General and Inorganic Chemistry

Equilibrium of Br^- and Cl^- exchange on strong-basic anion-exchanger

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The equilibrium of Br^- and Cl^- exchange is studied on the strong-basic anion-exchangers. Quantitative characteristics which can be used for elaboration of dual-temperature separation processes have been obtained. An empirical equation for the dehydration extent of an anion in a phase of a sorbent has been suggested, allowing one to calculate the Br^- and Cl^- exchange equilibrium constants on the anion-exchanger in a wide temperature range.

Key words: ion exchange; strong-basic anion-exchanger; dual-temperature processes; thermodynamic constants.

The creation of ecologically pure technological processes in the areas of purification and isolation of individual components from complicated mixtures has become possible in recent years owing to the development of dual-temperature ion-exchange methods of separation of substances in solutions.[1—2]

The concentration of bromides from natural water, for example, from the ocean water, using strong-basic anion-exchanger is one of the interesting problems.[3—5] For solution of this problem, data on the Br^- and Cl^- exchange equilibrium at different temperatures in solutions of different compositions and on different anion-exchangers are primarily needed.

The data presented in the known monographs on the ion exchange and in several articles are rather scarce.[6,7]

The temperature dependence of the exchange equilibrium constants is studied for bromide and chloride ions on the Dowex-1×10 anion-exchanger in acidic chloride solutions containing microadditions of bromides.[6]

Data on the exchange equilibrium of Cl^- and I^- ions to OH^- on the Dowex-1×4 and Dowex-1×10 anion-exchanger at temperatures below 328 K are available.[7]

In this work, exchange equilibria of Br^- and Cl^- on anion-exchanger are studied in a wide range of conditions with the purpose of obtaining values of parameters which can be used for the creation of the dual-temperature processes of concentration and separation.

Experimental

Strong-basic anion-exchanger with the parameters indicated in Table 1 were used.

The exchange equilibrium for Br^- and Cl^- was studied in model solutions with a total concentration of 0.5 g-eq. L^{-1} at different ratios of concentrations of exchanging ions.

Bromide in solution was analyzed by the known procedure[8] based on the oxidation of Br^- to Br_2 with chloramine T, decomposition of the oxidant excess, interaction of bromine formed with Phenol red, and photometry of the dye, tetrabromo-derivative. The relative error of determination of

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2083—2089, December, 1994.

Table 1. Parameters of sorbents

Sorbent	AB-17×8	Dowex-1×1	Dowex-1×4	Dowex-1×8	Dowex-1×16
Average grain size in air-dry state (*d*/mm)	0.75	0.20	0.10	0.10	0.20
Full exchange capacity of the Cl^--form in the air-dry state (mg-eq. g^{-1})	2.76	4.03	3.22	2.51	1.87
Full exchange capacity per 1 mL of the sorbent layer in 0.5 *N* NaCl (mg-eq. mL^{-1})	1.41	0.65	1.22	1.17	1.14

bromides by this method does not exceed 1—2 %. The content of Cl^- and Br^- ions was additionally determined by ion chromatography and potentiometric titration of the solutions of the mixtures of sodium chloride, bromide, and nitrate with an $AgNO_3$ solution, using a cell with a silver working electrode and a calomel reference electrode.[9] This procedure allows one to determine separately anions with a molar ratio of $[Br^-]$: $[Cl^-]$ within 1 : 20 to 10 : 1 with error no more than 1—2 %.

Coefficients of the ion-exchange equilibrium were found by the dynamic method, using ion-exchange columns with thermostated jackets and anion-exchanger layers: l = 12 to 20 cm, S = 0.40 to 0.60 cm^2.

Equilibrium coefficients were determined by direct frontal analysis and by the analysis of solutions after desorption of Br^- and Cl^- from an anion-exchanger. An initial solution with the concentration of salts $C_{0,Cl} + C_{0,Br} = C_0$ was passed through a column with an anion-exchanger in the Cl^--form with the total exchange capacity over the whole layer Q_0 (mg-eq.) containing V_0 (mL) of the free volume of 0.5 *N* NaCl solution. The solution was passed with linear velocity v = 60 to 100 cm h^{-1} (under the condition v/l = 5 h^{-1}) till the equilibrium with the anion-exchanger was achieved. The fractions of V_i in volume were collected, and the concentration of bromide in the fractions $C_{i,Br}$ was measured in parallel several times. After passage of the solution, whose volume exceeded the volume V_e corresponding to the equilibrium, the column was washed with distilled water until the salts were completely washed off, and desorption with 1 *N* $NaNO_3$ solution was performed till the bromide ion was not found in the eluate. The concentrations of Cl^- and Br^- ions in the total volume of the eluate ($C_{e,Cl}$ and $C_{e,Br}$) were determined in parallel several times.

