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Standard Potential of the AgCl/Ag Electrode and the Second Dissociation Constant of Phosphoric Acid in 20, 50, and 80 Mass % 2-Methoxyethanol + Water from −10 to +37 °C

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Solvents consisting of 2-methoxyethanol (20, 50, and 80 mass % + water were chosen in a continuing study designed to shed light on the behavior of electrolytes in mixed media at temperatures extending below 0 °C. Electromotive-force measurements of cells with hydrogen and AgCl/Ag electrodes in the range from −10 to +37 °C, together with a recalculation of earlier data in the literature, yielded values of the standard potential of the HCl in the mixed solvents. A disagreement of literature values for the standard potential in the 80 mass % solvent was resolved. A further series of measurements of phosphate buffer solutions in 20 and 50 mass % 2-methoxyethanol + water led to values for the dissociation constant (pK_2) and associated thermodynamic function for dissociation of the primary phosphate ion $H_2PO_4^-$ in these mixed solvents.

Introduction

Buffer solutions of controlled pH have been shown to be advantageous in the preservation of human tissues and organs at subzero temperatures (see, for example, refs 1 and 2). This observation has brought renewed interest in the properties of electrolytes at temperatures in the range −15–0 °C. For example, a recent contribution from this laboratory (*3*) reported the results of a study of the dissociation of acetic, propionic, and *n*-butyric acids in 25 and 50 mass % 2-propanol + water in the range −10 to +25 °C.

Acid–base behavior in mixtures of 2-methoxyethanol (20, 50, and 80 mass % ME) + water in the temperature range −10 to +37 °C was the subject of the present study. Measurements of the electromotive force (emf, *E*) of the following cells without liquid junction

$$\text{Pt;H}_2\text{(g, 101.325 kPa)}|\text{HCl } (m) \text{ in ME} + \text{H}_2\text{O}|\text{AgCl;Ag} \quad \text{(A)}$$

and

$$\text{Pt;H}_2\text{(g, 101.325 kPa)}|\text{KH}_2\text{PO}_4\ (m)\text{,Na}_2\text{HPO}_4\ (m)\text{, NaCl } (m) \text{ in ME} + \text{H}_2\text{O}|\text{AgCl;Ag} \quad \text{(B)}$$

where *m* is molality, were made over the range of temperatures included in the study. Values of the emf (*E*) of cell A were used to derive the standard emf ($E°$) of the cell, which is also the standard potential of the AgCl/Ag electrode, in the three solvent mixtures. With a knowledge of $E°$, measurements of cell B led to values of the dissociation constant and related thermodynamic functions for the dissociation of primary phosphate ion, $H_2PO_4^-$ in 20 and 50 mass % 2-methoxyethanol + water over a range of temperatures extending as low as −10 °C.

The standard potential of the AgCl/Ag electrode in 50 mass % 2-methoxyethanol + water from 5 to 45 °C was the subject of a study by Vega and Delgado (*4*). Other earlier work has included solvents more rich in the organic component. For example, Thun, Staples, and Bates (*5*) determined $E°$ in the 80 mass % solvent from 10 to 50 °C. In a more extensive study, Sadek, Tadros, and El-Harakany (*6*) used eight mixed solvents containing from 5 to 80 mass % 2-methoxyethanol + water over the temperature range 25–45 °C. Merken, Thun, and Verbeek (*7*) determined $E°$ for solvents in the composition range from 80 to 98 mass % 2-methoxyethanol at temperatures from 20 to 40 °C. In addition, Shanbhag, Vega, and Bates (*8*) studied the dissociation of acetic acid and protonated tris(hydroxymethyl)aminomethane in 80% 2-methoxyethanol from 10 to 50 °C.

With the present results, one can resolve with some certainty the disparity among literature values for $E°$ in the 80 mass % mixture of 2-methoxyethanol ("Methylcellosolve") + water. This mixture of solvents has found use in studies of the acid–base behavior of organic compounds that are of limited solubility in water (*9*).

