Letters to the Editor

Estimation of the clathrate aggregation of substances in solutions from ion-exchange equilibrium data

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So far, no experimental evidence for the formation of clathrate-like aggregates in the solution bulk on approaching the phase transition temperature from the high-temperature side has been obtained.[1,2] We developed a procedure for the experimental detection and investigation of this phenomenon using data on ion-exchange equilibria. As an example, we considered the $Bu_4NBr—KBr—H_2O$ system and slightly cross-linked Dowex 50Wx2 sulfopolysrtyrene cation exchanger (according to DTA, the temperature of precipitation of the crystalline tetrabutylammonium bromide polyhydrate ($Bu_4NBr \cdot nH_2O$) was ~—1 °C, the ionic strength of the solutions was 0.12, the solution volume was 50 mL, and the portions of the ion exchanger used in the K form were 1—5 g).

The accepted initial statements, the model, and the calculation procedure

1. If the clathrate polyhydrate $[Bu_4N^+][Br \cdot nH_2O]^-$ is formed in the solution, then, due to the specific features of its structure, it is electrically neutral, not dissociated, and the clathrated portion of Bu_4NBr does not participate in the ion exchange.[3]

2. The nonclathrated portion of Bu_4NBr in an aqueous solution is completely ionized and participates in the standard cation exchange.

3. When no clathrates are formed in the solution, the temperature has a slight influence on the ion exchange equilibrium, and the ion exchange isotherms taken at different temperatures coincide.[4]

Figure 1 shows the hypothetical model curves plotted in the $S_{Bu_4N^+}—L_{Bu_4N^+}$ coordinates (the equivalent fractions of the clathrate-forming ion in the ion exchange resin and in the solution, respectively); the curves represent the ion exchange isotherms without clathrate formation (curve *1*) and with the presumptive clathration of the Bu_4NBr salt in solution (curve *2*). Then, for identical solution compositions, for example $(L_{Bu_4N^+})_{B'}$, but different temperatures, one composition of the ion exchanger corresponds to ion exchange equilibrium without clathration in solution (curve *1*, point C), and the other one corresponds to the equilibrium when clathration takes place (curve *2*, point B).

If an equal-concentration line for the ion exchanger composition $(S_{Bu_4N^+})_{A,B}$ is drawn through point B, this line will intersect curve *1* at point A, corresponding to the ion exchange equilibrium without clathration for a solution composition of $(L_{Bu_4N^+})_{A'}$. Note that the $(L_{Bu_4N^+})_{A'}$ and $(L_{Bu_4N^+})_{B'}$ compositions found experimentally always correspond only to the overall concentrations of the clathrate-forming counter-ions.

The foregoing can be expressed as the following equations

$$(S_{Bu_4N^+})_{A,B} = (m_{Bu_4N^+})_A/(m_{Bu_4N^+} + m_{K^+})_A = \\ = (m_{Bu_4N^+})_B/(m_{Bu_4N^+} + m_{K^+})_B, \qquad (1)$$

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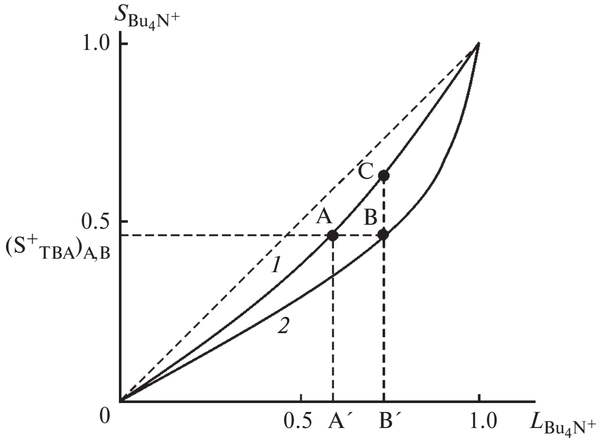

Fig. 1. Ion exchange isotherms in the absence of clathration (*1*) and with clathration of $\mathrm{Bu_4NBr}$ in solution (*2*).

$$(L_{\mathrm{Bu_4N^+}})_{A'} = (C_{\mathrm{Bu_4N^+}})_{A'}/(C_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{A'}, \tag{2}$$

$$(L_{\mathrm{Bu_4N^+}})_{B'} = (C_{\mathrm{Bu_4N^+}})_{B'}/(C_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{B'}, \tag{3}$$

where *m* and *C* are the ion concentrations in the ion exchanger and in the solution, respectively. The subscripts specify the ion type and the solution composition corresponding to the position of the given designation in Fig. 1.

