Experimental and Theoretical Elaboration of Phase Diagram for the Ternary System Ni(NO$_3$)$_2$-Al(NO$_3$)$_3$-H$_2$O at 20°C

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Abstract

The solid-liquid equilibrium of the ternary system of H$_2$O - Al(NO$_3$)$_3$ - Ni(NO3)$_2$ were studied using a synthesis process based on conductivity measurements. The isotherm was experimentally established at a 30 °C. The aim of our work is to validate the results obtained experimentally by an algorithm based on the Pitzer equations as well as the Nelder-Mead simplex method, which is an optimization method for multivariate function. A comparison between the obtained isotherm from the experimental data and the elaborated one using Pitzer model has confirmed our results.

Keywords: Pitzer model, solubility isotherms, Al(NO$_3$)$_3$ - Ni(NO$_3$)$_2$ -H$_2$O.

1. Introduction

A phase diagram is a thermodynamic tool, allowing after its analysis to give us a deep description about what happens at the microscopic level in the studied system. The liquid-solid phases equilibrium diagrams based on water and metal nitrates were the subject of many previous studies due to their properties, which give them opportunities for interesting industrial applications, especially for the synthesis of bi- or tri-metallic oxides (Goundali et al., 2006). Indeed Solubility equilibrium between solid salts, salt hydrates and water play an important role in different branches of applied chemistry such as, hydrometallurgy, geochemistry and oceanography, Hence thermodynamic models can be powerful predictive and interpretive tools to study the geochemistry of natural waters and mineral deposits, solve environmental problems and optimize industrial processes; indeed the Pitzer model is one of the most used ones, which has enjoyed remarkable success. It is especially popular with geochemists, waste chemists, and engineers for prediction of mineral solubilities and phase equilibrium.

2. Experimental work

Conductivity measurements were the basic synthetic method for the determination of solubility curves (Tenu et al., 1973; Kaddami et al., 1986; Tenu et al., 1979). It consists practically, in adding small amounts of water to the saturated solution in order to toggle it from its equilibrium state. Once the new equilibrium is restored after the addition of the water, the conductivity is measured and it is represented in terms of the quantity of added water (Laallam et al., 2004; Laallam et al., 2003; Laallam et al., 2011). Then, we follow for a set of poly-phase mixtures (liquid+ solid) of the appropriate composition, the variation of the liquid phase conductivity according to

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the dilution of the initial mixture. The electric conductivity-composition curve of solution introduces a discontinuity at each phase change. When the identification of the solid phase was too difficult with the previous method, the components were subjected to the dosage. Initially, salts are the Nickel nitrate with six water molecules and the Aluminum nitrate with nine water molecules. Water has been used bi-distilled.

The phase determination was our second step after the solubility limits definitions for a several mixed solution, indeed the identification of sold phase was a little difficult using conductivity measurements. Hence comes the metering method, which consists to identify the Nickel sulfate and the Aluminum sulfate using the wet residues and the "ensembles" methods (Chretien et al., 2011; Jouaiti et al., 1983; Schreinemakers et al., 1983). The Ni ions have been measured by molecular absorption spectrophotometry, the Al ions by volumetry using the EDTA.

In this study, we adopted definitions and notations of rectangular coordinates, we calculated the weight composition coordinates of considered mixture points by using the following expressions:

$$W\ (Al(NO_3)_3) = 100 * \frac{m(Al(NO3)3)}{mt}$$

$$W\ (Ni(NO_3)_2) = 100 * \frac{m(Ni(NO3)2)}{mt}$$
$$m_t = m(Al(NO3)3) + m(Ni(NO3)2) + m(H2O)$$

The experimental isotherm obtained at 20°C, (Jouaiti et al., 1983), is given in Table 1.

