Anion exchange in mixed solvent systems. II. Behaviour of anion exchangers in mixed solutions

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The swelling of the anion exchanger Dowex 2X-8 (100—200 mesh) was estimated in mixed solutions containing water, organic solvent (methyl alcohol, ethyl alcohol or acetone), and hydrochloric acid. The equilibrium distribution of macrocomponents of mixed solutions between the outer and inner solution of exchanger was determined. It appeared that the penetration of individual macrocomponents into exchanger depended largely on the composition of mixed solution and was quite different for organic solvent and for hydrochloric acid.

In a mixed solution containing water, organic solvent, hydrochloric acid as macrocomponents and eventually radioactive species as a microcomponent the ion exchanger starts to swell owing to osmotic differences and all the above-mentioned substances begin to separate between the phase of exchanger and that of neighbouring solution. The swollen exchanger may be considered to be a concentrated solution containing polyvalent cation and exchangeable counter-ions. The osmotic pressure of inner solution changes with the ionization of functional groups of exchanger. The swelling is due to the solvation of functional groups and counter-ions of exchanger [1, 2]. It depends both on the chemical characteristics of solvent and on the dielectric constant which has an influence upon the mutual electrostatic interaction of individual ions and ionic groups in exchanger.

The distribution of macrocomponents between the phase of exchanger and that of neighbouring solution proceeds in a quite different manner in the case of electrolyte and non-electrolyte.

In principle, the phenomena involving the penetration of electrolyte into exchanger may be taken for membrane equilibria. They are regulated by the equilibrium of opposite tendencies controlling the diffusion of unequally charged ions which is due to concentration gradient and interfacial potential. It seems that the formation of ion pairs is an important factor operating in the distribution of electrolytes from mixed solvent systems [3, 4].

The penetration of non-electrolyte is essentially governed by the physicochemical character of non-electrolyte and exchanger. As a rule, one component penetrates from mixed solution into exchanger in greater quantity and the composition of the inner solution of exchanger is different from that of neighbouring solution [5—7].

The concentration of macrocomponents in mixed solution determines the dielectric properties and ionic strength of solution which, on the other hand, are responsible for the chemical activity of the observed microcomponent in outer solution [8, 9]. The changes of the swelling of exchanger phase caused by the changes in outer solution, the swelling pressure and the molar volume of the electrolyte under investigation also affect the penetration of microcomponent into exchanger because they have influence upon the value of chemical potential of the microcomponent in exchanger phase [8, 9].

To clear up and support the qualitative and semiquantitative considerations we gathered primary information about the states and behaviour of a proper exchange medium.

In this study we tried to find out and give more precision to some data on the volume change of anion exchanger in mixed solutions containing water, hydrochloric acid, and methyl alcohol, ethyl alcohol or acetone as well as on the distribution of organic solvent and complex-forming agent between exchanger and neighbouring solution.

Experimental

Material, instruments, and equipment

We used:

— mineral acids — hydrochloric acid ($\varrho = 1.18$ g cm^{-3}), concentrated sulfuric acid (98 weight %);

— organic solvents — methyl alcohol, ethyl alcohol (96 weight %), acetone, toluene;

— volumetric solutions — 0.1 N-$AgNO_3$, 0.1 N-$Na_2S_2O_3$, 0.5 N-$K_2Cr_2O_7$, 0.1 N-I_2, 1 N-NaOH, 1 N-H_2SO_4;

— reagents and indicators — 10% solution of KI, 1% solution of K_2CrO_4, starch indicator;

— anion exchanger Dowex 2X-8 (100—200 mesh) in Cl^- form.

The particles below the lower limit of graininess of the exchanger were removed by countercurrent sedimentation. The suspension of exchanger was heated to 60°C and degased by a water pump. The exchanger was several times cyclically transformed into the form $Cl^- - OH^- - Cl^-$, washed with distilled water, dried at 60°C, and kept in desiccator over silica gel.

The separation of phases was carried out with a laboratory centrifuge or by sucking in a vessel with porous glass bottom.

Methods

The amount of 5—10 g of dry exchanger was allowed to swell in mixed solvent systems which contained organic solvent (methyl alcohol, ethyl alcohol or acetone), water, and hydrochloric acid in varying proportions. The mixed solutions were prepared by mixing the required volumes of individual components. The exact amounts of individual components were determined by weighing successively the system after the addition of each component. The swelling proceeded in 50-ml volumetric flasks for 48 hours.

