Anion exchange in mixed solvent systems. III.
Penetration of cations into anion exchanger

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The penetration of Na^+ cations into anion exchanger Dowex 2X-8 was investigated in mixed solvent systems: ethyl alcohol—hydrochloric acid——water. The functional relations which describe the change in equilibrium distribution coefficients were determined for varying concentrations of macrocomponents in mixed solution. By the Gibbs—Donnan equation the values of the mean activity coefficient of sodium chloride were calculated for the inner solution of exchanger. The basic causes which control the penetration of cations into anion exchanger are discussed.

The penetration of positively charged ions from aqueous solution into anion exchanger is usually small but in mixed solutions it may reach higher values according to the composition of mixed solvent systems. If a given cation does not produce any negatively charged complex forms under certain conditions, the penetration of positive ions into exchanger may significantly affect the value of the overall equilibrium distribution coefficient.

The concentration of macrocomponents in a mixed solution is responsible for the dielectric constant and ionic strength of solution. These basic characteristics, however, control the chemical affinity of the investigated microcomponent both in the outer and in the inner solution of exchanger. The change in the composition of outer solution produces some changes in the swelling and swelling pressure of the phase of exchanger as well as in the molar volume of the electrolyte under investigation. These quantities have also influence on the penetration of microcomponent into exchanger because they affect the value of chemical potential of the investigated microcomponent in the phase of exchanger. The study of the penetration of electrolytes into exchanger [1, 2] confirmed the validity of the Gibbs—Donnan equation for the equilibrium distribution of electrolyte between the outer and the inner solution of exchanger.

This paper presents a study of the penetration of Na^+ cations from mixed solutions consisting of water, hydrochloric acid, and ethyl alcohol into anion exchanger Dowex 2X-8. The aim of this study was to generalize the results obtained in order to describe the dependence of the penetration of cations into exchanger on the composition of mixed solution and express general relationships involved in this process.

Experimental

Material, instruments, and equipments

An anion exchanger Dowex 2X-8 (100—200 mesh) treated in the same way as in preceding studies [3, 4] and a stock solution of $^{24}NaCl$ with the concentration of 100 μCi ml^{-1} and 1 M concentration of isotopic carrier were used.

The measurement of the activity of dissolved radionuclides was made in 5-ml thin--walled glass ampoules Str-5. The scintillation probe NAG 232 with photomultiplier PK 411 and scintillation crystal NaI(Tl) of the type SKG 45/56 connected with a high voltage supply NBZ 411 and impulse counter Optima 403 was used for measurements as a detector. With this equipment the measurements of the activity of exchanger phase were carried out in vessels with porous glass bottom in which the exchanger was separated from neighbouring solution. In all cases the counting rate was estimated. The measurements were so performed that the relative error of measurement was smaller than 1%.

Working procedure

The investigation of the penetration of Na+ ion into anion exchanger was carried out by batch equilibration method. The system contained 1 g of dry exchanger and 50 ml of mixed solution. The mixed solution was prepared by mixing the relative amounts of water, concentrated hydrochloric acid (density 1.18 g cm^{-3}), ethyl alcohol (96 weight %), and the stock solution of ^{24}NaCl. The solutions thus prepared contained 0, 40, 65, 80, or 95 volume % of ethyl alcohol, 0.25—5.0 M hydrochloric acid and NaCl in 0.02 M concentration. All experiments were made twice. The equilibrium was established in 2 hours under constant shaking in 100-ml polyethylene vessels.

The corrections were made with respect to the different geometry during the measurements of counting rate of exchanger and solution samples as well as with respect to the decay of radionuclide ^{24}Na during the measurements.

On the basis of measurements the average values of equilibrium distribution coefficient were calculated.

Results

The penetration of cations into anion exchanger in dependence on the composition of mixed solvents

The penetration of Na+ cations into anion exchanger Dowex 2X-8 was expressed formally by the value of the equilibrium distribution coefficient K_d [ml g^{-1}] which was determined both from the activity decrease in outer solution and from the activity measurement of the phase of exchanger [3].

