Thermodynamics of ions precipitation in mixed-solvent mixtures

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Abstract

A framework derived from thermodynamic principles of solid–liquid equilibrium criteria was formulated to correlate and predict the precipitation of salts from aqueous solutions using organic solvents. The activity coefficient of a given salt in a mixed-solvent mixture was related to the activity coefficients of such a salt in each of the pure solvents (water and organic) using the excess Henry's constant approach (H_i^E). The Wohl's expansion was then employed to model the excess Gibbs free energy (g^E) function. Two equations were provided; the two-suffix equation, and the three-suffix equation. A previously acquired precipitation database was used to evaluate the correlative ability of the framework equations. The precipitation measurements were adequately correlated and predicted by the two interaction parameters equation; the two-suffix equation. However, the three-suffix equation, with three interaction parameters, was more accurate. The regressed interaction parameters can be used as predictive tools to estimate the precipitation fractions (P) for the tested systems for which no experimental data are available. Furthermore, such parameters can be employed to predict the solubilities of the tested salts in the organic solvent. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermodynamic framework; Salts solubilities; Mixed solvents

1. Introduction

The physical chemistry of inorganic–aqueous systems is complex due to phenomenon of interactions such as long-range electrostatic interactions between ions, solvation of ions, and the association between cations and anions. These interactions become more complicated for systems containing inorganic species in mixed-solvent mixtures. None

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of such interactions is sufficiently insignificant in relation to others so that it may be neglected.

Several theories have been proposed to describe the phase behavior of inorganic species in mixed-solvent mixtures (e.g. Ref. [1]). A sensitive test for the abilities of a given theory is its usefulness in understanding the effect of various forces and interactions on structural and thermodynamic properties. Yet, no theoretical treatment exists to fulfill such a purpose. However, various proposed empirical and semi-empirical models give reasonable approximation in targeted applications (e.g. Refs. [2–5]).

One goal of solution thermodynamics is to formulate models to describe quantitatively the phase behavior of pure fluids and mixtures. Most of these models are semi-empirical and their development and evaluation require phase equilibrium data, and proper mathematical and statistical tools. Therefore, in engineering applications, one of the main advantages of thermodynamic models is the reduction of experimental efforts [6].

The objective of this work was to formulate a thermodynamics framework as a means to predict the phase behavior of the precipitation process that we have developed in our previous work [7,8]. A previously acquired precipitation database [9] was employed to evaluate the framework equations. The impetus of this modeling effort was guided by the fact that precipitation measurements are costly and time consuming [9]. Thus, a practical framework with theoretical foundation, minimum empiricism, and acceptable prediction ability is needed.

2. Model development

The approach followed here is to transcend the complexity of inorganics phenomenon interactions (ion–ion and ion–solvent interactions), while providing a simple and practical model, using basic thermodynamic principles. As such, a system of a given salt in a mixed-solvent mixture (water and organic) is treated as a ternary system with explicit account only for solvent–solvent interactions. Following is a presentation of the developed model.

2.1. Salt solubility in a mixed-solvent mixture

The phase behavior of a given system can generally be described by the change in Gibbs free energy of mixing. For solid–liquid mixtures, the change in Gibbs free energy $(\mathrm{d}G)$ is given by equating chemical potentials or equivalent fugacities in the two phases:

$$\mathrm{d}G = \mu_i^s - \mu_i^L = RT\left[\ln \frac{f_i^s}{\hat{f}_i^L}\right] = 0 \tag{1}$$

or

$$f_i^s = \hat{f}_i^L, \tag{2}$$

where μ_i^s is the chemical potential of a solid salt, μ_i^L is the chemical potential of the salt in a liquid solution, R is the gas constant, T is the temperature, f_i^s is the fugacity of the solid salt, and $\hat{f}_i^{\ L}$ is the fugacity of the salt in a liquid solution. Eq. (1) or Eq. (2) can fundamentally be applied to virtually any given solute in a mixture [10,11], including salts [12]. In the case of a salt that forms crystal hydrate, however, Eq. (2) provides a fundamental relation, which crudely describes the essential behavior of a salt in the solid and liquid phases, considering the solid phase as a pure salt, but neglecting the crystal hydrate formation within the solid phase.

The fugacity of a salt in a liquid mixture ($\hat{f}_i^{\ L}$) can be given as follows:

$$\hat{f}_i^L = x_i \gamma_i f_i^o, \tag{3}$$

where x_i is the mole fraction of a salt, γ_i is the symmetric activity coefficient of a salt, and f_i^o is the hypothetical fugacity of the salt in the mixture. The solubility (mole fraction) of a given salt can thus be written as follows:

$$\ln x_i = \ln\left[\frac{f_i^s}{f_i^o}\right] - \ln \gamma_i. \tag{4}$$

The activity coefficient is either defined by Raoult's law with reference to an ideal solution (symmetric activity coefficient: $\gamma_i \to 1$ as $x_i \to 1$; $\gamma_i = \hat{f}_i^{\ L}/x_i f_i^o$), or by Henry's law with reference to an ideal dilute solution (unsymmetric activity coefficient: $\gamma_i^* \to 1$ as $x_i \to 0$; $\gamma_i^* = \hat{f}_i^{\ L}/x_i H_i$). The symmetric activity coefficient, however, is related to the unsymmetric activity coefficient by the following relation [13]:

$$\lim_{x_i \to 0} \ln \gamma_i = \ln \gamma_i - \ln \gamma_i^* \tag{5}$$

or

$$\lim_{x_1 \to 0} \ln \gamma_i = \ln\left[\frac{H_i}{f_i^o}\right], \tag{6}$$

where H_i is the Henry's constant of a salt in a mixture.

