

654. *The Absorption of Uncharged Molecules by Ion-exchange Resins.*

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Sorption of acetic, propionic, *n*-butyric, and benzoic acid, and of ethyl, *n*-propyl, and *n*-butyl alcohol, by sulphonated cross-linked polystyrene resins from aqueous solution at 25° is shown to be true and uniform absorption, and not confined to the surface of the resin particles. The distribution is influenced by, *inter alia*, the cationic form and degree of cross-linking of the resin, the chain length and polar group of the solute, and the concentration in solution. The operative factors are believed to be: (1) simple dissolution of the solute in the water present in the resin; (2) "salting-out" by the polar groups of the resin (the exact mechanism of this is not understood but it may be represented, in some cases, by the solvation of these polar groups); (3) London dispersion interactions between the hydrocarbon part of the organic solute and the benzene nuclei of the resin; (4) polar attractive interactions (in some cases); (5) an unidentified factor necessary to explain why, at high concentrations, the order of the molality ratios of acetic, propionic, and *n*-butyric acid is inverted, *n*-butyric acid being absorbed the least.

WHEN an ion-exchange resin is brought into contact with a solution containing ions and/or uncharged molecules, any or all of the following processes may occur: (1) Ion-exchange; (2) absorption (or desorption) of solvent, usually water, by (or from) the resin; (3) penetration of electrolyte into the resin; and (4) absorption of uncharged molecules by the resin. The present paper is concerned with the last of these.

The sorption of non-electrolytes by ion-exchange resins appears to have been discovered by Bhatnagar, Kapur, and Puri¹ in 1936, only a year after the first wholly synthetic ion-exchange resins were prepared.^{2a} Subsequent studies² enlarged our knowledge of this phenomenon particularly with respect to the effects with a wide variety of solutes. However, there appears to have been little or no systematic study of the effects arising from variation of the structure of the resin, and in particular, its degree of cross-linking. The present study was therefore undertaken primarily with this end in view. Other factors were also investigated, including the effects of varying the cationic form of the resin, and the chain length and polar group of the solute.

In the present work, three resins of the sulphonated polystyrene type, cross-linked with 5½, 10, and 15% of divinylbenzene (DVB) severally were used. These divinylbenzene contents are nominal since there is some uncertainty as to both the true composition of the copolymer and the amount of divinylbenzene that is actually effective in cross-linking. Nevertheless, reproducible correlations exist between the nominal divinylbenzene content and all the important properties of the resin, namely, swelling,³ ion-exchange equilibria,⁴ kinetics,⁵ and degree of penetration of electrolytes into the resins.³ The absorption of ethyl, *n*-propyl, and *n*-butyl alcohol from aqueous solution into these three resins (both hydrogen and sodium forms) have been measured at 25° at three concentrations. For acetic, propionic, and *n*-butyric acid it was only possible to use the hydrogen form of the resins (since ion-exchange would occur with other cationic forms). These acids too have been studied at three concentrations and, in addition, the absorption of acetic acid was studied down to very low concentrations (0.01M) and compared with that of benzoic acid at these concentrations. For the present purpose, all these carboxylic acids may be regarded as non-electrolytes since, even in aqueous solution of as low a concentration as 0.01M, only about 3%

¹ Bhatnagar, Kapur, and Puri, *J. Indian Chem. Soc.*, 1936, **13**, 679; cf. Bhatnagar, Kapur, and Bhatnagar, *ibid.*, 1939, **16**, 249, 261; 1940, **17**, 361.

² (a) Adams and Holmes, *J. Soc. Chem. Ind.*, 1935, **54**, 1; (b) Samuelson, *Ingen. Vetensk. Akad. Handl.*, 1945, No. 179, 24; Tolliday, Thompson, and Forman, *J. Soc. Leather Trades Chemists*, 1948, **32**, 291; Erler, *Z. analyt. Chem.*, 1949, **129**, 209; (c) 1951, **131**, 106; Gregor, Collins, and Pope, *J. Colloid Sci.*, 1951, **6**, 304; (d) Wheaton and Bauman, *Ann. New York Acad. Sci.*, 1953, **57**, 159.

³ Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.

⁴ (a) Reichenberg, Pepper, and McCauley, *J.*, 1951, 493; (b) Reichenberg and McCauley, *J.*, 1955, 2741.

