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Equilibria in Ion Exchanger–Aqueous Salt Solution Systems and Clathrate Formation

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Abstract—The new approach has been developed for the analysis of the data on the equilibria in the systems ionite–aqueous salt solution, based on the application of effective auxiliary functions. With the use of the procedure, that was worked out within the context of the mentioned approach, K^+ to Bu_4N^+ cation-exchange equilibria have been studied between slightly cross-linked sulfonated poly(sterene) cationite Dowex 50Wx2 and three component aqueous solutions of the salts Bu_4NBr, KBr. The formation of clathrate-like ion pairs, proposed earlier in the studied system (on the basis of general knowledge on clathrate hydrates), was not revealed in the solution. The suggested approach and procedure can be widely applied to the investigation of all specific cation–anion interactions in aqueous salt solutions.

Keywords: effective function; initial and detailed components; chemical species; ion-exchange equilibria; investigation technique

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The structure and physicochemical properties of crystalline clathrate hydrates of monomeric salts of quaternary alkylammonium bases with halide and carboxylate ions have been fairly extensively studied, and the relevant data have been summarized in multiple publications (see, e.g., [1–4]). It has been shown that the clathrate structures of crystalline hydrates are effectively stabilized by single salts based on tetrabutylammonium Bu_4N^+ and tetraisoamylammonium $i\text{-}Am_4N^+$ cations. The ability to form clathrate hydrates is also exhibited by salts of these cations with polymeric anions: linear polyacrylate ion [5] and cross-linked polyacrylate ions having low degrees of cross-linking with divinylbenzene or divinyl sulfide (the latter are polyacrylate carboxylic cation exchangers) [6]. For structure and physicochemical properties of this class of compounds, see [7–12].

It should be noted, however, that the idea that clathrate-like ion pairs are part of binary (or more-component) liquid aqueous salt phase in systems which, under certain (p, T, X) conditions, undergo incongruent and/or congruent formation of crystalline clathrate hydrates was advanced long ago.[1] This idea has long been a scientific hypothesis within the general knowledge of clathrate formation phenomena [1–9, 18–22], not without reasons, including the results of aqueous solution studies by physical methods [23–26].

In our opinion, it was not until 2001 that the first comprehensive effort was undertaken to estimate the

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[1] For example, considered in [1, 13] were moieties containing the Bu_4N^+ or $i\text{-}Am_4N^+$ cation and a monoatomic anion inside clathrate-like "water" frameworks with compartments, in which one (or more) water molecule is replaced by quaternary ammonium cation and/or the anion of the salt considered (e.g., halide). Naturally, macroensembles of these moieties (with interactions not included in the stoichiometric description and collectively termed "solvation" taken into account) can be regarded as ion pairs representing one of the types of stoichiometrically and structurally characterized chemical forms (species) [14–16] of a substance in solution. The concept of "ion pairs" (including "contact" ion pairs) in high-concentrated aqueous salt solution chemistry goes back a long way [17], though with the sum of knowledge about the clathrate formation phenomena uncalled. However, hydrogen bonding in water and aqueous solutions typically received attention in discussions of the structure of ion pairs.

extent of supposed clathrate formation in solution [in terms of the degree of Bu_4N^+ cation binding with bromide ions $\alpha^*(Bu_4N^+)$] from polythermal equilibrium examination for the K^+–Bu_4N^+ cation exchange between low-cross-linked polystyrene sulfonate cation exchanger Dowex 50Wx2 and three-component aqueous solutions of Bu_4NBr and KBr salts [27]. Importantly, in that study, the facts that an equivalent exchange of cations takes place and that the exchange capacity of the cation exchanger portions prepared by a standard procedure remains unchanged under the test conditions were experimentally substantiated (which demonstrates the solvability of the problem posed) as the first step and recorded with an acceptable degree of accuracy the isotherms in coordinates of $S(Bu_4N^+)$ (the "equivalent" proportion of the Bu_4N^+ions in the ion exchanger) vs. $L(Bu_4N^+)$ (the proportion of these same ions in the solution occurring in equilibrium with the ion exchanger) at temperatures of 0, 25, 50, and 60°C.

