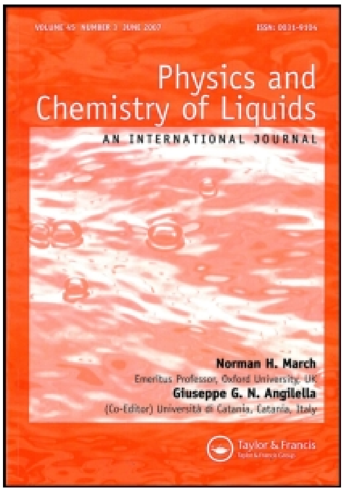

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DETERMINATION OF ACTIVITY COEFFICIENTS OF NH_4Cl IN METHANOL–WATER MIXED SOLVENTS AT 25°C BY ELECTROMOTIVE FORCE MEASUREMENTS

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Activity coefficients of NH_4Cl in methanol–water mixtures containing respectively 0, 10, 20, 30, 40, and 50 weight percent MeOH 25°C were determined using the Pitzer ion-interaction model and the electromotive force (emf) data of the following galvanic cell without a liquid junction: $NH_4^+(ISE)|\mathrm{NH_4}Cl(\mathrm{m}), \mathrm{H_2O}\ (1-x), \mathrm{MeOH}(x)|\mathrm{AgCl}|\mathrm{Ag}$. The experimental emf data were obtained using a solvent polymeric PVC ammonium selective membrane electrode containing a mixture of nonactin/monactin as ionophore and an Ag/AgCl electrode. Activity coefficients were determined over the molality range from dilute solution to near salt saturation (i.e. about 5.15 mol/kg in pure water or 2.44 mol/kg in 50% mixed MeOH–water solvent).

Keywords: Activity coefficient; Ammonium chloride; Ammonium-selective electrode; Mixed methanol–water solvent

1. INTRODUCTION

Since it has been first used in 1966 as ionophore in ion-selective electrodes (ISEs), carrier-based ion-selective solvent polymeric membranes have been shown to be useful devices, particularly, in analytical chemistry [1,2]. However, compared to cation responsive glass or solid state membrane electrodes, they were rarely [3] employed for the determination of activity coefficients in electrolytic solutions. *A fortiori*, and based on the examination of the related literature, these membranes seem to have never been used in mixed (organic-water) solvent systems for the determination of electrolytic activity coefficients. We report in the present work the results concerning the utilization of a solvent polymeric ammonium ion-selective membrane electrode for the determination of activity coefficients of NH_4Cl in mixed methanol–H_2O solvents at 25°C. The investigated methanol–H_2O mixed solvent systems contained 0, 10, 20, 30, 40 and 50 wt.% MeOH, respectively, in water. Activity coefficients were determined over the molality range from dilute solution to near salt saturation.

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2. METHOD

2.1. Determination of Mean Activity Coefficients ($\gamma_\pm$)

The Pitzer-interaction model has been successfully used both in aqueous solution and in mixed solvent for the determination of activity and osmotic coefficients of high concentrated pure and mixed electrolytes (e.g. [3–10]). For a single $M_{v+}X_{v-}$ electrolyte, the Pitzer equation is written as

$$\ln \gamma_\pm = |z_+ z_-| f^\gamma + m\left(\frac{2v_+v_-}{v}\right)B^\gamma + m^2\left(\frac{2(v_+v_-)^{3/2}}{v}\right)C^\gamma \tag{1}$$

where

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

$$B^\gamma = 2\beta^{(0)} + \frac{2\beta^{(1)}}{\alpha^2(I/m^0)}\left[1 - e^{-\alpha\sqrt{I/m^{\mathrm{n}}}}\left(1+\alpha\sqrt{I/m^0} - (1/2)\alpha^2(I/m^0)\right)\right] \tag{3}$$

$$C^\gamma = (3/2)C^\varphi \tag{4}$$

$\gamma_\pm$ is the molality-scale mean ionic activity coefficient of the electrolyte $M_{v+}X_{v-}$; Z the charge number of ion; $v = v_+ + v_-$ the number of ions dissociated in one unit electrolyte formula; m the molality of electrolyte (mol/kg); I the ionic strength on a molality scale; $\beta^{(0)}$, $\beta^{(1)}$ and $C^\phi$are the parameters of the Pitzer equation; $b = 1.2$ and $\alpha = 2$. A^ϕ is the Debye-Hückel coefficient for the osmotic coefficient defined as

$$A_\phi = \frac{1}{3}(2\pi N_A \rho_A)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_0 DkT}\right) \tag{5}$$

where the constants ε_0, k, N_A, D and ρ_A are vacuum permittivity, Boltzmann constant, Avogadro constant, dielectric constant and density of the mixed solvent, respectively.

