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A potentiometric method, a convenient and rapid technique for determination of the thermodynamics of ionization reactions for water, weak acids, and some slightly soluble salts in aqueous organic mixed solvents

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A POTENTIOMETRIC METHOD-A CONVENIENT AND RAPID TECHNIQUE FOR DETERMINATION OF THE THERMODYNAMICS OF IONIZATION REACTIONS FOR WATER, WEAK ACIDS, AND SOME SLIGHTLY SOLUBLE SALTS IN AQUEOUS ORGANIC MIXED SOLVENTS

A Dissertation
Presented to the
Department of Chemistry
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by

Charanai Panichajakul

August 1976

This dissertation, by Charanai Panichajakul, is accepted in its present form by the Department of Chemistry of Brigham Young University as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

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I. INTRODUCTION

Background

Harned and Owen (1) have described a variety of methods based on potentiometry, conductivity, and spectroscopy for determination of ionization constants. These methods lead to reasonably accurate values of equilibrium constants over rather wide ranges of temperatures, pressures, and dissolved salt concentrations. It has been established that there are several satisfactory methods for determination of K_w in aqueous solutions, though there is evidence (2) of a small error in the temperature dependence of these K_w values. Similar methods have been applied with considerable success to determination of ionization constants for various weak acids in aqueous solutions. The methods of investigation of ionization reactions in aqueous organic mixtures have always required a relatively great amount of laboratory work. Grunwald (3,4) used a differential potentiometric method to determine acid and base dissociation constants in mixed solvent systems. His method does not incorporate liquid junctions, and it is based upon measurement of the rate of change of pH as a function of neutralization near the equivalence point in pure water as solvent compared to that in the ethanol-water system. Frohliger and co-workers (5) devised a method to determine the ionization constants of monobasic acids in ethanol-water solvent by direct potentiometry utilizing glass electrodes. Their method did not require the conventional standardization of the electrodes. Spivey and Shedlovsky (6) have utilized conductance measurements on dilute solutions of acetic acid in ethanol-water mixtures to obtain ionization constants. Bates and co-workers (7-15) have made a great contribution to the study of ionic equilibrium. They have used several methods to investigate ionization reactions in aqueous organic mixed solvents.

Salomon (16) has studied the complex solubility of silver chloride in acetone-water by emf measurements with liquid junction. Feakins and co-workers (17-21) reported solubility products of silver chloride in methanol-water and dioxan-water solvents. Kratohvil and Tezak (22) have studied silver-anion complexes in mixtures of water with ethanol, methanol, and acetone. Anderson, Butler, and Woolley (23-27) have also made measurements of the complex solubility of silver halides in several aqueous organic mixed solvents at 25°C.

In spite of the excellent work cited above, the status of measurements leading to ionization constants in aqueous organic mixed solvents has not been developed nearly so well as similar measurements in water solutions. Experimental methods have been difficult and rather time-consuming, and those methods that make use of the hydrogen electrode can only be applied to systems in which there are no complications due to reduction at the hydrogen electrode.

Recently Woolley, Hurkot, and Hepler (28) developed a rapid and convenient potentiometric method for determination of the equilibrium constants for ionization of water in aqueous organic mixed solvent systems. Their method can be modified to make possible the determination of ionization constants of weak acids in these same solvent systems. The procedure makes use of the difference in two potentials, thereby eliminating the necessity to determine the standard potential as done by Harned and co-workers (29-30). In this method purely aqueous solvent solutions can be diluted by the organic co-solvents continuously and glass electrodes can be used instead of the hydrogen electrode. Woolley and co-workers (28,31-35) have also done many studies of ionization reactions of "very weak" ($pK_a \sim$ 12-16) acids in various mixtures of water and heavy water (D_2O) with organic solvents and the results are in satisfactory agreement with earlier work.

Scope and Purpose

The investigation reported in this dissertation is the result of an interest in the nature of ionization reactions in mixed solvent systems. The experimental method employed here was devised in order to enable the rapid and convenient determination of the ionization constants for water and for weak acids (36,37) and the solubility product constants for certain slightly soluble salts (37) in aqueous organic mixed solvents. Two features of the method are significantly different from earlier methods (1,3-22,29,30). First, provision is made to determine glass electrode responses. Second, the experimental procedure of diluting aqueous electrolyte solutions continuously with non-aqueous solvent component eliminates the need for most of the solution preparation and handling associated with the earlier methods. The potentiometric measurements at various solvent compositions can be obtained very rapidly from one experiment by adding the organic solvent into the purely aqueous solution until the desired composition is reached.

This dissertation reports the results of an investigation of the ionization constants for water, acetic acid, benzoic acid and phenol and the solubility product constant for silver chloride in mixtures of water with methanol, ethanol, acetone, tetrahydrofuran, and p-dioxane at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, and 70 mass percent organic co-solvent. The mixtures containing ethanol and acetone were studied at 10, 15, 20, 25, 30, 35, and 40°C and the mixtures containing methanol, tetrahydrofuran, and p-dioxane were studied at 15, 25, and 35°C. The ionic strength of the solutions was always less than 0.02M. Mean ionic activity coefficients were estimated from an extended form of the Debye-Hückel equation.

The purposes of this investigation are: (a) to describe the details of the method and calculations which have been devised, (b) to report on the application of this method to the determination of ionization constants and other thermodynamic properties of a variety of ionizing substances in several mixed solvents over a moderate temperature range, and (c) to discuss the meaning and significance of the results of this investigation.

II. EXPERIMENTAL

Materials

All chemicals used in this study were reagent grade or better and they were used without further purification. Furthermore, they were tested to be sure that they were free from significant quantities of potentially interfering impurities such as halide ions, acids, and bases: solutions were prepared from either doubly distilled water or deionized water which had a specific conductance less than 1.5 x 10^{-6} mho/cm at 25°C.

Preparation of Solutions

Glassware used to prepare and transfer solutions was thoroughly cleaned, rinsed with distilled water and acetone.

The following solutions were prepared volumetrically:

Soln A: $HCl(C_1), KNO_3(C_2)$
Soln B: $KOH(C_3), KCl(C_4)$
Soln C: $HA(C_5), KOH(C_6), KCl(C_7)$
Soln D: $AgNO_3(C_8), HNO_3(C_9)$

The maximum uncertainty in any of the concentrations in any of the solutions is estimated to be less than 0.5%.

For solution C, HA represents acetic acid, benzoic acid, or phenol throughout this dissertation. Total ionic strengths of solutions in the cells were varied from about 0.005M to about 0.02M. The concentrations of solutions in cell (C) were made so that the buffer ratio (36,37) always had a value between 0.4 and 0.6. Densities of tetrahydrofuran-water mixtures were determined pycnometrically at 15°C and at 35°C. Densities of all other solvent mixtures were obtained from the literature (38). All weighings were performed on a Mettler type B5 single-pan balance with 200 g capacity and readable to 0.1 mg, or on a Mettler P163 top-loading balance with 160 g capacity and readable to 1 mg.

Apparatus

Potential measurements were made on all cells with a Model E-436 Metrohm Potentiograph recording potentiometric titrator. The sensitivity was set to 50 mV-full scale so that potentials were readable to 0.1 mV. The glass electrodes used were several Fisher 13-639-1 and Coleman 3-472 wide pH range electrodes. Attempts were also made to use the Beckman 39004 and the Sargent 30050 glass electrodes. However, potential readings were very unstable with these electrodes in the mixed solvent solutions. Silver-silver chloride electrodes were prepared from Beckman 39261 Silver Billet Electrodes by electrolysis in chloride solution (7).

Method of Potentiometric Measurements

Experimental measurements were made by immersing a glass electrode - Ag/AgCl couple in a 15.0 ml portion of purely aqueous solution A, B, C or D and allowing the potential to stabilize. When the potential became stable, a portion of the non-aqueous co-solvent was added to the solution in the cell and the potential was again recorded when it became stable. This procedure was continued until 50.0 ml of the co-solvent had been added. The temperature of the cells was kept constant to within ± 0.05°C of the reported temperature throughout the experiments. The potential measurement-co-solvent addition experiments were performed at least twice and a different combination of glass and silver-silver chloride electrodes was used on independently prepared solutions with each set of measurements with a given co-solvent.

Calculations

In this investigation the ionization of a monobasic acid, HA, in solvent S is described by the equation:

$$HA(s) = H^{+}(s) + A^{-}(s) \qquad (1)$$

Several choices of standard state can be taken to define the equilibrium constant expression for equation (1). In this dissertation equation (2) will be used for the equilibrium constant expression

$$K_a = a_H a_A / a_{HA} = C_H C_A (\gamma\pm)^2 / C_{HA} \gamma_{HA} \qquad (2)$$

Where a_H, a_A, and a_{HA} are activities based on molar concentrations, C_H, C_A, and C_{HA}, of the species $H^+(s)$, $A^-(s)$, and HA(s), respectively, and where $\gamma\pm$ is the mean ionic activity coefficient for the ions and γ_{HA} is the activity coefficient of HA(s) molecules.

This study of the ionization of monobasic acids in aqueous organic mixed solvents is based on the potentials of the cells represented by:

glass electrode|Soln A: $HCl(C_1),KNO_3(C_2)$, in solvent S|AgCl,Ag (A)

glass electrode|Soln B: $KOH(C_3),KCl(C_4)$, in solvent S|AgCl,Ag (B)

glass electrode|Soln C: $HA(C_5),KOH(C_6),KCl(C_7)$, in solvent S|AgCl,Ag (C)

glass electrode|Soln D: $AgNO_3(C_8),HNO_3(C_9)$, in solvent S|AgCl,Ag (D)

In cells (A)-(D), C_1-C_9 represent total formal analytical concentrations.

A general expression for the potentials of these cells is given by

$$E = k_1 + k_2 \log(a_H a_{Cl}) \tag{3}$$

and a specific equation for cell (A) is

$$E_A = k_1 + k_2 \log(C_1)^2 + k_2 \log (\gamma\pm)_A^2 \tag{4}$$

A similar specific equation for cell (B) can be given in terms of an equilibrium constant expression for ionization of water in solvent S

$$H_2O(s) = H^+(s) + OH^-(s) \tag{5}$$

$$K_w = a_H a_{OH}/a_w = C_H C_{OH}(\gamma\pm)^2/a_w \tag{6}$$

In equation (6) the activity of water a_w is represented in terms of the standard state based on Raoult's law: that is, the activity of pure water is taken to be unity. With this choice we can calculate $a_w = P_w/P_w{}^\circ$ from vapor pressure data from Timmermans (37). The potential for cell (B) thus becomes (assuming that mean ionic activity coefficients for all the ions are equal):

$$E_B = k_1 + k_2 \log\ (K_w a_w C_4/C_3) \tag{7}$$

Combination of equations (4) and (7) leads directly to equation (8) when the solvent composition is the same in both cells.

$$k_2 = (E_A - E_B)/\log\ [(C_1)^2 C_3 (\gamma\pm)_A^2 / C_4 K_w (a_w)_B] \tag{8}$$

Values of K_w in solvent S can be obtained when k_2 is known. Equation (8) can be used to determine the "response" of the cell electrodes, k_2, by using: (a) measured potentials E_A and E_B in pure water, (b) known concentrations C_1, C_3, and C_4, (c) K_w values and $a_w \simeq 1$ from the literature (1,2,36), and (d) values of $\gamma\pm$ estimated from the Debye-Hückel equation

$$\log(\gamma\pm) = -\frac{354.5[\rho(s)/\varepsilon^3(s)]^{1/2}\ I^{1/2}}{1 + 13.31[\rho(s)/\varepsilon(s)]^{1/2}\ I^{1/2}} \tag{9}$$

In equation (9), $\rho(s)$ and $\varepsilon(s)$ represent the density and dielectric constant, respectively, of solvent S. Density and dielectric data for this study were taken from Timmermans (39) except that the density of tetrahydrofuran-water mixtures were found experimentally at 15° and 35°C.

The specific equation for the potential of cell (C) is

$$E_C = k_1 + k_2 \log[(C_H)_C C_7] + k_2 \log\ (\gamma\pm)_C^2 \tag{10}$$

where $(C_H)_C$ is the "unknown" concentration of $H^+(s)$ in the buffered cell (C). Combination of equations (4) and (10) gives, in the case where both cells have the same solvent composition,

$$\log(C_H)_C = (E_C - E_A)/k_2 + \log(C_1^2/C_7) + \log[(\gamma\pm)_A^2/(\gamma\pm)_C^2] \quad (11)$$

from which we can obtain a value of $(C_H)_C$. Substitution into equation (2) of: (a) this "measured" value of $(C_H)_C$, (b) a value of $(\gamma\pm)_C^2$ calculated from equation (9), (c) a value of $\gamma_{HA} = 1$ (1-15,40), and (d) the buffer ratio (41,36-37) calculated from

$$C_A/C_{HA} = (C_6 + C_H - C_{OH})/(C_5 - C_6 - C_H + C_{OH}) \sim C_6/(C_5 - C_6) \quad (12)$$

where C_{OH} can be obtained from equation (6), leads to a numerical value of K_a for the acid HA in solvent S.

The value of k_2 used in equation (11) can be taken as that value calculated from equation (8) or one could calculate a value of k_2 from equation (11) from known values of C_1, C_5, C_6, and C_7 in pure water and from measured values of E_A and E_C in pure water in conjunction with equations (2), (9), (11), and (12).

Values of K_h for the hydrolysis reaction

$$A^-(s) + H_2O(s) = HA(s) + OH^-(s) \quad (13)$$

can be obtained from known values of K_w and K_a by using equation (14)

$$K_h = a_{HA}a_{OH}/a_A\ a_w = \frac{K_w}{K_a} = K_b \quad (14)$$

The solubility reaction for a non-hydrolyzing and non-complexing salt in solvent S is

$$MX(s) = M^+(s) + X^-(s) \quad (15)$$

where

$$K_s = a_M a_X/a_{MX} = C_M C_X(\gamma\pm)^2/a_{MX} \tag{16}$$

The specific equation for the potential of cell (D) is (again assuming that mean ionic activity coefficients for all the ions are equal)

$$E_D = k_1 + k_2\log[K_s\ C_9/C_8] \tag{17}$$

Combination of equations (4) and (17) leads to equation (18) when the solvent composition is the same in cells (A) and (D).

$$pK_s = (E_A - E_D)/k_2 - \log[(C_1)^2 C_8(\gamma\pm)_A^2/C_9 a_{MX}] \tag{18}$$

Values of K_s can be obtained from measured E_A and E_D values in any solvent S when the analytical concentrations C_1, C_8, and C_9 are known, when a_{MX} is known, and where $\gamma\pm$ is calculated from equation (9). In this work, a_{MX} is taken to be unity.

The value of k_2 used in equation (18) may be taken as that value calculated from equations (8) or (11) or one could calculate a value of k_2 from equation (18), a known value of K_s in pure water, and from measured values of E_A and E_D in pure water in conjunction with equation (9) (30-37).

The methods outlined above for obtaining ionization constants in mixed solvents are based on the following assumptions.

1. That all electrolytes (except HA and MX) are completely dissociated in the solutions that are used. This assumption is most valid at low total formal analytical concentrations and in solutions of high water content (high dielectric constant).

2. That glass electrode junction potentials, asymmetry

potentials, and responses (k_2) are the same in all four cells (or at least constant in the pair of cells used to calculate each ionization constant) and that they do not change with solvent composition. To minimize possible errors in this assumption, the ionic strengths in all three cells were made small and identical by insuring that $C_1 + C_2 = C_3 + C_4 = C_6 + C_7 = C_8 + C_9 \leq 0.02$ at each solvent composition.

3. That mean ionic activity coefficients [calculated by equation (9)] are identical for each univalent electrolyte used in this study. This assumption is also most reasonably valid at low ionic strengths and at high water concentrations.

Assumptions 1 and 3 are commonly made and they have been shown to be valid in many studies in solvent compositions identical to (or similar to) those of this study (1-15,31-34,36,37). Assumption 2 has also been shown to give K_w, K_a, and K_h values that are consistent, within experimental uncertainties, with results obtained without the use of glass electrodes (31-34,36,37). The fact that the pK values calculated using the above assumptions are in good agreement with those values reported in the literature is a probable indication that any errors resulting from the making of these assumptions are probably relatively small.

The calculation of $\Delta H°$ and $\Delta S°$ values from the pK temperature data in each solvent mixture was performed by the non-empirical method of Clarke and Glew (42) as simplified by Bolton (43). In this method the thermodynamic parameters are considered to be continuous, well-behaved functions of temperature and their values are expressed as perturbations of their values at the same reference temperature, θ, by a Taylor's series expansion. The basic equation is:

$$R\ln K = - \frac{\Delta G^{\circ}_{\theta}}{\theta} + \frac{\Delta H^{\circ}_{\theta}}{\theta} t_1 + \Delta C^{0}_{p,\theta} t_2 + \frac{\theta}{2} \left(\frac{\partial \Delta C^{\circ}_{p}}{\partial T}\right)_{\theta} t_3 + - - - - - - - - - - - - - \tag{19}$$

when the thermodynamic parameters are the regression coefficients and the terms, t_i, are the temperature dependent variables. All equilibrium constants were converted to the molality scale prior to the above analysis (2,38,40). Values of K, ΔG° and ΔS° were then converted to the molarity scale and are expressed on that basis in the Results section.

When the pK versus temperature data were treated according to other polynomial equations, such as those used by Harned and Owen (1), it was found that only two parameters were required with any of the equations. These two parameters gave numerical values of $\Delta G^{\circ}_{\theta}$ and $\Delta H^{\circ}_{\theta}$ that are nearly identical to those obtained by use of equation (19).

III. RESULTS

Density and dielectric constant data at different solvent compositions and temperatures are summarized in Appendix A. Potentiometric data for each series of measurements on all cells are tabulated in Appendix B.

Values of k_2 obtained from equations (8), (11), and (18) are given in Appendix C . Theoretical k_2 = 2.303RT/F values are also given in Appendix C . The deviations of experimental k_2 values from the theoretical values may be the result of: (a) small amounts of impurities in reagents such that concentrations are slightly different from the formal analytical concentrations used in the calculations, and/or (b) drift in potentials, simultaneously on all cells with the same cell electrodes. Glass electrode potentials are known to drift, and often this drift increases with changes in solvent composition. The slightly larger deviations of k_2 values obtained with benzoic acid solutions and with dioxan mixtures could indicate impurities in these two reagents. The rest of the scatter of k_2 values is likely attributable to item (b) above and to the fact that the response of glass electrodes may be different in solutions of widely varying pH. In summary, these problems probably have little effect on resulting pK values, as evidenced by the agreement with literature values.

All pK values are presented in Appendix D. Each one is the average result of at least two independent series of measurements using different combinations of Fisher and Coleman glass electrodes and different solutions in cells. All these replicate measurements led to pK values which have average deviations of less than 0.03 in solvent mixtures containing up to 50 mass % organic component and less than 0.05 in solutions of higher organic co-solvent content In most cases, these average deviations were less than 0.02 and 0.03 in those two regions, respectively.

In Table I the "best" values of thermodynamic functions are the results obtained by reading large scale plots of the experimental values of pK and ΔH° at 25°C versus solvent composition at round solvent composition -- that is, at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, and 70 mass percent c0-solvent composition. Figure 1 shows an example of a plot from which the best values of pK_s for silver chloride were obtained in mixtures of methanol with water. Plots of pK versus mole fraction of water at 25°C are also given in Figures 2 to 6.

Standard deviations in the pK temperature correlation, as analyzed according to equation (19), did not decrease significantly from the two-parameter values when terms involving ΔC_p° were included. Standard deviations of between 0.01 and 0.04 (in pK versus t) were obtained in all cases when only the two parameters ΔG_θ° and ΔH_θ° were included in equation (19). More accurate pK measurements are necessary to determine ΔC_p° values (2,38,40,42,43).

Statistical standard deviations (41,43) in ΔH_θ° and ΔS_θ° values typically ranged from 0.2 to 0.5 kcal and from 1 to 2 cal/°K, respectively. However, statistical standard deviations in ΔH_θ° values

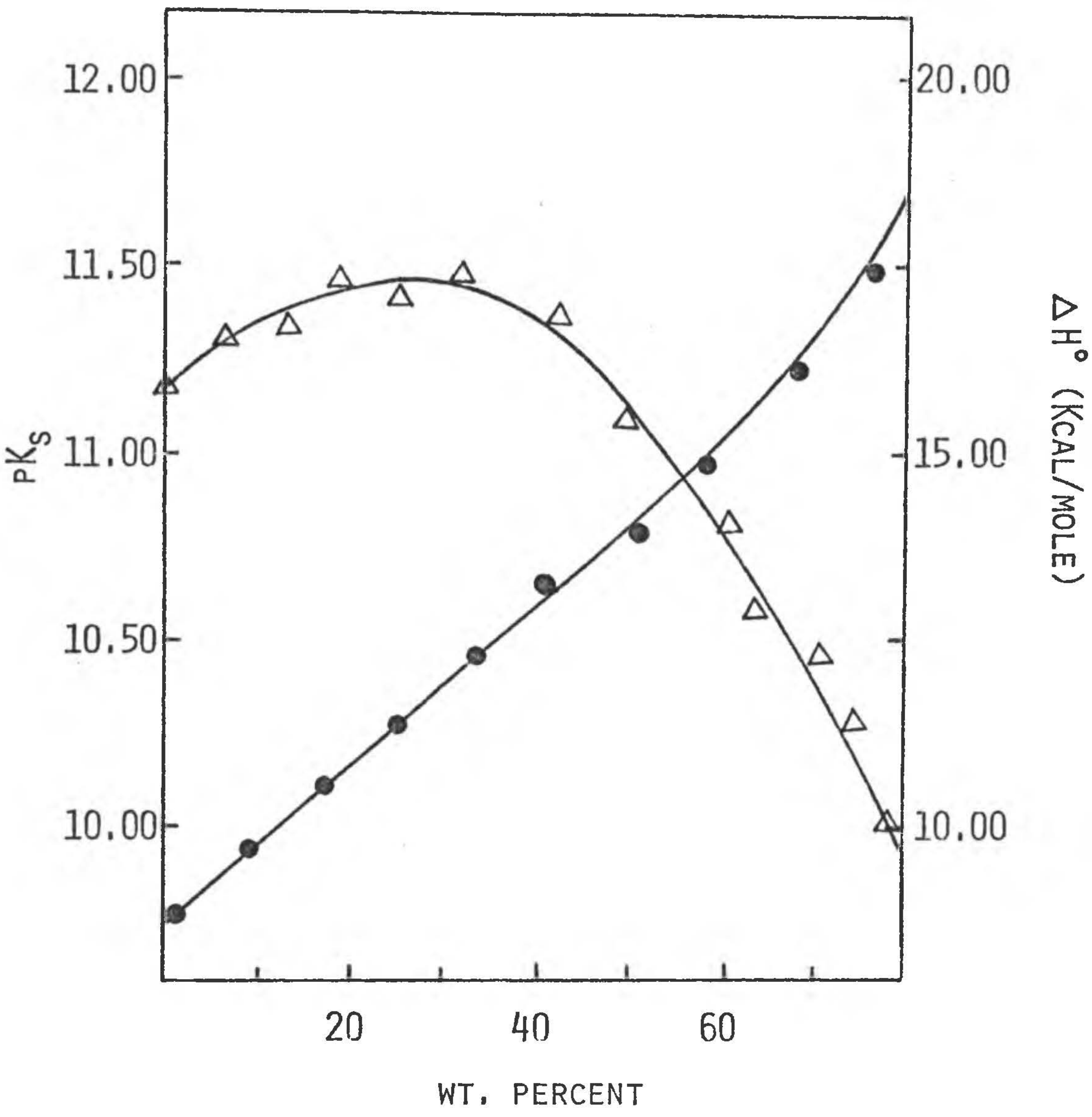

Fig. 1. The experimental values of pK and ΔH° at 25°C for AgCl versus the wt. percent of methanol. The "best" values were read from each line.

● pK

△ ΔH°

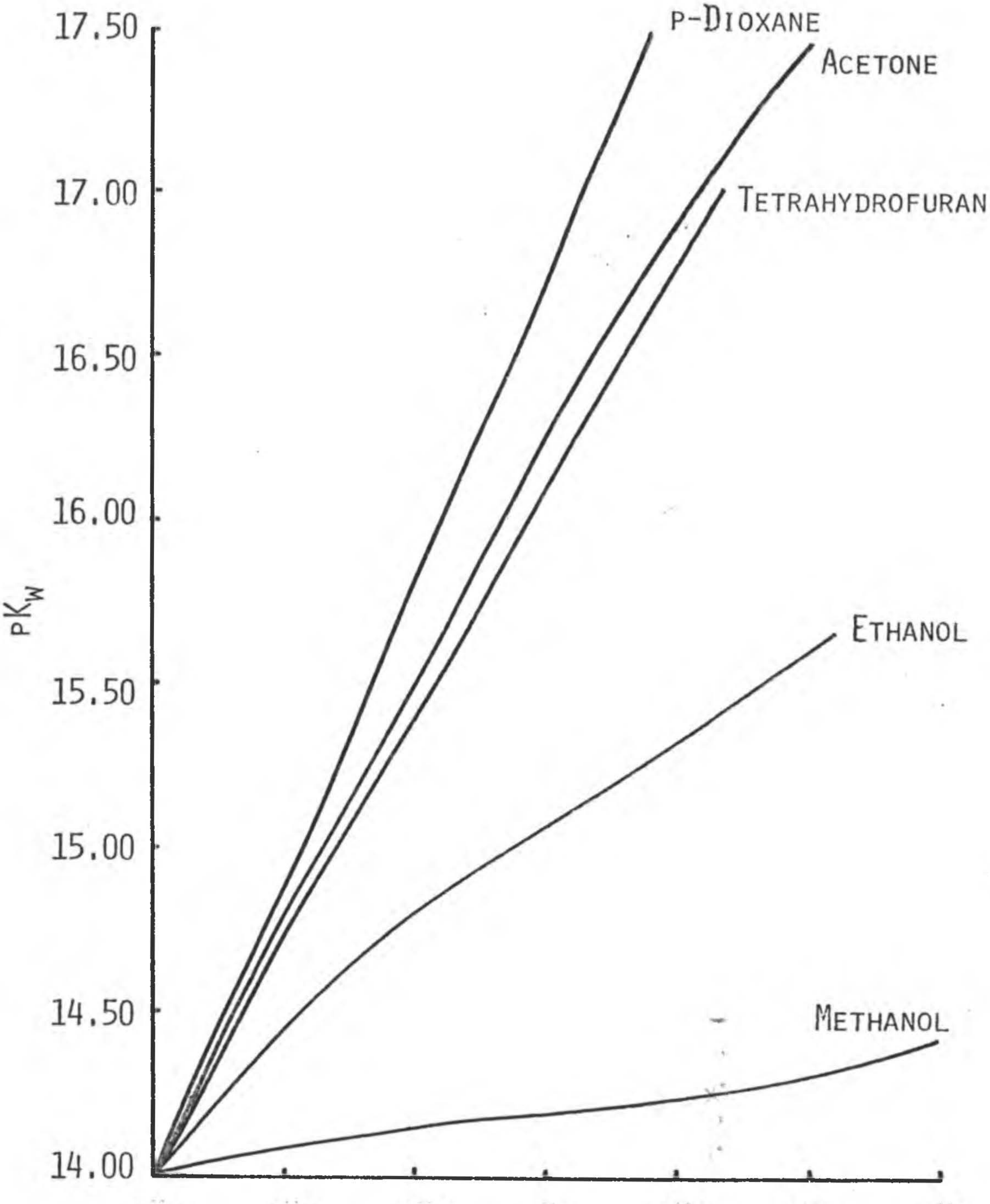

Fig. 2. pK values for ionization of water in aqueous organic mixed solvents against the mole fraction of water.

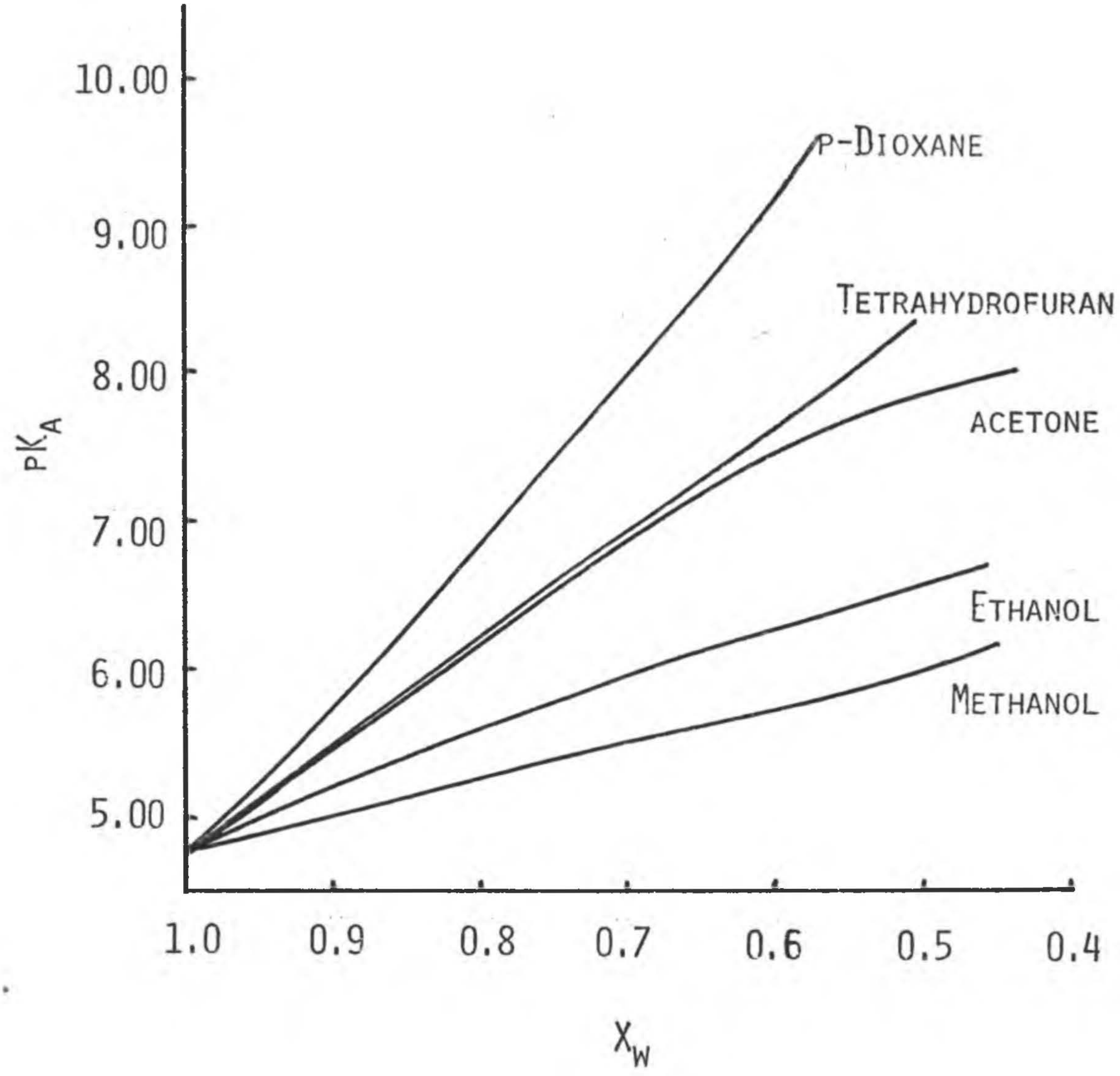

Fig. 3. pK values for ionization of acetic acid in aqueous organic mixed solvents against the mole fraction of water.