From the values of the equilibrium distribution coefficient K_d given in Table 1 the amount of sodium chloride in exchanger $\bar{G}_{NaCl}$ [mol g^{-1}] was estimated for a given composition of mixed solution according to the expression

$$\bar{G}_{NaCl} = K_d\, c_{NaCl}, \tag{1}$$

where c_{NaCl} is the concentration of sodium chloride in neighbouring solution [mol l^{-1}]. The results of this estimation are presented in Table 2.

It was found that at a certain concentration of hydrochloric acid the amount of sodium chloride in exchanger increased proportionally to the molar fraction of organic solvent in outer solution. This dependence is presented in Fig. 1.

At the same time it appeared (Fig. 2) that the values of ln $\bar{G}_{NaCl}$ as well as the values of ln K_d^{-1} change proportionally to the logarithm of the hydrochloric acid concentration (ln c) in outer solution.

The relationships presented in Figs. 1 and 2 may be described by the following equations

The calculated and the experimental values of $\bar{G}_{NaCl}$ for varying
composition of mixed solvent systems

Experiment	Composition of outer solution		K_d [ml g^{-1}]	x ethyl alcohol	$\bar{G}_{NaCl} \cdot 10^6$ calculated [mol g^{-1}]	$\bar{G}_{NaCl}$ found [mol g^{-1}]
	ethyl alcohol [volume %]	c_{HCl} [mol l^{-1}]				
1	0	0.25	0.260	0.000	5.54	5.20
2	0	0.50	0.288	0.000	5.67	5.76
3	0	1.00	0.297	0.000	5.81	5.94
4	0	2.00	0.303	0.000	5.95	6.06
5	0	5.00	0.344	0.000	6.15	6.88
6	40	0.25	0.393	0.164	8.42	7.86
7	40	0.50	0.465	0.165	9.42	9.30
8	40	1.00	0.512	0.165	10.5	10.2
9	40	2.00	0.588	0.165	11.8	11.8
10	40	4.00	0.621	0.167	13.2	12.4
11	65	0.25	0.690	0.346	13.9	13.8
12	65	0.50	0.842	0.346	17.1	16.8
13	65	1.00	1.043	0.347	20.5	20.9
14	65	2.00	1.172	0.349	25.9	23.5
15	65	3.00	1.441	0.351	28.8	28.8
16	80	0.25	1.103	0.515	20.6	22.0
17	80	0.50	1.536	0.517	29.4	30.7
18	80	1.00	1.954	0.519	36.7	39.1
19	80	1.50	2.379	0.520	47.3	47.6
20	80	2.00	2.457	0.522	51.1	49.2
21	95	0.25	1.991	0.780	40.9	39.8
22	95	0.37	2.210	0.781	55.9	44.2
23	95	0.50	2.320	0.782	63.1	46.4

$$\ln \bar{G}_{NaCl(x,\, c)} = k'_{(c)} x + b'_{(c)}, \qquad (2)$$

$$\ln \bar{G}_{NaCl(x,\, c)} = k_{(x)} \ln c + b_{(x)}, \qquad (3)$$

where $\bar{G}_{NaCl}$ denotes the number of micromoles of sodium chloride in the exchanger at
equilibrium with neighbouring solution, c is the concentration of hydrochloric acid
[mol l^{-1}] (in Table 1 denoted c_{HCl}) and x is the molar fraction of ethyl alcohol in outer
solution (in Table 1 denoted $x_{ethyl\ alcohol}$). The slope $k'_{(c)}$ depends on the concentration
of hydrochloric acid in outer solution while the slope $k_{(x)}$ is fixed by the molar fraction
of ethyl alcohol in mixed solvent system.