Experimental Section

A spectrophotometric grade of 2-methoxyethanol, obtained from Aldrich Chemical Co., Inc., was subjected to fractional distillation. Stock solutions of hydrochloric acid (Ultrex, J. T. Baker) were prepared and standardized by titration with a carbonate-free solution of sodium hydroxide. Potassium hydrogen phosphate and disodium hydrogen phosphate were NBS Standard Reference Materials. Procedures for the preparation of the hydrogen electrodes and the AgCl/Ag electrodes have been described elsewhere (*10*). The 3.5% solution of chloroplatinic acid (with addition of 0.03% lead acetate) was prepared by dissolving scrap platinum in aqua regia, followed by repeated evaporation with concentrated HCl. The silver chloride electrodes were made by the thermal decomposition of thoroughly washed Ag_2O on platinum helixes at 500 °C, with partial chloridization in a 1 M solution of HCl.

Solutions for the measurements of cell A were prepared from stock solutions of HCl in water by adding the amount of 2-methoxyethanol required for the solvent composition under study. The solutions for cell B were made by adding the three salts to weighed quantities of water and 2-methoxyethanol. Measurements of emf were made with a Fluke Model 8800A digital voltmeter. The constant-temperature bath contained a mixture of water and ethylene glycol; its temperature was measured with an Omega Model 5800 digital thermometer. Other procedural details have been described earlier (*3, 4*).

Densities of the solvent mixtures were measured at 20, 25, 30, and 35 °C with a Mettler/Paar digital density meter. Vapor pressures and dielectric constants were taken from the literature (*4–7, 11*), with extrapolation where necessary. These properties of the solvent mixtures are summarized in Table I. The last two columns list the constants *A* and *B* of the Debye–Hückel theory, on the scale of molality, calculated from the temperature, dielectric constant, and density (10); the values

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Table I. Properties of Mixtures of 2-Methoxyethanol + Water

T, K	density/ (g mL^{-1})	dielectric constant	p/kPa	A^a/ (kg$^{1/2}$ mol$^{-1/2}$)	B^a/(kg$^{1/2}$ mol$^{-1/2}$ nm^{-1})
		20 Mass % 2-Methoxyethanol + Water			
263.15	1.0260	78.8	0.36	0.6186	3.537
268.15	1.0226	77.7	0.51	0.6133	3.523
273.15	1.0193	76.6	0.72	0.6084	3.509
278.15	1.0159	75.5	1.01	0.6041	3.497
283.15	1.0125	74.4	1.36	0.6002	3.486
288.15	1.0092	73.3	1.84	0.5969	3.476
293.15	1.0057	72.2	2.47	0.5940	3.466
298.15	1.0025	71.1	3.15	0.5918	3.458
		50 Mass % 2-Methoxyethanol + Water			
263.15	1.0397	61.8	0.27	0.8977	4.022
268.15	1.0349	60.3	0.40	0.9025	4.023
273.15	1.0301	58.9	0.56	0.9084	4.025
278.15	1.0253	57.4	0.83	0.9155	4.029
283.15	1.0205	56.0	1.15	0.9241	4.036
288.15	1.0157	54.5	1.59	0.9341	4.044
293.15	1.0109	53.1	2.19	0.9456	4.054
298.15	1.0059	51.6	2.92	0.9589	4.066
310.15	0.9945	48.1	5.91	0.9979	4.105
		80 Mass % 2-Methoxyethanol + Water			
263.15	1.0249	37.8	0.23	1.8624	5.105
268.15	1.0195	37.0	0.33	1.8646	5.098
273.15	1.0140	36.1	0.49	1.8768	5.100
278.15	1.0086	35.0	0.71	1.9081	5.119
298.15	0.9868	31.5	2.51	1.9919	5.155

[a] Constant of the Debye–Hückel theory.

Table II. Emf of the Cell Pt;H_2(g, p = 101.325 kPa)|HCl (m) in 2-Methoxyethanol + Water|AgCl;Ag from 263.15 to 310.15 K