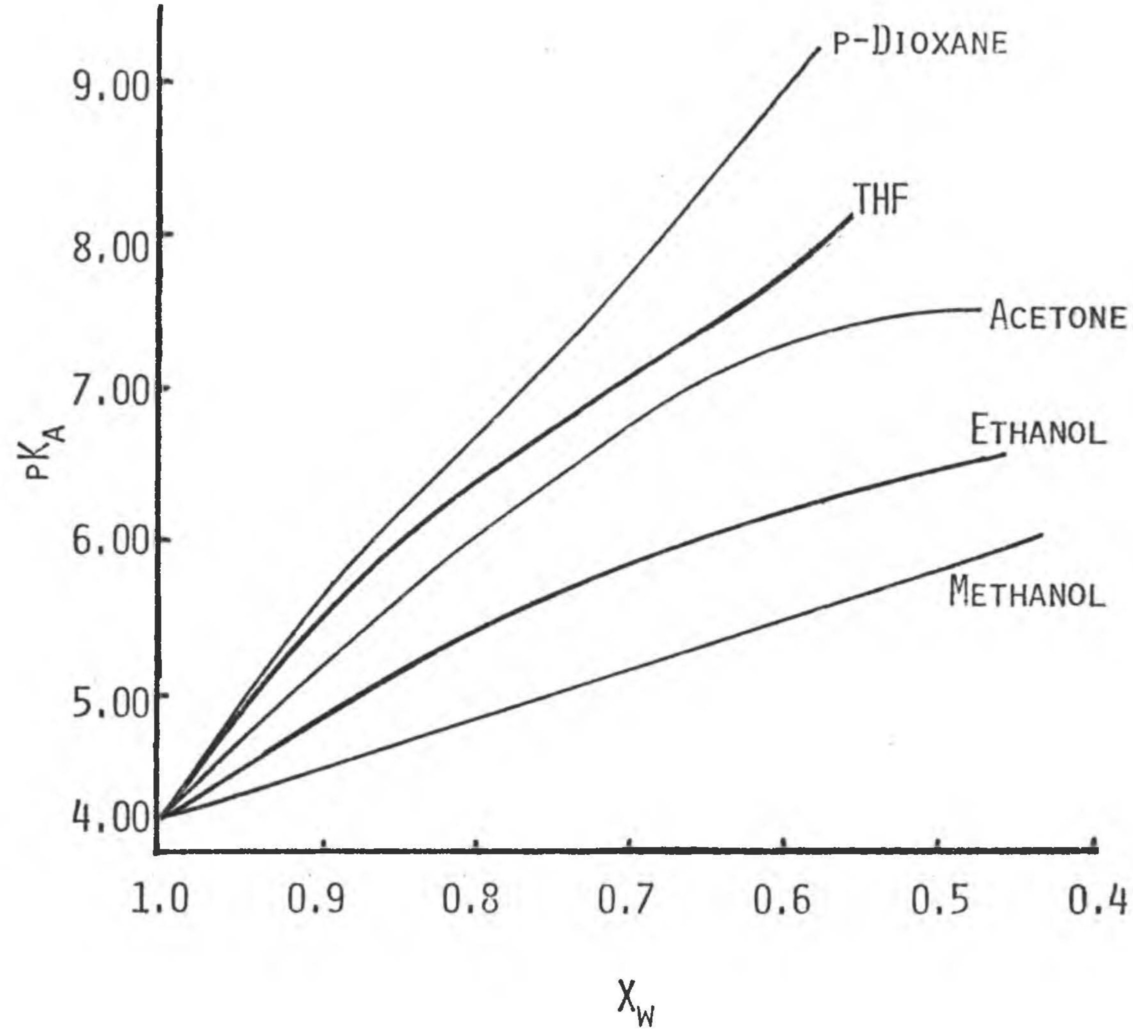

Fig. 4. pK values for ionization of benzoic acid in aqueous organic mixed solvents against the mole fraction of water.

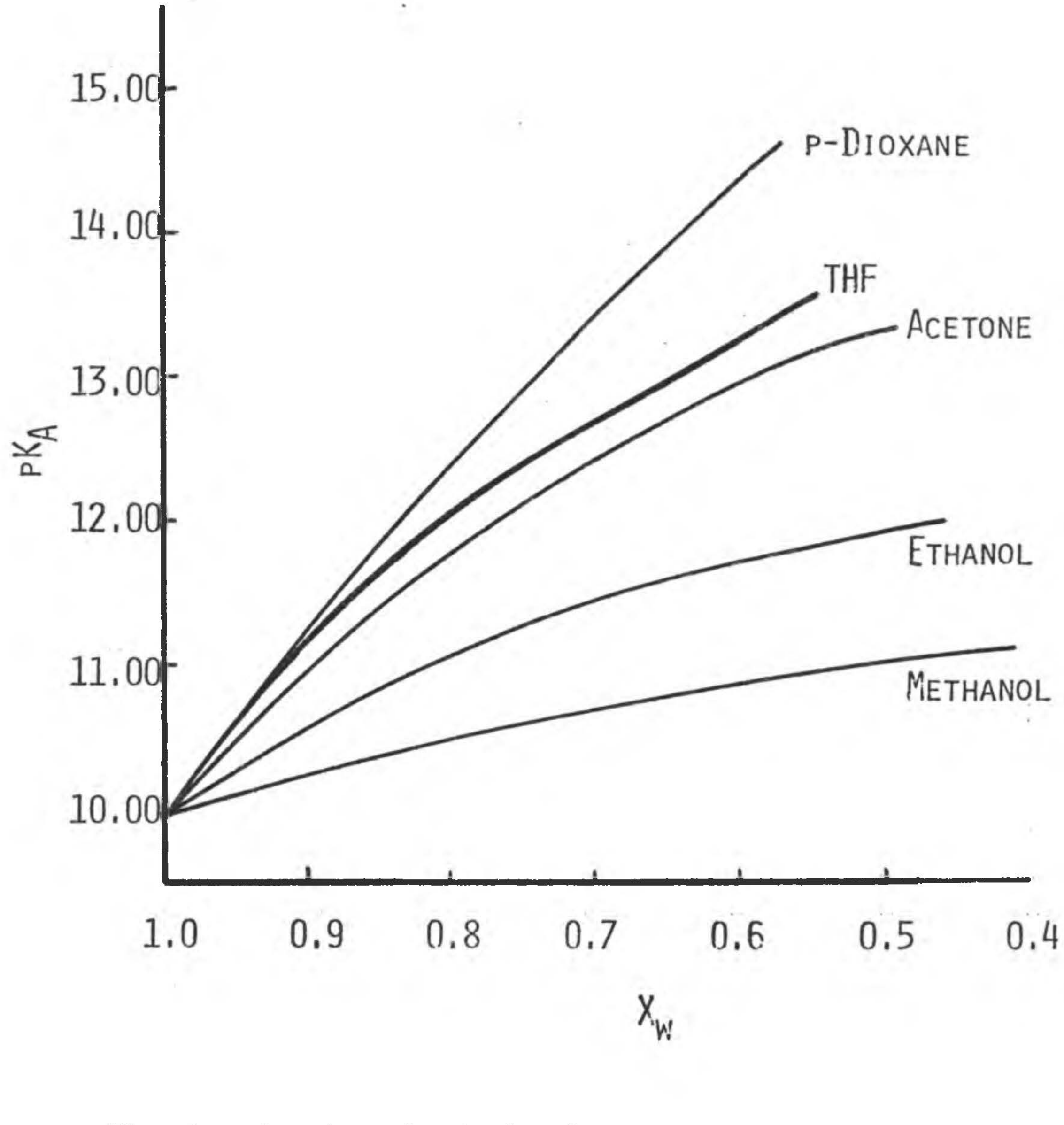

Fig. 5. pK values for ionization of phenol in aqueous organic mixed solvents against the mole fraction of water.

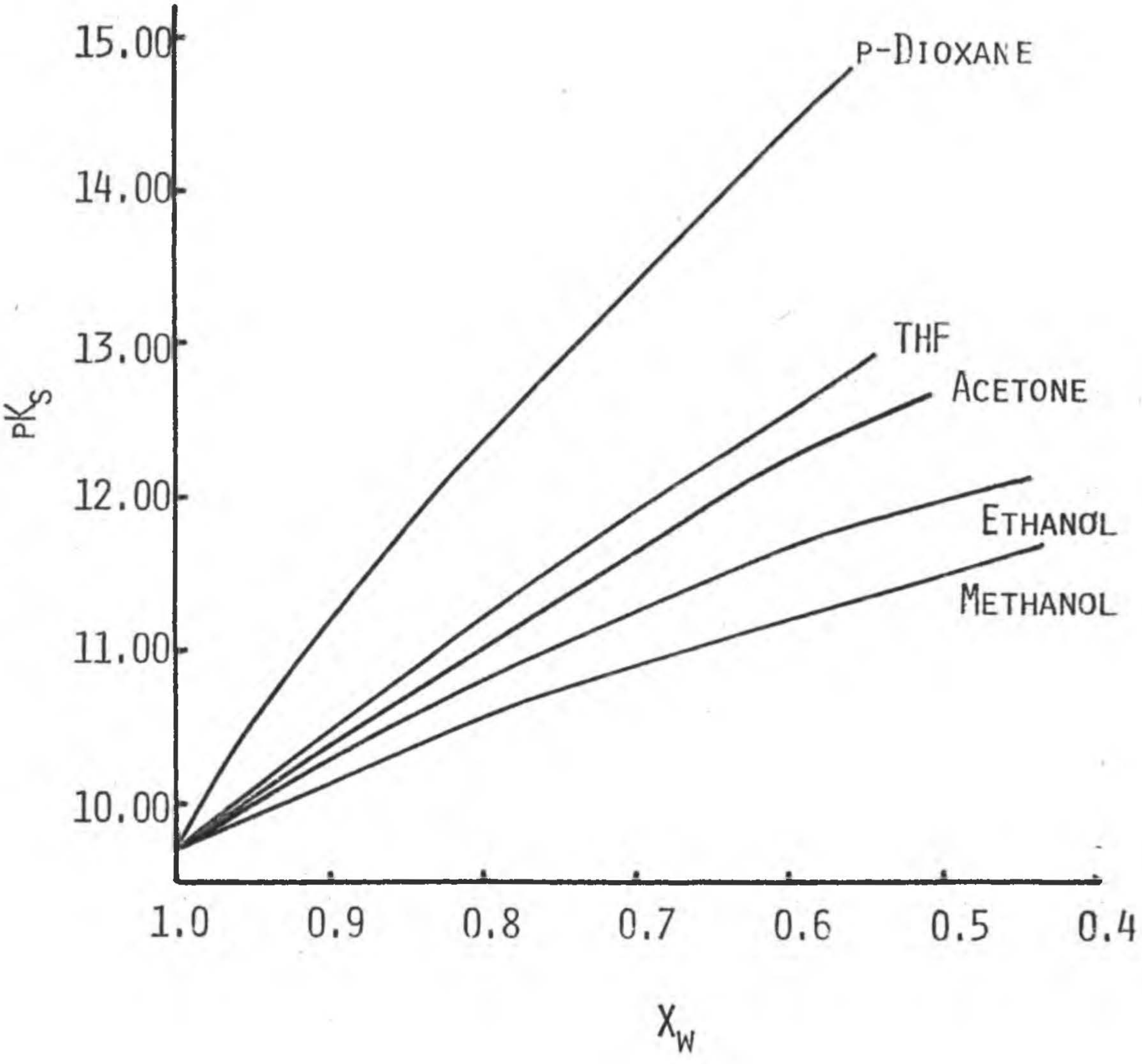

Fig. 6. pK values for ionization of silver chloride in aqueous organic mixed solvents against the mole fraction of water.

did increase, generally, from about 0.2 to 0.5 kcal as the mass percent organic content was increased from 0 to 70. The total uncertainties in ΔG°_θ are estimated to be ± 60 cal at all solvent compositions. The total uncertainties in the values of ΔH°_θ and $\Delta S^\circ_\theta = (\Delta H^\circ_\theta - \Delta G^\circ_\theta)/\theta$ ($\theta = 298.15°K$) that are given in Table I are estimated to be approximately the same at all solvent compositions: ± 0.5 kcal for ΔH°_θ and ± 2 cal/°K for ΔS°_θ.

The results of all pK determinations are summarized graphically in figures 2-14. Figures 2-6 show pK values of water, acetic acid, benzoid acid, phenol, and silver chloride against the more fraction of water in the mixed solvent. Figures 7-10 and 14 contain the "transfer" thermodynamic functions (for ionization reactions of the above substances) from water to the organic cosolvent mixtures. The results are represented as

$$\delta G = \Delta G^\circ(s) - \Delta G^\circ(w) \tag{20}$$

$$\delta H = \Delta H^\circ(s) - \Delta H^\circ(w) \tag{21}$$

$$\delta S = \Delta S^\circ(s) - \Delta S^\circ(w) \tag{22}$$

In equations (20-26) the s and w refer to values in solvent S and pure water, respectively. Values of ΔG°, ΔH°, and ΔS° for all five ionization reqctions]equations (1), (5), and (15)] in pure water solvent are given in Table II. Values of ΔG°, ΔH°, and ΔS° for the hydrolysis reactions]equation (13)] of acetic acid, benzoic acid, and phenol in pure water can be obtained by combinations of the values for ionization of water and for ionization of each acid. The transfer thermodynamic functions for the hydrolysis reactions of the three acids are summarized graphically in Figures 11-13.

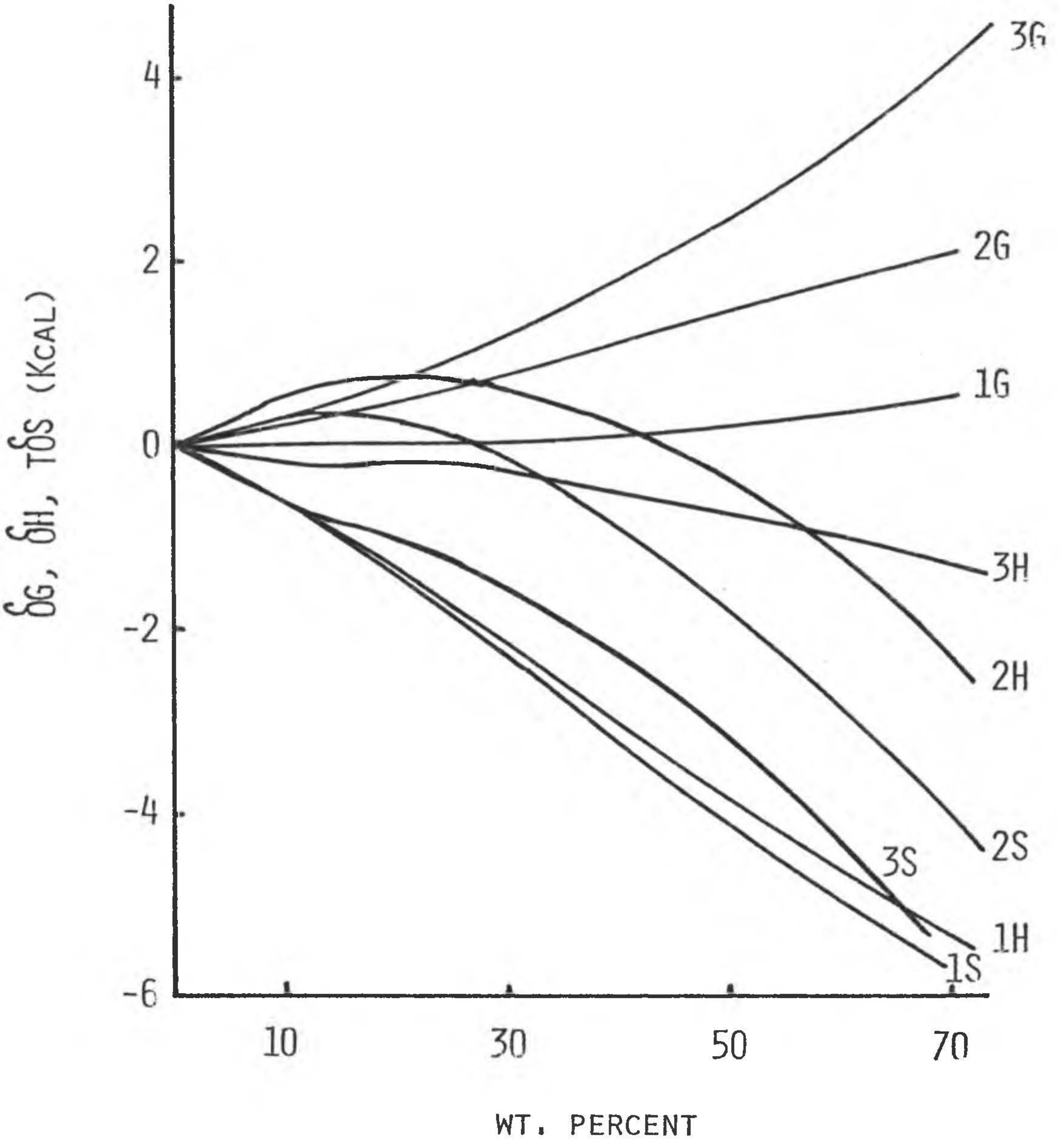

Fig. 7(a) Thermodynamics for $H_2O(s) = H^+(s) + OH^-(s)$ versus wt% organic solvent component. Equations (5), (6), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

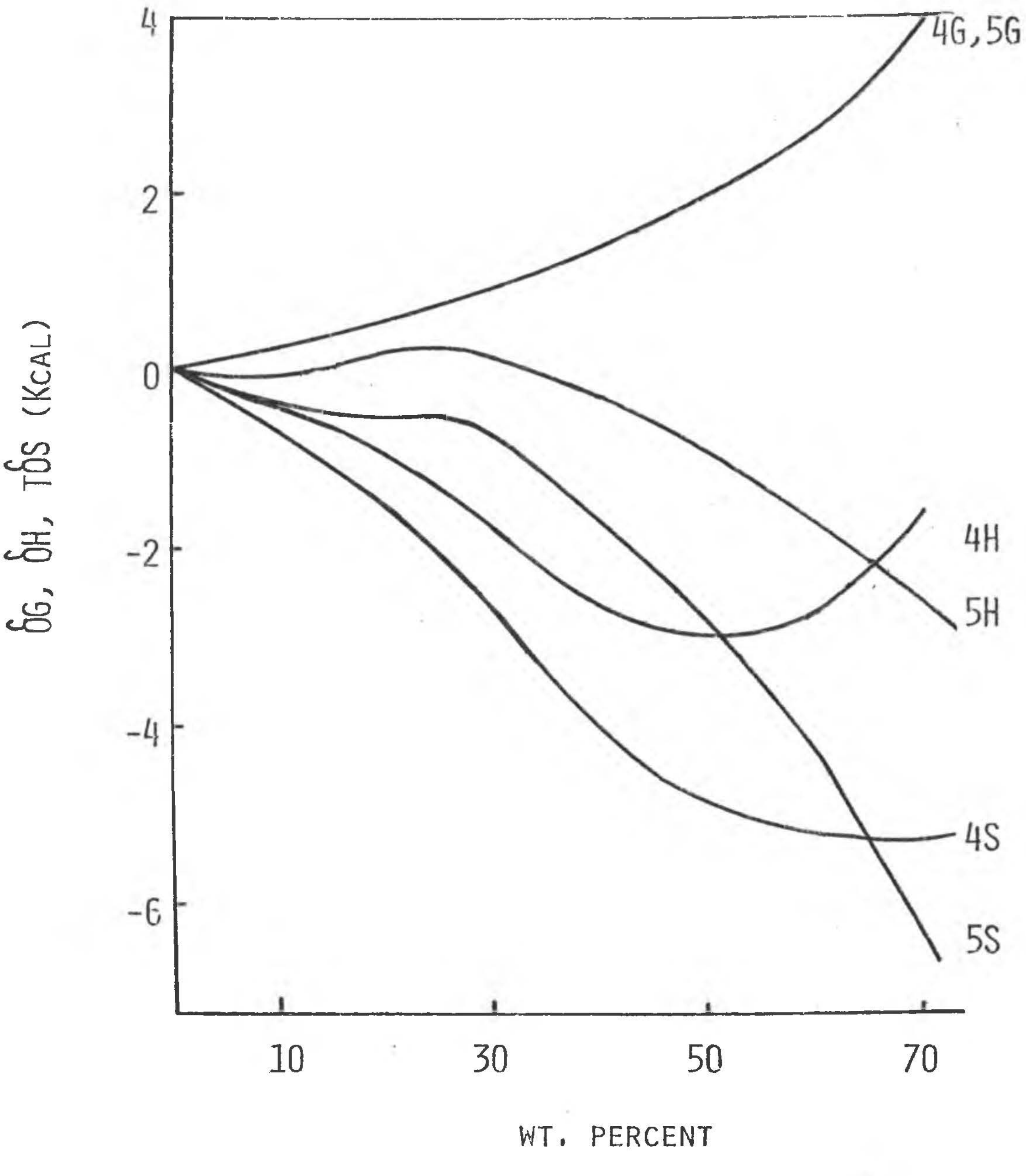

Fig. 7(b) Thermodynamics for $H_2O(s) = H^+(s) + OH^-(s)$ versus wt% organic solvent component. Equations (5), (6), (20)-(22): 4 = THF-water, 5 = dioxane-water; G = δG, H = δH, S = TδS.

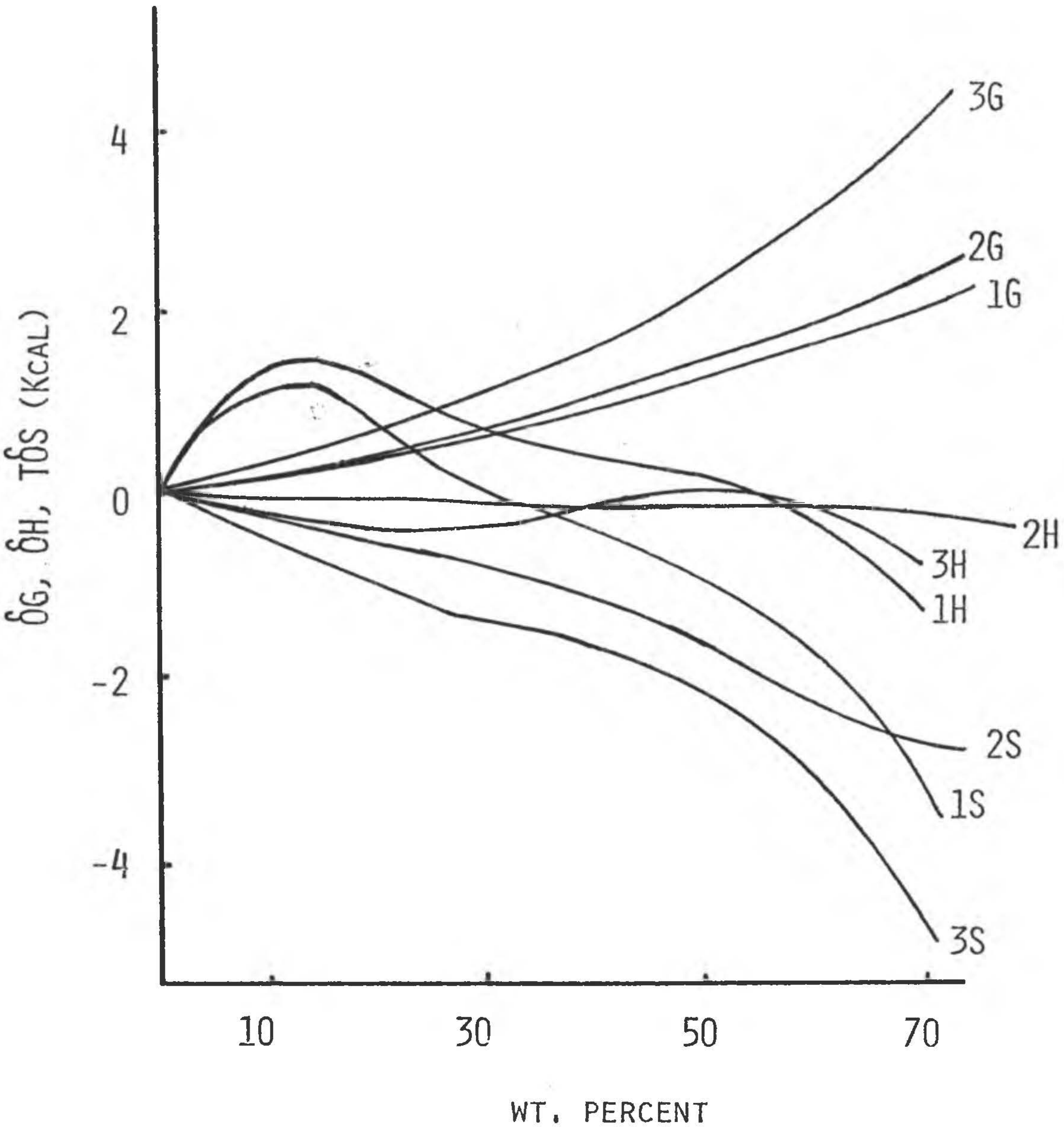

Fig. 8(a). Thermodynamics for HAc(s) = H^+(s) + Ac^-(s) where Ac = acetate versus wt% organic solvent component. Equations (1), (2), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

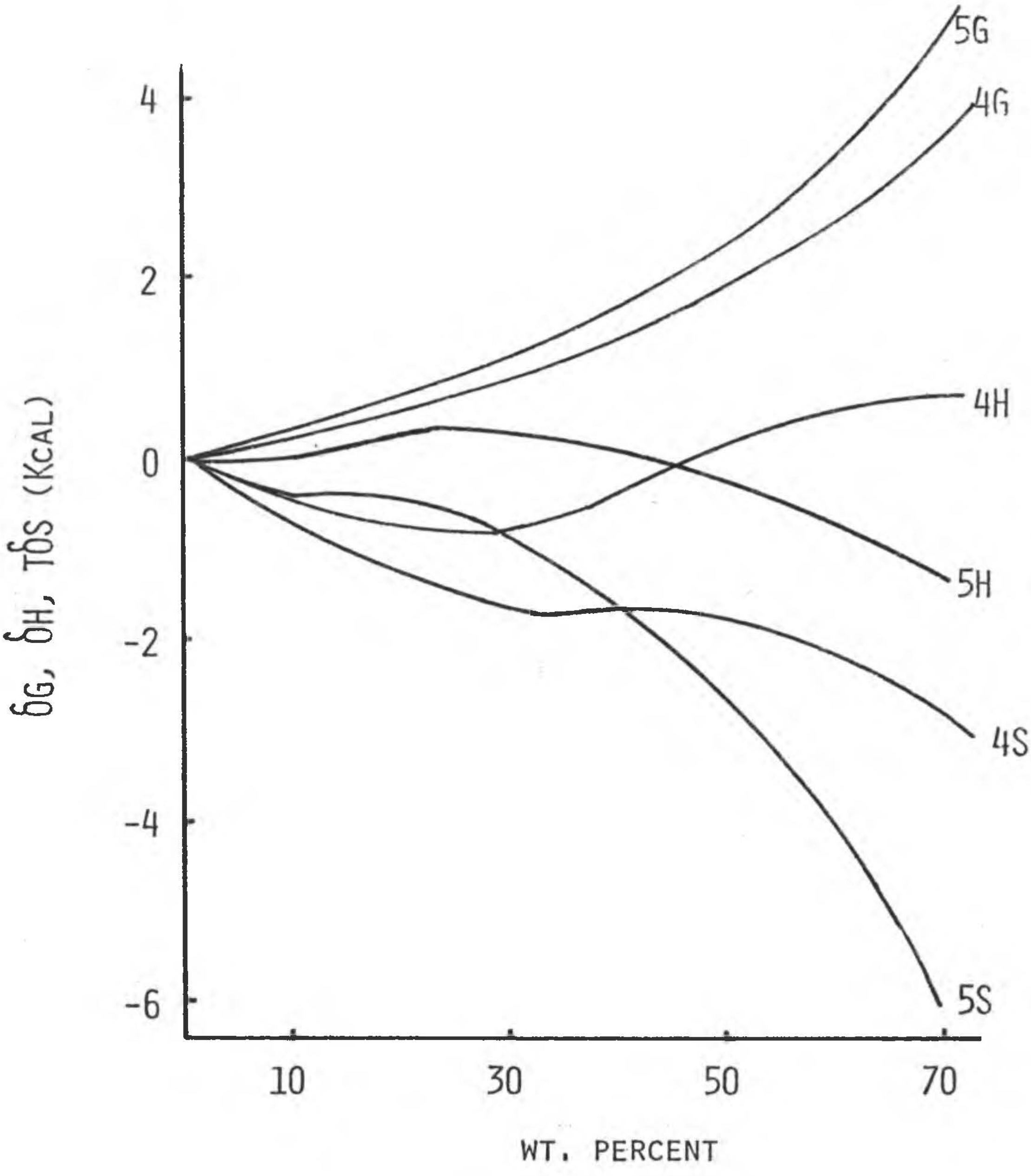

Fig. 8(b). Thermodynamics for HAc(s) = H^+(s) + Ac^-(s) where Ac = acetate versus wt% organic solvent component. Equations (1), (2), (20)-(22): 4 = THF-water, 5 = dioxane-water; G = δG, H = δH, S = TδS.

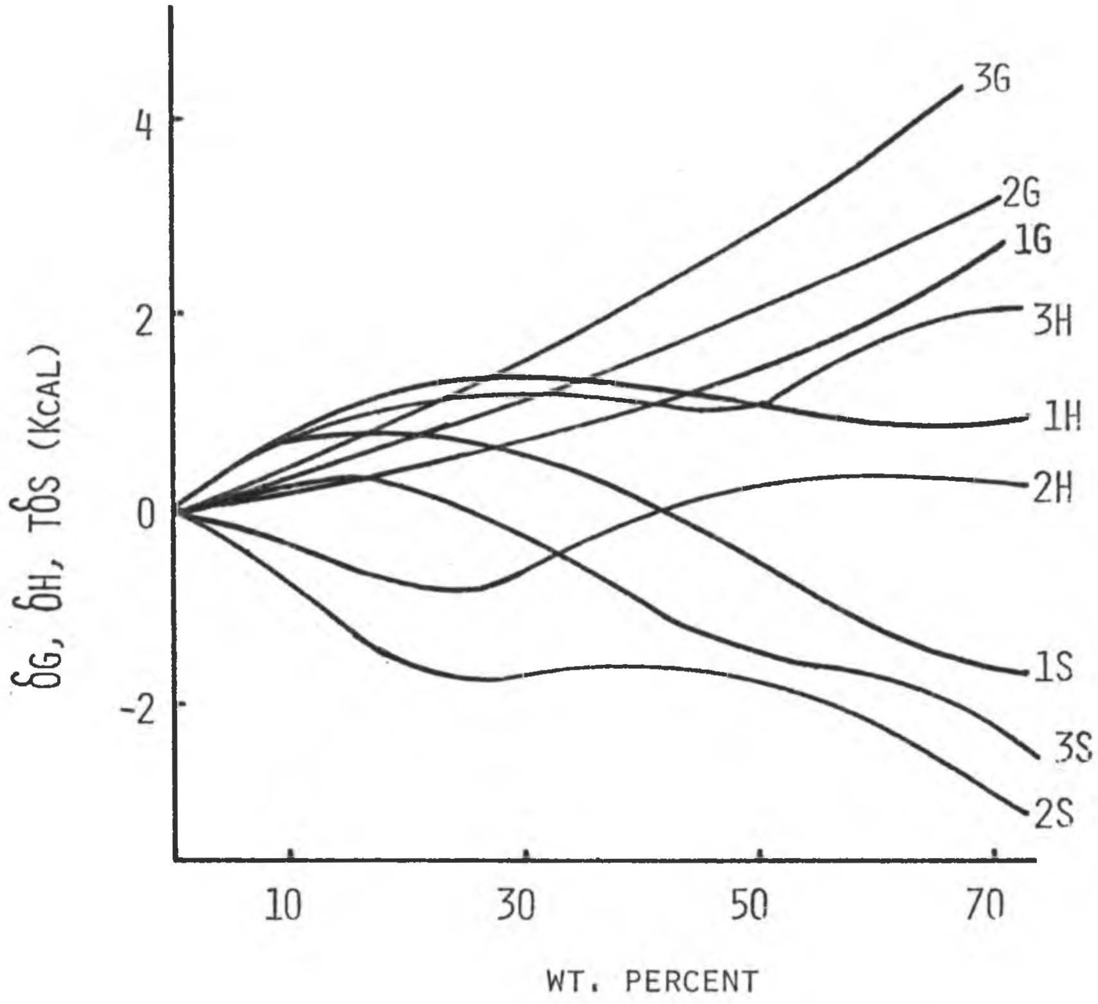

Fig. 9(a). Thermodynamics for $HBz(s) = H^{+}(s) + Bz^{-}(s)$ where Bz = benzoate versus wt% organic solvent component. Equations (1), (2), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = $T\delta S$.