In this work the mean activity coefficients of NH_4Cl in methanol–water mixtures have been determined at 25°C from the electromotive force (emf) of a galvanic cell without a liquid junction combining a solvent polymeric PVC ammonium selective membrane electrode and an Ag/AgCl electrode

$$NH_4^+(ISE)|\mathrm{NH_4Cl}(m), \mathrm{H_2O}(1-x), \mathrm{MeOH}(x)|\mathrm{AgCl}|\mathrm{Ag} \tag{6}$$

where x is the wt.% of MeOH in water. The emf of this cell can be represented by the Nernst relation

$$E = E' + 2s\ln(\gamma_\pm m) \tag{7}$$

where E' represents the cell constant potential and $s = (RT/F)$, in which the symbols have their usual meanings. The emf of the cell (2) was first measured at a series of electrolyte molalities in pure and mixed solvents and the root mean square deviation of E, calculated by Eqs. (1) and (3), from the measured E' was minimized by changing the value of the parameters $\beta^{(0)}$, $\beta^{(1)}$, C^ϕ, E' and s by an iteration procedure employing the Microsoft Excel (Solver) program. The concentration of electrolyte 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 previously utilized in the cell.

3. EXPERIMENTAL

3.1. Reagents

Ammonium ISE membranes were prepared using high molecular poly(vinyl chloride) (PVC), mixture of nonactin (72%) and monactin (28%) as ionophore, *bis*(2-ethylhexyl)sebacate and tetrahydrofuran (THF), all of Selectophore grade from Fluka (Buchs, Switzerland). Stock solution of NH_4Cl, Microselect quality from Fluka with analytical grade (wt.%) >99.5, was prepared in triply distilled water in MeOH–water mixtures. Methanol of analytical grade (wt.%) >99.5, from Kiankaveh (Iran), was fractionally distilled and only the intermediate fraction was used.

3.2. Preparation of the Ammonium Membranes Electrodes

Poly(vinyl chloride) based ammonium ion-selective membrane electrodes were prepared [11–13] with the following composition (wt.%): 1.05% of the mixture of nonactin (72%) and monactin (28%), 67.07% *bis*(2-ethylhexyl)sebacate and 31.88% PVC dissolved previously in THF as a solvent. The final assembled electrodes had membranes disks with 6 mm diameters and about 200 μm thicknesses, which were glued to PVC bodies with an outer diameter of 8 mm and inner diameter of 6 mm. The electrodes were each time back-filled for each series of measurements with 0.01 M NH_4Cl internal filling solution, in the appropriate pure water or water–MeOH mixed solvent. An Ag/AgCl wire was used as internal reference electrode.

In order to check the response of the fabricated electrode, it was initially conditioned normally for 48 h in 0.01 M NH_4Cl aqueous electrolyte solution and then calibrated using NH_4Cl test solutions, with concentration ranging from 10^{-6} to 1 M [14]. A double junction Ag/AgCl electrode (Fluka, Switzerland), with 1 M lithium acetate as a bridge electrolyte, was used as an external reference. By the application of this standard procedure, with corrections for liquid junction potentials, a slope of 57.27 mV/(decade change of activity) was obtained for the fabricated ammonium ISE. Ag/AgCl electrodes were prepared essentially as described elsewhere by electrolysis of Ag wire in 0.1 M HCl *versus* a Pt electrode [15]. Both ammonium and Ag/AgCl electrodes were conditioned overnight in the appropriate MeOH–water mixed solvent before each series of measurements.

