The Distribution of Polyalcohols between Organic Ion Exchangers and Water

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The distribution of glycol, glycerol and sorbitol between an aqueous solution and different types of ion exchange resin has been studied. It has been found that the concentration is lower in the resin phase than in the outer solutions. The counter ions and the degree of cross-linking of the resin have a considerable influence. The application of the Gibbs-Donnan theory is discussed.

The distribution of non-electrolytes between an ion exchanger and an aqueous solution has been dealt with by many authors. Polyalcohols have been subjected to investigations with respect to their sorption as borate complexes on anion exchangers [1-3], and their distribution between ion exchangers and solutions in pure water has also been studied [4,5]. The aim of the present work is to give an idea of the factors which influence the distribution, through a more detailed investigation of a small number of compounds, namely ethylene glycol, glycerol and sorbitol using water as solvent.

EXPERIMENTAL PART

The ion exchanger was shaken with the solution for a time, long enough to attain equilibrium. The two phases were then separated by centrifugation and analysed. Experiments were performed with a single polyalcohol in the solution, not with mixtures of them.

Ion Exchange Resins. The anion exchanger Dowex 2 and the cation exchanger Dowex 50 were used. Of the latter, resins with varying degrees of cross-linking (X), 0.5, 1, 2 and 8 % DVB (divinylbenzene) were studied. In order to obtain as good reproducibility of centrifugation as possible, spherical resin particles were used. The anion exchanger and the cation exchanger, X8, with a normal degree of cross-linking had the particle size 0.2−0.4 mm (40/70 mesh) in an air-dried state and the other resins 0.14−0.29 mm (50/100 mesh). Very fine particles were washed out with water. The cation exchangers were washed with hydrochloric acid and the anion exchanger alternately with hydrochloric acid and sodium hydroxide solutions. The resins were transformed into their ionic states and air-dried in the usual way [6].

Equilibration. The equilibrium experiments were performed in 50 ml test tubes. The solutions of polyalcohols were freshly prepared from c.p. chemicals by dilution with

boiled-out distilled water. On prolonged storage at room temperature the solutions are liable to microbial destruction. In each experiment 40 ml solution and 0.5 – 2 g air-dried resin were added, the lower amount being used for the resins which swell most. The test tubes were rotated slowly in an air thermostat kept at $25.0 \pm 0.1°C$. The time of contact had to be chosen long enough to obtain equilibrium, but not so long that the polyalcohols were destroyed by microbes. Other authors have reported as short times as a few minutes for obtaining equilibrium between ion exchangers and aqueous solutions of non-electrolytes [4], but in the present work some systems were found to require longer times. The potassium form of normally cross-linked Dowex 50 and a solution of sorbitol attained equilibrium within one hour. The corresponding value for the perchlorate form of Dowex 2 was 10 h. The differences between various systems may be explained by differences in the molecular size of the solutes and in the swelling of the resins. To secure equilibrium the contact time was chosen as long as 40 h.

Separation of the Resin. After equilibration the resin was transferred to a weighed centrifuge basket, made of stainless steel and fitted with a bottom of wire-netting. The solution was collected in a 50 ml conical flask and stored in a refrigerator until analysed. The basket with the resin was placed in a centrifuge tube, closed with a rubber cap, and subjected to centrifugation for 40 min at 2 000 r/min, corresponding to a centrifugal acceleration of about 600 g. After the run, the basket with resin was weighed in a closed weighing bottle. Subsequently the resin was transferred by washing to a column of 10 mm diameter and 120 mm height fitted with glass filter bottom. The polyalcohol was eluted with water until the volume of the eluate was 100 ml. The solution was kept in a refrigerator until analysis could be performed.

Analyses. The concentration of glycol, glycerol and sorbitol in the equilibrium solution and in the eluate was determined by oxidation with periodic acid [cf. Ref.[7]]. Samples containing less than 30 mg ethylene glycol, 20 mg glycerol or 15 mg sorbitol were mixed in conical flasks with 25 ml of a solution of periodic acid, made by dissolving 5 g HIO_4. $2H_2O$ in 200 ml distilled water and filling up to one litre with glacial acetic acid. Fresh solution was made every day. The flasks were shaken vigorously and then kept well closed at room temperature. After 30 min, 10 ml potassium iodide solution (270 g/l) was added, and the liberated iodine was titrated with 0.1 N sodium thiosulfate solution. In order to obtain as good accuracy as possible, a 10 ml burette fitted with a 40 ml pipette on the top was used. As an indicator, 10 ml starch solution (2 g/l) was added. The discoloration was best observed in the light from a blue bulb. On each solution 2 or 3 determinations were made, and 4 to 7 blanks were run in each series of 17 to 25 titrations in all. For the calculation of the concentration of polyalcohol from the sodium thiosulfate consumption, factors taken from the literature were used [8]. These factors deviated only slightly from the theoretical ones. A control showed that they gave satisfactory results.