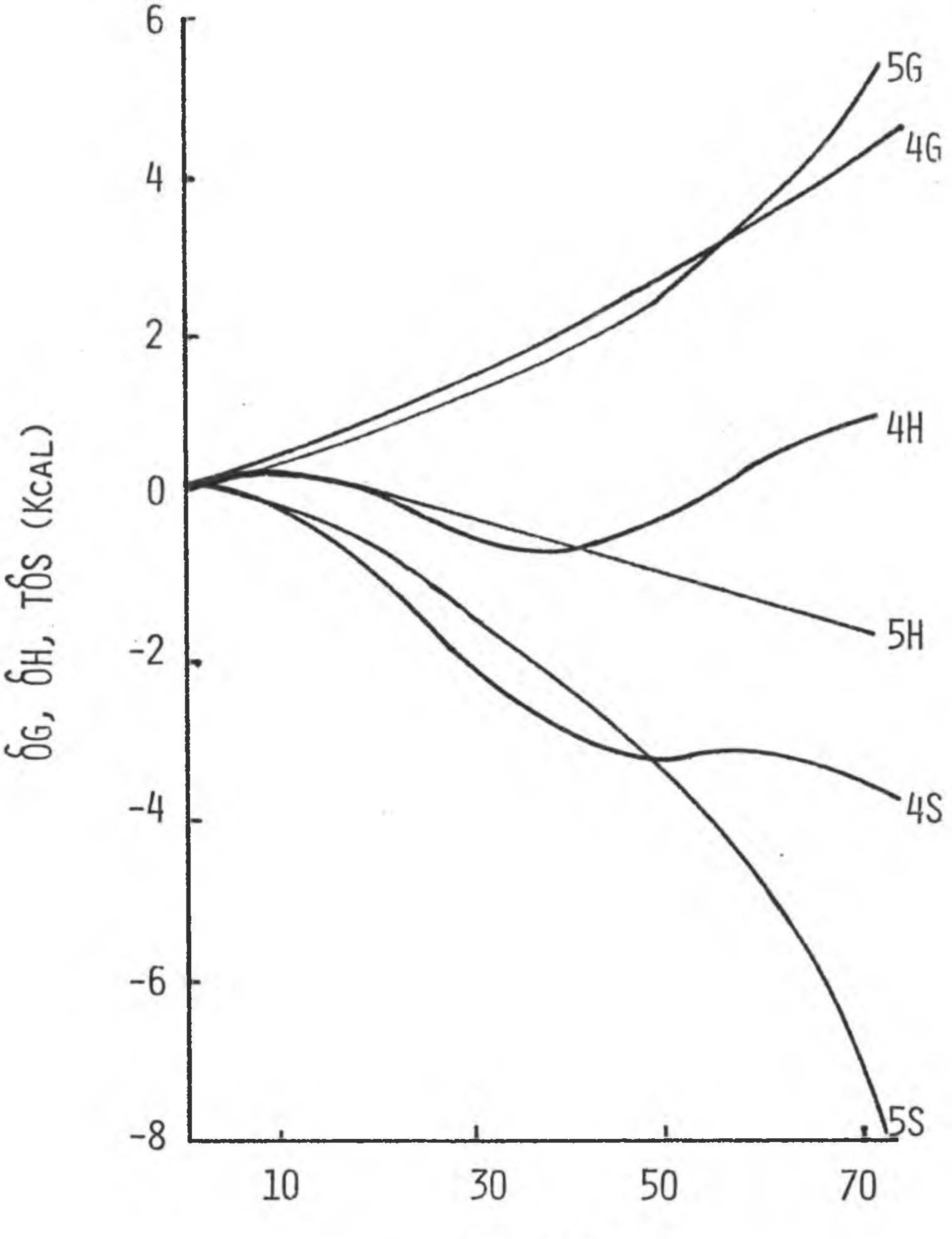

Fig. 9(b). Thermodynamics for HBz(s) + H^+(s) + Bz^-(s) where Bz = benzoate versus wt% organic solvent component. Equations (1), (2), (20)-(22): 4 = THF-water, 5 = dioxane-water, G = δG, H = δH, S = TδS.

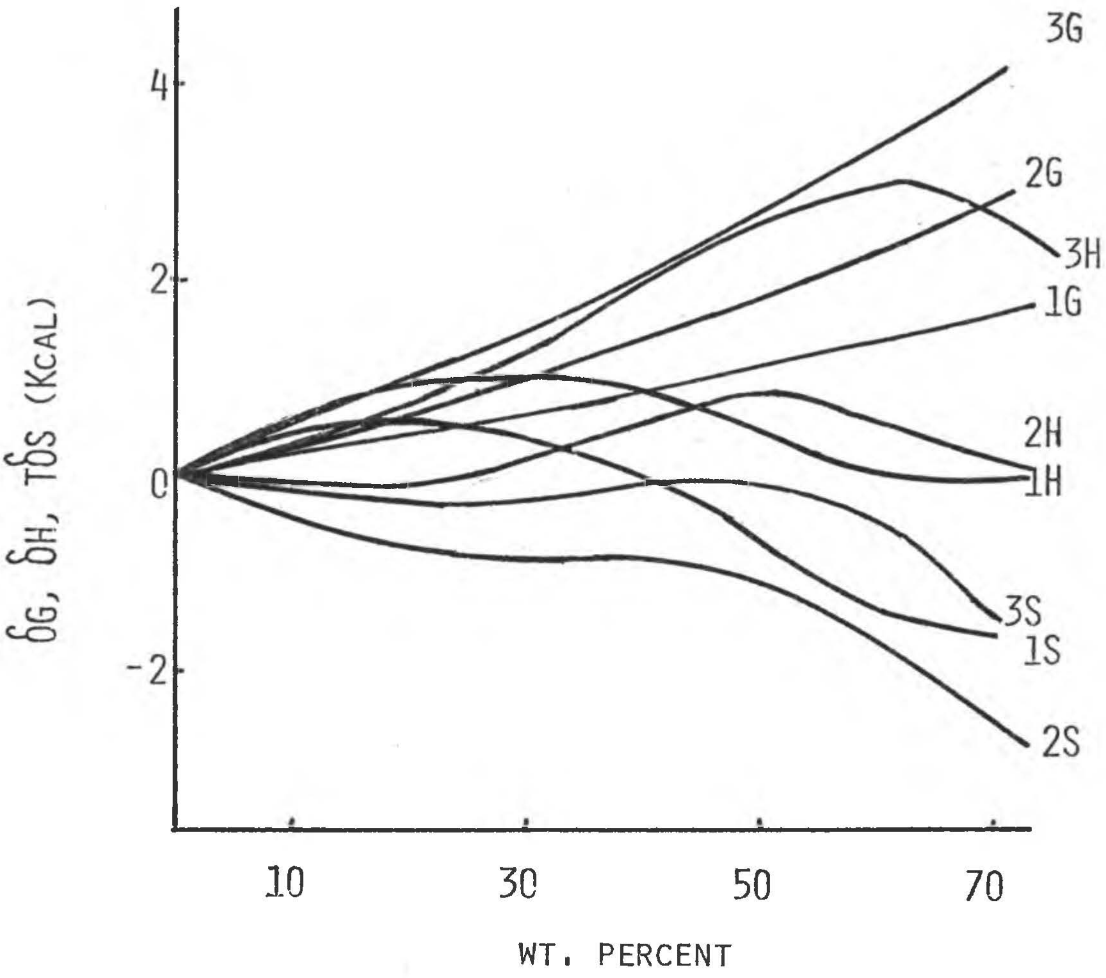

Fig. 10(a). Thermodynamics for HPh(s) = H^+(s) + Ph^-(s) where Ph = phenolate versus wt% organic solvent component. Equations (1), (2), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

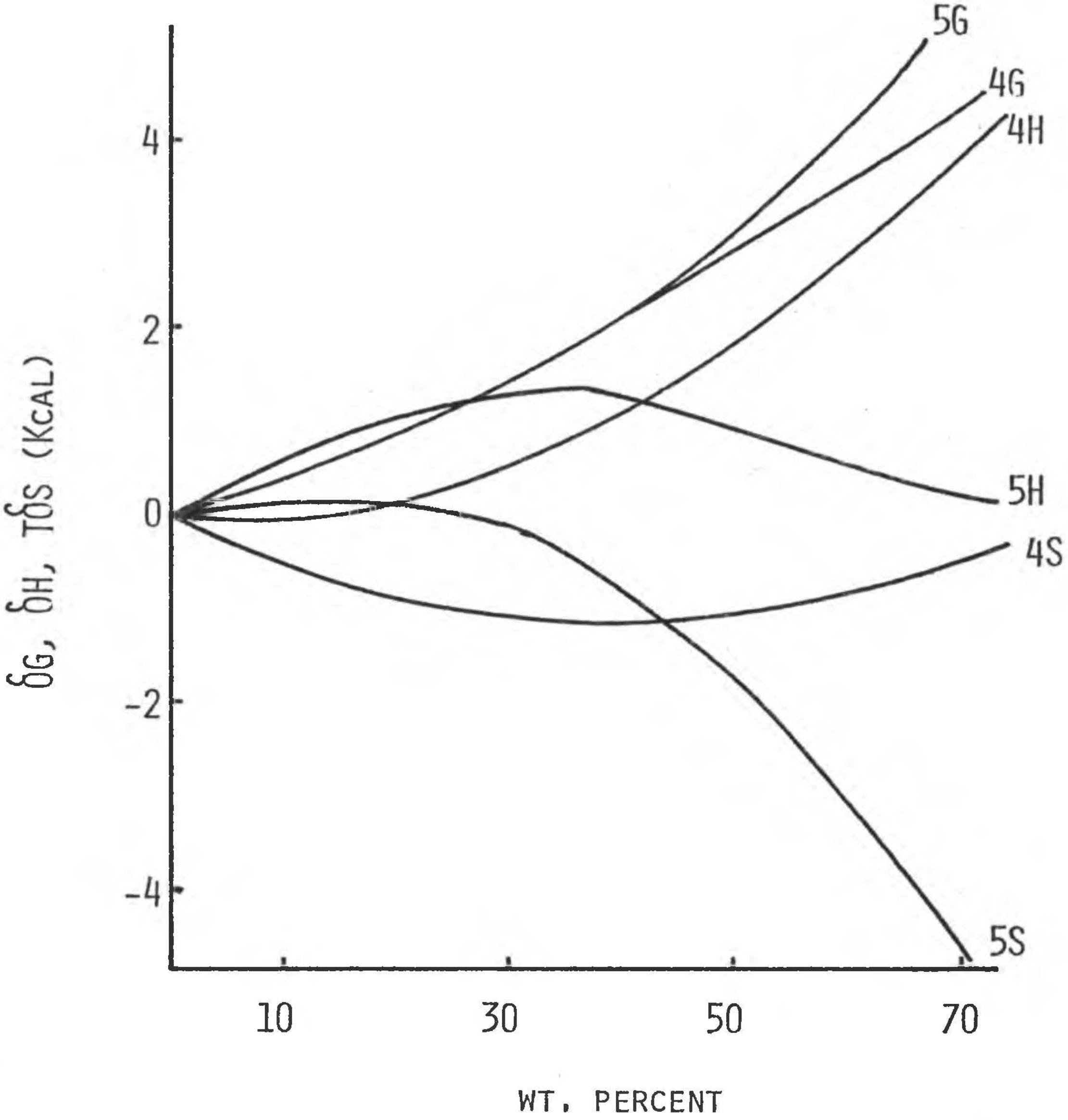

Fig. 10(b). Thermodynamics for HPh(s) = H^+(s) + Ph^-(s) where Ph = phenolate versus wt% organic solvent component. Equation (1), (2), (20)-(22): 4 = THF-water, 5 = dioxan-water; G = δG, H = δH, S = TδS.

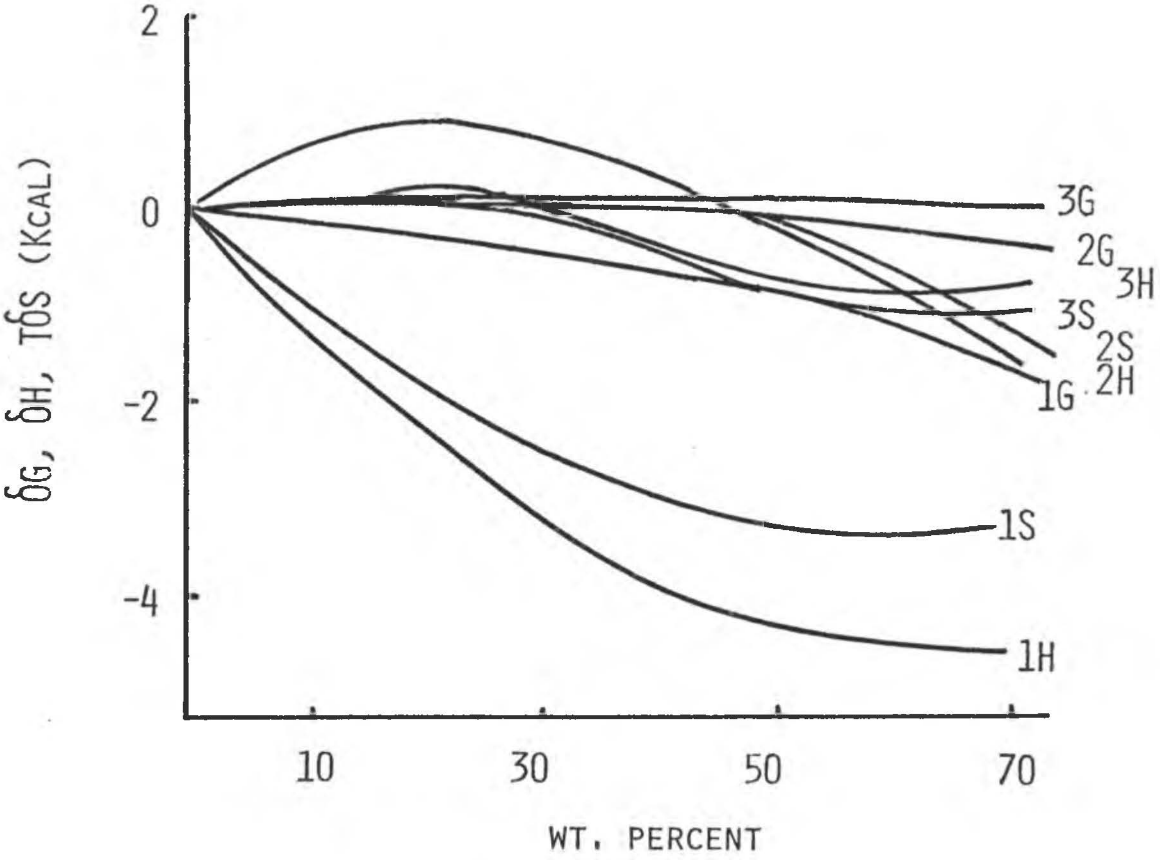

Fig. 11(a). Thermodynamics for $Ac^-(s) + H_2O(s) = HAc(s) + OH^-(s)$ where Ac = acetate versus wt% organic solvent component. Equation (13), (14), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

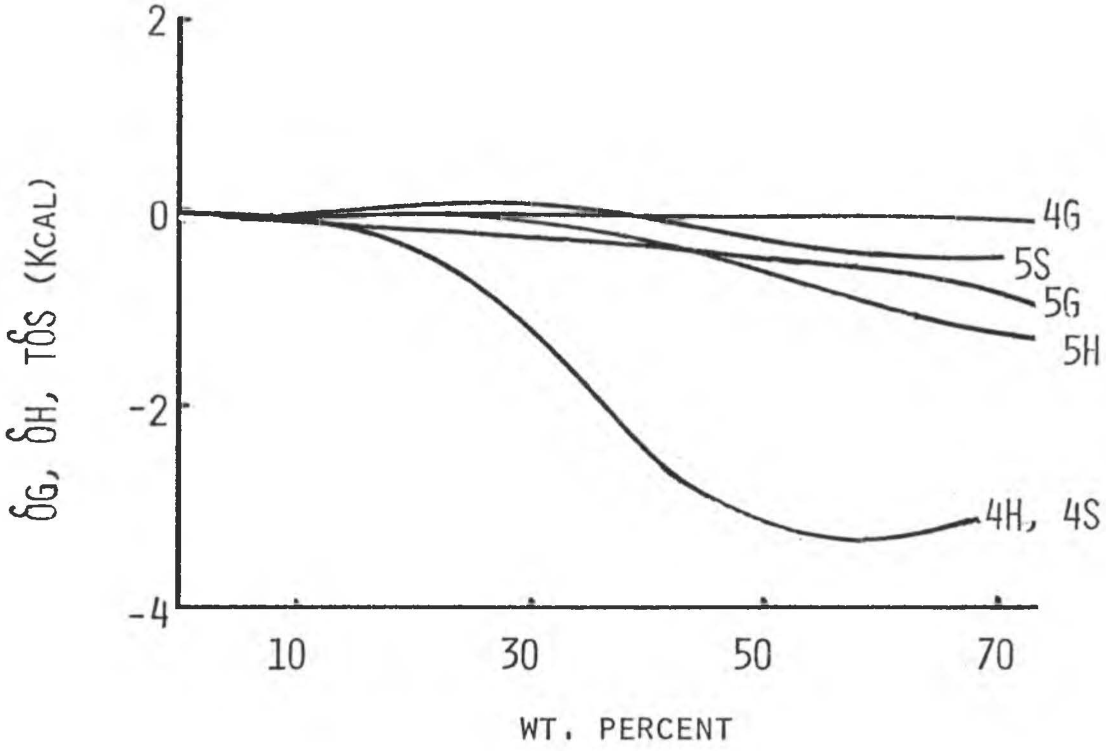

Fig. 11(b). Thermodynamics for $Ac^-(s) + H_2O(s) = HAc(s) + OH^-(s)$ where Ac = acetate versus wt% organic solvent component. Equations (13), (14), (20)-(22): 4 = THF-water, 5 = dioxane-water, G = δG, H = δH, S = $T\delta S$.

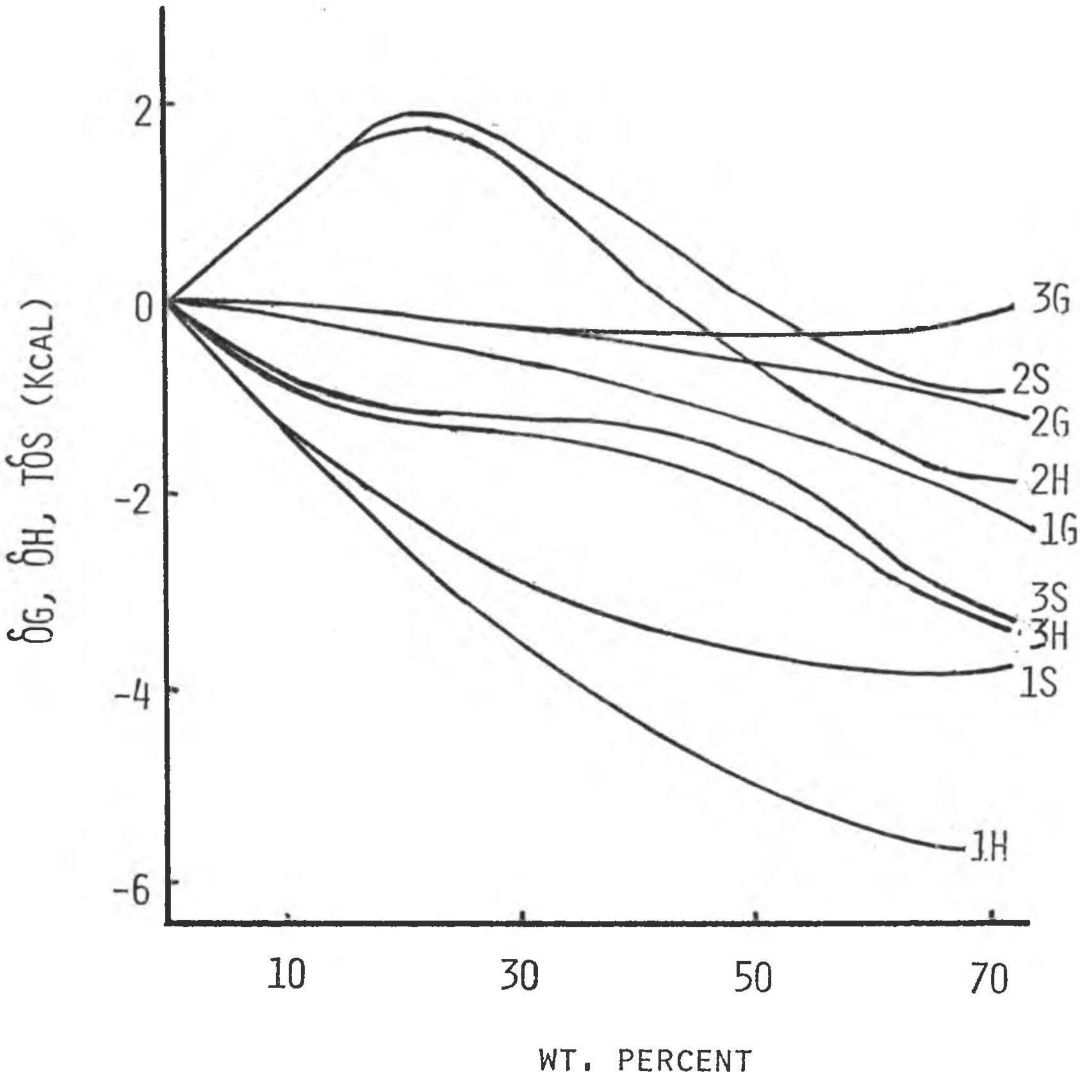

Fig. 12(a). Thermodynamics for $Bz^-(s) + H_2O(s) = HBz(s) + OH^-(s)$ where Bz = benzoate versus wt% organic solvent component. Equations (13), (14), (20-(22). 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

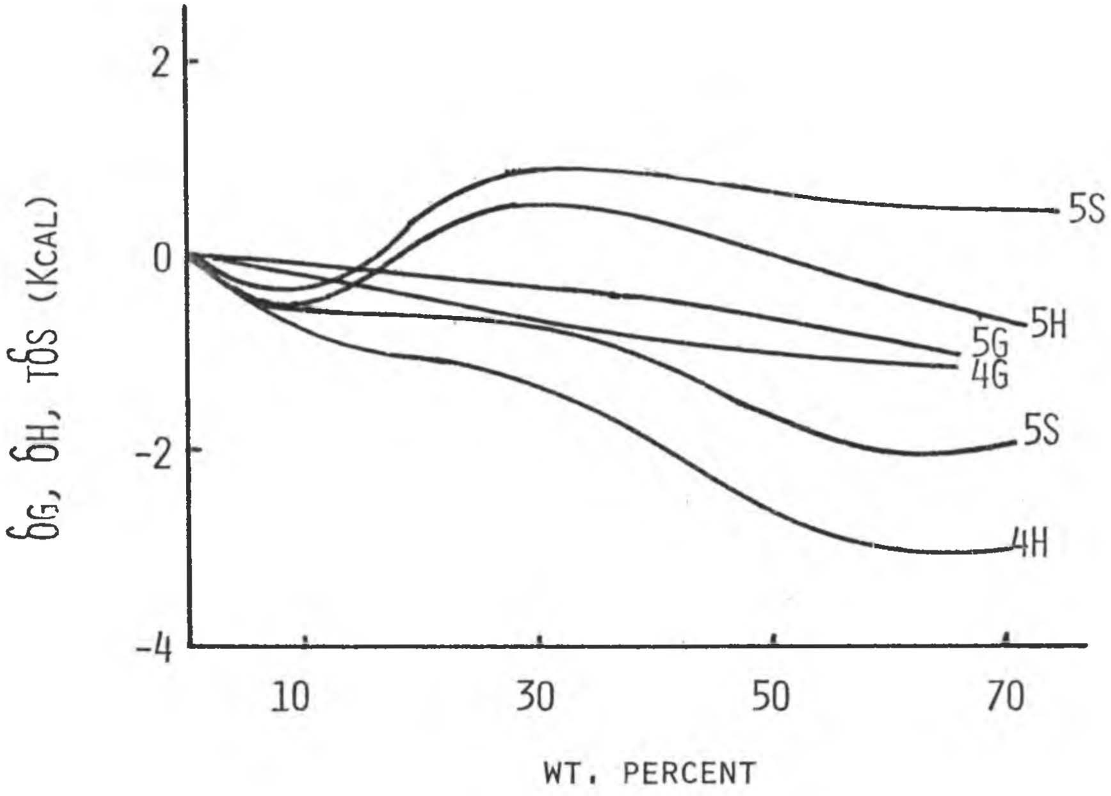

Fig. 12(b). Thermodynamics for Bz^-(s) + H_2O(s) = HBz(s) + OH^-(s) where Bz = benzoate versus wt% organic solvent component. Equations (13), (14), (20)-(22): 4 = THF-water, 5 = dioxane-water, G = δG, H + δH, S + TδS.

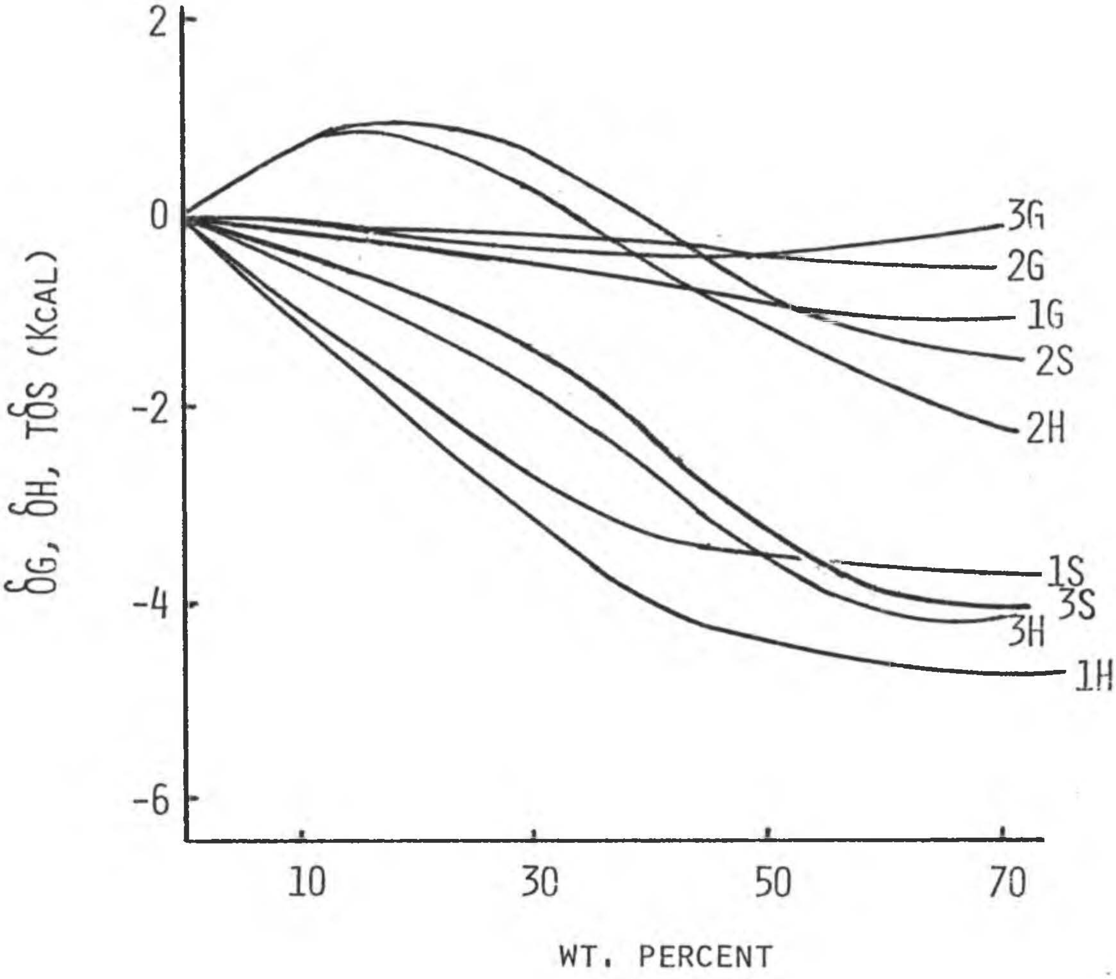

Fig. 13(a). Thermodynamics for $Ph^-(s) + H_2O(s) = HPh(s) + OH^-(s)$ where Ph = phenolate versus wt% organic solvent component. Equation (13), (14), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

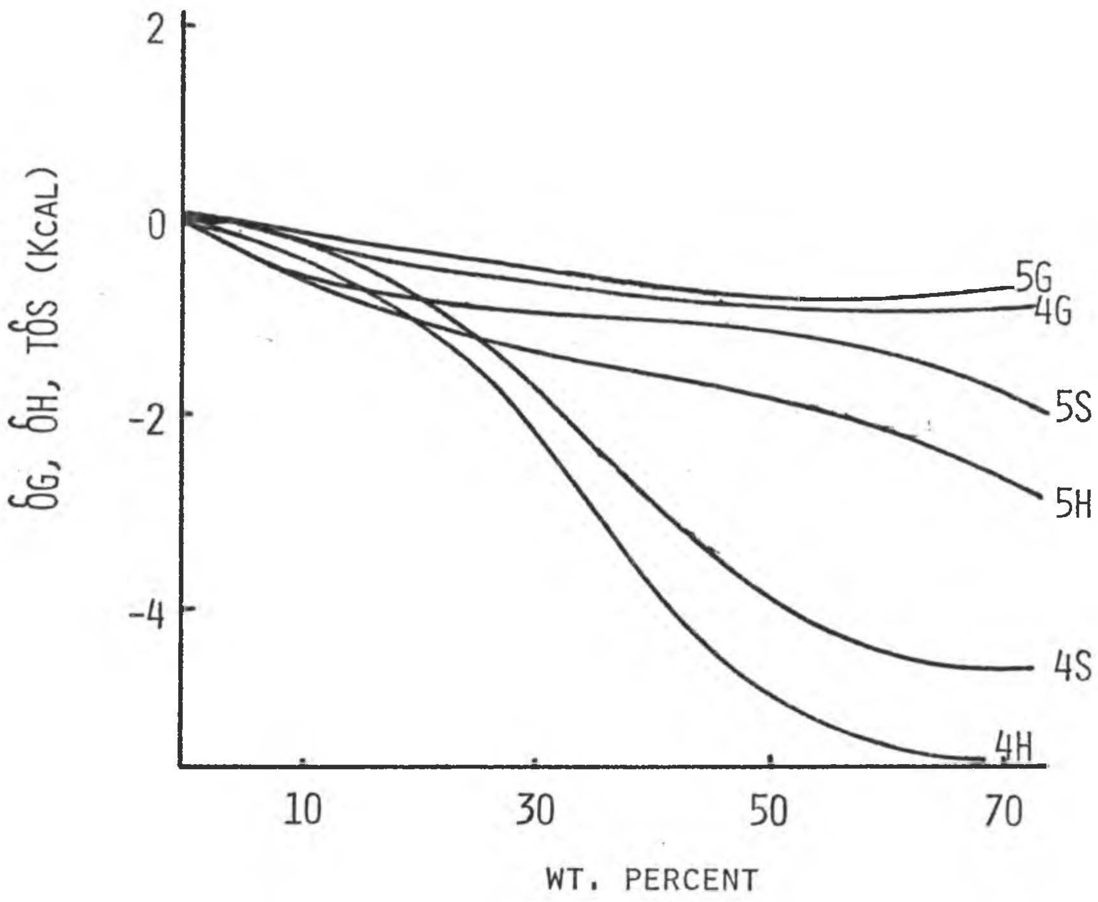

Fig. 13(b). Thermodynamics for $Ph^-(s) + H_2O(s) = HPh(s) + OH^-(s)$ where Ph = phenolate versus wt% organic solvent component. Equations (13), (14), (20)-(22); H = THF-water, 5 = dioxane-water; G = δG, H = δH, S = TδS.

