J. Chem. Eng. Data 1987, 32, 158–161

Thermodynamics of Transfer of Hydrogen Chloride in Water–Dimethylformamide Mixtures from Electromotive Force Measurements

D. Muralimohan Rao and C. Kalidas*

Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

The standard potentials of Ag–AgCl electrodes in water–dimethylformamide (DMF) mixtures in the composition range 10–70 wt % DMF have been determined at four different temperatures from 15 to 30 °C by emf measurements using the cell Pt,H_2(g, 1 atm)|$HCl_{(m)}$,$DMF_{(x)}$–$H_2O_{(y)}$|AgCl–Ag. The primary medium effects and the mean molal activity coefficients in the concentration range 0.01–0.02 mol kg^{-1} at 25 °C have been evaluated. The standard molal potential $_sE°_m$ has been expressed as a function of temperature. The thermodynamic parameters for the transfer of HCl from water to water–DMF mixtures have been evaluated 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 tetraphenylarsonium tetraphenylborate (TATB) reference electrolyte method. The significance of the various thermodynamic quantities associated with the transfer process has been discussed.

Introduction

Electromotive force measurements on galvanic cells employing hydrogen and silver–silver halide electrodes have been widely used in recent years (*1–9*) to determine the thermodynamics of hydrogen halides in aqueous, mixed aqueous and nonaqueous media. Such studies enable us to understand the electrolyte–solvent interactions and also to evaluate the thermodynamics of ion–solvent interactions employing suitable extra thermodynamic assumptions. In previous investigations from this laboratory (*4*, *6*, *7*) the standard potentials of silver–silver chloride electrode in several water–diethylene glycol, ethylene glycol–diethylene glycol, and water–propylene glycol mixtures have been reported. The measurements have now been extended to water–DMF mixtures and the results on the standard potentials of silver–silver chloride electrode in these mixtures of varying composition (10–70 wt % of DMF) in the temperature range 15–30 °C are reported. It may be mentioned at this juncture that although some work has been reported on the standard potentials of silver–silver chloride electrode in dipolar aprotic solvents (*10*) and aqueous–dipolar aprotic solvent mixtures such as water–acetonitrile (*11*), water–acetone (*12*), and water–Me_2SO (*13*, *14*), only a few reports involving aqueous DMF mixtures (*15*, *16*) and other binary mixtures (*17*) containing DMF are available in literature. Hence the results on the cell

$$\mathrm{Pt,H_2(g,\ 1\ atm)|HCl_{(m)}\text{–}DMF_{(x)}\text{–}H_2O_{(y)}|AgCl\text{–}Ag} \qquad (1)$$

in water–DMF mixtures are presented in order to have a comprehensive understanding of ion–solvent interactions in these mixed solvents.

Experimental Section

DMF (Merck, India) was purified according to the method of Faulkner and Bard (*18*) and the distilled sample was stored in an amber-colored bottle, out of contact with air. It had a boiling point of 45 °C under 15 mmHg pressure, refractive index n^{25}_D = 1.4300, and density d^{25} = 0.9445 g·cm^{-3} in good agreement with the reported values in literature (*19*) (lit. values n^{25}_D = 1.4269, d^{25} = 0.9443 g·cm^{-3}). Doubly distilled water in 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 is similar to that described earlier (*20*). The Ag–AgCl electrodes were of the thermal-electrolytic type (*21*) and had bias potentials less than 0.05 mV 3 days after electrolysis. The hydrogen electrodes were prepared in accordance with the method of Hills and Ives (*22*). Fresh hydrogen electrodes were used for each measurement. All measurements were made with two hydrogen electrodes and four Ag–AgCl electrodes. The cells were kept at each temperature within 0.05 °C. The emfs of the cell were measured at 15, 20, 25, and 30 °C with a Leeds and Northrup K_5 potentiometer in conjunction with a Keithley 602 solid-state electrometer as a null detector. The Ag–AgCl electrodes were stable over the entire temperature range, and the constancy of cell emf to ±0.05 mV for about 30 min was taken as a criterion of equilibrium. The emf value measured initially at 25 °C was further determined twice, viz., while changing the temperature from 15 to 30 °C as well as during cooling in order to verify the reproducibility of the silver,silver chloride electrodes. All the values agreed to within ±0.1 mV. In the range of solvent compositions 60 and 70 wt % DMF, the coating of platinum black on the hydrogen electrode was found to deteriorate with time leading to a drift of the emf. Hence only lightly coated electrodes were used in these compositions and no difficulty in recording stable emf's was encountered by this procedure. Nernst equation has been found to be valid in all the mixed solvents. The dielectric constants of all H_2O–DMF mixtures in the given temperature range have been determined with a DK meter (Model 60 GK, Franz Küstner Nachf. KG Dresden) after calibrating the meter with methanol, acetonitrile, and water at 30 °C as calibration liquids. The dielectric constants are accurate to within ±0.2%. The 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 solvent mixtures have been calculated by assuming the applicability of Raoult's law. The vapor pressure of pure DMF at different temperatures required for this purpose has been computed from the data of Geller et al. (*23*). The physical constant data of the solvent mixtures at different temperatures are presented in Table I.

