

Distribution of Methanol-Water and Ethanol-Water Mixtures in Strongly Basic Polystyrene Anion Exchangers in Free Base Form

EERO SJÖSTRÖM*, LALLI NYKÄNEN** and PEKKA LAITINEN

Lääketehtäs Orion Oy, Helsinki, Finland

The distribution of methanol-water and ethanol-water mixtures in two strongly basic anion exchange resins (hydroxyl form) cross-linked with 7.5 % and 0.5 % divinylbenzene has been studied. Centrifugation was used to separate the resin from the surrounding solution and the concentrations in the resin phase were determined after the elution of the solvent components. The hydroxyl-alkoxide ion equilibrium, $\text{ROH} + \text{OH}^- \rightleftharpoons \text{RO}^- + \text{H}_2\text{O}$, was taken into consideration in the final calculations. For this an equation was derived for the calculation of the hydroxyl and alkoxide ion contents of the resin.

The water concentration was found to be higher inside the resin than in the surrounding solution over the whole solvent composition range. Compared with the same resin in chloride form, the salting-out effect of the hydroxyl resin is greater up to a certain alcohol concentration (about 70 % (w/w) methanol and 83 % (w/w) ethanol) but smaller at higher concentrations. A reasonable explanation for this observation seems to be that the hydroxyl ions are converted into alkoxide ions, as a result of which the ability of the resin to take up alcohol is increased.

The internal solution volumes of the resins were calculated at various alcohol concentrations. The data revealed that, compared with the chloride resin, the hydroxyl resin takes up more solvent and that only small changes take place in the swollen volume with varying alcohol concentration.

Although many investigations have been published on the distribution of solvent mixtures in ion exchange resins in various ionic states (see, *e.g.*, Refs.¹⁻³), only very few experiments seem to have been carried out with anion exchange resins in the free base form. The main reason is that an anion

Present address: * (E.S.) Stora Kopparbergs Bergslags AB, Central Laboratory, Falun, Sweden.

** (L.N.) Research Laboratories of the State Alcohol Monopoly, Helsinki, Finland.

exchange resin in its hydroxyl form is more or less unstable to organic solvents. This special case is, however, of considerable interest from the standpoint of a fundamental understanding of the catalysis of reactions by ion exchange resins, for the rate and even the mechanism of a reaction depends on the composition of the solvent in the reacting phase ⁴. The present investigation was started in connection with our kinetic studies on resin-catalyzed ester hydrolysis in alcohol-water mixtures.

EXPERIMENTAL

Resins. Two strongly basic polystyrene anion exchange resins cross-linked with 7.5 % and 0.5 % divinylbenzene were used. The former resin, a commercial sample of Dowex 1 (20 to 50 mesh), was ground and sieved in the air-dry state to a particle size of 0.15 to 0.30 mm before use. After the usual purification procedure the resin was air-dried in chloride form and transferred to a glass bottle. The moisture content of the resin, determined by drying to constant weight *in vacuo* over magnesium perchlorate at 60°, was 12.0 %. The total capacity of the dry resin was 2.91 mequiv./g.

The resin containing 0.5 % divinylbenzene was prepared by a method similar to that described by Gregor *et al.*⁵ 49.55 g of styrene (Th. Schuchardt) and 0.45 g of a polymer mixture containing 55 % divinylbenzene (Th. Schuchardt) were heated together with 0.5 g of benzoyl peroxide and 400 ml of water to 90° in a 1-l three-necked flask. The mixture was then vigorously stirred for 15 min. After 5 g of soluble starch powder had been added, the stirring was continued for 3 h. The reaction mixture was kept at 90° for a further 24 h after which the product was separated, washed with water, and dried.

The chloromethylation process was exactly the same as described by Pepper, Paisley and Young⁶ and Samelson and Hammet⁷. The degree of chloromethylation was determined by burning a sample of the product in the presence of ethylene glycol and sodium peroxide in an IKA-bomb and titrating the residue potentiometrically with silver nitrate. The chloride content was found to be 24.3 % (theoretical value 23.1 %).

