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Thermodynamic Modeling of Apparent Molal Volumes of Bivalent Metal Nitrate Salts with Pitzer Model

Mouad Arrad

Equipe Energie et Procedes Propres, Department of Process Engineering, National School of Mines of Rabat, Rabat BP 753, Morocco; mouadarrad@hotmail.com

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Abstract: The apparent molal volumes of selected bivalent metal nitrate salts, $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Mg(NO_3)_2$, in water have been assessed from the available density measurements of their aqueous solutions at 25 °C over a wide molality range. The values of ${}^{\phi}V$ have been fitted to the Pitzer model using its volumetric contributions. The model parameters $\beta^{(0)V}$, $\beta^{(1)V}$, $C^{\varphi V}$ and $\overline{V}^{0}$ were determined for each aqueous electrolyte, over the composition range from 0 to about 4.5 $mol{\cdot}kg^{-1}{\cdot}H_2O$. The new experimental data and parameters obtained will be useful to extend the present database of electrolyte solutions and provide a reliable model for industrial use, which could be extended to other thermodynamic properties.

Keywords: cobalt nitrate; nickel nitrate; magnesium nitrate; density; aqueous solution; Pitzer; apparent molal volume

1. Introduction

Metal nitrate salts are widely used in several industrial applications; we can cite their presence in material processing such as Ferrites technology [1].

The volumetric properties of solutions are an important source of information about the interaction between species in solution. Density and apparent molal volumes could help derive other thermodynamic properties that are not always easy to measure.

In this study, the proposed thermodynamic model is Pitzer [2] model, because of its large popularity in the scientific community, its flexibility and relative simplicity have led to several investigations concerning different properties of electrolyte solutions but only few papers were interested to volumetric properties, we could cite here Kumar et al. [3], Krumgalz et al. [4], May et al. [5], Rodriguez et al. [6] and our recent study [7].

Krumgalz et al. [4] present volumetric Pitzer parameters for the investigated binaries, and later, May et al. [5] provide an update of Pitzer parameters. the starting point was identical for both papers. It was based on available experimental data, but those data are scarce or difficult to access. The majority of experimental points were taken from the ICT [8] compilation or belonged to restricted authors [9−13]. Our contribution aims to provide more experimental density measurement data for the investigated electrolytes and the determination of Pitzer parameters at 25 °C and atmospheric pressure based on the best experimental data available in the literature and our experimental findings.

2. Experimental

The chemicals, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ were supplied by Sigma-Aldrich and $Mg(NO_{3)2}{\cdot}6H_2O$, from Riedel-de Haën, and used as delivered. According to the supplier, these reagents have a purity higher than 99%, and water was distilled twice before use.

Electrolyte solutions were prepared gravimetrically, considering the resolution of the balance. The relative uncertainty in the concentration is estimated to be less than ± 0.1% for the investigated molalities. Densities of

aqueous solutions were measured using a single-flask type pycnometer of 25 mL of volume. The uncertainty of the density measurements was found to be less than ± 0.0005 g·cm^{-3}. The solutions of salts were prepared by dissolving the chemical in bi-distilled water.

The pycnometer method for the measurement of the density of aqueous salt solution is very simple to use, but the experiments should be carried out with the highest care. In order to validate the experimental procedure, a sample test of the measurement of the sodium chloride—water system was carried out using a thermostat in order to control the temperature. The obtained results are aligned with the literature data in the ICT [8], showing a deviation of less than 1.5%.

3. Results

The measurement method was identical to the method described by Sohnel et al. [9]. The only difference was that solutions were kept 30 min in the constant temperature bath using a thermostat with an accuracy of ± 0.1 °C.

The density of pure water used in the calculations of the density of solution was taken from [14], the value used was 997.047 kg·m^{-3} at 25 °C.

The apparent molal volume $^{\phi}V$ (cm^3·mol^{-1}) of the salt in the solution was calculated from the measured density of the solution using the equation:

$$^{\phi}V = 1000(\rho^0 - \rho)/(m\rho^0\rho) + M/\rho \quad (1)$$

where M is the molecular weight of the salt 182.943 g·mol^{-1}, 182.703 g·mol^{-1}and 148.3 g·mol^{-1} respectively for $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Mg(NO_3)_2$ and m is molality of the solution (mol·kg^{-1}), ρ is the density of the solution and ρ^0 is density of pure water at the given temperature of 25 °C given in g·cm^{-3}.