The value of $b'_{(c)}$ can be determined if we take the value of $\ln \bar{G}_{NaCl\,(x,\, c)}$ for $x = 0$.
By solving equations (2) and (3) we obtain

$$b'_{(c)} = k_{(0)} \ln c + b_{(0)}. \qquad (4)$$

For $c = 1$ it follows from equations (2) and (3)

$$b'_{(1)} = \ln \bar{G}_{NaCl(0,\, 1)} = b_{(0)}. \qquad (5)$$

By substituting from equations (4) and (5) into equation (2) we obtain

$$\ln \bar{G}_{NaCl(x,\, c)} = k'_{(c)} x + k_{(0)} \ln c + \ln \bar{G}_{NaCl(0,\, 1)}. \qquad (6)$$

Table 2

Swelling of exchanger Dowex 2X-8 in mixed solvent systems
Amounts of concentrations of sodium chloride in exchanger

Experiment	Composition of solution		$\bar{G}_{NaCl} \cdot 10^6$ [mol g^{-1}]	V_e [ml mol^{-1}]	Δv_i [ml g^{-1}]	$c_{NaCl} \cdot 10^3$ [mol l^{-1}]	ϱ_i [kg l^{-1}]	$\bar{m}_{NaCl} \cdot 10^3$ [mol kg^{-1}]
	ethyl alcohol [volume %]	c_{HCl} [mol l^{-1}]						
1	0	0.25	5.20	445	0.475	10.95	0.999	10.96
2	0	0.50	5.76	443	0.469	12.28	1.004	12.23
3	0	1.00	5.94	439	0.456	13.02	1.012	12.86
4	0	2.00	6.06	435	0.446	13.58	1.027	13.23
6	40	0.25	7.86	451	0.494	15.91	0.984	16.68
7	40	0.50	9.30	457	0.512	18.16	0.959	18.94
8	40	1.00	10.24	469	0.548	18.68	0.967	19.38
9	40	2.00	11.76	467	0.542	21.70	0.982	22.10
11	65	0.25	13.80	445	0.474	29.11	0.927	31.40
12	65	0.50	16.84	450	0.489	34.44	0.931	36.99
13	65	1.00	20.86	457	0.510	40.90	0.938	43.60
14	65	2.00	23.46	459	0.516	45.42	0.953	47.66
16	80	0.25	22.06	438	0.453	48.70	0.908	53.63
17	80	0.50	30.72	440	0.459	66.93	0.911	73.47
18	80	1.00	39.08	439	0.456	85.72	0.918	93.38
20	80	2.00	49.14	446	0.477	103.01	0.935	110.17
21	95	0.25	39.82	422	0.405	98.32	0.862	114.06
23	95	0.50	46.40	421	0.402	115.42	0.866	133.28

The functional relationship $k'_{(c)}$ was determined by means of the experimental relations presented in Fig. 1. Using equation (2) the values of k' were calculated for the concentration range from 0.25 to 2 M-HCl. The values of $k'_{(c)}$ were expressed by the simple expression

$$k'_{(c)} = k'_{(1)} + k'' \ln c, \tag{7}$$

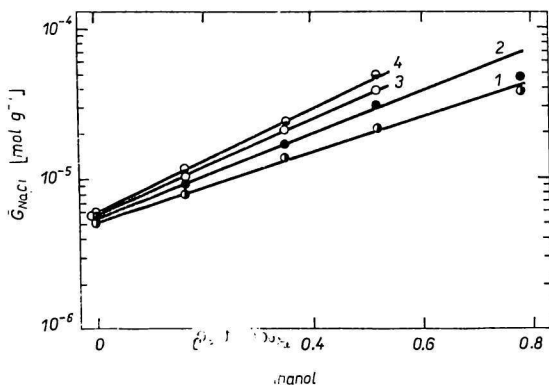where k'' is the slope of the curve presented in Fig. 3.

