J. Chem. Eng. Data **2004,** *49,* 1185−1188

Determination of Activity Coefficients, Osmotic Coefficients, and Excess Gibbs Free Energies of HCl in *N,N*-Dimethylformamide−Water Mixed Solvent Systems by Potentiometric Measurements

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Mean activity coefficients ($\gamma_{\pm}$), osmotic coefficients (φ), and excess Gibbs free energies (G^{E}) of HCl in mixed-solvent systems containing (0, 0.1, 0.2, 0.3, and 0.4) mass fractions (w) of *N*,*N*-dimethylformamide (DMF) in water were determined at 25 °C using the Pitzer ion-interaction model. These parameters were obtained from the experimental potentiometric data of the galvanic cell Ag|AgCl|HCl(m), DMF(w), $H_2O(1 - w)$|H^+(glass membrane ISE) over the molality range from dilute solution to about 4 mol/kg in these mixed-solvent systems.

Introduction

The prediction of thermodynamic properties of various electrolytes in water−organic solvent mixtures is of interest in many chemical applications in industrial and in environmental processes. The Pitzer ion-interaction model has been successfully used both in aqueous and in mixed-solvent systems for the determination of various thermodynamic properties of concentrated pure and mixed-electrolyte solutions.[1−9] In this work, using the Pitzer ion-interaction model, the activity and osmotic coefficients along with the excess Gibbs free energies of HCl in mixtures containing successively (0, 0.1, 0.2, 0.3, and 0.4) mass fractions of DMF in H_2O were determined at 25 °C. The determination was based on a potentiometric technique using both a pH glass membrane electrode and a Ag/AgCl electrode. The electrolyte concentration was changed using a standard addition technique over the molality range up to about 4 mol/kg in these aqueous and mixed-solvent systems.

Experimental Section

Reagents. All reagents were of analytical grade from Merck (Germany) or Fluka (Switzerland). Bidistilled water with an electrical conductivity of less than 1.5 $\mu S \cdot cm^{-1}$ was used for the preparation of electrolytes in pure- and mixed-solvent systems. DMF of analytical grade from Fluka (mass % > 99.5) was fractionally distilled, and only the intermediate fraction was used. HCl of analytical grade (mass % > 99.5) was also used for the preparation of different primary concentrated stock solutions in doubly distilled water or in DMF−water mixtures. The concentration of HCl in the prepared primary concentrated stock solution was checked by titration with NaOH (“Titrizol” Merck standard).

Potentiometric Measurements. The potentiometric cell data were measured using a high input impedance (>1 TΩ) Topward multimeter (model 1304, Taiwan, Korea) with ±0.01-mV resolution. All measurements were performed under stirring conditions, and the temperature was kept constant at (25 ± 0.1) °C by employing a thermostated bath (Thelco, Precision Scientific Co.) connected to a double-walled electrochemical cell. The electrodes and a glass thermometer (±0.05 °C) were immersed in the solution through a lid preventing solvent evaporation. The pH (glass membrane) electrode was from Metrohm (model 6.0238.000, Switzerland). The Ag/AgCl electrodes were prepared essentially as described elsewhere by the electrolysis of Ag wire in 0.1 M HCl versus a Pt electrode.[10] Both the pH and Ag/AgCl electrodes were conditioned overnight in the appropriate (DMF + water) mixed solvent before each series of measurements. In each mixed-solvent system and for each molality, the corresponding stabilized potential value was recorded after about 20 min.

Method

For a single $M_{\nu+}X_{\nu-}$ electrolyte, Pitzer equations for the excess Gibbs free energy (G^{E}), osmotic coefficient (φ), and mean ionic activity coefficient ($\gamma_{\pm}$) are as follows:[1−2,9]

$$\frac{G^{E}}{n_{w}RT} = f^{Gx} + m^{2}(2\nu_{+}\nu_{-})B^{Gx} + m^{3}[2(\nu_{+}\nu_{-})^{3/2}]C^{Gx} \quad (1)$$

$$\phi - 1 = |z_{+}z_{-}|f^{\phi} + m\left(\frac{2\nu_{+}\nu_{-}}{\nu}\right)B^{\phi} + m^{2}\left(\frac{2(\nu_{+}\nu_{-})^{3/2}}{\nu}\right)C^{\phi} \quad (2)$$

$$\ln \gamma_{\pm} = |z_{+}z_{-}|f^{\gamma} + m\left(\frac{2\nu_{+}\nu_{-}}{\nu}\right)B^{\gamma} + m^{2}\left(\frac{2(\nu_{+}\nu_{-})^{3/2}}{\nu}\right)C^{\gamma} \quad (3)$$