The chloromethylated resin was ammoniated as follows (*cf.* Ref.⁸). 20 g of the chloromethylated resin was added to 500 ml of dioxane and the mixture cooled in an ice bath. After 250 ml of dry trimethylamine (Fluka, purum) had been added, the reaction was allowed to proceed for 48 h with occasional shaking. The ammoniated resin was purified by alternate treatments with 1 N sodium hydroxide, 5 N hydrochloric acid, and water. The resin was then washed in its chloride form with water to remove excess acid, air-dried to a constant weight, and transferred to a glass bottle. The moisture content of the air-dried resin was found to be 11.7 % by drying at 60° *in vacuo* over magnesium perchlorate to constant weight. The total capacity of the dry resin was 3.80 mequiv./g.

Distribution experiments. Each experiment comprised four steps: (1) equilibration of the resin with a solvent; (2) separation of the outer phase from the resin by centrifugation; (3) elution of the solvent from the resin (water with methanol and alcohol with water); (4) determination of the water and alcohol in the effluents.

In detail, the experiments were carried out as follows. A sample of the air-dried resin (1.000 g of the 7.5 % and 0.1000 g of the 0.5 % cross-linked resin) was introduced into a glass filter-tube (10 × 90 mm) fitted with a sintered glass disc of porosity 1. The resin was allowed to swell in water for 18 to 20 h. It was then converted into the hydroxyl form with 100 ml of 1 N sodium hydroxide solution and washed free of excess alkali with de-ionized water. The resin tube was then placed in an air thermostat maintained at 25 ± 0.2°, and 200 ml of an aqueous alcohol solution at the same temperature was passed through the resin bed at a flow rate of about 0.5 ml/min. The equilibrated resin was allowed to stand for 18 to 20 h, after which it was washed with a further 100 ml of the mixed solvent. The tube was then loosely stoppered, transferred to a centrifuge (Martin Christ, Universal Junior I) and centrifuged for 30 min at a speed of 1 700 r.p.m., which corresponds to 480 g. After the centrifugation the water was displaced from the resin phase with absolute methanol into a 100-ml volumetric flask. Similarly, water was used to displace the alcohol. Since duplicate determinations were always performed, four samples in all were required to determine the distribution of the components of each solvent mixture.

The alcohol-water mixtures were prepared by weighing and were allowed to stand several hours in the 25-degree air thermostat before use. Methyl alcohol (guaranteed reagent; water content < 0.03 %) from E. Merck AG, Darmstadt, and ethyl alcohol (quality AaS; water content \simeq 0.5 %) from Oy Alkoholiliiike Ab, Helsinki, were used in all the experiments. The water used was de-ionized by mixed-bed ion exchange and had a specific conductivity of less than 10^{-6} ohm $^{-1}$ cm $^{-1}$.

Analytical methods. Water was determined by the Karl Fischer method as modified by Johansson⁸. The difference between duplicate determinations was less than 2 %. Methanol was determined by the chromotropic acid method described by Ahlén and Samuelson⁹. A standard and a blank solution were prepared simultaneously with the sample. The measurements were performed at 570 m μ with a Unicam SP 500 spectrophotometer fitted with 1-cm absorption cells. The difference between duplicate determinations did not exceed 2 %. Ethanol was determined by titration with potassium dichromate^{1,10}. The duplicate determinations differed less than 2 %.

CALCULATIONS

When a strongly basic anion exchange resin in hydroxyl form is equilibrated with an aqueous alcohol solution, the hydroxyl ions are partly replaced by alkoxide ions⁴:



Consequently, when the water is displaced from the resin with methanol in the elution step, the hydroxyl ions are converted into an equivalent amount of water. Correspondingly, the alkoxide ions form an equivalent amount of alcohol when the resin is eluted with water. The water and alcohol thus formed must be subtracted from the original water and alcohol contents in order to obtain correct results for the solvent composition in the resin phase. The hydroxyl and alkoxide ion contents of the resin can be calculated as follows.