The concentration equilibrium constant (equilibrium coefficient) in the direct method was found as follows:

$$K_{Cl}^{Br} = \frac{Q_{Br}}{Q_0 - Q_{Br}} \frac{C_{0,Cl}}{C_{0,Br}} ,$$

where Q was calculated from the balance correlation:

$$Q_{Br} = (V_e - V_0)C_{0,Br} - \sum_{i=1}^{n} V_i C_{i,Br} ,$$

where n is the number of fractions.

Under the conditions of the experiments performed and taking into account the errors of the analytical procedures used, the errors of determination of K_{Cl}^{Br} by this method (estimated by the rules of calculation of the limiting errors for functions of several arguments) do not exceed 10—15 %, and in the case where $C_{0,Br} << C_0$ they are not more than 5—8 %.

For the solutions with a comparable concentration of exchanged anions, the values of the equilibrium coefficients obtained from the analysis of the eluate solutions after desorption of both anions are the most reliable. They were calculated by the formula

$$K_{Cl}^{Br} = \frac{Q_{Br}}{Q_{Cl}} \frac{C_{0,Cl}}{C_{0,Br}} = \frac{C_{e,Br}}{C_{e,Cl}} \frac{C_{0,Cl}}{C_{0,Br}} .$$

The maximum errors of determination of K_{Cl}^{Br} in this method do not exceed 4—6 %.

The equilibrium coefficients found by both of the methods in all cases coincided with an error < 10 %.

Equilibrium coefficients were additionally determined under static conditions by the known procedure.[7] The accuracy of the results obtained by this method is comparable with the accuracy of dynamic methods only under the condition of the independent analysis of the anionic composition of the sorbent phases and the equilibrium solution. These data were used only as reference in the analysis of only one of the ions and in the calculation of the equilibrium coefficient taking into account the mass balance.

Results and Discussion

The elution curves presented in Fig. 1 show that the sorption capacity of strong-basic anion-exchanger to Br^- ions to a great extent depends on temperature. The results of the determination of equilibrium Br^- and Cl^- exchange coefficients on anion-exchanger are presented in Table 2.

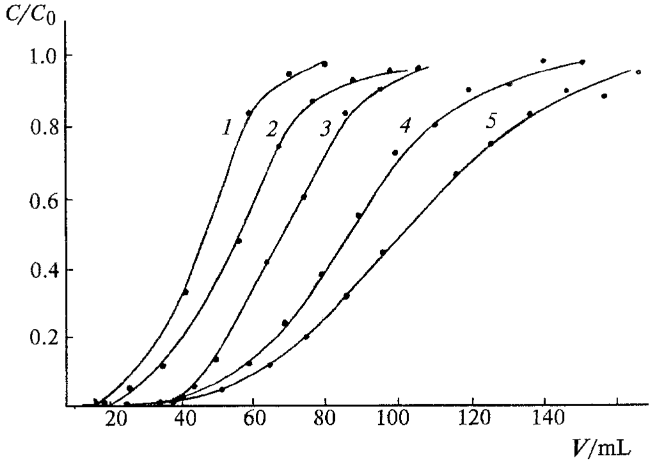

Fig. 1. Elution curves for Br^- sorption on the AB-17×8 anion-exchanger in the Cl^--form from the solution: NaBr, $8 \cdot 10^{-4}$; NaCl, 0.5 g-eq. L^{-1}; *T*/K: 363 (*1*); 344 (*2*); 328 (*3*); 297 (*4*); and 282 (*5*).

The study of AB-17×8 and Dowex-1×16 anion-exchanger in equilibrium with the solutions with different ratios of $[Br^-]$: $[Cl^-]$ attests that the selectivity of anion-exchanger depends on the exchange extent within errors of determination.

