



Determination and modeling of activity coefficients of the ionic liquid 1-ethyl-3-methylimidazolium chloride in the (water + formamide) mixed solvent system at 298.2 K

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ABSTRACT

In this work, the results relating to the mean activity coefficient measurements for 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) in the (formamide + water) mixed solvent system using the potentiometric method have been reported. The electromotive force (emf) measurements were performed on the galvanic cell of the type: Ag|AgCl|[EMIm]Cl (m), formamide (wt.%), H₂O (1 – wt %) |EMIm-ISE, in various mixed solvent systems containing 0, 10, 20, 30, and 40% mass fractions of formamide over ionic strength ranging from 0.0010 to 2.5000 mol·kg⁻¹ at T=298.2 K. The modeling of this ternary system was made based on the Pitzer ion-interaction model. The values of the mean activity coefficients, the osmotic coefficients, the excess Gibbs free energy and the solvent activity together with Pitzer ion-interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for the series under investigated system were determined.

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1. Introduction

Recently, ionic liquids due to some green characteristics such as negligible volatility, high thermal and chemical stability, large liquid range and strong solubility power are of crucial importance. The presence of ionic liquids (ILs) in different processes needs a deeper knowledge about the nonideality of these mixtures, essentially about their thermodynamic behavior [1,2]. Up to now, the general methods such as the isopiestic vapor pressure [3,4], gas–liquid chromatography [5,6] conductmetric [7,8] and volumetric techniques [9,10] have been used to measure the thermodynamic properties of mixtures containing ionic liquids. Up to this point the study of the thermodynamic properties of these mixtures in the potentiometric method has not been used. However, the electromotive force (emf) method presents advantages such as rapidity and relative simplicity to generate experimental data in comparison with the other techniques [11–13].

In this study for the first time, the results relating to the mean activity coefficient measurements for 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) in (formamide + water) mixtures using the potentiometric method have been reported. The system of the present study, [EMIm]Cl + formamide + water, is one of the systems that the thermodynamic data has not been reported in the literatures. In this work, the mean activity coefficients of [EMIm]Cl in the [EMIm]Cl + formamide +

water system were determined on a galvanic cell containing an ionic liquid ion selective electrode (IL-ISE) and Ag/AgCl electrode at T=298.2 K. The electrodes used in this work were prepared in our laboratory and had a reasonably good Nernst response. In our previous papers, we have reported the ability of the solvent polymeric membrane electrode for the determination of activity coefficient for binary, ternary and quaternary electrolyte mixtures [14–17]. In this article, the determination of activity coefficients for [EMIm]Cl in various formamide–water mixed solvent systems containing 0, 10, 20, 30, and 40% mass fractions of formamide over ionic strength ranging from 0.0010 to 2500 mol·kg⁻¹ has been reported. The modeling of this ternary system was made based on the Pitzer ion-interaction model. For the system under investigation from experimental data the Pitzer ion-interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) were evaluated. The values of the osmotic coefficients, the solvent activity and the excess Gibbs free energy for the series of under investigated system were determined.

2. Experimental

2.1. Chemicals used

Formamide and [EMIm]Cl were purchased from Merck and were of > 0.995 and 0.9975 mass fraction purities respectively. Double distilled water throughout all experiments was used. Dibutyl phthalate (DBP), potassium tetrakis (p-chlorophenyl) borate (KTP CIPB), high molecular weight poly(vinylchloride) (PVC), and tetrahydrofuran (THF) used were purchased from Merck and Fluka chemical company and all of them were of analytical reagent grade. The stock aqueous

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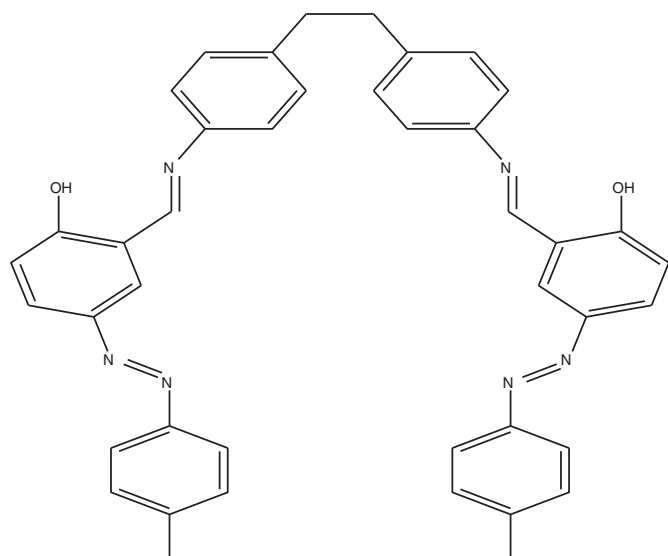
solutions of electrolyte were prepared from [EMIm]Cl, formamide and double-distilled water whose specific conductance was less than $2.0 \times 10^{-4} \text{ S m}^{-1}$ by adding weighted amounts of [EMIm]Cl and formamide into the proportion volume of double-distilled water.