The equilibrium constant for reaction (1) may be written:

$$\frac{[\text{RO}^-][\text{H}_2\text{O}]}{[\text{ROH}][\text{OH}^-]} = K \quad (2)$$

For one equivalent of resin the sum of hydroxyl and alkoxide ion concentrations

$$\begin{aligned} [\text{OH}^-] + [\text{RO}^-] &= 1 \\ \text{hence } [\text{RO}^-] &= 1 - [\text{OH}^-] \end{aligned} \quad (3)$$

If $[\text{ROH}]_t$ and $[\text{H}_2\text{O}]_t$ denote the total numbers of moles of alcohol and water found in the effluent per equivalent of resin, then

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_t - [\text{OH}^-] \quad (4)$$

and

$$[\text{ROH}] = [\text{ROH}]_t - (1 - [\text{OH}^-]) \quad (5)$$

When $[\text{RO}^-]$, $[\text{H}_2\text{O}]$ and $[\text{ROH}]$ are eliminated from eqn. (2) by means of (3), (4) and (5), one obtains

$$\frac{(1 - [\text{OH}^-])([\text{H}_2\text{O}]_t - [\text{OH}^-])}{([\text{ROH}]_t + [\text{OH}^-] - 1)[\text{OH}^-]} = K \quad (6)$$

After rearrangement, it is found that

Table 1. Distribution of methanol-water mixtures in Dowex 1 (OH).*

Solution	Experimental values				Resin Phase										
	MeOH g	H ₂ O g	MeOH Moles	H ₂ O Moles	HO ⁻ Equiv.	MeO ⁻ Equiv.	MeOH g	H ₂ O g	Total solvent g	MeOH wt. %	MeOH Moles	H ₂ O Moles	Total solvent Moles	X _{MeOH}	V _s ml
0	—	425	—	23.6	1.000	0.000	—	407	407	—	—	22.6	22.6	0	408
1	5.70	427	0.178	23.7	0.942	0.058	3.84	410	414	0.928	0.120	22.8	22.9	0.0053	415
2	11.5	443	0.358	24.6	0.891	0.109	7.97	427	435	1.83	0.249	23.7	24.0	0.0104	437
3	17.4	437	0.544	24.3	0.837	0.163	12.2	423	435	2.80	0.381	23.5	23.8	0.0160	438
4	20.5	428	0.640	23.8	0.810	0.190	14.4	414	428	3.36	0.450	23.0	23.4	0.0192	431
5	25.9	423	0.810	23.5	0.767	0.233	18.5	409	428	4.32	0.577	22.7	23.3	0.0248	431
7.5	38.1	418	1.19	23.2	0.686	0.314	28.0	405	433	6.45	0.876	22.5	23.4	0.0374	439
10	50.2	407	1.57	22.6	0.612	0.388	37.8	396	434	8.71	1.18	22.0	23.2	0.0509	441
12.5	62.4	392	1.95	21.8	0.547	0.453	48.0	383	431	11.1	1.50	21.3	22.8	0.0658	439
15	74.2	387	2.32	21.5	0.492	0.508	57.9	378	436	13.3	1.81	21.0	22.8	0.0794	447
17.5	84.8	373	2.65	20.7	0.450	0.550	67.2	365	432	15.6	2.10	20.3	22.4	0.0938	444
20	93.8	362	2.93	20.1	0.415	0.585	75.2	355	430	17.5	2.35	19.7	22.0	0.107	443
30	138	324	4.31	18.0	0.295	0.705	115	319	434	26.5	3.60	17.7	21.3	0.169	454
40	179	283	5.59	15.7	0.213	0.787	154	279	433	35.6	4.80	15.5	20.2	0.238	460
50	221	232	6.92	12.9	0.151	0.849	194	229	423	45.9	6.07	12.7	18.8	0.323	458
60	248	198	7.76	11.0	0.120	0.880	220	196	416	52.9	6.88	10.9	17.8	0.387	458
70	283	148	8.84	8.24	0.081	0.919	253	147	400	63.3	7.91	8.16	16.1	0.491	451
80	333	105	10.4	5.81	0.050	0.950	302	104	406	74.7	9.45	5.76	15.3	0.622	472
90	365	52.7	11.4	2.93	0.023	0.977	333	52.4	385	86.5	10.4	2.91	13.3	0.782	464
100	362	—	11.3	—	0.000	1.000	330	—	330	100	10.3	—	10.3	1.000	417