For each molality, three independent density measurements were conducted, and the obtained average value of density with the experimental uncertainty is presented. The apparent molal volume is also presented in Tables 1–3 for Cobalt nitrate, Nickel nitrate, and Magnesium nitrate, respectively.

Table 1. Measured density values at 25 °C as a function of molality for $Co(NO_3)_2$. The listed density is an average value of three measurements.

m (mol kg^{-1})	Density ρ (g cm^{-3})	$^{\phi}V$ (cm^{3}mol^{-1})
3.9199	1.4547	45.26
3.5983	1.4245	44.79
2.6776	1.3309	43.50
1.2947	1.1693	40.01
1.0688	1.1438	39.57
0.9744	1.1319	39.02

Standard uncertainties u are u(m) = 0.001 mol·kg^{-1} u(T) = 0.1 K, and the expanded uncertainties of measured densities are u(ρ) = 0.0005 g·cm^{-1}.

Table 2. Measured density values at 25 °C as a function of molality for $Ni(NO_3)_2$. The listed density is an average value of three measurements.

m (mol kg^{-1})	Density ρ (g cm^{-3})	$^{\phi}V$ (cm^{3}mol^{-1})
3.0501	1.3846	39.80
2.4266	1.3177	38.32
1.9153	1.2562	37.51
1.2955	1.1768	35.98
0.8915	1.1237	34.47
0.4757	1.0678	33.78

Standard uncertainties u are u(m) = 0.001 mol·kg^{-1} u(T) = 0.1 K, and the expanded uncertainties of measured densities are u(ρ) = 0.0005 g·cm^{-1}.

Table 3. Measured density values at 25 °C as a function of molality for $Mg(NO_3)_2$. The listed density is an average value of three measurements.

m (mol·kg^{-1})	Density ρ (g cm^{-3})	$^{\phi}V$ (cm^{3}mol^{-1})
4.1211	1.3470	47.20
3.5067	1.3019	46.94
2.6876	1.2400	46.49
2.2303	1.2041	45.83
		44.83
1.9357	1.1819	42.35
		41.31
1.0076	1.0993	
0.6172	1.0613	

Standard uncertainties u are u(m) = 0.001 mol·kg^{-1} u(T) = 0.1 K, and the expanded uncertainties of measured densities are u(ρ) = 0.0005 g·cm^{-1}.

4. A Review of Published Volumetric Data

Densities of metal nitrate solutions with water have been determined in the literature by a few experimental groups only, as stated in our previous paper [7]. For that purpose and to be able to choose the most accurate experimental points for modeling, the experimental method should be accurate, and the calculation of experimental apparent molal volume should be consistent with the density values. we have faced this problem in the evaluation of old and new data as well.

We have noticed that the investigated bivalent nitrate systems are not well covered by the open literature, we can cite some experimental works from, Herz [10,11], Spitzer et al. [12] and Doan et al. [13] or ICT [8] compilation but we were not able to find any complete study covering a wide range of concentration starting from very dilute regions to saturation. This problem is related especially to the nature of experimental methods to cover dilute and concentrated regions; the vibrating tube densimeter was used by Spitzer et al. [12] to measure the density of solutions at low concentration, while Sohnel et al. [9] and Arrad et al. [7] have used pycnometry to cover wide concentration ranges. This fact may lead to a large discrepancy if the revision of results is not carried out very carefully.

Concerning the investigated metal nitrate salts, an evaluation of experimental data to determine the accepted ones to be used for modeling the apparent molal volumes was carried out before the modeling of any system. Data from Sohnel et al. [9] were used concerning cobalt nitrate, while ICT [8] values were excluded for nickel nitrate since no agreement was found between the data; this problem could be related to the combination of different sets of data from different sources.

Herz [10,11] data were also excluded from the assessment for the same problem of conversion to apparent molal volume, which gives us an idea about the accuracy of density measurement.

After this analysis, we have used reliable data from the literature in addition to our experimental data in the modeling of apparent molal volume with Pitzer equations. Tables 4–6 summarize sources of the experimental data points used in the assessments:

Table 4. Apparent molal volume data used in the assessment for $Co(NO_3)_2$.