Fig. 1. Effect of the concentration of ethyl alcohol in mixed solution upon the amount of NaCl in exchanger.
The penetration of NaCl from 0.02 M-NaCl containing water, ethyl alcohol, and hydrochloric acid with concentration.
1. 0.25 M; *2.* 0.50 M; *3.* 1.0 M; *4.* 2.0 M.

By substituting from equation (6) into equation (7) we obtain the resulting expression

$$\ln \bar{G}_{NaCl(x,\, c)} = x\, k'' \ln c + k'_{(1)} + k_{(0)} \ln c + \ln \bar{G}_{NaCl(0,\, 1)}, \qquad (8)$$

which describes the penetration of NaCl from mixed organic-aqueous solvent systems into anion exchanger in dependence on the concentration of individual macrocomponents in mixed system.
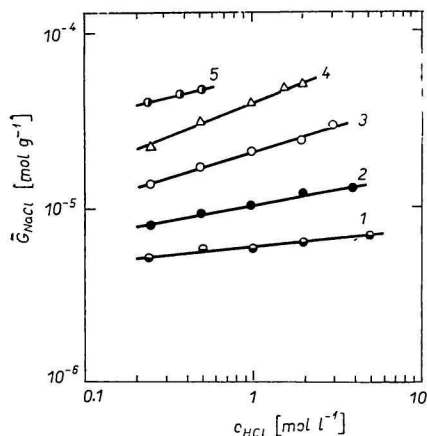

Fig. 2. Effect of the concentration of hydrochloric acid in mixed solution upon the amount of NaCl in exchanger.
The penetration of NaCl from 0.02 M-NaCl containing water, hydrochloric acid, and ethyl alcohol.
1. 0 volume %; *2.* 40 volume %; *3.* 65 volume %; *4.* 80 volume %; *5.* 95 volume %.
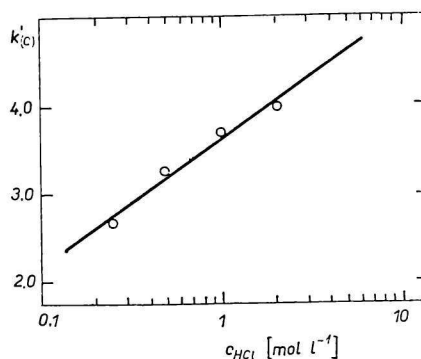
Fig. 3. Variation of $k'_{(c)}$ with the concentration of hydrochloric acid in mixed solution.

The values of the constants in equation (8) were: $k'' = 0.748$, $k'_{(1)} = 3.60$, $k_{(0)} = 0.0347$, and $\ln \bar{G}_{NaCl(0,\, 1)} = 1.760$. The values of $\bar{G}_{NaCl}$ calculated according to equation (8) for various compositions of solvent system are given in Table 1.

The comparison of the values of $\bar{G}_{NaCl}$ calculated according to equation (8) with the values found experimentally which are given in the last column of Table 1 showed a very good agreement between the results calculated and measured even for extreme contents of individual macrocomponents in mixed solutions.

Estimation of the activity coefficients of microcomponent and volume factors

To appreciate the effect of the change in activity coefficients and the volume factors on the value of equilibrium distribution coefficient, the adar⁺ ᵗʰᵉrmodynamic relationship was applied to express the equilibrium

$$\bar{\bar{\gamma}}_{\pm \text{NaCl}} = \frac{m_{\text{NaCl}}}{\overline{m}_{\text{NaCl}}} \, \gamma''_{\pm \text{NaCl}} \exp\left(-\frac{P \, \overline{V}_{\text{NaCl}}}{R \, T}\right), \tag{9}$$

where $\overline{m}_{\text{NaCl}}, m_{\text{NaCl}}$ — molality of NaCl in exchanger and in outer solution, respectively,

$\gamma''_{\pm \text{NaCl}}$ — mean activity coefficient of NaCl in outer solution,

$\bar{\bar{\gamma}}''_{\pm \text{NaCl}}$ — mean activity coefficient of NaCl in exchanger,

P — swelling pressure of anion exchanger [atm],

$\overline{V}_{\text{NaCl}}$ — partial molar volume of sodium chloride in the inner solution of exchanger [cm³],

R — gas constant (82.056 cm³ atm K⁻¹ mol⁻¹),

T — temperature in absolute temperature scale (298 K).

