Activity Coefficients of NaCl in H_2O + MeOH + EtOH by Electromotive Force at 298.15 K

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Activity coefficients of NaCl in water + methanol + ethanol solutions have been determined from electromotive force (emf) measurements at 298.15 K. We have used a cell [ISE Na^+|NaCl, H_2O, MeOH, EtOH|ISE Cl^-] to obtain the emf of eight mixture series containing 10 to 40 (w/w) of methanol + ethanol at molalities up to 2.0 of NaCl. A modified Pitzer equation is used together with the Nernst equation to obtain the mean activity coefficient.

Introduction

The design of extractive distillation,[1] food processes,[2,3] and brine preparation processes[4] requires of the thermodynamic properties of electrolyte solutions. One of these properties is the activity coefficient needed to estimate the nonideality of the mixture in equilibrium. Many of the activity coefficients of electrolytes in the literature are in aqueous solutions, and only a few determinations are done in mixed solvents. Ethanol (EtOH) and/or methanol (MeOH) mixed with water are common solvents used for the calculation of the mean activity coefficient. Åkerlöf[5] calculated the activity coefficient of sodium chloride in water + methanol solutions at 298.15 K. Recently, Yao et al.[6] obtained the activity coefficients of the same system by electromotive force measurements at (308.15 and 318.15) K. Activity coefficients of NaCl with ethanol and water have been determined at 298.15 K and alcohol mass fractions from (10 to 100) % by several authors.[7−10] The molalities considered in these works are up to 1 mol·kg^{-1}. Lopes et al.[11] measured electromotive force (emf) data for NaCl in water + ethanol solutions at mass fractions of ethanol from (5 to 20) % and from (298.15 to 373.15) K. To the best of our knowledge, there are not emf measurements and mean activity coefficients for sodium chloride in water + methanol + ethanol solutions.

In this work, we have measured the emf in a cell [ISE Na^+|NaCl, H_2O, MeOH, EtOH|ISE Cl^-] at 298.15 K and calculated the mean activity coefficient of sodium chloride in eight mixed solvents of water + methanol + ethanol using a modified Pitzer equation together with the Nernst equation. The molalities of NaCl considered in this work are up to 2 mol·kg^{-1}.

Experimental Section

J.T. Baker supplied purified methanol, anhydrous ethanol, and ACS certified grade sodium chloride. The stated mole fraction purity for methanol and ethanol was 99.9 % for both of them. The mass fraction purity of sodium chloride is 99.5 %. We use deionized water supplied by Omnichem with a specific conductivity of 1 μS·m^{-1}. Sodium chloride was dried over 6 h at 423.15 K and placed in a desiccator for 1.5 h. We weighed it with an analytical balance (Sartorius model BP61S) with a precision of ± 0.1 mg. This procedure was repeated until two consecutive weights did not change, and then it was stored in a desiccator before use. We prepared the mixtures gravimetrically, and the overall uncertainty in the molal compositions is ± 0.1 %.

We used a cell [ISE Na^+|NaCl(m), H_2O, MeOH, EtOH|ISE Cl^-] to measure the emf of aqueous solutions of NaCl in mixed solvents. In this work, we considered eight aqueous MeOH/EtOH mixtures with alcohol mass fractions of (5/5, 10/10, 10/5, 15/15, 20/20, 5/10, 15/25, and 10/40) % and molalities of NaCl of up to 2 ± 0.1 %. The electrodes were chloride and sodium ion-selective electrodes from Orion (Nos. 9617 and 8611). The cell is a glass double-walled vessel of a capacity of 90 mL that has a top lid with three holes that allows positioning of the electrodes and a thermometer. We used a PolyScience 9500 series bath to maintain a constant temperature using circulating coolant fluid through the vessel walls. A digital thermometer measures the temperature with an accuracy of 0.1 °C.

The emf was measured using an Orion 920A plus ion-meter with an uncertainty of ± 0.2 mV. Voltage readings were considered valid when the value did not change for at least 5 min. We have standardized both electrodes. The chloride and sodium electrodes were standardized according to the procedure of the manufacturer using a 0.1 M standard solution of NaCl.

We measured the density of the mixtures using an Anton Paar (DMA 5000) vibrating-tube densimeter.[12] The densimeter has an uncertainty reported by the manufacturer of ± 0.005 kg·m^{-3}, but we believe it is ± 0.03 kg·m^{-3}. A platinum resistance thermometer with an uncertainty of ± 0.01 K on ITS-90 provides temperature measurements. The repeatability in the density and temperature measurements is ± 0.001 kg·m^{-3} and ± 0.001 K, respectively. The manufacturer has calibrated the apparatus with ultrapure water and air. The principle of measurements has been reported in our previous work[12] together with measured water densities to test the calibration.