Source	Number of Data Used
This study	6/6
ICT [8]	3/5
Spitzer et al. [12]	7/8
Sohnel et al. [9]	5/5

Table 5. Apparent molal volume data used in the assessment for $Ni(NO_3)_2$.

Source	Number of Data Used
This study	6/6
Spizer et al. [12]	5/8

Table 6. Apparent molal volume data used in the assessment for $Mg(NO_3)_2$.

Source	Number of Data Used
This study	7/7
ICT [8]	12/12
Doan et al. [13]	6/6

5. Discussion of the Results

We have fitted the experimental apparent molal volume ${}^{\phi}V$ data to the following Equations (2)–(4) based on the Pitzer extended virial coefficient equation for aqueous electrolyte solutions 2,

$$ {}^{\phi}V = \overline{V}^{0} + \nu \left| z_M z_X \right| (A_V / 2b) \ln(1 + bI^{1/2}) + \nu_M \nu_X RT \left[2mB^{V}_{MX} + m^2 (\nu_M \nu_X)^{1/2} C^{\varphi V}_{MX} \right] \quad (2) $$

where:

$$ B^{V}_{MX} = \beta^{(0)\mathrm{V}}_{MX} + \beta^{(1)\mathrm{V}}_{MX} g(\alpha_1 I^{1/2}) + \beta^{(2)\mathrm{V}}_{MX} g(\alpha_2 I^{1/2}) \quad (3) $$

$$ g(x) = 2\left[1 - (1 + x)\exp(-x)\right] / x^2 \quad (4) $$

In Equations (2)–(4) the symbols z_M and z_X are the charges of the cation and anion in the electrolyte, ν_M and ν_X are the stoichiometric coefficients of the ions in the salt, with the notation $\nu = \nu_M + \nu_X$, and I is the stoichiometric ionic strength of the solution, $R = 8.314$ J·K^{-1}·mol^{-1} is the gas constant.

Since we have only electrolyte of the type 1–2, α_2 and $\beta^{(2)V}$ are not included in the Pitzer expressions used in this work.

The internal parameters used in this work, b = 1.2 (kg mol^{-1})1/2, α_1 = 2.0 (kg. mol^{-1})$^{1/2}$, are the standard values proposed by Pitzer. The theoretical Debye–Hückel slope, A_V calculated using the formulation of Pierrot et al. [15], is A_v = 1.8743 cm^3·kg^{-1}·mol$^{-3/2}$ at 25 °C, and $\overline{V}^{0}$ in Equation (3) is the partial molal volume of the electrolyte at infinite dilution, at the prevailing temperature and pressure.

The Pitzer volume parameters $\beta^{(0)V}$, $\beta^{(1)V}$, $C^{\varphi V}$ and $\overline{V}^{0}$ determined in this work at 25 °C are given in Table 7. The obtained values were calculated using an unweighted least squares method and the experimental data given in Tables 4–6. In all cases, the partial molal volume at infinite dilution $\overline{V}^{0}$ was fitted as an adjustable parameter.

Table 7. Pitzer model parameters at 25 °C obtained for the investigated electrolytes [a].

Electrolyte	$\overline{V}^{0}$	$\beta^{(0)V}$	$\beta^{(1)V}$	$C^{\varphi V}$	Objective Function
$Co(NO_3)_2$	33.32	0.00018138	−0.00090391	−0.000004012	1.23
$Ni(NO_3)_2$	29.59	0.000157933	−0.00091177	0.000001775	0.36
$Mg(NO_3)_2$	38.69	0.000324709	−0.00320280	−0.00002110	0.93

Units: $\overline{V}^{0}$ in cm^{3}mol^{-1}; $\beta^{(0)V}$ and $\beta^{(1)V}$ in kg mol^{-1}bar^{-1}; $C^{\varphi V}$ in kg^{2}mol^{-2}bar^{-1}.

The quality of the fit was checked for each system using the standard deviation. The results are 2.8%, 0.9%, and 1.8% respectively for cobalt nitrate, nickel nitrate, and aqueous magnesium nitrate. The variation of the objective function could lead to different results, but the presented results were based on the best possible representation due to the very limited amount of experimental data.

