



## Determination of thermodynamic properties of the ternary electrolyte system $\{\text{CoCl}_2 + \text{Co}(\text{NO}_3)_2 + \text{H}_2\text{O}\}$ by the potentiometric method at $T = 298.15$

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### ARTICLE INFO

#### Article history:

Received 28 June 2012

Received in revised form 21 August 2012

Accepted 16 September 2012

Available online 9 October 2012

#### Keywords:

Thermodynamic properties

$\text{CoCl}_2$

$\text{Co}(\text{NO}_3)_2$

Pitzer model

Potentiometric method

### ABSTRACT

In this work, the Pitzer ion interaction model and Harned rule were used to illustrate the ternary electrolyte system  $\{\text{CoCl}_2 + \text{Co}(\text{NO}_3)_2 + \text{H}_2\text{O}\}$ . The activity coefficients were determined using a potentiometric method. The galvanic cell used had no liquid junction of type:  $\text{Co}^{2+}\text{-ISE}|\text{CoCl}_2 (m_A), \text{Co}(\text{NO}_3)_2 (m_B), \text{H}_2\text{O}|\text{Ag,AgCl}$ . The measurements were performed at  $T = 298.15$  K and at total ionic strengths from 0.001 to 6.000 mol · kg<sup>-1</sup> for different series of salt ratios  $r = \frac{m_{\text{CoCl}_2}}{m_{\text{Co}(\text{NO}_3)_2}} = 1.00, 2.50, 5.00, 7.50, 10.00$  and 15.00. The PVC based cobalt ion-selective electrode ( $\text{Co}^{2+}\text{-ISE}$ ), the PVC based nitrate ion-selective electrode ( $\text{NO}_3^- \text{-ISE}$ ) and the Ag/AgCl electrode used in this work were prepared in our laboratory and showed a reasonably good Nernst response. The experimental results showed that both Pitzer model and Harned rule were suitable to be used satisfactorily to describe this ternary system.

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### 1. Introduction

In the last decades, a series of ion-interaction models for electrolyte solutions have been proposed to predict the activity coefficient of each solute and the osmotic coefficient of aqueous systems. One of the most famous and useful models is that proposed by Pitzer [1–3]. This model accounts for long-range forces by a classical Debye–Hückel term, while short-range forces are included via semi empirical parameters. The most common methods for the determination of thermodynamic properties in mixed electrolyte solutions are the isopiestic vapor pressure [4–7], vapor-pressure lowering [8–10], potentiometric techniques (emf) [11–16] and the use of the electrodynamic balance [17].

The potentiometric method using a galvanic cell without liquid junction was found to be an attractive experimental technique for studying the thermodynamic properties of electrolytic solutions [18,19]. Compared to the isopiestic method, this technique presents advantages, such as rapidity and relative simplicity to generate experimental electromotive force (emf) data. Different types of cation and anion selective electrodes were designed and used for such purposes. Examples of cation reversible electrodes are the hydrogen, metal amalgam, glass, liquid ion exchange and finally neutral carrier-based membrane electrodes. Examples of anion reversible electrodes include the silver–silver halide, metal amalgam–metal anion, liquid ion exchange and solid state membrane electrodes [19]. Among this type of electrodes, the ion-exchange

membrane and carrier based membrane ion-selective electrodes (ISE) were the least used for the determination of activity coefficients of electrolyte solutions [19–21]. However, carrier-based membrane-type electrodes are comparatively more selective, stable, and efficient than ion-exchange-type membrane electrodes.