A similar conclusion has previously been made in the study of the exchange of Br^-, NO_3^-, and IO_3^- to Cl^- on the Dowex-2×8 anion-exchanger and attests to the symbate character of the changes in the ratio of activity coefficients of resinates and electrolytes and in their ratio in equilibrium solutions.[10] For Cl^- and Br^- ions, the corresponding salts of alkaline metals in solutions are characterized[11] by almost the same values of average ionic activity coefficients up to a concentration of 1 g-eq. L^{-1}. Therefore, the thermodynamic equilibrium constant for the Cl^- and Br^- exchange is related to the concentration constant independently of the temperature by the following correlation:

$$\ln\overline{K}_{\mathrm{Cl}}^{\mathrm{Br}} = \ln K_{\mathrm{Cl}}^{\mathrm{Br}} + \ln\frac{(\bar{\gamma}^{\pm})^2_{\mathrm{R-Br}}}{(\bar{\gamma}^{\pm})^2_{\mathrm{R-Cl}}} , \qquad (1)$$

where $\overline{K}$ is the thermodynamic constant, $(\bar{\gamma}^{\pm})_{\mathrm{R-Br}}$ and $(\bar{\gamma}^{\pm})_{\mathrm{R-Cl}}$ are the average ionic activity coefficients of resinates. Based on the results of Table 2, one should assume that the latter term of Eq. (1) retains a constant value independently on the extent of exchange.

The calculation of $\overline{K}$ according to (1) can be performed by different approaches at different standard states of an ion-exchanger.

A general thermodynamic method for the calculation of selectivity coefficients for strong-basic anion-exchanger is known,[12] which is based on the Gregor osmotic theory. However, this method requires information about water sorption with mixed forms of ion-exchangers and for the exchange of ions similar in properties, which are Br^- and Cl^-, it turns out to be too cumbersome and does not allow one to predict the equilibrium in a wider range of conditions, based on a limited number of experiments.

Table 2. Average values of the equilibrium Br^- and Cl^- exchange coefficients on anion-exchanger

Anionite	Molar fraction of Br^- in equilibrium solution	K_{282}	K_{363}
Dowex-1×1	$1.6 \cdot 10^{-3}$	2.50±0.25	1.94±0.19
Dowex-1×4	$1.6 \cdot 10^{-3}$	3.75±0.38	2.46±0.25
Dowex-1×8	$1.6 \cdot 10^{-3}$	4.90±0.25	2.81±0.14
AB-17×8	$1.6 \cdot 10^{-3}$	4.80±0.24	2.79±0.14
AB-17×8	$8.3 \cdot 10^{-3}$*	—	2.82±0.28
AB-17×8	$3.8 \cdot 10^{-2}$*	5.02±0.50	—
AB-17×8	$4.5 \cdot 10^{-2}$*	—	2.85±0.29
AB-17×8	$7.7 \cdot 10^{-2}$	5.32±0.53	—
AB-17×8	$9.1 \cdot 10^{-2}$*	—	2.79±0.28
AB-17×8	$1.6 \cdot 10^{-1}$	4.84±0.24	2.68±0.13
AB-17×8	$2.1 \cdot 10^{-1}$*	5.28±0.53	—
AB-17×8	$3.2 \cdot 10^{-1}$	4.75±0.24	2.77±0.14
AB-17×8	$6.0 \cdot 10^{-1}$	4.85±0.24	2.81±0.14
Dowex-1×16	$1.6 \cdot 10^{-3}$	6.92±0.35	3.52±0.18
Dowex-1×16	$3.2 \cdot 10^{-1}$	6.83±0.34	3.51±0.18
Dowex-1×16	$6.0 \cdot 10^{-1}$	6.70±0.34	3.40±0.18

* Experiments under static conditions.

When the approach based on the osmotic theory is used, standard states for a solution and an ion-exchanger are chosen in similar way (indeed, they cannot be achieved for an ion-exchanger): $\gamma = 1$ for pure solvent and for a solute in a definitely dilute solution.