$\gamma_{\pm}$ is the molality-scale mean ionic activity coefficient of the electrolyte $M_{\nu+}X_{\nu-}$; z_{+} and z_{-} are the respective charges of the ions in electrostatic units; n_{w} is the number of kilograms of solvent; m is the molality of the electrolyte;

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10.1021/je034184j CCC: $27.50

$\nu = \nu_+ + \nu_-$ is the number of ions dissociated in one unit electrolyte formula. The other quantities have the following forms:

$$f^{Gx} = -A_\phi\left(\frac{4(I/m^0)}{b}\right)\ln(1 + b\sqrt{I/m^0}) \qquad (4)$$

$$f^\phi = -A_\phi\frac{\sqrt{I/m^0}}{1 + b\sqrt{I/m^0}} \qquad (5)$$

$$f^\gamma = -A_\phi\left[\frac{\sqrt{I/m^0}}{1 + b\sqrt{I/m^0}} + \frac{2}{b}\ln(1 + b\sqrt{I/m^0})\right] \qquad (6)$$

$$B^{Gx} = \beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2(I/m^0)}[1 - e^{-\alpha\sqrt{I/m0}}(1 + \alpha\sqrt{I/m^0})] \qquad (7)$$

$$B^\phi = \beta^{(0)} + \beta^{(1)}e^{-\alpha\sqrt{I/m0}} \qquad (8)$$

$$B^\gamma = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2(I/m^0)}[1 - e^{-\alpha\sqrt{I/m0}}(1 + \alpha\sqrt{I/m^0} - (1/2)\alpha^2(I/m^0))] \qquad (9)$$

$$C^{Gx} = (1/2)C^\phi \qquad (10)$$

$$C^\gamma = (3/2)C^\phi \qquad (11)$$

I is the ionic strength on a molality scale; $\beta^{(0)}$(kg/mol), $\beta^{(1)}$(kg/mol), C^ϕ (kg/mol)^2, and the constants $b = 1.2$ (kg/mol)$^{1/2}$ and $\alpha = 2$ (kg/mol)$^{1/2}$ are the parameters of the Pitzer equations; and A_ϕ(kg/mol)$^{1/2}$ is the Debye−Hückel coefficient for the osmotic coefficient defined as

$$A_\phi = \frac{1}{3}(2\pi N_A\rho_A)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2} \qquad (12)$$

where k is the Boltzmann constant, N_A is Avogadro's number, e is the electronic charge, D is the solvent dielectric constant, T is the temperature (K), and ρ_A is the solvent density, respectively.

In this work, the mean activity coefficients of HCl in (DMF + water) mixed solvents have been determined at 25 °C from the potentiometric data of a galvanic cell combining a glass membrane pH electrode and a Ag/AgCl electrode

$$\text{Ag}|\text{AgCl}|\text{HCl}(m),\ \text{DMF}(w),\ \text{H}_2\text{O}(1 - w)|\text{H}^+(\text{glass membrane ISE}) \qquad (13)$$

where w is the mass fraction of DMF in a water mixed solvent. The potentiometric data of this cell can be represented by the Nernst relation

$$E = E' + 2s\ln(\gamma_\pm m) \qquad (14)$$

where E' represents the cell constant potential and $s = (RT/F)$ represents the ideal Nernst slope, in which the symbols have their usual meanings. The electrolyte concentration in the cell was varied continuously by a standard addition method by adding each time a varying volume of a concentrated stock electrolyte solution having the same solvent mixture composition as that initially introduced into the cell. The accurate way to obtain experimentally the correct value of the electrode slope is to combine, each time, the experimental cell with the hydrogen gas electrode (Pt|H_2 (p = 101.325 kPa)|HCl(m)) or to use an indirect method using selected molalities of the electrolyte with known accurate values of mean activity coefficients. However, some authors used in their calculations a fixed Nernstian[6,8,11−13] or a regressed electrode slope.[14−16] In this work, for the operational simplicity and also in the absence of the related data in the used solvent systems, in addition to $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ, both E' and s were also each time included as regression parameters in the minimization procedures. The potentiometric data of the cell (eq 13) were first measured at a series of electrolyte molalities (in pure and in mixed solvents), and the root-mean-square of the summed deviations of E_{Th}, calculated by eqs 3 and 14 from