Results and Discussion

The emf data for the cell 1 in various solvent mixtures corrected for a partial pressure of 1 atm of hydrogen are given in Table II. The standard molal potentials, $_sE°_m$, of the cell in the various solvent mixtures were determined by the extrapolation of the function

$$E°' = E + 2K \log m - \frac{2KA'C^{1/2}}{1 + aB'C^{1/2}} - 2K \log (1 + 0.002mM_{xy}) = {}_sE°_m - 2Kbm \qquad (2)$$

0021-9568/87/1732-0158$01.50/0

Table I. Physical Constants and Other Data of Water–Dimethylformamide Mixtures[a]

wt % dimethylformamide		15 °C	20 °C	25 °C	30 °C	M_{xy}
10	D	80.10	79.05	78.00	76.60	19.47
	A'	0.5206	0.5174	0.5147	0.5158	
	$10^{-8}B'$	0.3311	0.3304	0.3298	0.3301	
20	D	79.50	78.40	76.90	75.70	
	A'	0.5265	0.5229	0.5257	0.5251	21.19
	$10^{-8}B'$	0.3324	0.3318	0.3322	0.3321	
40	D	70.95	69.60	68.50	66.90	25.77
	A'	0.6245	0.6263	0.6254	0.6320	
	$10^{-8}B'$	0.3518	0.3521	0.3519	0.3532	
60	D	60.80	59.65	58.15	56.80	32.86
	A'	0.7872	0.7894	0.7996	0.8079	
	$10^{-8}B'$	0.3800	0.3804	0.3820	0.3833	
70	D	57.50	56.60	55.30	54.15	38.10
	A'	0.8559	0.8541	0.8622	0.8679	
	$10^{-8}B'$	0.3908	0.3905	0.3917	0.3926	

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

Table II. Emf Data of Cell 1 (Corrected for 1 atm Pressure of H_2) from 15 to 30 °C in Various Water–Dimethylformamide Mixtures[a]

	emf, V			
m(HCl)	15 °C	20 °C	25 °C	30 °C
		x = 10 wt %		
0.010 24	0.466 52	0.467 46	0.468 55	0.468 74
0.012 13	0.457 66	0.458 79	0.459 86	0.460 28
0.018 04	0.438 67	0.439 40	0.439 99	0.440 15
0.020 13	0.434 73	0.435 31	0.435 77	0.435 90
0.029 61	0.416 20	0.416 52	0.416 87	0.416 69
0.034 81	0.409 27	0.409 48	0.409 65	0.409 10
		x = 20 wt %		
0.010 09	0.468 36	0.469 36	0.470 06	0.470 48
0.014 18	0.452 89	0.453 71	0.454 05	0.454 26
0.016 48	0.445 64	0.446 02	0.446 32	0.446 39
0.017 80	0.441 66	0.442 24	0.442 60	0.442 56
0.019 84	0.435 70	0.435 98	0.436 22	0.436 07
		x = 40 wt %		
0.010 11	0.474 42	0.475 38	0.475 54	0.476 07
0.012 12	0.468 24	0.468 28	0.467 85	0.467 14
0.015 09	0.455 32	0.455 39	0.455 27	0.454 79
0.019 01	0.446 71	0.446 38	0.445 68	0.443 63
0.025 06	0.431 52	0.430 80	0.429 86	0.429 34
		x = 60 wt %		
0.009 02	0.470 87	0.469 22	0.467 26	0.465 50
0.010 15	0.467 83	0.467 46	0.464 74	0.463 06
0.012 39	0.455 59	0.454 86	0.453 46	0.451 48
0.015 08	0.448 41	0.446 69	0.445 13	0.443 00
0.016 09	0.444 21	0.443 82	0.443 02	0.440 25
0.020 39	0.432 46	0.431 98	0.430 98	0.429 65
		x = 70 wt %		
0.006 19	0.471 50	0.470 88	0.470 76	0.470 46
0.007 22	0.466 64	0.466 60	0.464 59	0.461 89
0.007 76	0.460 25	0.457 82	0.456 09	0.455 19
0.009 21	0.453 85	0.451 85	0.450 16	0.448 06
0.010 49	0.442 30	0.442 00	0.443 48	0.443 47