Correlation

The Nernst equation relates the electromotive force to the mean activity coefficient as

$$E = E_0 - \frac{\upsilon_{MX} RT}{nF} \ln(m_{\pm} \gamma_{MX}^{\pm}) \qquad (1)$$

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Table 1. Mean Activity Coefficients for NaCl at (298.15 and 308.15) K in H_2O and H_2O + Methanol, Respectively

m/mol·kg^{-1}	E/V	$\gamma^{\pm}_{MX}$	m/mol·kg^{-1}	E/V	$\gamma^{\pm}_{MX}$
NaCl + H_2O			NaCl + H_2O + MeOH		
0.05	0.0172	0.8152	0.0500	0.0365	0.8062
0.10	0.0502	0.7732	0.0527	0.0380	0.8028
0.20	0.0828	0.7313	0.0700	0.0528	0.7845
0.30	0.1023	0.7085	0.0800	0.0584	0.7757
0.40	0.1164	0.6938	0.1010	0.0685	0.7602
0.50	0.1272	0.6835	0.3000	0.1235	0.6907
0.60	0.1352	0.6760	0.4000	0.1366	0.6750
0.70	0.1433	0.6704	0.5498	0.1530	0.6603
0.80	0.1481	0.6663	0.8000	0.1710	0.6481
0.90	0.1561	0.6632	0.8989	0.1776	0.6458
1.00	0.1631	0.6611	1.0000	0.1828	0.6445
1.10	0.1654	0.6597	1.2000	0.1917	0.6445
1.20	0.1708	0.6589	1.4000	0.1995	0.6471
1.30	0.1726	0.6587	1.5157	0.2085	0.6495
1.40	0.1743	0.6589	1.8000	0.2142	0.6578
1.50	0.1782	0.6596	1.9865	0.2197	0.6649
1.60	0.1855	0.6606	2.0000	0.2230	0.6654
1.70	0.1889	0.6620			
1.80	0.1906	0.6637			
1.90	0.1946	0.6658			
2.00	0.1980	0.6681			

Table 2. Parameters for the Pitzer Equation Used in the Calculation of the Activity Coefficient of NaCl[a]

solvent	E_0/mV	$\beta^{(1)}_{MX}$	$\beta^{(2)}_{MX}$	C_{MX}	sum of squares
H_2O	181.7877	0.0763	0.4051	0	3.73×10^{-5}
	(1.9185)	(0.0208)	(0.1852)		
H_2O + MeOH	206.2775	0.0926	0.3204	0	2.23×10^{-5}
	(1.4570)	(0.0193)	(0.1604)		

[a] Values in parentheses are the asymptotic standard error of the parameter.

where E_0 is the standard potential of the cell, υ is the sum of stoichiometric coefficients of the ions, R is the universal gas constant, T is the temperature in Kelvin, F is the Faraday constant, $m_{\pm}$ is the mean ionic molality, and $\gamma^{\pm}_{MX}$ is the mean activity coefficient. The mean activity coefficient is calculated with a model for the activity coefficients. In this work, we use the equation given by Pitzer[13] and a modified Pitzer equation[14] for 1:1 type strong electrolytes. The Pitzer equation[13] is

$$\ln \gamma^{\pm}_{MX} = |z_M z_X| f^{\gamma} + \left(\frac{2\nu_M \nu_X}{\nu_{MX}}\right) m_{MX} B^{\gamma}_{MX} + \left(\frac{2(\nu_M \nu_X)^{3/2}}{\nu_{MX}}\right) {m_{MX}}^2 C^{\gamma}_{MX} \quad (2)$$

with

$$f^{\gamma} = -A_{\phi}\left[\frac{I^{1/2}}{1 + bI^{1/2}} + \left(\frac{2}{b}\right) \ln(1 + bI^{1/2})\right] \quad (3)$$

$$B^{\gamma}_{MX} = 2\beta^{(0)}_{MX} + \frac{2\beta^{(1)}_{MX}}{\alpha^2 I}\left[1 + \frac{1}{2}(2 - \alpha^2 I + 2\alpha I^{1/2}) \exp(-\alpha I^{1/2})\right] \quad (4)$$

$$C^{\gamma}_{MX} = 3|z_M z_X|^{1/2} C_{MX} \quad (5)$$

and

$$I = \sum_i m_i {z_i}^2 \quad (6)$$

In eqs 2 to 6, I is the ionic strength; z is the ion valence; A_{ϕ} is the Debye−Hückel coefficient; b is the maximum approach parameter; α is a fixed parameter; ν is the stoichiometric coefficient; m is the molality; and $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$, and C_{MX} are fitting parameters that can be found by regressing the emf data. The subscripts M, X, and MX represent cation, anion, and neutral electrolyte, respectively. In eqs 2 to 6, we have considered b and α equal to 1.2 and 2.0, respectively, as