m/ (mol kg^{-1})	emf							
	263.15 K	268.15 K	273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	310.15 K
			20 Mass % 2-Methoxyethanol + Water						
0.010 320	0.438 42	0.440 45	0.442 40				0.447 41	0.448 26	
0.020 08	0.410 49	0.411 84	0.413 23	0.414 45	0.415 15	0.415 81	0.416 27	0.416 50	
0.030 17	0.392 88	0.394 27	0.395 29	0.396 11	0.396 58	0.397 14		0.397 53	
0.040 19	0.380 26	0.381 03	0.381 99	0.382 57	0.382 55	0.382 68	0.382 71	0.382 45	
0.059 96	0.363 23	0.363 93	0.364 59	0.364 80	0.364 98	0.364 88	0.364 60	0.364 14	
0.079 98	0.350 65	0.351 41	0.351 95	0.352 15	0.351 89	0.351 60	0.351 27	0.350 56	
0.100 05	0.340 28	0.340 73	0.341 05					0.339 14	
			50 Mass % 2-Methoxyethanol + Water						
0.005 260	0.455 96	0.456 69	0.457 56	0.458 05	0.458 25	0.458 55	0.458 44	0.457 40	
0.010 320	0.426 63	0.427 01	0.427 40	0.427 53	0.427 38	0.427 03	0.426 45	0.425 82	
0.028 62	0.384 14	0.383 81	0.383 28	0.382 56		0.380 39	0.379 72	0.378 24	0.374 19
0.040 65	0.370 62	0.370 03	0.369 28	0.368 26	0.367 22	0.365 90	0.364 43	0.362 75	0.357 94
0.070 86	0.347 62	0.346 58	0.345 47	0.344 00	0.342 58	0.340 77	0.338 84	0.336 70	0.331 42
0.089 32	0.337 79	0.336 55	0.335 50	0.333 84	0.332 24	0.330 29	0.328 28	0.325 98	0.320 29
0.107 98	0.330 40	0.328 99	0.327 62	0.325 94	0.324 14	0.322 06	0.319 90	0.317 35	0.311 29
			80 Mass % 2-Methoxyethanol + Water						
0.005 260	0.407 16	0.404 91	0.402 32	0.399 84				0.387 32	
0.015 370	0.362 57	0.359 87	0.356 09	0.351 95				0.341 59	
0.027 35	0.339 84	0.337 45	0.334 06	0.330 81				0.315 68	
0.044 51	0.324 34	0.320 91	0.317 26	0.313 33				0.296 22	
0.059 90	0.311 06	0.307 70	0.304 11	0.300 34				0.284 05	
0.071 86	0.303 19	0.299 70	0.295 90	0.291 92				0.274 62	

of B are to be used with ion sizes in nanometers.

Results and Calculations

The observed values of the emf of cells A and B, corrected to a hydrogen partial pressure of 101.325 kPa (1 atm), are collected in Tables II and III, respectively.

Standard Potential in 20 and 50 Mass % ME. The dielectric constant of these solvents exceeds 48, and complete dissociation of HCl was assumed. The values of the standard emf $E°$, which is, by convention, the standard potential of the AgCl/Ag electrode, were obtained by an extrapolation of a function of the emf (E) and m to zero molality. This often-repeated procedure has been set forth in a recent contribution from this laboratory (*12*). When the activity coefficient of HCl in the equation for the cell emf is expressed by the "extended" Debye–Hückel formula, one obtains

$$E° - 2k\beta m = E + 2k \log m - \frac{2kAm^{1/2}}{1 + B\mathring{a}m^{1/2}} \qquad (1)$$

In eq 1, k is the Nernst slope (RT ln 10)/F, $\mathring{a}$ is the ion-size parameter, and β is the slope of the plot of the right side of eq 1 as a function of m. The best value of $\mathring{a}$ (and intercept $E°$) at each temperature was assumed to be that producing the smallest standard deviation for regression from a linear extrapolation plot. The results are summarized in the second and third columns of Table IV.

Standard Potential in 80 Mass % ME. Inasmuch as the dielectric constant of the 80 mass % mixture of 2-methoxy-

Table III. Emf of the Cell Pt;H_2(g, p = 101.325 kPa)|KH_2PO_4 (m), Na_2HPO_4 (m),NaCl (m) in 2-Methoxyethanol + Water|AgCl;Ag from 263.15 to 310.15 K