The swelling of exchanger was estimated as a difference between the volumes of swollen and dry exchanger related to the weight of dry exchanger. The specific volume of dry exchanger was established pycnometrically by toluene. The swollen exchanger was centrifuged for 15 minutes at 600 *g* (approximately 2000 rev. min^{-1}), weighted and its volume was established pycnometrically by water. The capacity of exchanger was determined after conversion of chloride form into hydroxyl form by argentometric titration of chloride ions in eluate.

The penetration of macrocomponents of mixed solutions into exchanger was determined by volumetric analysis of the phases of exchanger and neighbouring solution in equilibrium state. After the pycnometric estimation of volume change the swollen exchanger was quantitatively transferred into a column and washed with water until organic solvent and hydrochloric acid quantitatively passed into eluate (approximately 500—1000 ml).

The concentration of hydrochloric acid in the samples of solution or eluate was determined by argentometric titration. The content of ethyl alcohol or methyl alcohol was estimated by back iodometric titration after oxidation with potassium bichromate. The content of acetone was determined iodometrically by back titration of excessive iodine.

Each experiment was made four times at 25°C.

Results and discussion

Changes in basic characteristics of exchanger

It was found that the exchanger capacity of anion exchanger Dowex 2X-8 (100—200 mesh) was equal to 3.01 mg equiv. g^{-1}. One gramequivalent of dry exchanger represents 332.22 g and its volume V_0 has the value of 287.01 ml.

The increase in equivalent volume ΔV_e [ml] during swelling was determined. It is the difference between the volume of 1 gramequivalent of exchanger swollen in a certain mixed solution and its volume in dry state. The increments of equivalent volume due

Table 1

Changes in the swelling of anion exchanger Dowex 2X-8 in mixed solvent systems containing methyl alcohol

Methyl alcohol [volume %]	Molar fraction x	Molar fraction $\bar{x}$	ΔV_e [ml]	V_e [ml]	V_e^{ex} [ml]
0	0.000	0.000	162.3	447.7	278.7
10	0.047	0.051	151.7	434.1	290.1
20	0.098	0.110	157.3	444.8	279.6
30	0.154	0.159	181.9	468.9	281.9
40	0.218	0.192	174.7	461.8	278.3
50	0.291	0.240	158.4	445.4	271.4
60	0.375	0.283	171.1	477.5	280.6
70	0.481	0.340	179.7	456.7	280.1
75	0.533	0.365	175.5	462.5	272.9
80	0.605	0.413	150.3	437.3	293.9
85	0.679	0.475	168.6	455.5	271.5
90	0.759	0.558	158.3	445.3	272.5
95	0.840	0.680	159.3	446.3	274.3
100	1.000	1.000	148.3	435.3	272.7

x — molar fraction of organic solvent in equilibrium state,
$\bar{x}$ — molar fraction of organic solvent in the inner solution of exchanger,
ΔV_e — equivalent volume change after swelling [ml],
V_e — equivalent volume [ml],
V_0^{ex} — extrapolated volume of exchanger [ml],
m — molality of hydrochloric acid in the outer solution of exchanger,
$\bar{m}$ — molality of hydrochloric acid in the inner solution of exchanger.

Table 2

Changes in the swelling of anion exchanger Dowex 2X-8 in mixed solvent systems containing ethyl alcohol

Ethyl alcohol [volume %]	Molar fraction x	Molar fraction $\bar{x}$	ΔV_e [ml]	V_e [ml]	V_0^{ex} [ml]
0	0.000	0.000	162.3	447.7	278.8
10	0.032	0.035	164.8	447.4	275.6
20	0.066	0.072	166.7	450.7	274.1
30	0.109	0.112	180.2	463.4	279.1
40	0.161	0.152	167.7	452.7	275.5
50	0.213	0.172	168.5	450.6	277.4
60	0.272	0.208	179,3	464.2	273.1
70	0.345	0.244	165.5	448.1	276.5
75	0.419	0.272	166,7	453.7	269.4
80	0.448	0.282	163.7	446.3	276.5
85	0.513	0.308	168.2	455.3	274.5
90	0.614	0.355	153.4	438.2	277.9
95	0.722	0.456	137.4	424.4	267.9
100	0.883	0.680	116.1	401.0	271.4