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

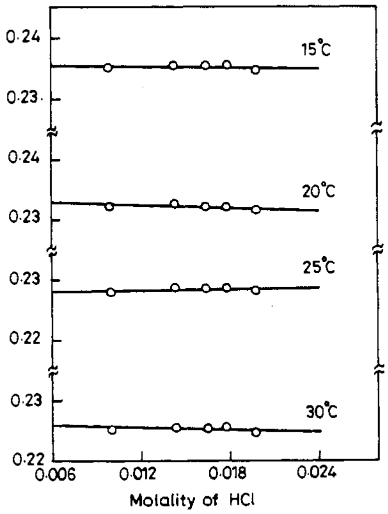

Figure 1. Extrapolation of plot of $E^{\circ\prime}$(V) (eq 2) against molality of HCl in water–DMF mixture (20 wt % DMF) at different temperatures.

to zero molality. Such a plot in 20 wt % DMF which is typical of the results in these mixtures is shown in Figure 1. 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 DMF and water, respectively, and M_x and M_y are the corresponding molecular weights. In the determination of ${}_sE^\circ_m$, $a = 5$ Å was used in all compositions, as this was found to give good linear plots with the least slope.

The ${}_sE^\circ_m$ values at different temperatures and also the standard potentials on molar (${}_sE^\circ_c$) and mole fraction (${}_sE^\circ_N$) scales calculated by using the equations

$${}_sE^\circ_c = {}_sE^\circ_m + 2K \log d_0 \tag{4}$$

$${}_sE^\circ_N = {}_sE^\circ_m - 2K \log (1000/M_{xy}) \tag{5}$$

are given in Table III. d_0 in eq 4 refers to the density of the solvent. The standard error in ${}_sE^\circ_m$ is about ±0.2 mV in all solvent mixtures at different temperatures. The ${}_sE^\circ_m$ has been expressed as a function of temperature according to

$${}_sE^\circ_{m,t} = E^\circ_{m,25} + b(t - 25) + c(t - 25)^2 \tag{6}$$

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 ${}_sE^\circ_{m,t}$ calculated from eq 6 were found to be within ±0.3 mV. The mean activity coefficients of HCl ${}_s\gamma_\pm$, referred to a value of unity at infinite dilution in each solvent, were calculated by using the equation

$$\log {}_s\gamma_\pm = ({}_sE^\circ_m - E)/2K - \log m \tag{7}$$

in the different 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.

Table III. ${}_sE^\circ_m$ at Different Temperatures and ${}_sE^\circ_c$ and ${}_sE^\circ_N$ at 25 °C in Various Water–Dimethylformamide Mixtures

wt % dimethylformamide	${}_sE^\circ_m$, V					
	15 °C	20 °C	25 °C	30 °C	${}_sE^\circ_{c,V(25°C)}$	${}_sE^\circ_{N,V(25°C)}$
10	0.233 23	0.230 27	0.227 37	0.223 67	0.227 18	0.025 08
20	0.235 50	0.233 00	0.228 27	0.226 27	0.228 09	0.030 35
40	0.241 70	0.239 07	0.235 17	0.231 18	0.234 99	0.047 28
60	0.232 18	0.225 95	0.217 87	0.211 21	0.217 51	0.041 77
70	0.220 52	0.214 71	0.205 53	0.198 18	0.204 84	0.037 73

Table IV. Coefficients of the Empirical Equation

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

wt % dimethylformamide	$_{s}E^{\circ}_{m,25^{\circ}C}$, V	-10^4b	-10^6c
0[a]	0.222 40	6.570	3.0
10	0.227 24	6.686	7.4
20	0.229 07	6.563	8.3
40	0.235 35	7.772	13.6
60	0.218 36	14.413	4.3
70	0.205 53	16.010	15.4

[a] See ref *28*, 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 Water–Dimethylformamide Mixtures at 25 °C

x[a]	0.01	0.012	0.014	0.015	0.02	log $_{m}\gamma_{\pm}$
10	0.896	0.889	0.882	0.878	0.860	−0.042
20	0.893	0.884	0.876	0.873	0.857	−0.049
40	0.917	0.903	0.891	0.887	0.867	−0.108
60	0.846	0.823	0.803	0.794	0.773	0.038

[a] x = weight percent of dimethylformamide.

