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Isopiestic study of the solutions of $MnCl_2$, $CoCl_2$ and $NiCl_2$ in methanol and ethanol at 298.15 K

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Abstract

Osmotic coefficients of the solutions of three divalent transition metal chlorides (MCl_2; M = Mn, Co, Ni) in methanol and ethanol have been measured by isopiestic method at 298.15 K. Vapor pressures of the solutions have been evaluated from osmotic coefficients and their depression was used for qualitative deduction of the solute–solvent interactions occurring in these solutions. The osmotic coefficients have been correlated using local composition models (including electrolyte non random two liquid (e-NRTL), non random factor (NRF) and modified NRTL (mNRTL) models) and the Pitzer model. The capability of the considered models was compared on the basis of the standard deviation in osmotic coefficients. The models give reliable results in correlation of the osmotic coefficients. However, the results show that the Pitzer and the mNRTL models successfully correlate the osmotic coefficients, however e-NRTL and NRF models give larger standard deviations.

Keywords: Isopiestic; Osmotic coefficients; Methanol; Ethanol; $MnCl_2$; $CoCl_2$; $NiCl_2$; Local composition models

1. Introduction

Thermodynamic properties of the non aqueous binary electrolyte solutions are useful in prediction of behavior of mixed-salt or mixed-solvent electrolyte systems, development the electrolyte solutions models, estimation of the interactions occurring in these solutions and so on. There is a growing interest in the study of non aqueous electrolyte solutions in the past two decades [1]. However, contrary to the solutions of 1:1 electrolytes, solutions of non 1:1 solutes in non aqueous solvents rarely have been studied. There are some reports in the literature for vapor pressure and osmotic coefficients of the solutions of $CaCl_2$, $Ca(NO_3)_2$, $CuCl_2$ and $ZnCl_2$ in methanol and ethanol [2–8]. However, there is not any report regarding to the thermodynamic properties of the solutions of the transition metal chlorides in alcohols.

In this work the osmotic coefficients of the solutions of $MnCl_2$, $CoCl_2$ and $NiCl_2$ in methanol and ethanol have been measured by the isopiestic method at 298.15 K. The osmotic coefficients of the solutions have been obtained from the isopiestic equilibrium molalities of the investigated solutions and the solution of NaI in methanol and ethanol served as isopiestic reference solution.

Osmotic coefficient data have been correlated using the local composition models and the ion interaction model of Pitzer [9]. The local composition models used for data correlation are electrolyte non random two liquid model (e-NRTL) [10], non random factor model (NRF) [11], and modified NRTL model (mNRTL) [12].

The results indicate that the models work properly in the present case. They correlate the osmotic coefficients of the studied solutions with acceptable precision.

2. Experimental

2.1. Apparatus and procedure

The isopiestic apparatus employed in the present work is essentially similar to the one used previously by Zafarani-Moattar and co-workers [5–7,13,14]. This apparatus consisted of a five-leg manifold attached to round-bottom flasks. The five

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Table 1
Isopiestic equilibrium molalities for the solutions of $MnCl_2$ in methanol at 298.15 K

m_r (mol kg^{-1})	m_{MnCl_2} (mol kg^{-1})
0.1565	0.1859
0.2012	0.2407
0.2510	0.3001
0.2930	0.3499
0.3060	0.3654
0.4045	0.4823
0.4570	0.5446
0.5429	0.6450
0.6605	0.7861
0.7195	0.8562
0.8100	0.9636
0.9275	1.1030
1.0280	1.2223
1.0695	1.2716
1.1730	1.3944
1.2690	1.5084
1.2985	1.5433
1.5097	1.7983
1.9721	2.3538
2.1533	2.5752
2.3752	2.8379
2.5466	3.0385
2.7324	3.2571
2.9981	3.5660
3.1598	3.7651
3.4782	4.1274
3.8593	4.5640

Table 2
Isopiestic equilibrium molalities for the solutions of $CoCl_2$ in methanol at 298.15 K

m_r (mol kg^{-1})	m_{CoCl_2} (mol kg^{-1})
0.2330	0.2377
0.2711	0.2917
0.2906	0.3191
0.3061	0.3411
0.4030	0.4787
0.4389	0.5281
0.5135	0.6342
0.6456	0.8211
0.6861	0.8764
0.7208	0.9289
0.7310	0.9421
0.7799	1.0120
0.8270	1.0774
0.9150	1.2021
0.8950	1.1738
0.9773	1.2902
0.9858	1.3024
1.0282	1.3623
1.0598	1.4070
1.0616	1.4091
1.0777	1.4322
1.0794	1.4348
1.0794	1.4348
1.1466	1.5286
1.1837	1.5827
1.2580	1.6871
1.2780	1.7150
1.3386	1.8014
1.4346	1.9396
1.5417	2.0886

flasks were typically used as follows. Two flasks contained the standard NaI solutions, two flasks contained transition metal chloride solution, and the central flask was used as a methanol or ethanol reservoir. The apparatus was held in a constant temperature bath for at least 120 h for equilibration at 298.15 ± 0.005 K. On the basis of the activity measurements, the maximum error has been previously verified ±0.0002 for the isopiestic technique used [15].

2.2. Chemicals

The alcohols and salts were obtained from Merck. They were all analytical pure grade reagents. (absolute ethanol, GR, minimum 99.8% by mass; NaI, GR, minimum 99.5% by mass; $MnCl_2$, $CoCl_2$, $NiCl_2$). Methanol and ethanol were dried by the method described by Vogel [16]. The density of pure methanol and ethanol were measured with a vibrating-tube densimeter as 787.70 and 785.12 kg m^{-3}, respectively, which are in reasonable agreement with the literature value of 787.36 kg m^{-3} for methanol [17] and 785.08 kg m^{-3} for ethanol [17].

3. Results and discussions

3.1. Experimental results

Isopiestic equilibrium molalities of the investigated solutions with reference standard solutions of NaI in methanol and ethanol as reported in Tables 1–6 enabled us the calculation of the osmotic coefficient of the investigated solutions, Φ^*, from

$$\Phi^* = \frac{\nu_r m_r}{\nu^* m^*} \Phi_r \tag{1}$$

in which ν and m are, respectively the total number of ions produced by one mole of the salt and the molality of the salt; r stands for isopiestic standard solution and strike indicates the transition metal chloride solution. Osmotic coefficients of the isopiestic reference solution in the isopiestic equilibrium at m_r were obtained from the fitted Pitzer equation including the $\beta^{(2)}$ term as described by Zafarani-Moattar and Nasirzadeh [13] for methanol solutions and by Zafarani-Moattar and Jahanbin [14] for ethanol solutions. The Pitzer parameters for reference solution in the case of methanol are $\beta^{(0)} = 0.40830$, $\beta^{(1)} = 1.04430$, $\beta^{(2)} = -0.875$ and $C^{\Phi} = -0.02224$, and in the case of ethanol are $\beta^{(0)} = 1.05886$, $\beta^{(1)} = 6.89558$, $\beta^{(2)} = -6.25702$ and $C^{\Phi} = -0.133017$. The optimum values of $\alpha(1)$, $\alpha(2)$ and b parameters in the Pitzer model are, respectively 2, 1.4 and 3.2 for all of the studied solutions. The osmotic coefficients of the reference solution, Φ_r, are reproduced with standard deviation of 0.005 for both methanol and ethanol solutions [13,14].

The osmotic coefficients obtained in this manner have been given in Tables 7–12. These Tables have also been contained the activity of solvent and the vapor pressure of the investigated solutions. The vapor pressures of the studied solutions, p, were