In most cases, when the swelling abilities of an ion-exchanger in different ionic forms differ slightly and at the mentioned choice of standard states $\overline{K} \approx 1$, and selectivity is completely determined by the ratio of activity coefficients.[13]

The energy factor

$$RT \ln[(\gamma^{\pm})^2_{\mathrm{R-A}} / (\gamma^{\pm})^2_{\mathrm{R-B}}]$$

can be calculated as the difference between the total energies of the interaction of A and B counterions with a polyion. This approach was used for the cationic exchange on sulfocation-exchangers.[13]

The thermodynamic constant becomes a real characteristic of the selectivity of the ion-exchange system, and the value of $RT\ln K$ can be calculated as some difference of the total energies of the interaction of counterions with a polyion, if standard states for resinates are chosen as follows:[14] $(\gamma^{\pm})_{\mathrm{R-A}} = 1$ at $N_{\mathrm{R-A}} = 1$, $(\gamma^{\pm})_{\mathrm{R-B}} = 1$ at $N_{\mathrm{R-B}} = 1$, where N is the equivalent fraction for a component in a mixed resinate, which is in equilibrium with a pure solvent.

In this case, $\overline{K}$ and K are interrelated with the correlation based on the Gibbs—Duegem equation:

$$\ln\overline{K}_{\mathrm{B}}^{\mathrm{A}} = \int_0^1 \ln K_{\mathrm{B}}^{\mathrm{A}}\, dN_{\mathrm{R-A}} . \qquad (2)$$

It should be mentioned that the problem of the calculation of $\overline{K}_{\mathrm{B}}^{\mathrm{A}}$ from $K_{\mathrm{B}}^{\mathrm{A}}$ was considered,[14] based on the assumption that an ion-exchanger is a two-component system of A and B resinates, and in the general case, taking into account the contents in an ion-exchanger of a solvent and an electrolyte absorbed without an exchange. A more precise analysis[15,16] shows that the values of $\overline{K}_{\mathrm{B}}^{\mathrm{A}}$, according to expression (2), can be used for the calculation of the Gibbs energy of the ion-exchange process with certain correction coefficients. For the exchange with participation of monovalent electrolytes in solution, the value of the correction coefficient can be evaluated from the literature data[15] and is equal to the ratio of the molar concentrations of A and B resinates in the corresponding pure A and B, monoforms of the ion-exchanger considered as a two-component system. In the general case, the correction coefficient is equal to the ratio of molar fractions of A and B resinates (taking account of a solvent) in the corresponding monoionic forms, which are in equilibrium with a solvent.[16]

For ions similar in properties, when the swelling abilities of ion-exchangers in different ionic forms differ slightly, and for the same standard states for a solvent in an ion-exchanger and in a bulk solution, Eq. (2) can be used for the calculation of thermodynamic exchange constants, taking into account the corrections[16] made for standard conditions for resinates (using γ_{R-A} instead of γ_A).

In this approach, it follows from the results presented in Table 2 and the data[10] on the Br^- and Cl^- exchange that

$$\overline{K}^{Br}_{Cl} \approx K^{Br}_{Cl}, \quad \left(\bar{\gamma}^{\pm}\right)_{R-Br} \Big/ \left(\bar{\gamma}^{\pm}\right)_{R-Cl} \approx 1 .$$

It is evident that this approach is the most convenient one for the system studied.

It is shown,[17] based on a detailed analysis of the regularities of the anionic exchange, that none of the accepted concepts, including the osmotic theory and the concepts about the formation of Coulomb ionic pairs or about the ion polarization, explains the experimentally observed selectivity of strong-basic anion-exchanger.

The most satisfactory results, which agree qualitatively with the known experimental data, were obtained from the calculation of full energies of the interaction of an anion with a polycation of a resin, including the energy of Coulomb interaction, the energy of the polarization interaction, and the enthalpy of the ion hydration.[17] The main assumption is the fact that the mechanism of selectivity of the anionic exchange is related to the partial dehydration of an anion in the ion-exchanger phase. According to this, we can write

$$RT \ln K^{A}_{B} = \Delta\Delta E_{el} - \sigma\Sigma\Delta\Delta H_{h}, \tag{3}$$

where $\Delta\Delta E_{el}$ is the difference of the energies of the Coulomb and polarization interactions of A and B with a polyion of an anion-exchanger, $\Delta\Delta H_h$ is the difference of the enthalpies of hydration of these ions, and σ is the extent of dehydration.

The quantitative calculations of σ and $\overline{K}$ are difficult, because the terms of the right part of Eq. (3) are greater values than the energy $RT \ln \overline{K}$. The values of the enthalpies and entropies of hydration for individual ions were multiply improved.[18] However, the accuracy of the determination of $\Delta\Delta E_{el}$ is associated with many additional assumptions.