2.2. Apparatus

All of the potentiometric measurements were made using a multimeter (Martini instruments Mi 180) whose resolution was 0.1 mV. The output of the multimeter was connected to a personal computer by the RS232 connector for data acquisition. The Mi 5200 software together with Microsoft Excel (Office 2007) software were used for data acquisition and calculations. The magnetic stirrer (Delta Model HM-101) was employed to avoid concentration gradients in the test solutions. The conductivity measurements were carried out by means of a Metrohm 660 conductometer with a type cell of constant cell of 1.17 cm^{-1} and having an uncertainty of 1%. Analytical balance (Sartorius GMBH 2842) with accuracy of 0.1 mg was used for preparation of the stock electrolyte solutions.

2.3. Preparation of electrodes and potentiometric measurements

The [EMIm]Cl selective electrode was prepared in accordance with the general procedure of PVC membrane construction. For this aim, an optimized mixture containing of 32 mg of powdered PVC, 60 mg of plasticizer DBP, 5.1 mg of additive KTpCIPB and 2.9 mg of EDBP (see Scheme 1) as an ionophore was dissolved in 2 ml of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm in diameter. The solvent was evaporated at the room temperature. After 2 h the polymer membrane could be easily removed from the plate. Then the transparent PVC membrane was taken up from the plate and attached to the end of a glass tube with a diameter of 1 cm and height of 5 cm by means of PVC-THF viscose solution. The Ag–AgCl wire electrodes were prepared basically as described elsewhere by electrolysis [18]. Both EMIm-ISE and Ag–AgCl electrodes were conditioned overnight in the appropriate mixed electrolyte system previous to each series of measurements. From the preliminary experimental tests performed with different concentrations of internal electrolyte filling solution the best results were those obtained with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ [EMIm]Cl electrolyte.



Scheme 1. Structure of EDBP.

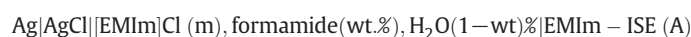
Table 1

The values of density (ρ), molar mass, relative permittivity (ϵ_r), Debye–Hückel constants (A_ϕ), as a function of the weight percentage formamide in formamide–water mixtures at 298.2 K taken from Ref. [20].

wt.%	ρ kg·m ⁻³	M g·mol ⁻¹	ϵ_r	A_ϕ^a kg ^{1/2} mol ^{-1/2}
0	0.9972	18.015	78.38	0.3915
10	1.0116	19.165	82.99	0.3618
20	1.0251	20.472	87.31	0.3376
30	1.0388	21.970	91.62	0.3162
40	1.0523	23.704	96.02	0.2966

^a The values calculated from [20].

The activity coefficients for [EMIm]Cl in the mixed solvent system were determined from the emf measurements using the following cell:



where w is the mass fraction of formamide in the mixed solvent system. The emf measurements of the galvanic cell (A) were made by using standard addition procedure. For this purpose, the concentrated electrolyte solutions were added into the cell containing a specified volume of the formamide–water as a mixed solvent. The standard addition steps were carried out using proper burette and suitable Hamilton syringes (CH-7402 Bonaduz). In each series and for each standard addition step, data collection was performed every 10 s interval and during 15 (for concentrated solutions) to 20 min (for dilute solutions) by using a multimeter connected to personal computer. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298.2 K (± 0.1 K), employing a double-wall container enabling the circulation of thermostat water from a Model GFL circulation.

3. Thermodynamics model

The Pitzer ion interaction model was used for the experimental data correlation and calculation of thermodynamic properties for under investigated system [19]. According to the Pitzer model, the mean molal activity coefficient (γ_{\pm}) for [EMIm]Cl in the mixed solvent is described as:

$$\ln \gamma_{\pm[\text{EMIm}]\text{Cl}} = f^\gamma + B_{[\text{EMIm}]\text{Cl}}^\gamma I + 1.5 C_{[\text{EMIm}]\text{Cl}}^\phi I^2 \quad (1)$$

where

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

$$B_{[\text{EMIm}]\text{Cl}}^\gamma = 2\beta_{[\text{EMIm}]\text{Cl}}^{(0)} + \frac{2\beta_{[\text{EMIm}]\text{Cl}}^{(1)}}{\alpha^2 I} \left[1 - \left(1 + \alpha\sqrt{I} - \frac{\alpha^2 I}{2} \right) e^{-\alpha\sqrt{I}} \right] \quad (3)$$

In these equations, α and b are assumed to be constant with values of 2.0 and $1.2 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$, respectively, both in water and in formamide–water mixtures; I indicates the total ionic strength on a molality scale. $\beta^{(0)}$, $\beta^{(1)}$ and C^ϕ show solute-specific interaction Pitzer parameters for electrolyte solution that their values should be determined for [EMIm]Cl in formamide–water mixtures. A_ϕ denotes the Debye–Hückel parameter for the osmotic coefficients defined by

$$A_\phi = \frac{1.4006 \times 10^6 \rho^{1/2}}{(\epsilon_r T)^{3/2}} \text{ kg}^{1/2} \text{ mol}^{-1/2} \quad (4)$$

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