The determination of the quantities of the right-hand side of equation (9) enabled us to calculate the values of the mean activity coefficient of sodium chloride in the inner solution of exchanger. The values of these quantities were determined as follows.

The concentration of microcomponent in exchanger $\bar{c}_{\text{NaCl}}$ [mol l⁻¹] was determined from the values of the equilibrium weight distribution coefficient K_d using the expression

$$\bar{c}_{\text{NaCl}} = K_d \, c_{\text{NaCl}}(\varDelta v_i)^{-1}, \tag{10}$$

where c_{NaCl} is the concentration of sodium chloride in neighbouring solution the value of which was 2.0×10^{-2} mol l⁻¹ in all cases, the error being below 2%. $\varDelta v_i$ is the volume increase of 1 g of dry exchanger due to swelling. The values of $\varDelta v_i$ were found from the values of the equivalent swelling of exchanger V_e [4] in certain mixed solutions using the relation

$$\varDelta v_i = (V_e - V_0) \, c_0, \tag{11}$$

where V_e — volume of swollen exchanger [ml mol⁻¹],

V_0 — volume of dry exchanger (287 ml mol⁻¹),

c_0 — exchanger capacity of dry exchanger (3.01×10^{-3} mol g⁻¹).

For the composition of the inner solution of exchanger in investigated media [4] the densities of inner solutions ϱ_i [kg l⁻¹] were determined. These values were used for the calculation of the molal concentration of sodium chloride in the inner solution of exchanger $\overline{m}_{\text{NaCl}}$ according to the approximate expression

$$\overline{m}_{\text{NaCl}} = \bar{c}_{\text{NaCl}}(\varrho_i)^{-1}. \tag{12}$$

For the investigated concentrations of microcomponent the error involved in this expression was smaller than 1% in most cases.

The values of V_e, $\varDelta v_i$, $\bar{c}_{\text{NaCl}}$, ϱ_i, and $\overline{m}_{\text{NaCl}}$ are summarized in Table 2.

In a similar way, the values of the molal concentration of sodium chloride in outer solution m_{NaCl} were calculated by means of expression (12). These values are presented in Table 3.

The value of the activity coefficient of NaCl in outer solution was determined by calculation. The effect of the dielectric constant of medium on the value of activity coefficient was expressed by approximate formula

$$\ln \gamma''_i = \ln \gamma''_0 \left(\frac{\varepsilon_0}{\varepsilon_i}\right)^{3/2} \tag{13}$$

Table 3

Values of the mean activity coefficient of sodium chloride and hydrochloric
acid in mixed solvent systems