After the experiment, the resin was treated in the following manner: The cation exchangers were transformed into the hydrogen form and washed. The hydrogen ions were eluted with sodium chloride solution and titrated with 0.1 N sodium hydroxide solution to the color change of phenolphthalein. After being washed with water, the resin was transferred to a glass filter crucible and, after being dried for 6 days at $60 – 70°C$ over magnesium perchlorate under vacuum, the crucible and contents were weighed. In all cases the determinations of dry weight and capacity were checked by calculating the equivalent weight of the resin. The dry weight was recalculated to the actual ionic form.

The anion exchangers were transformed into the chloride form, washed and eluted with sodium nitrate solution. The chloride ions were determined by titration with silver nitrate solution according to Mohr [9]. After being washed, the resins were again transformed into the chloride form, washed, dried and weighed.

List of Symbols

x mole fraction of polyalcohol in the solution
x_r mole fraction of polyalcohol in the resin phase (ion exchanger not included)
K^* distribution coefficient $(= x_r/x)$
m   molality of polyalcohol in the solution

m_r molality of polyalcohol in the resin phase
f practical activity coefficient of polyalcohol in the solution
f_r practical activity coefficient of polyalcohol in the resin phase
π swelling pressure of the resin, atmospheres
$\bar{v}$ partial molal volume of polyalcohol, ml
$\bar{v}_o$ partial molal volume of polyalcohol in an infinitely diluted aqueous solution at atmospheric pressure, ml
R gas constant, ml-atmospheres per degree per mole
T absolute temperature, degrees
k_s salting out parameter
n_r normality of resinate, equiv./1 000 ml water

RESULTS AND DISCUSSION

The experimental data are presented in Tables 1—3. The polyalcohol concentration in the solution and in the resin phase is given as mole fractions x and x_r. In the calculation of x_r the ion exchanger has not been included but only water and polyalcohol. The distribution coefficient K^*, *i.e.* the ratio x_r/x, is also given in the tables. Furthermore, figures are given for the total swelling, expressed in grams of water plus polyalcohol per equivalent of ion exchange resin, and for the water content and the polyalcohol content of the resin phase in moles per equivalent of resin. The water content is calculated by the difference.

Table 1. Distribution of ethylene glycol between various forms of Dowex 50 or Dowex 2 and water.

Resin	$x \times 10^2$	$x_r \times 10^2$	K^*	Total swelling g/equiv. resin	Mole H_2O equiv. resin	Mole glycol equiv. resin
Dowex 50 Li+	0.901	0.617	0.68	204.0	11.09	0.0688
	2.67	1.99	0.75	204.4	10.60	0.216
Dowex 50 Na+	0.910	0.677	0.74	179.2	9.72	0.0662
	2.69	2.00	0.74	179.5	9.31	0.190
Dowex 50 K+	0.899	0.663	0.74	155.6	8.44	0.0563
	2.67	2.05	0.77	156.9	8.13	0.170
Dowex 2 SO_4^{2-}	0.337	0.242	0.72	270.4	14.88	0.0361
	1.51	1.22	0.81	270.9	14.42	0.178
	3.28	2.61	0.80	273.6	13.90	0.373
	0.338	0.275	0.81	238.5	13.11	0.0362
Dowex 2 Cl-	1.51	1.35	0.89	234.6	12.44	0.170
	3.27	2.79	0.85	242.7	12.26	0.352
	0.459	0.440	0.96	99.0	5.41	0.0239
Dowex 2 ClO_4^-	1.50	1.40	0.93	94.2	4.99	0.0707
	3.25	3.17	0.97	93.3	4.66	0.152

Table 2. Distribution of glycerol between various forms of Dowex 50 or Dowex 2 and water.

