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Activity Coefficients for NaCl in MeOH + H_2O by Electromotive Force Measurements at 308.15 K and 318.15 K

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Electromotive force (emf) measurements of the cell Na ion-selective electrode (glass)|NaCl, MeOH + H_2O|Cl ion-selective electrode (solid state) were made in methanol + water containing 0, 10, 30, 50, 70, and 90 mass % of methanol, at 308.15 K and 318.15 K, respectively. Using the Pitzer's equation calculations of standard cell potentials were made. The mean activity coefficients of NaCl were also derived.

The activity coefficient of the electrolyte in mixed solvents is an important thermodynamic property. Ion-selective electrodes can be used to form a galvanic cell, and through the measurement of its electromotive force, the activity coefficient of the electrolyte in the solution can be obtained. There are three types of cells employed (Hamer and Wu, 1972). They are a galvanic cell with transference (Butler and Gordon, 1948), a galvanic cell without liquid junction using one fluid (Han and Pan, 1993; Yan et al., 1994), and a galvanic cell without liquid junction using two fluids (Feakins and Voice, 1972; Esteso et al., 1989). The reliable performance of the ion-selective electrode makes it possible to determine the activity coefficients of electrolytes in mixed solvents. In this work the system NaCl + MeOH + H_2O was studied at 308.15 K and 318.15 K.

Materials and Methods

Methanol of analytical grade was fractionally distilled, and the intermediate fraction was used. Refractive index was used as a measure of purity. Deionized water was distilled twice in the presence of a small amount of $KMnO_4$. Its specific conductance was approximately 7×10^{-7} $S{\cdot}cm^{-1}$. NaCl of analytical grade was recrystallized twice from water and stored over silica gel in a desiccator before use.

Cl ion-selective electrode (solid state, Orion No.941700) and Na ion-selective electrode (glass, Orion No.971100) have been standardized before used; they both have good Nernst response (Han and Pan, 1993; Yan et al., 1994). We compared our data with reference data (Hamer and Wu, 1972) of NaCl activity coefficients in pure water at 298.15 K every week and found the ion-selective electrodes were very stable. Figure 1 illustrates the comparisons; it can be seen that $\delta\gamma_\pm$ were within ±0.003.

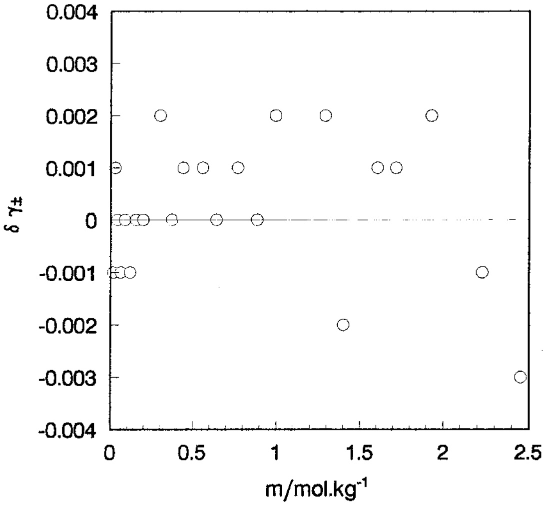

Figure 1. Comparisons between the experimental data and the reference data for mean activity coefficients of NaCl in water at 298.15 K.

The cell used in this work is as follows:

$$\text{Na ion-selective electrode}|\text{NaCl, MeOH} + H_2O|\text{Cl ion-selective electrode} \quad (1)$$

It belongs to the type of galvanic cell without liquid junction with only one fluid. It is simple and easy to operate. The solution is prepared by weighing (using a Sartorius-1712 electronic balance), whose accuracy was 0.1 mg.

The cell vessel has three holes on its top: two are used to plug ion-selective electrodes and the other is used to add solutions. The holes are sealed by Parafilm to prevent the solvent escaping. The electromotive force (emf) of this cell is measured by an Orion 811 ionalyzer, whose resolution is 0.1 mV. The vessel is put into the thermostat, which can maintain temperature within ±0.01 K by a standard Pt resistance thermometer. The solution is put into the thermostat for 0.5−1 h and stirred by a magnetic stirrer at a constant rate until the emf was stable at least 10 min, and then the data were taken.

