

# A STUDY OF THE USE OF SOLUBILITY ISOTHERMS TO OBTAIN INFORMATION ABOUT ION HYDRATION AND ION PAIRING IN CONCENTRATED SOLUTIONS OF ELECTROLYTES

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Computational analysis of solubility isotherms in ternary systems consisting of water and two solutes having a common ion was suggested and the respective software was developed. This hydration analysis was applied to model systems  $\text{NH}_4\text{CNS}-\text{NaCNS}-\text{H}_2\text{O}$  at 5, 25 and 50 °C and  $\text{NaX}-\text{KX}-\text{H}_2\text{O}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) at 25 °C. The results obtained are discussed and the way in which the hydration analysis gives information on ionic processes in saturated electrolyte solutions is demonstrated.

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Ion-hydration and ion-pair formation in concentrated solutions of electrolytes are topics of interest to inorganic as well as physical chemists. Some sophisticated experimental methods such as neutron and X-ray diffraction have been used to provide experimental data for these phenomena<sup>1</sup>. Such experimental results can be used together with molecular dynamics<sup>2</sup> and quantum mechanics<sup>3</sup> to give detailed structural information about these processes. However, these methods are time-consuming and require experimental equipment that is fairly expensive and not always readily available<sup>1</sup>. In contrast to that approach, a relationship between the shape of solubility curves and ion-hydration has been mentioned (often in terms of salt-in and salt-out effects<sup>4,5</sup>), but as far we are aware, no attempts have been made to present a quantitative discussion of this approach. It is the purpose of this paper to make such an attempt.

## THEORETICAL

In simple ternary systems consisting of water and two solutes having a common ion, solubility curves of the components will be analyzed. This may be done without considering the hydration of the solid phases. The only requirement is that the solubility isotherm begins with the solubility of a component in water. That is, we start with a saturated solution of component 1 ( $M_q X_p$ ) in water. Then, at constant temperature and pressure, component 2 ( $M'_q X'_p$ ) is added in such a way that the solution remains satu-

rated with respect to component 1. This is represented in Fig. 1 as going from point A to point B and may be continued until the nearest eutonic or peritonic point E is reached.

Point A, a saturated solution of component 1 in water is our reference point. The composition of the saturated solution given by the solubility of the respective component is  $w_1^A$  wt.% of the component 1 and  $w_0^A$  wt.% of water. Similarly, at each point of the solubility curve under consideration the composition of the saturated solution is known as  $w_1^B$  wt.% of the component 1,  $w_2^B$  wt.% of the component 2 and  $w_0^B$  wt.% of water.

Let us define an interaction parameter analogous to solubility product in molal scale as

$$K_s^A = q^q p^p (m_1^A)^{(p+q)}. \quad (1)$$

It is obvious that, in the point B

$$K_s^B = q^q (m_1^B)^q (pm_1^B + p'm_2^B)^p \neq K_s^A. \quad (2)$$

For our purposes we assume that this inequality is due to the fact that some water has changed its properties and is no longer "solvent" water. It means, the total analytical concentration of water has split into two terms

$$w_0^B = (w_0^B)_{\text{changed}} + (w_0^B)_{\text{solvent}} \quad (3)$$

from which only the latter is to be used in calculations of the molalities.

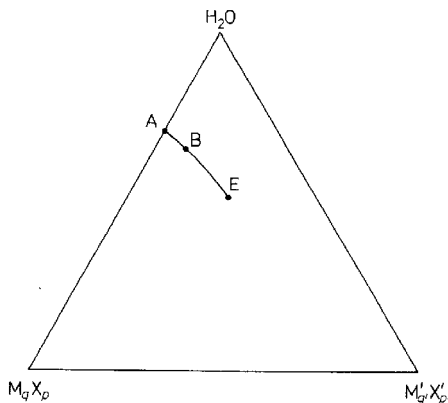


FIG. 1

A scheme specifying the part of solubility isotherm on which the hydration analysis is performed

The value  $(w_0^B)_{\text{solvent}}$  may be calculated as

$$(w_0^B)_{\text{solvent}} = \frac{(n_1^B)^{q/(p+q)} w_0^A}{p^{p/(p+q)} n_1^A} (pn_1^B + p'n_2^B)^{p/(p+q)}, \quad (4)$$

where

$$n_i^A = \frac{w_i^A}{(M_r)_i} \quad \text{and} \quad n_i^B = \frac{w_i^B}{(M_r)_i} \quad (i = 1, 2).$$

In most of the considerations on similar themes, the difference between  $w_0^B$  and  $(w_0^B)_{\text{solvent}}$  is incorporated in the activity coefficients. The water that has changed its properties may be considered as water of hydration where "hydration" is a broad term including, at one extreme, the mere restriction of the mobility and/or exchange reactions of the water molecules in the vicinity of ions, and at the other extreme, the formation of aqua complexes<sup>6</sup>.