⁵ Reichenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 589.

of dissociation occurs. In the resin phase, with its high concentration of hydrogen ions, the dissociation of the carboxylic acids will be much less.

EXPERIMENTAL

Resins.—The preparation of this type of resin in spherical beads has been described earlier.^{3,4} The 5½% and 15% divinylbenzene resins were identical with those used by Reichenberg and McCauley^{4b} for the study of ion-exchange relative affinities. The 10% resin, although not identical with, was very similar to that used in this previous work. Table I gives details of the properties of the resins.

TABLE I.

Nominal divinylbenzene content (%)	Particle diameter (swollen in water) (μ)	Specific capacity (mg.-equiv. per g. of dry H-form resin)	Wt. swelling : g. of water absorbed per amount of resin equiv. to 1 g. of dry H-form resin	
			H form	Na form
5½	180—280	5.40	1.49	1.26
10	220—320	5.30	0.84	0.73
15	190—310	5.24	0.60	0.53

Organic Solutes.—"AnalaR" glacial acetic acid was checked by titration and was used without further purification.

Commercial samples of propionic and *n*-butyric acid were purified by distillation. The purities were then checked by the refractive indices and by liquid-vapour chromatography.⁶

Ethyl alcohol was purified as described by Smith,⁷ then checked for its density, refractive index, and b. p.

Commercial samples of *n*-propyl and *n*-butyl alcohol were boiled with lime, then fractionally distilled. The refractive indices, densities, and b. p.s agreed with accepted values.

Determination of Absorption of Solutes by Resins.—The method used was essentially similar to that described³ for measuring the penetration of hydrogen chloride from aqueous solutions into ion-exchange resins. It permits simultaneous measurement of the uptake of both water and solute. Resin samples (each about 1 g. when swollen) were introduced into centrifuge sinter tubes and their amounts determined by conversion into the H-form, displacement with sodium chloride, and titration of the liberated acid with alkali. For an absorption measurement, the sample of resin was first converted into the desired cationic form and thoroughly washed with water. An aqueous solution containing the organic solute in known concentration was then passed through the column of resin until the resin was in sorption equilibrium with it, with respect both to water and the organic solute. This "conditioning" process was carried out in an air-thermostat at $25.0^\circ \pm 0.5^\circ$. Each experiment was repeated at the same flow-rate but with twice the volume of solution, in order to check for completeness of conditioning. The amounts of solution normally used contained at least 25 mmoles of solute; sometimes double this quantity was used. The conditioning period was always at least 4 hr. After the conditioning, the resin sample was centrifuged at 2000 r.p.m. for 30 min. at 25° and weighed. On the particular centrifuge used, 2000 r.p.m. corresponds to 340 g at the top of the resin bed and 380 g at the part in contact with the sinter. After the weighing, water was passed through the column of resin to wash out all the organic solute. The effluent was collected and analysed for the organic solute. For the carboxylic acids, this was done by titration with standard alkali and a mixed indicator of p_T 8.3. For the alcohols, the total effluent was made up to 100 ml. and the concentration of the resulting solution determined with a Rayleigh interference refractometer. From time to time, duplicate determinations of the exchange capacity of the resin samples were made to check against loss of resin. Also, blank experiments were run to determine the amounts of liquid remaining in the sinter and between the beads of resin after centrifuging.³ Thus were calculated the amounts of water and of organic solute held by the resin when in equilibrium with the conditioning solution. By repeating this with conditioning solutions of various concentrations, complete absorption isotherms for 25° were obtained.

RESULTS AND DISCUSSION

Careful consideration was given to whether the equilibrium amount of sorption was independent of the particle size of the resin. This was checked experimentally for sorption

⁶ James and Martin, *Biochem. J.*, 1952, **50**, 679.

⁷ Smith, *J.*, 1927, 1288.

from 2N-acetic acid. Table 2 shows that there is little or no effect of particle size on the sorption of either water or acetic acid and certainly no evidence in favour of decrease of sorption with increase of particle size. This proves that both the acetic acid and the water are uniformly *absorbed* throughout the interior of the resin particles and that *adsorption* on the surface of the particles plays a negligible part. This conclusion may also be drawn

TABLE 2. *Effect of particle size on the sorption of solvent and solute from 2N-acetic acid.*