Table 3

Changes in the swelling of anion exchanger Dowex 2X-8 in mixed solvent systems containing acetone

Acetone [volume %]	Molar fraction x	Molar fraction $\bar{x}$	ΔV_e [ml]	V_e [ml]	V_0^{ex} [ml]
0	0.000	0.000	162.3	447.7	278.8
10	0.026	0.025	164.8	451.8	286.2
20	0.056	0.052	146.0	433.0	267.5
30	0.092	0.073	168.3	455.3	278.3
40	0.133	0.095	171.9	467.9	274.7
50	0.186	0.115	184.9	471.9	286.9
60	0.249	0.110	147.8	434.7	266.4
70	0.337	0.120	159.5	446.4	272.3
75	0.380	0.123	155.3	442.2	277.9
80	0.459	0.125	143.2	430.2	257.9
85	0.517	0.130	132.6	419.6	272.4
90	0.638	0.140	107.8	394.2	277.4
95	0.754	0.164	103.4	390.4	266.8
98	0.824	0.215	79.3	365.3	266.8
100	1.000	1.000	15.4	303.4	277.6

to the swelling of exchanger in mixed solvent systems organic solvent—water are given in Tables 1—3 while Tables 4—6 contain these values for the systems water—organic solvent—hydrochloric acid.

If the equivalent volume is expressed by the formula

$$V_e = V_0^{ex} + \frac{\Delta G}{\varrho_i} = V_0 + \Delta V_e, \qquad (1)$$

where V_0 — volume of 1 gramequivalent of dry exchanger [ml],
V_0^{ex} — extrapolated volume of dry exchanger [ml],
ΔG — weight of solution with which 1 gramequivalent of exchanger is swollen [g],
ϱ_i — density of inner solution of exchanger [g ml^{-1}],
ΔV_e — equivalent volume change during swelling [ml],

the values V_0^{ex} obtained are without exception lower than the values of the volume of dry exchanger V_0 what indicates the negative deviations from the additivity of the volumes of individual components. These deviations are responsible for the contraction of the volume of system.

From the weight of solution with which 1 gramequivalent of exchanger was swollen the molal concentration of functional groups m_F with exchangeable ions (Cl^-) in the inner solution of exchanger was estimated:

$$m_F = 10^3[\Delta G]^{-1}. \qquad (2)$$

This is based on the assumption that counter-ions are totally dissociated since the anion exchanger Dowex 2X-8 behaves as a strong electrolyte.

Table 4

Composition of the outer and inner solution of anion exchanger Dowex 2X-8 after swelling in mixed solutions containing methyl alcohol

Outer solution		Molar fraction of methyl alcohol		Molality HCl		ΔV_e	V_0^{ex}
Methyl alcohol [volume %]	c_{HCl} [mol l^{-1}]	x	$\bar{x}$	m	$\bar{m}$	[ml]	[ml]
0	0.25	0.000	0.000	0.24	0.20	159.0	276.2
0	1.0	0.000	0.000	1.02	0.91	167.1	293.5
0	2.5	0.000	0.000	2.55	3.60	147.8	281.5
0	4.0	0.000	0.000	4.28	5.70	137.4	269.1
0	7.0	0.000	0.000	7.95	10.50	152.7	274.7
40	0.25	0.221	0.192	0.25	0.21	166.5	267.7
40	1.0	0.233	0.193	1.03	1.30	173.1	277.0
40	2.5	0.221	0.192	2.65	2.13	172.4	270.1
40	4.0	0.224	0.196	4.47	4.10	166.5	268.7
40	7.0	0.229	0.198	8.58	9.00	184.1	276.3
75	0.25	0.538	0.368	0.26	0.19	160.0	269.0
75	1.0	0.530	0.364	1.13	0.74	162.6	277.9
75	1.5	0.553	0.380	1.69	1.03	154.8	276.3
75	2.5	0.491	0.345	3.79	2.30	161.8	267.2
90	0.25	0.745	0.534	0.28	0.21	157.9	271.7
90	0.50	0.746	0.536	0.59	0.39	160.8	278.7
90	1.0	0.757	0.552	1.20	0.90	146.1	268.7
95	0.25	0.838	0.672	0.30	0.37	152.6	271.3
95	0.50	0.845	0.690	0.60	0.52	151.6	272.2

