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Activity Coefficients for NaCl in (*w*)*N*,*N*-Dimethylformamide + (1 − *w*)Water Mixtures at 25 °C

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Activity coefficients for NaCl in *N*,*N*-dimethylformamide + water mixtures containing 5, 7.5, 10, 15, 30, and 45 mass % DMF have been determined at 25 °C by emf measurements. A decrease of the activity coefficient for NaCl with the DMF increase in the mixture is observed. The activity coefficients at the concentration 0.10 mol·kg^{-1} have been correlated with those reported in the literature for other DMF compositions.

Introduction

In continuation of our previous investigations in the field of the thermodynamic properties of electrolytes in aqueous solutions of organic solvents (Sánchez-Montalvo et al., 1955; García-Pañeda et al., 1996, 1997; Muñoz de Miguel et al., 1997), we present in this paper stoichiometric activity coefficients for NaCl at different concentrations of *N*,*N*-dimethylformamide (DMF) + water mixtures from 5 to 45 mass % DMF. For this purpose, we carried out measurements of electromotric force (emf) of the galvanic cell

$$\text{(A) Na−glass}|\text{NaCl } (m),\ w\text{DMF} + (100 - w)\text{H}_2\text{O, AgCl}|\text{Ag};\ E\ (\text{V})$$

where *m* stands for the concentration (mol·kg^{-1}) of NaCl and *w* is the mass percent of *N*,*N*-dimethylfomamide (DMF) in the mixture. To eliminate the asymmetry potential of the Na−glass electrode (González-Diaz, 1995), cell A was combined with a reference cell (B)

$$\text{(B) Na−glass}|\text{NaCl } (m_{\text{ref}}),\ w\text{DMF} + (100 - w)\text{H}_2\text{O, AgCl}|\text{Ag};\ E_{\text{ref}}\ (\text{V})$$

where m_{ref} was kept at 0.10 mol kg^{-1}. The emf-obtained ΔE is the difference $E - E_{\text{ref}}$.

The aim of this work is to use activity coefficient data to calculate cation transference numbers for NaCl in the above mixtures from galvanic cells with transference. Transference numbers are a prerequisite for obtaining limiting single ion volumes of electrolytes by means of sedimentation potentials (Hirakawa, 1987). On the other hand, studies on activity coefficients for NaCl in DMF + water mixtures are restricted to regions with high DMF content (Lanier, 1965). Nevertheless, the results of this work combined with those of Lanier cover the entire range of the DMF + water mixture at 25 °C.

Experimental Section

Reagents. NaCl (Merck, suprapur) was used after drying it at 120 °C for 48 h in an oven. It was stored over P_2O_5 in a vaccum desiccator. *N*,*N*-Dimethylformamide (Carlo Erba, G.R. stated purity from GLC > 99.8 mol %, H_2O < 0.05%) was kept over thermally activated 4A molecular sieves prior to use. Water was obtained from a Milli-Ro and Milli-Q water system (Millipore, $\kappa < 10^{-6}$ S·cm^{-1}).

Apparatus. H-type cells were used (García-Pañeda, 1998). Sodium−glass electrodes from Metrohm (6.0501.100) and silver−silver chloride electrodes of thermal−electrolytic type made in our laboratory, according to the procedure described by Janz (1961), were used. Various batches of 12 electrodes were performed, and the electrodes remained shorted together for two weeks in opaque recipients with NaCl saturated with AgCl. Electrodes with bias potential greater than ±0.02 mV were rejected. The emf measurements were carried out with an electrometer (Keithley, model 614), which has resolution of ±0.01 mV. Stable emf readings were obtained by placing the apparatus into a Faraday cage.

Measurements. Solvents and stock electrolyte solutions were prepared by mass in a dry thermostated room (±0.5 °C). NaCl solutions were obtained by successive weight dilution from those stock solutions. Galvanic cells were introduced in a transformer oil bath whose temperature was mantained within (25.000 ± 0.003) °C by means of a temperature controller (Heto DBT) connected to a cooling unit (Hetofrig CB7). The temperature bath was monitored to ±0.001 °C with a platinum resistance probe connected to a ASL model F250 thermometer, which was calibrated by Isotech (England) with a precision of ±0.001 °C and an accuracy in absolute temperature of ±0.010 °C (ITS-90). The whole system was placed in a thermostated room at ±0.5 °C. After the cells were thermostated for 2 h, emf readings at 3 min intervals were recorded until they were constant within ±0.1 mV, i.e., for aproximately in 40 min. The reliability of the whole system was tested by measuring the activity coefficients of NaCl in water. A value of 0.777 ± 0.001 for the $\gamma_\pm$ (m = 0.10 mol·kg^{-1}) was obtained, which is in agreement with 0.779 from Hamer and Wu (1972).