Nominal divinylbenzene content (%)	5½		10		15	
Diam. of particles (swollen in water) (μ)	180—280	240—400	160—240	220—320	130—220	190—310
Acetic acid (mmoles) sorbed per g. of dry H-form resin	2.41	2.44	0.96	0.97	0.52	0.53
Water (g.) sorbed per g. of dry H-form resin	1.41	1.38	0.81	0.80	0.59	0.59

from the magnitude of the sorption of solute. In 0.5N-solution, the 15% resin (which sorbs the least) takes up 0.14 mmole of acetic acid per g. of the dry hydrogen-form resin. Even if the mean diameter of the swollen particles is assumed as low as 200 μ, adsorption would imply a surface concentration of about 23 molecules per Å² of the surface of the swollen resin particles. Even allowing acetic acid an area as low as 10 Å² per molecule, one would be compelled, on an adsorption basis, to postulate a multilayer 230 molecules deep. This is very much less probable than the concept of uniform absorption, even without evidence on the absence of any particle size effect. Since acetic acid is one of the least strongly sorbed solutes, uniform absorption may be taken as a general rule. It is

TABLE 3. *Absorption of water and organic solute from aqueous solutions of various concentrations.*

Solute	Form of resin	Molality in outside solution	<i>E</i> = wt. (g.) of H ₂ O absorbed *			<i>G</i> = amount (mmoles) of solute absorbed *		
			5½% DVB	10% DVB	15% DVB	5½% DVB	10% DVB	15% DVB
BzOH	H ⁺	0.0100	0.10	0.045	0.023	1.49	0.84	0.60
		0.0200	0.20	0.089	0.046	1.49	0.84	0.60
AcOH	H ⁺	0.0100	0.019	0.008	0.005	1.49	0.84	0.60
		0.0201	0.037	0.015	0.009	1.49	0.84	0.60
		0.0503	0.068	0.030	0.018	1.49	0.84	0.60
		0.101	0.13	0.059	0.034	1.48	0.84	0.60
		0.202	0.26	0.116	0.066	1.48	0.84	0.60
		0.514	0.64	0.27	0.14	1.46	0.83	0.59
		1.056	1.27	0.53	0.29	1.42	0.82	0.59
		2.234	2.41	0.97	0.53	1.35	0.80	0.58
Et·CO ₂ H	H ⁺	0.456	0.73	0.31	0.16	1.46	0.83	0.60
		0.941	1.45	0.54	0.28	1.43	0.82	0.59
		2.013	2.51	0.93	0.47	1.36	0.80	0.58
Pr·CO ₂ H	H ⁺	0.541	1.13	0.43	0.22	1.46	0.83	0.59
		1.134	1.95	0.74	0.33	1.42	0.82	0.59
		2.517	2.49	0.87	0.39	1.33	0.79	0.57
EtOH	H ⁺	0.519	0.83	0.41	0.26	1.46	0.83	0.59
		1.067	1.59	0.81	0.50	1.42	0.82	0.59
		2.262	2.88	1.43	0.89	1.34	0.79	0.58
	Na ⁺	0.519	0.44	0.23	0.14	1.22	0.71	0.52
		1.067	0.85	0.41	0.25	1.18	0.69	0.51
		2.262	1.81	0.74	0.51	1.09	0.64	0.48
PrOH	H ⁺	0.518	1.15	0.58	0.39	1.43	0.81	0.59
		1.075	2.33	1.12	0.73	1.36	0.79	0.57
		2.329	4.42	2.15	1.22	1.21	0.72	0.54
	Na ⁺	0.523	0.54	0.23	0.13	1.22	0.71	0.52
		1.084	1.01	0.42	0.24	1.18	0.69	0.51
		2.342	2.22	0.88	0.46	1.08	0.64	0.48
BuOH	H ⁺	0.210	0.60	0.30	0.17	1.44	0.82	0.60
		0.427	1.26	0.63	0.36	1.40	0.80	0.60
		0.886	2.68	1.27	0.74	1.29	0.76	0.59
	Na ⁺	0.210	0.29	0.13	0.06	1.23	0.72	0.53
		0.427	0.60	0.26	0.13	1.22	0.71	0.52
		0.886	1.37	0.60	0.30	1.15	0.70	0.51