The experiments were carried out with a prepared series of solutions which contained Bu_4NBr and KBr at a fixed total concentration (0.12 M) though in a variable ratio. By data processing with the use of the procedure described in [28, 29], the estimated $\alpha^*(Bu_4N^+)$ values were obtained. However, two of the four restrictions that underlie the $\alpha^*(Bu_4N^+)$ calculations (invariance of the cation exchange constant throughout the temperature range examined and the lack of significant manifestations of clathration at 60°C and above) were verifiable in principle, within a fairly correctly obtained set of monothermal functions $S(Bu_4N^+) = \varphi[L(Bu_4N^+)]$. Therefore, the aim of this study was, first, to develop a version of analysis of these functions without using the above-mentioned restrictions, second, to apply it to the array of existing data [27], and third, to design and conduct an additional study to obtain a reasonable answer to the question posed in [27–29] which still remains to be answered.[2]

Adjustment of the Technique for Analysis of the Equilibrium Data for Ion Exchanger–Aqueous Salt Solution Systems[3]

Our approach to adjustment of the technique consists in rejecting the two above-mentioned restrictions and performing the analysis of the ion-exchange equilibrium data obtained, as well as of the possible consequences of "clathration" in solution (in the general case, Bu_4N^+ binding into any other, along with $Bu_4N^+_{solv}$, species [14–16]) and any other effects (e.g., secondary medium effects [15] both in an aqueous solution and in the "ion-exchanger phase", or "clathration" in the ion exchanger) in terms of the experimentally detected variabilities in the apparent ion-exchange equilibrium constants:

$$(Bu_4N^+)^*_{solv} + K^+_{i.\text{-}ex.ph.} \rightleftarrows (Bu_4N^+)_{i.\text{-}ex.ph.} + K^+_{solv}, \qquad (1)$$

where i.-ex.ph is the ion-exchanger phase.

In Eq. (1) the stoichiometric formula of the Bu_4N^+ cation is bracketed and supplied with the superscript "*" in order to emphasize the facts that, first, this is a gross-reactant formed in an aqueous salt solution by the gross-component Bu_4N^+ [16], and, second, that this conditional reactant at a higher level of elaboration [14–16] can be represented as two species ($Bu_4N^+_{solv}$ and Bu_4NBr_{solv}). Based on the isothermal functions $S(Bu_4N^+) = \varphi_t[L(Bu_4N^+)]$[4] which were fairly correctly

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[2] Calculation of $\alpha^*(Bu_4N^+)$ in the framework of the model [28, 29] had brought the researchers in [27] to a conclusion that clathrates can be formed in the solutions studied already at 50°C and below, but the objectively existing opportunity to verify the restrictions underlying the calculation had escaped their attention. Hence, the question of presence/absence of significant clathration in solution is in fact still open, and the above-mentioned conclusion was wrong, as will be shown below.

[3] Naturally, in the adjustment we placed the focus only on provision of experimentally verifiable identifiability of the (p, T, X)-conditions (p = 1 atm, X is the vector of the composition of the aqueous salt solution in terms of the initial components [14–16]), under which ion pairs are formed along with the products of dissociation of salts exhibiting the behavior of strong electrolytes. The questions of their structure, with participation of water molecules in this process taken into consideration, in the framework of studies of the class of the compounds examined are still open.

[4] $L(Bu_4N^+) = C^*(Bu_4N^+)/[C^*(Bu_4N^+) + C(K^+)]$ is the proportion of the gross-amount {responsible for the molar gross-concentration $[C^*(Bu_4N^+) = C(Bu_4N^+) + C(Bu_4NBr)]$} of the Bu_4N^+ cations (of the total number of Bu_4N^+ and K^+ cations) in the portion of the solution brought in equilibrium with the cation exchanger, and $S(Bu_4N^+) = m(Bu_4N^+)_{i.\text{-}ex.ph.}/[m(Bu_4N^+)_{i.\text{-}ex.ph.} + mK^+_{i.\text{-}ex.ph.}]$, their is proportion in the portion of the cation exchanger (m_i are the molar amounts of cations in the ion exchanger). In each of the specific series of experiments, a portion of the cation exchanger in the K^+-form with a known total exchange capacity was introduced in the system, and at the end of the series the fact of its invariance, i.e., invariance of $[m(Bu_4N^+)_{i.\text{-}ex.ph.} + mK^+_{i.\text{-}ex.ph}]$ was controlled. The initial and equilibrium gross-concentrations of Bu_4N^+ $[C^*(Bu_4N^+)]$ in each series were determined analytically, and the remaining parameters [$C(K^+)$ and m_i], based on the balance calculation with the equivalence of exchange and invariance of the total amounts of the cations in both solution and cation exchanger taken into consideration.