Results and Discussion

The Nernst equation for cell 1 is

$$E = E° + 2k \ln(m\gamma_\pm) \quad (2)$$

where $k = RT/F$. R, F, and T are the universal gas constant, Faraday constant, and absolute temperature, respectively. $\gamma_\pm$ is the NaCl mean activity coefficient. $E°$ is the standard potential of cell 1. The emf values for each MeOH + H_2O mixture as a function of the NaCl molality m were listed in Table 1.

Pitzer's equation (Pitzer, 1973) was applied in describing the mean activity coefficients in our calculations.

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Table 1. Electromotive Force *E* and the Mean Activity Coefficients at the Different NaCl Molality *m* in Methanol + Water

m/(mol·kg^{-1})	E/mV	$\gamma_\pm$	m/(mol·kg^{-1})	E/mV	$\gamma_\pm$	m/(mol·kg^{-1})	E/mV	$\gamma_\pm$
$T = 308.15$ K								
100 mass % Water								
0.0406	114.5	0.835	0.3064	213.0	0.707	0.8822	265.7	0.662
0.0646	137.1	0.803	0.3682	222.1	0.698	0.9878	271.6	0.661
0.1052	160.9	0.771	0.4462	231.5	0.687	1.1500	279.7	0.661
0.1435	176.1	0.753	0.4907	236.2	0.683	1.4019	290.4	0.663
0.1821	187.6	0.737	0.5563	242.4	0.677	1.5349	295.5	0.667
0.2171	196.2	0.727	0.6733	252.0	0.670	1.8212	305.3	0.676
0.2606	205.1	0.716	0.7926	260.2	0.664	2.0651	313.1	0.690
10 mass % Methanol								
0.0235	103.2	0.856	0.2334	215.2	0.710	0.9166	283.2	0.650
0.0527	142.5	0.799	0.2854	225.0	0.698	1.0641	290.9	0.648
0.0800	163.0	0.774	0.3563	235.8	0.685	1.2226	298.2	0.647
0.1010	174.4	0.761	0.4365	245.7	0.674	1.5157	310.1	0.653
0.1262	185.1	0.745	0.5498	257.1	0.663	1.8707	322.1	0.663
0.1540	194.9	0.734	0.6480	265.3	0.657	1.9865	325.7	0.668
0.1910	205.4	0.721	0.7811	274.8	0.652	2.1734	330.2	0.665
30 mass % Methanol								
0.0147	118.2	0.865	0.1222	220.6	0.713	0.6348	300.0	0.613
0.0236	140.9	0.822	0.1561	232.2	0.695	0.7705	309.6	0.605
0.0301	152.6	0.806	0.1857	240.5	0.683	0.8831	316.5	0.601
0.0458	173.4	0.783	0.2301	250.7	0.668	1.0268	324.4	0.600
0.0549	182.2	0.770	0.2787	259.9	0.656	1.1959	332.6	0.601
0.0688	193.1	0.755	0.3723	273.8	0.638	1.2973	337.1	0.603
0.0965	209.4	0.732	0.5068	288.9	0.623	1.4833	344.5	0.606