We now introduce a parameter,  $P$ , which expresses the number of the moles of water that have changed its properties as a percentage of the total number of moles

$$P = \frac{(w_0^B)_{\text{changed}}}{(M_r)_{\text{H}_2\text{O}} \sum_{i=0}^2 n_i^B}. \quad (5)$$

From the definition and derivation of  $P$  it follows that positive values of  $P$  indicate that water molecules have been removed to the hydration sphere or envelope of ions added or formed in ternary solution. Values of  $P \approx 0$  may be expected when the added ion is unable to compete with ion  $M$  for attracting water molecules or  $X$  ions. Negative values of  $P$  are expected in two situations:

- a) the added ion  $M'$  is a structure breaking with respect to the saturated solution of  $M_q X_p$
- b) the addition of the component 2 may lead to ion-pairing replacing some water molecules that has previously been in hydration envelopes.

In real systems both hydration and ionic interaction occur simultaneously, and both of these are involved in the value of  $P$ , that is, the value of  $P$  is the result of two activities: a positive term related to hydration and a negative term related to ion-pairing. For that reason the values of  $P$  cannot be used solely as an indication of hydration.

Yet the values of  $P$  can provide valuable information about ionic processes in concentrated solutions of electrolytes, especially in the case when reasonably chosen series of systems are analyzed and the results are compared mutually. In making such a "hydration analysis" the analytical concentration of water is an important factor and must be taken into account.

## RESULTS

To illustrate the hydration analysis, following systems were chosen:

1) The solubility values of  $\text{NH}_4\text{CNS}$  in solutions of  $\text{NaCNS}$  at 5, 25 and 50 °C (ref.<sup>7</sup>). The results are given in Table I and the dependence of  $P/x_2$  on  $x_2$  is depicted in Fig. 2.

2) Solubility values for the  $\text{NaX-KX-H}_2\text{O}$  systems at 25 °C where  $\text{X} = \text{Cl}$  (ref.<sup>8</sup>),  $\text{Br}$  (ref.<sup>9</sup>) and  $\text{I}$  (ref.<sup>10</sup>). The values are given in Tables II and III and the hydration analysis of solubilities of potassium halides in solutions of sodium halides, which will be discussed in detail, is depicted in Fig. 3.

For the hydration analysis, a software was developed using the TNS computer and its MBASIC. The respective chart flow is depicted in Fig. 4.

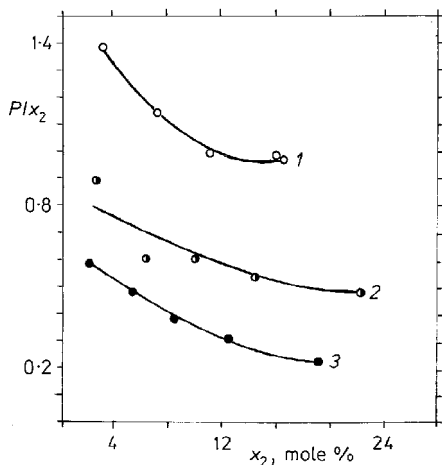


FIG. 2

The dependence of the ratio  $P/x_2$  on  $x_2$  at the solubility branch of  $\text{NH}_4\text{CNS}$  in solutions of  $\text{NaCNS}$ . 1  $T = 5$  °C, 2  $T = 25$  °C, 3  $T = 50$  °C

