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Determination and modeling of activity coefficients of cobalt chloride in the (water + ethanol) mixed solvent system by potentiometric method at 298.15 K

Q2 Mohammad A. Bagherinia*, Mohammad Pournaghdi

Department of Chemistry, Faculty of Science, Lahijan Branch, Islamic Azad University, Lahijan, Iran

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ABSTRACT

In this work, the thermodynamic properties of (CoCl₂ + C₂H₅OH + H₂O) system were investigated by potentiometric method and based on Pitzer ion interaction model. For this purpose, primarily the mean activity coefficients of CoCl₂ in pure water and ethanol–water mixture solvent were determined using a galvanic cell without liquid junction potential of type: Co²⁺-ISE|CoCl₂ (m), C₂H₅OH (wt.%), H₂O (100-wt.%) |Ag-AgCl. The measurements were performed at T = 298.15 K and at total ionic strengths from 0.001 to 6.000 mol·kg⁻¹ in various ethanol–water mixed solvent systems containing 0, 10, 20, 30, 40 and 50% mass fractions of ethanol. The mean activity coefficients measured were correlated with Pitzer ion interaction model and the Pitzer adjustable parameters were determined. Then these parameters were used to calculate the thermodynamics properties for under investigated system. The results showed that the Pitzer ion interaction model can satisfactory describe the investigated system. The modified three-characteristic-parameter correlation (TCPC) model was applied to correlate the experimental activity coefficient data for under investigation electrolyte system, too. The results showed that the modified TCPC model also was suitable in the case of the mixed solvent system.

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1. Introduction

The properties of electrolyte in mixed water–organic solvents are of particular interest in many industrial and environmental applications, particularly, for separation processes. Recently, there has been an increasing amount of work concerning the measurement of thermodynamic properties of electrolytes in mixtures of solvents [1–4]. To measure the thermodynamic properties of electrolytes in mixed solvent, the most common methods are the isopiestic vapor pressure [5,6] and potentiometric techniques [7,8]. Compared to the isopiestic method, the potentiometric method presents advantages, such as rapidity and relative simplicity to generate experimental electromotive force (emf) data. In this work, the results relating to the thermodynamic properties for CoCl₂ in (ethanol + water) mixtures using the potentiometric method are reported at T = 298.15 K. Thermodynamic properties of the mixed solvent solutions are useful in the prediction of the behavior of salt electrolyte in biological systems, development of the electrolyte solution models, estimation of the interactions occurring in these solutions and so on. However there is a growing interest in the study of mixed solvent solutions but have rarely been studies about cobalt chloride and according to our survey, there is not any report

regarding the thermodynamic properties of CoCl₂ + ethanol + H₂O system.

The main goal of this work was to provide precise thermodynamic data about the ternary system (CoCl₂ + ethanol (wt.%) + H₂O (100-wt.%)), which may allow modeling as its behavior. This paper is a continuation of the research on ternary aqueous electrolyte solutions with electrolytes having cobalt chloride [9,10]. The potentiometric measurements reported in this work were carried out with a galvanic cell containing a solvent polymeric membrane Co²⁺-ion selective electrode (Co²⁺-ISE) and Ag–AgCl electrode in which both of them were prepared in our laboratory and showed a reasonably good Nernst response. We have reported in our previous papers the ability of the solvent polymeric membrane electrode for the determination of the activity coefficient for binary and ternary electrolyte solutions [8,11,12]. The stock solution of electrolyte was prepared by adding weighted amounts of CoCl₂ into the proportion volume of the ethanol–water as a mixed solvent. It can be noted that all of the ethanol–water mixed solvents were separately prepared by direct weighting.

In this work, the resulting values of the mean activity coefficients of CoCl₂ in mixed solvent solution were determined using potentiometric model. The determination of the activity coefficient for CoCl₂ in various ethanol–water mixed solvent systems containing 0, 10, 20, 30, 40 and 50% mass fractions of ethanol over ionic strength ranging from 0.0001 to 6.0000 mol·kg⁻¹ was performed. The modeling of this ternary system was made based on the Pitzer ion-interaction model and the

* Corresponding author.

modified three-characteristic-parameter correlation (TCPC) model. Then, the Pitzer ion-interaction parameters (β^0 , β^1 and C^∞) and TCPC parameters (b, S) for the series under the investigated system were estimated by fitting experimental results with the models. Finally the excess Gibbs free energy and osmotic coefficient of water were calculated using the Pitzer ion-interaction parameters.

2. Experimental

2.1. Apparatus and reagents

All of the potentiometric measurements were made using a digital multimeter (Eutech 2100) with a resolution of 0.1 mV. The solutions were continuously stirred using a magnetic stirrer (Delta Model HM-101) at a slow constant rate to avoid concentration gradients in the test solutions. A Model GFL circulation water bath was used to control the temperature of the test solution at $298.15 \text{ K} \pm 0.1$. The conductivity measurements were carried out with a Metrohm 660 conductivity meter. An analytical balance (Sartorius GMBH 2842) with an accuracy of 0.1 mg was used throughout all experiments.