Figures 1–3 show the experimental apparent molal volumes of the electrolytes according to various authors as a function of molality, and the assessed value fitted with parameters of the Pitzer model, using Equations (2)–(4). The least squares fitting results are depicted as the solid line in each figure.

Due to the reduced number of experimental data the determination of reliable parameters in not an easy task however, Krumgalz et al. [4] have tried to model cobalt nitrate and nickel nitrate with Pitzer model, the recommended parameters concern only nickel nitrate since the set of parameters obtained for cobalt nitrate was not reliable according to their analysis.

Recently May et al. [5] have published an update of Pitzer parameters at 25 °C including the investigated salts, in this study, Pitzer parameters were obtained assuming a fixed value for the apparent molal volume at infinite

dilution using Marcus [16] values, another paper [17] presents a revision of the apparent molal volume at infinite dilution for magnesium nitrate using an extended version of the Debey-Huckel equation.

The value of apparent molal volume at infinite dilution is a determinant parameters in the prediction of the apparent molal volume, the adopted approach is to consider this value as an adjustable parameters in Pitzer equations and check the consistency of the obtained value with experimental data, this method enable the model to find the appropriate value at very dilute regions without imposing any predefined value since the used value in the previous studies are estimations using general regression or the use of the estimation of the anion and cation to estimate the apparent molal volume at the infinite dilution by adding the their given values [18].

As one can notice in Figures 1–3, a very good agreement is obtained between the calculated values of apparent molal volume and the selected experimental data used in the fitting of the three electrolyte systems investigated in this work.

Another remark concerning apparent molal volume values for nickel nitrate and magnesium nitrate at 0.35 MPa reported in [19,20], we have noticed that the small variation of pressure has a minor effect of density regarding the good agreement between data at atmospheric pressure and those at 0.35 MPa, the same conclusion was made previously by Rogers et al. [21].

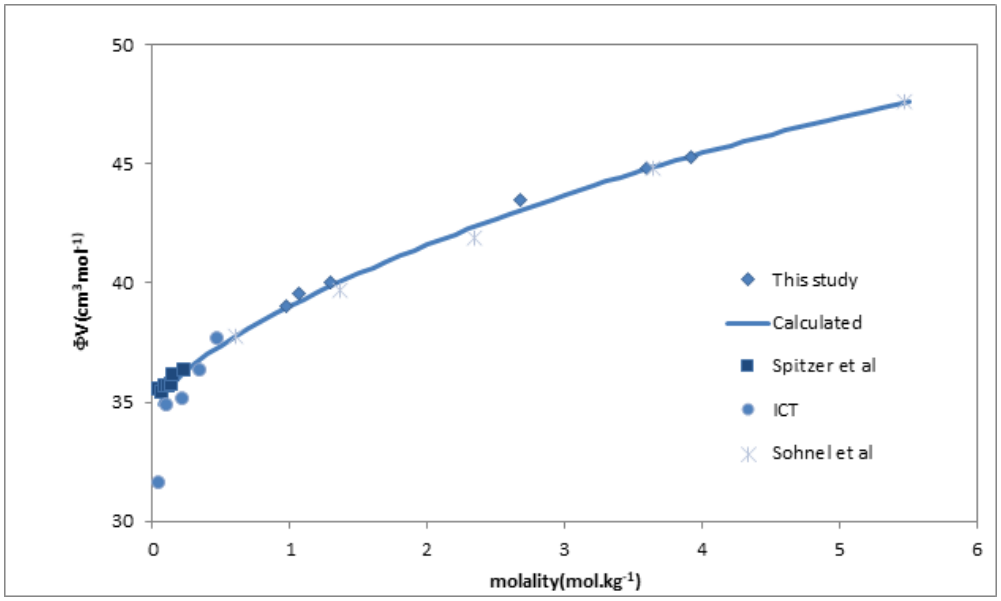

Figure 1. The experimental points and calculated value of apparent molal volume for $Co(NO_3)_2$ against molality at 25 °C [9,12].

