Contribution of the "Simple Solutions" Concept to Estimate Density of Actinides Concentrated Solutions.

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Abstract

In order to calculate criticality parameters of nuclear fuel solution systems, number density of nuclides are needed and they are generally estimated from density equations (1). Most of the relations allowing the calculation of the density of aqueous solutions containing the electrolytes HNO₃-UO₂(NO₃)₂-Pu(NO₃)₄, usually called "nitrate dilution laws" are strictly empirical. They are obtained from a fit of assumed polynomial expressions on experimental density data. Out of their interpolation range, such mathematical expressions show discrepancies between calculated and experimental data appearing in the high concentrations range.

In this study, a physico-chemical approach based on the isopiestic mixtures rule is suggested. The behaviour followed by these mixtures was first observed in 1936 by Zdanovskii (2) and expressed as: "Binary solutions (i.e. one electrolyte in water) having the same water activity are mixed without variation of this water activity value".

With regards to this behaviour, a set of basic thermodynamic expressions has been pointed out by Ryazanov and Vdovenko (3) in 1965 concerning enthalpy, entropy, volume of mixtures, activity and osmotic coefficient of the components. In particular, a very simple relation for the density is obtained from the volume mixture expression depending on only two physico-chemical variables: i) concentration of each component in the mixture and in their respectively binary solutions having the same water activity as the mixture and ii), density of each component respectively in the binary solution having the same water activity as the mixture.

Therefore, the calculation needs the knowledge of binary data (water activity, density and concentration) of each component at the same temperature as the mixture. Such experimental data are largely published in the literature and are available for nitric acid and uranyl nitrate. Nevertheless, nitric acid binary data show large discrepancies between the authors and need to be revised (4). In the field of this work, density data of uranyl nitrate binary solutions have been tabulated by incorporating recent experimental data to older published tables (5). Due to irreversible formation of colloidal or polymeric species leading to precipitation, plutonium(IV) nitrate binary solution does not exist. Nevertheless, binary data of "fictive" binary solution have be determined by Charrin (6).

The performance of this relation has been checked (5) on experimental density data of ternary solutions HNO₃-UO₂(NO₃)₂-H₂O available in the literature (7-10). The Ryazanov-Vdovenko relation has been also validated on new density data of quaternary mixtures HNO₃-UO₂(NO₃)₂-Pu(NO₃)₄-H₂O (11). The deviation between experimental and estimated values is always lower than 0.4 percent compared to the mean deviation of 0.6 per cent reached with Sakurai-Tachimori (12) mathematical relation.

Theory

Considering the experimental comportment of isopiestic solutions of electrolytes, the Zdanovskii's rule was postulated in 1936 (2). This empirical rule was expressed as,

"Binary solutions (i.e. one electrolyte in water) having the same water activity are mixed without any variation of this water activity value"

The linear relation (1) is the mathematical expression of empirical Zdanovskii's rule:

\[ \sum_{i} \frac{C_i}{C_{i}^{bi}} = 1 \quad \text{(Eq. 1)} \]

In 1965, Ryazanov and Vdovenko (3) demonstrated that the calculation of thermodynamic properties of mixtures is solved most simply when Zdanovskii's rule holds. For example, the volume of a mixture obtained from two binary solutions can be expressed as the additive relation (Eq. 2) involving binary thermodynamic properties of the mixture's components:

\[ V = \frac{C_1}{C_{1}^{bi}} \cdot V_{1}^{bi} + \frac{C_2}{C_{2}^{bi}} \cdot V_{2}^{bi} \quad \text{(Eq. 2)} \]

This additive relation means that the mixture exhibits no excess volume. It has similarly been demonstrated that excess enthalpy of isopiestic mixtures following Zdanovskii's rule is null. Therefore, thermodynamic properties of such
systems also called "simple systems" are similar to those of "ideal systems" apart from the fact that isopiestic binary mixtures instead of pure components mixtures are here taken into account.

Relation (2) has been reformulated by Ryazanov and coll. to expressed density of a mixture of i electrolytes as:

\[ \rho = \frac{\sum C_i (1000 + M_i C_i^b)}{\sum C_i^b \left( \frac{1000 + M_i C_i^b}{\rho_i^b} \right)} \]  

(Eq. 3)

Equation (3) is thermodynamically rigorous on condition that Zdanovskii's experimental comportment holds. This behaviour is followed by many nitrate salts mixtures (13, 14). It must be pointed out that, at the opposite of empirical dilution laws, Ryazanov-Vdovenko (RV) relation doesn't need any density measurement for mixtures. By keeping the same form whatever the nature and the number of the mixture's electrolytes are, this concept is widespread.

Calculation

In the field of the present study, the application of (Eq. 3) only need the knowledge of the following physicochemical data;

- concentration of nitric acid and actinide nitrate in the mixture \((C_{H}, C_{An})\),
- concentrations and densities of the nitric acid and actinide nitrate binary solutions having the same water activity as the mixture respectively noted as \((C_{H}^b, \rho_{H}^b)\) and \((C_{An}^b, \rho_{An}^b)\).