If the salt is labeled as species 1, water as species 2, and organic solvent as species 3, expressions for the solubilities of the salt in the: (1) water solvent ($x_{1,2}$); (2) organic solvent ($x_{1,3}$); and (3) mixed-solvent ($x_{1,m}$) can be derived, respectively, as follows:

$$\ln x_{1,2} = \ln\left[\frac{f_1^s}{H_{1,2}}\right], \tag{7}$$

$$\ln x_{1,3} = \ln\left[\frac{f_1^s}{H_{1,3}}\right], \tag{8}$$

$$\ln x_{1,m} = \ln\left[\frac{f_1^s}{H_{1,m}}\right]. \tag{9}$$

The fundamental application of the above equations hinges on the validity of Henry's law. Henry's law provides a good approximation for the solubility of a given solute in a

solution at ''low'' concentrations. The term ''low'', however, depends on the chemical identities of both solute and solvents. In this work, the initial concentrations, $x_{1,2}$, of the tested salts in pure water (chloride ions: 5000 and 10,000 mg/l, $\approx 10^{-3}$ to 10^{-4}; sulfate ions: 1000 mg/l, $\approx 10^{-4}$ to 10^{-5}) to be suppressed by adding an organic solvent is very low, and decrease ($x_{1,m}$) as the amount of the organic solvent increases. Furthermore, the solubility of the tested salts in the organic solvent ($x_{1,3}$) is extremely low. As such, the use of Henry's Law is valid for the tested systems ($x_{1,3} < x_{1,m} < x_{1,2}$: 10^{-3} to 10^{-5}).

In most problems involving the solubility of a solid solute in a mixed-solvent mixture, the solvent compositions are approximated by their solute-free volume fractions [10,13]. The volume fraction is given as follows:

$$\theta_i = \left[\frac{x_i v_i}{\displaystyle\sum_{i=2}^{3} x_i v_i} \right], \tag{10}$$

where v_i is the pure solvent molar volume. As $x_{1,m}$ decreases ($x_{1,m}$ or $\theta_1 \to 0$) with the increase in the volume of the organic solvent, the volume fractions of the mixed solvents become approximately salt-free ($\theta_2 + \theta_3 \approx 1$).

Using Eqs. (7) and (8), expressions for the f_i^s can be derived in terms of the salt-free volume fractions of the solvents as follows:

$$\ln f_1^s = \theta_2 \left[\ln x_{1,2} + \ln H_{1,2} \right] + \theta_3 \left[\ln x_{1,3} + \ln H_{1,3} \right]. \tag{11}$$

Substituting Eq. (11) into Eq. (9), leads to

$$\ln x_{1,m} = \theta_2 \ln x_{1,2} + \theta_3 \ln x_{1,3} - \ln H_1^E, \tag{12}$$

where H_1^E is the excess Henry's constant and given as follows:

$$\ln H_1^E = \ln H_{1,m} - \theta_2 \ln H_{1,2} - \theta_3 \ln H_{1,3}. \tag{13}$$

2.2. The excess gibbs free energy (g^E) function

To use Eq. (12), an expression for the H_i^E in terms of activity coefficients is needed. The g^E function can be employed to obtain such an expression. Models such as the one-term Margules, van Laar, Wohl expansion, Kirkwood–Buff, Wilson, T–K–Wilson, and others can be employed to express the g^E function [10,11,13]. These models involve semi-empirical correlations for activity coefficients with the exception of the Kirkwood–Buff model, which is based on the statistical mechanical theory [11].

The Wohl expansion model and its special cases (e.g. the one-term Margules and the van Laar models) do not require knowledge of the solute–solvent interactions. In contrast, knowledge of such interactions is needed for models such as the Wilson or the T–K–Wilson to characterize the nonideality of the system. As such, the simplicity of the Wohl's expansion model compared to other models makes it more appropriate as a general form to model the H_i^E of a salt in a mixed-solvent mixture.