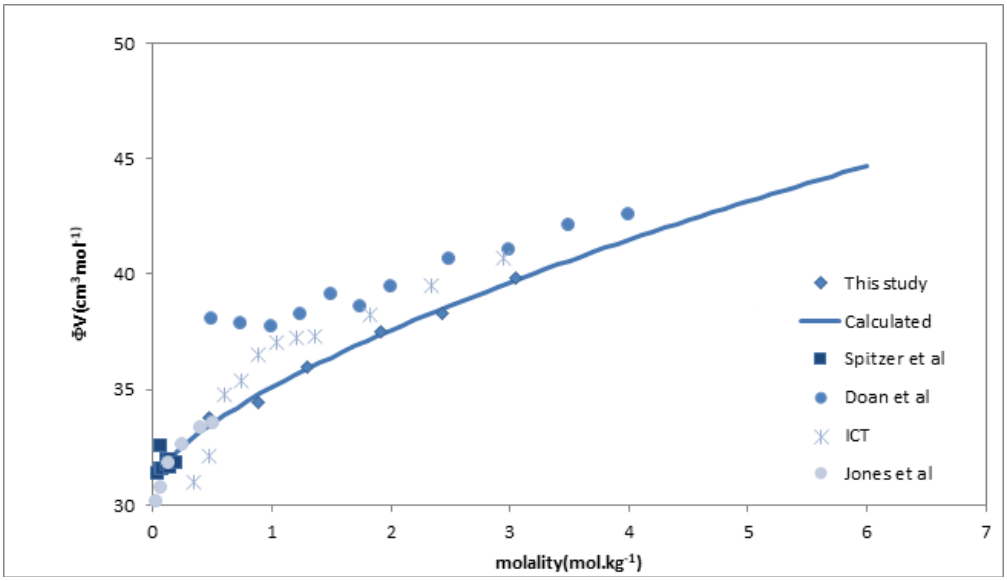

Figure 2. The experimental points and calculated value of apparent molal volume for $Ni(NO_3)_2$ against molality at 25 °C [13,19].

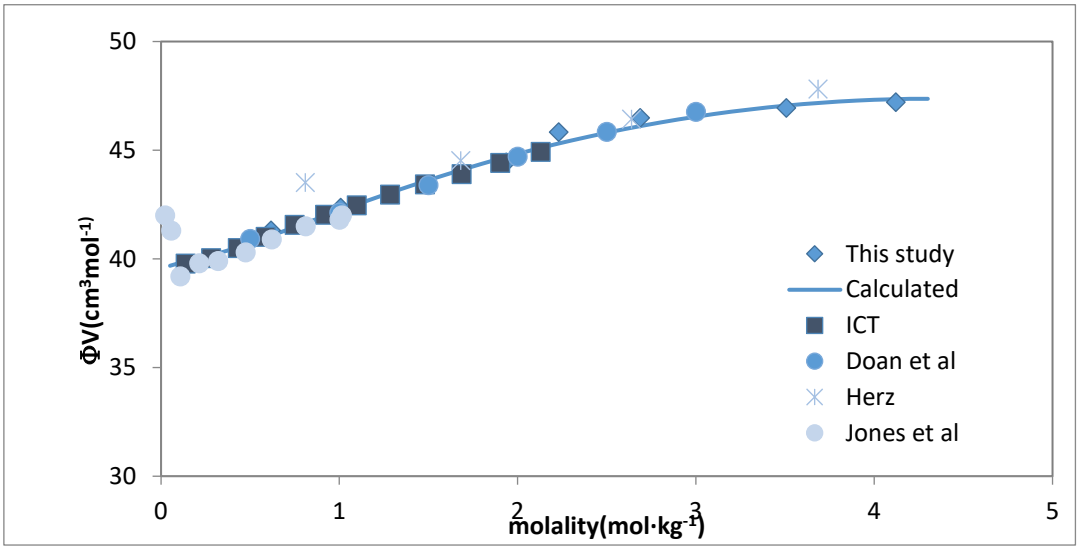

Figure 3. The experimental points and calculated value of apparent molal volume for $Mg(NO_3)_2$ against molality at 25 °C [13,19].

6. Conclusions

This study presents density measurements for three important bivalent metal nitrate salts covering a wide range of concentrations.

Using our set of experimental data and reliable density measurements, we were able to provide volumetric Pitzer parameters with good accuracy.

We should note, however, that new experimental data at wide temperature and concentration ranges are highly recommended.

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Conflicts of Interest

The author has no conflict of interest.

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