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SELECTIVE SWELLING OF ION EXCHANGERS IN MIXED SOLVENTS AND THE EFFECT OF SWELLING ON THE SORPTION OF IONS

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SUMMARY

The swelling of KU-2 cation exchanger and AV-17 anion exchanger in the hydrogen, chloride, nitrate, sulphate and perchlorate forms were measured in mixed solvents. In mixed aqueous–organic solvents, preferential swelling by water was found. For the perchlorate form of the resin, the selective uptake of organic solvent was observed at $N_{\text{MeOH}} < 0.2$ and at $N_{\text{Me}_2\text{O}} < 0.5$. The addition of mineral acids decreased the selective uptake of water by resins, especially in the case of resins in the sulphate form. This can be explained by the capability of the anion exchanger to take up mineral acids. The preferential sorption of water strongly influences the sorption of Ni(II), Co(II) and Cu(II) ions.

INTRODUCTION

The swelling behaviour of ion exchangers has been measured by numerous workers^{1–8} using mixed solvents. Most of them found that up to fairly high mole fractions of solvent in the solvent–water mixture there is a strong preference for water in the resin phase. The selective uptake of water by the exchanger is lower for anion exchangers than for cation exchangers² and depends on the ionic form of the exchanger^{1,2} and the degree of cross-linking of the resin³. Rückert and Samuelson⁴ determined the swelling of the Li⁺, Na⁺ and K⁺ forms of Dowex 50 resin and the Cl[–], SO₄^{2–} and ClO₄[–] forms of Dowex 2 resin in ethanol–water mixtures. The order of swelling found for Dowex 50 was Li⁺ > Na⁺ > K⁺ and for Dowex 2 SO₄^{2–} > Cl[–] > ClO₄[–]. However, with decreasing water content, the order of swelling for the SO₄^{2–} and Cl[–] forms was reversed, which was explained by the different degrees of hydration of counter ions and their different salting-out effects with ethanol. An empirical equation valid in the mole fraction of organic solvent range 0.2–0.8, in the intermediate region of solvent mixtures, was found to describe the swelling of ion exchangers. This equation was used to describe swelling in other solvent mixtures also^{5,7}. Marcus and Naveh⁷ determined the swelling of the Cl[–] and ClO₄[–] forms of Dowex 1 resin of various degrees of cross-linking in several solvents and their mixtures in water. In mixed aqueous–organic solvents, alcohols are sorbed preferentially at low mole fractions (up to about 0.2). The same behaviour was ob-

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served for an isopropanol–water mixture⁸. At higher mole fractions, water was sorbed to a greater extent. The results were explained in terms of the effect of the organic solvent on the structure of water and the selective ion solvation effects. The selective sorption of acetone was observed on the strongly basic anion exchanger AV-17 (CdI_3^-) up to 0.5 mole fraction of acetone, whereas in the Cl^- form water was preferentially sorbed⁶.

Although many investigations have been carried out on the sorption and separation of ions in water–organic solvent–mineral acid mixtures, there have been no investigations on the effect of mineral acids on the distribution of organic solvents and water between the resin and the liquid phase. We therefore determined the swelling of ion exchangers in the presence of mineral acids in mixtures which we have investigated previously⁹. Because of the lack of swelling data in the literature for all the systems investigated, for comparison we studied binary mixtures also.

EXPERIMENTAL

The swelling of KU-2-X8 cation exchanger and AV-17-X8 anion exchanger in the hydrogen, chloride, nitrate, sulphate and perchlorate forms was measured in water and in methanol–water and acetone–water mixtures and in solutions of different mineral acids (perchloric, sulphuric, nitric and hydrochloric) in methanol–water and acetone–water mixtures.

We also studied systematically the sorption of Cu(II), Co(II) and Ni(II) ions from organic solvent–mineral acid–water mixtures by the cation exchanger KU-2-X8 and the anion exchanger AV-17-X8.

The weight swelling of exchangers was determined by the standard centrifugation method (1500 g for 45 min). After centrifugation, the components were measured in the swollen resin phase. The acetone and methanol were determined by the iodine¹⁰ and potassium dichromate¹¹ methods, respectively. The sorbed acid was titrated with alkali. In some instances, the Karl Fischer method was adopted for determining the water bound by the ion exchanger. Equilibrium ion-exchange measurements were performed under static conditions.