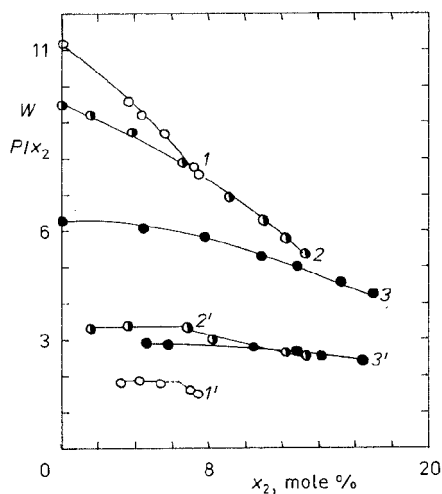


FIG. 3

Hydration analysis of the solubility of  $\text{KX}$  in solutions of  $\text{NaX}$  at 25 °C. 1, 1'  $\text{X} = \text{Cl}$ ; 2, 2'  $\text{X} = \text{Br}$ ; 3, 3'  $\text{X} = \text{I}$ . 1, 2, 3  $W$  is the dependent variable; 1', 2', 3'  $P/x_2$  is the dependent variable

## DISCUSSION

The data in Table I indicate that in the  $\text{NH}_4\text{CNS}-\text{NaCNS}-\text{H}_2\text{O}$  system the  $\text{Na}^+$  ions are hydrated at the expense of the other ions. The values of  $P$  are positive and decrease as the temperature increase. At 50 °C the values of  $P$  range from 0.01 to 0.04 and this could be considered essentially  $P \approx 0$ . In this case, the plot of  $P/x_2$  vs  $x_2$  ( $x_2$  is the molar fraction of the component 2) has proven to be useful. This plot is a smooth curve even at 50 °C. This confirms that the hydration of  $\text{Na}^+$  destroys the hydration sphere of the  $\text{NH}_4^+$  and  $\text{CNS}^-$  ions even under these circumstances.

TABLE I  
Hydration analysis of the solubility of  $\text{NH}_4\text{CNS}$  in  $\text{NaCNS}$  solutions

| $\text{NH}_4\text{CNS}$<br>wt. % | $\text{NaCNS}$<br>wt. % | $\text{H}_2\text{O}$<br>wt. % | $\text{NaCNS}$<br>mole % | $W$<br>mol/mol solute | $P$  | $P/x_2$ |
|----------------------------------|-------------------------|-------------------------------|--------------------------|-----------------------|------|---------|
| $T = 5\text{ }^\circ\text{C}$    |                         |                               |                          |                       |      |         |
| 56.20                            | 0.00                    | 43.80                         | 0.00                     | 3.30                  | 0.00 | –       |
| 49.00                            | 7.70                    | 43.30                         | 3.02                     | 3.26                  | 0.04 | 1.40    |
| 40.20                            | 17.90                   | 41.90                         | 7.17                     | 3.11                  | 0.08 | 1.16    |
| 33.00                            | 26.80                   | 40.20                         | 11.02                    | 2.92                  | 0.11 | 1.02    |
| 24.00                            | 38.00                   | 38.00                         | 16.18                    | 2.69                  | 0.16 | 1.01    |
| 23.10                            | 39.40                   | 37.50                         | 16.91                    | 2.64                  | 0.16 | 0.97    |
| $T = 25\text{ }^\circ\text{C}$   |                         |                               |                          |                       |      |         |
| 64.40                            | 0.00                    | 35.60                         | 0.00                     | 2.34                  | 0.00 | –       |
| 58.60                            | 6.20                    | 35.20                         | 2.73                     | 2.31                  | 0.02 | 0.90    |
| 51.40                            | 14.60                   | 34.00                         | 6.56                     | 2.21                  | 0.04 | 0.62    |
| 45.00                            | 22.00                   | 33.00                         | 10.06                    | 2.13                  | 0.06 | 0.61    |
| 37.50                            | 31.20                   | 31.30                         | 14.70                    | 1.98                  | 0.08 | 0.53    |
| 26.60                            | 45.00                   | 28.40                         | 22.35                    | 1.74                  | 0.11 | 0.48    |
| $T = 50\text{ }^\circ\text{C}$   |                         |                               |                          |                       |      |         |
| 73.80                            | 0.00                    | 26.20                         | 0.00                     | 1.50                  | 0.00 | –       |
| 69.40                            | 4.60                    | 26.00                         | 2.35                     | 1.49                  | 0.01 | 0.59    |
| 63.60                            | 10.90                   | 25.50                         | 5.63                     | 1.46                  | 0.03 | 0.48    |
| 58.60                            | 16.60                   | 24.80                         | 8.70                     | 1.41                  | 0.03 | 0.38    |
| 52.50                            | 23.70                   | 23.80                         | 12.68                    | 1.35                  | 0.04 | 0.30    |
| 42.90                            | 35.10                   | 22.00                         | 19.51                    | 1.23                  | 0.04 | 0.22    |