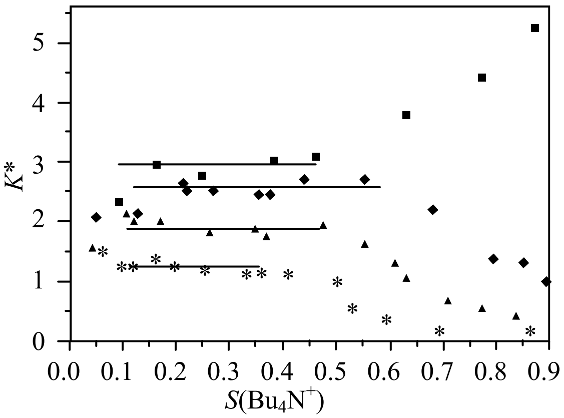

Fig. 1. The K^*–$S(\text{Bu}_4\text{N}^+)$ isotherms. (■) 60°C, (♦) 50°C, (▲) 25°C, and (*) 0°C.

obtained in [27], for each temperature in the temperature series (t) examined the following conditional equilibrium constant can be associated with process (1):

$$K^* = S(\text{Bu}_4\text{N}^+)[1 - L(\text{Bu}_4\text{N}^+)]/[1 - S(\text{Bu}_4\text{N}^+)]L(\text{Bu}_4\text{N}^+). \quad (2)$$

Introduction of the constant K^* was appropriate [30–32] because it is accessible for correct experimental determination. Moreover, its variability as a function of $S(\text{Bu}_4\text{N}^+)$ (at each particular temperature) is informative in terms of, first, possible consequences of the medium effects in the aqueous phase and in the ion exchanger (due to changes in the Bu_4N^+ to K^+ concentration ratio at their fixed total concentration both in solution and in the ion exchanger) and, second, possible significance of the contribution from the presumed $\text{Bu}_4\text{N}^+_{\text{solv}}$ binding into the $\text{Bu}_4\text{NBr}_{\text{solv}}$ ion pair. The appropriateness of the constant K^* [Eq. (2)] (efficiency in the above-mentioned respects) can be understood more clearly if, in accordance with the hypothesis about the states of the substance in the heterogeneous system examined, that is being verified, it will be associated with one homogeneous and two heterogeneous processes, which, naturally, are not independent:

$$\text{Bu}_4\text{N}^+_{\text{solv}} + \text{Br}^-_{\text{solv}} \rightleftarrows \text{Bu}_4\text{NBr}_{\text{solv}},\ K_3, \quad (3)$$

$$\text{Bu}_4\text{N}^+_{\text{solv}} + \text{K}^+_{\text{i.-ex.ph.}} \rightleftarrows (\text{Bu}_4\text{N}^+)_{\text{i.-ex.ph.}} + \text{K}^+_{\text{solv}},\ K_4, \quad (4)$$

$$\text{Bu}_4\text{NBr}_{\text{solv}} + \text{K}^+_{\text{f.i.}} \rightleftarrows (\text{Bu}_4\text{N}^+)_{\text{i.-ex.ph.}} + \text{K}^+_{\text{solv}} + \text{Br}^-_{\text{solv}},\ K_5. \quad (5)$$

Therefore, the equilibrium constants of reactions (3)–(5) are related as ($K_3 = K_4/K_5$). Any pair of the three constants in reactions (3)–(5), as being fixed parameters[5] of the model considered, can be easily incorporated into Eq. (2) basing on the law of mass action for equilibria (3)–(5) and the mass balance equation in terms of the initial and detailed components [15]. In particular, taking constants for equilibria (3) and (4), associated with particular temperature and level of the secondary medium effects both in solution and in the ion exchanger (i.e., $K^{\varnothing}_3$ and $K^{\varnothing}_4$ [15]), and using Eq. (2) we will get at:

$$K^* = K^{\varnothing}_4\alpha(\text{Bu}_4\text{N}^+), \quad (6)$$

where $\alpha(\text{Bu}_4\text{N}^+) = 1/[1 + K^{\varnothing}_3C(\text{Br}^-)]$; $C(\text{Br}^-) = C(\text{Bu}_4\text{N}^+) + C(\text{K}^+) = C^*(\text{Bu}_4\text{N}^+)\alpha(\text{Bu}_4\text{N}^+) + C(\text{K}^+)$.