In this work, the results relating to the thermodynamic properties for the ternary solutions of  $\{(1 - y) \text{CoCl}_2 + y \text{Co}(\text{NO}_3)_2\}_{(\text{aq})}$  ( $y = 3m_{\text{Co}(\text{NO}_3)_2}/I$ ) using the potentiometric method and based on the Pitzer ion interaction model are reported at  $T = 298.15$  K. Thermodynamic properties of the aqueous binary and ternary electrolyte solutions are useful in the prediction of behaviour of mixed salt electrolyte systems, development the electrolyte solutions models, estimation of the interactions occurring in these solutions and so on. However there is a growing interest in the study of aqueous electrolyte solutions but have rarely been studied about common cobalt cation [22]. According to our survey, there are a few reports in the literature for activity and osmotic coefficients of the solutions of  $\text{CoCl}_2, \text{CoSO}_4$  and  $\text{Co}(\text{ClO}_4)_2$  [23–24] and there is not any report regarding the thermodynamic properties of aqueous  $\text{CoCl}_2$  and  $\text{Co}(\text{NO}_3)_2$  solutions using the potentiometric method. The main goal of this work is to provide precise thermodynamic data about the ternary system  $(\text{CoCl}_2 + \text{Co}(\text{NO}_3)_2 + \text{H}_2\text{O})$ , which may allow modelling its behaviour. This paper is a continuation of the research on ternary aqueous electrolyte solutions with electrolytes having a common cobalt cation and a chloride anion [25]. The main objectives are to determine thermodynamic properties for the ternary aqueous solution of chloride cobalt and nitrate cobalt. The potentiometric measurements reported in this work were carried out with a galvanic cell containing a solvent polymeric membrane

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TABLE 1

Provenance and purity of the materials.

Component	Company	Mass fraction purity
Dibutyl phthalate	Fluka	≥ 0.99
Potassium tetrakis( <i>p</i> -chlorophenyl) borate	Fluka	≥ 0.98
Poly(vinyl chloride)	Fluka	High molar
Tetrahydrofuran	Fluka	≥ 0.99.5
CoCl <sub>2</sub> ·6H <sub>2</sub> O	Merck	≥ 0.99
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Merck	≥ 0.98

TABLE 2

The Harned interaction coefficient ( $\alpha_{AB}$ ) and the linear regression coefficient ( $R^2$ ) of the plot of  $\ln \gamma_{\pm A}$  versus ( $yI$ ).

$I/(\text{mol} \cdot \text{kg}^{-1})$	$\alpha_{AB}$	$R^2$
2.0000	0.0328	0.8175
3.0000	0.0343	0.9635
4.0000	0.0419	0.9286
5.0000	0.0519	0.9242
6.0000	0.0522	0.9624

Co<sup>2+</sup>-ion selective electrode (Co<sup>2+</sup>-ISE) and Ag–AgCl electrode and various series of this mixed salt electrolyte system, at ionic strengths of 0.001 to 6.000 mol · kg<sup>-1</sup>. A series of concentrated mixed electrolyte solutions, characterized by their mole salt ratio ( $r = \frac{m_{\text{CoCl}_2}}{m_{\text{Co(NO}_3)_2}} = 1.00, 2.50, 5.00, 7.5, 10.00, 15.00$ ) was used in a standard addition technique to modify the molality of the mixed electrolyte in the experimental cell. The resulting values of mean activity coefficients, osmotic coefficients and excess Gibbs energies were reported for the whole series of these studied ternary mixed electrolyte systems.

## 2. Experimental

### 2.1. Apparatus and reagents

All of the potentiometric measurements were made using a digital multimeter (Eutech 2100) with 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 ± 0.1) K. The conductivity measurements were carried out with a Metrohm 660 conductivity meter. An analytical balance (Sartorius GMBH 2842) with accuracy 0.1 mg was used throughout all experiments.

Dibutyl phthalate (DBP), potassium tetrakis(*p*-chlorophenyl) borate (KT<sub>p</sub>CIPB), high molar poly(vinyl chloride) (PVC), tetrahydrofuran (THF), cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and all other reagents used were purchased from Merck and Fluka and all of them were of analytical reagent grade (table 1). All aqueous solutions were prepared by using doubly distilled water whose specific conductance was less than 2.0 · 10<sup>-4</sup> S · m<sup>-1</sup>. The stock aqueous solution of cobalt chloride was prepared using CoCl<sub>2</sub>·6H<sub>2</sub>O. The concentration of cobalt chloride (aq) was determined by the potentiometric titration method using a standard solution of silver nitrate. Working solutions were prepared by adding weighed amounts of solid

cobalt nitrate and double-distilled water to the stock aqueous solution of cobalt chloride to give the desired ionic strengths fractions.

