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Thermodynamics of Hydrogen Chloride in Propylene Glycol–Water Mixtures from Electromotive Force Measurements

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The standard potentials of Ag–AgCl electrodes in propylene glycol (PG)–water mixtures in the composition range 20–90 wt % propylene glycol have been determined from 15 to 45 °C by emf measurements using the cell Pt,H_2(g, 1 atm)/HCl(m),propylene glycol(x)–water(y)|AgCl–Ag. The primary medium effects and the mean molal activity coefficients, in the concentration range 0.005–0.05 mol kg^{-1} at 25 °C, have been evaluated. The standard molal potential ${}_{s}E_{m}{}^{\circ}$ has been expressed as a function of temperature. The thermodynamic parameters for transfer of HCl from water to propylene glycol–water mixtures have been calculated from emf data at 25 °C on the mole fraction scale. The transfer energies of hydrogen and chloride ions have also been determined by employing the ferrocene reference method. The significance of the various thermodynamic quantities associated with the transfer process has been discussed. From the slope of the linear plot between $\Delta G_{t}{}^{\circ}{}_{c}$ and log ϕ_w (ϕ_w = volume fraction of water), in the various solvent mixtures, n, the number of water molecules coordinated to HCl, was evaluated.

Introduction

Electromotive force measurements on galvanic cells involving hydrogen, silver–silver halide electrodes have been widely used in recent years (*1–8*) to determine the thermodynamics of hydrogen halides in aqueous and nonaqueous media. Such studies not only enable one to understand the electrolyte–solvent interactions but also can be utilized to evaluate the thermodynamics of ion–solvent interactions employing suitable extrathermodynamic assumptions. In previous investigations from our laboratory (*7*, *9*) the standard potentials of silver–silver chloride electrodes in several diethylene glycol–water and diethylene glycol–ethylene glycol mixtures have been reported. In the present paper, we present the results on the standard potentials of silver–silver chloride electrodes in propylene glycol–water mixtures of varying composition (20–90 wt %) in the temperature range 15–45 °C. Despite the well-known industrial and pharmaceutical applications of propylene glycol as a solvent (*10*), very few emf data are available (*11*) in binary mixtures containing this solvent. The results on the cell

$$\mathrm{Pt,H_2(g,\ 1\ atm)|HCl}(m)\mathrm{,propylene\ glycol}(x)\mathrm{–water}(y)\mathrm{|AgCl–Ag} \qquad (1)$$

are reported.

Experimental Section

The method of purification of propylene glycol (BDH, LR) was similar to that employed in the case of ethylene glycol reported earlier (*12*). The distilled glycol had a boiling point of 186 °C, $n^{25}{}_{D}$ = 1.4222, d^{25} = 1.036 g cm^{-3}, in agreement with literature values (*13*) and it was always stored in a desiccator. Doubly distilled water over an all-glass apparatus was used in the preparation of various solvent mixtures, which were prepared by weight. The method of preparation and estimation of the stock hydrochloric acid solution in the different solvent compositions was similar to that described earlier (*12*). The Ag–AgCl electrodes were of the thermal electrolytic (*14*) type and had asymmetric potentials less than 0.05 mV 2 days after preparation. The hydrogen electrodes were lightly coated with platinum black before each measurement according to the method of Hills and Ives (*15*). All measurements were made with two hydrogen electrodes and four Ag–AgCl electrodes. The cells were thermostated at each temperature with an accuracy of ±0.05 °C. The emf's of the cell were measured at 15, 25, 35, and 45 °C, with a Leeds and Northrup K5 potentiometer in conjunction with a Keithley 602 solid-state electrometer as null detector. The Ag–AgCl electrodes were stable over the entire temperature range and constancy of the cell emf to ±0.05 mV for about 0.5 h was considered as an adequate criterion of equilibrium. The emf value recorded initially at 25 °C was redetermined while increasing the temperature from 15 to 45 °C and finally again at the end. All the values agreed within ±0.1 mV. The dielectric constants of the aqueous mixtures from 15 to 45 °C were determined with a DK 03 Dekameter (Wissenschaftliche Technische Werkstatten, West Germany) after checking the meter with methanol and water as calibration liquids at 30 °C. The dielectric constants are accurate within ±0.2%. Densities of all solvent mixtures at different temperatures were measured with a pyknometer of 5-mL capacity, having a 10-cm long neck with 1-mm diameter and calibrated into 0.1-cm divisions. The vapor pressures of the mixed solvents were obtained from the data of Gallant (*16*), except in the case of 20 wt % propylene glycol, which was, however, calculated by assuming the applicability of Raoult's law. Other experimental details are similar to those reported earlier (*7*). The physical-constant data of the solvent mixtures are presented in Table I.