Experiment	m_{HCl} [mol kg^{-1}]	m_{NaCl} [mol kg^{-1}]		γ''_{HCl} inter-polated	γ''_{HCl} calculated		$\gamma''^{0}_{\pm NaCl}$	$\gamma''_{\pm NaCl}$
1	0.251	0.0201	78.52	0.764	0.764	0.0565	0.717	0.741
2	0.505	0.0202	78.52	0.757	0.757	0.0573	0.679	0.726
3	1.020	0.0206	78.52	0.809	0.809	0.0580	0.656	0.750
4	2.081	0.0208	78.52	1.040	1.040	0.0580	0.672	0.888
6	0.273	0.0218	58.85	0.633	0.660	0.0567	0.599	0.620
7	0.550	0.0220	58.70	0.648	0.650	0.0574	0.549	0.590
8	1.112	0.0222	58.51	0.693	0.719	0.0580	0.519	0.595
9	2.276	0.0228	58.00	0.898	—	0.0580	0.535	0.725
11	0.289	0.0231	44.69	0.548	0.534	0.0569	0.461	0.748
12	0.581	0.0232	44.44	0.529	0.521	0.0575	0.403	0.436
13	1.176	0.0235	44.14	0.570	0.604	0.0580	0.367	0.430
14	2.410	0.0241	43.38	0.778	—	0.0580	0.380	0.524
16	0.300	0.0240	36.03	0.445	0.421	0.0570	0.343	0.357
17	0.601	0.0242	35.82	0.418	0.406	0.0575	0.285	0.309
18	1.218	0.0244	35.31	0.445	0.495	0.0580	0.247	0.292
20	2.498	0.0250	34.33	0.667	—	0.0580	0.254	0.354
21	0.310	0.0248	27.90	0.310	0.281	0.0570	0.208	0.217
23	0.623	0.0249	27.59	0.282	0.264	0.0576	0.157	0.170

γ''_i being the mean molal activity coefficient of electrolyte in mixed solution, γ''_0 the activity coefficient in aqueous solution while ε_j and ε_i are the corresponding values of the dielectric constant of solvent system.

Equation (13) may be used for mixed solvent system in the range $\gamma''_0 \leq 1$. It also express the approximate value of the activity coefficient of electrolyte in a mixed solution for the region beyond the validity of limiting law. The accuracy of the description of real state based on equation (13) may be demonstrated by means of a comparison between column 5 and column 4 in Table 3. The former contains the values of the activity coefficient of hydrochloric acid calculated according to expression (13) while the values obtained by graphical interpolation from the tabulated data available [5], obtained by conductivity measurements, are in column 4.

The values of the activity coefficient of sodium chloride in mixed solvent systems ethyl alcohol—water are in column 7 of Table 3.

The effect of the concentration of hydrochloric acid on the value of the activity coefficient of sodium chloride in mixed solvent systems was determined according to the rule of Harned

$$\log \gamma''_{\pm NaCl} = \log \gamma''^{0}_{\pm NaCl} - \alpha_{Na-H}\, m_{HCl}, \tag{14}$$

where $\gamma''_{\pm NaCl}$ — mean activity coefficient of sodium chloride in mixed solutions NaCl—HCl of the overall molality $m = m_{NaCl} + m_{HCl}$,

$\gamma''^{0}_{\pm NaCl}$ — activity coefficient of NaCl in a solution containing single electrolyte (NaCl) in the concentration m,

α_{Na-H} — interaction coefficient determined from the data available [6].

The values of the activity coefficients of sodium chloride in a solvent system with dielectric constant ε_i, corrected for the interaction with hydrochloric acid are given in the last column of Table 3, the overall molality of electrolytes being m at 25°C.

The value of the term involving pressure and volume in equation (9) valid for the penetration of sodium chloride into exchanger was calculated for the given characteristics of exchanger in mixed solutions. The values used for calculation are given in Table 4.

Table 4

Values of the mean activity coefficient of sodium chloride in the phase of exchanger and the pressure volume term of the Gibbs—Donnan equation