* The values are given per one equivalent of resin

Table 2. Distribution of ethanol-water mixtures in Dowex 1 (OH).*

Solution	Experimental values					Resin Phase									
	EtOH g	H ₂ O g	EtOH Moles	H ₂ O Moles	OH ⁻ Equiv.	EtO ⁻ Equiv.	EtOH g	H ₂ O g	Total solvent g	EtOH wt. %	EtOH Moles	H ₂ O Moles	Total solvent Moles	X _{EtOH}	V _s ml
0	—	425	—	23.6	1.00	0.00	—	407	407	—	—	22.6	22.6	0.000	408
5	22.7	427	0.492	23.7	0.99	0.01	22.2	409	431	5.15	0.482	22.7	23.2	0.0208	436
8	35.0	414	0.760	23.0	0.96	0.04	33.2	396	429	7.74	0.720	22.0	22.7	0.0317	435
11	49.3	401	1.07	22.3	0.96	0.04	47.5	383	431	11.0	1.03	21.3	22.3	0.0462	440
15	65.4	385	1.42	21.4	0.95	0.05	63.1	367	430	14.7	1.37	20.4	21.8	0.0628	441
20	80.2	364	1.74	20.2	0.94	0.06	77.4	347	424	18.3	1.68	19.3	21.0	0.0800	436
30	115	342	2.50	19.0	0.91	0.09	111	326	437	25.4	2.41	18.1	20.5	0.118	454
40	138	313	3.00	17.4	0.88	0.12	133	297	430	30.9	2.88	16.5	19.4	0.148	452
50	157	290	3.40	16.1	0.86	0.14	150	274	424	35.4	3.26	15.2	18.5	0.176	449
60	175	265	3.79	14.7	0.83	0.17	167	250	417	40.0	3.62	13.9	17.5	0.207	446
70	191	227	4.15	12.6	0.79	0.21	182	212	394	46.2	3.94	11.8	15.7	0.251	427
76	220	200	4.77	11.1	0.77	0.23	209	185	394	53.0	4.54	10.3	14.8	0.307	434
80	238	177	5.16	9.81	0.70	0.30	224	164	388	57.7	4.86	9.11	14.0	0.347	435
83	263	156	5.70	8.64	0.65	0.35	246	144	380	64.7	5.35	7.99	13.3	0.402	432
86	286	125	6.20	6.94	0.58	0.42	266	114	380	70.0	5.78	6.36	12.1	0.478	438
90	320	97.7	6.94	5.43	0.49	0.51	296	88.9	385	76.9	6.43	4.94	11.4	0.564	455

* The values are given per one equivalent of resin

Table 3. Distribution of methanol-water mixtures in Dowex 1 (Cl).*

Solution		Resin Phase								
MeOH wt. %	X _{MeOH}	MeOH g	H ₂ O g	Total solvent g	MeOH wt. %	MeOH Moles	H ₂ O Moles	Total solvent Moles	X _{MeOH}	V _s ml
0	0.000	—	286	286	—	—	15.9	15.9	0.000	259
20	0.123	51.8	230	282	18.4	1.62	12.8	14.4	0.112	261
30	0.194	78.1	202	280	27.9	2.44	11.2	13.6	0.179	265
50	0.360	122	130	252	48.4	3.82	7.23	11.1	0.346	248
70	0.568	147	87.1	234	62.8	4.60	4.84	9.44	0.487	238
90	0.835	187	34.4	221	84.6	5.84	1.91	7.75	0.753	239
100	1.000	214	—	214	100.0	6.70	—	6.70	1.000	245

* The values are given per one equivalent of resin.

$$[\text{OH}^-] = \frac{(K - K[\text{ROH}]_t - [\text{H}_2\text{O}]_t - 1) + \sqrt{(K - K[\text{ROH}]_t - [\text{H}_2\text{O}]_t - 1)^2 + 4[K - 1][\text{H}_2\text{O}]_t}}{2(K - 1)} \quad (7)$$