Table I. Physical Constants and Other Data of Propylene Glycol-Water Mixtures[a]

propylene glycol, wt %		15 °C	25 °C	35 °C	45 °C	M_{xy}
20	D	75.15	71.90	68.65	65.50	21.24
	A'	0.5724	0.5811	0.5928	0.6063	
	$B' \times 10^{-8}$	0.3418	0.3435	0.3458	0.3484	
40	D	66.25	62.65	59.65	56.60	25.91
	A'	0.6915	0.7145	0.7319	0.7548	
	$B' \times 10^{-8}$	0.3640	0.3680	0.3709	0.3748	
75	D	46.75	43.75	41.75	39.75	42.12
	A'	1.1666	1.2244	1.2499	1.2825	
	$B' \times 10^{-8}$	0.4333	0.4403	0.4434	0.4472	
90	D	37.50	35.25	33.25	31.60	57.53
	A'	1.6239	1.6929	1.7587	1.8095	
	$B' \times 10^{-8}$	0.4838	0.4906	0.4968	0.5016	

[a] D = dielectric constant; A' and B' = Debye–Hückel constants on the molality scale; M_{xy} = mean molecular weight.

Results and Discussion

The emf data for cell 1 in the various solvent mixtures corrected for a partial pressure of 1 atm of hydrogen are given in Table II. The standard molal potentials, ${}_{s}E_{m}{}^{\circ}$, of the cell in

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Table II. Emf Data of Cell I (Corrected for 1-atm Pressure of H_2) from 15 to 45 °C in Various Propylene Glycol-Water Mixtures[a]

m_{HCl}	emf, V 15 °C	25 °C	35 °C	45 °C
	x = 20 %			
0.020 71	0.413 13	0.414 33	0.415 05	0.414 88
0.029 85	0.396 23	0.396 92	0.396 97	0.396 15
0.033 19	0.391 59	0.392 11	0.391 79	0.390 80
0.037 88	0.385 06	0.385 25	0.385 41	0.384 30
0.046 12	0.375 83	0.375 76	0.375 40	0.373 82
0.055 45	0.367 33	0.366 97	0.366 39	0.364 70
0.064 46	0.360 33	0.359 64	0.358 96	0.356 85
0.074 44	0.354 03	0.353 16	0.352 07	0.349 67
	x = 40 %			
0.013 46	0.420 35	0.421 55	0.421 82	0.421 84
0.020 59	0.401 10	0.401 61	0.401 78	0.400 79
0.032 44	0.379 75	0.379 94	0.379 10	0.377 44
0.037 56	0.372 89	0.373 18	0.372 31	0.370 37
0.041 52	0.368 77	0.368 58	0.367 37	0.365 22
0.050 33	0.360 23	0.359 71	0.358 25	0.356 03
0.057 13	0.354 16	0.353 31	0.351 63	0.349 39
0.061 42	0.350 89	0.349 79	0.348 30	0.345 77
	x = 75 %			
0.005 455	0.428 85	0.426 97	0.424 90	0.421 86
0.007 999	0.411 79	0.409 71	0.407 01	0.403 54
0.014 36	0.385 06	0.381 76	0.378 49	0.374 10
0.023 41	0.363 42	0.359 79	0.355 84	0.350 99
0.028 72	0.353 35	0.349 62	0.345 15	0.340 70
0.034 71	0.344 60	0.339 59	0.335 88	0.331 92
0.041 74	0.338 38	0.334 11	0.329 03	0.323 31
0.050 15	0.329 03	0.324 28	0.319 03	0.313 32
	x = 90 %			
0.006 192	0.375 95	0.370 57	0.365 46	0.359 27
0.010 85	0.351 87	0.345 61	0.340 30	0.333 67
0.018 32	0.330 05	0.323 29	0.317 16	0.309 97
0.024 61	0.316 71	0.310 43	0.303 70	0.295 94
0.027 60	0.312 68	0.306 37	0.298 74	0.290 25
0.031 56	0.307 34	0.300 27	0.293 05	0.285 08
0.034 47	0.303 70	0.296 76	0.289 34	0.281 40
0.051 58	0.287 98	0.280 26	0.272 72	0.264 99