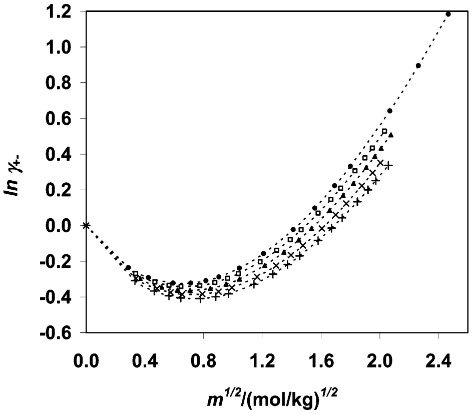

Figure 1. Resulting ln $\gamma_\pm$(HCl) values versus the square root of HCl molality for various values of w (DMF mass fractions) in the (DMF + water) mixed-solvent system at 25 °C: ●, w = 0; □, w = 0.1; ▲, w = 0.2; ×, w = 0.3; +, w = 0.4.

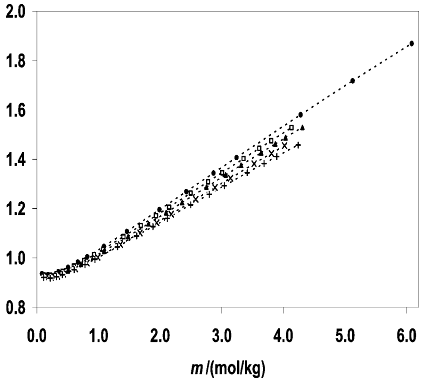

Figure 2. Calculated osmotic coefficient (φ) values versus HCl molality for various values of w (DMF mass fractions) in the (DMF + water) mixed-solvent system at 25 °C: ●, w = 0; □, w = 0.1; ▲, w = 0.2; ×, w = 0.3; +, w = 0.4.

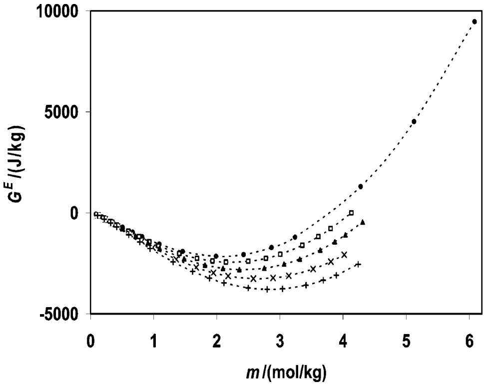

Figure 3. Calculated excess Gibbs free energy (G^E) values versus HCl molality for different values of w (DMF mass fractions) in the (DMF + water) mixed-solvent system at 25 °C: ●, w = 0; □, w = 0.1; ▲, w = 0.2; ×, w = 0.3; +, w = 0.4.

Table 1. Potentiometric Cell Data (E), Mean Activity Coefficients ($\gamma_\pm$), Excess Gibbs Free Energies (G^E), and Osmotic Coefficients (φ) Different Molalities of HCl for Various Values of w (DMF Mass Fractions) in the (DMF + Water) Mixed Solvent System at 25 °C