According to the Wohl's expansion model [14], the g^E of a ternary mixture (three-suffix) is expressed in terms of increasing powers of the volume fractions (θ) of the treated species as follows:

$$\frac{g^E}{RT[\,x_1 v_1 + x_2 v_2 + x_3 v_3\,]} = 2a_{12}\theta_1\theta_2 + 2a_{13}\theta_1\theta_3 + 2a_{23}\theta_2\theta_3$$

$$+\, 3a_{112}\theta_1^2\theta_2 + 3a_{122}\theta_1\theta_2^2 + 3a_{113}\theta_1^2\theta_3$$

$$+\, 3a_{133}\theta_1\theta_3^2 + 3a_{223}\theta_2^2\theta_3 + 3a_{233}\theta_2\theta_3^2$$

$$+\, 6a_{123}\theta_1\theta_2\theta_3, \tag{14}$$

where the v's are the effective volume or cross-section of the molecules, and the a's are the interaction parameters. The ratio of the v's is assumed to be the same as the ratio of the pure component liquid molar volumes [13]. The following abbreviations can be introduced [14]:

$$v_1[2a_{12} + 3a_{122}] = \Lambda_{12}, \tag{15}$$

$$v_2[2a_{12} + 3a_{112}] = \Lambda_{21}, \tag{16}$$

$$v_1[2a_{13} + 3a_{133}] = \Lambda_{13}, \tag{17}$$

$$v_3[2a_{13} + 3a_{113}] = \Lambda_{31}, \tag{18}$$

$$v_2[2a_{23} + 3a_{233}] = \Lambda_{23}, \tag{19}$$

$$v_3[2a_{23} + 3a_{223}] = \Lambda_{32}, \tag{20}$$

$$\Lambda_1\left[\frac{v_2}{v_1}\right] = \Lambda_2. \tag{21}$$

The activity coefficient is related to the g^E by the following relation [13]:

$$RT \ln \gamma_i = \left[\frac{\partial g^E}{\partial x_i}\right]_{T,p,x_1}. \tag{22}$$

The Wohl's definition of g^E is based on the symmetric activity coefficients, and thus in this case, the unsymmetric activity coefficients are already related to those of the symmetric ones. Therefore, the activity coefficient of a given salt (γ_1) in a mixed-solvent mixture can be obtained by differentiating Eq. (14) with respect to x_1 (θ_1) using the abbreviations given by Eqs. (15)–(21):

$$\ln \gamma_1 = \theta_2^2\left\{\Lambda_{12} + 2\theta_1\left[\Lambda_{21}\left(\frac{v_1}{v_2}\right) - \Lambda_{12}\right]\right\} + \theta_3^2\left\{\Lambda_{13} + 2\theta_1\left[\Lambda_{31}\left(\frac{v_1}{v_3}\right) - \Lambda_{13}\right]\right\}$$

$$+\, \theta_2\theta_3\left\{\Lambda_{21}\left(\frac{v_1}{v_2}\right) + \Lambda_{13} - \Lambda_{32}\left(\frac{v_1}{v_3}\right) + 2\theta_1\left[\Lambda_{31}\left(\frac{v_1}{v_3}\right) - \Lambda_{13}\right]\right.$$

$$\left. +\, 2\theta_3\left[\Lambda_{32}\left(\frac{v_1}{v_3}\right) - \Lambda_{23}\left(\frac{v_1}{v_2}\right)\right] - \Lambda_1(1 - 2\theta_1)\right\}. \tag{23}$$

The number of adjustable parameters can be reduced by neglecting the third body of interactions between the salt and each of the solvents [14]:

$$a_{122} = a_{112}, \tag{24}$$

$$a_{113} = a_{133}. \tag{25}$$

It should be pointed out that the van Laar equation [15] can be obtained if the same justification is applied to the solvent–solvent interaction parameters (Λ_{23} and Λ_{32}) by setting [14]:

$$a_{223} = a_{233}. \tag{26}$$

The approximations given by Eqs. (24) and (25), lead to

$$\frac{\Lambda_{21}}{\Lambda_{12}} = \frac{v_2}{v_1}, \tag{27}$$

$$\frac{\Lambda_{31}}{\Lambda_{13}} = \frac{v_3}{v_1}. \tag{28}$$

As x_1 (θ_1) approaches zero, and by introducing Eqs. (27) and (28) into Eq. (23), expressions for the activity coefficients of a given salt in the: (1) water solvent ($\gamma_{1,2}$); (2) organic solvent ($\gamma_{1,3}$); and (3) mixed-solvent mixture ($\gamma_{1,m}$) can be given as follows:

$$\lim_{x_1 \to 0} \ln \gamma_{1,2} = \Lambda_{12}, \tag{29}$$

$$\lim_{x_1 \to 0} \ln \gamma_{1,3} = \Lambda_{13}, \tag{30}$$

$$\lim_{x_1 \to 0} \ln \gamma_{1,m} = \Lambda_{12}\theta_2 + \Lambda_{13}\theta_3 + \Lambda_{32}\theta_2\theta_3\frac{v_1}{v_3}[2\theta_3 - 1]$$

$$- \Lambda_{23}2\theta_2\theta_3^2\frac{v_1}{v_2} - \Lambda_1\theta_2\theta_3, \tag{31}$$

where Λ_{12} and Λ_{13} are interaction parameters between the salt and the solvents, Λ_{23} and Λ_{32} are interaction parameters between the solvents, and Λ_1 is the salt binary-solvent interaction parameter (ternary constant). Eq. (31) reveals that the salt–solvents interaction parameters (Λ_{21} and Λ_{31}) are canceled out. This demonstrates the simplicity of the Wohl expansion model [14] over, for instance, the Wilson equation [16] or the T–K–Wilson equation [17].