Table 5

Composition of the outer and inner solution of anion exchanger Dowex 2X-8 after swelling in mixed solutions containing ethyl alcohol

Outer solution		Molar fraction of ethyl alcohol		Molality HCl		ΔV_e	V_0^{ex}
Ethyl alcohol [volume %]	c_{HCl} [mol l^{-1}]	x	$\bar{x}$	m	$\bar{m}$	[ml]	[ml]
40	0.25	0.150	0.117	0.26	0.28	159.0	269.6
40	1.0	0.154	0.119	1.01	0.73	167.1	259.6
40	2.5	0.157	0.135	2.74	2.80	147.8	243.7
40	4.0	0.158	0.123	4.50	5.13	137.9	231.5
40	7.0	0.163	0.118	8.75	10.63	142.7	241.2
75	0.25	0.407	0.288	0.26	0.26	150.8	270.0
75	1.0	0.422	0.297	1.15	0.88	159.9	273.3
75	1.5	0.430	0.316	1.62	1.34	157.6	269.0
75	2.5	0.420	0.292	2.91	2.98	166.8	270.5
90	0.25	0.604	0.402	0.29	0.32	142.2	272.5
90	0.50	0.629	0.392	0.58	0.48	153.6	269.1
90	1.0	0.620	0.373	1.19	1.22	133.0	265.2
95	0.25	0.724	0.435	0.29	0.23	128.4	263.5
95	0.50	0.707	0.499	0.58	0.47	135.6	271.0

Table 6

Composition of the outer and inner solution of anion exchanger Dowex 2X-8 after swelling in mixed solutions containing acetone

Outer solution		Molar fraction of acetone		Molality HCl		ΔV_e	V_0^{ex}
Acetone [volume %]	c_{HCl} [mol l^{-1}]	x	$\bar{x}$	m	$\bar{m}$	[ml]	[ml]
40	0.25	0.132	0.094	0.26	0.04	167.9	275.2
40	1.0	0.134	0.096	1.08	0.55	150.8	270.7
40	2.5	0.134	0.095	2.63	2.52	152.8	273.5
40	4.0	0.135	0.097	4.53	4.83	153.6	264.6
40	7.0	0.141	0.097	8.53	10.38	161.0	259.1
75	0.25	0.385	0.124	0.28	0.51	149.3	270.8
75	1.0	0.388	0.124	1.14	1.52	132.0	269.5
75	2.5	0.379	0.123	2.88	4.98	125.1	253.5
90	0.25	0.635	0.132	0.29	1.37	120.1	283.9
90	0.50	0.626	0.130	0.58	2.54	117.8	270.9
90	1.0	0.625	0.130	1.19	4.81	117.3	265.3
95	0.25	0.734	0.148	0.30	2.65	98.9	267.9
95	0.50	0.753	0.162	0.62	4.54	113.4	269.6

From Table 1 it is obvious that initially the swelling of exchanger increases with the portion of organic solvent in mixed solution and reaches a maximum at about 40—60 volume %. At higher concentrations of organic solvent, the higher the proportion of organic solvent in mixed solution, the more the swelling decreases.

The swelling of exchanger in mixed solutions consisting of water, organic solvent, and hydrochloric acid has a similar character with respect to the proportion of organic solvent (Tables 4—6). Since the swelling is determined by the value of osmotic differences between exchanger and solution, for which a different concentration of osmotically effective components is responsible, it may be expected that the exchanger should swell more in solutions containing electrolyte than in pure solvent. Tables 4—6 show that V_e of exchanger in mixed solutions is in most cases smaller than in the binary mixture organic solvent—water of equal composition.

On the basis of the values of equivalent volume the internal pressure of swelling of exchanger may be determined [10]. The swelling pressure of exchanger P [atm] is in principle the osmotic pressure of inner solution and is a linear function of the volume of swollen exchanger V_e

$$P = a(V_e - b), \tag{3}$$

where V_e — equivalent volume [ml],
a, b — coefficients depending on the kind of exchanger and the degree of crosslinking [10].

The coefficient a depends distinctly on the crosslinking of exchanger. We used the same value $a = 1.24$ [atm mol cm^{-3}] which had been found for cation exchanger Dowex 50X-8 [10]. The coefficient b [cm^3 mol^{-1}] was determined from the value of equivalent volume of exchanger in distilled water (Tables 1—3) and the swelling pressure found by isopiestic measurements [11] the value of which was 1.026×10^5 torr for Dowex 2X-8.