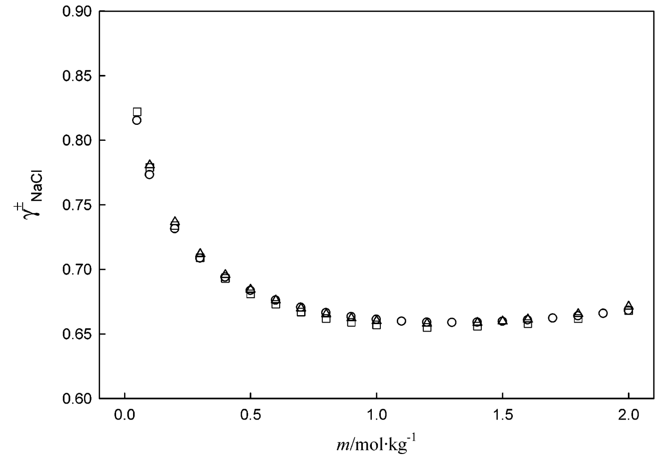

Figure 1. Mean activity coefficient of NaCl in water at 298.15 K: ○, this work; △, ref 19; □, ref 18.

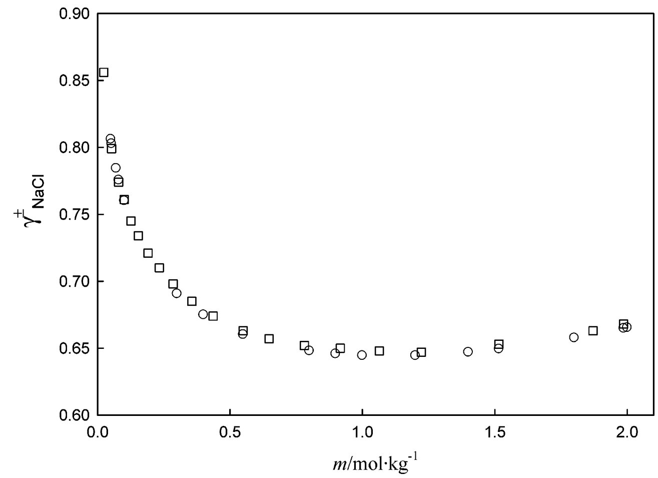

Figure 2. Mean activity coefficient of NaCl in water + methanol at 308.15 K: ○, this work; □, ref 6.

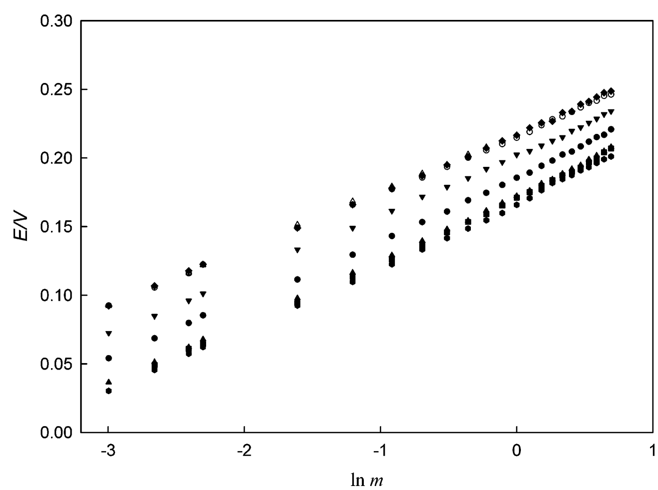

Figure 3. Linear behavior of the experimental emf as a function of the logarithm of the molality. Composition are given in mass fraction (% H_2O/% MeOH/% EtOH): ■, 90/5/5; ●, 80/10/10; ▲, 85/10/5; ▼, 70/15/15; ◆, 60/20/20; ⬣, 85/5/10; ○, 60/15/25; △, 60/10/30.