Substituting Eqs. (29)–(31) into Eq. (13) through the use of Eq. (6), leads to

$$\ln H_1^{\mathrm{E}} = \theta_2\theta_3[2\theta_3 - 1]\Lambda_{32}\frac{v_1}{v_3} - 2\theta_2\theta_3^2\Lambda_{23}\frac{v_1}{v_2} - \theta_2\theta_3\Lambda_1. \tag{32}$$

It should be noted that the f_1^{o} is canceled out in the final expression of the H_1^{E}. This demonstrates the convenience of using the H^{E} approach (the numerical value of f_1^{o} is not of concern). Substituting Eq. (32) into Eq. (12), leads to the three-suffix equation for the solubility of a given salt in a mixed-solvent mixture:

$$\ln x_{1,m} = \theta_2 \ln x_{1,2} + \theta_3 \ln x_{1,3} - \theta_2\theta_3[2\theta_3 - 1]\Lambda_{32}\frac{v_1}{v_3}$$

$$+ 2\theta_2\theta_3^2\Lambda_{23}\frac{v_1}{v_2} + \theta_2\theta_3\Lambda_1. \tag{33}$$

Rearranging Eq. (33), leads to

$$\ln\left[\frac{x_{1,m}}{x_{1,2}}\right] = \theta_3 \ln\left[\frac{x_{1,3}}{x_{1,2}}\right] - \theta_2 \theta_3 [2\theta_3 - 1] \Lambda_{32} \frac{v_1}{v_3} + 2\theta_2 \theta_3^2 \Lambda_{23} \frac{v_1}{v_2} + \theta_2 \theta_3 \Lambda_1.$$

(34)

The precipitation measurements are presented in terms of salts precipitation fractions (P) upon the addition of an organic solvent to an aqueous solution. Therefore, the left-hand side of Eq. (34) can be related to the P as follows [9]:

$$\ln\left[\frac{x_{1,m}}{x_{1,2}}\right] = \ln[1 - P].$$

(35)

As such, the final expression for the ternary three-suffix equation for the precipitation measurements is given as follows:

$$\ln[1 - P] = \theta_3 \ln\left[\frac{x_{1,3}}{x_{1,2}}\right] - \theta_2 \theta_3 [2\theta_3 - 1] \Lambda_{32} \frac{v_1}{v_3} + 2\theta_2 \theta_3^2 \Lambda_{23} \frac{v_1}{v_2} + \Lambda_1 \theta_2 \theta_3.$$

(36)

Similarly, a ternary two-suffix equation can also be obtained by ignoring the third body of interactions in Eq. (14), and following the same procedure that led to Eq. (36). Accordingly, the final expression for the ternary two-suffix equation can be given as follows:

$$\ln[1 - P] = \theta_3 \ln\left[\frac{x_{1,3}}{x_{1,2}}\right] + \theta_2 \theta_3 \Lambda_{32} \frac{v_1}{v_3}.$$

(37)

2.3. Solvent–solvent interaction parameters

If the solubility of a tested salt in an organic solvent is available ($x_{1,3}$), the solvent–solvent interaction parameters (Λ_{23} and Λ_{32}) can be obtained from the vapor–liquid equilibrium data. The vapor–liquid equilibrium data can be used to fit the g^E to any suffix equation. The g^E for the ternary three-suffix equation is given as follows:

$$\frac{g^E}{RT} = \theta_2 \theta_3^2 \Lambda_{23}\left[\frac{x_2 v_2 + x_3 v_3}{v_2}\right] + \theta_2^2 \theta_3 \Lambda_{32}\left[\frac{x_2 v_2 + x_3 v_3}{v_3}\right]$$

(38)

and the g^E for the ternary two-suffix equation is given as follows:

$$\frac{g^E}{RT} = \theta_2 \theta_3 \Lambda_{23}\left[\frac{x_2 v_2 + x_3 v_3}{v_3}\right],$$

(39)

where

$$\frac{g^E}{RT} = \sum_{i=2}^{3} x_i \ln \gamma_i = x_2 \ln \gamma_2 + x_3 \ln \gamma_3.$$

(40)

As shown by Eq. (40), the activity coefficients of the salt-free solvents (water–organic) are needed. The UNIFAC model, which is a group contribution method, can be used to estimate the activity coefficients of organic–aqueous systems (e.g., Refs. [18–20]). The UNIFAC model should provide good estimates for the activity coefficients of miscible organics in aqueous systems, since such systems are relatively simple [6]. The solvent–solvent properties (γ_i, x_i, and v_i) can then be employed to estimate Λ_{23} and Λ_{32} by combining either Eq. (38) or Eq. (39) with Eq. (40).