Then we obtained the following expression for the relationship between the swelling pressure and the equivalent volume of exchanger presented in Tables 1—6.

$$P = 1.24(V_e - 338.8). \tag{3a}$$

It follows from this expression that the swelling pressure in mixed solutions varies over a wide range of values, *i.e.* from 3.90×10^4 to 1.14×10^5 torr (50—150 atm).

Distribution of organic solvent

Provided an exchanger is in contact with mixed solution, the organic solvent, in general, becomes unevenly separated between both phases. The concentrations of organic solvent (methyl alcohol, ethyl alcohol or acetone) at equilibrium in mixed solution were determined and by computation the values of organic solvent concentration in the inner solution of exchanger were obtained. The organic solvent concentrations after elution from swollen exchanger were also determined (Tables 1—6). Fig. 1 shows the dependence of the molar fraction of organic solvent in the exchanger phase $\bar{x}$ on the molar fraction of this solvent in outer solution.

The increase in the swelling of exchanger which was observed up to the content of about 40 volume % of organic solvent (Table 1) results in the decrease of the concentration of ions in the inner solution of exchanger and thus in the decrease of the salting effect with respect to the organic component of mixed solution. Conversely, the swelling pressure increases initially, reaches its maximum at about 40 volume % and then decreases, as evident from Table 7.

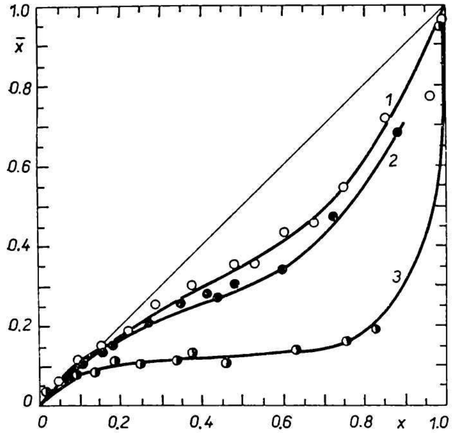

Fig. 1. Equilibrium distribution of organic solvent between the outer and the inner solution of the anion exchanger Dowex 2X-8.
1. methyl alcohol; *2.* ethyl alcohol; *3.* acetone.

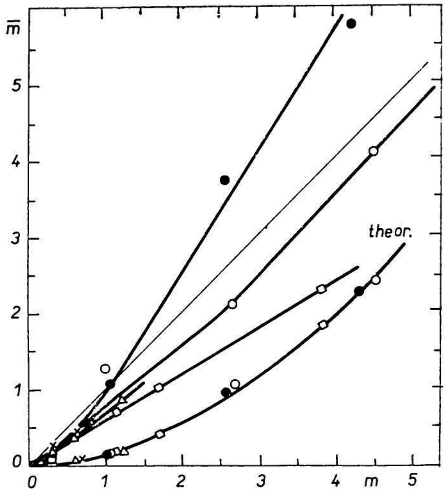

Fig. 2. Equilibrium distribution of hydrochloric acid between anion exchanger Dowex 2X-8 and mixed solution containing methyl alcohol.
● 0%; ○ 40%; □ 75%; △ 90% ; × 95% of organic solvent.

Table 7

Swelling and swelling pressure of anion exchanger Dowex 2X-8 in mixed solutions containing organic solvent and water

Organic solvent [volume %]	Methyl alcohol		Ethyl alcohol		Acetone	
	V_e [ml]	$P \cdot 10^{-5}$ [torr]	V_e [ml]	$P \cdot 10^{-5}$ [torr]	V_e [ml]	$P \cdot 10^{-5}$ [torr]
0	447.7	1.026	447.7	1.026	447.7	1.026
10	449.0	1.038	448.0	1.029	450.8	1.055
20	453.2	1.078	450.7	1.054	455.2	1.106
30	456.5	1.109	456.2	1.106	460.0	1.142
40	459.9	1.141	458.0	1.123	463.5	1.175
50	462.3	1.164	457.5	1.118	464.4	1.183
60	462.1	1.162	457.0	1.114	459.2	1.144
70	459.5	1.137	455.0	1.095	447.2	1.022
75	457.0	1.114	452.7	1.073	442.2	0.974
80	452.8	1.074	447.8	1.027	430.2	0.861
85	448.5	1.034	443.8	0.989	422.3	0.787
90	445.2	1.012	438.2	0.937	402.8	0.603
95	440.9	0.962	424.4	0.807	380.9	0.397
100	435.3	0.909	401.0	0.586	303.4	—