The hydroxyl ion content of the normal resin (Dowex 1), in equilibrium with an aqueous alcohol solution, cannot be exactly calculated using earlier reported values for K . The condition in the resin phase is far from ideal and when the unknown activities are neglected, the K in eqn. (2) will not represent a true thermodynamic equilibrium constant and will probably vary with solvent composition. However, by using earlier reported values for K , it is possible to approximately estimate the influence of the chemical reaction on the analytical figures. Kinetic measurements with a porous resin have given a value of 11.8 for K for methanol-water mixtures¹¹ (*cf.* Ref.¹²); from other studies the K value for ethanol-water mixtures again, can be evaluated as approximately 0.8¹³ (*cf.* Ref.¹⁴). As can be seen from Table 1 the calculated values based on these constants differ considerably from experimental values, especially for methanol-water mixtures of low methanol content (Table 1). For ethanol-water mixtures, however, the corrections are smaller owing to the lower K value (Table 2).

Considering a porous resin with an extremely large swollen volume, the additional amounts of water or methanol resulting from chemical reaction can obviously be neglected within the limits of experimental error. For instance, when the hydroxyl ion content of the porous resin in equilibrium with a methanol-water mixture containing not more than 5% methanol is calculated from eqn. (7) using for K a value of 12, it is seen that the methanol and water formed in the elution step correspond to less than 0.3% and 3% of the total (found) methanol and water contents, respectively. For methanol concentrations exceeding 5% the corresponding figures are 0.2% and 2%.

RESULTS AND DISCUSSION

All the experimental data obtained with the normal resin (Dowex 1) and the calculated values are summarized in Tables 1 and 2. For comparison, the

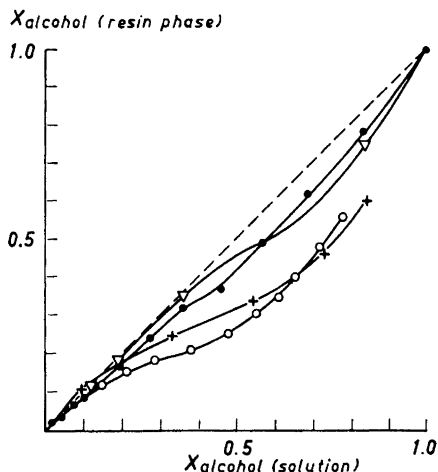


Fig. 1. Distribution of alcohol-water mixtures in Dowex 1.

- Methanol-water mixtures. Resin in OH-form.
- ▽ Methanol-water mixtures. Resin in Cl-form.
- Ethanol-water mixtures. Resin in OH-form.
- + Ethanol-water mixtures. Resin in Cl-form. (Dowex 2). According to data of Rückert and Samuelson¹.

distribution of methanol-water mixtures in the same resin in chloride form was also determined (Table 3). For the ethanol-water mixtures the distribution data reported by Rückert and Samuelson¹ for a resin (Dowex 2) in chloride form were used. The mole fractions of methanol and ethanol in the external solution are plotted against the mole fractions in the resin phase in Fig. 1. It is seen, in agreement with general rules presented earlier (see, *e.g.*, Ref.¹⁵), that the resin favours the more polar solvent component water throughout the whole solvent composition range. The salting-out effect is, of course, more pronounced in ethanol-water mixtures than in methanol-water mixtures. The dipole moments of water, methanol and ethanol are of same order of magnitude ($\mu_{\text{H}_2\text{O}} = 1.85$ D, $\mu_{\text{MeOH}} = 1.68$ D and $\mu_{\text{EtOH}} = 1.70$ D)¹⁶ but owing to its largest molar volume, ethanol has the lowest dielectric constant $\epsilon_{\text{H}_2\text{O}} = 78.0$ ¹⁷, $\epsilon_{\text{MeOH}} = 32.6$ ¹⁸, and $\epsilon_{\text{EtOH}} = 24.3$ ¹⁸ at 25°).