Under clathration conditions,

$$(C_{\mathrm{Bu_4N^+}})_{B'} = (C^{\circ}_{\mathrm{Bu_4N^+}} + C^{*}_{\mathrm{Bu_4N^+}})_{B'}, \tag{4}$$

where $(C_{\mathrm{Bu_4N^+}})_{B'}$ is the analytical concentration of $\mathrm{Bu_4NBr}$ in solution B´; $(C^{\circ}_{\mathrm{Bu_4N^+}})_{B'}$ is the ionized and $(C^{*}_{\mathrm{Bu_4N^+}})_{B'}$ is the clathrated component of the total analytical concentration of $\mathrm{Bu_4NBr}$ in solution B´. Then Eq. (3) can be written in the form

$$(L_{\mathrm{Bu_4N^+}})_{B'} = \frac{(C^{\circ}_{\mathrm{Bu_4N^+}} + C^{*}_{\mathrm{Bu_4N^+}})_{B'}}{(C^{\circ}_{\mathrm{Bu_4N^+}} + C^{*}_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{B'}}, \tag{5}$$

$$(L^{\circ}_{\mathrm{Bu_4N^+}})_{B'} = (C^{\circ}_{\mathrm{Bu_4N^+}})_{B'}/(C^{\circ}_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{B'}, \tag{6}$$

where $(L^{\circ}_{\mathrm{Bu_4N^+}})_{B'}$ is the equivalent fraction of $\mathrm{Bu_4N^+}$ in the solution of composition B´ calculated taking into account only ionized species participating in the ion exchange process.

The equality

$$(S_{\mathrm{Bu_4N^+}})_{A} = (S_{\mathrm{Bu_4N^+}})_{B} \tag{7}$$

should imply equal ratios of the equivalent fractions of ions participating in the ion exchange both in solution A´ and in solution B´, *i.e.*,

$$(L_{\mathrm{Bu_4N^+}})_{A'} = (L^{\circ}_{\mathrm{Bu_4N^+}})_{B'} = (C_{\mathrm{Bu_4N^+}})_{A'}/(C_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{A'} = \\ = (C^{\circ}_{\mathrm{Bu_4N^+}})_{B'}/(C^{\circ}_{\mathrm{Bu_4N^+}} + C_{\mathrm{K^+}})_{B'}. \tag{8}$$

Table 1. Degree of clathration of $\mathrm{Bu_4NBr}$ at various temperatures

$(S_{\mathrm{Bu_4N^+}})_{A,B}$	$(C^{*}_{\mathrm{Bu_4N^+}})_{B'}/(C^{\circ}_{\mathrm{Bu_4N^+}} + C^{*}_{\mathrm{Bu_4N^+}})_{B'}$		
	50 °C	25 °C	0 °C
0.1	—	—	0.44
0.2	—	0.14	0.50
0.3	0.12	0.36	0.59
0.5	0.21	0.47	0.70
0.7	0.52	0.84	0.95
0.9	0.80	0.92	0.97

* At a temperatures of 60 °C or higher, no clathrate aggregation takes place in the solutions, and ion exchange isotherms coincide

Thus the $(L_{\mathrm{Bu_4N^+}})_{A'}$ and $(C_{\mathrm{K}}{}^{+})_{B'}$ values can be found from the compositions of solutions A´ and B´ in Fig. 1, and the $(C^{\circ}_{\mathrm{Bu_4N^+}})_{B'}$ value can be calculated using Eq. (8). Finally, taking into account the ionic strength of the solution (*I*)

$$I = (C_{\mathrm{Bu_4N^+}})_{A'} + (C_{\mathrm{K^+}})_{A'}, \tag{9}$$

and the validity (only in the numerical form) of the relation

$$(C^{\circ}_{\mathrm{Bu_4N^+}} + C^{*}_{\mathrm{Bu_4N^+}})_{B'} + (C_{\mathrm{K^+}})_{B'} = I, \tag{10}$$

one can calculate the desired $(C^{*}_{\mathrm{Bu_4N^+}})_{B'}$ value. The results of calculations of the degree of clathration of $\mathrm{Bu_4NBr}$ in KBr—$\mathrm{Bu_4NBr}$ mixed aqueous solutions carried out by the developed procedure using data on ion-exchange equilibria are presented in Table 1.

When the data for mixed solutions given in the Table are extrapolated to the data for a pure solution of $\mathrm{NH_4Br}$, it can be seen that the degree of clathration of $\mathrm{NH_4Br}$ in a pure solution tends to unity at any temperature.

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