At a high content of organic solvent in mixed solution, the number of ionic groups formed by dissociation decreases considerably what causes the decrease of salting effect and a relatively higher amount of organic solvent goes into exchanger. This phenomenon is especially effective if the concentration of organic component in the outer solution is higher than 80—90%.

Since the swelling pressure as well as the concentration of ions in exchanger is dependent on the equivalent swelling of exchanger, the distribution of the organic component of solvent system is also affected by swelling. The comparison of Table 1 to Fig. 2 shows that the positive penetration of organic component into exchanger corresponds to the increased swelling of exchanger while the negative penetration corresponds to the decrease in swelling.

Penetration of hydrochloric acid into anion exchanger

The concentration of hydrochloric acid in the anion exchanger and the neighbouring solution was determined at equilibrium distribution. The dependence of the molality of hydrochloric acid in the inner solution of exchanger on the molality of hydrochloric acid in the outer solution is given in Figs. 2—4 for different organic components of mixed solution.

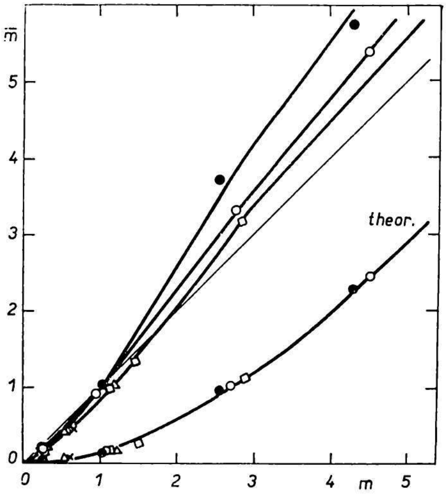

Fig. 3. Equilibrium distribution of hydrochloric acid between anion exchanger Dowex 2X-8 and mixed solution containing ethyl alcohol.
● 0%; ○ 40%; □ 75%; △ 90%; × 95% of organic solvent.

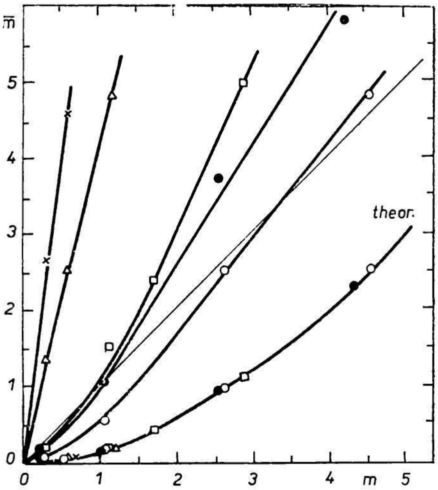

Fig. 4. Equilibrium distribution of hydrochloric acid between anion exchanger Dowex 2X-8 and mixed solution containing acetone.
● 0%; ○ 40%; □ 75%; △ 90%; × 95% of organic solvent.

For comparison, the approximate values of the hydrochloric acid concentration in exchanger which may be expected owing to the penetration of an electrolyte having a common ion with the counter-ion of exchanger were calculated by the expression for Donnan equilibrium:

$$\bar{m}_{\mathrm{HCl}} = -\frac{m_{\mathrm{F}}}{2} + \left(\frac{m_{\mathrm{F}}^2}{4} + m_{\mathrm{HCl}}^2\right)^{\frac{1}{2}}, \tag{4}$$

where m_{HCl} — molality of HCl in mixed solution,
$\bar{m}_{\mathrm{HCl}}$ — molality of HCl in inner solution of exchanger,
m_{F} — concentration of functional groups of exchanger.