An interesting difference is noted when data for the hydroxyl resin are compared with data for the chloride resin. As can be seen from Figs. 1 and 2, the salting-out effect of the hydroxyl resin is greater than that of the chloride resin only up to a certain alcohol concentration. The solvent distributions in the hydroxyl and the chloride resins are equal when the methanol concentration in the external solution is about 70% ($X_{\text{MeOH}} = 0.57$) and when the ethanol concentration is 83% ($X_{\text{EtOH}} = 0.66$). At higher alcohol concentrations the distribution is reversed. The experiments of Rückert and Samuelson¹ have shown that the salting-out effect of an anion exchange resin in various ionic states increases for ethanol-water mixtures in the order: $\text{ClO}_4^- < \text{Cl}^- < \text{SO}_4^{2-}$,

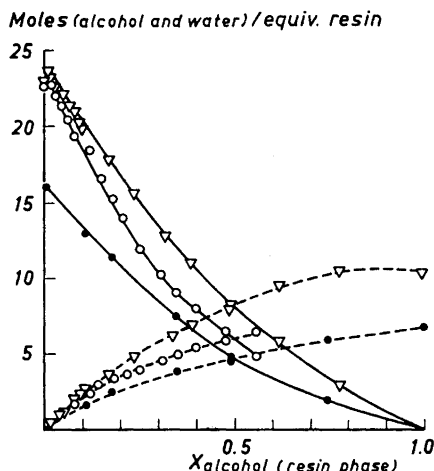


Fig. 2. Uptake of alcohol and water by Dowex 1 as a function of mole fraction of alcohol in the resin phase.

∇ --- ∇ Methanol, ∇ --- ∇ Water. Resin in OH-form.
 \bullet --- \bullet Methanol, \bullet --- \bullet Water. Resin in Cl-form.
 \circ --- \circ Ethanol, \circ --- \circ Water. Resin in OH-form.

and that this order prevails throughout the whole solvent composition range. The exceptional behaviour of the hydroxyl resin can be explained by the fact that the hydroxyl ions are replaced by alkoxide ions more and more when the alcohol content of the solvent mixture increases. Consequently the hydroxyl resin is able to take up more alcohol than the chloride resin.

The uptake of water and alcohol (methanol or ethanol) in moles is plotted against the mole fraction of the component in the internal solution in Fig. 2. That the uptake of water by the hydroxyl resin slightly increases with increasing alcohol concentration is indicated by the hardly perceptible maximum at the beginning of the water curve. For comparison, the values from the experiments with the chloride resin are plotted in Fig. 2. It is seen that the hydroxyl resin takes up considerably more solvent than the chloride resin, which is a natural consequence of the greater solvation tendency of the hydroxyl ion compared with that of the chloride ion.

The experiments of Pepper, Reichenberg and Hale¹⁹ with cation exchange resins have shown that there is a linear relationship between the total volume of the system (V_{tot}) and the weight of water absorbed by the resin (W) given by the equation $V_{\text{tot}} = W/\rho + \text{const.}$, where ρ is the density of water at the temperature in question. The value of the constant in this equation was found to be about 10 % lower than the specific volume of the dry resin as determined pycnometrically. This indicates that when a dry resin is allowed to swell in water the total volume of the system first undergoes a contraction. However, as shown by Boyd and Soldano^{20,21}, this contraction is in general considerably smaller for anion than for cation exchange resins.

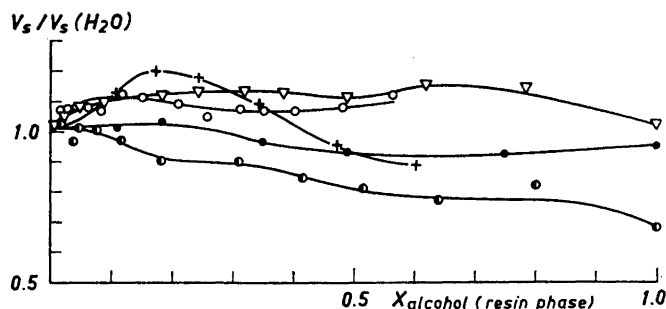


Fig. 3. Relative volume change of the internal solution as a function of alcohol concentration (mole fraction) in the resin phase.

V_s = internal solution volume for alcohol-water mixtures.

$V_s(H_2O)$ = internal solution volume in water.