### 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) and tridodecylmethylammonium chloride (TDMACl) were used as the ionophore and they act as neutral ion carrier in plasticized polymeric membranes for fabrication of the Co<sup>2+</sup>-selective and NO<sub>3</sub><sup>-</sup>-selective electrodes, respectively. The general procedure used to prepare the PVC membrane [26] was by mixing thoroughly optimized amounts of 32 mg of powdered PVC, 60 mg plasticizer DBP and 5 mg additive KT<sub>p</sub>CIPB in 1 cm<sup>3</sup> of dry freshly distilled THF. To this solution for fabrication of the Co<sup>2+</sup>-selective 3 mg of BMPHB and for fabrication of the NO<sub>3</sub><sup>-</sup>-selective 3 mg TDMACl as an ionophore were 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 Co<sup>2+</sup>-selective electrodes were each time backfilled with a CoCl<sub>2</sub> internal filling solution of 0.01 mol · dm<sup>-3</sup> and the NO<sub>3</sub><sup>-</sup>-selective electrodes were each time backfilled with a Co(NO<sub>3</sub>)<sub>2</sub> internal filling solution of 0.01 mol · dm<sup>-3</sup>. The electrodes were conditioned in 0.01 mol · dm<sup>-3</sup> solution of CoCl<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> for 48 h, respectively. Both the Co<sup>2+</sup>-selective electrode and the NO<sub>3</sub><sup>-</sup>-selective electrode were calibrated versus a saturated calomel reference electrode in the 1–10<sup>-4</sup> mol · dm<sup>-3</sup> concentration range of a solution of pure Co(NO<sub>3</sub>)<sub>2</sub> before using each series of measurements. The Co<sup>2+</sup>-ISE and NO<sub>3</sub><sup>-</sup>-ISE electrodes were then conditioned overnight in the appropriate mixed electrolyte system before each series of measurements.

For fabrication of the Ag–AgCl electrode, an Ag wire was electrolyzed in 0.1 mol · dm<sup>-3</sup> HCl solution, as described in Ref. [27]. The Ag–AgCl electrode prepared was used as both the internal reference and chloride selective electrode. The Ag–AgCl electrode was calibrated versus a saturated calomel reference electrode in the 1–10<sup>-4</sup> mol · dm<sup>-3</sup> concentration range of a solution of pure CoCl<sub>2</sub> before using each series of measurements. The Ag–AgCl electrode was conditioned overnight in the appropriate mixed electrolyte system before each series of measurements.

### 2.3. Potentiometric measurements

The cell arrangements in this work were as follows:

- (A) Co-ISE | CoCl<sub>2</sub> ( $m_{A0}$ ) | Ag–AgCl
- (B) Co-ISE | Co(NO<sub>3</sub>)<sub>2</sub> ( $m_{B0}$ ) | Ag–AgCl
- (C) Co-ISE | CoCl<sub>2</sub> ( $m_A$ ), Co(NO<sub>3</sub>)<sub>2</sub> ( $m_B$ ) | Ag–AgCl
- (D) Co-ISE | Co(NO<sub>3</sub>)<sub>2</sub> ( $m_{B0}$ ) | NO<sub>3</sub>-ISE

The above galvanic cells had no liquid junction, where  $m_{A0}$  and  $m_{B0}$  represent molalities of CoCl<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> as single salts in water, respectively. The  $m_A$  and  $m_B$  represent the molalities of CoCl<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> in the mixture, respectively. The electromotive force (emf) of cell (A) was measured so as to calibrate the electrode pair

TABLE 3

The values of Pitzer empirical parameters for pure salt ( $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $\beta^{(2)}$  and  $C^\phi$ ), maximum molality ( $m_{\text{max}}$ ) of solution and the standard deviation ( $\sigma$ ) of the fits.

Electrolyte	$\beta^0$ (kg · mol <sup>-1</sup> )	$\beta^1$ (kg · mol <sup>-1</sup> )	$\beta^2$ (kg · mol <sup>-1</sup> )	$C^\phi$ (kg <sup>2</sup> · mol <sup>-2</sup> )	$m_{\text{max}}$ (mol · kg <sup>-1</sup> )	$\sigma$	Reference
CoCl <sub>2</sub>	0.34723	1.66470	-0.00350	0.00559	4.26	0.00079	[29]
Co(NO <sub>3</sub> ) <sub>2</sub>	0.3167	1.0725		-0.0106	2	0.0005	This work

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