[a] x = weight percent of propylene glycol; m = molality.

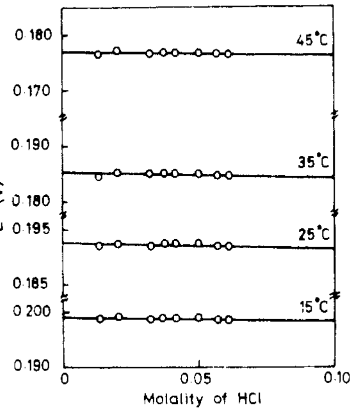

Figure 1. Extrapolation of plot of $E^{o'}$ (V) (eq 2) against molality of HCl in propylene glycol-water mixtures (40 wt % propylene glycol) at different temperatures.

the various solvent mixtures were determined by extrapolation of the function

$$E^{o'} = E + 2k \log m - \frac{2kA'c^{1/2}}{1 + ab'c^{1/2}} - 2k \log (1 + 0.002mM_{xy}) = {}_sE_m{}^\circ - 2kbm \tag{2}$$

to zero molality. Such a plot in 40 wt % propylene glycol which is typical of the results in these mixtures is shown in Figure 1.

Table III. ${}_sE_m{}^\circ$ at Different Temperatures and ${}_sE_c{}^\circ$ and ${}_sE_N{}^\circ$ at 25 °C in Various Propylene Glycol-Water Mixtures

propylene glycol, wt %	${}_sE_m{}^\circ$, V 15 °C	25 °C	35 °C	45 °C	${}_sE_c{}^\circ$, V	${}_sE_N{}^\circ$, V
20	0.2133	0.2070	0.2010	0.1938	0.2079	0.0091
40	0.1989	0.1923	0.1849	0.1767	0.1938	0.0046
75	0.1618	0.1504	0.1389	0.1264	0.1524	−0.0124
90	0.1109	0.0959	0.0813	0.0653	0.0978	−0.0509

Table IV. Coefficients of Empirical Equation

$${}_sE_m{}^\circ = {}_sE_m{}^\circ{}_{25\,^\circ C} + b(t - 25) + c(t - 25)^2$$

propylene glycol, wt %	${}_sE_m{}^\circ{}_{25\,^\circ C}$	$-b \times 10^4$	$-c \times 10^6$
0[a]	0.2224	6.400	2.98
20	0.2070	6.22	2.425
40	0.1923	6.991	3.95
75	0.1504	11.49	2.65
90	0.09585	14.89	2.323

[a] See ref *23*, p 716.

Table V. Mean Activity Coefficients (${}_s\gamma_\pm$) at Rounded Molalities and Primary Medium Effect of HCl (log ${}_m\gamma_\pm$) in Various Propylene Glycol-Water Mixtures at 25 °C

x[a]	${}_s\gamma_\pm$ 0.005	0.01	0.02	0.03	0.04	0.05	0.06	log ${}_m\gamma_\pm$
20	0.955	0.890	0.841	0.817	0.803	0.791	0.783	0.130
40	0.945	0.864	0.812	0.782	0.762	0.749	0.741	0.254
75	0.842	0.793	0.751	0.717	0.694	0.675		0.609
90	0.781	0.713	0.644	0.599	0.562	0.538		1.069

[a] x = weight percent of propylene glycol.