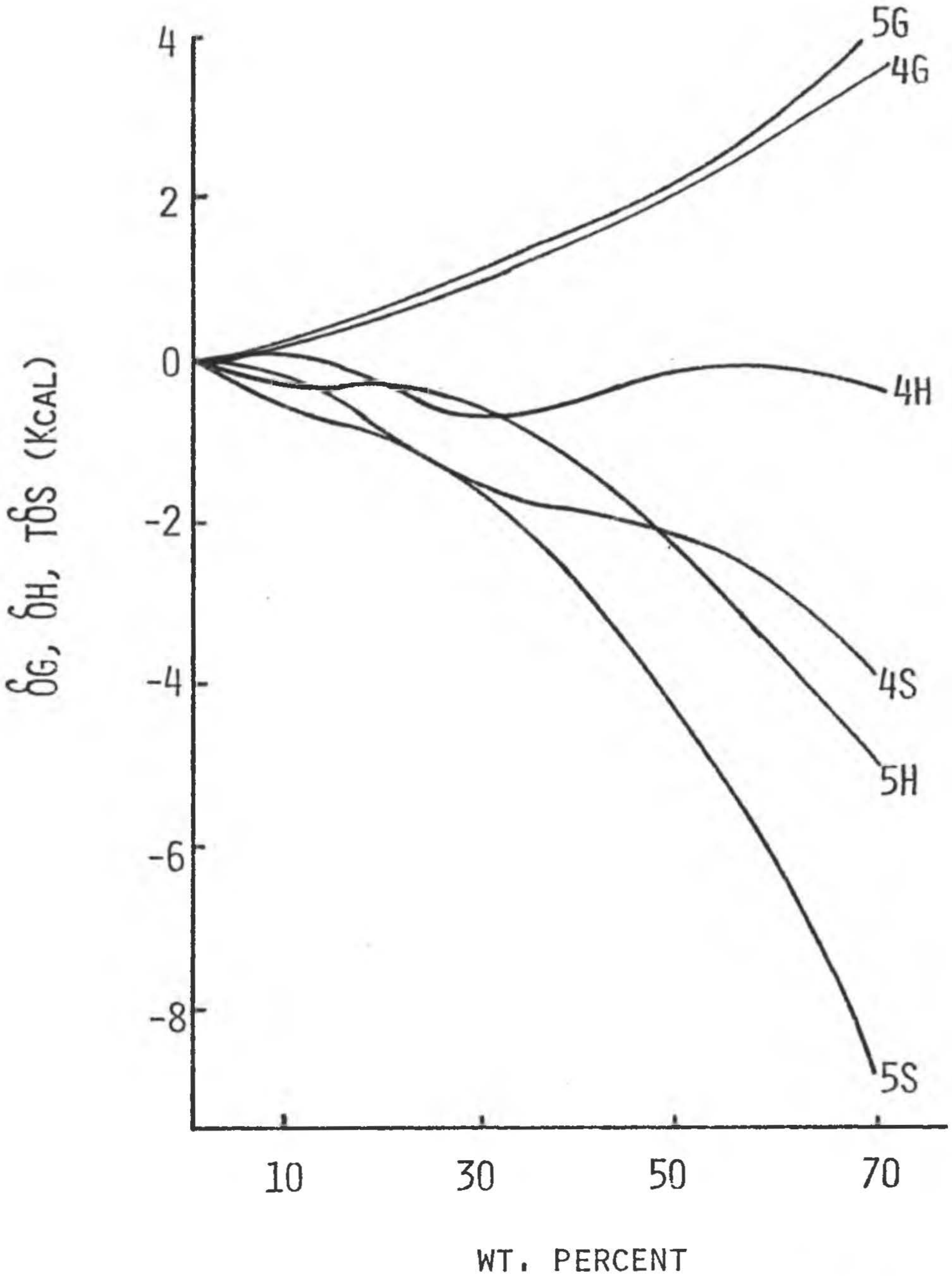

Fig. 14(b). Thermodynamics for AgCl(s) = Ag^+(s) + Cl^-(s) versus wt% organic solvent component. Equations (15), (16), (20)-(22): 4 = THF-water, 5 = dioxane-water; G = δG, H = δH, S = TδS.

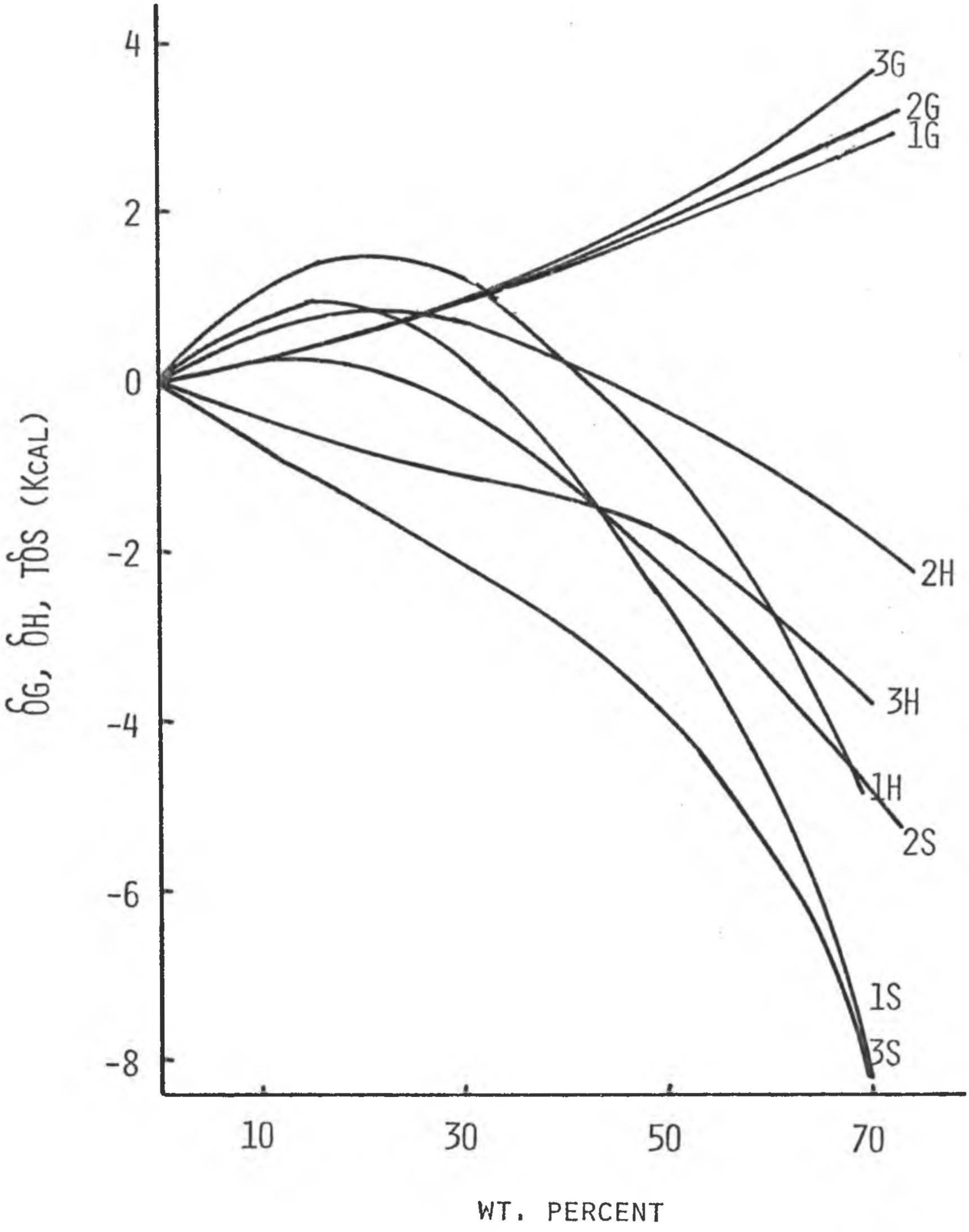

Fig. 14(a). Thermodynamics for AgCl(s) = $Ag^+(s) + Cl^-(s)$ versus wt% organic solvent component. Equations (15), (16), (20)-(22): 1 = methanol-water, 2 = ethanol-water, 3 = acetone-water; G = δG, H = δH, S = TδS.

IV. DISCUSSION

Comparison of Results of This Work with Literature Values

Values of pK_w at 25°C in methanol-water, ethanol-water, acetone-water, and THF-water are in good agreement with results obtained by the same method (28,31) and so are the values in ethanol-water as obtained by Gutbezahl and Grunwald (45). However, the values of pK_w in p-dioxane-water are slightly lower as a result of the somewhat large k_2 values used in equation (8). Values of ΔH_w° are in fair agreement with earlier calorimetric values (46). Values obtained in this work are more positive by about 1 kcal at the highest ethanol compositions.

The pK_a values for acetic acid and benzoic acid in methanol-water are in excellent agreement with those reported previously (47-53), especially those reported by Grunwald and his co-workers (52). The values in ethanol-water also agree well with those obtained by other investigators (1,2,5,6,36,37): the pK values of acetic acid in p-dioxane-water are identical (within experimental error) as the values reported by Harned and co-workers (54).

pK values of phenol in methanol-water are somewhat lower than those reported by Parson and Rochester (55), with the difference being as large as 0.1 log unit.

The pK_s values of AgCl in these solvent systems at 25°C are in fair agreement with previously reported values (24,27,56-59), but they are slightly lower in the acetone mixtures. Deviations are less than 0.10 in all cases where there is more than 50 mass percent water present.

Interpretation of Results

Figures 2 to 6 show the pK values of water, acetic acid, benzoic acid, and phenol, and the pK_s values of silver chloride, respectively at 25°C which increase with increasing organic content in the solvent systems, as expected, on the basis of the decreasing dielectric constant of the medium. Comparison of ionization or solubility, in terms of organic content in these solvent mixtures is in the order MeOH > EtOH > THF ≈ acetone > p-dioxane. Yasuda (60) predicts that a carboxylic acid has almost the same dissociation constant in various mixed solvents having the same dielectric constant. This is not true for pK values of acetic acid and benzoic acid in the mixtures of water with ethanol and acetone which were obtained in this work.

The transfer process for ionization and hydrolysis reactions from water to the aqueous-organic mixtures is demonstrated in Figures 7 to 14. The transfer free energy, δG, of ionization is positive for all weight percentages of all solvent systems, which indicates that these acids or salts are in higher free energy states in the mixed solvent than in water, or that the transfer is not favored. Contrarily the δG for hydrolysis reactions seem to be small and negative.

Some useful insight with regard to the changes in the structural features of the solvents might be obtained from observation of the change of the enthalpy, $\Delta H°$, and the change of the entropy, ΔS°, since the Gibbs free energy of transfer is not particularly sensitive to structural factors, because of partial cancellation of enthalpy and entropy contributions, while the enthalpy and the entropy are. Feakins (61), Franks and Ives (62), and Bates (63) and many other investigators emphasized the use of these thermodynamic quantities (ΔH°, ΔS°) besides ΔG°, to explain the structural effects of the solvents involved on the transfer process.

One can interpret the trends in δH and δS in Figures 7 to 14 in terms of solvation of the reactants and/or products (36,37). The negative values of δH are possible indication that the products in the reaction are more strongly solvated in solvent S than they are in water. Positive δH values also might indicate that reactants in the reaction are more strongly solvated in water than in solvent S. Positive δH may also indicate a structure-breaking process, which is endothermic, in which the net amount of order created by the ions in the mixed solvent is thus less than in water. Conversely, negative δH may indicate a structure-forming process, which is exothermic, where the ions create more order in the mixed solvent S than in water (61,68). Another possible factor in the interpretation of δH versus solvent composition data is the possibility of large contributions of solvent-solvent interactions.

Similar complicated possibilities exist in interpreting δS data, for one must consider the total entropy change for the reaction, including reactants, products, and solvent.

As we can see from Figures 7 to 14, the δG curves for the transfer ionization and hydrolysis reactions vary in a simple way as the organic content increases while the δH and TδS curves do not have uniform shapes. The structural features of solvents probably have some influence on δH and δS, because of the interaction between ions and solvents. Detailed discussion of the possible interpretation follows.

The ionization of acetic acid in the mixed solvents, as shown in Figures 8(a) and 8(b) (the values of the transfer energy, δG,) indicates that in the overall process the ionization in water is more favorable than in the mixed solvents. We may assume that there are two additive parts of thermodynamic functions contributing to the free energy of an ion in the transfer process, electrostatic (el) and chemical or non-electrostatic (chem). (There will be an interaction between the change on the ion and the dipolemoment of the solvent molecules.) The electrostatic effect is caused predominantly by the change in the dielectric constant of the medium. The chemical contribution mainly reflects the solvating capacity as well as specific chemical interactions (basicity). These involve the destruction of one type of solvation shell and the creation of another; the hydrogen bonds will be made or broken, strengthened or weakened. By the use of the Gibbs energy transfer we obtain the following equation (63,69-70):

$$\Delta G^\circ_t = (RT \ln 10)[pK_s - pK_w] = \Delta G^\circ_t(el) + \Delta G^\circ_t\,(chem) \qquad (23)$$

where w and s refer, respectively, to water and water-organic mixture. The electrostatic part of the free energy changes can be computed approximately from the Born equation (24), (71)

$$\Delta G^\circ_t(el) = (Ne^2/2)[\varepsilon(s)^{-1} - \varepsilon(w)^{-1}](r_+^{-1} + r_-^{-1}) \qquad (24)$$

where N is Avogadro's number, e is the unit of charge, r_+ and r_- are the effective radii of the cation and the anion and $\varepsilon(s)$ and $\varepsilon(w)$ are the dielectric constants of the mixed solvent and water, respectively. The non-electrostatic part of the thermodynamic quantities, can be obtained by subtracting $\Delta G_t^\circ(el)$ from the total values, ΔG_t°.

The equations (23) and (24) were applied to the transfer free energy data of acetic acid in the mixed solvents and the results are in Table III. For this comparison, pK values on the molarity scale were used, and the radii of solvated proton and acetate ions were taken as 2.8 and 1.82 A°, respectively (72).

We can see from Table III that the values of $\delta G_t^\circ(chem)$ are always less than those of $\delta G_t^\circ(el)$, this makes the electrostatic contribution predominate the over all free energy of transfer. In addition to the smooth curves of δG and the atypical curves of δH and δS, we may assume that the free energy of transfer is not particularly affected by structural factors as much as the enthalpy and entropy are.

The electrostatic part of the free energy change in these mixed solvents increases uniformly as the organic content increases, owing to the decrease in the dielectric constants of the media. The chemical part in the methanol, ethanol, and acetone-water mixtures is also positive, indicating the transfer process from water to the mixed solvents is not favorable, or the mixtures are less "basic" than water (61-68). Both effects, electrostatic and chemical, contribute to the positive values of the total transfer free energy; however, both of them are small in these three mixtures. It is interesting to note that in THF-water and p-dioxane-water mixtures, the non-electrostatic part, ΔG_t°(chem), of the free energy change, ΔG_t°, is fairly uniform and becomes negative as the mole fraction increases, whereas the electrostatic part, ΔG_t°(el) becomes more positive owing to the great difference in dielectric constants of the organic solvents and water. The negative ΔG_t°(chem) suggests that the transfer process from water to the solvent mixture is favorable insofar as the chemical interaction is concerned. Thus, tetrahydrofuran and p-dioxane promote the ionization process more effectively in mixed solvents and they show greater "basicity" than water. However, the large electrostatic effect predominates entirely over the chemical interaction or solvation causing an unfavorable effect in the overall process. Comparison of the "basicity" of these five solvent mixtures, shows that p-dioxane > THF > ethanol > methanol > acetone.

The Gibbs free energy claculations based on Born's model are fairly good to draw some general conclusions of a qualitative nature, but the uncertainties in the entropies and enthalpies are greater, chiefly because of the "arbitrary" choices of the ionic radii in the Born equation and the dielectric constant of the medium.

More possible interpretation of the data might be as follows The δG, δH, and $T\delta S$ for the total transfer process will be used.

Acetic Acid

From Figures 8(a) and 8(b), we see that δH and δS for the ionization of acetic acid are different in different solvent systems. In water-methanol, there is a maximum in δH at about 13% alcohol.

The transfer enthalpy is endothermic up to ~ 60% alcohol, which indicates that in the water-rich region, acetic acid meets more structure resistance than in the alcohol-rich region (61,62,73,74). The proton and acetate ions are less solvated in the water-methanol mixture than in pure water. When the co-solvent composition increases, the decreasing values of δH and $T\delta S$ support the view that the proton and acetate ions are solvated more as a result of hydrogen bonding interactions of the ions with solvent molecules (61,62,73). As the organic content increases, the water-methanol mixture becomes less associated than pure water. We may say that the acetic acid "breaks more structure" (62) in the mixed solvent in the water-rich region than in pure water and "breaks more structure" in pure water than the mixture in the alcohol-rich region.

In the mixtures of water-ethanol, the δH curves do not show maxima as found with other acids by some workers (62,75-77). The $T\delta S$ values predominantly contribute to the unfavorable δG. The solvation of proton and acetate ions appears to be stronger in the mixed solvent than in water (or the acetic acid is more strongly solvated in water than in the mixed solvent) all the way through the solvent composition. This trend seems to be stronger than in water-methanol. Hydrogen bond formation between the ions and ethanol molecules is stronger than with methanol, since the inductive effect from the ethyl group is more than from the methyl group.

Acetone and ethanol are nearly isodielectric, but the former is a dipolar aprotic solvent and the latter is an amphiprotic solvent (7). The δH and $T\delta S$ curves in these two solvents are quite different.

It is interesting that the curves of acetone-water and THF-water mixtures are somewhat similar. The transfer of acetic acid from water to water-acetone mixtures and to water-THF mixtures is at first an exothermic process. The enthalpy of transfer is at a minimum in the range 15 to 25 mass percent for the former and 25 to 35 mass percent of the organic content for the latter. The process becomes endothermic at about 40% for acetone and 45% for THF. It is likely that the proton and acetate ions are more strongly solvated at first in these two mixtures than in water and become less solvated as the organic co-solvent composition increases. In acetone, there is even a maximum and the values become exothermic again. It is not easy to explain this kind of behavior of the solutes and solvent right at this time.

In the mixtures of water-ethanol, the δH curves do not show maxima as found with other acids by some workers (75-77). The $T\delta S$ values predominantly contribute to the unfavorable δG. The solvation of proton and acetate ions appears to be stronger in the mixed solvent than in water (or the acetic acid is more strongly solvated in water than in the mixed solvent) all the way through the solvent composition. This trend seems to be stronger than in water-methanol. Hydrogen bond formation between the ions and ethanol molecules is stronger than with methanol, since the inductive effect from the ethyl group is more than from the methyl group.

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THF-water mixtures are somewhat similar. The transfer of acetic acid from water to water-acetone mixtures and to water-THF mixtures is at first an exothermic process. The enthalpy of transfer is at a minimum in the range 15 to 25 mass percent for the former and 25 to 35 mass percent of the organic content for the latter. The process becomes endothermic at about 40% from acetone and 45% for THF. It is likely that the proton and acetate ions are more strongly solvated at first in these two mixtures than in water and become less solvated as the solvent composition increases. In acetone, there is even a maximum and the values become exothermic again. It is not easy to explain this kind of behavior of the solutes and solvent right at this time.

In water–dioxane mixtures, the enthalpy takes positive values and passes through a maximum in the water-rich region. The increase in organic solvent content causes δH to become negative. This may be explained in the same way as was done for water-methanol mixtures by earlier workers (61-64, 77-79). The addition of the original co-solvent to water at first results in mixtures of higher structural order than that of water alone. In such mixtures the ions meet more structural resistance to their own tendency to make structure than in water, and their enthalpy rises. As more organic solvent is added, the structure of the mixed solvent breaks down relative to that of water, and ions find it easier to create their own structure. Thus their enthalpy falls. The rapid decrease in $T\delta S$ supports this view. The maximum of the δH curve is in the range 20 to 30 wt. percent. Since dioxane is an "inert" solvent (64), the mixture is less structured than water. Hence, in the mixed solvent, the proton and acetate ions will lose at least part of the structure-breaking enthalpy they had in water. Because of the inductive effect of the methylene groups, the negative charge on an oxygen is greater in the dioxane molecule than in the water molecule. Further, a dioxane molecule can induce in a water molecule hydrogen-bonded to it an increased negative charge on the oxygen atom and a decreased positive charge on the hydrogen atoms. These effects are likely to make a water-dioxane mixture more "basic" and less "acid" than pure water (64). As can be seen from Figure 8(b), beyond 45% the δH and $T\delta S$ decrease rapidly, indicating the solvation in the p-dioxane-water mixture is more than in water and the ions tend to cause the mixture to be more structured than they tend to cause water to be more structured.

It is difficult to compare the degree of solvation of acetic acid, the proton, and acetate ions in these five solvent systems. The values of δH and $T\delta S$ vary non-uniformly with solvent composition in these solvents. Thus, the general trend that can be given for the ionization of acetic acid in these solvents is that δG decreases in the mixture in the order p-dioxane > acetone > THF > ethanol > methanol.

Benzoic Acid

The ionization of benzoic acid is shown in Figures 9(a) and 9(b). The decrease in the transfer free energy, δG is in the order THF > acetone > p-dioxane > ethanol > methanol (but p-dioxane values increase rapidly beyond 60%).

In methanol-water mixture, the transfer enthalpy is endothermic with a maximum in the range of 20 to 30%. The benzoate ions and the proton meet more structure resistance than in pure water and the mixture becomes less associated as the organic content increases (61-63,74,78,80,81). The proton and the benzoate ions are less strongly solvated in the solvent mixture than in pure water. Also the ions tend to cause less structuring in the mixed solvent than in water or the benzoic acid "breaks more structure" in water than in the mixed solvent.

In ethanol-water mixtures, the δH and TδS show opposite directions of curvature from that found with other acids in aqueous alcohol solutions. Usually the transfer enthalpy is at first endothermic, but here it is exothermic with a minimum and it gradually increases as the solvent composition increases. This implies that the proton and the benzoate ions are more strongly solvated in the mixture at first than in pure water.

In acetone-water solvent mixture, the δH of the reaction is endothermic, indicating the ions break more structure in the mixture than in the water. The positive δH and the negative TδS contribute effectively to the large δG. Benzoic acid is more solvated in the mixed solvent than in water, but the proton and the benzoate ions are solvated in water more than the mixed solvent.

The δH curve in the THF-water mixture is irregular in going from positive to negative values. However, the net result in δG suggests that the ionization of benzoic acid in the mixture is unfavored relative to that in pure water.

The ionization in p-dioxane-water mixtures demonstrates a regular type which is found as in acetic acid. The large negative values of TδS have an effect on the large δG.

Phenol

Figures 10(a) and 10(b), show the ionization of phenol in the mixed solvents. The enthalpy changes in methanol and ethanol-water mixtures are similar to those of benzoic acid. This might link to the ring structure and size of these two acids, which, not too surprisingly, seem to be more closely related to one another than acetic acid. The enthalpy change in acetone-water mixture is large and positive. Also the transfer enthalpy of the phenol reaction in THF-water solvent is quite large and positive. The δH in p-dioxane-water mixture still shows a maximum, but it is positive up to 70 wt. % indicating the acid breaks more structure in acetone, THF, and p-dioxane in water than in the mixtures, or that the proton and phenolate ions are less strongly solvated in the mixtures than in water.

It is interesting to note that if we roughly compare the ionization of acetic acid, benzoic acid, and phenol, we might find that the ionization of acetic acid > benzoic acid > phenol. The solvation of the proton and the three ions in the solvent mixtures are in the same order. The structure of these acids have an important effect on the interactions between the solute and solvent. Benzoic acid is intermediate between acetic acid and phenol, since it contains both a carboxyl group and a ring. If one wishes to compare the ionization in these solvent mixtures there are many factors contributing to the whole process. Methanol, which has a dielectric constant closest to that of water is least favorable to the transfer process. We still need more information to explain in more detail the solvent-solvent and also the solute-solvent interactions in these mixed solvents.

The ioselectronic reaction is one in which a proton is transfered without the creation of a new electric field; for example,

$$CH_3COO^- + H_2O \leftrightarrows OH^- + CH_3COOH$$

The electrical work of transfer is small, but not zero. If this approach were valid, we would expect to see the values of δG for the hydrolysis reaction of acetic acid, benzoic acid, and phenol nearly zero in all solvents. The fact that the trends, including δH and $T\delta S$ are generally somewhat smaller in magnitude for these hydrolysis reactions than for the ionization reaction (see Figures 7 to 14) lends some support of this idea.

The transfer free energies of the three acids are small and negative in all solvents, as the organic solvent content increases. The negative values of δG indicate that the acid itself (and maybe the hydroxyl ion on the right-hand side of the reactions) is more strongly solvated in the mixed solvent than in pure water in the transfer process. The transfer process is favorable in all cases. Comparison of δG for acetic acid shows the trend acetone > THF > ethanol >p-dioxane > methanol. In Figure 11(a) and (b) the hydrolysis reaction of the acetate ion in water-methanol solvent and THF-water mixture shows the strongest solvation among these five solvents. The values of δH and $T\delta S$ suggest that the unionized acetic acid is more strongly solvated in the organic mixture than in pure water. The acetic acid can cause the solvent mixture to be more structured than it tends to cause water to be structured. The acetate ions are more strongly solvated in pure water than in the mixed solvent and tend to cause the water to be more structured than they tend to do to the mixed solvents. The effect of solvation in these mixtures is in the order methanol > THF > p-dioxane ~ acetone > ethanol.

In Figures 12(a) and 12(b), the δG for the hydrolysis reaction of benzoic acid is in this order: acetone > p-dioxan > THF > ethanol > methanol. The solvation of benzoic acid in the solvent mixtures is approximately in the order methanol > THF > acetone > ethanol > p-dioxane.

For the mixtures of methanol-water, THF-water, and acetone-water, the δH and TδS are all negative, indicating that benzoic acid is more strongly solvated in the mixtures than in water, and that it also causes the mixture to be more structured. The values of δH and TδS in ethanol-water solvent are positive and have a maximum in the range 20 to 30 wt. percent and become negative between 50-60 wt. percent. The δH and TδS values in p-dioxane are at first exothermic, then become endothermic at about 15% dioxane.

For phenol, the values of δG are in this order: acetone ~ ethanol > dioxane > THF > methanol. The δH and TδS values in all solvents, except for ethanol-water, are negative, suggesting that phenol is more strongly solvated in the mixed solvent than in pure water and also tends to cause more structure. The mixtures of ethanol with water show at first a positive enthalpy change which becomes negative between 40-50 wt. percent alcohol.

The study of solubility of silver chloride in the aqueous organic mixtures is shown in Figures 14(a) and 14(b). The transfer free energies of silver and chloride ions from water to the mixed solvents are all positive, implying the process is unfavorable. The δG values in the five solvents are not much different and the order is acetone ~ dioxane > THF > ethanol > methanol.

In aqueous mixtures of methanol and ethanol, the transfer enthalpy shows a typical pattern as found in aqueous alcohol solvents, (62,75-77) silver and chloride ions lose their enthalpy and entropy in water more than in methanol-water mixtures. The δH and $T\delta S$ values in acetone-water are all negative. The Ag^+ and Cl^- ions seem to be more strongly solvated in these solvents than in water and they tend to cause the mixed solvents to be more structured than they tend to cause water to be structured.

V. SUMMARY AND CONCLUSION

A new rapid and convenient method is described for obtaining relatively precise values of ionization constants for water, weak acids (or bases), and certain solids in aqueous-organic mixed solvents. The method has been applied to determination of ionization constants for water, acetic acid, benzoic acid, and phenol and the solubility product constant for silver chloride in mixtures of water with methanol, ethanol, acetone, tetrahydrofuran, and dioxane containing from 0 to 70 mass percent organic co-solvent at several temperatures between 10 and 40°C. Results are used in conjunction with the van't Hoff relationship to obtain ΔH° values for the ionization reactions in each mixture. The thermodynamic properties are discussed relative to various topics of ion-ion, ion-solvent, ion-molecule, molecule-solvent, and solvent-solvent interactions on the basis of theories of electrostatics, solvation, and solvent and solution structure.

TABLE I

THE BEST VALUES OF THERMODYNAMIC FUNCTIONS[a]

FOR WATER IN WATER-ETHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	14.00	19.11	13.50	18.8
5.0	14.09	19.23	13.85	18.0
10.0	14.20	19.38	14.13	17.6
15.0	14.28	19.49	14.30	17.4
20.0	14.39	19.64	14.35	17.7
25.0	14.49	19.78	14.31	18.3
30.0	14.59	19.92	14.17	19.3
35.0	14.70	20.07	13.95	20.5
40.0	14.81	20.22	13.69	21.9
45.0	14.93	20.38	13.42	23.3
50.0	15.04	20.53	13.10	24.9
55.0	15.17	20.71	12.75	26.7
60.0	15.28	20.86	12.38	28.4
65.0	15.43	21.06	11.97	30.5
70.0	15.56	21.24	11.58	32.4

TABLE I--Continued

FOR WATER IN WATER-ACETONE MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.00	14.00	19.11	13.50	18.8
5.00	14.14	19.30	13.38	19.9
10.00	14.27	19.48	13.26	20.9
15.00	14.42	19.68	13.24	21.6
20.00	14.57	19.89	13.33	22.0
25.00	14.73	20.11	13.27	22.9
30.00	14.90	20.34	13.18	24.0
35.00	15.09	20.60	13.08	25.2
40.00	15.28	20.86	12.98	26.4
45.00	15.51	21.17	12.87	27.8
50.00	15.76	21.51	12.76	29.3
55.00	16.04	21.89	12.65	31.0
60.00	16.36	22.33	12.53	32.9
65.00	16.70	22.83	12.40	35.0
70.00	17.16	23.42	12.28	37.4

TABLE I--*Continued*

FOR WATER IN WATER-METHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.00	14.00	19.11	13.50	18.8
5.00	14.02	19.14	13.26	19.7
10.00	14.04	19.16	12.96	20.8
15.00	14.05	19.18	12.60	22.1
26.00	14.07	19.21	12.20	23.5
25.00	14.08	19.22	11.78	25.0
30.00	14.11	19.26	11.36	26.5
35.00	14.13	19.29	10.90	28.1
40.00	14.16	19.33	10.47	29.7
45.00	14.18	19.36	10.05	31.2
50.00	14.22	19.41	9.64	32.3
55.00	14.26	19.46	9.27	34.2
60.00	14.30	19.52	8.97	35.4
65.00	14.35	19.59	8.74	36.4
70.00	14.40	19.66	8.54	37.3

TABLE I--Continued

FOR WATER IN WATER-THF MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	$-\Delta S^\circ$
0.00	14.00	19.11	13.50	18.8
5.00	14.09	19.23	13.30	19.9
10.00	14.20	19.38	13.07	21.2
15.00	14.31	19.53	12.85	22.4
20.00	14.42	19.68	12.56	23.9
25.00	14.54	19.85	12.18	25.7
30.00	14.67	20.02	11.66	28.0
35.00	14.83	20.24	11.15	30.5
40.00	14.98	20.45	10.78	32.4
45.00	15.17	20.71	10.58	34.0
50.00	15.39	21.01	10.50	35.3
55.00	15.64	21.35	10.57	36.2
60.00	15.93	21.74	10.92	36.3
65.00	16.25	22.18	11.40	36.2
70.00	16.60	22.66	11.90	36.1

TABLE I--Continued

FOR WATER IN WATER-p-DIOXAN MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	14.00	19.11	13.5	18.8
5.0	14.10	19.25	13.37	19.7
10.0	14.20	19.38	13.30	20.4
15.0	14.31	19.52	13.40	20.5
20.0	14.43	19.70	13.77	19.9
25.0	14.55	19.86	13.84	20.2
30.0	14.69	20.05	13.68	21.4
35.0	14.84	20.26	13.45	22.8
40.0	15.02	20.50	13.20	24.5
45.0	15.21	20.76	12.92	26.3
50.0	15.45	21.09	12.60	28.5
55.0	15.74	21.49	12.25	31.0
60.0	16.08	21.95	11.88	33.8
65.0	16.48	22.50	11.47	37.0
70.0	16.95	23.14	11.03	40.6

TABLE I--Continued

FOR ACETIC ACID IN WATER-ETHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	-ΔH°	-ΔS°
0.0	4.75	6.48	0.10	22.1
5.0	4.82	6.58	0.12	22.5
10.0	4.90	6.69	0.14	22.9
15.0	4.99	6.81	0.18	23.4
20.0	5.08	6.93	0.19	23.9
25.0	5.20	7.10	0.22	24.6
30.0	5.32	7.26	0.23	25.1
35.0	5.45	7.44	0.18	25.6
40.0	5.57	7.60	0.15	26.0
45.0	5.72	7.18	0.13	26.6
50.0	5.87	8.01	0.20	27.5
55.0	6.03	8.23	0.42	29.0
60.0	6.18	8.44	0.57	30.2
65.0	6.35	8.67	0.59	31.1
70.0	6.53	8.91	0.35	31.1

TABLE I--Continued

FOR ACETIC ACID IN WATER-ACETONE MIXTURES AT 25°C

wt%	pK	ΔG°	-ΔH°	-ΔS°
0.0	4.75	6.48	0.10	22.1
5.0	4.86	6.63	0.23	23.0
10.0	4.98	6.80	0.34	23.9
15.0	5.11	6.98	0.45	24.9
20.0	5.24	7.15	0.50	25.7
25.0	5.38	7.34	0.51	26.3
30.0	5.54	7.56	0.45	26.9
35.0	5.73	7.82	0.34	27.4
40.0	5.92	8.08	0.23	27.9
45.0	6.14	8.38	0.15	28.6
50.0	6.37	8.70	0.08	29.4
55.0	6.65	9.08	0.06	30.7
60.0	6.95	9.49	0.18	32.4
65.0	7.29	9.95	0.53	35.2
70.0	7.66	10.46	0.78	37.7