By contrast the condition of  $P \approx 0$  appears when potassium halide is added to a saturated solution of sodium halide (Table II). In these systems  $K^+$  ions are unable to compete with  $Na^+$  ions for either water or halide ions. In this special case of  $P \approx 0$ , Eq. (2) may be used for correlation and/or prediction of solubility in ternary systems. Accordingly, the solubility values for NaCl in solutions of KCl were calculated at 40 and 70 °C and compared with values in the literature<sup>11</sup>. This is illustrated in Fig. 5. The correlation is essentially the same as that of Vojtisek et al.<sup>12</sup>. However, these authors

TABLE II

Hydration analysis of the solubility isotherm in the NaX-KX-H<sub>2</sub>O (X = Cl, Br, I) system at 25 °C. Solubility of potassium halides in solutions of sodium halides

| KXwt.% | NaX<br>wt.% | H <sub>2</sub> O<br>wt.% | NaX<br>mole % | W<br>mol/mol solute | P    | P/x <sub>2</sub> |
|--------|-------------|--------------------------|---------------|---------------------|------|------------------|
| X = Cl |             |                          |               |                     |      |                  |
| 26.46  | 0.00        | 73.54                    | 0.00          | 11.50               | 0.00 | –                |
| 19.30  | 8.45        | 72.05                    | 3.36          | 9.83                | 0.06 | 1.83             |
| 17.66  | 10.74       | 71.60                    | 4.18          | 9.46                | 0.08 | 1.90             |
| 15.30  | 14.12       | 70.58                    | 5.53          | 8.78                | 0.10 | 1.85             |
| 12.98  | 18.26       | 68.76                    | 7.26          | 7.85                | 0.11 | 1.56             |
| X = Br |             |                          |               |                     |      |                  |
| 40.60  | 0.00        | 59.40                    | 0.00          | 9.67                | 0.00 | –                |
| 34.40  | 6.40        | 59.20                    | 1.71          | 9.36                | 0.06 | 3.32             |
| 26.80  | 14.60       | 58.60                    | 3.92          | 8.87                | 0.13 | 3.34             |
| 18.40  | 24.60       | 57.00                    | 6.71          | 8.04                | 0.22 | 3.26             |
| 12.40  | 33.20       | 54.40                    | 9.35          | 7.08                | 0.28 | 3.04             |
| 10.10  | 37.70       | 52.20                    | 10.93         | 6.43                | 0.30 | 2.75             |
| 8.20   | 41.20       | 50.60                    | 12.20         | 5.99                | 0.33 | 2.68             |
| 6.70   | 44.40       | 48.90                    | 13.46         | 5.57                | 0.35 | 2.58             |
| X = I  |             |                          |               |                     |      |                  |
| 59.78  | 0.00        | 40.22                    | 0.00          | 6.21                | 0.00 | –                |
| 42.08  | 17.60       | 40.32                    | 4.50          | 6.04                | 0.13 | 2.87             |
| 29.79  | 30.55       | 39.66                    | 7.88          | 5.75                | 0.22 | 2.83             |
| 21.43  | 40.11       | 38.46                    | 10.56         | 5.39                | 0.29 | 2.74             |
| 15.90  | 46.91       | 37.19                    | 12.64         | 5.06                | 0.34 | 2.68             |
| 10.60  | 54.49       | 34.91                    | 15.36         | 4.54                | 0.39 | 2.52             |
| 7.59   | 59.35       | 33.06                    | 17.38         | 4.16                | 0.42 | 2.41             |
| 7.06   | 59.71       | 33.23                    | 17.42         | 4.19                | 0.44 | 2.50             |

concluded that the solubility values are higher than those calculated in solutions of nitrates, iodates, cyanides and rhodanides while lower values were found in solutions of lithium and sodium halides.

These deviations can now be explained in terms of the parameter  $P$ . Solubility values greater than theoretical imply negative values of  $P$  and that is to be expected with nitrates and iodates which are known water-breakers and with cyanides and rhodanides which are typical complexing ligands. On the other hand lower experimental solubility values imply positive values for  $P$  which is true for solutions of strongly hydrated ions (here  $\text{Na}^+$  and  $\text{Li}^+$ ).