50 mass % Methanol								
0.0169	164.9	0.816	0.1152	255.2	0.655	0.4708	320.6	0.549
0.0223	178.2	0.795	0.1408	264.5	0.638	0.5194	325.4	0.545
0.0334	197.3	0.760	0.1706	273.3	0.622	0.5956	331.4	0.532
0.0416	207.6	0.741	0.2058	281.9	0.606	0.6587	335.8	0.523
0.0518	218.0	0.723	0.2446	289.9	0.593	0.7470	342.3	0.521
0.0741	234.7	0.692	0.3258	303.3	0.573	0.8060	345.9	0.517
0.0879	242.7	0.678	0.4176	314.9	0.556	0.9169	352.8	0.517
70 mass % Methanol								
0.0059	161.8	0.865	0.0429	252.9	0.663	0.2249	327.7	0.518
0.0076	172.9	0.834	0.0476	257.2	0.658	0.2437	331.3	0.511
0.0102	187.0	0.803	0.0653	273.3	0.640	0.2631	334.8	0.506
0.0164	208.7	0.757	0.0894	286.6	0.601	0.2847	338.4	0.500
0.0195	216.8	0.741	0.1222	300.2	0.568	0.3073	341.9	0.495
0.0264	230.8	0.711	0.1471	308.3	0.549	0.3294	345.2	0.491
0.0330	241.0	0.689	0.1793	317.6	0.537	0.3507	348.3	0.489
90 mass % Methanol								
0.0049	205.1	0.809	0.0169	261.0	0.665	0.0447	303.6	0.561
0.0066	218.7	0.772	0.0195	267.4	0.651	0.0514	309.5	0.545
0.0081	228.7	0.748	0.0230	274.6	0.632	0.0578	314.6	0.533
0.0099	237.5	0.726	0.0259	279.7	0.618	0.0615	317.3	0.529
0.0118	244.8	0.705	0.0293	285.3	0.606	0.0671	321.3	0.522
0.0140	252.5	0.685	0.0388	297.5	0.576	0.0751	326.6	0.515
$T = 318.15$ K								
100 mass % Water								
0.0226	83.0	0.859	0.2953	212.6	0.699	1.0358	277.8	0.654
0.0508	124.3	0.812	0.3449	220.5	0.691	1.1696	284.4	0.654
0.0875	151.8	0.778	0.4268	231.4	0.682	1.2757	289.2	0.654
0.1098	163.1	0.762	0.5173	241.2	0.672	1.4127	296.0	0.669
0.1638	183.2	0.737	0.5953	248.5	0.668	1.6371	304.4	0.673
0.2045	194.2	0.722	0.8150	264.9	0.658	1.7984	310.2	0.681
0.2395	202.1	0.712	0.9849	275.0	0.654	2.0748	319.1	0.694
10 mass % Methanol								
0.0349	127.4	0.822	0.2568	226.7	0.685	1.0819	301.0	0.630
0.0493	144.6	0.797	0.3088	235.9	0.673	1.2476	309.0	0.632
0.0700	162.2	0.774	0.3788	246.1	0.661	1.3946	315.4	0.636
0.0947	177.2	0.753	0.4338	252.9	0.654	1.5006	319.6	0.638
0.1113	185.2	0.741	0.4961	259.7	0.647	1.6327	324.5	0.641
0.1365	195.4	0.728	0.6833	276.1	0.634	1.8915	333.6	0.653
0.1716	206.7	0.711	0.7887	283.6	0.626	2.0909	339.9	0.663
0.2072	216.0	0.698	0.9193	291.3	0.626			