TABLE I--Continued

FOR ACETIC ACID IN WATER-METHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.75	6.48	-0.10	22.1
5.0	4.82	6.58	0.82	19.3
10.0	4.89	6.67	1.35	17.8
15.0	4.97	6.78	1.39	18.1
20.0	5.05	6.89	1.09	19.5
25.0	5.13	7.00	0.66	21.3
30.0	5.22	7.13	0.52	22.2
35.0	5.31	7.25	0.67	22.1
40.0	5.41	7.38	0.81	22.0
45.0	5.52	7.53	0.79	22.6
50.0	5.64	7.70	0.61	23.8
55.0	5.77	7.88	0.27	26.4
60.0	5.93	8.09	-0.23	27.9
65.0	6.07	8.29	-0.85	30.7
70.0	6.24	8.52	-1.23	32.7

TABLE I--Continued

FOR ACETIC ACID IN WATER-THF MIXTURES AT 25°C

wt%	pK	$\Delta G°$	$\Delta H°$	$-\Delta S°$
0.0	4.75	6.48	-0.10	22.1
5.0	4.84	6.61	-0.35	23.3
10.0	4.94	6.74	-0.56	24.5
15.0	5.05	6.89	-0.71	25.5
20.0	5.16	7.04	-0.79	26.3
25.0	5.28	7.21	-0.84	27.0
30.0	5.43	7.41	-0.83	29.9
35.0	5.57	7.60	-0.73	27.9
40.0	5.77	7.88	-0.44	27.9
45.0	5.96	8.14	-0.14	27.8
50.0	6.19	8.45	0.08	28.1
55.0	6.45	8.80	0.26	28.6
60.0	6.73	9.19	0.43	29.4
65.0	7.05	9.62	0.57	30.4
70.0	7.39	10.09	0.69	31.5

TABLE I--Continued

FOR ACETIC ACID IN WATER-p-DIOXANE MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.75	6.48	0.10	22.1
5.0	4.87	6.65	0.13	22.7
10.0	5.00	6.83	0.18	23.5
15.0	5.14	7.02	0.14	24.0
20.0	5.28	7.21	-0.23	23.4
25.0	5.44	7.42	-0.29	23.9
30.0	5.62	7.67	-0.22	24.3
35.0	5.82	7.94	-0.12	26.2
40.0	6.02	8.22	-0.02	27.5
45.0	6.26	8.54	0.12	29.0
50.0	6.53	8.91	0.27	30.8
55.0	6.85	9.35	0.49	33.0
60.0	7.22	9.86	0.74	35.6
65.0	7.65	10.44	1.10	38.7
70.0	8.29	11.32	1.34	42.5

TABLE I--Continued

FOR BENZOIC ACID IN WATER-ETHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.20	5.73	0.10	18.9
5.0	4.32	5.90	-0.06	20.0
10.0	4.46	6.09	-0.24	21.2
15.0	4.60	6.28	-0.67	23.3
20.0	4.74	6.47	-0.80	24.4
25.0	4.88	6.66	-0.75	24.9
30.0	5.04	6.88	-0.50	24.8
35.0	5.19	7.08	-0.14	24.2
40.0	5.35	7.30	0.07	24.2
45.0	5.52	7.53	0.24	24.5
50.0	5.70	7.78	0.36	24.9
55.0	5.88	8.03	0.43	25.5
60.0	6.07	8.29	0.44	26.3
65.0	6.26	8.54	0.34	27.5
70.0	6.47	8.83	0.03	29.5

TABLE I--Continued

FOR BENZOIC ACID IN WATER-ACETONE MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.20	5.73	0.10	18.9
5.0	4.35	5.94	0.52	18.2
10.0	4.53	6.18	0.80	18.0
15.0	4.70	6.42	1.05	18.0
20.0	4.88	6.66	1.17	18.4
25.0	5.07	6.92	1.24	19.1
30.0	5.28	7.21	1.26	20.0
35.0	5.49	7.49	1.23	21.0
40.0	5.73	7.82	1.19	22.2
45.0	5.97	8.15	1.12	23.6
50.0	6.23	8.50	1.03	25.1
55.0	6.53	8.91	1.55	24.7
60.0	6.81	9.30	1.97	24.6
65.0	7.12	9.72	2.14	25.4
70.0	7.47	10.20	2.23	26.7

TABLE I--Continued

FOR BENZOIC ACID IN WATER-METHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	$-\Delta S^\circ$
0.0	4.20	5.73	0.10	18.9
5.0	4.27	5.83	0.70	17.2
10.0	4.36	5.95	1.04	16.5
15.0	4.46	6.09	1.28	16.1
20.0	4.56	6.22	1.42	16.1
25.0	4.66	6.36	1.46	16.4
30.0	4.77	6.51	1.14	17.0
35.0	4.89	6.67	1.42	17.6
40.0	5.03	6.87	1.35	18.5
45.0	5.17	7.06	1.26	19.5
50.0	5.34	7.29	1.15	20.6
55.0	5.51	7.52	1.04	2.17
60.0	5.68	7.75	0.95	22.8
65.0	5.87	8.01	0.93	23.7
70.0	6.07	8.29	1.07	24.2

TABLE I--Continued

FOR BENZOIC ACID IN WATER-THF MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.20	5.73	0.10	18.9
5.0	4.37	5.97	0.42	18.6
10.0	4.56	6.22	0.47	19.3
15.0	4.75	6.48	0.36	20.5
20.0	4.96	6.77	0.12	22.3
25.0	5.16	7.04	-0.19	24.2
30.0	5.37	7.33	-0.42	27.6
35.0	5.60	7.64	-0.56	27.5
40.0	5.83	7.96	-0.58	28.6
45.0	6.06	8.27	-0.46	29.3
50.0	6.32	8.63	-0.16	29.5
55.0	6.59	9.00	0.23	29.4
60.0	6.86	9.36	0.58	29.4
65.0	7.16	9.77	0.85	29.9
70.0	7.48	10.21	1.07	30.7

TABLE I--Continued

FOR BENZOIC ACID IN WATER-p-DIOXAN MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	4.20	5.73	0.10	18.9
5.0	4.34	5.92	0.46	18.3
10.0	4.48	6.11	0.47	18.9
15.0	4.64	6.33	0.28	20.3
20.0	4.80	6.55	0.09	21.7
25.0	4.98	6.80	-0.06	23.0
30.0	5.16	7.04	-0.21	24.3
35.0	5.37	7.33	-0.33	25.7
40.0	5.59	7.63	-0.44	27.1
45.0	5.85	7.98	-0.59	28.7
50.0	6.15	8.39	-0.77	30.7
55.0	6.49	8.86	-0.95	32.9
60.0	6.90	9.42	-1.16	35.5
65.0	7.41	10.11	-1.39	38.6
70.0	8.07	11.01	-1.63	42.4

TABLE I--Continued

FOR PHENOL IN WATER-ETHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	9.97	13.61	5.58	26.9
5.0	10.08	13.76	5.53	27.6
10.0	10.22	13.95	5.50	28.3
15.0	10.35	14.13	5.51	28.9
20.0	10.47	14.29	5.53	29.4
25.0	10.62	14.50	5.65	29.7
30.0	10.75	14.67	5.81	29.7
35.0	10.90	14.89	5.97	30.0
40.0	11.04	15.07	6.14	30.0
45.0	11.18	15.26	6.33	30.0
50.0	11.34	15.48	6.44	30.3
55.0	11.48	15.67	6.35	31.3
60.0	11.64	15.89	6.17	32.60
65.0	11.79	16.09	5.97	33.9
70.0	11.95	16.31	5.77	35.4

TABLE I--Continued

FOR PHENOL IN WATER-ACETONE MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	9.97	13.61	5.58	26.9
5.0	10.14	13.84	5.73	27.2
10.0	10.33	14.10	5.90	27.5
15.0	10.52	14.36	6.12	27.6
20.0	10.72	14.63	6.35	27.8
25.0	10.93	14.92	6.63	27.8
30.0	11.13	15.19	6.96	27.6
35.0	11.33	15.47	7.30	27.4
40.0	11.53	15.74	7.68	27.0
45.0	11.76	16.05	8.05	26.8
50.0	12.00	16.38	8.42	26.7
35.0	12.25	16.72	8.61	27.2
60.0	12.52	17.09	8.70	28.1
65.0	12.78	17.44	8.58	29.7
70.0	13.08	17.85	8.28	32.1

TABLE I--Continued

FOR PHENOL IN WATER-METHANOL MIXTURES AT 25°C

wt%	pK	$\Delta G°$	$\Delta H°$	$-\Delta S°$
0.0	9.97	13.61	5.58	26.9
5.0	10.04	13.70	5.95	26.0
10.0	10.12	13.81	6.23	25.42
15.0	10.19	13.91	6.37	25.29
20.0	10.28	14.03	6.47	25.36
25.0	10.36	14.14	6.54	25.49
30.0	10.45	14.26	6.58	25.76
35.0	10.54	14.39	6.57	26.23
40.0	10.64	14.52	6.48	26.97
45.0	10.73	14.65	6.33	27.91
50.0	10.82	14.77	6.07	27.18
55.0	10.92	14.91	5.76	30.69
60.0	11.01	15.03	5.60	31.63
65.0	11.10	15.15	5.60	32.03
70.0	11.20	15.29	5.67	32.27

TABLE I--Continued

FOR PHENOL IN WATER-THF MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	9.97	13.61	5.58	26.9
5.0	10.12	13.81	5.47	28.0
10.0	10.29	14.05	5.48	28.7
15.0	10.47	14.29	5.56	29.3
20.0	10.66	14.55	5.72	29.6
25.0	10.86	14.82	5.89	20.0
30.0	11.08	15.12	6.08	30.3
35.0	11.31	15.43	6.31	30.6
40.0	11.55	15.76	6.64	30.6
45.0	11.80	16.11	7.04	30.4
50.0	12.06	16.46	7.48	30.1
55.0	12.32	16.82	7.93	29.8
60.0	12.60	17.20	8.40	29.5
65.0	12.88	17.58	8.88	29.2
70.0	13.18	17.99	9.28	29.2

TABLE I--Continued

FOR PHENOL IN WATER-p-DIOXAN MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	-ΔS°
0.0	9.97	13.61	5.58	26.9
5.0	10.12	13.80	5.85	26.7
10.0	10.27	14.01	6.14	26.4
15.0	10.44	14.24	6.39	26.3
20.0	10.62	14.49	6.60	26.5
25.0	10.32	14.82	6.77	24.5
30.0	11.02	15.03	6.93	27.2
35.0	11.24	15.33	7.01	27.9
40.0	11.47	15.65	6.86	29.5
45.0	11.75	16.03	6.72	31.2
50.0	12.03	16.40	6.55	33.0
55.0	12.34	16.83	6.37	35.1
60.0	12.68	17.30	6.17	37.3
65.0	13.10	17.87	5.97	39.9
70.0	13.57	18.51	5.77	42.7

TABLE I--Continued

FOR SILVER CHLORIDE IN WATER-ETHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	ΔS°
0.0	9.75	13.31	15.83	8.4
5.0	9.87	13.47	16.14	9.0
10.0	9.98	13.62	16.34	9.1
15.0	10.12	13.81	16.53	9.1
20.0	10.24	13.98	16.64	8.9
25.0	10.36	14.14	16.66	8.5
30.0	10.49	14.32	16.51	7.3
35.0	10.64	14.52	16.27	5.9
40.0	10.78	14.71	16.06	4.5
45.0	10.94	14.93	15.69	2.5
50.0	11.12	15.18	15.38	0.7
55.0	11.32	15.45	15.07	-1.3
60.0	11.52	15.72	14.74	-3.3
65.0	11.73	16.01	14.38	-5.5
70.0	11.97	16.34	14.05	-7.7

TABLE I--Continued

FOR SILVER CHLORIDE IN WATER-ACETONE MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	ΔS°
0.0	9.75	13.31	15.83	8.4
5.0	9.84	13.43	15.63	7.4
10.0	9.96	13.60	15.31	5.7
15.0	10.08	13.76	15.10	4.5
20.0	10.20	13.92	14.99	3.6
25.0	10.34	14.11	14.88	2.6
30.0	10.48	14.31	14.74	1.4
35.0	10.59	14.46	14.57	0.4
40.0	10.83	14.78	14.44	-1.14
45.0	11.03	15.06	14.28	-2.6
50.0	11.27	15.38	14.05	-4.5
55.0	11.53	15.74	13.63	-7.1
60.0	11.80	16.11	13.07	-10.2
65.0	12.11	16.53	12.62	-13.1
70.0	12.43	16.97	12.22	-15.9

TABLE I--Continued

FOR SILVER CHLORIDE IN WATER-METHANOL MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	ΔS°
0.0	9.75	13.31	15.83	8.4
5.0	9.87	13.47	16.45	10.0
10.0	9.98	13.62	16.90	11.0
15.0	10.11	13.80	17.27	11.6
20.0	10.22	13.95	17.43	11.7
25.0	10.34	14.11	17.35	10.9
30.0	10.46	14.28	17.08	9.4
35.0	10.58	14.44	16.64	7.4
40.0	10.73	14.65	16.07	6.4
45.0	10.87	14.84	15.47	2.1
50.0	11.03	15.06	14.87	-0.6
55.0	11.20	15.29	14.16	-3.8
60.0	11.37	15.52	13.37	-7.2
65.0	11.54	15.75	11.62	-13.8
70.0	11.73	16.01	10.61	-18.1

TABLE I--Continued

FOR SILVER CHLORIDE IN WATER-THF MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	ΔS°
0.0	9.75	13.31	15.83	8.4
5.0	9.87	13.47	15.95	8.3
10.0	9.98	13.62	15.84	7.4
15.0	10.11	13.80	15.68	6.3
20.0	10.23	13.96	15.44	5.0
25.0	10.36	14.14	15.15	3.4
30.0	10.50	14.33	15.14	2.7
35.0	10.66	14.55	15.24	2.3
40.0	10.83	14.78	15.35	1.9
45.0	11.02	15.04	15.49	1.5
50.0	11.21	15.30	15.62	1.1
55.0	11.45	15.63	15.68	0.2
60.0	11.71	15.98	15.75	-0.7
65.0	12.02	16.41	15.67	-2.5
70.0	12.38	16.90	15.40	-5.0

TABLE I--Continued

FOR SILVER CHLORIDE IN WATER-p-DIOXAN MIXTURES AT 25°C

wt%	pK	ΔG°	ΔH°	ΔS°
0.0	9.75	13.31	15.83	8.4
5.0	9.84	13.43	15.69	7.6
10.0	9.96	13.60	15.45	6.2
15.0	10.07	13.75	15.39	5.5
20.0	10.20	13.92	15.40	5.0
25.0	10.34	14.11	15.41	4.4
30.0	10.47	14.29	15.23	3.2
35.0	10.65	14.54	14.91	1.2
40.0	10.82	14.77	14.46	-1.0
45.0	11.04	15.07	13.97	-3.7
50.0	11.24	15.34	13.48	-6.2
55.0	11.55	15.77	12.95	-9.5
60.0	11.90	16.24	12.37	-13.0
65.0	12.37	16.89	11.62	-17.7
70.0	12.47	17.02	10.71	-21.2

[a] See discussion in "Results" regarding uncertainties for data given in Table I.

TABLE II

THERMODYNAMIC PARAMETERS AT 25°C FOR EQUATIONS (8), (11), AND (18) IN PURE WATER AS SOLVENT

Reaction	$\Delta G°$[a] (kcal)	$\Delta H°$ (kcal)	$\Delta S°$[a] (cal/°k)	References
$H_2O = H^+ + OH^-$	19.11	13.34	-19.3_5	2
$AgCl = Ag^+ + Cl^-$	13.31	15.65	7.8_5	44
$HAc = H^+ + Ac^-$	6.46	-0.10	-22.0_7	2
$HBz = H^+ + Bz^-$	5.73	0.10	-18.8_8	2
$HPh = H^+ + Ph^-$[b]	13.61	5.48	-27.2_7	2

[a] Standard states of all ions and acid solutes based on molarities. Standard states of water and silver chloride are chosen so that both activities are unity.

[b] Ac is acetate, Bz is benzoate, and Ph is phenolate.

TABLE III

THE TRANSFER FREE ENERGY OF ACETIC ACID IN MIXED SOLVENTS

Solvent	X	δG(el)	δG(chem)
Methanol	0.1	0.2	0.1
	0.2	0.4	0.3
	0.3	0.7	0.4
	0.4	1.0	0.4
	0.5	1.3	0.5
	0.6	1.6	0.5
Ethanol	0.1	0.4	0.2
	0.2	0.8	0.3
	0.3	1.3	0.4
	0.4	1.7	0.4
	0.5	2.2	0.4
Acetone	0.1	0.5	0.8
	0.2	1.0	0.9
	0.3	1.5	1.2
	0.4	2.1	1.6
	0.5	2.5	1.8
THF	0.1	0.8	0.2
	0.2	1.7	0.1
	0.3	3.4	-0.4
	0.4	5.0	-1.0
p-Dioxan	0.1	1.2	0.2
	0.2	3.4	-0.2
	0.3	5.7	-1.4
	0.4	12.7	-6.4

EXPLANATION TO APPENDICES

Appendix A	Densities and Dielectric Constants
Appendix B	EMF measurements All potentials are in mV. E_A, E_B, E_C, and E_D stand for potential readings for cells A, B, C, and D, respectively. Beginning with 15.00 ml at 25°C of pure aqueous solutions in each of the following cells: Cell A: $HCl(C_1)$, and $KNO_3(C_2)$ Cell B: $KOH(C_3)$, and KCl C C_4 Cell C: $HA(C_5)$, $KOH(C_6)$, and $KCl(C_7)$ Cell D: $AgNO_3(C_8)$, $HNO_3(C_9)$ where $C_1 = C_2 = C_3 = C_4 = C_6 = C_7 = C_8 = C_9 =$ 0.0100_0 F at 25°C values of C_5 for each acid are acetic acid 0.0099_7 F benzoic acid 0.0099_0 F phenol 0.0099_0 F Potentials were read where, 0, 1.25, 2.50, 3.75, 5.00, 7.50, 10.00, 15.00, 20.00, 25.00, 30.00, 35.00, 40.400, and 50.00 ml organic co-solvent were added. (Volumes added at 25°C)
Appendix C	Theoretical and experimental k_2 values at various temperatures.
Appendix D	pK values in mixed organic co-solvents at various temperatures. See discussion in "Results" regarding uncertainties.
Appendix E	A brief account on dimerization of some carboxylic acids by calorimetric technique with references.

APPENDIX A

DENSITIES AND DIELECTRIC CONSTANTS

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 10°C

Ethanol			Acetone		
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	84.1	0.9997	0.00	84.1	0.9997
6.16	80.8	0.9895	6.15	81.4	0.9915
11.61	77.5	0.9835	11.60	79.3	0.9862
16.45	74.7	0.9765	16.44	75.4	0.9835
20.80	71.8	0.9710	20.79	71.7	0.9800
28.26	67.8	0.9615	28.24	67.2	0.9675
34.43	64.2	0.9520	34.42	64.6	0.9571
44.06	57.4	0.0365	44.05	57.3	0.9402
51.23	53.6	0.9230	51.21	55.3	0.9265
56.76	48.5	0.9085	56.75	48.8	0.9145
61.17	46.3	0.8975	61.16	45.2	0.9051
64.76	44.0	0.8900	64.76	44.3	0.8960
67.75	42.3	0.8845	67.74	42.8	0.8894
72.42	39.6	0.8730	72.41	39.7	0.8871

APPENDIX A--Continued

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 15°C

	Ethanol			Acetone	
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.0	8.23	0.9991	0.00	82.3	0.9991
6.16	78.7	0.988	6.15	78.5	0.992
11.61	75.3	0.981	11.60	76.0	0.985
16.45	72.7	0.976	16.44	72.6	0.977
20.80	70.2	0.971	20.79	69.8	0.973
28.26	65.7	0.961	28.24	65.3	0.963
34.43	62.3	0.948	34.42	62.4	0.953
44.06	55.5	0.932	44.05	55.2	0.937
51.23	51.6	0.916	51.21	52.2	0.923
56.76	47.2	0.903	56.75	46.7	0.911
61.17	44.7	0.893	61.16	43.6	0.901
64.76	42.6	0.882	64.76	42.0	0.893
67.75	40.8	0.877	67.74	40.4	0.884
72.42	38.4	0.867	72.41	37.5	0.883

APPENDIX A--Continued

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 20°C

Ethanol			Acetone		
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	80.4	0.9982	0.00	80.4	0.9982
6.16	76.9	0.9876	6.15	76.6	0.9913
11.61	73.6	0.9824	11.60	73.4	0.9835
16.45	70.8	0.9735	16.44	70.4	0.9765
20.80	68.2	0.9657	20.79	67.9	0.9713
28.26	63.8	0.9548	28.24	63.7	0.9585
34.43	60.2	0.9435	34.42	60.4	0.9512
44.06	53.7	0.9265	44.05	53.5	0.9335
51.23	49.0	0.9208	51.21	49.8	0.9188
56.76	45.6	0.8955	56.75	45.1	0.9085
61.17	43.5	0.8857	61.16	41.8	0.8975
64.76	41.3	0.8757	64.76	39.6	0.8885
67.75	39.7	0.8725	67.74	38.1	0.8815
72.42	37.3	0.8615	72.41	35.5	0.8655

APPENDIX A--*Continued*

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 25°C

	Ethanol			Acetone	
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	78.5	0.9971	0.00	78.5	0.9971
6.16	75.2	0.988	6.15	75.1	0.988
11.61	72.0	0.977	11.60	72.3	0.981
16.45	69.3	0.972	16.44	69.5	0.974
20.80	66.7	0.966	20.79	66.8	0.968
28.26	62.3	0.958	28.24	62.6	0.958
34.43	58.2	0.947	34.42	58.6	0.948
44.06	52.3	0.923	44.05	52.4	0.929
51.23	48.3	0.907	51.21	47.7	0.913
56.76	44.4	0.893	56.75	43.8	0.903
61.17	42.4	0.884	61.16	41.2	0.893
64.76	4.13	0.875	64.76	39.2	0.885
67.75	38.5	0.868	67.74	37.3	0.877
72.42	36.0	0.858	72.41	34.4	0.865

APPENDIX A--Continued

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 30°C

Ethanol			Acetone		
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	76.8	0.9957	0.00	76.8	0.9957
6.16	73.4	0.9846	6.15	73.0	0.9869
11.61	70.4	0.9738	11.60	69.5	0.9795
16.45	67.4	0.967	16.44	67.5	0.9719
20.80	65.1	0.9416	20.79	65.1	0.9659
28.26	61.1	0.9475	28.24	60.7	0.9543
34.43	57.5	0.9375	34.42	56.9	0.9440
44.06	51.3	0.9175	44.05	50.9	0.9249
51.23	47.1	0.9025	51.21	46.4	0.9089
56.76	43.1	0.8862	56.75	42.8	0.8962
61.17	41.2	0.8810	61.16	40.3	0.8808
64.76	39.3	0.8691	64.76	37.6	0.8722
67.75	37.7	0.8638	67.74	35.8	0.8669
72.42	35.3	0.8525	72.41	33.2	0.8508

APPENDIX A--Continued

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 35°C

Ethanol			Acetone		
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	75.0	0.9941	0.00	75.0	0.9941
6.16	71.5	0.983	6.15	71.6	0.985
11.61	68.6	0.974	11.60	68.4	0.978
16.45	65.7	0.967	16.44	65.7	0.970
20.80	63.3	0.961	20.79	63.3	0.964
28.26	59.3	0.947	28.24	59.4	0.951
34.43	55.5	0.937	34.42	55.6	0.941
44.06	49.4	0.916	44.05	49.6	0.921
51.23	45.7	0.899	51.21	45.3	0.904
56.76	42.2	0.884	56.75	41.7	0.891
61.17	39.9	0.877	61.16	39.3	0.881
64.76	38.1	0.868	64.76	36.8	0.877
67.75	36.5	0.860	67.74	35.1	0.867
72.42	34.3	0.849	72.41	32.4	0.856

APPENDIX A--*Continued*

MIXTURES OF WATER WITH ETHANOL AND ACETONE AT 40°C

Ethanol			Acetone		
wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	73.3	0.9925	0.00	73.3	0.9925
6.16	69.8	0.9773	6.15	70.2	0.9842
11.61	66.8	0.9691	11.60	67.3	0.9772
16.45	63.9	0.9587	16.44	64.5	0.9703
20.80	61.5	0.9582	20.79	62.1	0.9615
28.26	57.6	0.9408	28.24	58.2	0.9503
34.43	54.3	0.9325	34.42	54.5	0.9385
44.06	48.4	0.9136	44.05	48.6	0.9175
51.23	44.4	0.8965	51.21	44.4	0.8994
56.76	41.5	0.8828	56.75	40.9	0.8863
61.17	39.0	0.8779	61.16	38.5	0.8725
64.76	37.1	0.8676	64.76	36.3	0.8631
67.75	35.7	0.8569	67.74	34.5	0.8564
72.42	33.6	0.8471	72.41	31.7	0.8415

APPENDIX A--Continued

MIXTURES OF WATER WITH METHANOL, THF AND p-DIOXAN AT 15°C

Methanol			THF			p-Dioxan		
wt%	ε	(g/ml)	wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	82.3	0.9991	0.00	8.23	0.9991	0.00	82.3	0.9991
6.21	78.6	0.9885	6.23	77.5	0.9980	7.91	75.6	1.0068
11.68	75.9	0.9835	12.82	73.6	0.9963	14.66	69.1	1.0133
16.57	73.4	0.9790	18.08	68.3	0.9940	20.49	63.5	1.0190
20.93	70.3	0.9750	22.73	65.8	0.9930	25.58	59.0	1.0237
28.42	66.9	0.9670	30.62	59.2	0.9890	34.02	49.9	1.0304
34.62	61.4	0.9610	37.04	53.8	0.9840	40.74	44.6	1.0355
44.26	56.2	0.9470	46.88	44.5	0.9760	50.76	35.4	1.0410
51.43	55.3	0.9340	54.06	37.8	0.9690	57.89	29.3	1.0439
56.96	53.1	0.9235	59.53	33.8	0.9590	63.21	24.3	1.0450
61.36	51.4	0.9135	63.84	30.8	0.9560	67.34	21.6	1.0457
64.95	49.9	0.9075	67.31	28.9	0.9485	70.64	18.6	1.0458
67.93	48.3	0.9020	70.18	25.7	0.9445	73.33	16.9	1.0457
72.58	45.4	0.8925	74.63	23.2	0.9360	77.46	13.3	1.0455

APPENDIX A--Continued

MIXTURES OF WATER WITH METHANOL, THF AND p-DIOXAN AT 25°C

Methanol			THF			p-Dioxan		
wt%	ε	(g/ml)	wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	78.5	0.9971	0.00	78.5	0.9971	0.00	78.5	0.9971
6.21	75.4	0.988	6.23	73.6	0.995	7.91	7.15	1.004
11.68	72.8	0.982	12.82	69.3	0.991	14.66	64.4	1.009
16.57	70.3	0.977	18.08	64.3	0.991	20.49	60.6	1.014
20.93	68.1	0.972	22.73	6.13	0.988	25.58	55.6	1.020
28.42	64.5	0.962	30.62	55.8	0.981	34.02	48.2	1.025
34.62	63.7	0.953	37.04	49.8	0.976	40.74	42.3	1.029
44.26	58.4	0.941	46.88	42.2	0.967	50.76	33.7	1.034
51.43	52.8	0.928	54.06	36.4	0.952	57.89	28.1	1.036
56.96	50.4	0.918	59.53	32.0	0.947	63.21	23.5	1.037
61.36	48.7	0.908	63.84	28.5	0.942	67.43	19.8	1.037
64.95	46.9	0.899	67.31	26.3	0.937	70.64	16.8	1.037
67.93	45.8	0.893	70.18	24.5	0.933	73.33	14.5	1.037
72.58	42.5	0.883	74.63	21.5	0.926	77.46	10.3	1.036

APPENDIX A--Continued

MIXTURES OF WATER WITH METHANOL, THF AND p-DIOXAN AT 35°C

Methanol			THF			p-Dioxan		
wt%	ε	(g/ml)	wt%	ε	(g/ml)	wt%	ε	(g/ml)
0.00	75.0	0.9941	0.00	75.0	0.9941	0.00	75.0	0.9941
6.23	72.6	0.984	6.23	71.3	0.9930	7.91	68.5	1.0001
11.68	70.1	0.981	12.82	66.8	0.9910	14.66	62.6	1.0050
16.57	67.6	0.974	18.08	62.3	0.9890	20.49	57.6	1.0093
20.93	65.4	0.968	22.73	59.3	0.9830	25.58	53.4	1.0128
28.42	62.1	0.958	30.62	53.8	0.9780	34.02	45.7	1.0194
34.62	59.3	0.949	37.04	48.5	0.9690	40.74	40.1	1.0222
44.26	54.7	0.938	46.88	40.5	0.9585	50.76	31.7	1.0267
51.43	51.4	0.922	54.06	34.9	0.9465	57.89	26.1	1.0287
56.96	48.7	0.908	59.53	31.2	0.9420	63.21	21.6	1.0292
61.36	46.8	0.901	63.84	28.2	0.9340	67.34	18.1	1.0292
64.95	44.7	0.893	67.31	25.9	0.9310	70.64	15.3	1.0283
67.93	43.4	0.885	70.18	23.1	0.9265	73.33	12.8	1.0278
72.58	41.5	0.877	74.63	21.1	0.9215	77.46	9.1	1.0260

APPENDIX B

EMF DATA

IN WATER-ETHANOL MIXTURES AT 10°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	186.2	389.8	-38.3	-65.5	262.3	162.9
	6.16	188.3	392.0	-36.7	-62.4	267.4	167.3
	11.61	190.0	393.8	-34.9	-59.7	272.2	171.1
	16.45	191.0	395.5	-33.1	-57.0	276.7	174.6
	20.80	191.3	396.8	-31.1	-54.4	281.0	177.7
	28.26	190.7	398.5	-36.8	-46.7	288.6	183.1
	34.43	189.6	399.7	-22.4	-39.9	295.2	187.6
	44.06	188.8	400.8	-13.9	-28.7	301.3	194.2
	51.23	188.5	401.6	-6.9	-16.8	305.3	199.1
	56.76	188.0	402.3	-1.2	-8.3	30912	203.4
	61.17	187.4	402.9	4.1	-1.8	312.9	207.4
	64.76	186.7	403.3	9.1	-3.7	316.6	211.2
	67.75	186.0	403.8	13.7	8.5	320.2	214.8
	72.42	184.6	404.6	21.9	15.8	326.6	221.0
Coleman	0.00	166.2	407.5	-18.5	-51.1	281.8	181.5
	6.16	168.4	410.1	-17.2	-47.1	285.7	185.8
	11.61	170.1	412.1	-15.5	-43.6	289.4	189.4
	16.45	171.1	413.7	-13.7	-40.1	292.8	192.6
	20.80	171.6	415.1	-11.2	-36.7	296.1	195.6
	28.26	171.2	416.9	-5.3	-30.4	305.3	200.3
	34.43	169/5	417.3	1.3	-24.5	313.9	203.3
	44.06	167.4	418.1	12.3	-14.1	324.0	209.1
	51.23	166.4	418.9	20.4	-5.8	332.3	214.2
	56.76	165.6	419.7	27.0	5.5	338.8	318.4
	61.17	164.7	420.4	32.4	-12.6	342.9	222.3
	64.76	163.8	421.0	36.9	17.9	346.8	225.9
	67.75	163.0	421.4	40.7	22.6	350.2	229.3
	72.42	161.3	421.8	46.4	30.6	355.5	234.9

APPENDIX B--Continued

IN WATER ETHANOL MIXTURES AT 15°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	189.0	393.0	-37.1	-66.0	265.6	145.0
	6.16	190.6	395.4	-35.6	-64.0	271.6	158.2
	11.61	191.8	397.1	-33.2	-60.4	276.9	161.2
	16.45	192.5	398.5	-30.9	-55.8	282.1	164.2
	20.80	192.7	399.7	-27.3	-48.9	287.2	167.1
	28.26	191.5	402.1	-20.3	-34.9	298.1	172.5
	34.43	189.7	403.9	-12.9	-22.5	307.0	178.2
	44.06	187.0	405.5	-1.6	-6.0	319.7	186.9
	51.23	185.5	405.9	6.5	3.6	327.3	192.8
	56.76	184.6	405.9	12.6	9.9	332.0	197.5
	61.17	184.2	405.7	17.7	14.9	335.2	201.0
	64.76	184.0	405.0	21.9	19.0	338.0	204.3
	67.75	184.0	408.4	25.7	22.4	340.1	206.7
	72.42	184.0	404.2	31.8	28.1	343.9	210.3
Coleman	0.00	172.6	406.7	-20.4	-46.0	287.4	171.5
	6.16	174.5	408.6	-18.0	-44.8	291.2	173.8
	11.61	175.8	410.3	-15.2	-42.0	295.4	176.4
	16.45	176.4	411.6	-12.4	-37.5	300.2	179.3
	20.80	176.6	413.0	-9.4	-31.8	305.5	182.3
	28.26	175.4	415.2	-2.7	-17.6	315.5	187.9
	34.43	173.7	417.0	4.0	-5.4	324.8	193.7
	44.06	170.5	418.6	15.3	10.2	338.1	202.8
	51.23	169.0	419.2	23.5	20.5	346.3	208.8
	56.76	168.2	419.4	29.6	27.8	351.3	213.1
	61.17	167.8	419.4	34.6	33.5	354.6	216.1
	64.76	167.7	419.3	38.8	37.0	357.2	218.2
	67.75	167.7	419.0	43.5	40.5	360.0	220.4
	72.42	167.8	418.4	50.0	46.4	362.5	224.0