3. Results and discussion

3.1. Database used

Previously acquired experimental precipitation measurements on chloride and sulfate salts using isopropylamine (IPA) as a precipitation solvent [9] were employed to evaluate the framework equations. The measurements include: (1) chloride ions at 5000 mg/l: magnesium, magnesium–sodium, magnesium–potassium, calcium, calcium–sodium, calcium–potassium, calcium–magnesium, calcium–barium, and calcium–strontium; (2) chloride ions at 10,000 mg/l: magnesium, magnesium–sodium, magne-

Table 1
The two-suffix equation (Eq. (37)) representation of the tested systems
$c_1 = \ln[x_{1,3}/x_{1,2}]$; $c_2 = \Lambda_{32}$.

System	Model's parameters		RMSE	%AAD	NP
	c_1	c_2			
Chloride ions at 5000 mg/l					
Magnesium	−1.0561	−1.8747	0.0479	6.65	8
Magnesium–Sodium	−1.1476	−0.4333	0.0545	8.22	8
Magnesium–Potassium	−1.1674	−0.0054	0.0517	8.19	8
Calcium	−1.0619	−1.7106	0.0559	8.20	8
Calcium–Sodium	−1.0386	−2.1482	0.0551	8.87	8
Calcium–Potassium	−1.0357	−2.1331	0.0549	8.48	8
Calcium–Magnesium	−1.0911	−1.4655	0.0564	8.29	8
Calcium–Barium	−1.0834	−1.3221	0.0539	8.74	8
Calcium–Strontium	−1.0279	−1.9949	0.0566	9.12	8
Chloride ions at 10,000 mg/l					
Magnesium	−1.1179	−0.6211	0.0533	8.10	8
Magnesium–Sodium	−1.1211	−0.4171	0.0423	5.72	8
Magnesium–Potassium	−1.1033	−1.1037	0.0448	6.93	8
Calcium	−1.1015	−0.7582	0.0488	6.97	8
Calcium–Sodium	−1.1148	−1.0236	0.0429	7.36	8
Sulfate ions at 1000 mg/l					
Magnesium	−1.4701	1.1334	0.0289	6.47	8
Calcium–Magnesium	−2.2507	0.2566	0.0372	4.47	8
Calcium–Sodium	−2.1647	−1.1747	0.0616	4.58	7
Calcium–Potassium	−4.5601	7.8052	0.3085	10.02	7
Calcium	−6.5038	5.8016	0.1264	3.90	8

sium–potassium, calcium, and calcium–sodium; and (3) sulfate ions at 1000 mg/l: calcium, magnesium, calcium–magnesium, calcium–sodium, and calcium–potassium. Detailed information regarding the tested precipitation database can be found elsewhere [9]. It should be pointed out that species 1, which is given in Section 2, is referred to the chloride or sulfate ion in any given salt system.

3.2. Data reduction procedure

Regressions of the precipitation measurements were performed using the weighted least squares objective function (SS). A Marquardt nonlinear regression procedure was employed in the precipitation calculations [21]. The objective function, SS, used for the evaluation of the model equations is given as follows:

$$SS = \sum_{i=1}^{NP} \left[\frac{Y_{cal} - Y_{exp}}{Y_{exp}} \right],$$ (41)

where Y_{cal} is the calculated variable, and Y_{exp} is the experimental variable, and given as follows:

$$Y = \ln[1 - P].$$ (42)

According to Eq. (41), the root mean square error (RMSE) provides an appropriate

Table 2
The three-suffix equation (Eq. (36)) representation of the tested systems
$c_1 = \ln[x_{1,3} / x_{1,2}]$; $c_2 = \Lambda_{32}$; $c_3 = \Lambda_{23}$.

System	Model's parameters			RMSE	%AAD	NP
	c_1	c_2	c_3			
Chloride ions at 5000 mg/l						
Magnesium	−2.3042	2.5413	3.5875	0.0129	2.07	8
Magnesium–Sodium	−2.7322	5.2114	4.9460	0.0123	2.19	8
Magnesium–Potassium	−2.5727	5.1708	4.4624	0.0180	3.18	8
Calcium	−2.6175	3.7341	4.5919	0.0096	1.53	8
Calcium–Sodium	−2.7405	3.5254	4.9728	0.0172	2.17	8
Calcium–Potassium	−2.7263	3.4764	4.9418	0.0186	3.23	8
Calcium–Magnesium	−2.7404	4.2334	4.9415	0.0158	2.30	8
Calcium–Barium	−2.7466	4.3612	5.0166	0.0180	2.55	8
Calcium–Strontium	−2.6893	3.6870	4.8689	0.0100	1.67	8
Chloride ions at 10,000 mg/l						
Magnesium	−2.5388	4.5891	4.3836	0.0078	1.34	8
Magnesium–Sodium	−2.1536	3.4519	3.1999	0.0124	2.17	8
Magnesium–Potassium	−2.2357	3.0572	3.3753	0.0090	1.72	8
Calcium	−2.3912	3.9640	3.9432	0.0048	0.87	8
Calcium–Sodium	−2.2308	3.0538	3.3416	0.0138	2.44	8
Sulfate ions at 1000 mg/l						
Magnesium	−2.3699	2.2162	1.1202	0.0264	4.18	8
Calcium–Magnesium	−3.0013	1.1303	0.3901	0.0310	4.22	8
Calcium–Sodium	−4.2572	−0.7614	1.8197	0.0156	1.08	7
Calcium–Potassium	−9.1327	16.4653	5.8814	0.0507	3.35	7
Calcium	−9.0664	9.4756	3.3240	0.0785	3.03	8

measure for the overall performance of the model for a given data set more so than the percentage average absolute deviation (%AAD).