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

wt % dimethylformamide	ΔG°_{tr}, J mol^{-1}	ΔS°_{tr}, J K^{-1} mol^{-1}	ΔH°_{tr}, J mol^{-1}	$T\Delta S^{\circ}_{tr}$, J mol^{-1}
10	−864	0.13	−825	39
20	−1371	2.77	−545	826
40	−3006	−5.62	−4682	−1676
60	−2542	−66.00	−22115	−19573
70	−2084	−79.00	−25533	−23449

This table also contains the primary medium effects (log $_{m}\gamma_{\pm}$) of HCl at 25 °C in various solvent mixtures, calculated from

$$\log {}_{m}\gamma_{\pm} = {}_{w}E^{\circ}_{m} - {}_{s}E^{\circ}_{m}/2K \tag{8}$$

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

$$\text{HCl(water)} = \text{HCl(water-DMF)} \tag{9}$$

The Gibbs energy of transfer, ΔG°_{tr}, 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

$$\Delta G^{\circ}_{tr} = F({}_{w}E^{\circ}_{N} - {}_{s}E^{\circ}_{N}) \tag{10}$$

where $_{w}E^{\circ}_{N}$ and $_{s}E^{\circ}_{N}$ represent the standard emfs of the cell 1 in water and 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 split the free energy into an electrostatic part, $\Delta G^{\circ}_{tr,el}$ and a nonelectrostatic part, $\Delta G^{\circ}_{tr,nonel}$. While the former arises due to the difference in the dielectric constants of the solvents, the latter arises due to the contributions of solvation and other specific ion–solvent interactions which depend on the solvent basicity. Thus

$$\Delta G^{\circ}_{tr} = \Delta G^{\circ}_{tr,el} + \Delta G^{\circ}_{tr,nonel} \tag{11}$$

The standard entropy of transfer, ΔS°_{tr}, was calculated from

$$\Delta S^{\circ}_{tr} = -\frac{d}{dt}F({}_{w}E^{\circ}_{N} - {}_{s}E^{\circ}_{N})$$

$$= F[(b_s - b_w) + 2(c_s - c_w)(t - 25) + (K_w - K_s)] \tag{12}$$

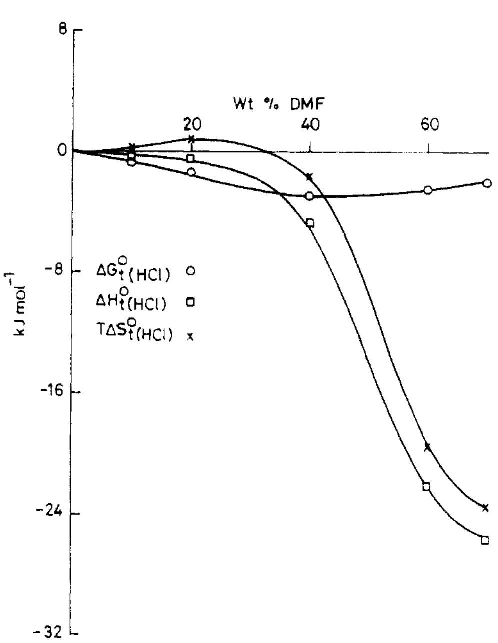

Figure 2. Variation of the various thermodynamic quantities (mole fraction scale) of transfer of HCl in water–DMF mixtures.