IN WATER-ETHANOL MIXTURES AT 20°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	183.4	387.5	-27.8	-57.5	268.0	147.0
	6.16	184.7	389.8	-23.5	-54.2	272.6	150.8
	11.61	186.0	391.8	-23.5	-52.6	277.4	154.1
	16.45	186.6	393.4	-21.2	-47.2	284.0	157.1
	20.80	186.6	395.1	-18.7	-41.4	287.0	159.9
	28.26	185.8	397.4	-13.1	-25.6	295.8	164.6
	34.43	184.4	398.7	-7.0	-19.8	301.6	168.4
	44.06	182.4	400.1	3.1	-7.9	309.8	174.4
	51.23	181.2	400.5	11.2	-0.6	314.8	179.2
	56.76	180.6	400.8	18.0	7.1	319.1	183.3
	61.17	180.4	401.1	23.5	14.1	322.0	187.2
	64.76	180.4	401.3	27.9	20.4	325.2	191.0
	67.75	180.6	401.4	31.8	25.8	328.8	194.8
	72.42	181.2	401.2	37.8	34.0	335.8	201.6
Coleman	0.00	167.6	401.5	-19.1	-42.0	286.6	163.4
	6.16	169.2	404.3	-17.1	-39.3	290.0	166.6
	11.61	170.4	406.0	-14.8	-36.0	294.2	170.0
	16.45	171.0	407.7	-12.3	-31.2	298.6	173.0
	20.80	171.2	409.0	-9.7	-24.0	301.4	176.2
	28.26	170.4	411.6	-3.4	-12.0	311.2	181.6
	34.43	169.0	413.5	3.7	-1.3	319.4	186.4
	44.06	167.7	415.2	13.5	11.1	327.4	194.0
	51.23	166.2	416.4	20.8	17.2	332.7	198.2
	56.76	165.7	416.8	26.8	24.0	337.2	202.7
	61.17	165.6	416.9	31.9	33.3	341.2	207.4
	64.76	165.1	416.7	36.9	35.7	344.8	210.7
	67.75	165.1	416.8	42.5	40.9	348.5	215.7
	72.42	164.8	416.0	48.6	48.0	354.4	218.0

APPENDIX B--*Continued*

IN WATER-ETHANOL MIXTURES AT 25°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	193.6	386.9	-26.6	-69.3	269.9	140.0
	6.16	194.5	388.4	-34.6	-65.0	274.7	143.1
	11.61	195.3	390.2	-32.1	-60.1	279.8	146.0
	16.45	195.5	392.0	-29.1	-54.9	284.9	148.8
	20.80	195.6	393.4	-25.8	-49.1	289.9	151.4
	28.26	194.6	395.9	-18.8	-35.4	301.1	157.4
	34.43	193.4	397.6	-12.1	-24.5	309.8	162.8
	44.06	192.0	399.4	-3.0	-11.0	321.0	170.9
	51.23	191.3	400.3	4.0	-2.1	328.1	176.9
	56.76	190.9	400.0	10.0	4.7	332.4	181.5
	61.17	190.9	401.1	15.5	9.9	336.3	185.3
	64.76	190.9	401.3	19.8	13.1	339.4	188.6
	67.75	191.0	401.3	23.4	17.8	341.9	191.3
	72.42	192.3	401.4	29.5	23.0	344.3	194.8
Coleman	0.00	177.0	401.4	-20.8	-52.2	286.3	157.8
	6.16	177.3	403.4	-18.9	-48.4	290.9	160.6
	11.61	177.7	405.5	-16.2	-43.8	295.7	164.2
	16.45	178.0	407.2	-13.2	-38.6	301.1	167.5
	20.80	178.1	408.7	-9.7	-33.7	307.6	170.6
	28.26	177.5	411.4	-1.7	-19.1	318.6	180.4
	34.43	176.4	413.2	5.1	-8.4	326.5	185.5
	44.06	175.0	414.9	15.4	7.8	337.6	194.1
	51.23	174.2	415.9	22.7	16.0	344.2	200.2
	56.76	174.0	416.4	28.4	22.5	348.5	204.3
	61.17	173.9	416.5	33.3	28.0	351.9	208.1
	64.76	173.9	416.5	37.4	32.9	344.6	211.0
	67.75	173.9	416.5	40.9	36.4	356.8	213.6
	72.42	175.0	416.6	46.7	42.0	360.4	217.5

APPENDIX B--Continued

IN WATER-ETHANOL MIXTURES AT 30°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	191.2	386.0	-31.6	-64.2	274.0	135.8
	6.16	191.7	388.2	-28.9	-60.0	278.8	139.6
	11.61	192.5	390.0	-25.8	-55.2	283.6	143.6
	16.45	192.8	391.8	-22.9	-50.6	288.2	147.4
	20.80	192.9	393.1	-20.0	-44.2	292.8	151.4
	28.26	192.6	395.2	-14.1	-32.3	299.4	154.5
	34.43	192.2	396.6	-8.4	-21.0	304.2	159.2
	44.06	191.2	398.6	0.2	-6.9	315.1	169.2
	51.23	191.0	399.4	7.8	0.8	320.4	174.1
	56.76	191.0	399.7	13.6	6.8	324.1	179.1
	61.17	191.4	400.2	18.2	11.8	326.8	183.3
	64.76	192.2	400.5	22.4	15.6	328.8	186.5
	67.75	193.9	400.5	25.7	18.8	330.0	189.2
	72.42	400.3	31.8	24.4	331.6	192.8	
Coleman	0.00	177.4	399.2	-16.8	-50.0	289.8	150.0
	6.16	178.3	401.2	-14.4	-45.0	294.0	155.0
	11.61	178.7	403.4	-11.4	-40.0	298.4	159.0
	16.45	179.0	405.2	-8.4	-35.0	300.7	162.4
	20.80	179.1	406.7	-5.6	-30.0	306.5	165.5
	28.26	178.8	409.2	0.0	-20.0	312.7	171.1
	34.43	178.2	411.0	4.8	-14.1	315.7	175.6
	44.06	177.5	413.1	15.1	2.8	328.7	184.0
	51.23	177.5	414.2	22.7	11.5	334.5	190.8
	56.76	177.4	414.6	28.3	18.5	338.2	196.2
	61.17	177.4	414.7	32.9	23.8	340.3	201.4
	64.76	178.0	414.8	37.0	27.4	342.0	202.4
	67.75	178.8	414.8	40.3	30.9	343.1	205.0
	72.42	190.4	414.3	45.5	36.8	344.7	208.3

APPENDIX B--Continued

IN WATER-ETHANOL MIXTURES AT 35°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	195.6	381.0	-35.5	-67.3	274.5	125.1
	6.16	196.2	382.8	-32.2	-62.6	280.0	129.1
	11.61	196.4	384.5	-28.9	-56.8	286.0	132.9
	16.45	196.4	386.2	-25.5	-50.3	291.8	136.5
	20.80	196.4	387.7	-21.8	-43.6	297.4	139.9
	28.26	195.6	390.2	-14.2	-31.2	308.1	146.2
	34.43	194.5	391.7	-7.8	-20.6	315.8	151.5
	44.06	193.3	393.7	5.7	-8.0	326.2	159.4
	51.23	193.6	395.0	9.4	1.8	332.7	165.4
	56.76	193.7	395.6	15.4	7.9	337.0	170.0
	61.17	194.2	395.8	20.3	12.4	340.2	173.5
	64.76	195.1	395.8	24.2	16.1	342.8	176.4
	67.75	196.0	395.8	27.5	19.4	344.5	178.6
	72.42	197.6	395.9	32.9	24.9	348.1	181.6
Coleman	0.00	182.0	395.1	-19.9	-50.6	288.2	142.6
	6.16	182.8	396.5	-16.4	-45.0	298.0	145.5
	11.61	183.0	398.7	-13.1	-39.4	305.0	148.2
	16.45	183.0	400.9	-9.6	-33.7	311.1	149.7
	20.80	183.0	402.8	-6.1	-28.1	316.6	153.5
	28.26	182.2	406.0	1.2	-16.3	325.8	160.1
	34.43	181.3	408.3	7.6	-8.5	333.0	165.3
	44.06	180.3	410.3	17.5	5.4	343.4	173.5
	51.23	180.0	411.5	24.9	14.0	349.4	179.5
	56.76	180.2	412.2	30.7	20.3	353.8	184.1
	61.17	180.3	412.9	35.5	25.2	356.9	187.5
	64.76	181.4	413.1	39.6	29.0	249.5	190.3
	67.75	182.3	413.3	43.0	32.5	361.5	192.6
	72.42	183.9	413.5	49.5	38.0	364.5	196.4

APPENDIX B--Continued

IN WATER-ETHANOL MIXTURES AT 40°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	201.1	370.9	-34.0	-69.0	271.0	116.2
	6.16	301.4	374.0	-30.2	-63.8	278.2	119.7
	11.61	202.4	376.6	-26.6	-58.2	283.4	122.8
	16.45	202.3	378.7	-23.2	-51.4	289.8	125.7
	20.80	201.4	380.3	-19.8	-45.0	295.6	128.5
	28.26	200.1	383.2	-13.2	-32.8	305.8	133.6
	34.43	199.7	385.1	-7.4	-23.6	313.2	138.1
	44.06	199.4	387.8	-1.4	-10.0	323.0	145.9
	51.23	199.7	388.9	9.6	-2.0	318.9	152.2
	56.76	200.6	389.4	15.3	3.9	332.9	156.8
	61.17	201.9	389.8	20.1	8.4	336.1	160.7
	64.76	202.8	390.0	39.6	12.2	338.4	163.9
	67.75	203.9	390.0	43.1	15.5	340.4	166.4
	72.42	206.1	390.1	48.8	20.9	343.2	170.5
Coleman	0.00	184.2	388.8	-12.5	-54.9	293.5	135.4
	6.16	185.2	390.9	-9.3	-50.7	297.9	139.3
	11.61	186.5	392.7	-6.1	-47.8	304.8	143.1
	16.45	186.1	394.3	-3.6	-44.0	310.8	146.6
	20.80	186.5	395.7	-0.6	-39.9	316.0	150.4
	28.26	184.3	397.9	8.2	-31.9	325.0	156.2
	34.43	183.6	399.7	15.0	-26.3	332.3	160.6
	44.06	183.2	401.8	24.7	-18.3	343.1	167.3
	51.23	183.6	402.8	31.6	-12.6	349.2	172.3
	56.76	184.4	403.1	37.6	-7.9	353.6	176.4
	61.17	185.4	403.2	41.8	-4.0	356.8	180.1
	64.76	186.3	403.3	45.6	-0.7	359.3	183.4
	67.75	187.3	403.2	49.1	2.1	361.2	186.2
	72.42	189.2	403.0	54.9	6.1	364.1	190.1

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 10°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	188.8	392.8	-37.6	-66.7	265.0	163.4
	6.15	188.6	399.2	-32.4	-60.0	266.4	166.3
	11.60	188.3	403.7	-27.3	-52.4	286.6	169.2
	16.44	188.2	408.8	-22.1	-42.9	294.5	172.1
	20.79	188.0	413.4	-17.0	-34.6	301.9	174.7
	28.24	188.0	421.7	-6.8	-20.6	316.5	179.3
	34.42	188.2	428.9	2.5	-10.1	328.5	183.3
	44.05	189.6	440.7	17.6	9.2	344.5	190.1
	51.21	192.3	449.2	29.1	21.8	356.8	195.7
	56.75	197.2	456.1	38.2	31.0	364.1	200.4
	61.16	200.2	462.0	45.9	38.0	370.6	204.3
	64.76	204.4	467.2	42.3	43.4	375.8	207.5
	67.74	208.7	471.6	57.7	48.0	380.0	210.0
	72.41	216.9	478.3	65.8	54.8	386.0	213.6
Coleman	0.00	168.4	408.5	-21.8	-47.5	282.6	178.6
	6.15	168.3	414.9	-16.1	-41.2	292.0	182.6
	11.60	168.2	420.8	-10.6	-34.2	301.9	186.1
	16.44	168.1	426.1	-5.2	-26.6	310.8	189.1
	20.79	168.2	430.9	0.1	-18.8	319.4	191.8
	28.24	168.4	439.3	9.6	-5.6	333.2	196.5
	34.42	168.9	446.1	18.4	4.5	341.4	200.0
	44.05	170.7	456.9	32.9	20.8	360.1	209.2
	51.21	173.3	464.9	43.5	33.2	372.6	215.4
	56.75	176.6	471.5	51.8	42.3	382.1	220.2
	61.16	180.6	477.0	59.0	48.9	388.6	224.1
	64.76	184.6	481.7	65.5	54.1	394.0	227.2
	67.74	188.8	485.8	71.0	58.5	398.5	229.7
	72.41	197.6	492.6	79.4	65.3	405.0	232.7

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 15°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	187.6	389.8	-39.2	-69.2	266.3	153.9
	6.15	187.6	395.0	-32.7	-61.1	277.6	157.0
	11.60	187.7	401.2	-26.6	-52.5	287.4	159.9
	16.44	187.8	406.5	-20.9	-42.8	296.6	162.8
	20.79	188.0	411.0	-15.2	-34.8	305.5	165.6
	28.24	188.6	418.7	-5.1	-20.5	315.1	171.0
	34.42	189.4	425.2	4.0	-8.4	332.3	176.1
	44.05	191.8	434.9	18.5	8.7	348.8	184.9
	51.21	195.4	442.5	29.8	20.5	360.0	191.3
	56.75	199.1	448.6	38.2	29.0	268.0	196.0
	61.16	203.3	453.5	44.6	37.6	374.1	199.5
	64.76	207.7	458.2	49.9	39.6	378.4	202.2
	67.74	212.1	462.4	54.5	43.3	381.6	204.3
	72.41	221.3	469.4	61.5	49.9	386.5	207.0
Coleman	0.00	171.9	406.5	-19.6	-49.4	283.7	168.2
	6.15	172.1	412.1	-14.6	-41.8	299.0	171.6
	11.60	172.4	417.8	-8.7	-33.5	308.5	174.4
	16.44	172.6	423.0	-2.9	-25.3	318.2	177.2
	20.79	172.9	428.0	3.0	-17.2	335.7	180.3
	28.24	173.8	436.1	13.1	-2.5	340.5	186.2
	34.42	174.7	442.9	21.8	9.3	351.8	191.7
	44.05	177.0	453.0	36.4	26.9	369.0	200.2
	51.21	179.9	460.9	47.4	39.0	379.8	206.4
	56.75	183.4	467.0	55.8	47.3	387.8	210.8
	61.16	187.4	472.1	62.4	53.4	393.2	214.5
	64.76	191.8	476.4	68.0	58.2	397.2	216.9
	67.74	196.7	480.1	72.5	61.6	400.3	218.6
	72.41	205.7	486.8	79.8	66.7	405.0	221.3

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 20°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	182.4	390.4	-30.8	-59.8	270.0	149.7
	6.15	183.0	397.1	-25.4	-54.0	276.6	152.8
	11.60	183.1	400.7	-19.6	-46.0	283.2	155.7
	16.44	183.3	404.2	-14.0	-38.0	289.2	158.7
	20.79	183.4	407.9	-8.0	-32.4	295.0	161.3
	28.24	183.8	415.2	0.2	-19.0	307.9	166.5
	34.42	184.2	422.6	9.2	1.6	319.1	171.1
	44.05	184.5	437.6	24.0	8.8	334.5	178.7
	51.21	191.5	444.7	34.2	20.4	356.3	184.3
	56.75	196.3	451.1	41.8	28.2	354.9	188.3
	61.16	200.6	456.8	48.9	35.0	361.3	191.6
	64.76	205.7	461.6	55.0	40.1	365.0	194.4
	67.74	210.8	465.7	60.2	44.3	368.6	196.6
	72.41	220.6	473.6	64.2	50.0	373.6	199.6
Coleman	0.00	166.0	406.7	-13.8	-45.2	282.6	163.2
	6.15	166.4	411.4	-11.0	-37.6	290.6	164.8
	11.60	166.8	415.6	-4.2	-29.6	298.0	167.2
	16.44	167.2	419.8	-0.3	-21.0	303.8	169.6
	20.79	167.6	424.0	4.3	-13.0	310.2	171.8
	28.24	168.7	432.4	14.3	1.8	321.6	176.0
	34.42	170.0	441.0	23.1	9.8	331.6	180.0
	44.05	172.9	440.3	37.1	27.2	345.0	187.0
	51.21	176.6	432.1	47.1	37.2	357.0	193.0
	56.75	181.0	425.1	55.5	45.2	365.9	197.5
	61.16	185.0	419.9	62.7	51.9	372.9	201.9
	64.76	189.8	417.6	68.7	56.7	378.5	204.7
	67.74	194.4	411.3	75.6	60.7	383.0	207.3
	72.41	204.2	405.7	80.7	66.5	390.3	210.9

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 25°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	198.8	388.1	-39.1	-69.3	267.6	141.4
	6.15	190.2	393.5	-33.6	-60.6	277.7	143.9
	11.60	190.8	398.3	-27.8	-52.3	286.6	146.3
	16.44	191.3	403.2	-22.2	-43.8	295.7	148.5
	20.79	191.9	407.3	-16.6	-36.3	304.1	150.4
	28.24	193.2	414.2	-6.8	-21.9	317.3	156.8
	34.42	194.7	420.3	1.6	-10.4	327.6	161.7
	44.05	198.3	429.7	15.2	5.9	343.5	169.6
	51.21	202.7	437.3	25.7	16.7	351.9	175.0
	56.75	207.7	443.3	34.2	24.7	359.5	179.0
	61.16	212.8	448.3	41.1	30.1	365.0	181.6
	64.76	217.9	450.9	46.9	35.7	369.1	183.5
	67.74	223.0	455.1	51.5	39.2	372.4	185.4
	72.41	232.7	464.1	58.4	40.7	376.9	187.9
Coleman	0.00	173.8	380.3	-26.7	-52.2	282.6	156.2
	6.15	174.2	387.0	-20.9	-41.7	289.9	159.6
	11.60	174.4	392.8	-15.4	-32.7	300.5	161.8
	16.44	174.8	397.8	-10.5	-24.5	310.6	165.8
	20.79	175.2	403.6	-5.9	-17.0	318.8	168.6
	28.24	176.2	410.9	3.9	-3.5	333.3	174.0
	34.42	177.4	417.6	12.9	9.6	345.5	178.9
	44.05	180.7	428.0	27.0	26.0	361.9	187.1
	51.21	184.8	435.7	37.5	37.8	374.8	192.6
	56.75	190.0	446.1	45.7	46.0	380.4	196.2
	61.16	195.3	451.1	52.2	52.2	385.9	198.8
	64.76	200.5	453.7	57.8	57.0	389.9	201.3
	67.74	205.4	457.9	62.3	60.5	393.0	203.3
	72.41	215.3	466.9	69.9	65.0	397.3	205.7

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 30°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	197.8	382.1	-35.7	-69.9	270.2	129.2
	6.15	198.1	388.2	-29.4	-61.0	281.6	132.4
	11.60	198.5	394.0	-23.6	-53.4	291.0	135.7
	16.44	199.0	397.8	-18.4	-48.5	298.4	138.8
	20.79	199.5	401.0	-13.8	-40.9	302.4	141.6
	28.24	200.8	411.2	-5.4	-26.9	315.8	146.5
	34.42	202.2	422.0	-2.0	-16.6	325.8	150.5
	44.05	205.9	434.8	12.0	-0.8	342.1	159.0
	51.21	211.1	443.9	26.7	11.0	352.9	165.2
	56.75	217.6	456.4	34.1	19.4	360.9	169.6
	61.16	224.1	462.2	41.9	25.4	367.3	173.0
	64.76	229.6	467.6	48.1	31.1	371.7	175.8
	67.74	236.4	472.6	53.5	35.2	375.8	178.0
	72.41	245.9	481.0	62.3	41.6	381.9	180.9
Coleman	0.00	181.3	400.6	-21.0	-53.0	287.8	146.4
	61.5	181.7	407.0	-21.8	-46.2	297.8	149.4
	11.60	182.3	412.1	-16.6	-37.2	306.4	152.2
	16.44	182.9	416.7	-12.2	-28.6	317.4	153.8
	20.79	183.6	420.8	-8.4	-20.6	324.4	157.4
	28.24	185.3	428.1	1.4	-6.4	337.6	162.2
	34.42	187.2	434.5	9.6	4.6	347.5	166.9
	44.05	191.8	445.6	22.0	20.4	363.1	175.0
	51.21	197.2	455.0	31.3	32.5	371.1	181.2
	56.75	203.3	462.4	40.0	41.4	382.0	185.4
	61.16	208.3	468.6	47.4	47.6	388.0	188.5
	64.76	213.5	473.8	53.8	52.8	392.9	191.2
	67.74	218.6	478.6	59.2	56.8	397.0	193.4
	72.41	229.1	486.1	68.4	60.6	403.2	196.6

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 35°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	196.4	384.4	-33.4	-66.3	274.7	127.5
	6.15	196.7	388.4	-27.9	-58.4	286.1	131.1
	11.60	197.0	392.1	-21.6	-48.8	295.4	134.0
	16.44	197.5	395.4	-15.7	-40.3	304.6	137.4
	20.79	198.1	398.8	-9.2	-32.7	312.5	140.8
	28.24	199.4	404.2	0.0	-18.9	325.7	146.5
	34.42	201.0	408.1	8.1	-8.0	335.9	149.1
	44.05	205.3	413.7	20.9	5.3	349.7	156.7
	51.21	210.4	217.6	31.3	15.7	358.9	162.1
	56.75	214.1	421.6	39.2	23.3	364.7	166.2
	61.16	221.9	425.1	45.1	29.0	369.6	169.4
	64.76	227.7	428.4	50.1	33.3	373.6	171.9
	67.74	233.4	432.9	54.7	36.6	376.7	174.1
	72.41	245.7	440.6	61.9	40.7	381.5	177.1
Coleman	0.00	181.5	398.1	-19.1	-50.9	290.6	143.0
	6.15	181.5	402.1	-13.2	-41.7	300.7	146.3
	11.60	181.6	405.2	-7.5	-32.7	310.8	149.9
	16.44	182.0	408.0	-2.2	-23.2	320.0	152.9
	20.79	182.7	410.4	4.1	-17.0	327.9	156.0
	28.24	184.1	414.4	14.4	-2.7	339.4	161.8
	34.42	185.8	417.9	22.9	7.8	349.3	166.8
	44.05	189.6	423.8	35.8	23.2	364.0	174.6
	51.21	195.7	429.1	45.1	33.4	373.4	180.4
	56.75	201.6	434.2	53.2	40.5	379.2	184.1
	61.16	208.0	439.5	59.2	45.8	483.8	187.1
	64.76	214.3	445.2	64.2	50.1	387.6	189.5
	67.74	221.0	450.8	68.7	53.3	390.6	191.2
	72.41	232.8	460.7	75.7	58.3	395.3	194.0

APPENDIX B--Continued

IN WATER-ACETONE MIXTURES AT 40°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	203.7	382.2	-34.2	-70.4	292.8	118.5
	6.15	204.1	388.5	-29.2	-63.0	301.4	123.0
	11.60	204.6	393.7	-22.0	-56.4	312.0	127.2
	16.44	205.3	398.3	-16.0	-48.5	321.6	131.6
	20.79	206.0	403.0	-10.5	-39.5	329.2	136.0
	28.24	207.7	410.8	-1.2	-25.1	340.4	144.8
	34.42	209.8	417.3	7.0	-15.7	35.14	149.5
	44.05	215.4	427.3	19.4	5.1	367.7	156.8
	51.21	221.5	435.1	29.2	9.9	377.5	162.6
	56.75	227.7	441.7	37.2	17.5	385.0	167.1
	61.16	233.9	447.1	43.8	23.3	390.8	170.8
	64.76	240.1	452.1	49.3	27.5	395.2	173.6
	67.74	246.0	456.5	54.0	31.8	398.9	175.8
	72.41	257.5	463.6	61.8	37.6	464.8	178.2
Coleman	0.00	186.2	399.5	-12.9	-49.5	276.1	135.5
	6.15	186.5	405.7	-8.0	-42.0	286.8	139.7
	11.60	186.9	411.9	-3.8	-33.0	294.4	144.0
	16.44	187.5	417.9	-0.8	-24.2	303.0	148.3
	20.79	188.1	421.5	7.8	-15.9	312.4	150.8
	28.24	189.7	428.9	18.0	-2.2	325.8	155.4
	34.42	191.7	435.4	26.2	10.2	336.0	159.4
	44.05	196.9	445.8	39.4	26.2	349.7	167.1
	51.21	203.1	453.8	48.2	37.0	359.9	172.8
	56.75	209.4	460.4	56.0	45.3	67.4	177.1
	61.16	215.8	466.0	61.4	51.3	374.0	180.4
	64.76	222.0	470.9	67.8	55.8	378.0	182.9
	67.74	228.1	475.4	72.7	59.6	381.7	185.0
	72.41	238.5	483.0	80.6	65.3	386.9	188.1

APPENDIX B--Continued

IN WATER-METHANOL MIXTURES AT 15°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	188.7	387.6	-38.3	-69.8	265.8	151.7
	6.21	189.7	382.9	-34.9	-66.0	276.1	156.4
	11.68	190.7	379.9	-31.6	-62.0	280.1	160.4
	16.57	191.0	376.7	-28.4	-59.0	283.7	164.0
	20.93	191.3	373.8	-25.4	-53.6	287.1	167.2
	28.42	191.0	369.1	-20.0	-46.6	293.1	171.6
	34.62	190.3	265.5	-14.8	-36.6	298.3	176.7
	44.26	187.0	361.0	-5.6	-24.2	305.7	185.4
	51.43	186.0	357.2	1.2	-14.4	311.1	191.8
	56.96	182.1	354.1	8.0	-7.8	314.7	197.0
	61.36	180.6	351.3	13.6	-2.0	316.8	201.4
	64.95	169.5	349.3	18.0	3.0	318.4	204.8
	67.93	168.7	347.3	22.0	7.2	319.5	207.5
	72.58	167.8	343.3	28.3	14.0	320.9	211.0
Coleman	0.00	171.6	405.6	-20.4	-50.2	283.2	170.1
	6.21	172.8	403.2	-17.4	-46.8	286.1	174.2
	11.68	173.8	398.9	-14.6	-43.0	289.0	178.1
	16.57	174.3	395.1	-11.8	-39.3	292.0	182.0
	20.93	174.4	392.0	-9.1	-35.5	295.0	185.6
	28.42	173.6	387.5	-4.2	-27.7	299.5	191.4
	34.62	172.8	383.8	0.4	-19.9	304.4	194.4
	44.26	169.7	379.2	7.7	-5.6	311.2	203.0
	51.43	166.9	375.4	15.6	1.9	316.5	310.1
	56.96	164.8	372.3	21.8	9.6	319.8	215.9
	61.36	163.5	369.4	26.9	15.6	322.0	220.6
	64.95	162.7	367.0	31.1	20.5	323.6	224.1
	67.93	162.0	364.9	34.7	24.7	324.7	226.4
	72.58	161.2	361.1	40.2	31.1	325.7	229.3

APPENDIX B--Continued

IN WATER-METHANOL MIXTURES AT 25°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	192.2	369.4	-34.7	-66.9	272.5	140.5
	6.21	192.8	367.1	-32.3	-63.0	276.0	144.3
	11.68	193.4	364.8	-29.7	-59.0	279.0	148.0
	16.57	193.8	362.4	-27.2	-55.2	282.0	150.8
	20.93	193.8	360.1	-24.5	-51.2	284.6	154.0
	28.42	193.4	355.1	-19.4	-41.4	289.4	159.6
	34.62	192.8	352.5	-14.2	-34.0	293.0	163.6
	44.26	191.3	349.2	-3.8	-24.3	301.1	170.0
	51.43	189.1	345.9	3.3	-17.6	307.6	179.5
	56.96	188.0	342.7	9.1	-11.9	310.9	182.0
	61.36	186.3	339.5	14.1	-4.7	313.0	186.0
	64.95	186.0	336.3	18.9	1.3	314.3	189.4
	67.93	185.6	333.7	22.9	6.7	314.9	192.0
	72.58	185.3	329.7	29.4	14.7	315.8	195.2
Coleman	0.00	176.4	400.5	-19.8	-50.8	288.0	155.4
	6.21	177.2	398.2	-17.9	-48.6	291.3	159.6
	11.68	178.0	395.3	-14.4	-44.8	294.4	163.4
	16.57	178.0	393.0	-11.7	-41.0	297.4	167.0
	20.93	178.2	390.6	-9.0	-37.2	299.3	171.0
	28.42	177.5	386.6	-3.6	-29.6	305.3	176.8
	34.62	176.6	383.4	0.3	-22.0	309.9	179.4
	44.26	174.5	378.7	10.5	-6.6	327.3	187.0
	51.43	172.5	375.5	17.5	1.4	322.1	193.4
	56.96	171.0	372.5	22.7	8.2	325.7	198.7
	61.36	169.8	369.5	28.1	14.0	327.7	203.4
	64.95	169.2	366.5	33.1	19.2	329.1	207.0
	67.93	168.8	363.6	37.3	23.8	329.9	209.7
	72.58	168.4	359.6	44.5	31.6	330.8	213.6

APPENDIX B--Continued

IN WATER-METHANOL MIXTURES AT 35°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	196.5	380.9	-33.0	-66.5	275.6	123.3
	6.21	194.0	37.95	-30.6	-62.5	280.0	128.6
	11.68	195.8	378.2	-27.6	-58.0	283.8	133.3
	16.57	195.2	376.8	-24.0	-54.2	287.0	137.2
	20.93	194.8	375.6	-20.8	-53.3	290.0	140.7
	28.42	194.0	373.2	-14.8	-43.8	295.4	145.9
	34.62	193.1	370.9	-8.8	-35.3	299.8	153.3
	44.26	191.4	366.4	-1.0	-22.6	307.3	163.5
	51.43	190.1	362.8	9.7	-14.9	312.4	170.7
	56.96	189.0	359.4	13.8	-8.1	315.4	176.3
	61.36	188.4	356.0	18.4	-2.3	317.4	211.7
	64.95	188.4	373.8	22.8	2.7	318.2	214.9
	67.93	188.2	371.8	26.8	7.1	318.7	217.5
	72.58	187.8	367.5	33.6	13.1	319.2	221.4
Coleman	0.00	180.2	397.4	-19.0	-50.9	290.0	140.0
	6.21	180.1	395.0	-16.0	-47.7	293.6	144.4
	11.68	179.9	393.2	-13.0	-43.5	296.8	148.5
	16.57	179.7	391.6	-10.0	-38.7	303.4	151.2
	20.93	179.5	389.9	-6.8	-35.1	309.0	154.6
	28.42	179.0	386.8	-1.5	-26.9	308.9	160.6
	34.62	178.6	384.0	4.1	-18.9	313.4	166.2
	44.26	177.1	379.6	14.3	-4.6	320.2	187.6
	51.43	175.0	376.2	21.8	-3.2	325.1	194.5
	56.96	174.6	273.9	27.9	3.2	327.9	199.4
	61.36	170.0	369.8	32.7	9.4	329.5	203.8
	64.95	173.6	367.2	37.1	22.4	330.6	207.0
	67.93	173.4	364.6	41.0	26.6	331.3	209.0
	72.58	173.3	360.4	46.1	32.9	331.9	211.7