Table 1. The measured solubility data of ternary system $Al(NO_3)_3+ Ni(NO_3)_2 + H_2O$ at 20°C

W (Al(NO3)3),%	W (Ni(NO3)2),%	Limit domains
0	47.98	Liq+Ni6
4.33	43.18	--
8.6	38.1	--
11.2	36.22	$AL9 + Ni_6 + Liq$
13.11	33.84	Liq+Al9
16.9	28.1	--
23.9	17.1	--
30.9	8.5	--
38.37	0	--

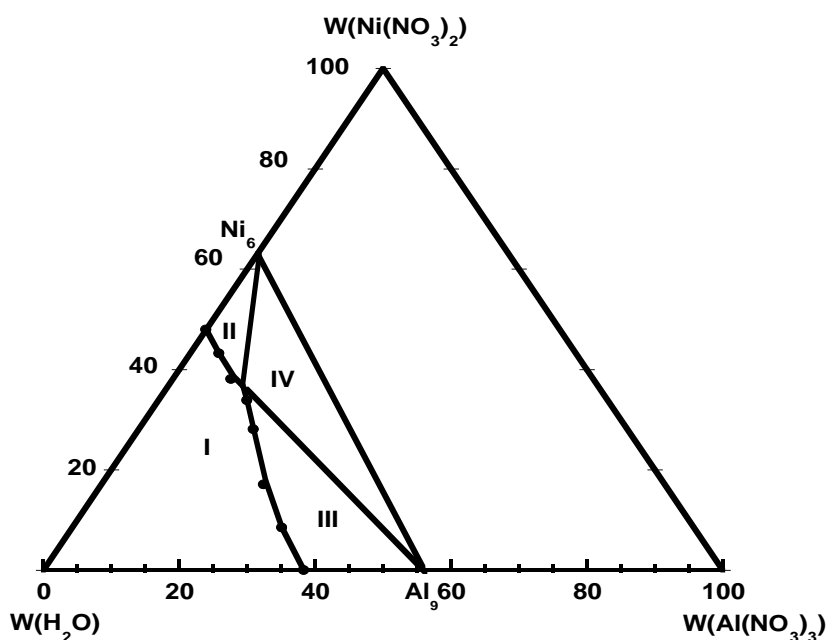The experimental results of the solubility isotherm obtained at 20°C are given in Figure 1.

Fig. 1. The 20°C solubility isotherm of $Al(NO_3)_3$-$Ni(NO_3)_2$-H_2O ternary system

3. Page and column layout

The details of ion- interaction have already been discussed in preceding PITZER publication, the following equation 1, 2 and 3 are the main equations employed in our calculations.

$$(\varphi_{osmotic} - 1) = \frac{2}{\Sigma_i m_i} \begin{bmatrix} \frac{-A_\phi I^{\frac{3}{2}}}{\left(1+bI^{\frac{1}{2}}\right)} + \Sigma_c \Sigma_a m_c m_a \left(B_{ca}^\phi + ZC_{ca}\right) \\ + \Sigma_{c<} \Sigma_{c'} m_c m_{c'} \left(\phi_{cc'}^\phi + \Sigma_a m_a \psi_{cc'a}\right) + \\ \Sigma_{a<} \Sigma_{a'} m_a m_{a'} (\phi_{aa'}^\phi + \Sigma_c m_c \psi_{caa'}) \end{bmatrix} \tag{1}$$

$$\ln(\gamma_M) = z_M^2 F + \Sigma_a m_a (2B_{Ma} + ZC_{Ma}) + \Sigma_c m_c (2\phi_{Mc} + \Sigma_a m_a \psi_{Mca}) \tag{2}$$
$$+ \sum_{a<} \sum_{a'} m_a m_{a'} \psi_{Maa'} + z_M \sum_c \sum_a m_c m_a C_{ca}$$

$$\ln(\gamma_X) = z_X^2 F + \Sigma_c m_c (2B_{cX} + ZC_{cX}) + \Sigma_a m_a (2\phi_{Xa} + \Sigma_c m_c \psi_{cXa}) \tag{3}$$
$$+ \sum_{c<} \sum_{c'} m_c m_{c'} \psi_{cc'X} + |z_X| \sum_c \sum_a m_c m_a C_{ca}$$