Resin	$x \times 10^2$	$x_r \times 10^2$	$K *$	Total swelling g/equiv. resin	Mole H_2O equiv. resin	Mole glycerol equiv. resin
Dowex 50 Li+	0.367	0.209	0.57	201.2	11.05	0.0232
	1.43	0.845	0.59	206.8	11.0	0.0938
	3.00	1.86	0.62	206.7	10.46	0.198
Dowex 50 X2 Li+	0.360	0.323	0.90	767.5	41.90	0.136
	1.52	1.35	0.89	778.1	40.37	0.553
	3.39	3.02	0.89	788.4	37.75	1.18
Dowex 50 X1 Li+	0.360	0.351	0.97	1 804	98.37	0.346
	1.51	1.44	0.95	1 806	93.30	1.36
	3.39	3.24	0.95	1 830	86.72	2.90
Dowex 50 X 0.5 Li+	0.359	0.352	0.98	2 317	126.35	0.447
	1.51	1.47	0.98	2 343	120.84	1.80
	3.37	3.34	0.99	2 335	110.15	3.80
Dowex 50 Na+	0.370	0.212	0.57	181.7	9.97	0.0212
	1.43	0.836	0.59	182.2	9.70	0.0818
	3.01	1.86	0.62	182.2	9.22	0.175
Dowex 50 K+	0.368	0.236	0.64	159.0	8.72	0.0206
	1.42	0.939	0.66	158.6	8.40	0.0796
	2.98	2.00	0.67	158.8	7.98	0.163
Dowex 50 X2 K+	0.361	0.329	0.91	678.7	37.04	0.122
	1.52	1.39	0.91	678.4	35.12	0.495
	3.39	3.11	0.92	686.9	32.76	1.05
Dowex 50 X1 K+	0.360	0.352	0.98	1 687	91.95	0.325
	1.51	1.48	0.98	1 703	87.77	1.32
	3.37	3.29	0.98	1 708	80.78	2.75
Dowex 50 X0.5 K+	0.358	0.358	1.00	2 208	120.33	0.433
	1.50	1.49	0.99	2 234	115.11	1.74
	3.39	3.33	0.98	2 261	106.70	3.68
Dowex 2 $SO_4{}^{2-}$	0.334	0.234	0.70	270.8	14.85	0.0349
	1.52	1.11	0.73	271.7	14.26	0.160
	3.38	2.49	0.74	277.0	13.60	0.347
Dowex 2 Cl-	0.336	0.242	0.72	248.2	13.61	0.0330
	1.52	1.11	0.74	251.5	13.20	0.149
	3.37	2.50	0.74	257.8	12.65	0.324
Dowex 2 $ClO_4{}^-$	1.51	1.02	0.67	99.0	5.22	0.0536
	3.36	2.28	0.68	95.3	4.73	0.110

The distribution coefficient is a function of solute concentration [4], but from the data given in Tables 1—3 it is evident that within the examined range of concentration — up to 3.5 mole per cent in the outer solution — this dependence is small. For the normally cross-linked cation exchange resins the

Table 3. Distribution of sorbitol between various forms of Dowex 50 or Dowex 2 and water.

Resin	$x \times 10^2$	$x_r \times 10^2$	K^*	Total swelling g/equiv. resin	Mole H_2O equiv. resin	Mole sorbitol equiv. resin
Dowex 50 Li$^+$	0.262	0.0948	0.36	206.9	11.38	0.0108
	1.15	0.432	0.37	209.3	11.13	0.0483
	2.67	1.06	0.40	213.2	10.68	0.114
Dowex 50 X2 Li$^+$	0.357	0.280	0.78	776.8	41.93	0.118
	1.52	1.21	0.79	794.5	39.25	0.480
	3.54	2.80	0.79	824.4	35.45	1.02
Dowex 50 X1 Li$^+$	0.355	0.323	0.91	1 798	96.63	0.314
	1.51	1.39	0.92	1 837	89.21	1.26
	3.56	3.22	0.91	1 884	78.24	2.61
Dowex 50 Na$^+$	0.260	0.113	0.43	182.9	10.04	0.0114
	1.15	0.522	0.45	184.5	9.73	0.0510
	2.65	1.22	0.46	188.1	9.29	0.114
Dowex 50 K$^+$	0.260	0.134	0.52	157.7	8.64	0.0116
	1.15	0.601	0.52	159.5	8.34	0.0504
	2.64	1.42	0.54	163.1	7.90	0.114
Dowex 50 X2 K$^+$	0.358	0.319	0.89	675.7	36.33	0.116
	1.53	1.35	0.88	704.8	34.37	0.470
	3.48	3.13	0.90	723.0	30.25	0.977
Dowex 50 X1 K$^+$	0.352	0.342	0.97	1 699	91.15	0.313
	1.50	1.45	0.96	1 752	84.69	1.24
	3.52	3.34	0.95	1 824	75.01	2.59
Dowex 50 X0.5 K$^+$	0.350	0.351	1.00	2 225	119.27	0.420
	1.51	1.48	0.98	2 274	109.58	1.65
	3.53	3.40	0.97	2 355	96.38	3.40
Dowex 2 SO$_4^{2-}$	0.258	0.158	0.61	271.4	14.83	0.0234
	1.14	0.683	0.60	276.6	14.36	0.0987
	2.64	1.59	0.60	285.3	13.61	0.220
Dowex 2 Cl$^-$	0.259	0.136	0.53	239.1	13.09	0.0178
	1.16	0.601	0.52	240.3	12.57	0.0760
	2.67	1.41	0.53	246.1	11.94	0.170
Dowex 2 ClO$_4^-$	0.258	0.095	0.37	91.5	5.03	0.0048
	1.14	0.471	0.41	87.0	4.61	0.0218
	2.63	1.03	0.39	89.1	4.47	0.0466