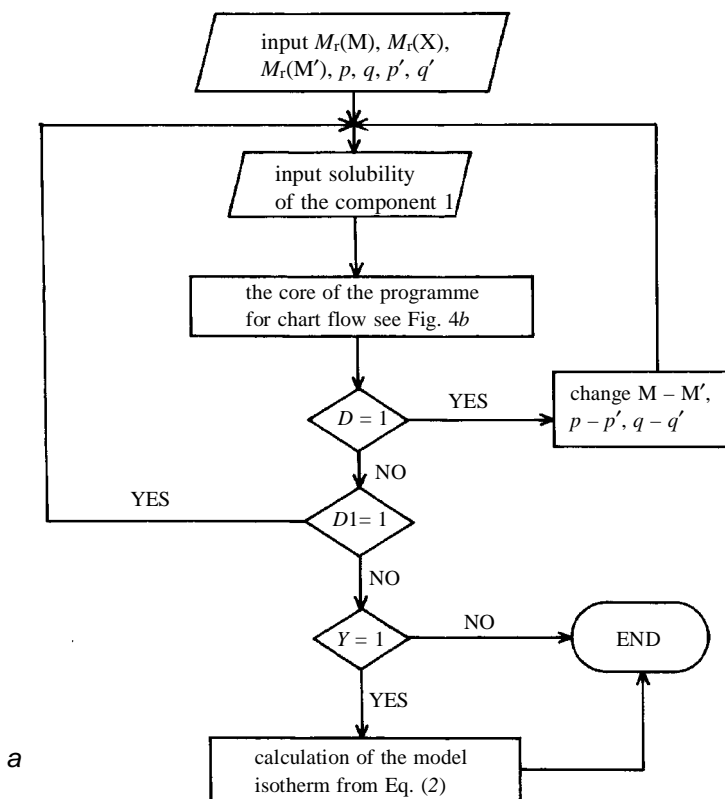
We now consider the solubility values of potassium halides in solutions of sodium halides at 25 °C (Table II, Fig. 3). Again, the value  $P/x_2$  has proven to be more useful

TABLE III  
Hydration analysis of the solubility isotherm in the  $\text{NaX-KX-H}_2\text{O}$  ( $X = \text{Cl, Br, I}$ ) system at 25 °C. Solubility of sodium halides in solutions of potassium halides

| NaX<br>wt.%       | KX<br>wt.% | H <sub>2</sub> O<br>wt.% | KX<br>mole % | $W$<br>mol/mol solute | $P$   | $P/x_2$ |
|-------------------|------------|--------------------------|--------------|-----------------------|-------|---------|
| $X = \text{Cl}$   |            |                          |              |                       |       |         |
| 26.46             | 0.00       | 73.54                    | 0.00         | 9.02                  | 0.00  | –       |
| 24.19             | 3.61       | 72.20                    | 1.08         | 8.68                  | 0.01  | 1.32    |
| 23.56             | 5.23       | 71.21                    | 1.58         | 8.36                  | 0.00  | 0.22    |
| 21.25             | 9.39       | 69.37                    | 2.90         | 7.87                  | 0.01  | 0.37    |
| 20.46             | 11.12      | 68.42                    | 3.47         | 7.61                  | 0.01  | 0.19    |
| $X = \text{Br}^a$ |            |                          |              |                       |       |         |
| 48.60             | 0.00       | 51.40                    | 0.00         | 6.05                  | 0.00  | –       |
| 47.10             | 2.60       | 50.30                    | 0.67         | 5.83                  | –0.01 | –1.75   |
| 45.60             | 5.20       | 49.20                    | 1.36         | 5.61                  | –0.02 | –1.72   |
| 44.40             | 6.70       | 48.90                    | 1.76         | 5.57                  | –0.02 | –1.01   |
| $X = \text{I}^b$  |            |                          |              |                       |       |         |
| 64.72             | 0.00       | 35.28                    | 0.00         | 4.54                  | 0.00  | –       |
| 63.15             | 2.17       | 34.68                    | 0.55         | 4.44                  | –0.01 | –1.17   |
| 61.35             | 4.78       | 33.87                    | 1.24         | 4.30                  | –0.02 | –1.41   |
| 60.74             | 5.44       | 33.82                    | 1.41         | 4.29                  | –0.01 | –0.02   |
| 59.97             | 6.80       | 33.23                    | 1.79         | 4.19                  | –0.03 | –1.48   |
| 59.71             | 7.06       | 33.23                    | 1.86         | 4.19                  | –0.02 | –1.32   |