The summations in Eqs (1), (2) and (3) over c and a respectively are summations over the cations and the anions respectively present in the solution. The various terms in Eqs. (1), (2) and (3) are defined as follows:

$$I = 1/2 \Sigma_i m_i z_i^2 \tag{4}$$
$$Z = \Sigma_i m_i |z_i| \tag{5}$$
$$F = f^\gamma + \Sigma_c \Sigma_a m_c m_a B'_{ca} + \Sigma_{c<} \Sigma_{c'} m_c m_{c'} \phi'_{cc'} + \Sigma_{a<} \Sigma_{a'} m_a m_{a'} \phi'_{aa'} \tag{6}$$
$$f^\gamma = -A_\phi \left[\frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] \tag{7}$$
$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g\left(\alpha_1 I^{\frac{1}{2}}\right) + \beta_{MX}^{(2)} g(\alpha_2 I^{1/2}) \tag{8}$$
$$C_{MX} = C_{MX}^\phi / 2|Z_M Z_X|^{1/2} \tag{9}$$
$$g(x) = 2[1 - (1-x)e^{-x}]/x^2 \tag{10}$$

$$B'_{MX} = \beta_{MX}^{(1)} g'\left(\alpha_1 I^{\frac{1}{2}}\right) + \beta_{MX}^{(2)} g'(\alpha_2 I^{1/2}) \tag{11}$$

$$g'(x) = -2[1 - (1 + x + 1/2x^2)e^{-x}]/x^2 \tag{12}$$

$$\phi_{ij}^{\phi} = \theta_{ij} + {}^{E}\theta_{ij}(I) + I {}^{E}\theta'_{ij} \tag{13}$$

$$\phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij}(I) \tag{14}$$

$$\phi'_{ij} = {}^{E}\theta'_{ij}(I) \tag{15}$$

The ion-interaction model gives an equation for the activity and osmotic coefficient of electrolyte solution depending to four binary parameters, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ} and two ternary ones ψ and θ. These parameters allow us the calculation of the equilibrium constant of each component in the systems at different temperature.

The solubility of hydrated salt in electrolyte solutions can be calculated from thermodynamic equations. For a hydrated salt, $v\,M(NO_3)_{v_M, v_w}H_2O$, the solubility at a given temperature for the dissolution reaction:

$$vM(NO_3)_{v_M, v_w}H_2O \leftrightarrow M^{v_{M^+}} + {}_{v_M}NO_3^- + {}_{v_w}H_2O$$
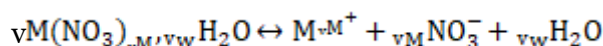
Is given by:

$$K_t = a_{M^+}.\left(a_{NO_3^-}\right)^{v_M}.a_w^{v_w}$$

Where a_i and a_w represent respectively the activity of the ion i and water.

$$K_t = m_{M^+}.\gamma_{M^+}.(m_{NO_3^-}.\gamma_{NO_3^-})^{v_M}(a_w)^w$$

Where m_i and γ_i, represent respectively, the molality and the activity coefficient of the ions i. The activity of water is related to the osmotic coefficient (Pitzer et al., 1977) by the given equation:

$$\ln a_w = -\frac{\phi.\sum_i m_i.M_w}{1000}$$

In which:

M_w Represents the molecular mass of water, the sum covers all solute spices. Activity and osmotic coefficients are calculated by using the PITZER model (Jouaiti et al., 2017; Pitzer et al., 1977).

4. Theoretical model

In this work, the algorithm used is already establshed in a previous article (Jouaiti et al., 2018). One of the most basic parts of this algorithm is on finding the Pitzer parameters for a system that we know the experimental data.

The principle is to change the values of these parameters so that it can minimize the objective function, indeed this function is expressed in terms of the difference between the experimental and theoretical values calculated from the Pitzer parameters at each iteration (Jouaiti et al., 2018).

In the following, we will mainly consider the studied ternary system with a common ion, in this case we're facing three binary PITZER parameters which are already known from literature, and tow ternary ones which are the aim of the present work. The idea is to calculate the equilibrium constant Kb for the binary system for an initial Pitzer parameters, then, the equilibrium constant Kt for the ternary system is calculated from for all experimental molality data (Jouaiti et al., 2018). At the end, the objective function can be calculated as follow:

$$\sum_{i=1}^{N} (K_t(m_c, m_{c'}, m_a) - K_b)^2$$

Where:

N: number of data points in the solubility isotherm.

mc, mc': experimental molality of cation.

ma: experimental molality of anion it can be determined directly from mc and mc'.