The exchange of Br^- and Cl^- is a convenient model for the calculation of σ, because the value of $\Delta\Delta E_{el}$ for this system is almost equal to zero.[17]

Our selected experimental data on the equilibrium constants of the Br^- and Cl^- exchange at some fixed values of temperature for anion-exchanger with different contents of the linking agent, divinylbenzene (DVB), were used for the calculation of σ. Most of them are presented in Table 2. The calculations were performed using the correlation

$$RT \ln K^{Br}_{Cl} = \sigma\left[(\Delta H_{h,Br} - \Delta H_{h,Cl}) - T(\Delta S_{h,Br} - \Delta S_{h,Cl})\right] = \\ = \sigma\Delta\Delta G_{h} . \tag{4}$$

The dehydration extent is determined as follows:

$$\sigma = (\Delta G_h - \Delta G_{h,R})/\Delta G_h, \tag{5}$$

where ΔG_h is the change in the Gibbs energy for hydration of an ion in water (for the ion transfer from the gaseous phase to water), $\Delta G_{h,R}$ is the change in the Gibbs energy for hydration of an ion in an anion-exchanger.

As so doing, expression (3) (when the $\Delta\Delta G_h$ values are used in it instead of $\Delta\Delta H_h$) retains the form and the physical meaning of the previously known equations for the ion exchange constants of Panchenkov and Gorshkov, Izmailov, and Eisenman analyzed previously.[11,19]

The following equation for A and B ions should be written using a rigid approach:

$$RT \ln K^{A}_{B} = \sigma_A\Delta G_{h,A} - \sigma_B\Delta G_{h,R} . \tag{6}$$

Correlation (4) was used for the following reasons. Different data on hydration expressed in the form of $\Delta\Delta G_h$ are more reliable and agree well with each other, because the value of $\Delta\Delta G_h$ is, in fact, the difference between the hydration energies of two salts with the common ion, which allows one to unambiguously interpret this parameter. At the same time, data on the thermodynamic parameters of hydration of ions may significantly differ in different works, which is associated with the different choice of standard states and different methods for the separation of hydration energies for anions and cations.[11,18,20] On the other hand, our calculations of σ_{Cl} and σ_{Br}, using different tabulated data, showed that in all cases $\sigma_{Cl} \approx \sigma_{Br}$.

The starting material[18] for further calculations of correlation (4) contained, in addition to the values of the standard enthalpies and entropies of ion hydration, the thermal coefficients as follows:

$$\Delta c^{0}_{p} = \left(\frac{\partial\Delta H^{0}_{h}}{\partial T}\right)_{p}, \quad \Delta e^{0} = \left(\frac{\partial T\Delta S^{0}_{h}}{\partial T}\right)_{p} . \tag{7}$$

The results of the calculations of the thermodynamic parameters for Br^- and Cl^- hydration at different temperatures based on the mentioned data are presented in Table 3. The calculations are performed in an approximation in which the values of the changes in heat capacity and entropy capacity determined under standard conditions by correlations (7) remain constant in the range from 273 to 373 K. This assumption is acceptable, because it is seen from Table 3 that the values of ΔH_h and $T\Delta S_h$ are weakly temperature-dependent. The use of empirical equations,[18] which take into account

Table 3. Thermodynamic parameters of hydration for Br^- and Cl^- ions (kJ mol^{-1}) at different temperatures (calculated using the data on thermal coefficients under standard conditions[18])

T/K	$\Delta H_{h,Br}$	$T\Delta S_{h,Br}$	$\Delta H_{h,Cl}$	$T\Delta S_{h,Cl}$	$\Delta G_{h,Br}$	$\Delta G_{h,Cl}$	$\Delta\Delta G_h$
273.0	110.0	−61.70	81.30	−63.20	171.70	144.50	−27.20
282.0	109.3	−63.09	80.60	−64.64	172.40	145.20	−27.20
298.0	107.9	−65.59	79.50	−67.14	173.50	146.60	−26.90
308.0	107.0	−67.20	78.80	−68.70	174.20	147.50	−26.70
328.0	106.2	−68.70	78.10	−70.30	174.90	148.40	−26.50
363.5	102.4	−75.90	74.90	−77.40	178.30	152.30	−26.00
373.0	101.6	−77.39	74.10	−78.94	178.99	153.04	−25.95

the temperature dependence of Δc_p and Δe, does not affect the results of the calculations. Taking into account that the tabulated data on enthalpy and entropy of hydration of Br^- and Cl^- ions are characterized[18] by relative errors of 1—1.5 %, one should expect that the relative error of the $\Delta\Delta G_h$ values in Table 3 is less than 10 %. A comparison of the results obtained at different reference states for the change in the Gibbs energy for hydration of individual ions[11,18,20] indicates also that the values of $\Delta\Delta G_h$ under standard conditions differ by less than 10 %.