In the above equation, $k = RT \ln 10/F$, m is the molality of HCl (mol kg^{-1}), A' and B' are the Debye–Hückel constants on the molal scale, a is the ion size parameter (Å), b is the coefficient occurring in the expression for activity coefficient as a function of molality, and M_{xy} is the mean molecular weight of the solvent defined as

$$M_{xy} = 100/(x/M_x + y/M_y) \tag{3}$$

where x and y are the weight percentages of propylene glycol and water, respectively, and M_x and M_y are the corresponding molecular weights. In the determination of ${}_sE_m{}^\circ$, a = 5 Å was used in all solvent compositions, as this was found to give good linear plots with the least slope.

The ${}_sE_m{}^\circ$ values at different temperatures and also the standard potentials on molar (${}_sE_c{}^\circ$) and mole fraction (${}_sE_N{}^\circ$) scales calculated by using the equations

$${}_sE_c{}^\circ = {}_sE_m{}^\circ + 2k \log d_0 \tag{4}$$

$${}_sE_N{}^\circ = {}_sE_m{}^\circ - 2k \log (1000/M_{xy}) \tag{5}$$

are given in Table III where d_0 refers to the density of the solvent. The standard error in ${}_sE_m{}^\circ$ is about ±0.2 mV in all solvent mixtures at different temperatures. The ${}_sE_m{}^\circ$ has been expressed as a function of temperature according to

$${}_sE_m{}^\circ = E_m{}^\circ{}_{25} + b(t - 25) + c(t - 25)^2 \tag{6}$$

where t is the temperature in °C, and b and c are empirical coefficients. These data are recorded in Table IV. The standard deviations in ${}_sE_m{}^\circ$ calculated from eq 6 were found to be within ±0.05 mV. The mean activity coefficients of HCl, ${}_s\gamma_\pm$, referred to a value of unity at infinite dilution in each particular solvent, were calculated by using the equation

$$\log {}_s\gamma_\pm = ({}_sE_m{}^\circ - E)/2k - \log m \tag{7}$$

Table VI. Thermodynamic Quantities for the Transfer of HCl from Water to Various Propylene Glycol + Water Mixtures at 25 °C on Mole Fraction Scale

propylene glycol, wt %	ΔG_t°, J mol^{-1}	$10^2\Delta S_t^\circ$, J K^{-1} mol^{-1}	ΔH_t°, J mol^{-1}	$T\Delta S_t^\circ$, J mol^{-1}
20	665	448	2 000	1 336
40	1104	34	1 205	101
75	2744	−3500	−7 690	−10 435
90	6456	−6262	−12 213	−18 670
100[a]	17401	+8458	+42 618	+25 217

[a] Calculated with data from ref *24*.

in various solvent mixtures at 25 °C. The $_s\gamma_\pm$ values taken at rounded molalities from a large-scale plot of data at 25 °C are given in Table V. This table also contains the primary medium effects (log $_m\gamma_\pm$) of HCl at 25 °C in various solvent mixtures, calculated from

$$\log {}_m\gamma_\pm = ({}_wE_m^\circ - {}_sE_m^\circ)/2k \qquad (8)$$

The primary medium effect is a measure of the Gibbs free energy change associated with the transfer of 1 mol of HCl from water to the given solvent at infinite dilution according to

$$\text{HCl(water)} = \text{HCl(propylene glycol–water mixture)} \qquad (9)$$

The Gibbs free energy of transfer ΔG_t° for the process given by eq 9 was calculated on the mole fraction scale for the various solvent mixtures at 25 °C from the equation

$$\Delta G_t^\circ = F({}_wE_N^\circ - {}_sE_N^\circ) \qquad (10)$$

where $_wE_N^\circ$ and $_sE_N^\circ$ represent the standard emf's of cell 1 in water and the solvent, respectively, on the mole fraction scale and are given in Table VI.