The volume changes were included into the concentration changes of exchangeable ions of exchanger m_{F}. The calculated values of $\bar{m}_{\mathrm{HCl}}$ are given in Figs. 2—4 by the curve denoted "theoretical". The experimentally found concentrations of hydrochloric acid in exchanger presented in Figs. 2—4 show that the penetration from the aqueous solutions of hydrochloric acid as well as from the mixed solutions containing organic solvent is over the whole concentration range much higher than the corresponding values obtained by calculation. Provided the concentration of hydrochloric acid is higher than 1—2 M, the concentration of acid in exchanger is even higher than that in outer solution. This effect may be attributed to the decrease in the concentration of ionic groups because

Table 8

Effect of the composition of mixed solution on the formation of ion pairs

Organic solvent [volume %]		Association constant K_{as}		
		0.1 M-HCl $\mathring{a}$ = 4.6 Å	1.0 M-HCl $\mathring{a}$ = 4.3 Å	3.0 M-HCl $\mathring{a}$ = 3.6 Å
0	80.37	0	0	0
20 Me	71.02	0	0	0.45
20 Et	68.66	0	0	0.57
20 Ac	68.58	0	0	0.58
40 Me	61.24	0	0.59	1.22
40 Et	56.49	0.83	1.14	1.96
40 Ac	56.00	0.88	1.22	2.06
55 Me	54.30	1.13	1.46	2.48
65 Me	48.99	2.21	2.72	4.36
55 Et	47.52	2.66	3.24	5.08
55 Ac	46.22	3.13	3.83	5.85
75 Me	43.96	4.25	5.07	7.51
65 Et	41.90	5.59	6.65	9.29
65 Ac	39.72	7.46	8.72	11.82
85 Me	39.13	8.13	9.38	12.50
90 Me	36.80	11.22	12.79	—
75 Et	36.51	11.95	13.25	16.69
95 Me	34.57	15.26	17.03	—
75 Ac	33.42	17.88	19.61	24.97
85 Et	31.46	23.51	25.48	32.83
90 Et	29.03	32.58	36.23	—
85 Ac	27.47	41.98	46.55	62.81
95 Et	27.01	47.87	49.55	—
90 Ac	24.61	68.59	76.98	—
95 Ac	22.08	115.47	131.40	—

Me — methyl alcohol, Et — ethyl alcohol, Ac — acetone, ε — relative dielectric constant of medium, $\mathring{a}$ — distance of the nearest approach.

of the growing formation of ion pairs due to increased concentration of hydrochloric acid in outer solution.

The concentration of ionic groups, however, depends mainly on the dielectric properties of the solution with which the exchanger swells. The decrease in the value of dielectric constant of mixed solution promotes the association of hydrochloric acid in the outer and inner solutions of exchanger as well as the formation of pairs counter-ion—functional group in exchanger.

In order to clear up the possible effect of these factors on the penetration of electrolyte into exchanger, we estimated the formation of pairs as a function of dielectric constant according to the relation [12]

$$-\log K = 6.124 - 3 \log \varepsilon + \log Q(b), \qquad (5)$$

where K is the equilibrium dissociation constant for the pair H^+Cl^-, ε is the relative dielectric constant of medium and $Q(b)$ are tabulated values for $b > 2$ [12].

The values of the parameter b depend on the dielectric constant and the distance of the nearest approach $\mathring{a}$

$$-\log b = 5.245 + \log \varepsilon + \log \mathring{a}. \qquad (6)$$

The data about the association of hydrochloric acid in mixed solutions calculated according to equations (5) and (6) are presented in Table 8.

From Table 8 it can be seen that the formation of associated molecules increases considerably with the concentration of hydrochloric acid and with the decreasing dielectric constant of medium what may enhance the penetration of hydrochloric acid into exchanger.

It is obvious from Figs. 2—4 that the penetration of electrolyte from mixed solutions into exchanger depends on the composition of system but is quite irregular. In general, it may be alleged that the penetration of hydrochloric acid into exchanger (at a given concentration of hydrochloric acid in outer solution) decreases with increasing content of organic solvent in mixed solution until the value of the molar fraction of organic solvent equals 0.5. On the other hand, provided the concentration of organic solvent is higher than 70—80%, the penetration of hydrochloric acid relatively increases with the portion of organic solvent in solution. This phenomenon is to be observed with all mixed systems studied but it is the most marked in the case of systems containing acetone (Fig. 4).