The dependences of the extent of dehydration of the anion in the ion-exchanger on the content of DVB at different temperatures are presented in Fig. 2. The empirical equation for σ, which can be used for the calculation of the Br^- and Cl^- exchange equilibrium constants, including constants for other conditions that were not studied experimentally, has the form

$$\sigma = 8.31\cdot10^{-2}\sqrt[4]{\chi} - 7\cdot10^{-5}\sqrt{\chi}(T-273)\ , \qquad (8)$$

where χ is [DVB] in the anion-exchanger, %.

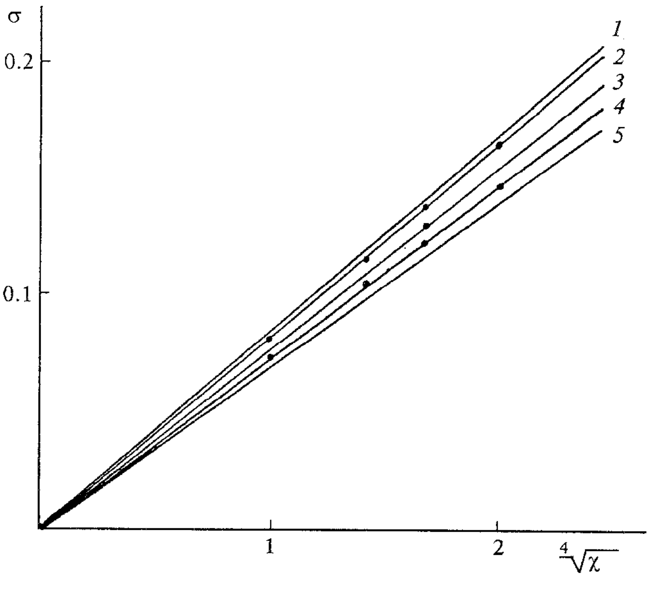

Fig. 2. Dependence of the extent of dehydration of Br^- and Cl^- ions on the content of DVB (χ(%)) in the anion-exchanger. T/K: 273 (*1*); 282 (*2*); 328 (*3*); 363 (*4*); and 373 (*5*). The results of the calculation from the experimental plots are presented by points.