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 in eq 12 arises in the conversion of $_{s}E^{\circ}_{m}$ to $_{s}E^{\circ}_{N}$. The standard enthalpy of transfer was calculated from the expression

$$\Delta H^{\circ}_{tr} = \Delta G^{\circ}_{tr} + T\Delta S^{\circ}_{tr} \tag{13}$$

Both the thermodynamic quantities ΔH°_{tr} and ΔS°_{tr} are recorded in Table VI. Figure 2 shows the variation of the transfer parameters with solvent composition. The ΔG°_{tr} values are accurate to ±20 J and the expected errors in ΔS°_{tr} and ΔH°_{tr} are ±0.5 J deg^{-1} and ±150 J, respectively. It is seen that the ΔG°_{tr} values gradually decrease, becoming increasingly negative upto 40 wt % DMF, and then increase at 60 and 70 wt % DMF, the values, however, being still negative. A comparison of ΔG°_{tr} values in the present work with those of Smits et al. (*15*) shows good agreement between the two sets of data upto about 20 wt % DMF but the differences are somewhat large (~1.5 kJ) at higher compositions. These results indicate that the transfer of HCl from water to the mixed solvent is a spontaneous process throughout the composition range. Qualitatively, it may be expected that $\Delta G^{\circ}_{tr,el}$ will be increasingly positive with the addition of DMF due to the resulting decrease in the dielectric constant of the medium while $\Delta G^{\circ}_{tr,nonel}$ possibly decreases continuously under the same conditions. The predominantly negative values of ΔG°_{tr} suggest a dominant contribution of nonelectrostatic over electrostatic interactions in this case. Utilizing the Gibbs transfer energies of the proton, $\Delta G^{\circ}_{tr(H^+)}$ (mole fraction scale) reported earlier (*24*) on the basis of TATB reference electrolyte method in these media at 25 °C, the transfer energy of Cl^- ion in the different solvent mixtures on the mole fraction scale has been evaluated from the relation

$$\Delta G^{\circ}_{tr,(HCl)} = \Delta G^{\circ}_{tr(H^+)} + \Delta G^{\circ}_{tr(Cl^-)} \tag{14}$$

and the results are given in Table VII. It is seen that $\Delta G^{\circ}_{tr(H^+)}$ is negative throughout and decreases continuously upto 80 wt % DMF but increases slightly in pure DMF, the value still being negative. The transfer energy of chloride ion is positive and increases continuously under the same conditions. The negative and continuously decreasing values of $\Delta G^{\circ}_{tr(H^+)}$ indicate that

J. Chem. Eng. Data 1987, 32, 161-163

Table VII. Transfer Free Energies of H^+ and Cl^- in Water-Dimethylformamide Mixtures at 25 °C on Mole Fraction Scale

wt % dimethylformamide	ΔG°_{tr}, J mol^{-1}	$\Delta G^\circ_{tr(H^+)}$, J g ion^{-1}	$\Delta G^\circ_{tr(Cl^-)}$, J g ion^{-1}
10	-864	-1400	536
20	-1371	-2900	1529
40	-3006	-9100	6094
60	-2542	-15900	13358
70	-2084	-17200	15116
80		-18400	
100		-17800	

the proton is better stabilized in the mixed solvents than in water. Thus all water-DMF mixtures including pure DMF are more basic than water. Das and Kundu (*17*) arrived at a similar conclusion and interpreted it on the basis of the good solvating nature of small cations in general and H^+ in particular by DMF through hydrogen-bonding stability in the mixed solvents and also on the more basic nature of DMF as compared to water. At the same time the hydrogen-bonding stability of Cl^- ion will decrease due to the increased anion-desolvating nature of mixed solvent. This is reflected in the increasing positive value of $\Delta G^\circ_{tr(Cl^-)}$ with the increasing proportion of DMF in the mixed solvents.

The ΔH°_{tr} values are negative throughout the composition range whereas $T\Delta S^\circ_{tr}$ values are positive upto 20 wt % of DMF and thereafter decrease, becoming increasingly negative upto 70 wt % of DMF. Franks and Ives (*25*) have emphasized the importance of these quantities in explaining the structural effects of the solvents on the transfer process. The large negative values of ΔH°_{tr} beyond 40 wt % DMF suggest the structure-making ion–solvent interactions which is also reflected in the large negative values of ΔS°_{tr} beyond 20 wt % DMF. This is also supported by the view (*26*) that all structure-forming processes, including solvation of ions, are exothermic and are accompanied by a decrease in entropy. However, the positive values of ΔS°_{tr} and the small negative values of ΔH°_{tr} upto 20 wt % DMF reflect the strong solvent–solvent interactions between water and DMF molecules in this composition region. In fact, complexes of water–DMF of the type water–$(DMF)_n$, where $n = 3$, have been reported (*27*) in this composition region, and HCl, on transfer from water to these mixtures, seems to be a better structure breaker, resulting in an increase of ΔS°_{tr}.