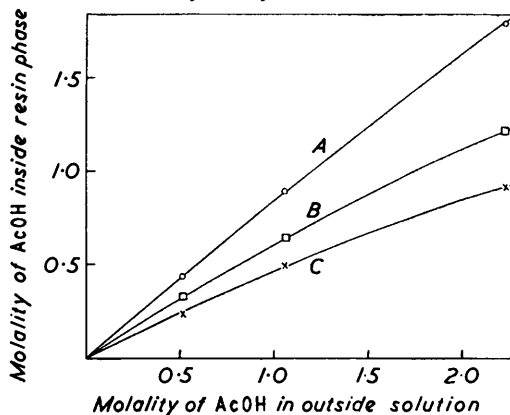
* By 1 g. of dry H-form resin or an equiv. wt. of dry Na-form resin.

only when the total sorption is very low that the possibility of adsorption need be considered seriously. Such cases will arise mainly where the solute molecules are too large to penetrate easily the molecular pores of the cross-linked resin. Possible cases of such adsorption have been indicated by Davies and Thomas.⁸

Erler^{2b} studied the sorption from aqueous solution of a number of organic acids on Wofatit F, a German resin of the phenolsulphonic type. He concluded that the sorption increased with increased particle size. This very surprising result is due to a fallacious experimental technique. Erler assumed, incorrectly, that after the solution had been shaken with resin for a few seconds there would be insufficient time for appreciable sorption to occur. He therefore calculated the total sorption from the difference between the titre (of an aliquot part) after 30 minutes' shaking and that after a few seconds' shaking. It is clear, therefore, that all his sorption values are too low, the error being greatest with the resins of the smallest particle size.

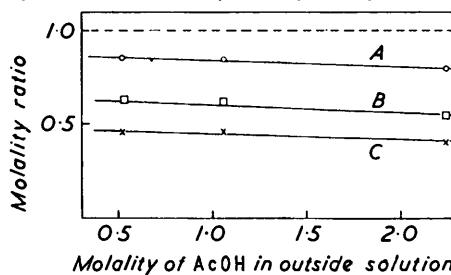
The results in Table 3 show that with each solute, at a given molality in the outside solution, the amounts of both water and solute absorbed by the resin decrease with increase

FIG. 1. Absorption of acetic acid at 25° by the H forms of resins.



A, 5½% DVB; B, 10% DVB; C, 15% DVB.

FIG. 2. Molality ratios expressing the absorption of acetic acid at 25° by the H forms of resins.



of cross-linking of the resin. The simplest explanation is to suppose that the resin absorbs the water which in turn dissolves the solute. If there were no other effects, the molality of the solute (*i.e.*, mmoles per g. of water) inside the resin should depend on the molality in solution but be independent of the degree of cross-linking. Fig. 1 shows that for acetic acid the molality inside the resin depends markedly on the degree of cross-linking and this has been found also for all the solutes investigated. For subsequent representation, we define the "molality ratio" as the molality of solute inside the resin divided by the molality in the outside solution. This may be regarded as a partition coefficient between the aqueous phase in the resin and that in the outside solution. Fig. 2 shows the molality ratio for acetic acid plotted against the molality in the outside solution.

The concept mentioned above may be refined a little by considering the amounts of solute and "resin material" associated with 1 g. of water inside the resin for a given concentration of solute in the outside solution. As the cross-linking is increased, the amount of "resin material" increases and the amount of solute decreases. On the assumption that the simultaneous increase of resin material and decrease of solute are related as cause and effect, the resin material may be regarded as having a "salting-out" effect on the solute. The simplest interpretation of salting-out is that the ions of the salt interact with a certain number of the solvent molecules in some way that prevents these molecules from fulfilling their normal function. Thus solvation of ions leaves less "free" solvent molecules for the solute to dissolve in.

⁸ Davies and Thomas, *J.*, 1951, 2624.

If 1 g. of dry H-form resin absorbs E mg.-equiv. of solute and G grams of water from a solution of molality m , the above hypothesis leads to the equation

$$E = am(G - G_0)$$

where G_0 is the number of grams of water withdrawn by solvation of the exchange groups of 1 g. of dry H-form resin. G_0 is related to n , the hydration number of the exchange

FIG. 3. Test of the simple "hydration" theory, using data on the absorption of acetic acid.