RESULTS AND DISCUSSION

The selective swelling of KU-2 cation exchanger is shown in Fig. 1. The curves are asymmetrical to the diagonal drawn in the \bar{N}_0/N_0 diagram. This effect is greater for an acetone–water mixture, and the positive deviation from ideal behaviour is higher in the case of this mixture. In the presence of perchloric acid, the preferential sorption of water decreases, especially at higher N_0 values and at higher acid concentrations. The uptake of perchloric acid is small ($2.7 \cdot 10^{-2}$ – $8.3 \cdot 10^{-1}$ mole per kilogram of resin). The same result was observed in nitric acid solution.

Fig. 2 demonstrates the sorption of Ni(II) ions on KU-2 cation exchanger from organic solvent–water–nitric acid mixtures as a function of organic solvent content. The distribution coefficients, D , increase in the order methanol < ethanol < propanol < acetone, and so does the selective uptake of water by the resin.

Selective swelling of an anion exchanger depends on the nature of the solvent mixture, the structure of the solution, the ionic form of the ion exchanger and the type

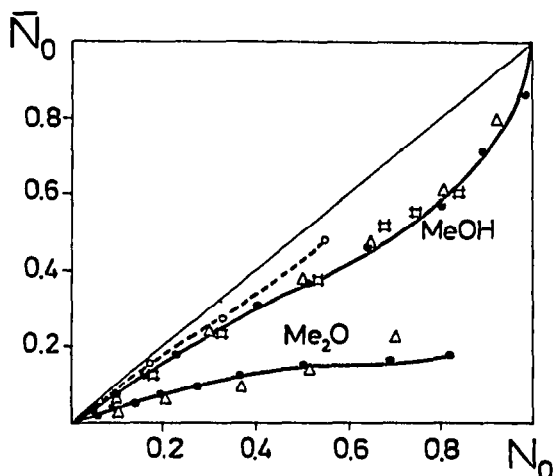


Fig. 1. Solvent selectivity, N_0 , as a function of N_0 for KU-2-X8 (H^+) resin in water-organic solvent-perchloric acid mixtures, with methanol and acetone as the organic solvents. N_0 and N_0 = mole fraction of organic solvent in the resin and in solution, respectively. Concentration of perchloric acid in both solvents: ●, 0; △, 0.5 N; □, 1.0 N; ○, 2.0 N.

of hydration of the counter ion. The uptake of water by anion exchangers depends on the counter ion: it increases in the order $ClO_4^- < NO_3^- < Cl^- < SO_4^{2-}$ form of the resin and is greater from acetone-water mixtures than from methanol-water mixtures, especially for higher N_0 values. The sorption of methanol in different forms of anion exchangers exhibits the same order as that of water, *i.e.*, $ClO_4^- < NO_3^- < Cl^- \approx SO_4^{2-}$, whereas the uptake of acetone by the anion exchanger is very low and

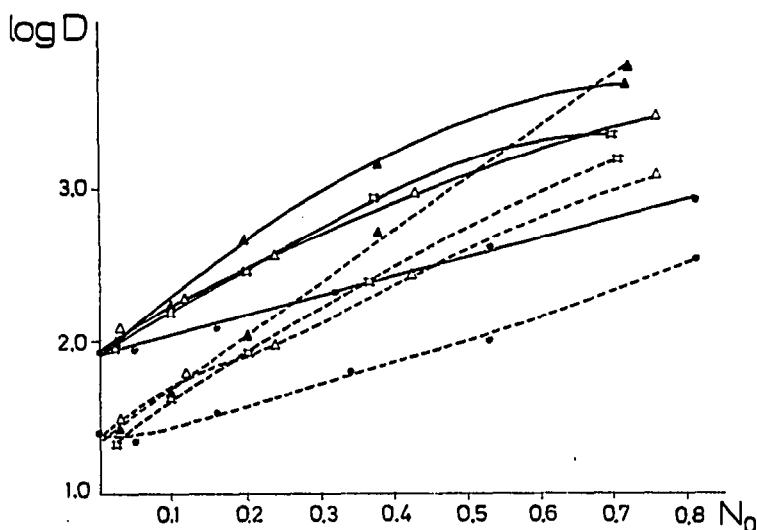


Fig. 2. Sorption of Ni(II) ions on KU-2-X8 cation exchanger from organic solvent-water-nitric acid mixtures. Solvent: ●, methanol; △, ethanol; □, propanol; ▲, acetone. Solid lines, 0.5 N nitric acid; broken lines, 1.0 N nitric acid. $D = (\mu g \text{ ion/g resin}) / (\mu g \text{ ion/ml solution})$.