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Table 1. Experimental Values of ΔE and $\gamma_\pm$ at Different Concentrations of NaCl in wDMF + (1 − w)Water Mixtures at 298.15 K

$w = 0.05$			$w = 0.10$			$w = 0.05$			$w = 0.10$		
$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$
1.0793	0.10709	0.896	1.0450	0.10795	0.900	5.9000	0.02495	0.810	5.0391	0.03251	0.811
1.9803	0.07712	0.875	1.8929	0.07929	0.868	7.6444	0.01298	0.789	6.5339	0.02017	0.795
2.8155	0.06041	0.852	2.6872	0.06221	0.853	7.9067	0.01136	0.788	7.8403	0.01149	0.784
3.7743	0.04633	0.836	3.4921	0.04984	0.835	9.5060	0.00267	0.776	8.8630	0.00585	0.774
4.5950	0.03698	0.823	4.3517	0.03945	0.820	10.00	0.0	0.777	10.000	0.0	0.769
5.0355	0.03251	0.819	4.7706	0.03501	0.816						

$w = 0.075$			$w = 0.15$			$w = 0.075$			$w = 0.15$		
$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$
0.9784	0.11112	0.903	1.1664	0.10227	0.902	32.391	−0.05489	0.690	33.290	−0.05624	0.691
1.017	0.10927	0.901	1.2957	0.09780	0.886	41.080	−0.06640	0.681	48.320	−0.07414	0.674
1.7445	0.08303	0.875	1.6921	0.08516	0.867	45.100	−0.07086	0.676	48.940	−0.07454	0.671
2.8029	0.06035	0.847	1.7586	0.08326	0.866	48.722	−0.07460	0.673	55.960	−0.08084	0.663
3.4136	0.05086	0.836	2.5270	0.06548	0.852	50.0.958	−0.07670	0.670	68.910	−0.09114	0.658
3.5090	0.04957	0.834	3.5243	0.04931	0.837	60.137	−0.08465	0.663	93.090	−0.10584	0.649
3.9226	0.04429	0.827	3.9415	0.04393	0.831	80.789	−0.09950	0.659	111.640	−0.11504	0.647
4.2065	0.04101	0.822	4.4830	0.03780	0.823	107.114	−0.11354	0.653	122.040	−0.11984	0.650
5.4830	0.02832	0.807	5.8507	0.02522	0.805	136.582	−0.12564	0.648	144.360	−0.12874	0.653
6.6865	0.01921	0.790	7.1225	0.01593	0.793	147.651	−0.12980	0.650	176.850	−0.13984	0.662
7.0214	0.01676	0.789	7.9287	0.01104	0.783	150.441	−0.13082	0.651	193.730	−0.14474	0.664
9.6120	0.00189	0.770	8.6110	0.00722	0.777	157.245	−0.13325	0.653			
10.000	0.0	0.768	9.1355	0.00442	0.773	167.484	−0.13660	0.654			
13.931	−0.01535	0.743	10.000	0.0	0.770	180.970	−0.14110	0.661			
18.000	−0.02718	0.724	10.650	0.00273	0.762	190.351	−0.14410	0.666			
21.484	−0.03490	0.705	28.650	−0.04880	0.694						

$w = 0.30$			$w = 0.45$			$w = 0.30$			$w = 0.45$		
$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$	$10^2 m/(\text{mol}\cdot\text{kg}^{-1})$	ΔE/V	$\gamma_\pm$
1.2392	0.09878	0.885	0.8015	0.12031	0.884	17.670	−0.02582	0.701	13.726	−0.01297	0.688
1.8243	0.08028	0.862	1.3587	0.09470	0.858	19.100	−0.02934	0.695	27.042	−0.04447	0.644
2.9383	0.05771	0.830	2.0189	0.07606	0.830	22.220	−0.03629	0.684	34.881	−0.05567	0.621
3.4395	0.05045	0.817	2.2304	0.07116	0.826	26.870	−0.04469	0.666	45.541	−0.06787	0.602
4.2295	0.04042	0.807	2.7512	0.06092	0.818	35.490	−0.05807	0.654	56.171	−0.07802	0.595
5.0664	0.03199	0.794	3.1060	0.05517	0.810	46.760	−0.07149	0.645	63.101	−0.08317	0.585
5.7021	0.02675	0.781	3.4381	0.05028	0.805	57.590	−0.08149	0.636	74.829	−0.09167	0.582
6.9878	0.01673	0.775	4.2856	0.04003	0.788	68.860	−0.08999	0.627	88.143	−0.09917	0.572
7.7652	0.01193	0.766	5.0825	0.03212	0.775	81.870	−0.09829	0.620	97.562	−0.10367	0.564
9.6890	0.00173	0.748	6.4325	0.02087	0.762	92.450	−0.10409	0.615	110.125	−0.11007	0.566
10.000	0.0	0.750	7.1504	0.01601	0.753	102.710	−0.10936	0.613	120.818	−0.11507	0.568
11.956	−0.00749	0.726	8.0890	0.01017	0.746	122.490	−0.11879	0.618	130.798	−0.11938	0.571
12.830	−0.01042	0.716	8.7450	0.00653	0.740	146.370	−0.12829	0.622			
13.510	−0.01265	0.710	10.000	0.0	0.735	166.710	−0.13559	0.629			