Registry No. HCl, 7647-01-0; H^+, 12408-02-5; Cl^-, 16887-00-6; DMF, 68-12-2; Hg, 7440-22-4; AgCl, 7783-90-6.

Literature Cited

(1) Kundu, K. K.; Chattopadyay, P. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1970**, *15*, 209.
(2) Kundu, K. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1974**, *19*, 329.
(3) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Soc. A*. **1971**, 1242.
(4) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1974**, *19*, 201.
(5) Khoo, K. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 554.
(6) Kalidas, C.; Sivaprasad, P. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2710.
(7) Sastry, V. V.; Kalidas, C. *J. Chem. Eng. Data* **1983**, *28*, 5.
(8) Roy, R. N.; Vernon, W.; Gibbons, J. J.; Bothwell, A. L. M. *J. Electroanal. Interfacial Electrochem.* **1972**, *34*, 101.
(9) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Electroanal. Interfacial Electrochem.* **1971**, *30*, 335.
(10) Rasmussen, S. E.; Everette, D. H. *J. Chem. Soc.* **1954**, 2812.
(11) Mussini, T.; Longhi, P.; Giammario, P. *La Chemica el Industria*, **1972**, *54*, 3.
(12) Feakins, D.; French, C. M. *J. Chem. Soc.* **1956**, 3168.
(13) Khoo, K. H. *J. Chem. Soc.* **1971**, 1177.
(14) Tayler, M. J. *J. Chem. Eng. Data* **1978**, *23*, 308.
(15) Smits, R.; Massart, D. L.; Julliard, J.; Morel, J. P. *Electrochim. Acta* **1976**, *21*, 431.
(16) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Soc. B*. **1971**, 2320.
(17) Das, K. A.; Kundu, K. K. *Electrochim. Acta* **1978**, *23*, 685.
(18) Faulkner, L. R.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 6284.
(19) Geller, B. E. *Russ. J. Phys. Chem.* **1961**, *35*, 1090.
(20) Kalidas, C.; Palit, S. R. *J. Chem. Soc.* **1961**, 3998.
(21) Janz, G. J.; Ives, D. J. G. *Reference Electrodes*; Academic: New York, 1961; p 209.
(22) Hills, G. J.; Ives, D. J. G. *J. Chem. Soc.* **1951**, 308.
(23) Geller, B. E.; Ivanova, T. M. *Russ. J. Phys. Chem.* **1961**, *35*, 598.
(24) Das, K.; Kundu, K. K. *Electrochim. Acta* **1981**, *26*, 479.
(25) Franks, F.; Ives, D. J. G. *Q. Rev. Chem. Soc.* **1966**, *20*, 1.
(26) Frank, H. S.; Evans, H. G. *J. Chem. Phys.* **1945**, *13*, 507.
(27) Singh, D.; Lal Bahadur; Ramanamurthy, M. V. *J. Solution Chem.* **1977**, *6*, 703.
(28) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; Reinhold: New York, 1958; p 716.

Received for review May 2, 1986. Accepted October 1, 1986.

Thermodynamics of Aqueous Mixtures of Nonelectrolytes. 1. Excess Volumes of Water + γ-Butyrolactone Mixtures at Several Temperatures

Mohamoud O. Abdullah

College of Engineering, Baghdad University, Baghdad, Iraq

Suham H. F. Al-Madafi and Akl M. Awwad*

Scientific Research Council, Petroleum Research Centre, Jadiriyah, Baghdad, Iraq

Excess molar volumes of water + γ-butyrolactone mixtures were obtained from precise density measurements over the entire mole fraction range and at 10 K intervals from 288.15 to 318.15 K. Partial molar excess volumes, excess coefficients of thermal expansion, and partial molar excess expansibilities at 298.15 K were derived from the results. The significance of these results is discussed in terms of the structural changes in the mixtures.

Introduction

In our program on the thermodynamic properties of mixed solvent systems of industrial importance, we have previously studied a number of thermodynamic properties of water with *N*-methylpyrrolidone (*1*) and *N*-formylmorpholine (*2*). In this paper we report excess volumes derived from precise density measurements of water + γ-butyrolactone mixtures at 10 K intervals from 288.15 to 318.15 K. The excess coefficient of thermal expansion α^E, partial molar excess expansibilities E_i^E,

0021-9568/87/1732-0161$01.50/0