3.3. Model evaluations

The acquired precipitation database was used to test and evaluate Eqs. (36) and (37). Tables 1 and 2 present a summary of the results of the tested equations (Eqs. (36) and (37)) for the studied systems. These tables include interaction parameters of the model equations and complete statistics.

Due to the lack of knowledge in the solubilities of the tested chloride and sulfate salts in IPA ($x_{1,3}$), Eqs. (38)–(40) were not used to estimate the solvent–solvent interaction parameters. The solvent–solvent interaction parameters (Λ_{23} and Λ_{32}) were obtained using the objective function of Eq. (41) through the precipitation calculations. However, $x_{1,3}$ can be reasonably estimated from the regressed parameters of Eq. (36) or Eq. (37).

As demonstration cases, Figs. 1–3 present samples of graphical representations (magnesium chloride: 5000 and 10,000 mg/l; magnesium sulfate: 1000 mg/l) that reveal the experimental precipitation measurements along with the fit of Eqs. (36) and (37). These figures exhibit plots of the left-hand side of these equations vs. the IPA salt-free volume fraction (θ_3). Without the addition of IPA, the left-hand side of these equations is zero, since there is no precipitation ($P = 0$). However, without the use of the solvent–solvent interaction parameters (Λ_{32} and/or Λ_{23}), the precipitation measure-
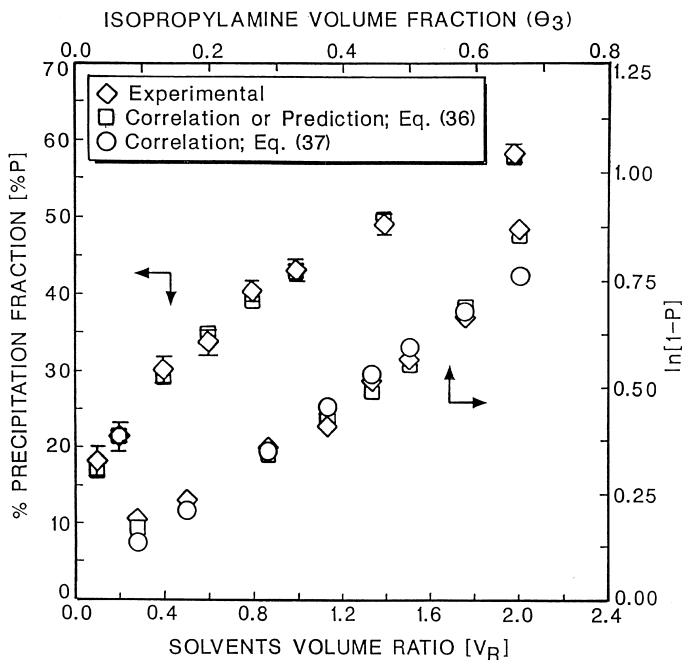

Fig. 1. Precipitation of 5000 mg/l of chloride ion from magnesium–chloride system.
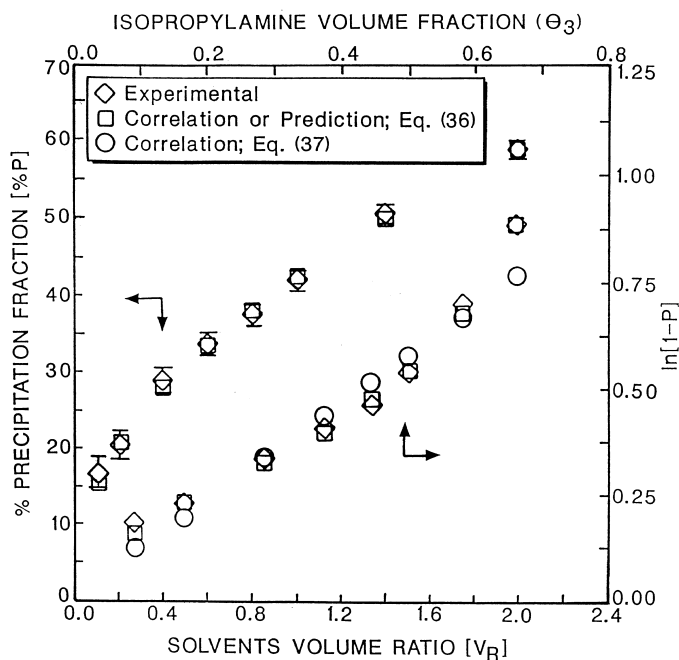
Fig. 2. Precipitation of 10,000 mg/l of chloride ion from magnesium–chloride system.

ments can be fit with a straight line. This situation is equivalent to the ideal mixture solubility based on Henry's law. To extend the model fitting to the maximum value of θ_3, the solvent–solvent interaction parameters are needed to account for the nonideality.