During calculation, the ternary Pitzer parameters change to minimize the objective function ω, by the NELDER MEAD method. So, the Pitzer parameters are now obtained by minimizing ω, and the resulting parameters are then considered acceptable for use in the Pitzer model.

**Table 2.** The binary Pitzer parameters for both binary systems Ni(NO3)2, and Al(NO3)3 (Jouaiti et al., 2018)

Salts	β^0	β^1	β^2	C^φ
Ni(NO3)2	0.288	1,437		-0,002
Al(NO3)3	0,703	1,890		0,075

Table 3. The ternary Pitzer parameters determining by iterative

Ternary parameters	$\theta_{Al,Ni}$	$\psi_{Al,Ni,NO3}$
Calculated	-0.267	-0.183

5. Comparison

Figure 2, shows the experimental isotherm for the studied ternary system in comparison with the theoretically elaborated one, using Pitzer model. As it's clear in the graph, the predicted solubilities agree very well with the experimental data.
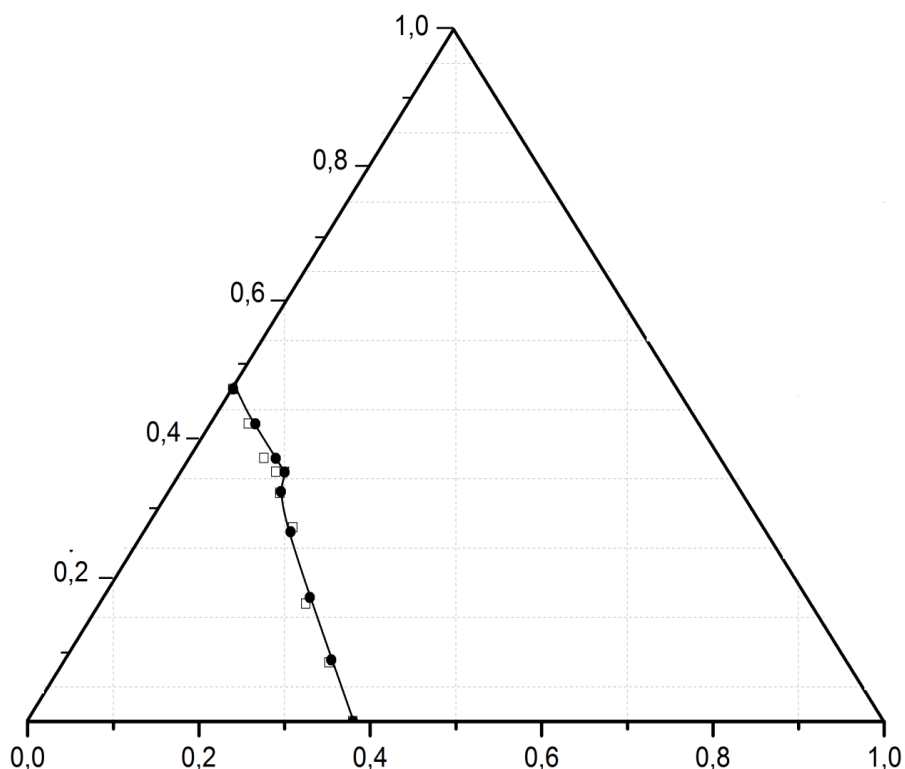
Fig. 2. Experimental and calculated solubility of Al(NO3)3,-Ni(NO3)2-H2O system at 20°C, (□: experimental data,—•— calculated results obtained by using the Pitzer parameters in Table 2)

6. Conclusion

Because of the low solubility of Al(NO3)3,9H2O, the Pitzer parameters cannot be determined from isopiestic measurements in the binary system. Therefore, solubilities in the ternary system

Al(NO3)3-Ni(NO3)2-H2O are applied to evaluate these parameters. Indeed, the successful calculations for the system proves that the obtained results experimentally are correct.

7. Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper. Also, they declare that this paper or part of it has not been published elsewhere.

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