Here, we implemented the above-described approach to analysis of the data {borrowed from [27] in terms of the $S(\text{Bu}_4\text{N}^+) = \varphi_t[L(\text{Bu}_4\text{N}^+)]$ functions} on the ion-exchange equilibria established at temperatures of 0, 25, 50, and 60°C and the total salt concentration of 0.12 M, and also analyzed the data obtained by us additionally for the same system at 25°C and several fixed total (KBr + Bu_4NBr) concentrations: 0.06, 0.12, and 0.24 M. For details on the techniques of the ion-exchange equilibrium experiment and the primary data processing up to the sought-for $S(\text{Bu}_4\text{N}^+) = \varphi_{25°\text{C}}[L(\text{Bu}_4\text{N}^+)]$ functions, that we borrowed for the purposes of this study, see [27].

Experimental Data and Their Analysis

Table 1 lists the results of transformation of the experimental data on the ion-exchange equilibrium [27] into K^* values according to Eq. (2).

The specific influence of temperature on the effective functions $K^* = f_t[S(\text{Bu}_4\text{N}^+)]$ can be better illustrated via graphical presentation (Fig. 1). Except for the first one or two points, each of the four isotherms comprises a clearly defined section of satisfactory (within the limits of the random errors) constancy of K^* at levels exhibiting a regular temperature dependence. The log K^* vs. $1/T$ function (Table 2)[6] is linear within the limits of the errors

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[5] Certainly, this concerns only the case of fixed secondary medium effects, and hence, fixed activity of H_2O in isothermal experiments. Importantly, specifically meeting the latter criterion allowed processes (3) and (5) to be presented without $\text{H}_2\text{O}_{\text{solv}}$, i.e., the presumed involvement of water molecules in formation of a clathrate-like ion pair to be included implicitly (without stoichiometric description) in the “solv” symbol substance.

[6] The constant K^* was estimated from the average values for the ranges indicated in Table 2. The information required for data processing (according to Van’t Hoff equation) by the linear least squares method is also presented in Table 2.

Table 1. The initial $S(Bu_4N^+) = \varphi_t[L(Bu_4N^+)]$ functions for a series of temperatures and the corresponding effective $K^* = f_t[S(Bu_4N^+)]$ functions. Dowex 50Wx2 cation exchanger–Bu_4NBr + KBr aqueous solution system

Temperature, °C											
60			50			25			0		
$L(Bu_4N^+$	$S(Bu_4N^+)$	K^*	$L(Bu_4N^+$	$S(Bu_4N^+)$	K^*	$L(Bu_4N^+$	S_{Bu4N+}	K^*	$L(Bu_4N^+$	$S(Bu_4N^+)$	K^*
0.041	0.090	2.31	0.024	0.048	2.05	0.030	0.045	1.52	0.041	0.061	1.52
0.062	0.164	2.97	0.060	0.120	2.14	0.054	0.107	2.10	0.075	0.096	1.31
0.109	0.250	2.72	0.094	0.213	2.61	0.064	0.120	1.99	0.090	0.111	1.26
0.171	0.381	2.98	0.101	0.220	2.51	0.092	0.167	1.98	0.120	0.158	1.38
0.215	0.457	3.07	0.129	0.273	2.54	0.165	0.263	1.81	0.161	0.194	1.25
0.310	0.631	3.81	0.182	0.354	2.46	0.220	0.344	1.86	0.220	0.254	1.21
0.429	0.769	4.43	0.197	0.376	2.46	0.248	0.371	1.79	0.293	0.328	1.18
0.562	0.870	5.22	0.228	0.442	2.68	0.317	0.469	1.90	0.325	0.358	1.16
0.702	0.949	7.90	0.311	0.548	2.69	0.432	0.551	1.61	0.363	0.404	1.19
0.848	0.986	12.6	0.354	0.583	2.55	0.537	0.604	1.32	0.491	0.502	1.04
			0.491	0.677	2.17	0.626	0.628	1.01	0.627	0.528	0.67
			0.734	0.792	1.38	0.782	0.701	0.65	0.816	0.589	0.32
			0.816	0.851	1.29	0.865	0.773	0.53	0.924	0.687	0.18
			0.890	0.891	1.01	0.923	0.833	0.42	0.970	0.862	0.19