▽ Methanol-water mixtures. Dowex 1 (OH).

● Methanol-water mixtures. Dowex 1 (Cl).

○ Ethanol-water mixtures. Dowex 1 (OH).

+ Ethanol-water mixtures. Dowex 2 (Cl). According to data of Rückert and Samuelson¹.

Methanol-water mixtures. Anion exchange resin with 0.5 % DVB (OH).

The volume of the solvent inside the resin (V_s) was calculated by assuming that its density was the same as that of the solvent in the free state. Thus

Table 4. Distribution of methanol-water mixtures in 0.5 % cross-linked resin (OH-form).*

Solution		Resin Phase								V_s ml
MeOH wt. %	X_{MeOH}	MeOH g	H ₂ O g	Total solvent g	MeOH wt. %	MeOH Moles	H ₂ O Moles	Total solvent Moles	X_{MeOH}	
0	0.000	—	5994	5994	—	—	333	333	0.000	6000
1	0.0057	61.1	5976	6037	1.01	1.91	332	334	0.0058	6060
2	0.0113	118	6084	6202	1.90	3.68	338	342	0.0107	6246
3	0.0171	152	5868	6020	2.52	4.76	326	331	0.0144	6060
4	0.0229	217	5868	6085	3.57	6.79	326	333	0.0204	6150
5	0.0287	279	5724	6003	4.65	8.71	318	327	0.0267	6060
7.5	0.0436	400	5292	5692	7.03	12.5	294	307	0.0407	5760
10	0.0588	541	5400	5941	9.11	16.9	300	317	0.0534	6030
15	0.0903	810	5040	5850	13.8	25.3	280	305	0.0826	6000
20	0.123	1059	4572	5631	18.8	33.1	254	287	0.115	5790
30	0.194	1434	3762	5196	27.6	44.8	209	254	0.177	5410
40	0.273	1808	3330	5138	35.2	56.5	185	242	0.233	5440
50	0.360	2256	2790	5046	44.7	70.5	155	226	0.313	5440
60	0.458	2592	2052	4644	55.8	81.0	114	195	0.415	5120
70	0.568	2784	1472	4256	65.4	87.0	81.8	169	0.515	4820
80	0.692	2992	938	3930	76.1	93.5	52.1	146	0.642	4590
90	0.835	3232	446	3678	87.9	101	24.8	126	0.802	4940
100	1.000	3264	—	3678	100.0	102	—	102	1.000	4090

* The values are given per one equivalent of resin.

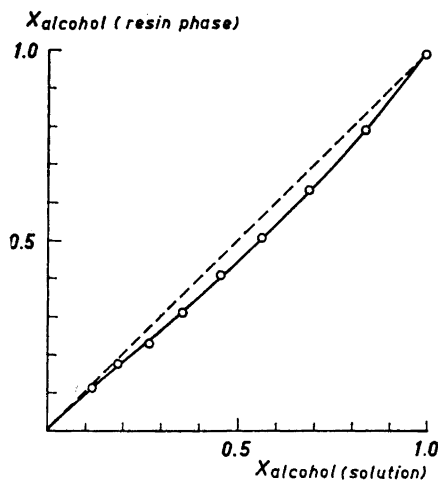


Fig. 4. Distribution of methanol-water mixtures in 0.5 % cross-linked resin (OH-form).

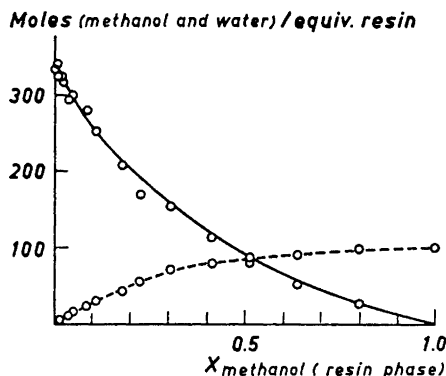


Fig. 5. Uptake of methanol and water by 0.5 % cross-linked resin (OH-form) as a function of mole fraction of methanol in the resin phase. ——— Methanol, ——— Water.