distribution coefficient increases slightly with increased concentration, but for the anion exchange resins and for the weakly cross-linked cation exchanger the variations are probably within the limits of experimental errors.

As may be seen, the concentration in the resin phase is in all cases lower than that in the outer solution. Thus the net effect may be considered as a salting out of the polyalcohol from the resin phase.

It may be of interest to apply the Gibbs-Donnan theory [10] to the distribution of the non-electrolyte between the two phases. Different approaches have recently been reviewed by Holm [11]. The distribution can be approximately represented by the following equation [cf. Ref.[11c] p. 464—465].

$$\ln \frac{m \cdot f}{m_r \cdot f_r} = \frac{\pi \cdot \bar{v}}{RT} \tag{1}$$

If the concentration of non-electrolyte is low in both phases, we may put m/m_r equal to x/x_r and $f = 1$. Consequently, the equation may be written

$$- \log K^* = \frac{\pi \bar{v}}{2.303 \ RT} + \log f_r \tag{2}$$

The first term on the right-hand side of eqn. (2) (the pressure term) accounts for the influence of the swelling pressure upon the distribution, whereas the second term (the interaction term) accounts for the interaction between the non-electrolyte and a hypothetical strain-less ion exchanger. The salting-out effect on non-electrolytes in common electrolyte solutions can, as a good approximation, be represented by the following eqn. (12)

$$\log f_i = k_s \ m_s \tag{3}$$

where f_i is the practical activity coefficient of the non-electrolyte, k_s a salting-out parameter and m_s the molal concentration of the salt. This equation is valid only at fairly low concentrations of the non-electrolyte. If eqn. (3) is applied to our problem, eqn. (2) may be written:

$$- \log K^* = \frac{\pi \bar{v}}{2.303 \ RT} + k_s \cdot n_r \tag{4}$$

The distribution coefficient, K^*, is obtained in the experiments. The swelling pressure, π, may be obtained from isopiestic measurements [13,14] and data for Dowex 50 X8 have been taken from the paper by Boyd and Soldano [14]. A few isopiestic measurements were made with the resin (Li-form) used in the present work and it was observed that the calculated osmotic pressure was somewhat lower than the data given by these authors. The deviations were less than 10 %. The non-electrolyte has within the actual range of concentration only a slight influence upon the swelling, and so the swelling pressures determined for pure water can be used.

The partial molal volume, $(\bar{v}_o)$, in aqueous solution at infinite dilution is reported by Riiber, Sörensen and Thorkelsen to be 54.28 ml per mole for glycol, 70.59 ml per mole for glycerol and 117.86 ml per mole for sorbitol [15]. As no data are available for the calculation of the partial molal volume, $(\bar{v})$, in the resin, the values, $\bar{v}_o$, for pure aqueous solutions at atmospheric pressure have been inserted in eqn. (2).

From these data f_r has been calculated according to eqn. (2). The calculation is based upon the values for K^* obtained at the lowest concentration under investigation. The results are given in Table 4. Although several objections might be raised to the calculations, this approach may serve as a basis for a discussion of the results obtained in the present work. First of all, it may be

Table 4. The magnitude of the pressure term and the interaction term.

	π	$-\log K^*$	$\dfrac{\pi \cdot \bar{v}_0}{2.303\ RT}$	$\log f_r$	k_s
Li$^+$, glycol	150	0.1675	0.1445	0.0230	0.005
Li$^+$, glycerol	150	0.2441	0.1880	0.0561	0.011
Li$^+$, sorbitol	150	0.4437	0.3138	0.1299	0.027
Na$^+$, glycol	124	0.1308	0.1195	0.0113	0.002
Na$^+$, glycerol	124	0.2441	0.1554	0.0887	0.016
Na$^+$, sorbitol	124	0.3665	0.2594	0.1071	0.019
K$^+$, glycol	99	0.1308	0.0956	0.0352	0.005
K$^+$, glycerol	99	0.1938	0.1243	0.0695	0.011
K$^+$, sorbitol	99	0.2840	0.2075	0.0765	0.012

pointed out that the pressure term has a predominating influence upon the distribution coefficient for the non-electrolytes studied in the present work, whereas in ion exchange equilibria the influence of the pressure term upon the equilibrium distribution is fairly small [13].