The three-suffix equation, Eq. (36), with four interaction parameters (including Λ_1) represents the ultimate correlative ability. Such a level of complexity may be excessive, since the RMSE for the precipitation measurements using Eq. (36) without Λ_1 are mostly within the expected experimental uncertainty in the combined precipitation data sets used. Hence, the salt binary-solvent interaction parameter (Λ_1) in Eq. (36) is neglected.

As shown in Table 1, Eq. (37), the two-suffix equation, with one solvent–solvent interaction parameter (Λ_{32}) provides good predictions over the entire range of θ_3. As given in Table 2, however, some improvements in the predictive ability were achieved when the two solvent–solvent interaction parameters were employed by Eq. (36), the three-suffix equation (e.g., for magnesium chloride system at 5000 mg/l; Eq. (37): RMSE = 0.0479, %AAD = 6.65; Eq. (36): RMSE = 0.0129, %AAD = 2.07). Such improvements were attributed to the unsymmetric solvent–solvent interaction parameters with respect to θ_3. The combination of these two solvent–solvent interaction parameters (Λ_{32} and Λ_{23}) in Eq. (36) provides good correlation for the precipitation measurements. While both the two-suffix and three-suffix equations are capable of correlating the solubility phase behavior of a salt in a mixed-solvent mixture, the three-suffix equation is statistically superior.
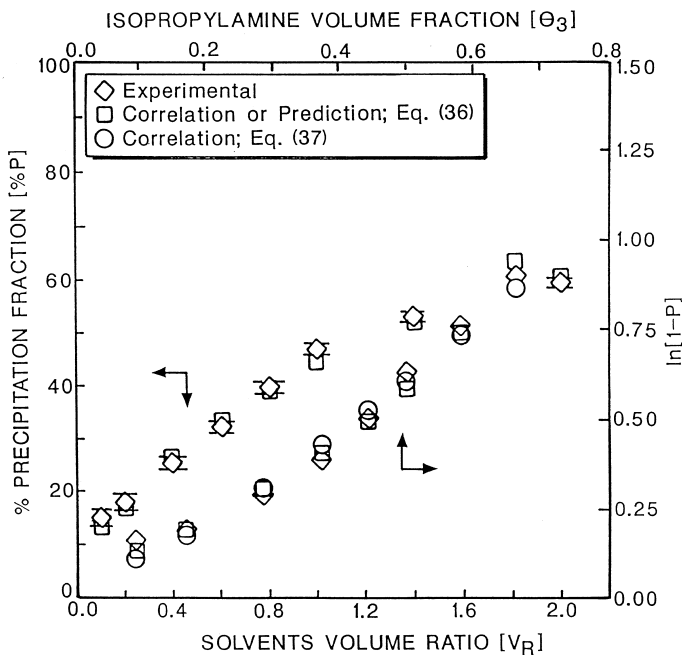
Fig. 3. Precipitation of 1000 mg/l of sulfate ion from magnesium–sulfate system.

Samples of graphical representations of the experimental P at different solvents volume ratio (V_R) along with their error intervals, and the predicted P by the optimum predictive equation, Eq. (36), are also given in Figs. 1–3. These figures, as demonstration cases, reveal the ability of Eq. (36), the three-suffix equation, to accurately predict the P of the studied systems.

Since the P of all chloride ions (at 5000 and 10,000 mg/l) are almost identical [9], general interaction parameters are regressed using all the chloride salts systems (14 systems). The general regressed parameters for all chloride using the three-suffix equation, the optimum predictive case, along with the statistics are given as follows: $C_1 = -2.0509$; $C_2 = 5.4493$; $C_3 = 3.0554$; RMSE = 0.0510; %AAD = 12.42; and NP = 112. These parameters can be used to estimate the P of the tested chloride systems at higher values of V_R (e.g., $V_R = 3.0$ or 4.0, etc.) or possibly at different chloride concentrations where no experimental data are available. This would provide economy of experimental effort and cost savings (not to waste the organic solvent).

Several factors would determine the suitability of a selected organic solvent for the precipitation process. However, one of the most important factors in selecting the organic solvent is the solubility of the targeted salt in such a solvent [22]. A further benefit of the model's interaction parameters is to provide a reasonable estimate for the solubility of the targeted salts in the organic solvent. The estimate of the salt solubility in the organic solvent would facilitate further interpretation to the controlling factors in the precipitation phenomenon.

Tables 3 and 4 present the estimated solubilities of chloride and sulfate salts in IPA ($x_{1,3}$ in terms of $C_{1,3}$) using the interaction parameter (C_1) of Eq. (36), the optimum predictive case. The solubility of a salt in a simple organic solvent is typically orders of magnitude less than the aqueous salt solubility [23]. As shown in Table 3, the solubilities of the chloride salts in IPA are about 7% of their aqueous solubilities. Table 4, however, indicates that solubilities of sulfate salts in IPA are appreciably varied, and are significantly lower than the solubilities of the chloride salts in IPA (the lower the $x_{1,3}$, the higher the P). This would explain: (1) the relatively low P of the tested chloride salts (e.g. $P \approx 60\%$) compared to the sulfate salts (e.g. $P \approx 98\%$) [9]; and (2) the precipitation orders of the sulfate salts (% P: magnesium sulfate < calcium–magnesium sulfate < calcium–sodium sulfate < calcium–potassium sulfate < calcium sulfate) [9].