Table 3. Densities Values (in $kg \cdot m^{-3}$) for the Different Solvent Mixtures[a]

	ρ/kg·m^{-3} (% H_2O/% MeOH/% EtOH)							
T/K	90/5/5	80/10/10	85/10/5	70/15/15	60/20/20	85/5/10	60/15/25	60/10/30
283.15	983.485	972.024		957.951	942.576	977.660	943.055	943.464
288.15	982.615	970.353		955.415	939.409	976.466	939.809	940.112
293.15	981.472	968.849	977.375	952.751	936.080	974.985	936.448	936.693
298.15	980.069	966.819	975.852	949.949	932.706	973.305	933.042	933.164
303.15	978.436	964.680	974.092	946.997	929.215		929.516	929.537
308.15	976.587			943.945	925.565		925.915	925.014
313.15	974.540			940.822			922.177	921.907
318.15				937.569			918.410	919.545
323.15				934.244			914.475	915.602
328.15				930.532			910.475	911.490
333.15							906.406	907.313

[a] Compositions are given in mass fraction.

Table 4. Calculated Dielectric Constant and Debye−Huckel Parameters for the Different Mixtures Considered in this Work

	% H_2O/% MeOH/% EtOH							
parameter	90/5/5	80/10/10	85/10/5	70/15/15	60/20/20	85/5/10	60/15/25	60/10/30
ϵ	71.2310	65.4060	68.5390	59.8630	54.5810	68.0270	54.1040	53.6270
A_ϕ	0.4499	0.5057	0.4736	0.5725	0.6516	0.4783	0.6603	0.6692

Table 5. Parameters for the Pizter and Modified Pitzer Equation

	Pitzer				modified Pitzer			
solvent % H_2O/% MeOH/% EtOH	E_0/mV	$\beta^{(1)}_{MX}$	$\beta^{(2)}_{MX}$	C_{MX}	E_0/mV	b_{MX}	B_{MX}	C_{MX}
90/5/5	199.573	0.1562	−0.1332	−0.0136	199.538	0.8456	0.1789	−0.0145
	(1.025)	(0.065)	(0.029)	(0.007)	(1.276)	(0.071)	(0.131)	(0.002)
85/5/10	197.727	0.1685	−0.1187	−0.0138	197.757	0.8622	0.1958	−0.0156
	(0.589)	(0.068)	(0.021)	(0.002)	(0.597)	(0.546)	(0.012)	(0.002)
85/10/5	203.379	0.0979	0.0310	0.0000	202.995	1.4076	0.0851	0.0000
	(0.514)	(0.014)	(0.010)		(1.203)	(0.331)	(0.024)	
80/10/10	221.924	0.1637	−0.2902	−0.0106	221.942	0.3728	0.2810	−0.0191
	(1.436)	(0.106)	(0.022)	(0.005)	(1.007)	(0.227)	(0.025)	(0.005)
70/15/15	239.879	0.0000	0.4102	0.0201	239.942	2.0182	0.0000	0.0141
	(0.705)		(0.071)	(0.004)	(0.732)	(0.183)		(0.005)
60/10/30	263.641	0.0000	0.5137	0.0176	263.538	2.1592	0.0000	0.0057
	(0.750)		(0.080)	(0.011)	(0.821)	(0.198)		(0.001)
60/15/25	265.046	0.1662	−0.2247	−0.0133	265.089	0.7468	0.2207	−0.0168
	(0.920)	(0.052)	(0.195)	(0.012)	(0.887)	(0.371)	(0.114)	(0.015)
60/20/20	265.884	0.2205	−0.3998	−0.0232	265.691	0.4867	0.3156	−0.0273
	(0.585)	(0.048)	(0.164)	(0.011)	(0.796)	(0.040)	(0.153)	(0.017)

suggested by Pitzer.[13] The mean activity coefficient from the modified Pitzer equation is given by

$$\ln \gamma^{\pm}_{MX} = |z_M z_X| f^{\gamma} + \left(\frac{4\nu_M \nu_X}{\nu_{MX}}\right) m_{MX} B_{MX} + \frac{6(\nu_M \nu_X)^{3/2}}{\nu_{MX}} |z_M z_X|^{1/2} m_{MX}^2 C_{MX} \quad (7)$$

with

$$f^{\gamma} = -A_\phi \left[\frac{I^{1/2}}{1 + b_{MX} I^{1/2}} + \frac{2}{b_{MX}} \ln(1 + b_{MX} I^{1/2})\right] \quad (8)$$

In eqs 7 and 8, the fitting parameters are b_{MX}, B_{MX}, and C_{MX}. The Debye-Hückel parameter has been calculated using

$$A_\phi = \left(\frac{1}{3}\right)(2\pi N_A \rho)^{1/2} \left[\frac{e^2}{(4\pi\epsilon_0 \epsilon k T)}\right]^{3/2} \quad (9)$$

where N_A is Avogadro's number, ρ is the solvent density, e is the electron charge, ϵ_0 is the vacuum dielectric constant, ϵ is the static dielectric constant, k is the Boltzmann constant, and T is absolute temperature.