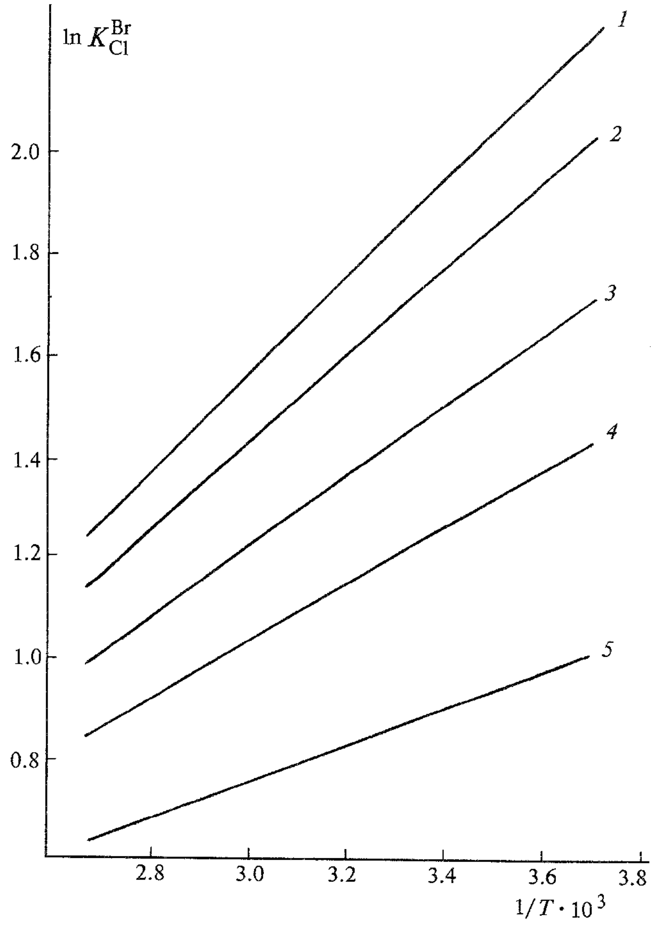

Fig. 3. Temperature dependence of the Br^- and Cl^- exchange interaction for anion-exchanger with [DVB] (%): 24 (*1*); 16 (*2*); 8 (*3*); 4 (*4*); and 1 (*5*).

Table 4. Calculated and experimental values of Gibbs energy for the Cl^- and Br^- exchange on anion-exchanger ($-\Delta G_{Cl}^{Br}$ /kJ mol^{-1})

T/K	Dowex-1×1		Dowex-1×4		Dowex-1×8		Dowex-1×16		Dowex-1×24
	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	calc.
273	—	2.26	—	3.20	—	3.80	—	4.52	5.00
282	2.15	2.23	3.10	3.15	3.72	3.75	4.49	4.45	4.92
298	—	2.19	—	3.06	3.65	3.63	—	4.28	4.73
308	—	2.15	—	3.00	3.55	3.54	—	4.18	4.59
328	—	2.10	—	2.90	3.38	3.41	—	4.00	4.38
363	2.00	2.00	2.72	2.70	3.13	3.16	3.75	3.68	3.99
373	—	1.97	—	2.66	—	3.11	—	3.59	3.89

At fixed temperatures these dependences are virtually linear and start from the beginning of coordinates, because the value of the first term of the right part of Eq. (8) considerably exceeds the value of the second term.

The results of the calculations of the Gibbs energy for the ion exchange on anion-exchanger, using Eq. (8) and the data on the difference of hydration energies of Br^- and Cl^- ions (see Table 3), are presented in Table 4. The dependences $\ln K_{Cl}^{Br}$ *vs.* $f(1/T)$ based on the calculated values of the ion-exchange equilibrium constants and those presented in Fig. 3 turned out to be linear for all of the anion-exchanger. This attests to the constancy of the ΔH_{Cl}^{Br} values in the studied temperature range, which seems to be related to the equal value of the sums of heat capacities of Br^- and Cl^- ions in anion-exchanger and solutions.

Thus,

$$\Delta H_{Cl}^{Br} = f[\sigma(T) \cdot \Delta\Delta G_h(T)] \neq f(T) \ .$$

The calculated values of enthalpies and entropies of the exchange on Dowex-1 anion-exchanger linearly depend on each other.

χ (%)	1	4	8	16	24
$-\Delta H$/ kJ mol^{-1}	3.05	4.68	5.70	7.04	8.05
$-\Delta S$/kJ mol^{-1} K^{-1}	2.89	5.42	6.95	9.25	11.16