Dibutyl phthalate (DBP), potassium tetrakis (*p*-chlorophenyl) borate (KT_pCIPB), high molecular weight poly(vinyl chloride) (PVC), tetrahydrofuran (THF), cobalt chloride hexahydrate (CoCl₂·6H₂O), ethanol and all other reagents used were purchased from Merck and Fluka and all of them were of analytical reagent grade. All aqueous solutions were prepared by using doubly distilled water whose specific conductance was less than $2.0 \times 10^{-4} \text{ S}\cdot\text{m}^{-1}$. The stock solution of cobalt chloride was prepared using CoCl₂·6H₂O in mixed solvent.

2.2. Preparation of the PVC membrane electrode and the Ag–AgCl electrode

The 1,4-bis(2-(5-methyl-4-phenylthiazol-2-yl)hydrazinyl) benzene (BMPHB) was used as the ionophore and it acted as neutral ion carrier in plasticized polymeric membranes for the fabrication of the Co²⁺-selective. The general procedure used to prepare the PVC membrane was mixing thoroughly optimized amounts of 32 mg of powdered PVC, 60 mg plasticizer DBP and 5 mg additive KT_pCIPB in 1 ml of dry freshly distilled THF. To this solution for fabrication of the Co²⁺-selective 3 mg of BMPHB as an ionophore was added and mixed very well. The resulting clear mixture was transferred into a glass dish of 2 cm 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 Co²⁺-selective electrodes were each time backfilled with a CoCl₂ internal filling solution of $0.01 \text{ mol}\cdot\text{dm}^{-3}$. The electrodes were conditioned in $0.01 \text{ mol}\cdot\text{dm}^{-3}$ solution of CoCl₂ for 48 h, respectively. The Co²⁺-selective electrode was calibrated versus a saturated calomel reference electrode in the $1\text{--}10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ concentration range of a solution of pure CoCl₂ before using each series of measurements. The Co²⁺-ISE was then conditioned overnight in the appropriate mixed solvent solution before each series of measurements.

For fabrication of the Ag–AgCl electrode an Ag wire was electrolyzed in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ HCl solution, as described in literature [13]. The Ag–AgCl electrode prepared was used as both internal reference and chloride selective electrode. The Ag–AgCl electrode was calibrated versus a saturated calomel reference electrode in the $1\text{--}10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ concentration range of a solution of pure CoCl₂ before using each series of measurements. The Ag–AgCl electrode was conditioned overnight in the appropriate mixed electrolyte system before each series of measurements, too.

Table 1

Values Debye–Hückel parameters for the osmotic coefficient (A^\ominus) the solvent relative permittivity (ϵ_r) and density (ρ) in different mass fraction (w) of EtOH–water mixed solvent systems at 298.15 K.

Ethanol (wt.%)	A^\ominus ($\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$)	ϵ_r	ρ ($\text{kg}\cdot\text{m}^{-3}$)
0	0.3915	78.38	997.2
10	0.4337	72.80	980.4
20	0.4877	67.00	966.4
30	0.5564	61.02	950.5
40	0.6437	55.00	931.5
50	0.7543	49.10	910.0

2.3. Potentiometric measurements

The cell arrangement for studying the (CoCl₂ + ethanol + water) system was described as follows:



where w was the mass fraction of ethanol in the mixed solvent. The emf measurements of the galvanic cell Eq. (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 ethanol–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 during 20 min by using a multimeter. As usual, all measurements were performed under stirring conditions and the temperature was kept constant at 298.15 K (± 0.1 K), employing a double-wall container enabling the circulation of thermostat water from a Model GFL circulation.

3. Thermodynamics models

3.1. Pitzer model

According to the Pitzer ion interaction model, the mean molal activity coefficient (γ_{\pm}) for CoCl₂ in the mixed solvent is inscribed as [14]:

$$\ln \gamma_{\pm\text{CoCl}_2}^o = 2f^\gamma + \frac{4}{9}B_{\text{CoCl}_2}^\gamma I + \frac{2\sqrt{2}}{9}C_{\text{CoCl}_2}^\phi I^2 \quad (1)$$

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

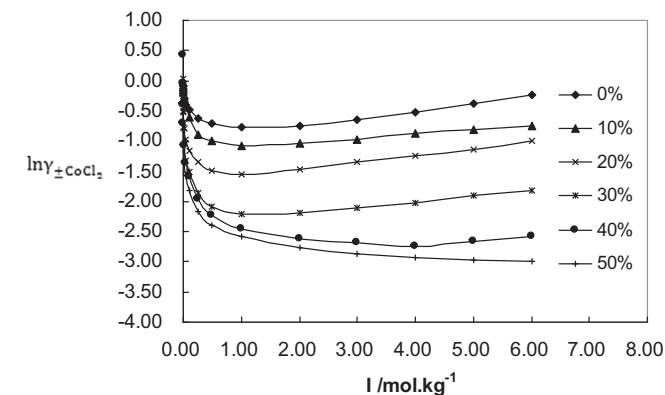


Fig. 1. The plot of the values of natural logarithm mean activity coefficients of CoCl₂ versus total ionic strength at different mass fractions of ethanol at 298.15 K.

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