The transfer process involves the transfer of charged species H^+ and Cl^- ions from water to the mixed solvents at infinite dilution. It is therefore reasonable to expect that it consists of an electrostatic part $\Delta G_t^\circ{}_{el}$ and a nonelectrostatic part $\Delta G_t^\circ{}_{nonel}$. While the electrostatic transfer free energy arises mainly due to the differences in the dielectric constants of the solvents, the nonelectrostatic part reflects the contributions of solvation and other specific ion–solvent interactions which depend on solvent basicity. Thus

$$\Delta G_t^\circ = \Delta G_t^\circ{}_{el} + \Delta G_t^\circ{}_{nonel} \qquad (11)$$

The standard entropy of transfer, ΔS_t°, was calculated from

$$\Delta S_t^\circ = -\frac{d}{dt}F({}_wE_N^\circ - {}_sE_N^\circ)$$
$$= F[(b_s - b_w) + 2(c_s - c_w)(t - 25) + (k_w - k_s)] \qquad (12)$$

where b_s, c_s, b_w, and c_w are the coefficients from Table IV in solvent and water, respectively, and

$$k_w = (2R/F)\ln(1000/18.016) = 6.92 \times 10^{-4}$$

$$k_s = (2R/F)\ln(1000/M_{xy})$$

The last term of eq 12 arises in the conversion of $_sE_m^\circ$ to $_sE_n^\circ$. The standard enthalpy of transfer was calculated from the expression

$$\Delta H_t^\circ = \Delta G_t^\circ + T\Delta S_t^\circ \qquad (13)$$

Both the thermodynamic quantities ΔH_t° and ΔS_t° are recorded in Table VI. Figure 2 shows the variation of the transfer parameters with solvent composition. The ΔG_t° values are accurate to ±30 J and the expected errors in ΔS_t° and ΔH_t° are ±0.5 and ±150 J, respectively. It is seen that ΔG_t° values are positive and increase with increasing amounts of propylene glycol, indicating that the transfer of HCl from water to the mixed solvent is not spontaneous. Qualitatively it may be expected that $\Delta G_t^\circ{}_{el}$ will be increasingly positive with the addition of propylene glycol due to the resulting decrease in the dielectric constant, while $\Delta G_t^\circ{}_{nonel}$ possibly decreases continuously under the same conditions. The predominantly positive values of ΔG_t° presumably indicate a dominant contribution of the electrostatic over the nonelectrostatic interactions in the present case. The Gibbs transfer energies of the proton, $\Delta G_t^\circ{}_{H^+}$ (molal scale) determined earlier (*17*) on the basis of the ferrocene reference method in these mixtures at 25 °C are given in Table VII. The transfer free energy data of chloride ion, $\Delta G_t^\circ{}_{Cl^-}$, obtained from eq 14 are also recorded in Table VII. It is seen

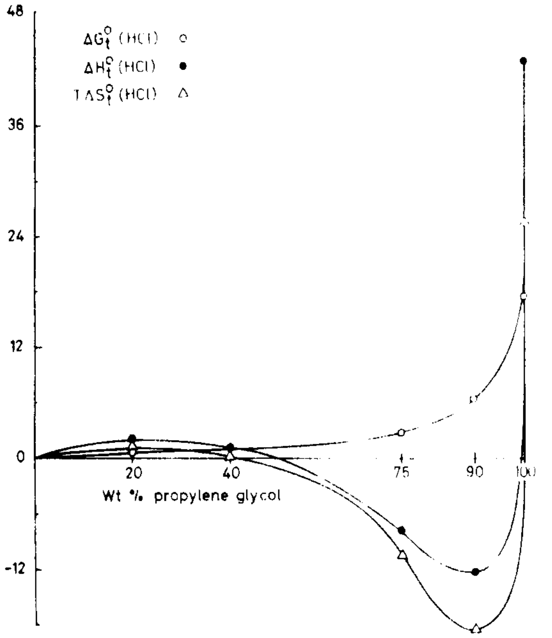

Figure 2. Variation of the various thermodynamic quantities (mole fraction scale) of transfer of HCl in propylene glycol–water mixtures.