<sup>a</sup>  $\text{NaBr} \cdot 2\text{H}_2\text{O}$  crystallizes as the equilibrium solid phase; <sup>b</sup>  $\text{NaI} \cdot 2\text{H}_2\text{O}$  crystallizes as the equilibrium solid phase.

for our discussion than the mere value of  $P$ . For chlorides and bromides, the value of  $P/x_2$  is constant in certain concentration ranges (curves 1 and 2 in Fig. 3). A further increase in the concentration of the sodium halide leads to a decrease in the value of  $P/x_2$ . For iodides (Fig. 3, curve 3) the value of  $P/x_2$  decreases continually. For the discussion of these results the total number of moles of water being at the disposal per mole of ions involved must be taken into account (curves 1', 2' and 3' in Fig. 3). Then the phenomena observed may be explained as follows. Saturated solution of KCl contains 11.5 mol  $H_2O$  per mole KCl, saturated solution of KBr contains 9.5 mol  $H_2O$  per mole KBr. The amount of water being at a disposal per mole of solute,  $W$ , decreases with increasing values of  $x_2$ . Figure 3 also shows that in both systems the decrease in the value of  $P/x_2$  begins in the region where  $W$  has a value close to 8 mol  $H_2O$  per mole of solute. Thus we may state that if more than 8 mol of water are available per mole of solute, then all ions can be hydrated in the normal extent and the value of  $P$  is positive





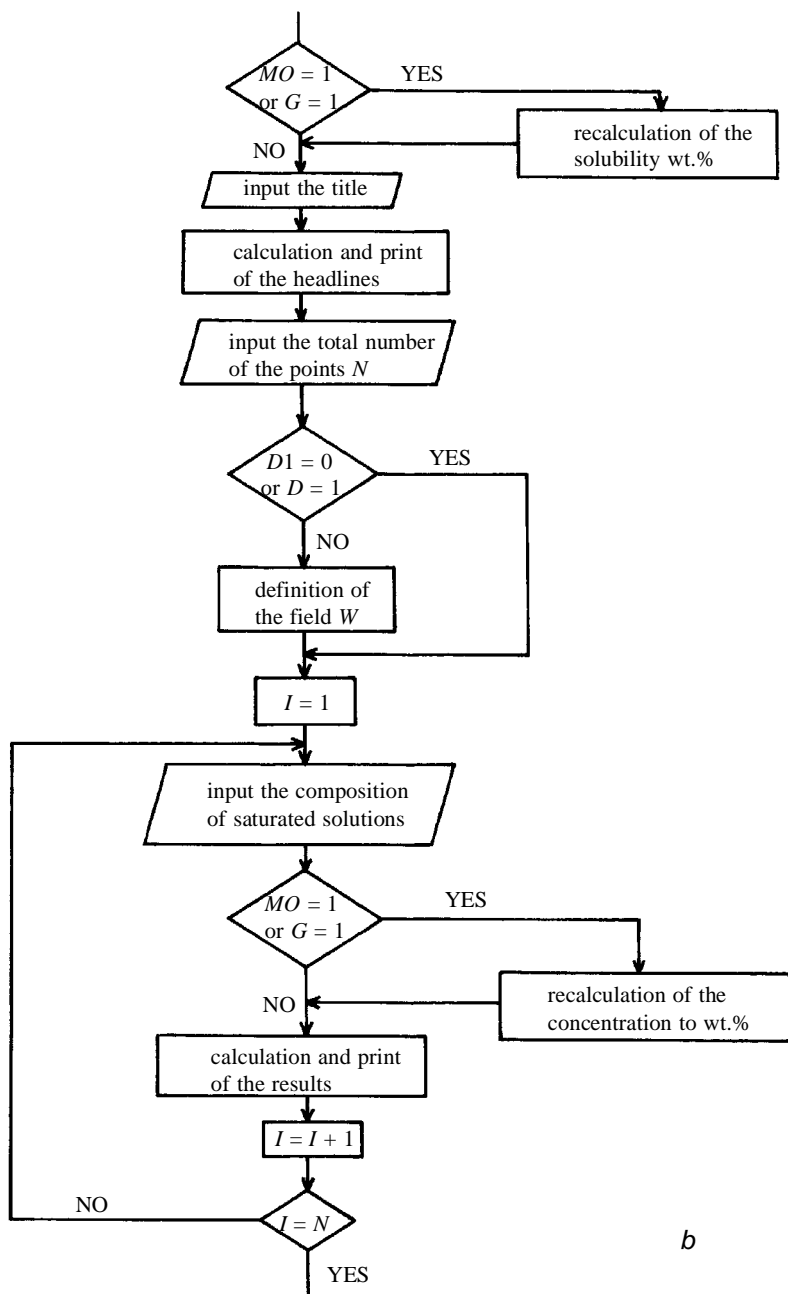


FIG. 4

The chart flow of the programme HYDRAN. *a* The overall chart flow; *b* the chart flow of the core of the programme