m	E			G^E	m	E			G^E	m	E			G^E
mol/kg	mV	$\gamma_\pm$	φ	J/kg	mol/kg	mV	$\gamma_\pm$	φ	J/kg	mol/kg	mV	$\gamma_\pm$	φ	J/kg
		0					0.1					0.2		
0.0831	256.2	0.7900	0.9367	−71.0	0.1135	285.8	0.7647	0.9300	−112.1	0.1350	300.2	0.7443	0.9256	−147.9
0.1796	292.5	0.7475	0.9325	−199.1	0.2189	316.5	0.7294	0.9305	−266.3	0.2641	332.1	0.7089	0.9271	−355.0
0.3514	325.9	0.7245	0.9439	−463.7	0.3197	334.6	0.7155	0.9386	−429.6	0.3865	350.7	0.6970	0.9364	−569.9
0.5082	345.0	0.7246	0.9618	−715.4	0.4175	347.7	0.7107	0.9496	−593.9	0.5021	363.9	0.6948	0.9484	−778.2
0.6662	359.0	0.7344	0.9829	−963.1	0.6002	366.2	0.7145	0.9747	−902.2	0.7157	382.7	0.7034	0.9748	−1158.8
0.8177	371.1	0.7497	1.0049	−1187.6	0.7692	379.6	0.7270	1.0008	−1177.2	0.9103	396.2	0.7204	1.0016	−1487.5
1.0899	388.2	0.7875	1.0470	−1544.5	0.9301	390.3	0.7442	1.0264	−1422.6	1.0910	407.0	0.7414	1.0278	−1768.9
1.4612	407.2	0.8551	1.1072	−1910.6	1.0776	399.1	0.7635	1.0510	−1629.4	1.4811	426.5	0.8000	1.0869	−2276.5
1.9893	429.9	0.9779	1.1954	−2148.0	1.4069	415.7	0.8164	1.1072	−2016.8	1.8126	440.7	0.8617	1.1386	−2583.0
2.4260	447.0	1.1023	1.2693	−2067.9	1.6877	428.2	0.8709	1.1560	−2254.9	2.0986	451.7	0.9229	1.1837	−2745.9
2.8664	461.3	1.2498	1.3439	−1718.8	1.9332	438.1	0.9249	1.1984	−2386.8	2.3572	461.0	0.9845	1.2246	−2807.5
3.2404	473.9	1.3938	1.4070	−1204.6	2.1464	446.1	0.9766	1.2354	−2440.8	2.7517	474.1	1.0902	1.2871	−2738.9
4.2807	504.0	1.8997	1.5803	1303.8	2.4979	458.3	1.0717	1.2966	−2401.6	3.0645	483.8	1.1844	1.3364	−2541.0
5.1256	525.5	2.4489	1.7176	4523.8	2.7789	467.7	1.1568	1.3450	−2252.1	3.3135	491.3	1.2663	1.3755	−2290.9
6.0852	549.8	3.2638	1.8690	9469.2	3.0066	474.7	1.2319	1.3842	−2052.3	3.6389	500.6	1.3832	1.4263	−1838.9
					3.3554	485.0	1.3585	1.4437	−1607.3	3.8685	506.9	1.4727	1.4619	−1434.0
					3.6102	492.4	1.4602	1.4866	−1174.6	4.0363	511.5	1.5420	1.4877	−1092.9
					3.8044	498.0	1.5433	1.5190	−783.5	4.3100	518.7	1.6624	1.5295	−454.0
					4.1328	506.9	1.6956	1.5734	−0.4					
		0.3					0.4							
0.1152	299.2	0.7443	0.9235	−124.9	0.1105	304.23	0.7353	0.9214	−125.4					
0.2320	332.1	0.7029	0.9213	−315.0	0.2164	335.76	0.6934	0.9189	−305.9					
0.3323	349.0	0.6875	0.9267	−496.5	0.3181	354.18	0.6751	0.9242	−500.0					
0.4285	361.9	0.6809	0.9347	−677.9	0.4159	367.30	0.6668	0.9323	−696.1					
0.6261	380.7	0.6809	0.9559	−1055.9	0.6050	386.34	0.6641	0.9525	−1085.3					
0.8133	395.4	0.6910	0.9792	−1406.7	0.7802	399.91	0.6709	0.9739	−1443.1					
0.9878	405.9	0.7060	1.0026	−1717.5	0.9429	410.50	0.6822	0.9951	−1764.9					
1.3553	425.7	0.7501	1.0546	−2299.3	1.3084	430.07	0.7198	1.0453	−2426.9					
1.6738	439.0	0.7990	1.1015	−2704.6	1.6183	443.87	0.7615	1.0892	−2901.9					
1.9465	450.4	0.8477	1.1423	−2968.4	1.8843	454.43	0.8034	1.1274	−3235.6					
2.1803	458.6	0.8942	1.1777	−3129.2	2.1152	462.89	0.8439	1.1607	−3464.7					
2.5782	471.7	0.9834	1.2381	−3256.7	2.4960	475.78	0.9190	1.2154	−3711.6					
2.8897	481.9	1.0623	1.2854	−3223.1	2.7972	485.23	0.9856	1.2585	−3785.4					
3.1403	489.0	1.1317	1.3234	−3108.8	3.0414	492.51	1.0445	1.2931	−3763.6					
3.5247	500.3	1.2491	1.3815	−2779.2	3.4147	503.10	1.1430	1.3454	−3584.4					
3.8066	507.9	1.3440	1.4238	−2417.2	3.6875	510.49	1.2219	1.3831	−3339.6					
4.0188	513.3	1.4208	1.4554	−2076.9	3.8937	515.91	1.2855	1.4112	−3089.6					
					4.2396	524.56	1.4004	1.4577	−2542.7					