It should be pointed out that no experimental data are available regarding the solubilities of the tested salts in IPA to draw a conclusion about the reliability of the

Table 3
Estimation of the solubility of the tested chloride salts in IPA using Eq. (36)

System	$C_{1,2}$ (mg/l)	$C_{1,3}$ (mg/l)
Magnesium		
$MgCl_2 – 6H_2O$	14,340	1432
Magnesium– Sodium		
$MgCl_2 – 6H_2O/$	7163	466
NaCl	4125	268
Magnesium– Potassium		
$MgCl_2 – 6H_2O/$	7163	547
KCl	5246	400
Calcium		
$CaCl_2 – 2H_2O$	10,365	757
Calcium– Sodium		
$CaCl_2 – 2H_2O/$	5184	335
NaCl	4124	266
Calcium– Potassium		
$CaCl_2 – 2H_2O/$	5182	339
KCl	5272	345
Calcium– Magnesium		
$CaCl_2 – 2H_2O/$	5184	335
$MgCl_2 – 6H_2O$	7165	463
Calcium– Barium		
$CaCl_2 – 2H_2O/$	5183	333
$BaCl_2 – 2H_2O$	8616	553
Calcium– Strontium		
$CaCl_2 – 2H_2O/$	5185	352
$SrCl_2 – 6H_2O$	9406	639

Table 4
Estimation of the solubility of the sulfate salts in IPA using Eq. (36)

System	$C_{1,2}$ (mg/l)	$C_{1,3}$ (mg/l)
Magnesium		
$MgSO_4-7H_2O$	2565	239.80
Calcium–Magnesium		
$CaSO_4$ /	711	35.40
$MgSO_4-7H_2O$	1283	63.80
Calcium–Sodium		
$CaSO_4$ /	708	10.00
Na_2SO_4	749	10.60
Calcium–Potassium		
$CaSO_4$ /	705	0.10
K_2SO_4	905	0.11
Calcium		
$CaSO_4$	1412	0.16

estimated values by the model equation. However, it appears that Eq. (36) is capable of predicting the expected trend and providing acceptable estimates.

4. Conclusions

A semi-empirical framework derived from thermodynamic principles was developed to model the precipitation measurements. The framework was based on the criteria of solid–liquid equilibria employing the approach. The Wohl's expansion was used to express the g^E function. The framework provided two flexible and general correlative equations (the two-suffix and three-suffix equations). Both equations were adequate for correlating the precipitation data as well as for estimating optimum interaction parameters. However, the three-suffix equation with three interaction parameters, is quantitatively better than the two-suffix equation with two interaction parameters. The regressed parameters can be used to estimate: (1) the P of studied systems at different concentrations (salt or organic solvent) where no experimental data were available; and (2) solubility of the studied salts in the organic solvent.

Notation

a	Constant characteristic of the interaction between molecules
%AAD	Percentage average absolute deviation
C_i	Model's regression (interaction) parameters
$C_{i,j}$	Concentration of species i in solvent j, mg/l
dG	Change in Gibbs free energy
f_i^s	Fugacity of a pure solute (solid)

$\hat{f}_i^{\,L}$	Fugacity of species i in a liquid solution
$f_i^{\,o}$	Fugacity of the hypothetical pure liquid
g^E	Excess Gibbs free energy function
H_i^E	Excess Henry's constant of species i in liquid solution
H_i	Henry's constant of species i in liquid solution
NP	Number of points
P	Precipitation fraction
R	Gas constant
RMSE	Root mean square error
SS	Objective function
T	Temperature
v_i	Molar volume of solvent i
V_R	Solvent volume ratio (organic/water)
x_i	Mole fraction (solubility) of species i in liquid solution
$x_{i,j}$	Mole fraction (solubility) of species i in solvent j
$x_{i,m}$	Mole fraction (solubility) of species i in mixed-solvent mixture m

Greek symbols

Λ_1	Salt binary-solvent interaction parameter (ternary constant)
Λ_{ij}	Wohl's interaction parameter of species i in solvent j
γ_i	Symmetric activity coefficient of species i in liquid solution
$\gamma_{i,j}$	Symmetric activity coefficient of species i in solvent j
$\gamma_{i,m}$	Symmetric activity coefficient of species i in mixed-solvent mixture m
γ_i^*	Unsymmetric activity coefficient of species i in liquid solution
μ_i^s	Chemical potential of pure solute
μ_i^L	Chemical potential of species i in liquid solution
θ_i	Volume fraction of solvent i

Subscripts

1	Salt species (chloride or sulfate ion)
2	Water solvent
3	Organic solvent
cal	Calculated
exp	Experimental
m	Mixed-solvent mixture

Superscripts

E	Excess
L	Liquid phase
s	Solid phase

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