3.3. Emf Measurement and Data Acquisition Process

The experimental cell potentials were measured using a high input impedance ($>1\,G\Omega$) Topward multimeter (model 1304, Taiwan, Korea) with a ±0.01 mV resolution, interfaced with a GPIB Bus (1304 G) and connected to a personal computer (32 MHZ) for data acquisition and processing. All measurements were performed under stirring conditions and the temperature was kept constant at 25°C, employing a double-wall container enabling the circulation of thermostated water from a bath (Thelco, Precision

Scientific Co., USA). The electrodes and a glass thermometer (±0.05°C) were immersed in the solution through a lid preventing from solvent evaporation. In each mixed solvent system and for each molality, data acquisition were performed every 4 s interval and during 20 min. From data processing a resulting final potential mean value with a standard deviation never exceeding 0.2 mV during 4 min was accepted for each concentration.

4. RESULTS AND DISCUSSION

The resulted emf values of the cell (6) and the calculated mean activity coefficients of NH_4Cl electrolyte in different mixed MeOH–water solvent systems at 25°C are reported in Table I. The variation of natural logarithm of NH_4Cl mean activity coefficient *versus*

TABLE I The emf *versus* molality and the corresponding mean activity coefficients for NH_4Cl in various (wt.%) mixed MeOH–water solvent systems, at 25°C

m (mol/kg)	E (mV)	$\gamma_\pm$	m (mol/kg)	E (mV)	$\gamma_\pm$	m (mol/kg)	E (mV)	$\gamma_\pm$
0 wt.% wt. MeOH			10 wt.% wt. MeOH			20 wt.% wt. MeOH		
0.0018	−84.4	0.9536	0.0014	−69.8	0.9561	0.0009	−114.9	0.9596
0.0051	−33.7	0.9259	0.0029	−38.5	0.9375	0.0028	−64.8	0.9329
0.0127	10.6	0.8904	0.0087	5.1	0.8990	0.0074	−20.0	0.8961
0.0255	43.9	0.8550	0.0212	40.3	0.8544	0.0170	16.7	0.8536
0.0378	62.5	0.8319	0.0336	58.2	0.8264	0.0265	36.2	0.8257
0.0993	107.2	0.7668	0.0899	95.7	0.7563	0.0732	79.7	0.7497
0.2180	143.0	0.7081	0.1938	124.2	0.6947	0.1628	113.0	0.6809
0.4407	174.7	0.6554	0.3845	149.4	0.6388	0.3305	141.8	0.6174
0.6470	192.0	0.6284	0.5605	163.2	0.6092	0.4852	157.3	0.5837
1.0179	212.5	0.5998	0.8713	179.4	0.5769	0.7614	175.5	0.5460
1.4179	227.8	0.5822	1.1965	191.1	0.5561	1.0565	188.7	0.5208
2.0603	245.4	0.5672	1.7156	204.6	0.5361	1.5218	203.7	0.4958
2.7582	259.5	0.5602	2.2732	215.4	0.5239	2.0183	215.4	0.4794
3.3966	269.8	0.5580	2.7753	223.3	0.5174	2.4631	223.9	0.4696
4.0136	278.3	0.5580	3.2550	229.6	0.5137	2.8861	230.7	0.4630
4.5172	284.3	0.5589	3.6406	234.2	0.5117	3.2264	235.6	0.4590
4.9009	288.5	0.5597	3.9345	237.3	0.5107	3.4828	238.9	0.4566
5.1479	291.1	0.5603	4.1222	239.2	0.5102	3.6463	241.0	0.4552
			4.2202	240.2	0.5100	3.6720	241.3	0.4550
30 wt.% wt. MeOH			40 wt.% wt. MeOH			50 wt.% wt. MeOH		
0.0009	−68.7	0.9568	0.0007	−48.0	0.9565	0.0007	−208.9	0.9523
0.0024	−39.1	0.9304	0.0015	−29.5	0.9397	0.0020	−173.8	0.9209
0.0061	−12.7	0.8950	0.0037	−5.3	0.9083	0.0054	−142.5	0.8770
0.0155	13.5	0.8445	0.0074	12.6	0.8758	0.0123	−117.3	0.8268
0.0247	26.2	0.8135	0.0074	12.6	0.8758	0.0187	−104.6	0.7952
0.0708	54.4	0.7286	0.0366	52.8	0.7650	0.0505	−75.3	0.7050
0.1568	74.9	0.6544	0.0723	69.1	0.7026	0.1082	−53.9	0.6237
0.3149	92.5	0.5867	0.1416	84.7	0.6346	0.2182	−35.1	0.5437
0.4577	101.8	0.5509	0.1416	84.7	0.6346	0.3096	−25.9	0.5034
0.7114	112.7	0.5104	0.2715	99.4	0.5654	0.4646	−15.6	0.4571
0.9807	120.6	0.4830	0.3326	103.9	0.5437	0.6395	−7.6	0.4216
1.4054	129.6	0.4549	0.6043	116.9	0.4807	0.9909	3.1	0.3749
1.8582	136.7	0.4357	0.8306	123.7	0.4484	1.3642	10.8	0.3428
2.2632	141.7	0.4238	1.0219	128.1	0.4280	1.6835	15.8	0.3226
2.6529	145.8	0.4152	1.3277	133.6	0.4033	1.9754	19.6	0.3078
2.9595	148.7	0.4099	1.5613	137.0	0.3886	2.2011	22.1	0.2981
3.1923	150.7	0.4065	1.7456	139.4	0.3788	2.3678	23.8	0.2916
3.3313	151.9	0.4046	1.7456	139.4	0.3788	2.4720	24.8	0.2879
						2.4899	25.0	0.2873