Experiment	$P \cdot 10^{-3}$ [torr]	C_F [mol l^{-1}]	$\bar{c}_{HCl}$ [mol l^{-1}]	$\bar{V}_{NaCl}$ [cm^3]	$\exp\left(-\dfrac{P\,\bar{V}}{R\,T}\right)$	$a_{NaCl} \cdot 10^3$	$\bar{\gamma}''_{\pm NaCl}$
1	100	6.34	0.20	22.33	0.8866	14.89	1.5322
2	98.2	6.41	0.40	22.53	0.8878	14.66	1.3446
3	94.3	6.58	0.90	23.01	0.8896	15.15	1.3237
4	90.6	6.76	2.71	24.37	0.8880	18.47	1.5730
6	105.6	6.10	0.20	22.22	0.8814	13.52	0.9196
7	111.3	5.88	0.40	22.30	0.8749	12.98	0.7834
8	122.6	5.49	0.90	22.57	0.8616	13.21	0.7936
9	120.7	5.56	2.56	23.86	0.8620	16.53	0.8677
11	99.9	6.34	0.20	22.33	0.8869	11.04	0.3963
12	104.7	6.13	0.40	22.41	0.8814	10.12	0.3103
13	111.3	5.88	0.90	22.73	0.8728	10.10	0.2653
14	113.2	5.82	2.45	23.88	0.8646	12.63	0.3065
16	93.4	6.63	0.20	22.45	0.8933	8.57	0.1787
17	95.2	6.54	0.40	22.59	0.8907	7.48	0.1142
18	94.3	6.58	0.90	23.01	0.8897	7.12	0.0856
20	100.9	6.29	2.32	23.95	0.8781	8.85	0.0914
21	78.3	7.41	0.20	22.78	0.9085	5.38	0.0518
23	77.3	7.47	0.40	22.96	0.9089	4.23	0.0349

The swelling pressure P [atm] was computed for the systems under investigation using the equation

$$P = 1.24(V_e - 338.8), \qquad (15)$$

presented in preceding paper [4]. It was assumed that this relationship should also be valid for the mixed solutions containing a small amount of hydrochloric acid. The values of the equivalent volume of exchanger V_e [ml mol^{-1}] given in Table 2 were used for the computation of swelling pressure.

The values of the partial molar volume $\bar{V}_{NaCl}$ of sodium chloride were calculated for the conditions in exchanger by means of the expression

$$\bar{V}_{NaCl} = \bar{V}^0_{NaCl} + \frac{3}{2} S_v \left(\frac{C_F}{2} + \bar{c}_{HCl}\right)^{1/2} \qquad (16)$$

where $\bar{V}^0_{\text{NaCl}}$ — partial molar volume of sodium chloride at infinite dilution 16.4 cm³,

S_v — coefficient 2.153,

C_F — concentration of the exchangeable ions Cl⁻ in exchanger [mol l⁻¹],

$\bar{c}_{\text{HCl}}$ — number of moles of hydrochloric acid which penetrated into exchanger during swelling in the mixed solution of a certain composition [mol l⁻¹].

From the values $\bar{V}_{\text{NaCl}}$ and P the term of the Gibbs—Donnan equation involving pressure and volume was determined. Its values are given in column 5 of Table 4 for the media under investigation.

On the basis of the calculated values of the mean activity coefficient of sodium chloride in outer solution $\gamma''_{\pm\text{NaCl}}$ (Table 3), the molality of sodium chloride in outer mixed solution m_{NaCl} (Table 3), the molality of sodium chloride in inner solution $\bar{m}_{\text{NaCl}}$ (Table 2) and of the term $P\,\bar{V}(R\,T)^{-1}$ involving pressure and volume (Table 4), the values of the mean activity coefficient in the phase of exchanger $\bar{\gamma}''_{\pm\text{NaCl}}$ were calculated by equation (9). These values are presented in the last column of Table 4.

The values of the important (otherwise inaccessible) quantities were thus obtained. These values were used in the discussion on the effect of individual factors controlling the equilibrium distribution of the ions of microcomponent between the outer mixed solution and the inner solution of exchanger.

Discussion

A relationship between the equilibrium weight distribution coefficient K_d and the quantities characterizing an exchange system was deduced in order that the effect of individual factors controlling the penetration of microcomponent might be discussed.