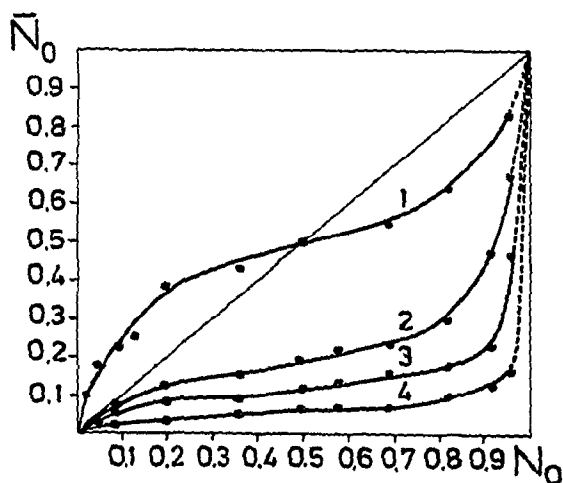


Fig. 3. Solvent selectivity, \bar{N}_0 , as a function of N_0 for different forms of AV-17-X8 resin in water-acetone mixtures. Form of resin: 1, ClO_4^- ; 2, NO_3^- ; 3, Cl^- ; 4, SO_4^{2-} .

varies only slightly with the mole fraction of solvent in the solution, and the order is opposite to that with water and methanol. This phenomenon is related to the different solvating ability of the two solvents¹². Fig. 3 shows the $\bar{N}_0 - N_0$ curves obtained with different forms of the anion exchanger in an acetone-water mixture. The greater the hydration energy and the stronger the positive hydration of the counter ion, the higher is the selective water sorption coefficient, K_0^w , of the resin:

$$K_0^w = \frac{\bar{N}_w \cdot N_0}{N_0 \cdot N_w}$$

where \bar{N}_w and N_w are the mole fraction of water in the resin and in solution, respectively. For N_0 values lower than 0.5 on the perchlorate form of the resin, selective adsorption of acetone can be observed. The component present in a smaller amount is better sorbed. Perchlorate ion does not show a salting-out effect with acetone because, as its hydration is negative, it shows a water structure breaking effect. Similarly, in a methanol-water mixture, for $N_0 < 0.2$, selective sorption of methanol was observed. The same result was obtained by Marcus and Naveh⁷ on Dowex 1 resin, and they attributed this result to the effect of the low methanol concentration on the structure of water.

The presence of mineral acid affects the selective uptake of water by anion exchangers to a greater extent than that by cation exchangers. This difference is related to the higher acid uptake by anion exchangers. Figs. 4 and 5 show the water uptake by different forms of the anion exchanger from methanol-water and acetone-water mixtures, respectively, and from 1 *N* solutions of mineral acids in the same solvent mixtures. The water uptake by the SO_4^{2-} form of the resin decreased to a great extent in the presence of sulphuric acid. There is virtually no difference between the two curves for the perchlorate form of the resin. Sulphuric acid is bound to a greater extent with formation of HSO_4^- ions in the resin phase: 0.8–1.0 equiv. acid/equiv. resin. Negative hydration is characteristic of the HSO_4^- ion in contrast to the SO_4^{2-}

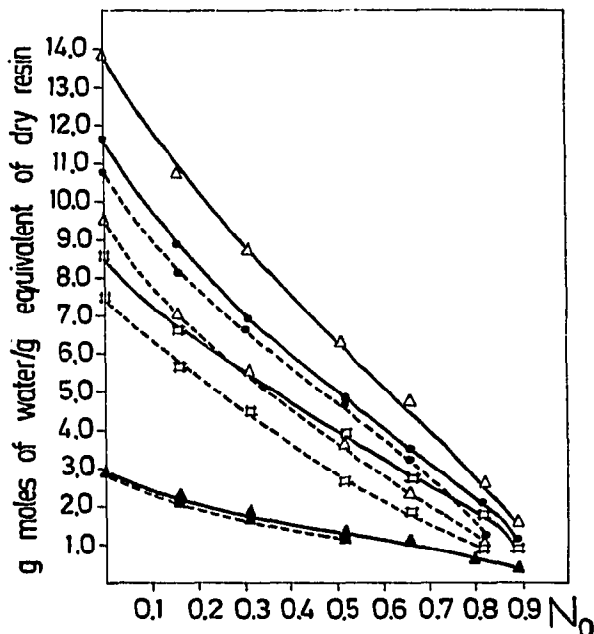


Fig. 4. Water uptake (moles of water per equivalent of dry resin) by different forms of the resin: \blacktriangle , ClO_4^- ; \square , NO_3^- ; \bullet , Cl^- ; \triangle , SO_4^{2-} . Solid lines, water-methanol; broken lines, water-methanol-1 N acid (HClO_4 , HNO_3 , HCl or H_2SO_4 , corresponding to the salt form of the anion exchanger).