Table 2. The $\log K^* = f(1/T)$ function obtained from data processing by the least squares method[a]

$S(Bu_4N^+)$ range	Number of points	t, °C	$1/T$(K), 10^{-3}	K^*	$\log K^*$
0.111–0.404	7	0	3.66	1.23±0.07	0.090
0.120–0.469	6	25	3.36	1.89±0.09	0.276
0.213–0.583	8	50	3.10	2.56±0.09	0.408
0.164–0.457	4	60	3.00	2.94±0.15	0.468

[a] The errors are the rms deviations.

(Fig. 2). As a result, we obtained a fairly stable estimate of the apparent enthalpy [30] of process (4) (for the conditions in the ion exchanger and in the solution within the $S(Bu_4N^+)$ ranges indicated in Table 2):

$$\Delta H^* = 2.6 \pm 0.2 \text{ kcal mol}^{-1}.$$

It should be noted that analysis of the data reported by Bogatyrev et al. [27] clearly showed that the condition of temperature independence of the cation-exchange constant (K_4) behind the calculation of $\alpha^*(Bu_4N^+)$ was incorrect. Specifically for this reason, a conclusion was made in [27] about a considerable contribution made by the Bu_4NBr_{solv} ion pair to the mass balance of the Bu_4N^+ cation in the aqueous salt solution. The variation of log K^* with reciprocal temperature [naturally, this concerns the average values for the sections inside which K^* does not vary with $S(Bu_4N^+)$ and, consequently, with $L(Bu_4N^+)$] is complaint with Van't Hoff equation (see Fig. 2), which led us to the opposite conclusion.

Naturally, $\alpha(Bu_4N^+)$ [and hence $\alpha^*(Bu_4N^+)$] can also be estimated in the isothermal version of the experiment. In particular, we studied the ion-exchange

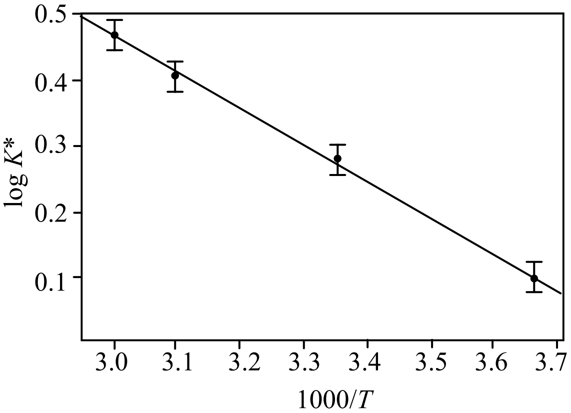

Fig. 2. Influence of $1/T$ on the average log K^* values within the $S(Bu_4N^+)$ ranges indicated in Table 2.

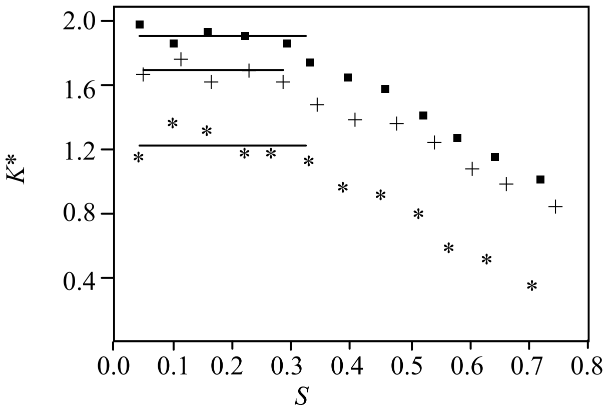

Fig. 3. The $K^* = \varphi[S(Bu_4N^+)]$ dependences. (■) K006, (+) K012, and (*) K024. The plots for the total salt concentrations of 0.12 and 0.24 M are shifted by –0.3 and –0.6 units along the ordinate, respectively.

equilibria at several fixed total KBr + Bu_4NBr concentrations under conditions of sequential increase in $L(Bu_4N^+)$ and, correspondingly, in $S(Bu_4N^+)$. The data on the $K^* = f_t[S(Bu_4N^+)]$ functions are presented in Table 3 and Fig. 3 (25°C isotherms).