m/ (mol kg^{-1})	emf 263.15 K	268.15 K	273.15 K	278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	310.15 K
				20 Mass % 2-Methoxyethanol + Water					
0.0019834	0.75985	0.76632	0.77281	0.77950	0.78433	0.78952			
0.003027	0.74967	0.75907	0.76523	0.77138	0.77645		0.78785	0.79317	
0.003997	0.74664	0.75330	0.75925	0.76565	0.77067	0.77661	0.78241	0.78780	
0.004982							0.77524	0.78046	
0.005986			0.75136	0.75917	0.76430	0.76969	0.77516	0.78019	
0.007372	0.74191	0.74921	0.75330	0.76054	0.76405	0.76797	0.77220	0.77548	
0.008396		0.75125		0.75643	0.76046	0.76361			
				50 Mass % 2-Methoxyethanol + Water					
0.0019314					0.82984	0.83516			0.85715
0.003075			0.80803	0.81286		0.82210	0.82672	0.83030	
0.004014	0.79100		0.80038	0.80492	0.80956	0.81453	0.81949	0.82397	0.83496
0.006023	0.77885	0.78336	0.78829	0.79269	0.79703	0.80151	0.80593		0.82106
0.007042	0.77391	0.77744	0.78234	0.78634	0.78965			0.80184	
0.008018		0.77315	0.77869	0.78300	0.78717	0.79152	0.79575	0.79982	0.80969
0.010029	0.76041	0.76490	0.76945	0.77395	0.77832	0.78258	0.78702	0.79108	
0.010069									0.80249
0.015423		0.75044	0.75438	0.75875	0.76228	0.76620	0.77009	0.77423	0.78256

Table IV. Standard Potential ($E°$) of the AgCl/Ag Electrode in Three Mixtures of 2-Methoxyethanol (ME) + Water

	20 mass % ME		50 mass % ME		80 mass % ME[b]			
T/K	$E°$/V	σ/mV	$E°$/V	σ/mV	$\mathring{a}$/nm	K_d	$E°$/V	σ/mV
263.15	0.2262	0.23	0.2116	0.25	0.82	0.093	0.1563	1.1
268.15	0.2241	0.27	0.2078	0.23	0.76	0.088	0.1493	0.9
273.15	0.2220	0.26	0.2040	0.21	0.79	0.084	0.1417	1.0
278.15	0.2196	0.35	0.1998	0.20	0.77	0.079	0.1337	1.2
283.15	0.2168	0.45	0.1956	0.19	0.73	0.0752	0.12769	0.05
288.15	0.2140	0.52	0.1909	0.25	0.75	0.0710	0.11984	0.04
293.15	0.2104	0.34	0.1863	0.18	0.71	0.0669	0.11156	0.04
298.15	0.2076	0.38	0.1811	0.27	0.69	0.0631	0.10301	0.03
303.15					0.62	0.0572	0.09456	0.06
308.15					0.59	0.0537	0.08579	0.06
310.15			0.1690	0.23				
313.15					0.56	0.0512	0.07684	0.08
318.15					0.57	0.0467	0.06750	0.09
323.15					0.52	0.0414	0.05796	0.16

[a] σ = standard deviation of the intercept ($E°$). [b] For temperatures from 283.15 to 323.15 K, the data are from ref 5, recalculated with K_d from ref 13.

ethanol + water is in the range 31–38; some ion-pairing of HCl is to be expected. If K_d represents the dissociation constant for ion pairs, the "true" molality m' of HCl is given by

$$m' = \frac{K_d + (K_d^2 + 4mK_d\gamma')^2}{2(\gamma')^2} \qquad (2)$$

where the mean activity coefficient of HCl at the molality m' is designated γ' and that of the ion pairs is assumed to be 1. The values of γ' were derived from the equation

$$\log \gamma' = \frac{-A(m')^{1/2}}{1 + Ba_d(m')^{1/2}} \qquad (3)$$

The true molality m' was then used in eq 1 to perform the extrapolation to $m'' = 0$. In eq 3, a_d is an ion-size parameter, not necessarily the same as $\mathring{a}$ in eq 1. A computer program performed four iterations for each set of K_d and a_d values. The "best" values of m' and $E°$ were those that, when used in eq 1, provided the smallest standard deviation of regression from the linear extrapolation plot.

A similar procedure was used by Thun, Staples, and Bates (*5*) to derive values of the standard potential at temperatures from 10 to 50 °C. Since neither parameter was known independently, sets of K_d and a_d were sought to provide the minimum deviation from the extrapolation line. Studies by Merken, Thun, and Verbeek (*13*, *14*) and others (*15*) have now made available, from conductivity measurements, values of K_d in the temperature range 20–50 °C. We have recalculated $E°$ from the earlier data, using these newer values for the ion-pair dissociation constant. For K_d at 10 and 15 °C, an extrapolation was needed, and for the data listed in Table I, it was necessary to extrapolate K_d to −10 °C. Nevertheless, K_d varies only by 0.026 between 20 and 50 °C, and it was shown that an uncertainty of 0.01 introduces an error of only 0.2–0.4 mV in $E°$, or considerably less than the uncertainty in the emf data at the lower temperatures.

