CHEMISTRY

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1963

SovietRxiv

Abstract

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CHEMISTRY

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STUDY OF THE COCRYSTALLIZATION OF IONIC COMPOUNDS FROM ORGANIC SOLVENTS

(Presented by Academician V. I. Spitsyn on 25 VI 1963)

At present, for the separation of chemical elements, along with other methods, the method of cocrystallization is widely used. The distribution of elements between the crystalline phase and the solution is determined by the practical cocrystallization coefficient (D_{pr}), the magnitude of which depends both on the choice of system and on the ratios of the active concentrations of ions in the solution. In the most frequently encountered case, when each component being separated dissociates into one cation and an equal number of identical anions, the practical cocrystallization coefficient, on the basis of Ratner' s equation (^{1}), can be calculated from the following equations:

$$D_{\text{pr}} = \frac{x}{y}\frac{C'}{C} = \left[\frac{x}{y}\frac{a'_+}{a_+}\right]\frac{\gamma_+}{\gamma'_+}; \tag{I}$$

$$D_{\text{pr}} = \left[\left(\frac{m'_0}{m_0}\frac{\gamma'_{0\pm}}{\gamma_{0\pm}}\right)^{\nu} e^{\frac{\Delta\mu^s}{RT}}\right]\frac{\gamma_+}{\gamma'_+}, \tag{II}$$

where x and y are the amounts of the micro- and macrocomponents in the solid phase, C and C' are the concentrations of the micro- and macrocomponents in solution, a_+ and a'_+ are the activities of the cations of the micro- and macroelements in solution, γ_+ and γ'_+ are, respectively, their activity coefficients, m_0, m'_0 and $\gamma_{0\pm}$, $\gamma'_{0\pm}$ are the solubilities and activity coefficients of the micro- and macrocomponents in their pure saturated solutions, and ν is the number of ions into which they dissociate, $\Delta\mu^s$ is the work of transferring one mole of the microcomponent from its pure crystals into the solid solution.

In equations (I) and (II), the expressions enclosed in square brackets represent the true thermodynamic cocrystallization coefficient (D_0). Then

$$D_{\text{pr}} = D_0\frac{\gamma_+}{\gamma'_+}. \tag{III}$$

The efficiency of separation of elements depends on the practical cocrystallization coefficient. As is evident from equations (I) and (II), the value of the practical cocrystallization coefficient is dependent on the ratio of the activity coefficients of the ions of the micro- and macrocomponents in their common solution. Consequently, a change in this quantity affects the efficiency of separation of elements (^{2}). In addition, the practical cocrystallization coefficient may be changed by introducing a complexing agent into the solution, which can also increase the efficiency of separation of elements (^{3}).

For the separation of elements by the cocrystallization method, the use of non-aqueous solvents may prove promising, since replacement of solvents leads to a change in the true thermodynamic cocrystallization coefficient as a consequence of a change in the ratio of the produc-

introduced activities of the compounds of the micro- and macrocomponents in pure saturated solutions. In addition, on going to low-polarity solvents, the incompleteness of dissociation of the compounds being separated has an effect, which influences the practical cocrystallization coefficient. This phenomenon had not previously been taken into account, since cocrystallization from aqueous solutions was studied, in which ionic compounds are dissociated practically

Table 1

Values of the practical cocrystallization coefficients in the systems studied at 25°

<table>
<tr><th>Systems</th><th>Determined by the isothermal evaporation method</th><th>Determined by the partial recrystallization method</th><th>Adopted values</th></tr>
<tr><td>Rb (K)Cl – ethyl alcohol</td><td>0.50$±0.015|0.55±0.04|0.50||Rb(K)Cl–acetone–watersolution|—|0.31±0.04|0.31||K(Rb)Cl–</td><td>0.85</td><td></td></tr>
</table>

almost completely. As is known, the activity of a substance in the ionic state can be expressed by the following formula: $a = (C \cdot \alpha \cdot \gamma_{\pm})^{\nu}$, and the active concentration of the cation is $a_{+} = C \cdot \alpha \cdot \gamma_{+}$; then equations (I) and (II) take the following form:

$$D_{\text{pr}} = \frac{x}{y}\frac{C'}{C} = \left[\frac{x}{y}\frac{C'\alpha'\gamma'_{+}}{C\alpha\gamma_{+}}\right]\frac{\alpha\gamma_{+}}{\alpha'\gamma'_{+}}; \qquad \text{(IV)}$$

$$D_{\text{pr}} = \left[\left(\frac{m'_0\alpha'_0\gamma'_{0\pm}}{m_0\alpha_0\gamma_{0\pm}}\right)^{\nu} e^{\Delta\mu^{S}/RT}\right]\frac{\alpha\gamma_{+}}{\alpha'\gamma'_{+}}, \qquad \text{(V)}$$

where: α_0 and α_0' are the degrees of dissociation of the micro- and macroelements in their pure saturated solutions, and α and $\alpha_\pm'$ are the degrees of dissociation of the micro- and macroelements in their common solution.