the square root of electrolyte molality in water and various wt.% MeOH–water mixed solvent are also illustrated in Fig. 1. Pitzer interaction parameters, computed by the minimization procedure for these systems are, as well, given in Table II. For the constants b and α, the values $b = 1.2$ and $\alpha = 2$ were used according to Koh *et al.* [6], who showed that these values, defined for aqueous systems, are still appropriate for

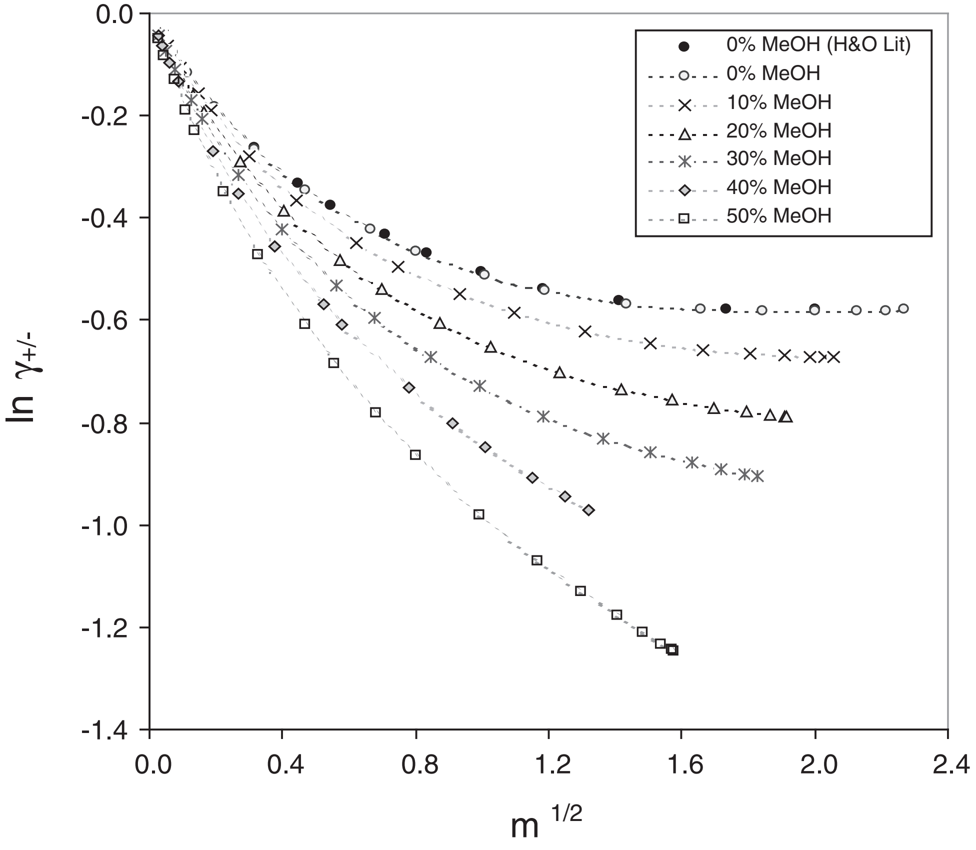

FIGURE 1 Natural logarithm of mean activity coefficient of NH_4Cl *versus* square root of molality in various mixed wt.% MeOH–water solvent systems, at 25°C. The corresponding literature data in pure water solvent at 25°C are those reported by Harned and Owen [17].