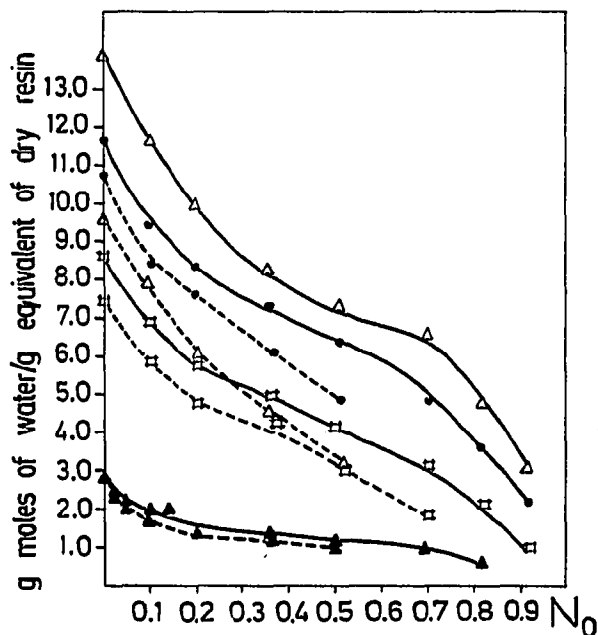


Fig. 5. Water uptake (moles of water per equivalent of dry resin) in different salt forms of the resin. Symbols for salt forms as in Fig. 4. Solid lines, water-acetone; broken lines, water-acetone-1 N acid (HClO_4 , HNO_3 , HCl or H_2SO_4 , corresponding to the salt form of the anion exchanger).

ion, and therefore the water uptake by the former is even less than that of the Cl^- form of the resin (Figs. 4 and 5).

The sorption of hydrochloric and nitric acid can be explained by the formation of HCl_2^- and $\text{H}(\text{NO}_3)_2^-$ ions, respectively, particularly at higher acid concentrations, in a similar manner to the result with liquid anion exchangers^{13,14}. The uptake of perchloric acid is very low (*ca.* 0.07 mole per equivalent of resin). Increasing the solvent concentration may enhance both the association and the acid sorption. The methanol uptake decreases in mixtures containing sulphuric acid compared with the binary mixtures, but it remains virtually unchanged in the Cl^- , ClO_4^- and NO_3^- forms of the resin. By addition of acid, the acetone uptake increases in the case of the SO_4^{2-} form of the resin, the salting-out effect of the HSO_4^- ion being weaker than that of the SO_4^{2-} ion.

The sorption of ions in the anion exchanger depends considerably on the selective swelling of the resin. Without the addition of acid, metal nitrates are sorbed only from acetone at very high concentrations, as the addition of water does not allow the formation of $\text{CoX}_3(\text{NO}_3)_3^-$ ions ($\text{X} = \text{acetone}$) in the resin phase because of selective adsorption of water by the resin. From sulphuric acid solutions, the elements are sorbed only at low acid concentrations ($<0.1 N$) and at high organic solvent concentrations ($N_0 > 0.5$). Under such conditions, the difference in solvent mixture composition is greatest between the resin and solution phase. Metal sulphates prefer the water-rich ion exchanger phase. The solubility of metal sulphates is much greater in water than in organic solvents. The distribution coefficients in acetone-water-hydrochloric acid mixtures are lower for Co(II) and Cu(II) than in mixtures containing alcohol, as the sorption of ions is hindered by the lower organic solvent content of the resin phase, which in turn is lower in acetone-water mixtures because of the enhanced water adsorption. Ions are not sorbed on the perchlorate form of the resin because neither complex formation nor a distribution mechanism is possible. The presence of metal ions (maximum 500 μg per 0.200 g of ion exchanger) has virtually no effect on the selective swelling of the ion exchangers.

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