Figure 3 shows that, despite a fourfold difference in the total concentration of the salts, all the three dependences not only belong to the same type but also are nearly identical quantitatively. The similarity of these dependences, as well as the constancy of K^* up to $S(Bu_4N^+) = 0.3$, would not be possible with the ion pair significantly contributing to the Bu_4N^+ balance in solution. This unambiguously demonstrated that only effects in the cation exchanger are responsible for the clearly detected regular decrease in K^* at $S(Bu_4N^+) > 0.35$, with these effects being possibly due to progressive involvement into the composition of the

Table 3. The equivalent equilibrium constant K^* in relation to the equivalent proportion of the Bu_4N^+ cations in the ion exchanger S and in the equilibrium solution L at three total KBr + Bu_4NBr concentrations (t = 25°C)

C(KBr + Bu₄NBr), M								
0.06			0.12			0.24		
L	S	K^*	L	S	K^*	L	S	K^*
0.0246	0.0474	1.975	0.0250	0.0483	1.979	0.0273	0.0465	1.737
0.0618	0.1086	1.850	0.0587	0.1138	2.059	0.0592	0.1095	1.954
0.0910	0.1613	1.922	0.0927	0.1652	1.936	0.0907	0.1605	1.918
0.1328	0.2254	1.899	0.1323	0.2320	1.982	0.1379	0.2203	1.766
0.1862	0.2975	1.851	0.1689	0.2853	1.964	0.1728	0.2710	1.779
0.2202	0.3313	1.754	0.2245	0.3431	1.804	0.2214	0.3303	1.734
0.2848	0.3958	1.645	0.2875	0.4076	1.705	0.2909	0.3877	1.543
0.3542	0.4622	1.566	0.3532	0.4787	1.681	0.3547	0.4553	1.521
0.4397	0.5228	1.396	0.4345	0.5443	1.555	0.4381	0.5156	1.365
0.5244	0.5834	1.270	0.5230	0.6054	1.399	0.5258	0.5716	1.204
0.6110	0.6434	1.149	0.6087	0.6681	1.294	0.6090	0.6320	1.102
0.7203	0.7186	0.992	0.7181	0.7459	1.153	0.7192	0.7057	0.936

Table 4. Silver bromide (E_{Br}) and glass (E_H) electrode potentials for a series of solutions $C(Bu_4NBr) + C(KBr) = 0.16$ and $C_{HCl} = 0.001$ M (25.0±0.1°C). The E_D column data were obtained by subtracting from the ($E_H - E_{Br}$) difference its average value (258.8 mV)

$C(Bu_4N^+)$, M	E_{Br}, mV	E_H, mV	($E_H - E_{Br}$), mV	E_D, mV	Proportion of K^+ replaced by Bu_4N^+, $\alpha(Bu_4NBr)$	$C(Bu_4N^+)$, M	E_{Br}, mV	E_H, mV	($E_H - E_{Br}$), mV	E_D, mV	Proportion of K^+ replaced by Bu_4N^+, $\alpha(Bu_4NBr)$
0.0000	–100.8	158.0	258.8	0.0	0.000	0.082	–96.6	162.1	258.7	–0.1	0.510
0.0119	–100.3	158.5	258.8	0.0	0.074	0.085	–96.2	162.4	258.6	–0.2	0.532
0.0221	–100.0	159.2	259.2	0.4	0.138	0.089	–96.0	162.8	258.8	0.0	0.556
0.0310	–99.5	159.8	259.3	0.5	0.194	0.093	–96.1	163.0	259.1	0.3	0.581
0.0388	–99.0	160.0	259.0	0.2	0.242	0.098	–95.7	163.2	258.9	0.1	0.610
0.0457	–98.7	160.2	258.9	0.1	0.286	0.103	–95.3	163.6	258.9	0.1	0.641
0.0519	–98.1	160.6	258.7	–0.1	0.324	0.108	–94.8	164.0	258.8	0.0	0.676
0.0574	–97.8	161.0	258.8	0.0	0.359	0.114	–94.7	164.6	259.3	0.5	0.714
0.0624	–97.4	161.2	258.6	–0.2	0.390	0.121	–94.2	165.0	259.2	0.4	0.758
0.0670	–97.1	161.4	258.5	–0.3	0.419	0.129	–93.2	165.6	258.8	0.0	0.806
0.0711	–96.6	161.6	258.2	–0.6	0.444	0.138	–92.8	166.1	258.9	0.1	0.862
0.0749	–96.4	161.9	258.3	–0.5	0.468	0.148	–91.6	166.9	258.5	–0.3	0.926
0.0784	–96.3	162.1	258.4	–0.4	0.490	0.160	–90.4	167.6	258.0	–0.8	1.000