A range of ion-size parameters a_d and $\mathring{a}$ was tried. Changing a_d from 0.4 to 0.6 nm (encompassing the usual values for HCl in several media) altered the value of $E°$ found by only 0.16 mV at 25 °C and was without effect on the deviation from linearity. Thus, a_d was fixed at a value of 0.5 nm in all cases, while $\mathring{a}$ in eq 1 was varied until the minimum standard deviation of regression was located and the best value of $E°$ identified. Similarly, when a_d was fixed at 0.5 nm, the standard deviation for values of $\mathring{a}$ in the range 0.68–0.72 nm differed from the minimum value (0.04 mV) by less than 0.01 at 25 °C. The results of the recalculation of the data (10–50 °C) of Thun et al. (*5*) and the present investigation (−10 to +5 °C) are summarized in Table IV.

The standard potentials can be expressed as a quadratic function of the thermodynamic temperature T as follows:

20 mass % ME

$$E°/\mathrm{V} = 0.01508 + 1.98190 \times 10^{-3}T - 4.4833 \times 10^{-6}T^2 \qquad \sigma/\mathrm{mV} = 0.21$$

50 mass % ME

$$E°/\mathrm{V} = 0.14420 + 1.24592 \times 10^{-3}T - 3.7608 \times 10^{-6}T^2 \qquad \sigma/\mathrm{mV} = 0.14$$

80 mass % ME

$$E°/\mathrm{V} = 0.23111 + 8.4121 \times 10^{-4}T - 4.2606 \times 10^{-6}T^2 \qquad \sigma/\mathrm{mV} = 0.10$$

The equation for $E°$ in 80 mass % ME was based on the results from 10 to 50 °C, that is, on the emf data from ref 5; σ is the standard deviation of fit. By application of the usual thermodynamic relationships, the standard changes of Gibbs energy, enthalpy, and entropy for the cell reaction were calculated and are listed in Table V.

Thermodynamic functions for the transfer process

$$\mathrm{HCl}(a = 1 \text{ in } H_2O) = \mathrm{HCl}(a = 1 \text{ in 2-methoxyethanol + water}) \qquad (4)$$

were derived as the difference between these quantities for the cell reaction in the mixed solvents and the corresponding quantity in water. For the water solvent (*16*)

$$E°/\mathrm{V} = 0.13174 + 1.25603 \times 10^{-3}T - 3.19286 \times 10^{-6}T^2 \qquad \sigma/\mathrm{mV} = 0.05$$

Values of the transfer Gibbs energy, enthalpy, and entropy for HCl at $T/\mathrm{K} = 298.15$ are given in Table VI. The last row of the table gives the value of $\log \gamma_t$, where γ_t is the transfer activity coefficient, calculated by

$$\log \gamma_t = \Delta_t G°/(2RT \ln 10) \qquad (5)$$

pK_2 for Phosphoric Acid in 20 and 50 Mass % ME + H_2O. The acidic dissociation constant of the primary phosphate ion ($H_2PO_4^-$) was derived from the emf of cells of type B, together with the standard potentials listed in Table IV. "Apparent" values of pK_2, designated pK_2', were extrapolated to zero ionic strength (I). Activity coefficients of chloride and phosphate anions were evaluated by the Debye–Hückel extended equation with an estimated ion-size parameter of 0.4 nm. Allowance was made for solvolysis of the $H_2PO_4^-$ ion, although the molality of hydrogen ion m_H, estimated from the emf, proved to be negligible.