Table 1 (Continued)

m/(mol·kg^{-1})	E/mV	$\gamma_\pm$	m/(mol·kg^{-1})	E/mV	$\gamma_\pm$	m/(mol·kg^{-1})	E/mV	$\gamma_\pm$
			30 mass % Methanol					
0.0208	134.5	0.829	0.1938	244.5	0.663	0.5994	299.8	0.588
0.0364	162.4	0.790	0.2241	251.4	0.650	0.6880	306.9	0.583
0.0629	189.4	0.748	0.2557	257.8	0.641	0.9319	322.4	0.571
0.0897	206.7	0.719	0.2976	265.1	0.629	1.0475	328.5	0.568
0.1137	218.3	0.701	0.3369	271.3	0.622	1.2637	339.1	0.571
0.1538	233.0	0.678	0.3784	277.0	0.614	1.4814	348.4	0.576
0.1681	237.3	0.670	0.4524	285.7	0.602	1.6602	354.9	0.580
			50 mass % Methanol					
0.0122	148.4	0.831	0.0848	242.3	0.666	0.3667	312.0	0.550
0.0165	163.2	0.811	0.1002	250.2	0.652	0.4443	321.3	0.538
0.0268	186.6	0.765	0.1204	259.0	0.637	0.5035	327.8	0.534
0.0358	200.9	0.742	0.1366	265.0	0.626	0.5808	335.0	0.528
0.0489	215.9	0.714	0.1726	276.1	0.607	0.6481	340.7	0.525
0.0591	224.9	0.697	0.2102	285.5	0.592	0.7632	348.3	0.512
0.0711	233.8	0.681	0.3017	302.8	0.565	0.8262	353.2	0.517
			70 mass % Methanol					
0.0106	187.6	0.773	0.0486	259.1	0.619	0.1376	307.4	0.527
0.0171	210.2	0.722	0.0546	264.5	0.608	0.1546	312.7	0.518
0.0239	226.0	0.689	0.0608	269.4	0.597	0.1722	317.8	0.509
0.0282	233.8	0.671	0.0716	277.0	0.583	0.2089	326.9	0.496
0.0311	238.4	0.663	0.0796	282.2	0.576	0.2295	331.3	0.489
0.0354	244.0	0.650	0.1025	293.9	0.553	0.2671	338.4	0.478
0.0427	253.2	0.632	0.1212	301.6	0.539	0.2928	342.9	0.474
			90 mass % Methanol					
0.0052	211.9	0.798	0.0179	268.1	0.643	0.0444	308.6	0.543
0.0071	225.8	0.754	0.0207	274.7	0.628	0.0495	313.2	0.530
0.0100	241.7	0.710	0.0250	283.4	0.609	0.0536	317.1	0.525
0.0124	251.4	0.686	0.0296	290.8	0.593	0.0575	320.4	0.520
0.0144	258.3	0.668	0.0333	296.2	0.578	0.0662	326.8	0.508
0.0163	263.9	0.655	0.0399	304.9	0.565	0.0747	332.5	0.499

For 1−1 type electrolyte, the Pitzer's equation is written as

$$\ln \gamma_\pm = f^\gamma + mB^\gamma + m^2C^\gamma \qquad (3a)$$

where

$$f^\gamma = -A_\phi[m^{1/2}/(1 + bm^{1/2}) + (2/b)\ln(1 + bm^{1/2})] \qquad (3b)$$

$$B^\gamma = 2\beta^{(0)} + 2\beta^{(1)}[1 - \exp(-\alpha m^{1/2})(1 + \alpha m^{1/2} - \alpha^2 m/2)]/(\alpha^2 m) \qquad (3c)$$

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

$\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ are the parameters of the Pitzer's equation, which were obtained by optimizing the experimental data. A_ϕ is the Debye−Huckel parameter for the osmotic function as defined by

$$A_\phi = (1/3)(2\pi N_A\rho)^{1/2}[e^2/(4\pi\epsilon_0 D k_0 T)]^{3/2} \qquad (4a)$$

where ϵ_0 is the permittivity of a vacuum, k_0 is the Boltzmann constant, N_A is Avogadro constant, D is dielectric constant, and ρ is the density of solvent mixtures (Bates, 1968). After the values of the fundamental physical constants are introduced to eq 4a, it becomes

$$A_\phi = 1.4006 \times 10^6 \rho^{1/2}/(DT)^{3/2} \qquad (4b)$$

The A_ϕ values in the different solvent compositions were listed in Table 2. The results obtained by Koh et al. (1985) show that $\alpha = 2.0$ and $b = 1.2$ of aqueous systems are still suitable for MeOH−H_2O mixed solvents systems. Introducing eq 3 into eq 2, $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ, and $E°$ could be optimized by the algorithm of the Nelder and Mead (1965) simplex method from emf data. The results and deviations were listed in Table 3.