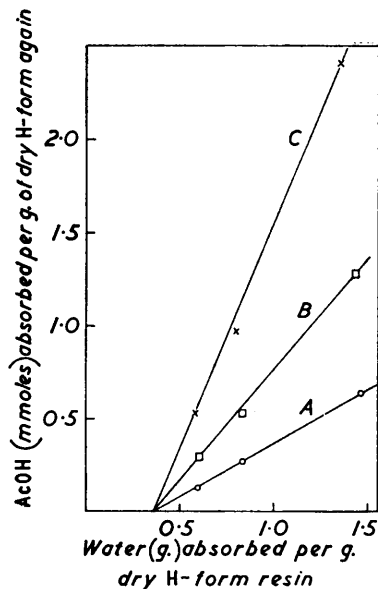
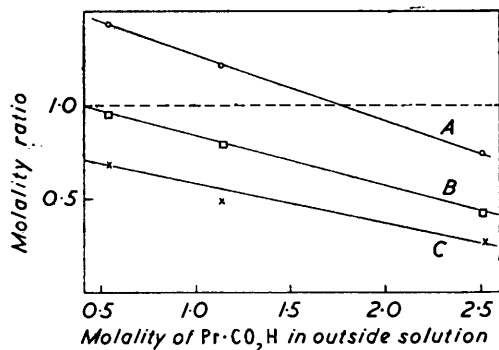


FIG. 5. Molality ratios for the absorption of n-butyric acid by the H-forms of resins.



For Fig. 3: A, 0.514m; B, 1.056m; C, 2.234m.

For Figs. 4-6: A, 5½% DVB; B, 10% DVB; C, 15% DVB.

FIG. 4. Molality ratios for the absorption of propionic acid by the H-forms of resins.

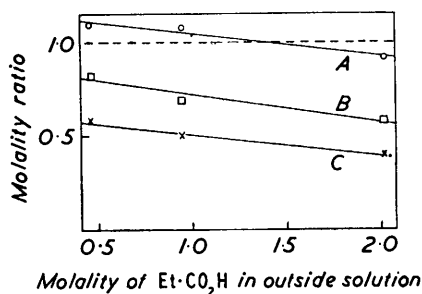
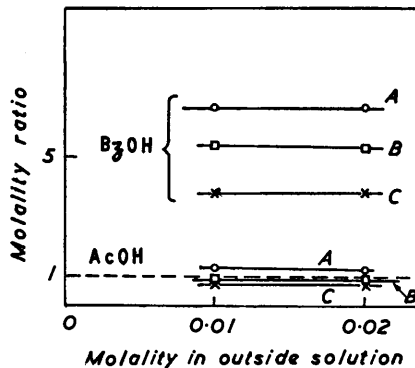


FIG. 6. Molality ratios for the absorption of benzoic and acetic acid from solutions of very low concentration.



groups of the resin, and n is assumed to be constant for a given solute and a given type of resin in a given cationic form. One may regard a as a rather abstract kind of partition coefficient representing the ratio of the molality of solute in the "free" water inside the resin to the molality in the outside solution. It may be noted that while the hypothesis involves the assumption that a is independent of the degree of cross-linking (at a given value of m) it does not involve assuming that a is independent of m (for a given degree of

cross-linking). This hypothesis predicts, therefore, that if, for each of a series of values of m , E is plotted against G , a series of straight lines should be obtained, all cutting the G -axis at the same value, G_0 . The plot in Fig. 3 for acetic acid shows that all these expectations are fulfilled. The value of G_0 corresponds almost exactly to a hydration number of 4 for the sulphonic acid group, a plausible value. From the slopes of the straight lines, values of a may be deduced: for acetic acid, a is constant and independent of the molality (although this is not an essential part of the hypothesis) and is close to unity at all concentrations at least up to 2 m .

The simple hypothesis fits equally well for propionic acid and fairly well for n -butyric acid. Again G_0 corresponds to a hydration number of about 4. With propionic acid, a has a value 1.4, independent of the molality, but with n -butyric acid, a varies markedly with m , decreasing from about 2 at low molalities to slightly less than 1 at $m = 2.5m$ in the outside solution.

Fig. 4 shows that with the 10% and the 15% resin propionic acid has a lower molality inside the resin than outside at all concentrations, but with the 5½% resin the molality ratio is greater than unity at molalities below 1.4. With the 15% resin, n -butyric acid (Fig. 5) has a lower molality inside the resin than outside at all concentrations but with the 5½% and the 10% resin the molality ratio is greater than unity at molalities below 1.75 and 0.4, respectively. Clearly, in addition to the salting-out effects, there must be positive interactions which tend to make the molality inside the resin greater than outside. These effects increase in the order acetic < propionic < n -butyric and are almost certainly due to London dispersion interactions between the hydrocarbon part of the solute molecules and the benzene nuclei of the resin. Fig. 6 shows that at very low concentrations the London interactions are very much greater with benzoic than with acetic acid. The molality ratios for acetic acid are appreciably higher at these very low concentrations than at >0.5 m . It also appears that with the 5½% resin the molality ratio for acetic acid exceeds unity at these very low concentrations, although this requires confirmation as the effect is only a little greater than the probable experimental error. The molality ratios for benzoic acid considerably exceed those for butyric acid, so that we may tentatively extend the series given above: acetic < propionic < n -butyric < benzoic.