There exist[15] few experimental values for the dielectric constant in pure water and water + alcohol solvents in the literature; however, there are not values for the dielectric constant in water + methanol + ethanol. In order to calculate the dielectric constant of this system, we use a procedure proposed by Wang and Anderko.[16] First the polarization per unit volume of each pure component is calculated using

$$P = \frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} \quad (10)$$

and the polarization of the mixture is estimated using the mixing rule suggested by Oster:[17]

$$P_m = \frac{\sum_{i=1}^{N} x_i \underline{\nu_i} P_i}{\sum_{i=1}^{N} x_i \underline{\nu_i}} \quad (11)$$

where x_i is the mole fraction of component i, $\underline{\nu_i}$ is the molar volume, P_i is the polarization of pure species i, and P_m is the polarization per unit volume of the mixture. Finally, we calculate the dielectric constant of the mixture using eq 10. In this work, we have obtained the regression parameters of each model and the standard potential of the cell by correlating the experimental emf measurements to eqs 1, 2, and 7.

Table 6. Experimental Electromotive Force Measurements at 298.15 K[a]

m	E/V		$\gamma^{\pm}_{NaCl}$		m	E/V		$\gamma^{\pm}_{NaCl}$		m	E/V		$\gamma^{\pm}_{NaCl}$	
$mol \cdot kg^{-1}$	1st test	2nd test	Pitzer	modified Pitzer	$mol \cdot kg^{-1}$	1st test	2nd test	Pitzer	modified Pitzer	$mol \cdot kg^{-1}$	1st test	2nd test	Pitzer	modified Pitzer
90 % Water, 5 % Methanol, 5 % Ethanol														
0.07	0.0471	0.0491	0.7511	0.7513	0.70	0.1527	0.1534	0.5723	0.5728	1.50	0.1900	0.1899	0.5574	0.5577
0.09	0.0604	0.0609	0.7296	0.7299	0.80	0.1592	0.1591	0.5671	0.5675	1.60	0.1917	0.1929	0.5577	0.5580
0.10	0.0648	0.0644	0.7204	0.7207	0.90	0.1641	0.1654	0.5634	0.5638	1.70	0.1963	0.1969	0.5580	0.5584
0.20	0.0941	0.0941	0.6595	0.6601	1.00	0.1703	0.1711	0.5609	0.5612	1.80	0.1993	0.1997	0.5584	0.5588
0.30	0.1134	0.1135	0.6260	0.6266	1.10	0.1738	0.1751	0.5592	0.5595	1.90	0.2020	0.2042	0.5588	0.5592
0.40	0.1260	0.1261	0.6045	0.6051	1.20	0.1786	0.1796	0.5581	0.5584	2.00	0.2052	0.2069	0.5591	0.5596
0.50	0.1368	0.1364	0.5899	0.5905	1.30	0.1824	0.1838	0.5576	0.5578					
0.60	0.1461	0.1459	0.5796	0.5802	1.40	0.1868	0.1873	0.5574	0.5576					
80 % Water, 10 % Methanol, 10 % Ethanol														
0.05	0.0541	0.0514	0.7456	0.7453	0.60	0.1610	0.1611	0.5085	0.5083	1.40	0.2025	0.2013	0.4798	0.4802
0.07	0.0686	0.0678	0.7133	0.7130	0.70	0.1692	0.1683	0.4993	0.4992	1.50	0.2047	0.2040	0.4802	0.4804
0.09	0.0798	0.0797	0.6880	0.6877	0.80	0.1746	0.1746	0.4925	0.4925	1.60	0.2084	0.2080	0.4809	0.4810
0.10	0.0854	0.0846	0.6772	0.6769	0.90	0.1804	0.1802	0.4877	0.4878	1.70	0.2119	0.2112	0.4819	0.4818
0.20	0.1115	0.1105	0.6053	0.6049	1.00	0.1856	0.1853	0.4843	0.4845	1.80	0.2152	0.2143	0.4831	0.4827
0.30	0.1295	0.1278	0.5651	0.5647	1.10	0.1893	0.1906	0.4820	0.4823	1.90	0.2169	0.2180	0.4846	0.4837
0.40	0.1432	0.1426	0.5392	0.5388	1.20	0.1943	0.1930	0.4806	0.4810	2.00	0.2209	0.2194	0.4861	0.4847
0.50	0.1533	0.1529	0.5213	0.5210	1.30	0.1981	0.1975	0.4799	0.4803					
85 % Water, 10 % Methanol, 5 % Ethanol														
0.05	0.0365	0.0367	0.7717	0.7740	0.60	0.1481	0.1480	0.5597	0.5658	1.40	0.1886	0.1844	0.5272	0.5318
0.07	0.0513	0.0504	0.7436	0.7465	0.70	0.1543	0.1544	0.5502	0.5563	1.50	0.1920	0.1918	0.5275	0.5316
0.09	0.0621	0.0627	0.7217	0.7250	0.80	0.1616	0.1617	0.5430	0.5490	1.60	0.1947	0.1948	0.5282	0.5320
0.10	0.0679	0.0679	0.7123	0.7158	0.90	0.1672	0.1671	0.5375	0.5434	1.70	0.1989	0.1944	0.5295	0.5329
0.20	0.0978	0.0972	0.6494	0.6541	1.00	0.1723	0.1722	0.5335	0.5392	1.80	0.2018	0.2015	0.5312	0.5341
0.30	0.1164	0.1163	0.6134	0.6188	1.10	0.1761	0.1761	0.5306	0.5361	1.90	0.2049	0.2040	0.5333	0.5357
0.40	0.1291	0.1291	0.5894	0.5952	1.20	0.1813	0.1771	0.5287	0.5339	2.00	0.2079	0.2070	0.5358	0.5377