The physicochemical data of binary solutions also called "binary data" are constituted of the triplet \((a_w, m, \rho)\). Therefore, these binary data are characteristics of an electrolyte at a given temperature. Such binary data have been tabulated by the National Bureau of Standards (NBS) for a lot of electrolytes and most often at the unique temperature of 25°C.

After having computed these data in electronic files, the density of electrolyte mixtures is calculated according to the following steps;

- water activity of the mixture is estimating by solving (Eq. 1) according to an iterative procedure,
- the knowledge of the water activity enables us to estimate the couples of data \((C_{H}^b, \rho_{H}^b)\) and \((C_{An}^b, \rho_{An}^b)\) by interpolating the binary data files of nitric acid and actinide nitrate.

Critical Analysis of Binary Data

An extensive study has been carried out to check binary data of nitric acid and actinide (U(VI) or Pu(IV)) nitrate solutions. This preliminary work is required to ensure that validation test of Ryazanov-Vdovenko relation can not be perturbed by eventual inaccuracy of the electrolytes binary data.

Nitric acid binary data \((a_w, m, \rho)\) tabulated by Davis and coll. (15), Redlich (16) and later by Hamer and coll. (17) at 25°C, exhibit large discrepancies. For this reason, Charrin (4) has proposed revised values by adopting a new methodology and taking into account recent experimental results. Density data tabulated in the International Critical Tables (ITC) at 25°C (18) have been successfully checked and has therefore been retained.

The physicochemical data available for uranyl nitrate binary solutions were exhaustively collected by Goldberg (19) for the NBS. Water activities were evaluated after a rigorous critical review of experimental data and thus have been chosen. At the opposite, the density data compiled in the ITC are inaccurate and need to be updated. More recent empirical relations were proposed by Söhnel (20) to describe concentration and temperature dependences of electrolyte solutions densities. Accuracy of such relations to estimate density of uranyl nitrate binary solutions at the unique temperature of 25°C is altered by the multi-temperature interpolation.

To overcome these discrepancies, the experimental densities data available for uranyl nitrate solutions at 25°C have been inventoried and interpolated with assumed polynomial expressions. Four new studies (7, 8, 21, 22) have been taken into account in addition to the two sources of Grant (23) and Kaputinskii (24) already exploited by Söhnel (20). Among the four references, the numerous data measured by Davis during liquid-liquid extraction with TBP have been ignored because of the solubility of the extractant in aqueous solutions. Experimental data have been interpolated as followed:
Plutonium (IV) nitrate dissolution in water results in the irreversible formation of colloidal or polymeric species leading to plutonium precipitation. Thus, preparation of plutonium (IV) nitrate binary solution is impossible. Such experimental limitation can nevertheless be overcome by applying the simple solutions concept to ternary mixtures \( \text{Pu(NO}_3\text{)}_4/\text{HNO}_3/\text{H}_2\text{O} \) (6). Finally, binary data \((C^b_i, a_w, \rho^b_i)\) obtained refer to a "fictive" binary solution.

Validation of Ryazanov-Vdovenko Relation

The performance of this relation has been checked on experimental density data of ternary solutions \( \text{HNO}_3-\text{UO}_2(\text{NO}_3)^2-\text{H}_2\text{O} \) available in the literature (7-10) as shown on Figure 2. The Ryazanov-Vdovenko relation has been also validated on new density data of quaternary mixtures \( \text{HNO}_3-\text{UO}_2(\text{NO}_3)^2-\text{Pu(NO}_3\text{)}_4-\text{H}_2\text{O} \) (11). The mean deviation between experimental and estimated values is always lower than 0.2 percent. This behaviour is greatly better than the one obtained by applying Sakurai mathematical relation which is currently considered to be the most accurate available model for such fissile mixtures.

Conclusions

The "Simple Solutions" concept has already shown its ability to quantify liquid-liquid extraction equilibrium (25), redox kinetics (26) and thermodynamic behavior of electrolytes (6) in highly concentrated media. This study demonstrates its performance in a new application field and confirms, once again, its ability to overcome the difficulties inherent to aqueous concentrated solutions. By avoiding the use of empirical parameters, such physicochemical approach is an attractive alternative to mathematical models.

Footnotes

\( a_w \) : Water activity
\( C_i \) : Molarity of component \( i \) in the mixture (mol.L\(^{-1}\))
\( m_i \) : Molality of component \( i \) in the mixture (mol.kg\(^{-1}\))
\( C_i^{bi} \): Molarity of component \( i \) in the binary solution at the same \( a_w \) as the mixture (mol.L\(^{-1}\))

\( V \): Mixture volume

\( V_i^{bi} \): Volume of the binary solution at the same \( a_w \) as the mixture

\( \rho \): Mixture density (g.cm\(^{-3}\))

\( \rho_i^{bi} \): Density of the binary solution at the same \( a_w \) as the mixture (g.cm\(^{-3}\))

\( M_i \): Molecular weight of component \( i \) (g.mol\(^{-1}\))

References