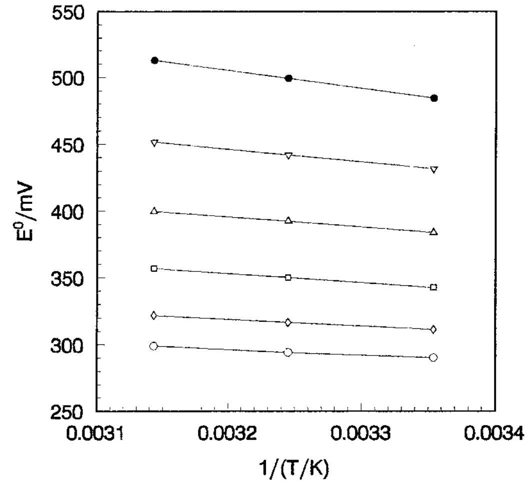

Figure 2. Linear correlation between $E°$ and $1/T$: −○−, 100% water; −◇−, 10% MeOH; −□−, 30% MeOH; −△−, 50% MeOH; −▽−, 70% MeOH; −●−, 90% MeOH.

Table 2. Values of the Dielectric Constant D, Density ρ, and the Parameter A_ϕ of Pitzer's Equation for Methanol + Water

mass %	T = 308.15 K			T = 318.15 K		
MeOH	ρ/(g·cm^{-3})	D	A_ϕ	ρ/(g·cm^{-3})	D	A_ϕ
0	0.9972	74.94	0.395 73	0.9965	71.50	0.408 73
10	0.9798	70.68	0.430 88	0.9786	67.32	0.441 58
30	0.9449	62.20	0.514 39	0.9405	58.97	0.529 93
50	0.9059	53.21	0.634 64	0.8995	50.29	0.656 06
70	0.8601	44.42	0.811 52	0.8526	41.83	0.842 81
90	0.8075	35.65	1.092 80	0.7992	33.53	1.036 20

As seen in Table 3, the Pitzer's equation could correlate the experimental data with very small errors, which tested the stability of ion-selective electrode during experiments. From the $E°$ values of Pitzer's equation, the experimental

Table 3. Values Obtained for the Parameters of the Pitzer Equation for the System NaCl + MeOH + H_2O

mass %	T = 308.15 K					T = 318.15 K				
MeOH	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	$E°$/mV	σ/mV	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	$E°$/mV	σ/mV
0	0.0763	0.2878	0.0057	294.26	0.07	0.0903	0.2650	0.0039	299.09	0.16
10	0.1001	0.3162	−0.0053	310.67	0.17	0.1101	0.2295	−0.0021	322.01	0.09
30	0.0849	0.4854	0.0129	350.10	0.17	0.1224	0.3464	−0.0075	356.99	0.46
50	0.1305	0.4653	−0.0034	392.44	0.23	0.2635	0.1978	−0.0865	399.80	0.21
70	0.3485	0.1772	−0.0057	441.91	0.62	0.5908	0.4560	0.0053	451.59	0.50
90	4.3647	−5.9872	0.0680	499.33	0.25	4.8090	−6.6811	0.0789	512.82	0.45

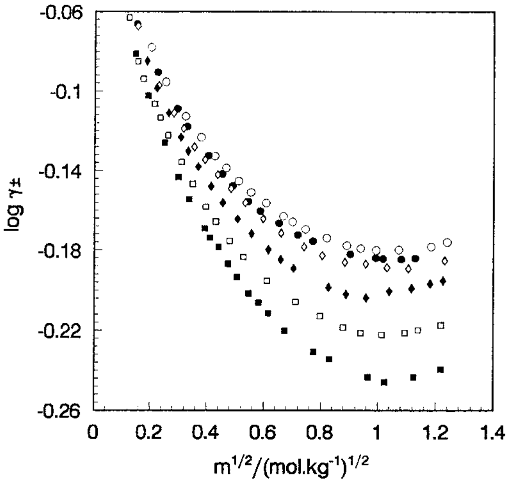

Figure 3. Comparisons of mean activity coefficients between 308.15 K and 318.15 K (100% water, 10% MeOH, 30% MeOH): ○, 100% water, 308.15 K; ●, 100% water, 318.15 K; ◇, 10% MeOH, 308.15 K; ♦, 10% MeOH, 318.15 K; □, 30% MeOH, 308.15 K; ■, 30% MeOH, 318.15 K.