0.50	0.1396	0.1395	0.5724	0.5784	1.30	0.1844	0.1802	0.5276	0.5325					
70 % Water, 15 % Methanol, 15 % Ethanol														
0.05	0.0725	0.0697	0.7414	0.7413	0.60	0.1789	0.1755	0.5021	0.5007	1.40	0.2151	0.2159	0.4445	0.4453
0.07	0.0849	0.0850	0.7114	0.7109	0.70	0.1853	0.1809	0.4884	0.4875	1.50	0.2197	0.2176	0.4432	0.4438
0.09	0.0961	0.0981	0.6880	0.6871	0.80	0.1920	0.1873	0.4772	0.4769	1.60	0.2224	0.2216	0.4428	0.4430
0.10	0.1012	0.1014	0.6780	0.6770	0.90	0.1970	0.1945	0.4681	0.4682	1.70	0.2257	0.2255	0.4433	0.4429
0.20	0.1333	0.1324	0.6100	0.6079	1.00	0.2024	0.2016	0.4607	0.4612	1.80	0.2286	0.2283	0.4446	0.4436
0.30	0.1490	0.1485	0.5694	0.5670	1.10	0.2050	0.2043	0.4548	0.4556	1.90	0.2319	0.2307	0.4469	0.4449
0.40	0.1615	0.1602	0.5408	0.5385	1.20	0.2090	0.2091	0.4502	0.4512	2.00	0.2341	0.2337	0.4499	0.4469
0.50	0.1718	0.1713	0.5192	0.5173	1.30	0.2125	0.2121	0.4468	0.4478					
60 % Water, 20 % Methanol, 20 % Ethanol														
0.05	0.0922	0.0927	0.6847	0.6862	0.60	0.1950	0.1951	0.4154	0.4174	1.40	0.2331	0.2328	0.3727	0.3739
0.07	0.1068	0.1062	0.6466	0.6484	0.70	0.2009	0.2016	0.4047	0.4065	1.50	0.2340	0.2363	0.3706	0.3718
0.09	0.1178	0.1176	0.6172	0.6192	0.80	0.2072	0.2065	0.3966	0.3981	1.60	0.2392	0.2393	0.3687	0.3700
0.10	0.1225	0.1222	0.6047	0.6068	0.90	0.2125	0.2124	0.3902	0.3916	1.70	0.2413	0.2420	0.3668	0.3682
0.20	0.1490	0.1489	0.5228	0.5254	1.00	0.2166	0.2165	0.3852	0.3865	1.80	0.2444	0.2438	0.3650	0.3665
0.30	0.1660	0.1656	0.4782	0.4807	1.10	0.2220	0.2218	0.3812	0.3824	1.90	0.2476	0.2470	0.3632	0.3648
0.40	0.1780	0.1775	0.4496	0.4519	1.20	0.2256	0.2254	0.3779	0.3790	2.00	0.2487	0.2495	0.3612	0.3630
0.50	0.1870	0.1871	0.4298	0.4319	1.30	0.2268	0.2276	0.3751	0.3762					
85 % Water, 5 % Methanol, 10 % Ethanol														
0.05	0.0303	0.0298	0.7670	0.7666	0.60	0.1416	0.1421	0.5649	0.5646	1.40	0.1846	0.1855	0.5467	0.5465
0.07	0.0456	0.0452	0.7384	0.7380	0.70	0.1486	0.1483	0.5580	0.5576	1.50	0.1875	0.1864	0.5474	0.5472
0.09	0.0574	0.0567	0.7162	0.7158	0.80	0.1546	0.1556	0.5532	0.5529	1.60	0.1910	0.1932	0.5483	0.5481
0.10	0.0623	0.0618	0.7068	0.7063	0.90	0.1599	0.1614	0.5500	0.5497	1.70	0.1933	0.1954	0.5493	0.5490
0.20	0.0925	0.0935	0.6446	0.6442	1.00	0.1659	0.1665	0.5479	0.5476	1.80	0.1964	0.1984	0.5504	0.5501
0.30	0.1097	0.1111	0.6107	0.6102	1.10	0.1707	0.1729	0.5467	0.5465	1.90	0.1991	0.2001	0.5515	0.5511
0.40	0.1226	0.1243	0.5893	0.5889	1.20	0.1765	0.1789	0.5463	0.5460	2.00	0.2011	0.2026	0.5526	0.5521
0.50	0.1334	0.1338	0.5749	0.5745	1.30	0.1818	0.1803	0.5463	0.5461					
60 % Water, 15 % Methanol, 25 % Ethanol														
0.05	0.0925	0.0911	0.6859	0.6855	0.60	0.1936	0.1933	0.4133	0.4129	1.40	0.2303	0.2302	0.3624	0.3622
0.07	0.1057	0.1054	0.6483	0.6479	0.70	0.2003	0.2008	0.4012	0.4009	1.50	0.2336	0.2336	0.3599	0.3597
0.09	0.1160	0.1167	0.6192	0.6188	0.80	0.2056	0.2053	0.3918	0.3914	1.60	0.2369	0.2371	0.3577	0.3575
0.10	0.1224	0.1209	0.6069	0.6064	0.90	0.2102	0.2084	0.3842	0.3839	1.70	0.2402	0.2383	0.3558	0.3555
0.20	0.1491	0.1500	0.5253	0.5248	1.00	0.2148	0.2151	0.3781	0.3777	1.80	0.2417	0.2418	0.3540	0.3537
0.30	0.1660	0.1659	0.4799	0.4794	1.10	0.2190	0.2183	0.3730	0.3727	1.90	0.2453	0.2444	0.3524	0.3521
0.40	0.1773	0.1762	0.4501	0.4497	1.20	0.2239	0.2221	0.3689	0.3686	2.00	0.2463	0.2460	0.3510	0.3506
0.50	0.1858	0.1856	0.4290	0.4286	1.30	0.2282	0.2267	0.3654	0.3651					
60 % Water, 10 % Methanol, 30 % Ethanol														
0.05	0.0922	0.0930	0.7065	0.7082	0.30	0.1685	0.1686	0.5213	0.5220	0.80	0.2079	0.2082	0.4222	0.4233
0.07	0.1068	0.1066	0.6737	0.6752	0.40	0.1794	0.1802	0.4910	0.4917	0.90	0.2123	0.2128	0.4118	0.4127
0.09	0.1161	0.1168	0.6483	0.6497	0.50	0.1888	0.1894	0.4679	0.4688	1.00	0.2166	0.2173	0.4030	0.4035
0.10	0.1220	0.1218	0.6374	0.6388	0.60	0.1952	0.1958	0.4496	0.4507					
0.20	0.1515	0.1534	0.5645	0.5653	0.70	0.2027	0.2031	0.4346	0.4358					