For resins with lower degrees of cross-linking the swelling pressure is much lower than for the X8 resin, and for this reason the pressure term will have lower values for these resins. On the other hand it must be expected that the interaction term is also lower for these resins. Because of the experimental difficulties involved in the determination of the swelling pressure for these resins the data published by different authors are contradictory. An attempt has been made to calculate the pressure term for the X2 resin. This calculation, which is based upon isopiestic measurements by Boyd [16], indicates that the relative magnitude of the pressure term is fairly large for this resin also. As the probable errors are considerable, these calculations are not included in the table.

From eqn. (2) it may be predicted that, if the interaction term is small or of the same order of magnitude for different non-electrolytes, the distribution coefficient will decrease for an increase in molecular size. It might therefore be expected that for all forms of the resin the distribution coefficient should increase according to the following sequence

$$\text{sorbitol} < \text{glycerol} < \text{glycol}$$

This is in agreement with the experimental results.

The influence of the degree of cross-linking can be predicted from eqn. (4). The pressure term decreases rapidly for a decrease in the degree of cross-linking. At the same time there is an increase in swelling, which means that n_r decreases. Consequently, it must be expected that for strongly polar non-electrolytes K^* is increased and approaches the value of unity at low degrees of cross-linking. This is in agreement with the experimental results given in Tables 2 and 3. In this connection it may be mentioned that also for less polar solutes (acetic acid and butyric acid), where, because of a van der Waals' adsorption on the resin matrix, K^* is larger than unity, the distribution coef-

ficient has been shown to be equal to unity for resins with a low degree of cross-linking [17],[18].

From Tables 2 and 3 it may also be seen that the degree of cross-linking does not affect the order of the effects of different counter ions upon the distribution of glycerol and sorbitol.

The influence of different counter ions upon the distribution coefficient compared at a constant degree of cross-linking is a more complicated matter. The swelling of the resin is dependent on the counter ions, which means that both π and n_r are affected. At a constant degree of cross-linking a higher swelling means an increase in swelling pressure but a decrease in inside concentration (n_r). This means that the pressure term and the interaction term are affected in opposite directions. Furthermore, it must be expected that, as in the case of normal electrolytes, the parameter, k_s, is different for different ions and also varies considerably for various non-electrolytes. Thus it might be expected that the effect of the counter ions upon the distribution coefficient might be different for different polar solutes. This is in agreement with the experimental data presented in the tables. This effect is most clearly demonstrated in the experiments with anion exchangers, where a reversed order between the counter ions is obtained for glycol and sorbitol.

It may be of interest to compare the results obtained in the present work with the data given in an earlier paper [19] on the distribution of glucose between different forms of the resins and an outer aqueous solution. The experimental technique was the same in both investigations and the results are comparable. It is found that the order of the different counter ions is the same for glucose as for sorbitol. For both solutes the distribution coefficients increase according to the following series:

$$\text{For Dowex } 50: \text{Li}^+ < \text{Na}^+ < \text{K}^+$$
$$\text{For Dowex } 2: \text{ClO}_4^- < \text{Cl}^- < \text{SO}_4^{2-}$$
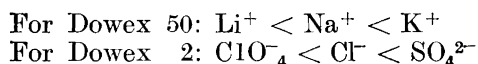
For the cation exchanger the sequence is in agreement with the order which can be calculated from the swelling pressure according to the method used in the present work, whereas for the anion exchanger a reversed order has been observed. This shows that it is not permissible to neglect the interaction term even if it is only desired to make predictions of a qualitative kind.

Some conclusions about the possibilities of adopting ion exchange resins for the separation of glycol, glycerol and sorbitol in aqueous solution can be drawn from the data given in the present paper. The ratio between the distribution coefficients has a predominating influence upon the separation [cf. Ref.[20]]. For the anion exchanger in the perchlorate form this ratio (the separation factor) is 1.4 for glycol/glycerol and 1.6 for glycerol/sorbitol indicating that a good separation can be obtained provided that the flow rate is not too high. It may also be concluded that the forms of the cation exchanger used in the present work will be less suitable, but from the data given for different degrees of cross-linking it may be anticipated that an increase in the degree of cross-linking would give more favorable results.

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