$V_s = W/\rho$, where W is the weight of solvent in grams absorbed by one equivalent of resin and ρ the density of the solvent at 25°. Even if this assumption is not fully correct, especially in view of the observations referred to above, the deviations from the true volumes are probably within the limits of the experimental error. The relative volume changes can be seen from Fig. 3, where the ratio $V_s/V_s(\text{H}_2\text{O})$ is plotted against the mole fraction of alcohol in the resin phase. It is seen that a slight increase in the internal volume of the hydroxyl resin takes place at very low methanol concentrations. Only a hardly perceptible volume change seems to occur when the methanol concentration is increased, but the volume is somewhat lower in pure methanol. Essentially the same behaviour is noted for the ethanol-water mixtures. Since the hydroxyl resin is not stable in pure ethanol, no experiments were carried out with ethanol concentrations exceeding 90 %. As far as the chloride resin is concerned, it is observed that its volume changes are greater and a maximum appears in the ethanol-water curve.

The solvent distribution data from the experiments with the porous resin are shown in Table 4. Here again, the methanol concentration is lower in the resin phase than in the external solution (Fig. 4). The salting-out effect is, however, much smaller than with the normal resin.

Due to its high degree of swelling, the porous resin absorbs much more solvent than the normal resin. The uptake of water and methanol in moles is plotted against the mole fraction of the internal solution in Fig. 5.

The volume of the solution in the porous resin is about 15 times as great as the volume of solution in the normal resin. Up to an internal methanol concentration of 10 % there is no marked change in the swelling, but then the volume decreases continuously with increasing methanol concentration and is about 33 % smaller in pure methanol than in water (*cf.* Fig. 3).

This work has been supported by *Finnish State Scientific Board*.

REFERENCES

1. Rückert, H. and Samuelson, O. *Acta Chem. Scand.* **11** (1957) 303.
2. Gregor, H. P., Nobel, D. and Gottlieb, M. H. *J. Phys. Chem.* **59** (1955) 10.
3. Gable, R. W. and Strobel, H. A. *J. Phys. Chem.* **60** (1956) 513.
4. Sjöström, E. and Nykänen, L. *J. Org. Chem.* **21** (1956) 1321.
5. Gregor, H. P., Bregman, J. I., Gutoff, F., Broadley, R. D., Baldwin, D. E. and Overberger, C. G. *J. Colloid Sci.* **6** (1951) 20.
6. Pepper, K. W., Paisley, H. M. and Young, M. A. *J. Chem. Soc.* **1953** 4097.
7. Samuelson, H. and Hammet, L. P. *J. Am. Chem. Soc.* **78** (1956) 524.
8. Johansson, A. *Svensk Papperstidn.* **50** No. 11 B (1947) 124.
9. Ahlén, L. and Samuelson, O. *Svensk Papperstidn.* **56** (1953) 81.
10. Nogare, S. D. *Anal. Chem.* **25** (1953) 1874.
11. Sjöström, E. and Nykänen, L. *To be published*.
12. Sjöström, E. and Nykänen, L. *Acta Chem. Scand.* **12** (1958) 141.
13. Caldin, E. F. and Long, G. *J. Chem. Soc.* **1954** 3737.
14. Koskikallio, J. *Suomen Kemistilehti* **32 B** (1959) 161.
15. Helfferich, F. *Ionen austauscher*. Band I. Grundlagen. Verlag Chemie Weinheim/Bergstr. 1959, pp. 96–98, 438.
16. Gurney, R. *Ionic Processes in Solution*, McGraw-Hill Book Co., New York 1953, p. 266.
17. *International Critical Tables*, Vol. VI, p. 78.
18. Weissberger, A. *Technique of Organic Chemistry*, Vol. VII, 2nd Ed., Interscience Publishers, Inc., New York 1955, pp. 90–91.
19. Pepper, K. W., Reichenberg, D. and Hale, D. K. *J. Chem. Soc.* **1952** 3129.
20. Boyd, G. E. and Soldano, B. A. *Z. Elektrochem.* **57** (1953) 162.
21. Soldano, B. A. and Boyd, G. E. *J. Am. Chem. Soc.* **75** (1953) 6099.

Received September 6, 1961.