The apparent dissociation constant at each finite ionic strength is given by

$$pK_2' \equiv pK_2 - \beta I = \frac{E - E°}{k} + \log\left(\frac{m(m - m_H)}{m + m_H}\right) + \frac{2AI^{1/2}}{1 + 0.4BI^{1/2}} \qquad (6)$$

where β is again the slope of the straight line used for extrapolation and $I = 5m$. The values of m_H are given by

$$-\log m_H = \frac{E - E°}{k} + \log m - \frac{2AI^{1/2}}{1 + 0.4BI^{1/2}} \qquad (7)$$

The results of the calculation of pK_2 are summarized in Table VII and compared with pK_2 in water (*16*). The functional relationships between pK_2 and the thermodynamic temperature T are as follows:

20 mass % ME

$$pK_2 = 629.0/T - 3.452 + 1.5333 \ln T \qquad (8)$$

50 mass % ME

$$pK_2 = 5427.5/T - 107.725 + 17.240 \ln T \qquad (9)$$

The standard deviations of fit were 0.014 and 0.013, respectively. The standard changes in Gibbs energy, enthalpy, and entropy for the process

$$H_2PO_4^- = HPO_4^{2-} + H^+ \qquad (10)$$

are given at the foot of the table and compared with the corresponding functions in water (*17*). These values were calculated in the usual way from the constants of eqs 8 and 9.

Table V. Comparison of the Standard Thermodynamic Functions at 298.15 K for the Cell Reaction $^1/_2H_2(g, p = 101.325 \text{ kPa}) + AgCl(s) = Ag(s) + HCl(a = 1)$ in Water, 20, 50, and 80 Mass % 2-Methoxyethanol (ME) + Water (Molality Scale)

solvent	$\Delta G°$/(kJ mol^{-1})	$\Delta H°$/(kJ mol^{-1})	$\Delta S°$/(J K^{-1} mol^{-1})
water	−21.458	−40.10	−62.5
20 mass % ME	−20.016	−39.91	−66.7
50 mass % ME	−17.498	−46.17	−96.2
80 mass % ME	−9.955	−58.84	−164.0

Table VI. Thermodynamic Quantities for the Transfer Process $HCl(a = 1 \text{ in } H_2O) = HCl(a = 1$ in 2-Methoxyethanol (ME) + Water) at 298.15 K (Molality Scale)

	20 mass % ME	50 mass % ME	80 mass % ME
$\Delta_t G°$/(kJ mol^{-1})	1.442	3.960	11.503
$\Delta_t H°$/(kJ mol^{-1})	0.19	−6.07	−18.75
$\Delta_t S°$/(J K^{-1} mol^{-1})	−4.2	−33.7	−101.5
$\log \gamma_t$	0.126	0.347	1.008

Table VII. Comparison of Thermodynamic Functions for the Second Dissociation of Phosphoric Acid in Water and in Water + 20 and 50 Mass % 2-Methoxyethanol (ME) in the Range 263.15–310.15 K (Molality Scale)

	water[a]	20 mass % ME		50 mass % ME	
T/K	pK_2	pK_2	σ[b]	pK_2	σ[b]
263.15		7.482	0.031	8.984	0.019
268.15		7.455	0.022	8.894	0.017
273.15	7.313	7.472	0.036	8.862	0.009
278.16	7.282	7.448	0.025	8.820	0.009
283.15	7.254	7.419	0.018	8.768	0.014
288.15	7.231	7.400	0.030	8.751	0.010
293.15	7.213	7.404	0.041	8.739	0.009
298.15	7.198	7.402	0.038	8.695	0.026
310.15	7.181			8.678	0.018
at 298.15 K:					
$\Delta G°$[c]	41.096	42.20		49.68	
$\Delta H°$[c]	4.086	3.29		5.50	
$\Delta S°$[c]	−124.1	−130		−148	

[a] Reference 17. [b] σ = standard deviation of the intercept (pK_2). [c] Units: for $\Delta G°$ and $\Delta H°$, kJ mol^{-1}; for $\Delta S°$, J mol^{-1} K^{-1}.

Discussion

The values of $E°$ in 50 mass % 2-methoxyethanol found earlier in this laboratory (*4*) are about 1.3 mV higher than those from the present investigation. Recalculation of the data at 25 °C lowers $E°$ by only 0.6 mV, and the standard deviation of the intercept is somewhat larger than that for the data of the present study. The lowest molality of HCl included was 0.019 mol kg^{-1}.