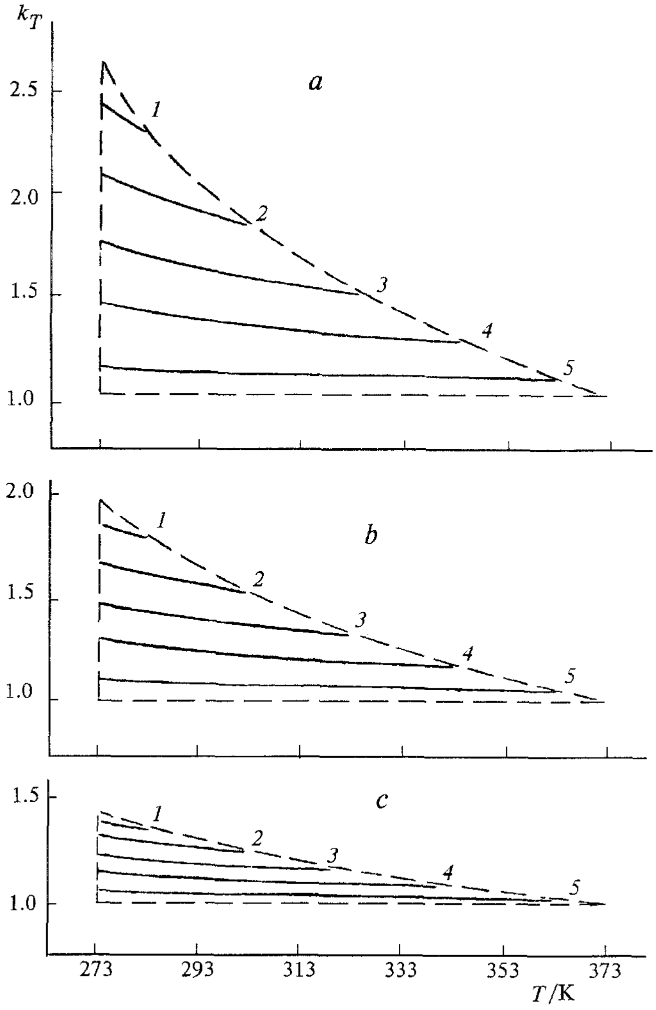

Fig. 4. Temperature dependence of the ratio of the equilibrium exchange coefficients k_T at different values of ΔT: 90 (*1*); 70 (*2*); 50 (*3*); 30 (*4*); and 10 (*5*); for anion-exchanger with [DVB] (%): 24 (*a*); 8 (*b*); and 1 (*c*). The area where dual-temperature methods are used is indicated by the dotted line.

This corresponds to the previously drawn conclusions that there is a linear dependence between the values of ΔH and ΔS in ion-exchange processes for monovalent ions on ion-exchangers with linkages of different extents.[16] The calculation of ΔH_{Cl}^{Br} for the Dowex-1×10 anion-exchanger satisfactorily coincides at 298 K with the previously obtained results[6] (6.2 and 6.4 kJ mol^{-1}); however, the estimate of the contribution of the entropy factor to the Gibbs energy for the Br^- and Cl^- exchange (55 %) seems overstated. According to our approximate calculations, the contribution of the entropy factor under standard conditions ranges from 30 % for weakly linked ion-exchangers to 40 % for strongly linked ion-exchangers. On the other hand, the temperature dependence of ΔH_{Cl}^{Br} in the range of 273—413 K found previously[6] can be explained by the fact that the authors compared the experimental data obtained at different pressures. The possibility of the influence of external pressure on the ion-exchange equilibrium is mentioned.[12]

Thus, the approach used allows one to calculate on the basis of empirical Eq. (18) and the tabulated thermodynamic data on the hydration of ions all parameters of the Br^- and Cl^- exchange equilibrium which are necessary for choosing conditions of the dual-temperature processes of concentration and separation of these ions.

The thermal coefficient is one of the main parameters used in dual-temperature methods

$$k_T = K(T)/[K(T + \Delta T)].$$

It is easy to show that

$$\ln k_T = -\frac{\Delta H\,\Delta T}{R}\,\frac{1}{T(T+\Delta T)}\,. \tag{9}$$

The diagrams presented as an example for some anion-exchanger in Fig. 4 are convenient for the estimation of the maximum extent of the concentration of bromide in the solution of a mixture of chloride and bromide, which is achieved for one stage of concentration in the dual-temperature process at the linear isotherm. It follows from these diagrams, for example, that the maximum extent of the bromide concentration is 2 when the solution of the mixture is passed through the layer of the AB-17×8 (or Dowex-1×8) anion-exchanger first at 273 K and then at 373 K. As seen from Fig. 4, the concentration extent is higher in the range of low temperatures at the same value of ΔT.

It should be mentioned in conclusion that the approach used in this work can also be useful for the study of the exchange equilibrium of other anions. In this case, a correlation of the type of Eq. (6) must be used with simultaneous account for the Coulomb component of the full energy of the interaction of ions and an anion-exchanger.[17] The data for Br^- and Cl^- obtained above may be used as one of the reference values of the extent of dehydration to increase the reliability of calculations. It is evident that, unlike the Br^-—Cl^- system, which is almost an ideal model (for this anion-exchanger, $\sigma_{Cl} \approx \sigma_{Br}$, $\overline{K} \approx K$, $\Delta H = \text{const}$), the study of other systems seems to be a considerably more difficult problem. Significant advances in this area are possible if reliable experimental and theoretical data on the thermodynamic parameters and thermal coefficients of hydration of monomeric analogs of strong-basic anion-exchanger (tetraalkyl ammonium salts) become available.

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Received February 8, 1994;
in revised form June 10, 1994