Table 2. Densities ρ, Dielectric Constants ϵ, and Debye−Hückel Constants Required to Apply Eq 2

w	$\rho^a/(\text{g}\cdot\text{cm}^{-3})$	ϵ^b	$A/(\text{kg}^{1/2}\cdot\text{mol}^{-1/2})$	$B/(\text{kg}^{1/2}\ \text{mol}^{-1/2}\cdot\text{cm}^{-1})$
0.05	0.99648	77.68	0.5167	0.3298
0.075	0.99632	77.22	0.5213	0.3308
0.10	0.99629	76.82	0.5264	0.3317
0.15	0.99623	75.72	0.5368	0.3341
0.30	0.99693	72.20	0.5768	0.3422
0.45	0.99680	67.18	0.6426	0.3547

[a] Determined with an Anton−Paar densimeter. [b] From Niazi et al., 1993.

Table 3. Mean Ionic Activity Coefficients of Reference $\gamma_{\pm\text{ref}}$ ($m_{\text{ref}} = 0.10$ mol·kg^{-1}), Mean Distance of Closest Approach a, and Standard Deviation of Fit $\sigma(\Delta E)$

w	x_{DMF}	$\gamma_{\pm\text{ref}}$	a/Å	$10^4\sigma(\Delta E)$/V
0.05	0.0128	0.777 ± 0.002	4.7 ± 0.2	1.4
0.075	0.0196	0.768 ± 0.001	4.2 ± 0.1	1.4
0.10	0.0267	0.769 ± 0.001	4.4 ± 0.1	1.1
0.15	0.0417	0.770 ± 0.002	4.8 ± 0.2	2.0
0.30	0.0955	0.750 ± 0.002	4.2 ± 0.2	2.0
0.45	0.1678	0.735 ± 0.001	5.4 ± 0.2	1.0

Results

Values of ΔE for NaCl in different DMF + water mixtures are summarized in Table 3. The mean ionic activity coefficients (molal scale) were calculated using the Nernst equation

$$\Delta E = 2k \log \frac{m_{ref}\gamma_{\pm\text{ref}}}{m\gamma_\pm} \qquad (1)$$

where $k = 2.303RT/F$ (V) and $\gamma_\pm$ and $\gamma_{\pm\ \text{ref}}$ stand for the mean ionic activity coefficients of NaCl at molalities m and m_{ref}, respectively. To calculate $\gamma_\pm$, it is necessary to know $\gamma_{\pm\text{ref}}$. An extended Debye−Hückel equation was used (Robinson and Stokes, 1965)

$$\log \gamma_\pm = -\frac{A\sqrt{m}}{1 + Ba\sqrt{m}} + Cm - \log(1 + 10^{-3}\ \nu m M_s) \qquad (2)$$

where M_s is the mean molar mass of the solvent, $\nu = 2$, and C is an adjustable parameter. A and B are Debye−Hückel constants, and a is the mean distance of closest approach of the ions (Horvath, 1985). The parameters required to calculate A and B are listed in Table 2.