Table VII. Transfer Free Energies of H^+ and Cl^- in Propylene Glycol-Water Mixtures at 25 °C

propylene glycol, wt %	ΔG_t°, J mol^{-1}	$\Delta G^\circ{}_{H^+}$, J mol^{-1}	$\Delta G^\circ{}_{Cl^-}$, J mol^{-1}
20	665	−2556	3 221
40	1104	−3318	4 422
75	2744	−8326	11 070
90	6456	−10439	16 895
100	17401	−5699	23 099

$$\Delta G_t^\circ{}_{HCl} = \Delta G_t^\circ{}_{H^+} + \Delta G_t^\circ{}_{Cl^-} \qquad (14)$$

that $\Delta G_t^\circ{}_{H^+}$ decreases continuously with the addition of propylene glycol, passes through a minimum at about 90 wt % PG, and then increases, while the transfer energy of chloride ion continuously increases. This suggests that all propylene glycol–water mixtures are more basic than water and supports the earlier conclusions regarding the variation of $\Delta G_t^\circ{}_{nonel}$. Similar conclusions have been reached about the basicity of several amphiprotic solvent–water mixtures and were explained (*1–8*) on the basis of the structural theory of ion solvation proposed by Feakins et al. (*18*).

ΔH_t° (Table VI) passes through an endothermic maximum around 20 wt % and becomes increasingly negative up to 90 wt % organic solvent and subsequently reaches a high positive value, a variation which has been observed (*7*) in many organic solvent–water mixtures. The variation in $T\Delta S_t^\circ$ is similar to that in ΔH_t°. Franks and Ives (*19*) and Feakins and Voice (*18*) have emphasized the importance of these quantities in explaining the structural effects of the solvents on the transfer process. The decrease of ΔH_t° beyond 40 wt % propylene glycol is associated with the structure-making ion–solvent interactions after this composition. The endothermic maximum

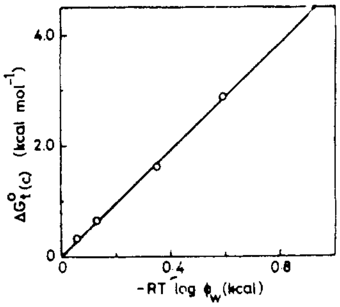

Figure 3. Extrapolation of plot of $\Delta G_t{}^\circ{}_c$ against $-RT \log \phi_w$ at 25 °C.

in $\Delta H_t{}^\circ$ around 20 wt % propylene glycol is due to the structure-breaking effect of the acid on the ordered structure in solvent mixtures of low propylene glycol content when the acid is transferred from water to these media. Addition of small amounts of alcohols promotes (*19*) the hydrogen-bonded structure of water and HCl is a better structure breaker in the mixed solvent than in water (*20*).

A plot of the standard molar free energy of transfer, $\Delta G_t{}^\circ{}_c$, against solvent composition in terms of volume fraction of water ϕ_w in these solvent mixtures (Figure 3) according to the relation

$$\Delta G_t{}^\circ{}_c = -2.303\, nRT \log \phi_w$$

is linear with $n = 2.0$. This value representing the number of water molecules coordinated to the hydrogen chloride is, however, small compared to the values (*21*) obtained in other media but is almost similar to values reported elsewhere (*22*).

Registry No. HCl, 7647-01-0; propylene glycol, 57-55-6; hydronium, 13968-08-6; chloride, 16887-00-6.