[a] Compositions are given in mass fraction.

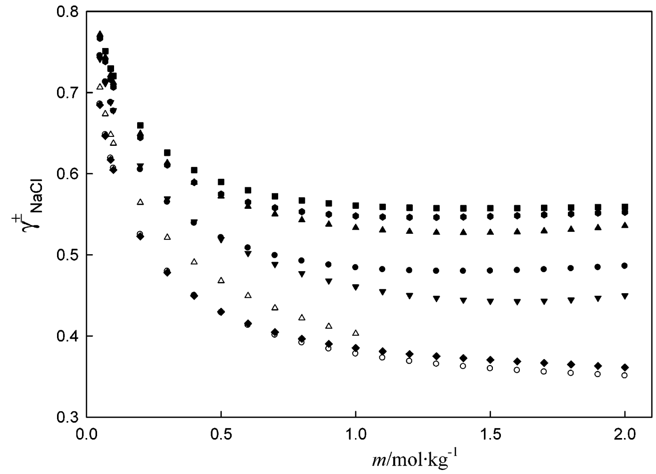

Figure 4. Mean activity coefficient of NaCl in water + methanol + ethanol at 298.15 K. Compositions are given in mass fraction (% H_2O/% MeOH/% EtOH): ■, 90/5/5; ●, 80/10/10; ▲, 85/10/5; ▼, 70/15/15; ◆, 60/20/20; ⬢, 85/5/10; ○, 60/15/25; △, 60/10/30.