and constant (indicating that  $\text{Na}^+$  has a greater hydration ability than  $\text{K}^+$ ). However, if the concentration of water decreases to less than 8 mol  $\text{H}_2\text{O}$  per mole of solute, then some adjustment has to be made such as a haring of hydration envelopes (the association part of  $P$  increases) and the value of both  $P$  and  $P/x_2$  begin to decrease. By contrast, a saturated solution of KI contains 5.3 mol of  $\text{H}_2\text{O}$  per mole KI and, therefore, the value of  $P/x_2$  begin decreasing as soon as NaI is added.

The values of  $P/x_2$  in the concentration-independent region (1.85 for chlorides, 3.3 for bromides and by far extrapolation to  $W = 8$  obtained value of about 4 for iodides) reflect the increase of the association term in  $P$  in the sequence  $\text{NaCl} > \text{NaBr} > \text{NaI}$ . Furthermore, in those solutions of chlorides and bromides when  $W$  is 8 mol  $\text{H}_2\text{O}$  per mole of solute the sum of molar fractions of the solutes is near the value of 11.1 mole %. This value is identical to that of "boundary of water-ressembling structure" calculated for many solutions of 1-1 electrolytes by Lyashchenko<sup>13</sup>. These calculations were based on geometrical assumptions only.

Both  $P$  and  $P/x_2$  are very sensitive to the precision of solubility measurements. Therefore, the parameter  $P$  may be used to determine the validity of solubility data. For example, solubility isotherms for the NaI–KI– $\text{H}_2\text{O}$  system at 25 °C were published by different authors<sup>10,14</sup>. The isotherms of both articles are compared graphically in Figs 6 and 7 as well as the respective  $P$  and  $P/x_2$ . The values of  $P$  and  $P/x_2$  calculated on the

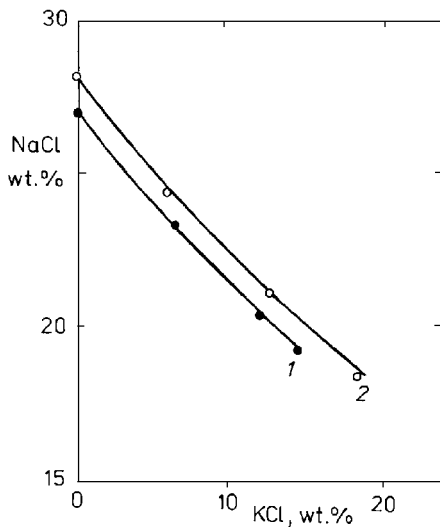


FIG. 5  
Calculated (—) and experimental<sup>11</sup> (○, ●) solubility of NaCl in solutions of KCl: 1 at 40 °C, 2 at 70 °C

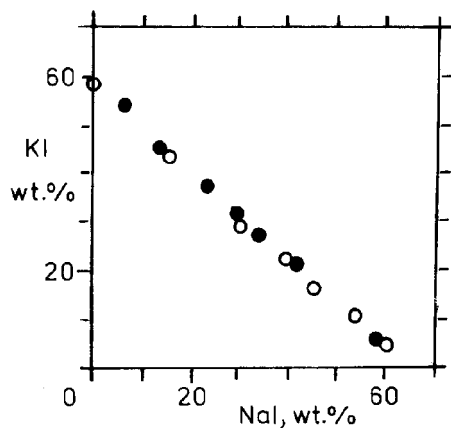


FIG. 6  
Solubility of KI in solutions of NaI at 25 °C measured by Hill et al.<sup>10</sup> (○) and Klebanov and Pinchuk<sup>14</sup> (●)

basis of the data of Klebanov and Pinchuk<sup>14</sup> are scattered and therefore the respective isotherm was rejected and the values of Kill and Wilson<sup>10</sup> were accepted. On the other hand this sensitivity of  $P$  and  $P/x_2$  to the experimental precision may be a source of difficulties. In the region of small values of  $x_2$  the experimental precision of solubility isotherms is generally less because of the analytical determination of one component in the presence of a large excess of the other. Furthermore, investigators often include a limited number of data points in these areas. In such cases, new measurements of higher precision are needed before the hydration analysis described in this paper can be applied. Such problems are similar to those encountered by Pitzer in his elegant calculations of solubility isotherms<sup>15</sup>, as shown recently by Kumar<sup>16</sup>.