Literature Cited

(1) Kundu, K. K.; Sen, U.; Das, M. N. *J. Phys. Chem.* **1967**, *71*, 3665.
(2) Kundu, K. K.; Chattopadhyay, P. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1970**, *15*, 209.
(3) Kundu, K. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1974**, *19*, 329.
(4) Bates, R. G.; Macaskill, J. B.; Sankar, M. *J. Solution Chem.* **1979**, *8*, 887-95.
(5) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Soc. A* **1971**, 1242-6.
(6) Elsemongy, M. M.; Fouda, A. S. *J. Electroanal. Chem.* **1980**, *25*, 114.
(7) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1974**, *19*, 201.
(8) Khoo, K. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 554.
(9) Kalidas, C.; Sivaprasad, P. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2710.
(10) Curme, G. O.; Johnston, F. "Glycols"; Reinhold: New York, 1952; pp 241-6.
(11) Claussen, B. B.; French, C. M. *Trans. Faraday Soc.* **1955**, *51*, 1124.
(12) Kalidas, C.; Palit, S. R. *J. Chem. Soc.* **1961**, 3998.
(13) Clendenning, K. A.; Macdonald, F. J.; Wright, D. E. *Can. J. Res., Sect. B* **1950**, *28*, 608.
(14) Janz, G. J.; Ives, D. J. G. "Reference Electrodes"; Academic Press: New York, 1961; p 209.
(15) Hills, G. J.; Ives, D. J. G. *J. Chem. Soc.* **1951**, 308.
(16) Gallant, R. W. *Hydrocarbon Process.* **1967**, *46*, 201.
(17) Kalidas, C.; Sivaprasad, P.; Venkatram, U. V. *Z. Naturforsch. A* **1977**, *32*, 791.
(18) Feakins, D.; Voice, P. J. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1390.
(19) Franks, F.; Ives, D. J. G. *Q. Rev., Chem. Soc.* **1966**, *20*, 1.
(20) Braude, E. A.; Stern, E. S. *J. Chem. Soc.* **1948**, 1976.
(21) Mussini, T. M.; Earmora, C.; Andrigo, P. *J. Electroanal. Chem.* **1971**, *33*, 189.
(22) Feakins, D.; French, C. *J. Chem. Soc. A* **1957**, 2581.
(23) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions"; Reinhold: New York, 1958; p 716.
(24) Kundu, K. K.; De, A. L.; Das, M. N. *J. Chem. Soc., Dalton Trans.* **1972**, 373.

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Solvation Energies and Solvent Transport Numbers of Silver Sulfate in Methanol, Ethanol, and Their Mixtures with Acetonitrile

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The solvent transport number, Δ, of acetonitrile (AN) and Gibbs solvation energies of Ag_2SO_4 in the binary solvent systems methanol + acetonitrile and ethanol + acetonitrile were determined at 30 °C by employing emf and solubility measurements. It was observed that the solubility of the salt increases up to $X_{AN} = 0.4$ in both systems and thereafter decreases with further addition of AN. Further, the Gibbs energy of transfer of silver ion, $\Delta G_t{}^\circ(Ag^+)$, decreases continuously while that of sulfate ion, $\Delta G_t{}^\circ(SO_4{}^{2-})$, increases with the addition of acetonitrile. The solvent transport number, Δ, passes through a maximum at $X_{AN} = 0.55$ and at $X_{AN} = 0.45$ in the case of MeOH-AN and EtOH-AN systems, respectively. These results have been interpreted in terms of a heteroselective solvation of the salt, the silver ion being selectively solvated by acetonitrile and the sulfate ion by the amphiprotic component of the solvent mixtures.

Introduction

Selective solvation of ions in mixed solvents profoundly influences solubilities of electrolytes, rates of chemical reactions, redox potentials, etc. (*1*). It also has potential technological value (*1-3*). As part of a program of work dealing with this subject, the selective solvation of silver bromate and iodate in H_2O-Me_2SO (*4*), MeOH-Me_2SO (*5*), and H_2O-AN (*6*) mixtures was reported earlier. In this paper the solvation behavior of Ag_2SO_4 in the binary mixtures of MeOH-AN and EtOH-AN is reported in order to throw light on the ion-solvent interactions in these systems.

Experimental Section

Materials. Acetonitrile (LR, BDH) was subjected to a preliminary distillation and the middle fraction collected was further purified, after drying over anhydrous potassium carbonate, by a second distillation in the presence of a few added crystals of silver nitrate following the procedure of Jayadevappa (*7*). It had a boiling point of 80 °C (reported (*8*) 80.1 °C) and a density $d^{25} = 0.7766$ g cm^{-3} (reported (*9*) 0.7768 g cm^{-3}). Methanol (LR, BDH) was first distilled and dried over heated anydrous sodium sulfate. The second distillation was carried out over magnesium turnings according to the procedure of Kolthoff and Chantooni (*10*) and the middle fraction, "boiling at 64-65 °C", was collected and stored out of contact with air. It had a density $d^{25} = 0.7867$ g cm^{-3} (reported (*11*) bp 64.6 °C and d^{25}

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