To verify the correctness of equations (IV) and (V), it is necessary to study the system using different solvents. Then, if the concentration of the microcomponent in the solid phase is small, constancy should be observed for the exponential term, which does not depend on the solvent

Table 2

Solubility of potassium and rubidium chlorides in anhydrous ethyl alcohol and in a mixture of acetone with 2.5% water at 25°

<table>
<tr><th>Solvent</th><th>Electrolyte</th><th>Solubility, mg-equiv/l</th></tr>
<tr><td>Ethyl alcohol</td><td>KCl</td><td>3.95$±0.20||Same|RbCl|5.45±0.15||Mixtureofacetonewith</td></tr>
</table>

$$e^{\Delta\mu^S/RT} = D_{\text{pr}}\frac{\alpha'\gamma_+'}{\alpha\gamma_+}\left(\frac{m_0\alpha_0\gamma_{0\pm}}{m_0'\alpha_0'\gamma_{0\pm}'}\right)^\nu . \tag{VI}$$

For the experimental verification of relations (IV) and (V), reciprocal systems of potassium and rubidium chlorides were chosen, since these salts do not form solvates, and, in addition, there are data in the literature on the thermodynamic study of these systems in aqueous solutions (4). Anhydrous ethyl alcohol (specific gravity 0.789) and a mixture of acetone with water containing 2.5% water were used as solvents. To calculate the value of $e^{\Delta\mu^S/RT}$, it was first necessary to determine the practical cocrystallization coefficient (D_{pr}). The practical cocrystallization coefficient in the systems $\text{Rb(K)Cl} - \text{C}_2\text{H}_5\text{OH}$ and $\text{K(Rb)Cl} - \text{C}_2\text{H}_5\text{OH}$ was determined by the isothermal evaporation method (5) and by the partial recrystallization method (6). In those cases where as the solvent were used-

was the mixture of acetone with water, the practical cocrystallization coefficient was determined only by the method of partial recrystallization, since the isothermal evaporation method is not applicable to mixed solvents. The data obtained are presented in Table 1.

The solubility data for potassium and rubidium chlorides that we needed and that were available in the literature differed greatly from one another. In this connection, experiments were carried out to determine these quantities. The solubilities of potassium and rubidium chlorides in anhydrous ethyl alcohol were determined by the radiometric method and by the dry residue, and in a mixture of acetone with 2.5% water only by the radiometric method. The quantities found are given in Table 2.

Table 3

Activity coefficients and degrees of dissociation of potassium and rubidium chlorides at 25°

Solvent	Electrolyte	Average activity coefficients ($\gamma_{0\pm}$)	Degree of dissociation (α_0)	Degree of dissociation of the microcomponent in the saturated solution of the macrocomponent (α)
Ethyl alcohol	KCl	0.698	0.99	–
Same	RbCl	0.671	0.89	0.92
Mixture of acetone with water	KCl	0.91	0.555	0.555
Same	RbCl	0.91	0.542	0.542

Using the solubility values obtained, the degrees of dissociation of each component in pure saturated solutions (α_0) were determined by the electrical-conductivity method. The degree of dissociation of the microcomponent in the saturated solution of the macrocomponent (α) was calculated from the dissociation constant of the microcomponent salt found by us. Since the solubility of potassium and rubidium chlorides in the solvents studied is small, the Debye–Hückel equation is applicable for calculating the average activity coefficients of the micro- and macrocomponents in pure saturated solutions ($\gamma_{0\pm}, \gamma'_{0\pm}$). For the same reason, the activity coefficients of the ions of the micro- and macrocomponents in their common solution are equal to one another. The data obtained are presented in Table 3.

Table 4

Calculated values of $\exp\dfrac{\Delta\mu^s}{RT}$ in the systems studied at 25°

System	$\exp\dfrac{\Delta\mu^s}{RT}$
Rb(K)Cl –H_2O	0.303*
Rb(K)Cl –ethyl alcohol	0.316
Rb(K)Cl –mixture of acetone with water	0.305
K(Rb)Cl –H_2O	0.574*
K(Rb)Cl –ethyl alcohol	0.88
K(Rb)Cl –mixture of acetone with water	0.86

Note. Values marked with an asterisk were taken from literature data.

On the basis of the data obtained, the values of $e^{\Delta\mu^s/RT}$ in the systems studied were calculated; they are presented in Table 4.

As can be seen from Table 4, the values found for different solvents agree well. However, the value of $e^{\Delta\mu^s/RT}$ determined by Makarov for the system K(Rb)Cl $-H_2O$ differs from that obtained by us for this same system in anhydrous ethyl alcohol and in a mixture of acetone with water. Evidently, this is connected with the difficulty of determining this quantity for aqueous solutions, in which the solubility of the salts is high.

Thus, the correctness of the equations proposed by us for calculating the cocrystallization coefficient from solutions in which the components are not completely dissociated has been experimentally confirmed. In addition, it should be noted that, with the aid of organic solvents, in which the solubility of ionic compounds is, as a rule, small, according to the equation

(VI) one can determine the work of formation of the solid solution. Knowing this quantity, one can calculate the true cocrystallization coefficient in any solvent, which is necessary for assessing the efficiency of using one or another solvent for the separation of elements. In addition, starting from the value $e^{\Delta\mu_s/RT}$, the thermodynamic characteristics of the system can be calculated.

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Received
25 VI 1963

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Note: Figure translations are in progress. See original paper for figures.