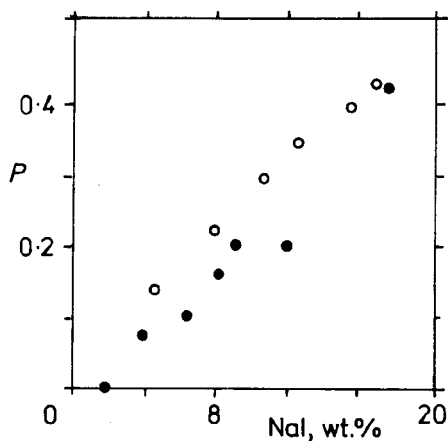


FIG. 7  
Concentration dependence of  $P$  on the isotherms depicted in Fig. 6

## SYMBOLS

|                |   |
|----------------|---|
| A              | binary saturated solution of the component 1  |
| B              | ternary saturated solution of the component 1                                       |
| $K_S^A, K_S^B$ | interaction parameters  |
| $m_i^A, m_i^B$ | molality of the component $i$ in the solution A and B, respectively                 |
| M              | common ion  |
| $(M_i)_i$      | relative molecular mass of the component $i$  |
| $n_i^A, n_i^B$ | number of moles of the component $i$ in 100 g of the solution A and B, respectively |
| $p, p'$        | stoichiometric coefficients   |
| $P$            | hydration parameter   |
| $q, q'$        | stoichiometric coefficients   |
| $w_i^A, w_i^B$ | wt.% of the component $i$ in the solution A and B, respectively                     |
| $x_2$          | molar fraction of the component 2 in the saturated solution                         |
| X, X'          | non-common ions   |

$W$  number of moles of water per one mole of solute

### Subscripts

|   |                          |
|---|--------------------------|
| 0 | solvent                  |
| 1 | solute                   |
| 2 | non-saturating component |

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### REFERENCES

1. Enderby J. E., Cummings S., Herdman G. J., Neilson G. W., Salmon P. S., Skipper N.: *J. Phys. Chem.* 91, 5851 (1987).
2. Bounds D. G.: *Mol. Phys.* 54, 1335 (1985).
3. Ortega-Blake J., Navarro O., Les A., Rybak S.: *J. Chem. Phys.* 76, 5405 (1982).
4. Lilich L. S., Chernykh L. V.: *Proceedings of the Conference Problemy sovremennoi khimii koordinatsionnykh soedinenii*, p.63. Izdatel'stvo Leningradskogo gosudarstvennogo universiteta, Leningrad 1968.
5. Zhdanovskii A. B.: *Zh. Neorg. Khim.* 32, 2327 (1987).
6. Samoilov O. I.: *Struktura vodnykh rastvorov elektrolitov*, p. 80. Izdatel'stvo AN SSSR, Moscow 1957.
7. Zhuravlev E. F., Bychkova M. N.: *Zh. Neorg. Khim.* 4, 2367 (1959).
8. *Spravochnik po rastvorimosti*. Table No. 3678, p. 1131. Nauka, Leningrad 1969.
9. Vlasov N. A., Bergman A. G.: *Dokl. Akad. Nauk SSSR* 38, 211 (1943).
10. Hill A.E., Willson H. S., Bishop J. A.: *J. Am. Chem. Soc.* 55, 420 (1933).
11. *Spravochnik po rastvorimosti*. Table No. 3688, p. 1136. Nauka, Leningrad 1969.
12. Vojtisek P., Havlicek D., Ebert M.: *Electrochim. Acta* 31, 1609 (1986).
13. Lyashchenko A. K.: *Izv. Akad. Nauk SSSR, Ser. Khim.* 1973, 287.
14. Klebanov G. S., Pinchuk G. J.: *Zh. Prikl. Khim.* 37, 289 (1964).
15. Pitzer K. S.: *Pure Appl. Chem.* 58, 1599 (1986).
16. Kumar A.: *J. Solution Chem.* 18, 481 (1989).

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