By the combination of equations (9), (10), and (12) we obtained

$$K_d = \frac{\varrho_i}{\varrho_e}\,\Delta v_i\,\frac{\gamma''_{\pm\text{NaCl}}}{\bar{\gamma}''_{\pm\text{NaCl}}}\exp\left(-\frac{P\,\bar{V}_{\text{NaCl}}}{R\,T}\right) \qquad (17)$$

All the factors in equation (17) affect to a certain extent the value of the equilibrium weight distribution coefficient K_d, but as evident from Fig. 4, it is the ratio of the mean activity coefficient of sodium chloride in the phase of outer solution to that in the phase of exchanger, that has the decisive influence on the value of K_d.

While the values of the exponential term and the ratio of densities vary with the composition of mixed solvent system only by a few percents (Table 4) and the values of swelling by 20—30% at the most, the value of the ratio of activity coefficients changes even tenfold and in principle equally as the value of the equilibrium weight distribution coefficient (Fig. 4).

The analysis of general relationship (17) also answers the question what penetration may be expected for other cations besides Na⁺ or its salts. The density of solutions, the swelling of exchanger and its inner pressure will be for a certain concentration of macrocomponent equal also in the case of other microcomponent. The characteristics of microcomponent will predetermine only the value of its molar volume inside the exchanger and of the activity coefficients. Since the value of the exponential term changes only by a few percents in the case of NaCl, a relatively small influence of this term on the value of K_d may be expected also in the case of other electrolytes though the values of the coefficient S_v in equation (16) may be several times higher provided the halogenides with multivalent cations are present. In general, the ratio of mean activity coefficients of microcomponent in outer solution to that in the inner solution of exchanger is the factor controlling the penetration of microcomponent from mixed solutions and the value of K_d as well.
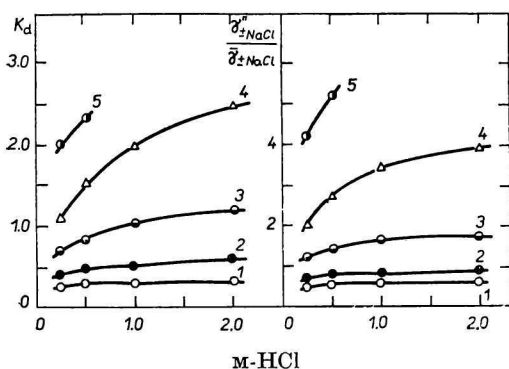
Fig. 4. Comparison of the equilibrium distribution coefficient with the ratio of activity coefficients of sodium chloride in the phases of mixed solution and exchanger.
1. 0 volume %; *2.* 40 volume %; *3.* 65 volume %; *4.* 80 volume %; *5.* 95 volume % of ethyl alcohol in mixed solution.

Because of these facts it may be assumed that the penetration of other simple or complex cations into anion exchanger shall be of equal order as found for sodium cations.

Although the value of the mean activity coefficient is, in the main, determined by the dielectric constant of medium and the ionic strength of solution, the interaction between electrolyte and macrocomponent and the changes in the hydration and association of ions have a considerable influence on the value of the activity coefficient of microcomponent in mixed solutions.

On the basis of a comparison between the activity coefficients of sodium chloride in the outer and the inner solution of exchanger it is obvious that the values of the activity coefficient of sodium chloride in exchanger are higher than those in outer solution provided the concentration of ethyl alcohol in mixed solution is within the range from 0 to 40 volume %. Conversely, the values of the activity coefficient of sodium chloride are lower in exchanger if the content of organic solvent in mixture exceeds 40 volume %

Conclusion

The study of the penetration of microcomponent, *i.e.* Na⁺ cations, from mixed solvent systems into anion exchanger has shown that the volume changes of exchanger have only a small effect on the value of equilibrium distribution coefficient. The ratio of the activity coefficients of sodium chloride in the outer and the inner solution has a prevailing effect on the equilibrium distribution coefficient.

A relationship has been deduced which expresses the dependence of the change in equilibrium distribution coefficient on the concentration of macrocomponents in a mixed solution.

It has been found that, in principle, the penetration of other simple or complex cations into anion exchanger shall be of equal order as the investigated penetration of sodium cations.

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