Furthermore, the standard potentials for the 80 mass % ME + water solvent found by Sadek, Tadros, and El-Harakany (*6*) differ by some 13 mV from those given by Thun et al. (*4*). At 25 °C, for example, the former group lists 0.0900 V while 0.10344 V was found in the latter investigation. To shed some light on the cause of the disagreement, we have compared these two sets of data with the emf data at 25 °C given in Table II, using $K_d = 0.0631$, $a_d = 0.5$ nm, and $\mathring{a} = 0.69$ nm in all three cases. The results were as follows: Thun et al., 0.10301 ± 0.00003 V; Sadek et al., 0.0943 ± 0.0003 V; this investigation, 0.1029 ± 0.0007 V. Furthermore, the newer set of emf data of Merken et al. (*7*) leads to a value of 0.103 19 ± 0.000 05 V. One may conclude that the discrepancy resides in the experimental measurements, rather than, as postulated by Merken et al. (*11*), in the failure of Sadek et al. to allow for ion pairing and their use of too low a value for the dielectric constant.

As expected, the transfer properties given in Table VI reflect the decreasing stabilization of HCl as water is replaced by the organic solvent. An increase of pK_2 as 2-methoxyethanol is added to the water solvent is evident in Table VII. Here, changes in the ion–solvent interaction pattern are presumably reinforced by enhanced ion–ion interaction favored by the decreasing dielectric constant of the medium.

Registry No. AgCl, 7783-90-6; Ag, 7440-22-4; HCl, 7647-01-0; H_2, 1333-74-0; PO_4^{3-}, 14265-44-2; $H_2PO_4^-$, 14066-20-7; KH_2PO_4, 7778-77-0; Na_2HPO_4, 7558-79-4; 2-methoxyethanol, 109-86-4.

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Vapor–Liquid Equilibrium Data for the NH_3–H_2O System and Its Description with a Modified Cubic Equation of State

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New pressure–temperature–overall composition vapor–liquid equilibrium (VLE) data are reported for the ammonia–water system at five temperatures between 20 and 140 °C and up to 500 psia. These data have been converted to *T–P–x* data, and vapor-phase compositions have been calculated by means of a Redlich-Kwong equation of state modified to include Peneloux's volume translation and a density-dependent mixing rule. In order to achieve agreement of calculated vapor-phase compositions with previous literature results, it was necessary to use different k_{ij} values in the vapor and liquid phases.

Introduction

There have been a number of experimental (*1–9*) and computational (*1*, *10–14*) efforts to characterize the vapor–liquid equilibrium (VLE) behavior of the NH_3–H_2O system. Gillespie et al. (*1*) point out that, prior to their work, there was disagreement between experimental and calculated vapor-phase compositions, especially at high ammonia concentrations. Some authors had attributed these discrepancies to thermodynamically inconsistent data (Edwards et al. (*14*), for example), others to shortcomings in existing models (Peng and Robinson (*12*) and Heidemann and Rizvi (*11*), for example). Gillespie et al. (*1*) were able to resolve this disagreement. They first took an extensive data set that included both total pressure and *T–P–x–y* data and then fit these data with an activity coefficient based model with three parameters for the liquid phase and an equation of state with an adjustable cross-virial coefficient for the vapor phase.

The objectives of the work described herein were three-fold. The first objective was to measure a set of pressure–total composition data that was more precise than those sets in the literature. This had already been done in our laboratory for other systems. The second objective was to correlate these data with an equation of state that included recent improvements in equation-of-state techniques. The third objective was to see if the improved accuracy of our *T–P–x* data and the improved equation of state methods could successfully remove discrepancies in the vapor-phase compositions, as Gillespie et al. (*1*) had done with their *T–P–x–y* data and activity coefficient model.

Experimental Section

Total composition–pressure–temperature data were determined at the nominal temperatures of 20, 50, 80, 110, and 140 °C and up to 500 psia. At the lowest three temperatures, the data covered the entire composition range, but the pressure limitation did not allow data to be taken over the entire range at the highest two temperatures. The VLE was established in cells that are shown in Figure 1. These cells, which are described in more detail in ref 15, consist of a sample compartment, a stainless steel diaphragm, and a transducer. Pressure was measured by adjusting the nitrogen pressure in the upper chamber of the cell until the diaphragm was forced into its null position, which was sensed by the transducer. The nitrogen pressure was measured with one of three digital pressure gauges, which had ranges of 0–20, 0–150, and 0–2500 psig

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