APPENDIX B--Continued

IN WATER-THF MIXTURES AT 15°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
	0.00	185.8	386.4	-37.8	-68.0	264.7	154.4
	6.23	185.9	388.7	-32.8	-59.4	276.4	159.6
	12.82	186.0	391.0	-28.0	-53.0	285.6	163.8
	18.08	186.1	393.2	-21.6	-45.0	294.0	167.6
	22.73	186.3	395.3	-17.8	-33.8	303.6	171.0
	30.62	186.9	399.3	-8.1	-14.0	320.0	176.4
	37.04	187.7	402.0	-0.2	0.0	332.0	180.8
	46.88	190.1	407.8	13.0	18.8	348.4	187.6
	54.06	193.6	413.0	22.4	2918	358.6	192.5
	59.53	198.2	417.4	39.4	36.4	365.8	196.1
	63.84	202.0	421.6	35.3	41.2	371.1	198.7
	67.31	206.1	424.4	40.7	45.9	375.1	200.8
	70.18	209.9	426.4	45.1	49.8	378.3	202.8
	74.63	216.9	428.8	52.8	55.2	382.8	206.0
Coleman	0.00	168.9	404.7	-19.3	-48.8	282.9	171.2
	6.23	168.9	407.2	-14.1	-43.0	292.1	175.4
	12.82	168.9	409.4	-9.0	-32.5	300.5	179.0
	18.08	169.0	411.6	-3.8	-21.0	311.9	182.4
	22.73	169.2	412.7	0.6	-10.0	322.1	185.2
	30.62	169.7	417.6	9.6	4.4	338.3	190.0
	37.04	170.5	421.2	17.5	19.0	350.2	194.4
	46.88	172.9	427.5	31.3	38.0	368.2	201.0
	54.06	176.4	432.6	40.7	49.0	379.1	206.6
	59.53	180.1	436.0	47.8	57.0	386.1	211.0
	63.84	183.9	440.4	53.0	62.4	391.4	214.6
	67.31	187.7	443.2	59.1	67.0	395.4	216.9
	70.18	191.5	444.2	63.5	70.8	398.2	219.2
	74.63	198.8	447.5	70.7	76.3	401.6	222.4

APPENDIX B--Continued

IN WATER-THF MIXTURES AT 25°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	190.00	385.4	-36.2	-66.7	270.3	139.0
	6.23	190.4	388.2	-31.0	-57.0	280.0	144.4
	12.82	190.7	390.9	-26.0	-49.4	290.0	149.0
	18.08	191.2	393.4	-21.0	-36.0	298.0	153.0
	22.73	191.6	296.0	-16.0	-23.5	312.6	156.2
	30.62	192.7	401.2	-6.8	-5.6	329.4	161.4
	37.04	194.0	406.6	1.4	7.4	342.2	165.6
	46.88	197.2	415.0	13.2	25.4	356.2	171.6
	54.06	200.7	420.6	23.0	33.4	365.0	177.0
	59.53	205.1	423.9	30.6	40.5	371.2	180.8
	63.84	210.3	426.9	36.5	45.6	375.8	184.0
	67.31	214.5	429.2	41.6	49.8	379.2	186.7
	70.18	219.1	430.2	46.0	53.2	381.9	188.8
	74.63	227.7	434.4	52.5	58.0	385.8	192.0
Coleman	0.00	174.3	399.4	-18.0	-48.8	285.6	152.8
	6.23	174.7	401.9	-13.0	-40.0	295.0	158.8
	12.82	175.0	405.9	-8.0	-31.2	303.2	163.0
	18.08	175.5	409.5	-3.0	-19.0	315.0	166.4
	22.73	176.0	412.7	3.0	-6.0	325.8	169.6
	30.62	177.0	418.7	12.4	11.6	341.8	174.6
	37.04	178.2	423.9	20.6	25.0	352.9	180.0
	46.88	181.1	432.9	33.6	41.6	368.4	185.8
	54.06	184.6	438.1	41.8	51.6	377.9	190.8
	59.53	188.7	441.9	48.2	58.7	383.9	194.7
	63.84	193.7	444.7	54.0	63.7	388.5	197.5
	67.31	197.6	446.6	58.6	68.0	392.0	199.9
	70.18	201.8	448.0	62.6	71.4	394.6	202.5
	74.63	210.4	450.8	69.6	76.4	397.9	211.1

APPENDIX B--Continued

IN WATER-THF MIXTURES AT 35°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	193.0	386.7	-32.0	-63.2	277.4	126.3
	6.23	193.4	389.7	-24.6	-52.4	287.6	131.2
	12.82	194.2	392.0	-18.8	-44.0	298.8	135.6
	18.08	194.8	394.4	-13.4	-32.0	309.0	140.0
	22.73	195.2	396.8	-8.6	-18.0	319.6	144.4
	30.62	196.0	404.6	1.0	-3.4	335.0	149.8
	37.04	197.0	408.5	8.4	9.2	345.9	154.2
	46.88	200.0	414.7	20.2	25.4	360.3	159.0
	54.06	204.8	419.5	20.0	35.2	368.9	163.2
	59.53	210.4	422.4	35.8	40.6	374.5	166.6
	63.84	215.2	424.2	41.0	46.0	378.5	169.2
	67.31	220.6	426.0	45.6	50.2	381.0	171.8
	70.18	225.8	427.9	49.6	53.2	383.4	174.2
	74.63	235.4	431.3	55.8	57.7	387.7	177.4
Coleman	0.00	178.1	398.0	-17.3	-48.8	292.6	142.4
	6.23	178.1	400.6	-12.0	-39.0	301.6	146.6
	12.82	178.2	404.6	-6.0	-27.4	312.0	150.4
	18.08	178.6	408.0	0.6	-16.0	322.2	154.4
	22.73	179.2	411.2	4.6	-3.0	333.0	157.4
	30.62	180.4	416.6	14.2	13.4	347.2	162.6
	37.04	182.0	421.0	21.6	26.0	360.2	166.6
	46.88	186.6	428.0	33.4	41.4	374.6	172.6
	54.06	191.6	432.8	41.2	48.2	383.6	176.9
	59.53	196.8	436.4	47.8	54.0	389.4	180.8
	63.84	199.3	439.0	53.2	58.8	393.8	183.8
	67.31	204.8	441.2	58.0	62.8	396.4	186.1
	70.18	209.8	443.0	62.0	65.8	398.8	188.3
	74.63	218.8	446.4	68.6	70.4	402.8	191.7

APPENDIX B--Continued

IN WATER-p-DIOXAN MIXTURES AT 15°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	196.6	395.6	-39.4	-74.9	262.6	151.2
	7.91	197.2	396.4	-33.4	-65.0	274.0	154.0
	14.66	198.2	404.2	-27.4	-57.2	286.5	156.6
	20.49	199.3	408.8	-21.4	-51.6	296.0	159.0
	25.58	200.3	412.2	-15.8	-43.2	303.5	161.4
	34.02	202.7	417.4	-5.4	-27.6	318.5	165.8
	40.74	205.1	421.0	4.2	-14.6	330.1	169.8
	50.76	211.4	426.1	19.6	-2.8	345.8	176.6
	57.89	219.9	429.4	30.7	3.6	358.0	182.0
	63.21	229.7	431.0	39.7	26.2	366.4	186.5
	67.34	238.0	431.4	47.0	33.5	371.8	209.0
	70.64	246.7	430.4	53.5	39.8	375.2	188.5
	73.33	254.7	428.2	59.2	45.0	377.1	188.3
	77.46	268.7	420.2	68.3	52.6	378.0	185.6
Coleman	0.00	177.1	408.8	-23.0	-49.3	282.8	171.1
	7.91	177.7	421.4	-17.0	-43.0	296.0	173.8
	14.66	178.2	426.8	-11.4	-33.2	306.4	176.6
	20.49	178.8	431.8	-6.0	-24.8	318.4	179.0
	25.58	179.6	435.6	-0.2	-16.2	326.4	181.5
	34.02	181.2	441.6	12.8	-2.8	339.8	186.0
	40.74	183.2	446.3	22.6	10.6	349.4	190.0
	50.76	188.6	450.8	38.0	29.6	365.8	196.6
	57.89	196.0	453.4	50.2	42.0	377.7	200.8
	63.21	204.4	454.5	59.6	51.4	386.4	204.8
	67.34	213.6	453.8	67.6	58.6	392.0	207.0
	70.64	222.6	442.0	74.0	64.3	395.6	208.5
	73.33	231.4	439.3	79.2	68.9	397.4	208.9
	77.46	246.6	441.3	87.0	75.6	397.2	207.2

APPENDIX B--Continued

IN WATER-p-DIOXAN MIXTURES AT 25°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	196.2	387.2	-34.5	-73.2	269.1	136.2
	7.91	197.7	391.0	-2719	-63.2	280.2	139.6
	14.66	198.9	394.8	-21.8	-56.3	289.9	142.6
	20.49	200.1	398.2	-15.6	-50.7	]97.6	145.3
	25.58	201.3	400.4	-9.9	-43.2	305.7	147.9
	34.02	204.3	404.4	0.6	-27.6	320.0	153.6
	40.74	207.6	408.7	9.8	-15.9	331.1	158.5
	50.76	216.3	413.3	24.2	0.6	347.3	166.3
	57.89	226.0	415.8	35.0	14.2	357.7	171.8
	63.21	236.9	416.7	43.4	24.6	364.4	175.7
	67.34	246.3	416.7	5018	31.9	368.6	178.3
	70.64	255.1	415.7	56.6	37.5	370.8	179.8
	73.33	263.8	413.1	61.2	41.2	371.4	180.6
	77.46	273.6	29.8	67.9	45.9	369.0	180.0
Coleman	0.00	180.0	404.8	-16.5	-53.6	286.8	155.4
	7.91	181.1	410.3	-9.9	-48.4	297.6	159.1
	14.66	182.2	414.4	-4.4	-42.7	307.5	162.3
	20.49	183.4	417.7	1.8	-32.8	316.9	165.3
	25.58	184.7	420.3	8.2	-23.5	325.2	168.1
	34.02	187.4	424.4	17.2	-9.7	338.0	173.1
	40.74	190.7	427.6	28.4	2.4	348.3	177.2
	50.76	200.0	432.3	42.5	19.9	365.1	183.4
	57.89	210.5	434.9	54.2	33.4	376.0	187.7
	63.21	220.5	434.8	64.5	43.8	382.8	190.9
	67.34	230.7	433.2	72.5	51.5	387.8	193.3
	70.64	240.3	430.5	78.4	56.8	391.0	194.9
	73.33	248.0	427.0	82.9	60.8	392.3	195.4
	77.46	262.8	418.1	89.4	66.0	391.6	194.9

APPENDIX B--*Continued*

IN WATER-p-DIOXAN MIXTURES AT 35°C

Electrode	wt%	E_A	$-E_B$	$-E_{C_1}$	$-E_{C_2}$	$-E_{C_3}$	$-E_D$
Fisher	0.00	200.6	384.6	-33.8	-68.4	272.3	121.3
	7.91	201.9	388.1	-27.0	-59.0	284.2	124.8
	14.66	203.2	391.0	-21.0	-51.2	293.8	127.8
	20.49	204.7	393.7	-15.6	-41.3	301.6	130.5
	25.58	206.4	396.1	-10.6	-32.5	309.6	132.9
	34.02	210.2	401.4	-2.1	-18.4	324.2	137.3
	40.74	215.0	405.4	7.1	-7.6	334.4	141.1
	50.76	225.0	409.3	20.7	9.7	349.3	147.3
	57.89	237.0	411.2	30.8	21.7	358.9	151.7
	63.21	247.8	411.2	39.2	30.6	363.8	154.8
	67.34	258.4	409.4	46.2	37.4	366.7	145.8
	70.64	268.6	406.5	51.7	42.8	367.6	158.2
	73.33	277.9	402.8	56.2	46.6	367.6	158.6
	77.46	294.0	393.5	62.3	51.2	364.0	158.8
Coleman	0.00	185.9	403.0	-14.8	-49.8	291.1	142.2
	7.91	186.5	409.9	-8.9	-412	303.2	145.6
	14.66	187.8	414.8	-4.2	-31.5	314.0	148.8
	20.49	189.2	418.7	-0.4	-22.4	323.8	150.4
	25.58	190.8	421.7	9.0	-14.2	331.8	152.8
	34.02	194.4	426.3	21.2	-1.1	343.1	156.8
	40.74	198.8	420.6	30.7	10.5	353.5	160.2
	50.76	209.8	433.4	45.1	27.4	369.1	166.2
	57.89	221.1	434.4	57.0	39.8	378.5	170.2
	63.21	232.8	433.6	65.4	49.2	383.7	173.4
	67.34	243.6	431.5	71.8	55.7	386.7	175.2
	70.64	253.4	428.5	76.8	60.5	387.8	176.1
	73.33	262.5	424.7	80.8	64.1	387.8	176.4
	77.46	279.1	416.1	86.8	68.7	384.8	176.5

APPENDIX C

k_2 VALUES IN VARIOUS MIXED SOLVENTS
(F = Fisher, C = Coleman)

Temperature		10°C	15°C	20°C	25°C	30°C	35°C	40°C
Theoretical k_2 Values		56.18	57.17	58.16	59.16	60.15	61.14	62.13
Ethanol-Water:								
from K_w	F	55.25	56.89	56.77	58.53	59.40	60.31	60.75
	C	55.03	56.63	56.59	58.75	59.34	60.36	60.86
from K_s	F	55.71	55.25	56.63	59.45	60.06	61.07	62.53
	C	55.49	56.92	56.73	59.24	60.21	61.82	62.98
from HAc	F	55.59	57.47	59.02	59.33	60.66	60.89	63.62
	C	55.52	57.59	56.33	59.64	61.04	61.65	65.16
from HBz	F	57.08	58.49	60.08	59.75	60.91	61.66	63.39
	C	54.43	60.20	59.94	59.51	61.10	63.15	62.04
from HPh	F	55.39	56.75	56.91	58.96	59.72	60.86	61.57
	C	55.33	57.42	57.27	58.99	59.98	60.88	62.30
Acetone-Water:								
from K_w	F	55.79	56.44	56.96	59.40	59.68	60.75	62.23
	C	55.34	56.54	56.95	56.08	59.89	60.62	62.21
from K_s	F	56.21	56.49	56.92	60.41	60.14	61.68	63.50
	C	55.38	56.26	56.43	58.60	60.27	61.80	63.40
from HAc	F	56.83	56.15	57.51	60.66	61.61	61.99	64.33
	C	55.10	57.63	57.73	55.88	60.93	61.76	65.77
from HBz	F	57.74	56.30	58.51	62.00	61.34	62.53	63.96
	C	57.17	58.25	57.65	58.22	61.53	62.77	65.59
from HPh	F	56.05	56.66	57.04	59.36	60.08	60.99	64.75
	C	55.70	56.87	56.56	58.08	60.23	61.12	60.29

APPENDIX C--Continued

Temperature		15°C	25°C	35°C
Methanol-Water:				
from K_w	F	56.33	56.83	60.39
	C	56.42	58.38	60.41
from K_s	F	56.31	59.08	60.90
	C	56.52	58.92	60.98
from HAc	F	56.91	59.83	62.18
	C	57.21	59.48	61.30
from HBz	F	56.54	59.99	62.48
	C	57.73	60.13	62.14
from HPh	F	56.73	59.14	61.12
	C	56.77	59.10	60.88
THF-Water:				
from K_w	F	55.93	58.23	60.63
	C	56.07	58.06	60.25
from K_s	F	56.27	58.42	60.81
	C	56.26	58.08	61.04
from HAc	F	56.00	58.42	61.23
	C	56.60	59.37	61.15
from HBz	F	56.01	59.03	62.38
	C	57.11	60.08	62.15
from HPh	F	56.23	58.58	60.90
	C	56.40	58.53	60.94

APPENDIX C--Continued

Temperature		15°C	25°C	35°C
p-Dioxan-Water:				
from K_w	F	57.89	59.04	61.21
	C	57.27	59.18	61.59
from K_s	F	57.53	59.02	61.30
	C	57.60	59.56	62.48
from HAc	F	59.48	61.42	63.43
	C	58.31	62.11	65.07
from HBz	F	57.87	58.89	63.54
	C	60.77	60.51	65.41
from HPh	F	57.32	69.22	61.23
	C	57.41	59.41	61.76

APPENDIX D

AVERAGE pK's

IN THE MIXTURES OF WATER-ETHANOL AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Water	0.00	14.53	14.34	14.17	14.00	13.84	13.69	13.55
	6.16	14.69	14.47	14.30	14.12	13.95	13.79	13.67
	11.61	14.81	14.59	14.42	14.23	14.06	13.89	13.79
	16.45	14.92	14.69	14.52	14.34	14.16	13.99	13.88
	20.80	15.01	14.77	14.60	14.43	14.23	14.07	13.95
	28.26	15.13	14.89	14.73	14.59	14.37	14.20	14.07
	34.43	15.20	14.98	14.83	14.70	14.48	14.31	14.18
	44.06	15.35	15.12	14.99	14.89	14.67	14.50	14.38
	51.23	15.49	15.24	15.11	15.04	14.82	14.66	14.55
	56.76	15.62	15.36	15.25	15.16	14.96	14.80	14.69
	61.17	15.72	15.45	15.35	15.28	15.07	14.92	14.82
	64.76	15.81	15.54	15.45	15.35	15.18	15.03	14.94
	67.75	15.91	15.64	15.56	15.45	15.29	15.12	15.04
	72.42	16.11	15.84	15.76	15.65	15.49	15.33	15.24
Acetic Acid	0.00	4.76	4.75	4.75	4.75	4.75	4.75	4.76
	6.16	4.86	4.83	4.80	4.84	4.84	4.85	4.87
	11.61	4.96	4.93	4.94	4.94	4.93	4.95	4.98
	16.45	5.04	5.02	5.02	5.03	5.02	5.04	5.06
	20.80	5.11	5.12	5.10	5.13	5.07	5.12	5.13
	28.26	5.25	5.29	5.24	5.32	5.24	5.29	5.29
	34.43	5.37	5.44	5.38	5.48	5.37	5.42	5.43
	44.06	5.61	5.78	5.62	5.72	5.60	5.71	5.65
	51.23	5.80	5.88	5.80	5.91	5.80	5.87	5.88
	56.76	5.97	6.04	5.97	6.07	5.97	6.04	6.05
	61.17	6.11	6.18	6.12	6.21	6.10	6.18	6.20
	64.76	6.23	6.30	6.25	6.33	6.23	6.31	6.31
	67.75	6.33	6.41	6.43	6.44	6.35	6.43	6.43
	72.42	6.51	6.60	6.56	6.62	6.54	6.63	6.63

APPENDIX D--Continued

IN THE MIXTURES OF WATER-ETHANOL AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Benzoic Acid	0.00	4.22	4.21	4.20	4.20	4.20	4.20	4.20
	6.16	4.35	4.31	4.32	4.34	4.32	4.34	4.33
	11.61	4.46	4.42	4.41	4.47	4.46	4.46	4.48
	16.45	4.56	4.54	4.55	4.60	4.58	4.60	4.60
	20.80	4.64	4.68	4.69	4.76	4.72	4.73	4.74
	28.26	4.92	4.96	4.98	5.04	4.94	4.96	4.97
	34.43	5.17	5.20	5.24	5.27	4.24	5.20	5.20
	44.06	5.54	5.52	5.53	5.58	5.55	5.55	5.56
	51.23	5.86	5.74	5.74	5.81	5.78	5.74	5.72
	56.76	5.95	5.91	5.93	5.98	5.93	5.91	5.90
	61.17	6.10	6.05	6.08	6.12	6.08	6.05	6.05
	64.76	6.21	6.17	6.20	6.23	6.20	6.18	6.18
	67.75	6.30	6.27	6.29	6.36	6.32	6.29	6.30
	72.42	6.52	6.45	6.48	6.54	6.51	6.50	6.51
Phenol	0.00	10.20	10.11	10.04	9.97	9.90	9.84	9.79
	6.16	10.34	10.27	10.19	10.10	10.03	9.98	9.92
	11.61	10.49	10.41	10.30	10.25	10.15	10.11	10.09
	16.45	10.60	10.54	10.44	10.38	10.34	10.24	10.21
	20.80	10.70	10.66	10.59	10.53	10.43	10.36	10.33
	28.26	10.90	10.88	10.83	10.77	10.67	10.58	10.50
	34.43	11.07	11.06	11.01	10.95	10.85	10.74	10.66
	44.06	11.36	11.32	11.28	11.22	11.12	10.99	10.92
	51.23	11.56	11.50	11.46	11.40	11.20	11.17	11.10
	56.76	11.67	11.64	11.60	11.54	11.43	11.31	11.25
	61.17	11.78	11.75	11.74	11.65	11.54	11.43	11.37
	64.76	11.89	11.84	11.84	11.75	11.64	11.54	11.48
	67.75	11.98	11.93	11.93	11.84	11.73	11.63	11.57
	72.42	12.12	12.06	12.06	11.97	11.86	11.79	11.73

APPENDIX D--Continued

IN THE MIXTURES OF WATER-ETHANOL AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Silver Chloride	0.00	10.37	10.16	9.95	9.75	9.56	9.38	9.21
	6.16	10.56	10.30	10.10	9.89	9.72	9.52	9.37
	11.61	10.71	10.44	10.24	10.03	9.86	9.64	9.51
	16.45	10.85	10.55	10.36	10.15	9.98	9.75	9.63
	20.80	10.97	10.66	10.48	10.26	10.07	9.87	9.75
	28.26	11.14	10.84	10.66	10.47	10.27	10.05	9.91
	34.43	11.26	11.01	10.82	10.65	10.43	10.23	10.06
	44.06	11.49	11.28	11.09	10.94	10.74	10.50	10.38
	51.23	11.70	11.50	11.22	11.17	10.98	10.74	10.57
	56.76	11.85	11.68	11.48	11.37	11.19	10.95	10.78
	61.17	12.05	11.84	11.66	11.54	11.38	11.12	10.95
	64.76	12.19	11.97	11.81	11.69	11.52	11.28	11.12
	67.75	12.32	12.09	11.98	11.83	11.68	11.42	11.27
	72.42	12.54	12.31	12.16	12.05	11.89	11.65	11.51

APPENDIX D--Continued

IN THE MIXTURES OF WATER-ACETONE AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Water	0.00	14.53	15.34	14.17	13.99	13.84	13.69	13.54
	6.15	14.71	14.51	14.32	14.16	14.01	13.85	13.72
	11.60	14.84	14.67	14.47	14.32	14.18	14.01	13.87
	16.44	14.99	14.83	14.60	14.48	14.31	14.17	14.02
	20.79	15.12	14.96	14.74	14.62	14.42	14.30	14.16
	28.24	15.37	15.21	14.97	14.87	14.71	14.55	14.41
	34.42	15.59	15.44	15.20	15.10	14.94	14.78	14.65
	44.05	15.99	15.85	15.63	15.50	15.37	15.19	15.07
	51.21	16.35	16.26	16.01	15.84	15.76	15.55	15.43
	56.75	16.67	16.59	16.34	16.15	16.12	15.88	15.77
	61.16	16.94	16.88	16.63	16.43	16.41	16.17	16.06
	64.76	17.20	17.05	1.690	16.66	16.68	16.44	16.34
	67.74	17.44	17.30	17.14	16.91	16.84	16.74	16.60
	72.41	17.98	17.84	17.68	17.38	17.34	17.28	17.06
Acetic Acid	0.00	4.76	4.75	4.75	4.75	4.75	4.75	4.75
	6.15	4.89	4.90	4.86	4.90	4.90	4.89	4.92
	11.60	5.00	5.04	5.00	5.03	5.03	5.02	5.05
	16.44	5.12	5.17	5.13	5.16	5.14	5.16	5.17
	20.79	5.24	5.23	5.25	5.27	5.26	5.30	5.32
	28.24	5.48	5.55	5.48	5.51	5.49	5.53	5.56
	34.42	5.69	5.77	5.70	5.73	5.67	5.75	5.77
	44.05	6.08	6.16	6.08	6.12	6.04	6.12	6.16
	51.21	6.39	6.49	6.43	6.45	6.41	6.45	6.48
	56.75	6.72	6.78	6.71	6.74	6.72	6.75	6.77
	61.16	6.97	7.03	6.98	6.01	7.00	7.01	7.03
	64.76	7.20	7.24	7.23	7.26	72.5	7.25	7.27
	67.74	7.42	7.45	7.44	7.48	7.48	7.47	7.49
	72.41	7.79	7.80	7.77	7.84	7.87	7.86	7.88

APPENDIX D--Continued

IN THE MIXTURES OF WATER-ACETONE AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Benzoic Acid	0.00	4.22	4.21	4.20	4.20	4.20	4.20	4.20
	6.15	4.39	4.39	4.38	4.38	4.37	4.38	4.36
	11.60	4.59	4.58	4.55	4.57	4.55	4.57	4.50
	16.44	4.78	4.77	4.74	4.77	4.68	4.75	4.66
	20.79	4.97	4.95	4.92	4.95	4.85	4.91	4.86
	28.24	5.28	5.27	5.25	5.27	5.16	5.22	5.21
	34.42	5.56	5.54	5.54	5.54	5.40	5.47	5.46
	44.05	6.01	5.99	5.91	5.98	5.92	5.95	5.92
	51.21	6.33	6.32	6.32	6.32	6.28	6.29	6.27
	56.75	6.62	6.60	6.60	6.61	6.50	6.55	6.52
	61.16	6.89	6.86	6.86	6.89	6.76	6.76	6.77
	64.76	7.03	7.05	6.97	7.05	7.01	7.02	7.04
	67.74	7.24	7.24	7.20	7.24	7.22	7.23	7.24
	72.41	7.60	7.59	7.52	7.60	7.58	7.60	7.58
Phenol	0.00	10.20	10.11	10.04	9.97	9.90	9.84	9.79
	6.15	10.41	10.37	10.26	10.21	10.11	9.95	9.90
	11.60	10.61	10.58	10.48	10.41	10.32	10.26	10.19
	16.44	10.80	10.78	10.71	10.61	10.53	10.47	10.39
	20.79	10.99	10.98	10.92	10.79	10.71	10.65	10.56
	28.24	11.33	11.30	11.16	11.03	10.93	10.87	10.80
	34.42	11.59	11.57	11.51	11.38	11.27	11.17	11.10
	44.05	11.99	11.95	11.86	11.73	11.64	11.51	11.45
	51.21	12.38	12.31	12.22	12.09	11.95	11.87	11.81
	56.75	12.60	12.56	12.46	12.33	12.20	12.11	12.05
	61.16	12.85	12.82	12.69	12.56	12.44	12.34	12.28
	64.76	13.06	13.04	12.92	12.79	12.68	12.57	12.50
	67.74	13.26	13.20	13.10	12.97	12.86	12.78	12.68
	72.41	13.61	13.52	13.44	13.31	13.22	13.13	13.04

APPENDIX D--Continued

IN THE MIXTURES OF WATER-ACETONE AT VARIOUS TEMPERATURES

Substance	wt%	10°C	15°C	20°C	25°C	30°C	35°C	40°C
Silver Chloride	0.00	10.37	10.16	9.95	9.75	9.56	9.38	9.21
	6.15	10.48	10.28	10.10	9.88	9.68	9.50	9.35
	11.60	10.58	10.39	10.20	10.00	9.80	9.62	9.49
	16.44	10.69	10.51	10.32	10.11	9.90	9.74	9.63
	20.79	10.79	10.62	10.42	10.22	10.02	9.86	9.73
	28.24	10.97	10.83	10.62	10.45	10.23	10.08	9.93
	34.42	11.14	11.03	10.80	10.66	10.44	10.26	10.13
	44.05	11.45	11.39	11.26	11.02	10.81	10.62	10.50
	51.21	11.73	11.70	11.46	11.34	11.15	10.95	10.74
	56.75	12.03	11.97	11.74	11.61	11.45	11.23	11.13
	61.16	12.26	12.22	11.99	11.85	11.70	11.50	11.40
	64.76	12.49	12.43	12.22	12.07	11.93	11.74	11.64
	67.74	12.69	12.64	12.42	12.28	12.14	11.96	11.86
	72.41	13.05	13.00	12.82	12.58	12.52	12.37	12.24

APPENDIX D--Continued

IN THE MIXTURES OF WATER-METHANOL AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Water	0.00	14.35	14.00	13.69
	6.17	14.36	14.04	13.71
	11.62	14.37	14.06	13.74
	16.47	14.38	14.08	13.77
	20.82	14.39	14.09	13.80
	28.29	14.39	14.11	13.83
	34.47	14.40	14.13	13.87
	44.10	14.42	14.18	13.93
	51.26	14.43	14.23	13.97
	56.80	14.45	14.26	14.03
	61.21	14.48	14.29	14.06
	64.80	14.51	14.32	14.10
	67.78	14.55	14.35	14.14
	72.45	14.61	14.42	14.21
Acetic Acid	0.00	4.75	4.75	4.75
	6.17	4.86	4.83	4.80
	11.62	4.96	4.94	4.90
	16.47	5.05	5.01	4.98
	20.82	5.14	5.09	5.05
	28.29	5.27	5.22	5.25
	34.47	5.35	5.31	5.33
	44.10	5.56	5.53	5.53
	51.26	5.72	5.69	5.71
	56.80	5.84	5.81	5.84
	61.21	5.96	5.94	5.96
	64.80	6.03	6.06	6.08
	67.78	6.12	6.16	6.18
	72.45	6.28	6.31	6.33

APPENDIX D--Continued

IN THE MIXTURES OF WATER-METHANOL AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Benzoic Acid	0.00	4.21	4.20	4.20
	6.21	4.33	4.29	4.27
	11.68	4.45	4.40	4.38
	16.57	4.53	4.49	4.48
	20.93	4.60	4.59	4.54
	28.42	4.81	4.75	4.72
	34.62	5.02	4.91	4.89
	44.26	5.23	5.22	5.20
	51.43	5.44	5.40	5.39
	56.96	5.56	5.54	5.51
	61.36	5.69	5.67	5.65
	64.95	5.81	5.80	5.80
	67.93	5.93	5.91	5.89
	72.58	6.14	6.11	6.09
Phenol	0.00	10.11	9.97	9.84
	6.21	10.22	10.07	9.91
	11.68	10.32	10.17	10.01
	16.57	10.41	10.26	10.11
	20.93	10.50	10.35	10.26
	28.42	10.61	10.46	10.29
	34.62	10.74	10.56	10.40
	44.26	10.88	10.72	10.57
	51.43	10.99	10.85	10.70
	56.96	11.06	10.93	10.79
	61.36	11.13	11.01	10.86
	64.95	11.19	11.07	10.92
	67.93	11.24	11.12	10.96
	72.58	11.31	11.21	11.05

APPENDIX D--Continued

IN THE MIXTURES OF WATER-METHANOL AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Silver	0.00	10.16	9.75	9.38
Chloride	7.91	10.32	9.90	9.51
	14.66	10.47	10.04	9.64
	20.49	10.60	10.15	9.75
	25.58	10.69	10.28	9.85
	34.02	10.89	10.46	10.03
	40.74	11.05	10.58	10.22
	50.76	11.30	10.83	10.56
	57.89	11.51	11.04	10.81
	63.21	11.67	11.22	11.10
	67.34	11.82	11.38	11.27
	70.64	11.98	11.53	11.38
	73.33	12.09	11.65	11.52
	77.46	12.17	11.86	11.71

APPENDIX D--Continued

IN THE MIXTURES OF WATER-THF AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Water	0.00	14.35	14.00	13.69
	6.85	14.46	14.12	13.80
	12.82	14.56	14.25	13.93
	18.08	14.67	14.37	14.05
	22.73	14.77	14.48	14.17
	30.62	14.96	14.71	14.41
	37.04	15.13	14.92	14.61
	46.88	15.48	15.30	14.97
	54.06	15.80	15.62	15.30
	59.53	16.10	15.89	15.58
	63.84	16.36	16.15	15.82
	67.31	16.59	16.37	16.05
	70.18	16.80	16.56	16.28
	74.63	17.16	16.94	16.67
Acetic Acid	0.00	4.75	4.75	4.75
	6.85	4.88	4.88	4.90
	12.82	5.00	5.00	5.04
	18.08	5.15	5.14	5.20
	22.73	52.6	5.26	5.30
	30.62	5.50	5.50	5.54
	37.04	5.71	5.72	5.75
	46.88	6.11	6.08	6.12
	54.06	6.44	6.40	6.44
	59.53	6.73	6.68	6.72
	63.84	6.98	6.95	6.95
	67.31	7.21	7.17	7.18
	70.18	7.44	7.38	7.42
	74.63	7.80	7.74	7.77