Table 2. Resulting Pitzer Parameters, Used Dielectric Constants (D), and Debye−Hückel Coefficients for the Osmotic Coefficient (A_ϕ) for the HCl Electrolyte for Different Values of w (DMF Mass Fractions) in the (DMF + Water) Mixed Solvent System at 25 °C

DMF				A_φ[a]		E'	$2s$	σ
(w)	$\beta(0)$	$\beta(1)$	C^φ	(kg/mol)$^{1/2}$	D[a]	mV	mV	(rmsd)
0[b]	0.20488	0.07662	−0.00377					
0	0.20362	0.07861	−0.00350	0.3915	78.54	396.0	118.3	0.31
0.1	0.19857	0.08388	−0.00355	0.4025	76.82	408.8	115.9	0.06
0.2	0.19649	0.09256	−0.00400	0.4192	74.64	417.9	117.9	0.02
0.3	0.19008	0.13023	−0.00367	0.4395	72.20	424.5	117.5	0.24
0.4	0.18921	0.18914	−0.00434	0.4687	69.06	433.2	118.2	0.02

[a] D: known literature[8] values and from fitting using eq 15, A_ϕ: known literature[8] values and using eq 16. [b] Pitzer parameter values for HCl in pure water (at 25 °C) reported by Marshall et al.[18]

the measured E_{exp}, was minimized by changing the value of parameters $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ, E', and s by an iteration procedure employing the Microsoft Excel (Solver) program. The obtained Pitzer parameters were then substituted into eqs 1 and 2 for the calculation of excess Gibbs free energies (G^E) and osmotic coefficients (φ) at each molality.

Results and Discussion

The experimental potentiometric data of the cell (eq 13) and the resulting mean ionic activity coefficients ($\gamma_\pm$), osmotic coefficients (φ), and excess Gibbs free energies (G^E) for the HCl electrolyte in different mixed-DMF−water solvent systems at 25 °C are reported in Table 1. Figures 1−3 show the variation of ln $\gamma_\pm$(HCl) versus the square root of the electrolyte molality and the osmotic coefficient (φ) and excess Gibbs free energy (G^E), both versus the electrolyte molality, respectively, in pure water and at various mass fractions of (DMF + water) mixed-solvent systems. Pitzer interaction parameters, computed by the minimization procedure for these systems, are also reported in Table 2. For constants b and α, the values $b = 1.2$ and $\alpha = 2$ were used according to Koh et al.,[3] who showed that these values (defined for aqueous systems) are still appropriate for mixed water−organic solvent systems.

The unknown values of D (dielectric constant) for different solvent compositions were obtained by a regressed equation derived from fitting discrete values reported in the literature[8] (Table 2). The best fit ($R^2 = 0.99993$) was obtained using the following equation:

$$D^{\mathrm{mix}} = -245.48616086(x_{\mathrm{DMF}})^3 + 48.96194578(x_{\mathrm{DMF}})^2 - 69.24715885x_{\mathrm{DMF}} + 78.57292256 \quad (15)$$

where x_{DMF} is the mole fraction of DMF in the mixed solvent. The values of A_ϕ for different solvent compositions (Table 2) were also obtained from the following equation:[7,17]

$$A_\varphi^{\mathrm{mix}} = A_\varphi^{\mathrm{w}}\left(\frac{D^{\mathrm{w}}}{D^{\mathrm{mix}}}\right)^{3/2}\left(\frac{\rho^{\mathrm{mix}}}{\rho^{\mathrm{w}}}\right)^{1/2} \quad (16)$$

where ρ^{mix} and ρ^{w} are the densities of the mixed solvent and water and D^{mix} and D^{w} are the dielectric constant of the mixed solvent and water, respectively.

Only the results obtained for HCl in pure water could be compared with the corresponding available literature data. Accordingly, Table 2 shows that the obtained values of Pitzer interaction parameters for the HCl electrolyte in pure water solvent are very close to those reported in the literature.[18]

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Received for review September 19, 2003. Accepted June 10, 2004.

JE034184J