In general, the sorption of solvent is controlled by the equilibrium of osmotic and electrostatic forces and the elasticity in the matrix of exchanger. The higher the polarity of the solvent used, the greater the amount of solvent sorbed by the phase of exchanger. The sorption of solvent and the swelling of exchanger, in principle, increase with growing similarity between the structure of solvent molecules and the structural and functional groups in the phase of exchanger. The functional groups of strongly basic anion exchangers have a high affinity with respect to alcohols by which the influence of the lower polarity of these mixed solutions is compensated. For the organic component of mixture, the matrix of exchanger is a more similar medium ($\varepsilon = 2-5$) whereas water is prone to hydrate the ions and ionic groups in exchanger. The affinity of solvents with respect to exchanger and the tendency to hydrate and dilute the highly concentrated solution of counter-ions and functional groups are simultaneously effective.

The distribution of organic solvent between outer solution and exchanger may be affected by the attractive forces of exchanger which may be either polar or van der Waals. It is the hydroxyl group of alcohols and the functional group of exchanger that could take part in polar interaction while the hydrocarbon parts of alcohols or acetone and the matrix of exchanger could be effective in van der Waals interaction. This fact might contribute to the positive sorption of organic solvent observed at lower concentrations of organic solvent. Simultaneously with attractive forces, the salting effect, caused by a high concentration of functional groups, upon the organic component of solvent system as well as the pressure-volume changes in exchanger is effective.

The uneven distribution of individual solvents at the swelling of exchanger in a mixture of solvents may be explained by the assumption that the inner solution of exchanger from functional point of view consists of an unbound and thus more freely mobile component of mixed solution and of a component bound in the solvate spheres of functional groups and dissociated counter-ions [13].

Because of the penetration of organic solvent, the strength of the hydrate sphere increases proportionally to the decrease of dielectric constant of the inner solution of exchanger. In accordance with that, the swelling of anion exchanger increases because a part of solution has been partially fixed by hydration as a solvent and is replaced by new penetration of the solvent into exchanger. Thus the swelling of anion exchanger increases.

Provided the portion of organic solvent in outer solution increases, it becomes more and more difficult for the organic solvent to get into exchanger because it has to take part in solvation and replace water in hydrate spheres. The molecules of methyl alcohol easily replace the molecules of water in solvate spheres and that is why the negative penetration is expressed only by a small deviation from a uniform distribution. In the case of mixed solutions containing acetone it may, however, be observed that the penetration of acetone into exchanger is extremely irregular at higher proportions of this substance in solution.

If the mixed solution contains only a small amount of water, which cannot provide for the hydration of counter-ions and ionic groups, an increased association of ionic components and thus a decrease in the portion of solvent functioning as a solvation solution appears. Since the solvation solution predominantly consists of water, this mechanism results in a relative enrichment of the inner solution by organic component.

The investigation of the penetration of organic component into exchanger in the solvent systems containing hydrochloric acid in addition to water and organic solvent shows that the replacement of water by hydrochloric acid does not significantly affect the distribution of organic solvent. In this case, the deviations from the distribution in binary systems organic solvent—water are in the range of experimental errors.

The sorption of complex-forming agent proceeds in conformity with the equilibrium of the opposite tendencies due to the values of concentration fall and interfacial potential. These quantities are responsible for the diffusion of unequally charged ions. It appeared that the penetration of hydrochloric acid from aqueous solutions is in the whole concentration range much higher in contrast to the values obtained by approximative calculations based on the relationship valid for the Donnan equilibrium. The increase in the concentration of hydrochloric acid as well as the decrease in the value of the dielectric constant of mixed solution promotes both the association of hydrochloric acid in the outer and inner solutions of exchanger and the formation of the pairs counter-ion—functional group of exchanger.

The swelling of exchanger decreases with increasing association of ions what corresponds to a decreasing number of solvated functional groups. With respect to the increasing swelling of exchanger, a relative decrease in the penetration of electrolyte may be expected in the initial stage. The activity of the electrolyte in exchanger adequately decreases with decreasing dielectric constant of solution owing to what the interfacial potential decreases considerably. That means that strong electrolytes should penetrate into exchanger in a high degree. These relations may be observed best in the case of mixed media containing acetone, as evident from Fig. 4.

In conclusion, it may be stated that the results of this investigation supplied a basis for the study of equilibrium states and states preceding equilibrium with respect to the adsorption of trace radionuclides from mixed solvent systems on anion exchanger.

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