APPENDIX D--Continued

IN THE MIXTURES OF WATER-THF AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Benzoic Acid	0.00	4.21	4.20	4.20
	6.23	4.44	4.42	4.22
	12.82	4.60	4.59	4.62
	18.08	4.87	4.86	4.86
	22.73	5.12	5.11	5.13
	30.62	5.51	5.50	5.50
	37.04	5.72	5.80	5.76
	46.88	6.21	6.23	6.20
	54.06	6.57	6.57	6.52
	59.53	6.86	6.84	6.86
	63.84	7.10	7.09	7.07
	67.31	7.31	7.29	7.29
	70.18	7.53	7.48	7.48
	74.63	7.89	7.88	7.87
Phenol	0.00	10.11	9.97	9.84
	6.23	10.34	10.18	10.03
	12.82	10.53	10.38	10.26
	18.08	10.74	10.59	10.48
	22.73	10.98	10.85	10.69
	30.62	11.32	11.21	11.02
	37.04	11.61	11.50	11.30
	46.88	12.04	11.90	11.71
	54.06	12.43	12.21	12.04
	59.53	12.71	12.47	12.31
	63.84	12.95	12.71	12.53
	67.31	13.15	12.90	12.72
	70.18	13.36	13.07	12.93
	74.63	13.65	13.39	13.25

APPENDIX D--Continued

IN THE MIXTURES OF WATER-THF AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Silver Chloride	0.00	10.16	9.75	9.38
	6.23	10.31	9.92	9.53
	12.82	10.44	10.07	9.67
	18.08	10.58	10.20	9.82
	22.73	10.69	10.32	9.95
	30.62	10.91	10.53	10.16
	37.04	11.11	10.75	10.37
	46.88	11.46	11.07	10.71
	54.06	11.78	11.38	11.03
	59.53	12.07	11.66	11.32
	63.84	12.32	11.91	11.56
	67.31	12.54	12.13	11.81
	70.18	12.78	12.34	12.04
	74.63	13.13	12.82	12.43

APPENDIX D--Continued

IN THE MIXTURES OF WATER-p-DIOXAN AT VARIOUS TEMPERATURES

Substances	wt%	15°C	25°C	35°C
Water	0.00	14.35	14.00	13.69
	7.95	14.51	14.17	13.86
	14.73	14.67	14.33	14.02
	20.57	14.84	14.47	14.17
	25.67	14.98	14.60	14.31
	34.13	15.24	14.84	14.58
	40.85	15.46	15.08	14.83
	50.89	15.87	15.53	15.29
	58.01	16.27	15.94	15.70
	63.33	16.66	16.31	16.08
	67.45	16.96	16.65	16.42
	70.74	17.27	16.99	16.74
	73.42	17.51	17.29	17.06
	77.55	18.05	17.89	17.73
Acetic Acid	0.00	4.75	4.75	4.75
	7.95	4.91	4.96	4.92
	14.73	5.06	5.12	5.07
	20.57	5.22	5.28	5.21
	25.67	5.42	5.45	5.41
	34.13	5.74	5.74	5.69
	40.85	6.00	6.03	6.01
	50.89	6.53	6.56	6.55
	58.01	7.00	7.08	7.05
	63.33	7.44	7.49	7.51
	67.45	7.91	7.91	7.94
	70.74	8.33	8.31	8.35
	73.42	8.76	8.70	8.70
	77.55	9.35	9.38	9.39

APPENDIX D--Continued

IN THE MIXTURES OF WATER-p-DIOXAN AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Benzoic Acid	0.00	4.21	4.20	4.20
	7.91	4.43	4.42	4.40
	14.66	4.63	4.59	4.62
	20.49	4.78	4.78	4.83
	25.58	4.99	4.99	5.04
	34.02	5.38	5.36	5.40
	40.74	5.71	5.69	5.74
	50.76	6.28	6.27	6.32
	57.89	6.77	6.79	6.83
	63.21	7.24	7.27	7.32
	67.34	7.68	7.70	7.75
	70.64	8.06	8.02	8.05
	73.33	8.40	8.46	8.50
	77.46	9.03	9.10	9.13
Phenol	0.00	10.11	9.97	9.84
	7.91	10.36	10.21	10.09
	14.66	10.63	10.45	10.32
	20.49	10.86	10.64	10.53
	25.58	11.04	10.84	10.73
	34.02	11.42	11.20	11.08
	40.74	11.73	11.51	11.40
	50.76	12.25	12.08	11.96
	57.89	12.74	12.56	12.44
	63.21	13.19	12.97	12.85
	67.34	13.54	13.36	13.22
	70.64	13.86	13.62	13.55
	73.33	14.13	14.02	13.86
	77.46	14.64	14.54	14.40

APPENDIX D--Continued

IN THE MIXTURES OF WATER-p-DIOXAN AT VARIOUS TEMPERATURES

Substance	wt%	15°C	25°C	35°C
Silver Chloride	0.00	10.11	9.97	9.84
	7.91	10.36	10.21	10.09
	14.66	10.63	10.45	10.32
	20.49	10.86	10.64	10.53
	25.58	11.04	10.84	10.73
	34.02	11.42	11.20	11.08
	40.74	11.73	11.51	11.40
	50.76	12.25	12.08	11.96
	57.89	12.74	12.56	12.44
	63.21	13.19	12.97	12.85
	67.34	13.54	13.36	13.22
	70.64	13.86	13.62	13.55
	73.33	14.13	14.02	13.86
	77.46	14.64	14.54	14.40

APPENDIX E

The following data are tabulated as $-\phi_L$, cal/mole. The extrapolated value of $-\phi_L$ for the titrant is equal to ΔH_0, and can be used in connection with equation (2) to obtain ΔH_i values. Asterisks indicate values of ϕ_L which were omitted from the calculation of K_2 and ΔH_2° values.

The least -square slope, intercept and standard deviation of the data when analyzed according to equation (10) are listed [$-\phi_L$ plotted against $(-\phi_L/M_A)^{1/2}$]. The units of the intercept and standard deviation are cal/mole. The standard deviations in ΔH_2° obtained from equations (12) and (14) are also given, in units of cal/mole. Values of ΔH_2° obtained from the two methods are given in kcal/mole dimer, while ΔS_2° is listed as cal/mole °K.

APPENDIX E--Continued

Benzene

0.2945 M Benzoic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
$0.3134\text{x}10^{-3}$	758*	$0.2612\text{x}10^{-2}$	361*
$0.7043\text{x}10^{-3}$	1124*	$0.6522\text{x}10^{-2}$	898
$0.1276\text{x}10^{-2}$	1524	$0.1042\text{x}10^{-2}$	1173
$0.2000\text{x}10^{-2}$	1799	$0.1561\text{x}10^{-2}$	1403
$0.2643\text{x}10^{-2}$	1968	$0.2077\text{x}10^{-2}$	1588
$0.3539\text{x}10^{-2}$	2137	$0.2591\text{x}10^{-2}$	1728
$0.4557\text{x}10^{-2}$	2270	$0.3105\text{x}10^{-2}$	1839
$0.5315\text{x}10^{-2}$	2354	$0.3743\text{x}10^{-2}$	1948
$0.6195\text{x}10^{-2}$	2425	$0.4379\text{x}10^{-2}$	2037
$0.7318\text{x}10^{-2}$	2504	$0.5012\text{x}10^{-2}$	2118
$0.8433\text{x}10^{-2}$	2570	$0.5642\text{x}10^{-2}$	2181
$0.9416\text{x}10^{-2}$	2619	$0.6395\text{x}10^{-2}$	2248
$0.1015\text{x}10^{-1}$	2615	$0.7268\text{x}10^{-1}$	2314
$0.1100\text{x}10^{-1}$	2684	$0.8316\text{x}10^{-1}$	2366
$0.1136\text{x}10^{-1}$	2697	$0.9367\text{x}10^{-1}$	2436
0.2945	3431	$0.1034\text{x}10^{-1}$	2481
		$0.1108\text{x}10^{-1}$	2514
		0.2945	3232*

Equation (10)

-slope	1.939	2.318
intercept	3641	3619
std. dev.	1.9	6.3
K_2	484	337
$-\Delta H_2$	7.28	7.24
$-\Delta S_2$	12.14	12.72

Equation (12) and (14)

std. dev.	86	420
K_2	490	350
$-\Delta H_2$	7.30	7.66

APPENDIX E--Continued

Benzene					
0.1296 M m-Toluic Acid				0.2019 M m-Toluic Acid	
Run 1		Run			
M	$-\phi_L$	M	$-\phi_L$	M	$-\phi_L$
$0.3669\text{x}10^{-3}$	834*	$0.4921\text{x}10^{-3}$	1036*	$0.2509\text{x}10^{-3}$	733*
$0.8164\text{x}10^{-3}$	1314	$0.8413\text{x}10^{-3}$	1403	$0.7197\text{x}10^{-3}$	1239
$0.1312\text{x}10^{-2}$	1619	$0.1238\text{x}10^{-2}$	1674	$0.1186\text{x}10^{-2}$	1596
$0.1902\text{x}10^{-2}$	1858	$0.1632\text{x}10^{-2}$	1854	$0.1959\text{x}10^{-2}$	1938
$0.2341\text{x}10^{-2}$	3001	$0.2024\text{x}10^{-2}$	1998	$0.2650\text{x}10^{-2}$	2131
$0.3354\text{x}10^{-2}$	2271	$0.2535\text{x}10^{-2}$	2143	$0.3487\text{x}10^{-2}$	2315
$0.3401\text{x}10^{-2}$	2238	$0.3090\text{x}10^{-2}$	2275	$0.4393\text{x}10^{-2}$	2461
$0.3925\text{x}10^{-2}$	2314	$0.3901\text{x}10^{-2}$	2417	$0.5365\text{x}10^{-2}$	2583
$0.4397\text{x}10^{-2}$	2380	$0.4421\text{x}10^{-2}$	2494	$0.6032\text{x}10^{-2}$	2653
$0.4866\text{x}10^{-2}$	2440	$0.4889\text{x}10^{-2}$	2546	$0.6768\text{x}10^{-2}$	2716
$0.1296\text{x}10^{-2}$	3527*	$0.5308\text{x}10^{-2}$	2591	$0.7934\text{x}10^{-2}$	2804
		$0.5770\text{x}10^{-2}$	2636	$0.8591\text{x}10^{-2}$	2848
		$0.1296\text{x}10^{-2}$	3662*	$0.2019\text{x}10^{-2}$	3632

Equation (10)

-slope	2.035	2.002	2.164
intercept	3889	3991	4086
std. dev.	22.8	5.2	9.2
K_2	469	498	436
$-\Delta H_2$	7.78	7.98	8.17
$-\Delta S_2$	13.86	14.43	15.33

Equation (12) and (14)

std. dev.	183
K_2	550
$-\Delta H_2$	8.03

APPENDIX E--Continued

Benzene

0.1577 M o-Toluic Acid

$\underline{M}$	$\underline{\bar{L}}$	$\underline{M}$	$\underline{\bar{L}}$
0.3366×10^{-3}	1020*	0.5743×10^{-3}	1148*
0.7021×10^{-3}	1304	0.8781×10^{-3}	1379
0.1005×10^{-2}	1556	0.1241×10^{-2}	1588
0.1428×10^{-2}	1802	0.1663×10^{-2}	1810
0.1728×10^{-2}	1903	0.1962×10^{-2}	1920
0.2266×10^{-2}	2083	0.2320×10^{-2}	2038
0.2801×10^{-2}	2219	0.3149×10^{-2}	2260
0.3390×10^{-2}	2334	0.3619×10^{-2}	2339
0.3858×10^{-2}	2415	0.4318×10^{-2}	2458
0.4428×10^{-2}	2505	0.4896×10^{-2}	2565
0.4902×10^{-2}	2569	0.5258×10^{-2}	2572
0.5246×10^{-2}	2611	0.1577	3775
0.1577	3664		

Equation (10)

-slope	1.946	2.215
intercept	3963	4126
std. dev.	15.2	21.1
K_2	523	420
$-\Delta H_2$	7.93	8.25
$-\Delta S_2$	14.15	15.68

Euqation (12 and (14)

std. dev.	519	1.130
K_2	550	400
$-\Delta H_2$	7.93	8.08

APPENDIX E--Continued

Benzene

0.2568 M o-Toluic Acid		0.1899 M o-Toluic Acid	
M	$-\phi_L$	M	$-\phi_L$
$0.3590\text{x}10^{-3}$	964	$0.5889\text{x}10^{-3}$	1140
$0.6574\text{x}10^{-3}$	1388	$0.1028\text{x}10^{-2}$	1542
$0.1153\text{x}10^{-2}$	1762	$0.1538\text{x}10^{-2}$	1842
$0.1548\text{x}10^{-2}$	1978	$0.2118\text{x}10^{-2}$	2046
$0.2139\text{x}10^{-2}$	2205	$0.2765\text{x}10^{-2}$	2252
$0.2531\text{x}10^{-2}$	2358	$0.3480\text{x}10^{-2}$	2404
$0.3409\text{x}10^{-2}$	2529	$0.4259\text{x}10^{-2}$	2537
$0.4281\text{x}10^{-2}$	2683	$0.5032\text{x}10^{-2}$	2641
$0.5147\text{x}10^{-2}$	2799	$0.5660\text{x}10^{-2}$	2717
$0.6103\text{x}10^{-2}$	2911	$0.6352\text{x}10^{-2}$	2787
$0.6956\text{x}10^{-2}$	2990	$0.7108\text{x}10^{-2}$	2849
$0.7616\text{x}10^{-2}$	3048	$0.7715\text{x}10^{-2}$	2900
$0.8366\text{x}10^{-2}$	3107	0.1899	3958
0.2568	4022		

Equation (10)		
-slope	2.037	2.244
intercept	4307	4274
std. dev.	26.7	11.8
K_2	519	424
$-\Delta H_2$	8.61	8.55
$-\Delta S_2$	16.47	16.65

Equation (12) and (14)		
std. dev.	--	--
K_2	--	--
$-\Delta H_2$	--	--

Toluene

0.4792 M Benzoic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
0.4097×10^{-3}	165	0.5208×10^{-3}	426*
0.9672×10^{-3}	204	0.1263×10^{-2}	519
0.1894×10^{-2}	408	0.2741×10^{-2}	787
0.3184×10^{-2}	583	0.3843×10^{-2}	911
0.4651×10^{-2}	732	0.5487×10^{-2}	1054
0.5745×10^{-2}	809	0.6758×10^{-2}	1129
0.7557×10^{-2}	902	0.8561×10^{-2}	1213
0.9535×10^{-2}	982	0.9994×10^{-2}	1266
0.1096×10^{-1}	1029	0.1142×10^{-1}	1310
0.1309×10^{-1}	1082	0.1354×10^{-1}	1364
0.1467×10^{-1}	1115	0.1512×10^{-1}	1397
0.1624×10^{-1}	1146	0.1686×10^{-1}	1430
0.1794×10^{-1}	1172	0.1793×10^{-1}	1447
0.4792	1687*	0.4792	2010*

Equation (10)

	Run 1	Run 2
-slope	3.127	2.616
intercept	1953	2195
std. dev.	113.6	4.7
K_2	100	160
$-\Delta H_2$	3.91	4.39
$-\Delta S_2$	3.95	4.63

Equation (12) and (14)

	Run 1	Run 2
std. dev.	517	360
K_2	160	145
$-\Delta H_2$	3.90	3.97

APPENDIX E--Continued

Toluene

0.3804 M Benzoic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
0.4728x10^{-3}	400	0.4138x10^{-3}	268
0.1356x10^{-2}	788	0.1444x10^{-2}	646
0.2089x10^{-2}	958	0.2031x10^{02}	781
0.3547x10^{-2}	1208	0.2761x10^{-2}	908
0.4561x10^{-2}	1319	0.3924x10^{-2}	1079
0.5856x10^{-2}	1421	0.5080x10^{-2}	1185
0.7000x10^{-2}	1494	0.6371x10^{-2}	1288
0.8702x10^{-2}	1580	0.7370x10^{-2}	1345
0.9689x10^{-2}	1620	0.9069x10^{-2}	1425
0.1095x10^{-1}	1664	0.1061x10^{-1}	1486
0.1275x10^{-1}	1718	0.1242x10^{-1}	1541
0.1427x10^{-1}	1754	0.1421x10^{-1}	1587
0.3804	2381*	0.3804	2193*

Equation (10)	Run 1	Run 2
-slope	2.383	2.834
intercept	2594	2548
std. dev.	8.15	10.6
K_2	228	159
$-\Delta H_2$	5.19	5.10
$-\Delta S_2$	6.61	7.02

Equation (12) and (14)	Run 1	Run 2
std. dev.	232	165
K_2	295	220
$-\Delta H_2$	5.20	5.16

APPENDIX E --Continued

Toluene

0.1296 M m-Toluic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
0.3669x10^{-3}	840	0.4921x10^{-3}	1036*
0.8164x10^{-3}	1321	0.8413x10^{-3}	1403
0.1312x10^{-2}	1625	0.1238x10^{-2}	1674
0.1902x10^{-2}	1864	0.1632x10^{-2}	1854
0.2341x10^{-2}	2007	0.2024x10^{-2}	1998
0.3353x10^{-2}	2277	0.2535x10^{-2}	2143
0.3401x10^{-2}	2244	0.3090x10^{-2}	2275
0.3925x10^{-2}	2320	0.3901x10^{-2}	2417
0.4397x10^{-2}	2386	0.4421x10^{-2}	2545
0.4866x10^{-2}	2446	0.4889x10^{-2}	2591
0.1296x10^{-2}	3533	0.5308x10^{-2}	2636
		0.5770	3622*

Equation (10)

-slope	2.005	2.002
intercept	3870	3991
std. dev.	20.9	5.2
K_2	481	498
$-\Delta H_2$	7.74	7.98
$-\Delta S_2$	13.69	14.43

Equation (12) and (14)

std. dev.	--	183
K_2	--	550
$-\Delta H_2$	--	8.03

APPENDIX E--Continued

Toluene

0.1333 M m-Toluic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
$0.1554\text{x}10^{-3}$	261*	$0.3104\text{x}10^{-3}$	961
$0.4650\text{x}10^{-3}$	729	$0.5679\text{x}10^{-3}$	1266
$0.8245\text{x}10^{-3}$	1020	$0.9268\text{x}10^{-3}$	1660
$0.1182\text{x}10^{-2}$	1193	$0.1284\text{x}10^{-2}$	1881
$0.1436\text{x}10^{-2}$	1317	$0.1639\text{x}10^{-2}$	2046
$0.1790\text{x}10^{-2}$	1431	$0.2042\text{x}10^{-2}$	2194
$0.2193\text{x}10^{-2}$	1548	$0.2543\text{x}10^{-2}$	2322
$0.2543\text{x}10^{-2}$	1638	$0.3040\text{x}10^{-2}$	2420
$0.2991\text{x}10^{-2}$	1711	$-.3533\text{x}10^{-2}$	2504
$0.3435\text{x}10^{-2}$	1791	$0.4023\text{x}10^{-2}$	2558
0.1333	2922	$0.4509\text{x}10^{-2}$	2625
		0.1333	3637

Equation (10)

	Run 1	Run 2
-slope	1.989	1.731
intercept	3219	3961
std. dev.	12.5	40.6
K_2	407	661
$-\Delta H_2$	6.44	7.92
$-\Delta S_2$	9.65	13.67

Equation (12) and (14)

	Run 1	Run 2
std. dev.	340	776
K_2	420	475
$-\Delta H_2$	6.46	7.91

APPENDIX E--Continued

Toluene

0.1523 M o-Toluic Acid

Run 1		Run 2	
M	$-\phi_L$	M	$-\phi_L$
0.4136×10^{-3}	907*	0.2366×10^{-3}	525*
0.7663×10^{-3}	1223*	0.1590×10^{-3}	760
0.1234×10^{-2}	1536	0.1059×10^{-2}	1050
0.1641×10^{-2}	1721	0.1699×10^{-2}	1319
0.1988×10^{-2}	1838	0.2276×10^{-2}	1509
0.2677×10^{-2}	2034	0.2849×10^{-2}	1645
0.3247×10^{-2}	2168	0.3417×10^{-2}	1742
0.3756×10^{-2}	2254	0.3925×10^{-2}	1825
0.4261×10^{-2}	2318	0.4596×10^{-2}	1909
0.4652×10^{-2}	2373	0.5096×10^{-2}	1961
0.5096×10^{-2}	2424	0.5691×10^{-2}	2020
0.5697×10^{-2}	2485	0.1523	3082
0.1523	3551		

Equation (10)

	Run 1	Run 2
-slope	2.101	2.362
intercept	3873	3426
std. dev.	7.5	13.9
K_2	439	307
$-\Delta H_2$	7.75	6.85
$-\Delta S_2$	13.89	11.60

Equation (12) and (14)

	Run 1	Run 2
std. dev.	295	221
K_2	4.30	330
$-\Delta H_2$	7.68	6.97

APPENDIX E--Continued

Toluene

0.1887 M o-Toluic Acid

Run 1 M	Run 1 $-\phi_L$	Run 2 M	Run 2 $-\phi_L$
$0.1292\text{x}10^{-3}$	534	$0.2994\text{x}10^{-3}$	737*
$0.4508\text{x}10^{-3}$	1227	$0.7871\text{x}10^{-3}$	1326
$0.8163\text{x}10^{-3}$	1699	$0.1075\text{x}10^{-2}$	1564
$0.1270\text{x}10^{-2}$	2082	$0.1437\text{x}10^{-2}$	1776
$0.1765\text{x}10^{-2}$	2354	$0.1796\text{x}10^{-2}$	1921
$0.2078\text{x}10^{-2}$	2462	$0.2243\text{x}10^{-2}$	2080
$0.2654\text{x}10^{-2}$	2638	$0.2641\text{x}10^{-2}$	2188
$0.2919\text{x}10^{-2}$	2698	$0.3125\text{x}10^{-2}$	2293
$0.3400\text{x}10^{-2}$	2804	$0.3604\text{x}10^{-2}$	2389
$0.3748\text{x}10^{-2}$	2893	$0.4166\text{x}10^{-2}$	2477
$0.4261\text{x}10^{-2}$	2945	$0.4500\text{x}10^{-2}$	2526
0.1187	4246	0.1184	3733*

	Run 1	Run 2
Equation (10)		
-slope	2.033	2.086
intercept	4652	4086
std. dev.	31.2	5.3
K_2	563	469
$-\Delta H_2$	9.31	8.17
$-\Delta S_2$	18.63	15.19
Equation (12) and (14)		
std. dev.	--	240
K_2	--	360
$-\Delta H_2$	--	8.08

APPENDIX F

I. INTRODUCTION

The idea of hydrogen-bond formation was introduced by Latimer and Rodebush in 1920 (82). For the last few decades, the subject has been of great interest to chemists and others and it has stimulated a large and growing number of studies (83).

There have been various techniques for studying the association of carboxylic acids in solution (83,87). These techniques include both spectroscopic (visible, ultraviolet, infrared, nuclear magnetic resonance) and non-spectroscopic (cryoscopy, boiling point elevation measurement, vapor measurement, dielectric constant measurement, self-diffusion, ultrasonic absorption, phase distribution, and calorimetry).

Calvet and Paoli (85) Levy et al (86) and Sturtevant et al (87) utilized a calorimetric method to obtain K and ΔH° of dimerization of some acids in organic solvents. However, there had been no systematic study of carboxylic acid association in organic solvents by calorimetry until the work of Zaugg and his co-workers (84,88,89). A calorimetric technique is the only method providing a direct measurement of association enthalpies. It has been developed to allow the simultaneous determination of equilibrium constants and enthalpies of association from calorimetric enthalpy of dilution data (88-93).

The purpose of the work reported in this appendix is intended only as a preliminary study of the thermodynamics of dimerization of benzoic acid, m-toluic acid, and o-toluic acid in benzene and in toluene at 25°C by a calorimetric technique. This is the result of my interest in studying calorimetry when I began my graduate work. Unfortunately, p-toluic acid is not soluble in these two solvents so it is not included in this study.

II. EXPERIMENTAL

Benzoic acid, m-toluic acid, and o-toluic acid used were reagent grade. Benzene and toluene were from Baker Chemical Company and were spectrophotometric or GC-Spectrophotometric quality, certified at least 99.9% pure.

Volumetric pipets and flasks used to prepare and transfer solutions were thoroughly cleaned, rinsed with acetone, and flushed with dry N_2. The concentration of acid solutions used in this experimental work were generally 0.1-0.5 F, as solubility permitted. Care was taken to prepare and keep solutions and solvents free from water. All weighings were performed on a Mettler type B5 single-pan balance with 200 g capacity and readable to 0.1 mg, or on a Mettler P163 top-loading balance with 160 g capacity and readable to 1 mg. All measurements were made at 25.00 ± 0.03°C.

Heats of dilution of all acid solutions in anhydrous benzene and toluene were measured with the Tronac 450 Titration Calorimeter (50 ml vessel) coupled to the Tronac 1040 Precision Temperature Controller and a Sargent-Welch SRG recorder. The apparatus was modified to include a Metrohm Herisau Dosimat piston buret. All concentrations are reported in terms of molarities and activity coefficients are assumed to be unity (10,11).

III. CALCULATIONS AND RESULTS

Heats of dilution results are reported and used in the form of ϕ_L values. The relative apparent molar enthalpy, ϕ_L is equal to the negative of the enthalpy of dilution of one mole of an acid for a solution of specified molarity to infinite dilution. The differences between actual ϕ_L values and $\phi_L = 0$ for ideal solutions are assumed to be caused only by dissociation of carboxylic acid dimers to monomers (91,92).

Values of ϕ_L are obtained as follows: As the solution of acid enters the pure solvent at a known rate, the enthalpy of dilution is recorded at regular intervals, corresponding to

$$M_t \longrightarrow M_1 \qquad \Delta H_1 \tag{1a}$$

$$M_t \longrightarrow M_2 \qquad \Delta H_2 \tag{1b}$$

$$\vdots$$

$$M_t \longrightarrow M_i \qquad \Delta H_i \tag{1i}$$

where the M_t is the formal acid concentration of the titrant. The enthalpy of dilution of the titrant to infinite dilution corresponds to

$$M_t \longrightarrow 0 \qquad \Delta H_0 = -\phi_{Lt} \tag{2}$$

Combination of equations (1) and (2) yields

$$M_1 \longrightarrow 0 \qquad -\phi_{L1} \tag{3a}$$

$$M_2 \longrightarrow 0 \qquad -\phi_{L2} \tag{3b}$$

$$\vdots$$

$$M_i \longrightarrow 0 \qquad -\phi_{Li} \tag{3i}$$

The correct value of ΔH_0 can be found by extrapolation of a plot of ΔH_i versus M_i to zero concentration.

A general equation can be obtained which relates heats of dilution to the thermodynamic properties K_2 and ΔH_2° for dimerization represented by the reaction

$$2A \rightleftarrows A_2 \tag{4}$$

$$K_2 = [A_2] / [A]^2 \tag{5}$$

In equation (5), $[A_2]$ and $[A]$ represent molarities of the acid dimer and monomer, respectively.

For the dilution of a solution containing an acid of initial molarity M to infinite dilution, we write

$$M\phi_L = \Delta H_2^\circ [A_2] \tag{6}$$

in which ΔH_2° represents the molar enthalpy of the reaction shown in equation (4). By rearranging equation (5) we obtain

$$[A_2] = K_2[A]^2 \tag{7}$$

Combination of equations (6) and (7) and subsequent rearrangement give us

$$[A] = (M\phi_L/\Delta H_2^\circ K_2)^{1/2} \tag{8}$$

Substitution of equations (7) and (8) into the equation for material balance

$$M = [A] + 2[A_2] \tag{9}$$

followed by rearrangement yields

$$\phi_L = (\Delta H_2^\circ/2) + (-\Delta H_2^\circ/4K_2)^{1/2}(-\phi_L/M)^{1/2} \qquad (10)$$

Plots of experimental values of $-\phi_L$ versus $(-\phi_L/M)^{1/2}$ lead to K_2 and ΔH_2° from slopes and intercepts, respectively, of straight lines.

Another way to calculate ΔH_2° and K_2 values from ϕ_L data is as follows. Since at any finite concentration there will be both monomeric and dimeric acid present, while at infinite dilution all dimers are dissociated to monomers, the enthalpy of dilution to infinite dilution may be expressed as

$$\phi_L = (\alpha/2)\Delta H_2^\circ \qquad (11)$$

where α represents the fraction of acid that is associated. Thus, $[A] = M(1-\alpha)$ and $[A_2] = \alpha M/2$, which can be substituted into equation (7) to obtain

$$K_2 = \alpha/2M(1-\alpha)^2 \qquad (12)$$

In an approach based on differences in ϕ_L at two molarities of the acid, one can obtain from equation (11)

$$\Delta H_2^\circ = 2(\phi_{L2} - \phi_{L1})/(\alpha_2 - \alpha_1) \qquad (13)$$

where ϕ_{L1} and ϕ_{L2} refer to relative apparent molar enthalpies, and α_1 and α_2 represent the fraction of monomers associated in the two solutions, respectively. By referring to equations (1) and (3), one sees readily that equation (13) is equivalent to

$$\Delta H_2^\circ = 2(\Delta H_i - \Delta H_j)/(\alpha_i - \alpha_j) \qquad (14)$$

Equations (11) - (14) provide an alternate method to the determination of K_2 and ΔH_2° where the necessity of finding ΔH_0 is eliminated.

Using the two methods based on equation (10) and equations (11) - (14) the "best" thermodynamic values for the self association of each of the acids in anhydrous benzene and toluene solvents at 25°C are given in Table IV. The ϕ_L and molarity data are tabulated at the end of this section.

TABLE IV

"BEST" VALUES OF THERMODYNAMIC FUNCTIONS FOR DIMERIZATION OF CARBOXYLIC ACIDS [EQUATION (4)] IN BENZENE AND TOLUENE AT 25°C[a]

Acid	K_2	$-\Delta G_2^\circ$ (kcal)	$-\Delta H_2^\circ$ (kcal)	$-\Delta S_2^\circ$ (cal)
Benzene				
Benzoic acid	414 (±100)	3.6 (±0.2)	7.5 (±0.4)	13.3 (±2)
m-Toluic acid	418 (±100)	3.7 (±0.1)	7.4 (±0.5)	12.7 (±2)
o-Toluic acid	380 (±100)	315 (±0.2)	7.7 (±0.3)	14.1 (±2)
Toluene				
Benzoic acid	202 (±50)	312 (±0.2)	4.8 (±0.5)	6.1 (±0.2)
m-Toluic acid	491 (±100)	3.7 (±0.1)	7.6 (±0.4)	13.1 (±2)
o-Toluic acid	389 (±60)	3.5 (±0.2)	7.4 (±0.4)	13.1 (±0.2)

[a] ± signs indicate uncertainty in values (91,92).

[b] values of K_2, ΔG_2°, and ΔS_2° are based on the molarity concentration scale for monomer and dimer (91,92).

IV . DISCUSSION

The values of K_2 for dimerization of benzoic acid in benzene have been investigated using various methods by several workers (83,99-101). However, the reported values range from about 100 to 1400 (2). The K_2 values for benzoic acid, m-toluic acid, and o-toluic acid in benzene shown in Table IV are somewhat lower than those calculated by Wall and Banes (95,96) utilizing the isopiestic method. The values of ΔG_2°, ΔH_2°, and ΔS_2° are also slightly lower than their previously reported values (95,96). The results in Table IV do not show a sufficient general trend to provide an understanding in the substituent effect of the methyl group on benzoic acid, nor an understanding of the solvent effect when benzene is compared to toluene.

All calculations in this study were made on the basis of a monomer-dimer model. Zaugg and co-workers have shown that aliphatic acids fit this model within experimental error. There is a possibility that other models, such as monomer-trimer and monomer-dimer-trimer, might be constrained to fit the data at higher concentrations but the uncertainties in our ϕ_L data do not permit us to pursue these models.

The study of hydrogen bonding of carboxylic acids in solutions of "inert" solvents and the effect of solvents and substituents is still a very interesting topic, and it is still open to more research.

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A POTENTIOMETRIC METHOD-A CONVENIENT AND RAPID TECHNIQUE FOR DETERMINATION OF THE THERMODYNAMICS OF IONIZATION REACTIONS FOR WATER, WEAK ACIDS, AND SOME SLIGHTLY SOLUBLE SALTS IN AQUEOUS-ORGANIC MIXED SOLVENTS

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ABSTRACT

A potentiometric method which is devised to be rapid and convenient for determining ionization constants for water, weak acids (or bases), and certain solids in mixed solvents is described. The method has been applied to the determination of ionization for water, acetic acid, benzoic acid, and phenol and the solubility product constant for silver chloride in mixtures of water with methanol, ethanol, acetone, tetrahydrofuran, and p-dioxane containing from 0 to 70 mass percent organic co-solvent at several temperatures between 10 and 40°C. Results are used to study the thermodynamics of ionization in each mixture which is discussed relative to various topics of ion-ion, ion-solvent, ion-molecule, molecule-solvent, and solvent-solvent interactions on the basis of theories of electrostatics, solvation, and solvent and solution structure.

A calorimetric technique applied to the investigation of dimerization of benzoic acid, m-toluic acid, and o-toluic acid in benzene and toluene at 25°C as a preliminary study of the author is briefly mentioned in Appendix E.