cation exchanger of water molecules with increasing degree of substitution of K^+ by Bu_4N^+ and to the conjugated rearrangement until a clathrate-like structure is formed.[7]

For aqueous salt solutions of the class of compounds of interest the presence/absence of significant manifestations of clathration as indicated by formation of significant amounts of the corresponding ion pair can be revealed by correct measurements of the activity of the anionic component (in our case, bromide ions [Eq. (3)]}. To this end, we examined potentiometrically the consequences of substitution of K^+ by Bu_4N^+ ions in an aqueous solution of their bromides using silver bromide (electrochemically prepared according to the known technique) and glass (ESL-63-07) electrodes. For details on this kind of research technique (with data putting in the form equivalent to that obtained for chains without transfer), developed by I.V. Mironov, see [33]. All the solutions tested were included into two chains with transfer (silver bromide–saturated calomel electrode or glass–saturated calomel electrode pair). The experimental data from a series of such measurements are presented in Table 4. In the series of the solutions tested the activity of the bromide ions remained constant within the limits of the errors, as follows from invariance of ln $\gamma\pm$ for H^+, Br^- (see the E_D column). From this it follows that $\gamma\pm$ is unaffected by substitution of K^+ by Bu_4N^+ at a fixed ionic strength (which conclusion is consistent with the existing generalizations [33]) and there is no significant sought-for binding of Bu_4N^+ and Br^-.

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[7] The possibility of this rearrangement is indicated by a drastic change in the form of the empirical function in the $S(Bu_4N^+) > 0.3–0.4$ area, detected by us (from constancy to within the limits of the errors to a regular growth at 60°C and decrease at 50°C and below, see Figs. 1 and 2), as well as by the available information on formation of clathrate-like solid polyhydrates in the cation exchanger–water systems. For example, it was found that, in the mixed [(H + Bu_4N) or (H + *i*-Am_4N)] form of polyacrylate carboxylic cation exchanger–aqueous solution systems at the degree of proton substitution by the Bu_4N^+ or *i*-Am_4N^+ cation equal to or above 0.4, crystalline polyhydrates are formed with the melting points increasing with increasing equivalent proportion of alkylammonium cation in the ion exchanger [7, 11, 12]. Formation of a solid polyhydrate with the melting point of +8°C was also derived in [8] from thermograms of samples of swollen grains of polystyrene sulfonate cation exchanger Dowex 50Wx2 in the *i*-Am_4N form.

To conclude, three points will be emphasized. First, the absence of significant manifestations of formation of the Bu_4NBr_{solv} ion pair in the composition of an aqueous solution of the heterogeneous system under study certainly does not exclude the possibility, in principle, of formation of clathrate-like structures for water molecules in the first hydration-solvation sphere of the $Bu_4N^+_{solv}$ particles in these same aqueous solutions. Second, under the (p, T, X) conditions closer to those of formation in the corresponding systems of solid clathrate polyhydrates, the possibility of formation of clathrate-like ion pairs in solution cannot be ruled out either. Third, though applicable in principle to the above-mentioned (p, T, X)-conditions, the technique that we developed needs adjustment with the view of its inclusion in the framework of specific models that take into account the secondary medium effects both in solution and in the ion exchanger (in the latter case, with the possibility of structural rearrangements taken into account).

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