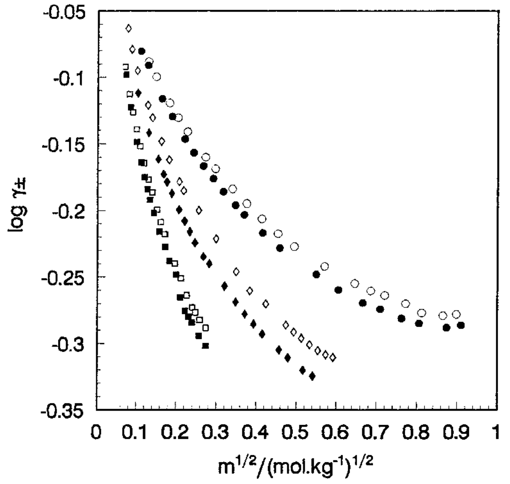

Figure 4. Comparisons of mean activity coefficients between 308.15 K and 318.15 K (50% MeOH, 70% MeOH, 90% MeOH): ○, 50% MeOH, 308.15 K; ●, 50% MeOH, 318.15 K; ◇, 70% MeOH, 308.15 K; ♦, 70% MeOH, 318.15 K; □, 90% MeOH, 308.15 K; ■, 90% MeOH, 318.15 K.

Table 4. Relationship of $E°$ and $1/T$ for the System NaCl + MeOH + H_2O

mass %	$E°$/mV		
MeOH	1/(T/K) = 0.003354	1/(T/K) = 0.003245	1/(T/K) = 0.003143
0	290.44	294.26	299.09
10	311.45[a]	316.67	322.01
30	342.81[a]	350.10	356.99
50	384.07[a]	392.44	399.80
70	431.75[a]	441.91	451.59
90	484.40	499.33	512.82

[a] Yan et al. (1994) interpolation.

values of the NaCl mean activity coefficients (listed in Table 1) could be calculated by eq 2.

Table 3 shows that the $E°$ values increase with an increasing of the methanol content in the solvent mixtures. To compare these values with those of 298.15 K (Yan et al., 1994) in the same systems, it can be seen that the $E°$ value and the value of $1/T$ have the linear correlation (listed in Table 4 and are shown in Figure 2). The linear relationships also indicate the good repeatability of the experiments. From Figure 3 and Figure 4, it can be seen that the activity coefficients decrease when the temperature is increased.

Since the instrumental precision was 0.1 mV, the calculations of activity coefficients may lead to 0.003 uncertainty.

Literature Cited

Bates, R. G. In *Hydrogen-Bonded Solvent Systems*; Covington, A. K., Jones, P., Eds.; Butterworth: London, 1968.

Butler, J. P.; Gordon, A. R. Thermodynamics of Sodium Chloride in 50 Mole Per Cent. Aqueous Methanol from E.m.f. Measurements on Cells with Transference. *J. Am. Chem. Soc.* **1948**, *70*, 2276−2278.

Esteso, M. A.; et al. Activity Coefficients for NaCl in Ethanol−Water Mixtures at 25 °C. *J. Solution Chem.* **1989**, *18*, 277−288.

Feakins, D.; Voice, P. J. Studies in Ion Solvation in Nonaqueous Solvents and Their Aqueous Mixtures. Part 14−Free Energies of Transfer of the Alkali-Metal Chlorides from Water to 10−99% (w/w) Methanol−Water Mixtures at 25 °C. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1390−1405.

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.

Han, S.; Pan, H. Thermodynamics of the Sodium Bromide-Methanol-Water and Sodium Bromide-Ethanol-Water Two Ternary Systems by the Measurements of Electromotive Force at 298.15 K. *Fluid Phase Equilib.* **1993**, *83*, 261−270.

Koh, D. S. P.; et al. The Application of the Pitzer Equations to 1−1 Electrolytes in Mixed Solvents. *J. Solution Chem.* **1985**, *14*, 635−651.

Nelder, J. A.; Mead, R. A Simplex Method for Function Minimization. *Computer J.* **1965**, *7*, 308−313.

Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268−277.

Yan, W.; et al. Activity Coefficients for NaCl in MeOH-H_2O Mixtures by the Measurements of Electromotive Force (298.15 K). *Acta Chim. Sin. (Chinese)* **1994**, *52*, 937−946.

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