TABLE II Values obtained for Pitzer parameters, dielectric constant (D), density (ρ_A) and Debye-Hückel coefficients for the osmotic coefficient (A_ϕ), for NH_4Cl at different wt.% of MeOH–water at 25°C

MeOH x% (wt.)	$\beta(0)$	$\beta(1)$	C^ϕ	A_ϕ	D	ρ_A (g/cm)^3
0[a]	0.05192	0.19346	−0.00298			
0	0.05188	0.19356	−0.00299	0.3915	78.54	0.997
10	0.05118	0.19362	−0.00302	0.4229	74.10	0.983
20	0.05020	0.19389	−0.00298	0.4661	69.18	0.967
30	0.04970	0.19455	−0.00292	0.5147	64.30	0.951
40	0.03491	0.19487	−0.00278	0.5618	59.55	0.934
50	0.03090	0.20361	−0.00305	0.6382	54.90	0.916

[a] The values of Pitzer parameters reported by Marshall *et al.* [18] for NH_4Cl in pure water at 25°C.

TABLE III The resulting fitted values of the *a*, *b*, *c*, *d*, *e* and *f* constants employed in the non-linear power series equation (8) used successively for the determination of A_ϕ, dielectric constant (D) and density (ρ_A), at different wt.% of mixed MeOH–water solvent systems at 25°C

	A_ϕ	D	ρ_A (g/mL)
a	−2.23E-10	1.52E-08	4.94E-11
b	5.14E-08	−3.28E-06	−1.05E-08
c	−3.44E-06	2.48E-04	7.19E-07
d	1.25E-04	−7.79E-03	−2.37E-05
e	2.28E-03	0.3878	−1.22E-03
f	0.3906	78.54	0.997

MeOH–water mixed solvents systems. The utilized values of A_ϕ, dielectric constant and density for different solvent compositions are also included in Table II. These constants were obtained from discrete values from the literature [16,17] that have been fitted perfectly ($R^2 \approx 1$) to the following non-linear power series equation

$$y = ax^5 + bx^4 + cx^3 + dx^2 + ex + f \tag{8}$$

where y represents successively: A_ϕ, dielectric constant (D) or density (ρ_A) in the corresponding composition of the mixed solvent system, and x the wt.% of methanol in the mixed MeOH–water solvent systems. Table III shows the obtained values of the *a*, *b*, *c*, *d*, *e* and *f* constants successively for A_ϕ, dielectric constant (D) and density (ρ_A) for different solvent compositions.

Only the results obtained for NH_4Cl in pure water could be compared with the corresponding available literature data. Figure 1 shows that the obtained values of mean activity coefficient for NH_4Cl match well with those previously reported in pure water [17]. Similarly, Table II shows that the obtained values of the Pitzer interaction parameters for NH_4Cl electrolyte in pure water solvent are also very close to those reported in the literature [18].

5. CONCLUSION

The results concerning the use of a solvent polymeric ammonium ion-selective membrane electrode for the determination of activity coefficients of NH_4Cl in mixed methanol–H_2O solvents at 25°C, using the Pitzer ion-interaction model and the electromotive force (emf) data of a galvanic cell without a liquid junction were reported. The used mixed solvent systems contained 0, 10, 20, 30, 40 and 50 wt.% MeOH, respectively, in water. Activity coefficients were determined over the molality range from dilute solution (i.e. about 0.0018 mol/kg in pure water) to near salt saturation (i.e. about 5.15 mol/kg in pure water or 2.44 mol/kg in 50% mixed MeOH–water solvent). A non-linear (5th order) power series equation was also presented for the determination of A_ϕ, dielectric constant and density for different compositions of mixed MeOH–water solvent. The resulted values of mean activity coefficient as well as the values of Pitzer interaction parameters obtained for NH_4Cl compared well with those previously reported in pure water [17,18]. This satisfactory agreement between our results, which are obtained in a more extended concentration range than those reported in the literature for pure water solvent [17], confirms the reliability of our results in mixed solvent systems.

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