By combining eqs 1 and 2,

$$\Delta E = -2k \log\frac{m}{m_{\text{ref}}} + 2k\left(\frac{A\sqrt{m}}{1 + Ba\sqrt{m}}\right) + 2k \log(1 + 0.002mM_s) + 2k \log \gamma_{\pm\text{ref}} - 2kCm \qquad (3)$$

where a, C, and $\gamma_{\pm\text{ref}}$ are obtained by a least-squares

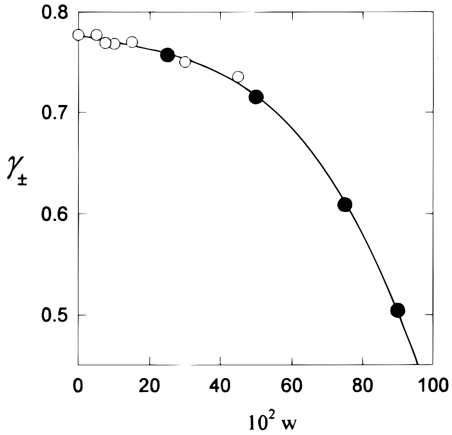

Figure 1. Variation of the activity coefficient $\gamma_\pm$ for NaCl (m = 0.10 mol·kg^{-1}) with mass fraction w at 25 °C: (●) Lanier; (○) this work; (—) second-order polynomial equation.

analysis. The values of a and $\gamma_{\pm\mathrm{ref}}$ and the standard deviations of the fit are listed in Table 3. From the $\gamma_{\pm\mathrm{ref}}$ values, the mean ionic activity coefficients for NaCl in the different DMF + water mixtures studied are calculated by means of eq 1, and they are shown in Table 1 along with the associated uncertainties.

Lanier has determined the activity coefficients of NaCl in DMF + water mixtures (25, 50, 75, and 90 DMF wt %) by emf measurements (Lanier, 1965). On the basis of our equations, we have calculated the Lanier activity coefficients at the NaCl concentration 0.10 mol·kg^{-1} (25%, 0.757; 50%, 0.715, 75%, 0.609; 90%, 0.504). In Figure 1 is shown a plot of $\gamma_\pm$ versus wt % DMF, in which are included our data and those calculated from the Lanier paper. A decrease of the activity coefficient value for NaCl with the DMF increase in the mixture is observed.

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Literature Cited

González-Díaz, O. M.; Fernández-Mérida, L.; Hernández-Luis, F. F.; Esteso M. A. *J. Solution Chem.* **1995**, *24*, 551−563.

García-Pañeda, E.; Muñoz de Miguel, E.; Yanes, C.; Maestre, A. Limiting Partial Molar Volumes of Tetra-*n*-alkylammonium Bromides in *x*Dimethylformamide + (1 − *x*)Water Mixtures at 298.15 K. *J. Chem. Eng. Data* **1997**, *42*, 441−445.

García-Pañeda, E. Estudio de Volúmenes Molares Parciales a Dilución Infinita de Electrolitos en Medios Acuoorgánicos: Análisis de Contribuciones Iónicas. Thesis, Universidad de Sevilla, Spain, 1998.

García-Pañeda, E.; Yanes, C.; Muñoz de Miguel, E.; Maestre, A. Limiting Molar Partial Volumes of Tetra-*n*-alkylammonium Bromides in Dimethyl Sulfoxide + Water Mixtures at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1149−1151.

Hamer, W. J.; Wu, Y.-C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047−1099.

Hirakawa, H. Measurement of Sedimentation Potential and its Aplication to the Determination of Individual Ionic Partial Molar Volumes. *J. Phys. Chem.* **1987**, *91*, 3452−3456.

Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions, Physical Properties, Estimation and Correlation Methods*; Ellis Horwood Ltd.: Chichester (England), 1985.

Janz, G. J. *Reference Electrodes, Theory and Practice*; Ives, G. J., Janz, G. J., Eds.; Academic Press: New York, 1961.

Lanier, R. D. Properties of Organic-Water Mixtures. III. Activity Coefficients of Sodium Chloride by Cation-Sensitive Glass Electrodes. *J. Phys. Chem.* **1965**, *69*, 2697−2706.

Muñoz de Miguel, E.; Yanes, C.; García-Pañeda, E.; Mozo-Llamazares; Maestre, A. Enthalpy of Interaction of Some Electrolytes with Dimethyl Sulfoxide in Water at 298.15 K. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2533−2536.

Niazi, M. S. K.; Jabeen, I.; Shah, S. S. Ionic Association and Conductances of Sodium Perchlorate in *N*,*N*-Dimethylformamide + Water and Tetrahydrofuran + Water at 298 K. *J. Chem. Eng. Data* **1993**, *38*, 285−287.

Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed. revised; Butterworth: London, 1965.

Sánchez-Montalvo, R.; Calvente, J. J.; Yanes, C.; Maestre, A. Enthalpy of Interaction of Some Electrolytes with 2-Methyl-2-butanol in Water at 25 °C. *J. Solution Chem.* **1995**, *24*, 953−965.

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