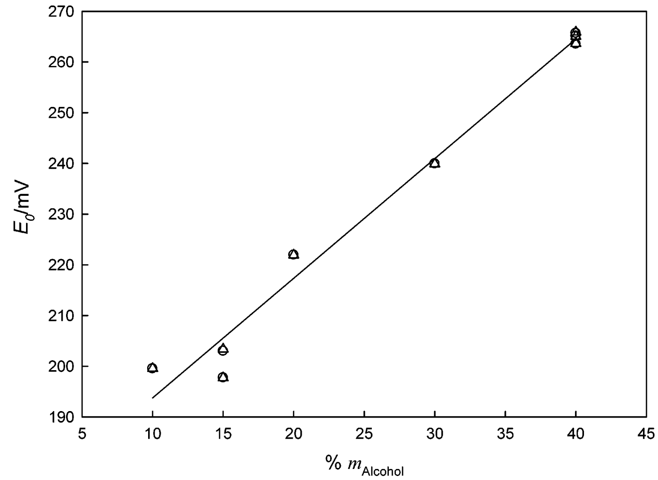

Figure 5. Standard potential of the cell as a function of the total alcohol percent weight concentration: △, from Pitzer equation; ○, from Modified Pitzer equation; —, linear equation.

Results

In order to check the calibration of the equipment, we have measured the emf and calculated the mean activity coefficient of NaCl in water and in a mixture of water + methanol at mass fractions of (10 and 90) % water and methanol, respectively. We have compared our mean activity coefficients values of NaCl with those of Hamer and Wu[18] and Gibbard et al.[19] at 298.15 K in aqueous solution and those of Yao et al.[6] at 308.15 K in water + methanol. Tables 1 and 2 show the experimental results and the parameters values for the Pitzer equation,[13] respectively. The mean activity coefficients of NaCl together with some literature values are shown in Figures 1 and 2. Also, we have measured the density of the mixed solvent at the molalities used in this work. Experimental density values are shown in Table 3. Unfortunately experimental values have not been reported in the literature; therefore, we have compared our results with those calculated from a procedure suggested by Spencer and Danner.[20] The absolute average percent deviation of the procedure from the experimental values is 0.38 %. The dielectric constant and the Debye−Hückel parameter used in this work are shown in Table 4. We have measured the emf for the quaternary system NaCl + H_2O + MeOH + EtOH and checked the linearity that follows according to the Nernst equation when plotted versus the logarithm of the molality. This linearity is shown in Figure 3 for all the mixtures. Then, we have calculated the mean activity coefficient using eqs 1, 2, and 7. Table 5 shows the parameters for each model together with their asymptotic error. Table 6 shows the experimental emf values and the mean activity coefficients. We can notice that the mean activity coefficient varies slightly depending on the model used in the curve fitting procedure even though both models pass through the data within the same level of accuracy as shown in Table 6. Figure 4 shows that the mean activity coefficients are grouped according to the alcohol concentration or the value of the dielectric constant of the solvent. This grouping occurs regardless of the activity coefficient model used in the calculation. The uncertainty in the activity coefficients is ± 0.001 due to the uncertainty of the ion-meter. For the mixture of H_2O (0.6) + MeOH (0.1) + EtOH (0.3), we only measure the emf up to 1 mol·kg^{-1} due to damage of the Na ion-selective electrode. It is important to notice that the standard potential of the cell seems to follow a linear function of the alcohol concentration as shown in Figure 5. This characteristic will be important in the generalization of an activity coefficient model in mixed solvents formed of alcohols and water.

Conclusions

We have measured the emf of a quaternary mixture of NaCl + H_2O + MeOH + EtOH at 298.15 and at molalities of NaCl up to 2. We used a Pitzer and a modified Pitzer model to calculate the mean activity coefficients from the emf measurements with an uncertainty of ± 0.001. It appears that the standard potential of the cell follows a linear function of the alcohol concentration. This particular behavior will be an attractive characteristic in the generalization of activity coefficient models in mixed solvent solutions of water + alcohols.

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