The equation $E = am(G - G_0)$ also fits fairly well the experimental data for the absorption of ethyl, n -propyl, and n -butyl alcohol. Table 4 summarises results obtained by drawing the best straight line through each set of three points representing a given molality in the outside solution.

TABLE 4.

Solute	Form of resin	G_0	a	Concn. range (molality in outside solution)
AcOH	H ⁺	0.36	1.1	0.5—2.2
Et·CO ₂ H	H ⁺	0.35—0.40	1.4	0.5—2.0
Pr·CO ₂ H	H ⁺	0.38—0.43	2—1	0.5—2.5
EtOH	H ⁺	0.25	1.3	0.5—2.3
PrOH	Na ⁺	0.23	0.9	0.5—2.3
	H ⁺	0.24	2.0	0.5—2.3
BuOH	Na ⁺	0.28—0.31	1.2	0.5—2.3
	H ⁺	0.26—0.32	2.5—3	0.2—0.9
	Na ⁺	0.33	1.5—1.8	0.2—0.9

If a mean specific capacity of 5.3 mg. equiv. per g. of dry H-form resin is assumed, hydration numbers of 2, 3, 4, and 5 correspond with G_0 values of 0.191, 0.286, 0.382, and 0.478, respectively. Thus for the three acids with the resins in the hydrogen form, G_0 corresponds with a hydration number of 4. For the alcohols, G_0 corresponds more closely with a hydration number between 2 and 3, with both the hydrogen and the sodium forms of the resins: a possible reason for this is discussed below.

The most striking effect in connection with the absorption of alcohols is the effect of the cationic form of the resin. Fig. 7 shows that the hydrogen form of the 5½% resin absorbs n -butyl alcohol nearly twice as strongly as does the sodium form. This effect is exhibited also by the 10% and the 15% resin and applies also to ethyl and n -propyl alcohol.

Fig. 8 shows that for acetic, propionic, and butyric acid at low molalities the absorption increases with chain length, though this effect diminishes with increasing concentration and is even reversed at high concentrations. Clearly yet another factor is operative, though its nature is not clear. It might perhaps be thought to correspond with the co-volume term in the van der Waals equation of state for gases. The intersection point for the molality ratios of propionic and *n*-butyric acid occurs at a molality of 2.0 in the outside solution (1.8 inside the resin) with the 5½% resin. This corresponds with about 0.5 molecule of solute per sulphonic acid group. It is reasonable to expect the size of the solute molecules to have some effect in this range. A possible objection is that similar plots for ethyl, *n*-propyl, and *n*-butyl alcohol with the 5½% resin in either the hydrogen (Fig. 9) or the sodium form show no sign of any such convergence even though in the former case the highest concentration of *n*-butyl alcohol in the resin corresponds to 0.5 molecule per sulphonic acid group and that of *n*-propyl alcohol to about 0.85 molecule. However, this

FIG. 7. Molality ratios for the absorption of *n*-butyl alcohol by (A) the H- and (B) the Na-form of a 5½% DVB resin.

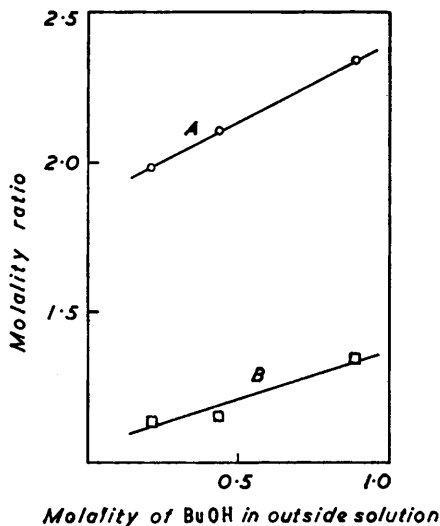
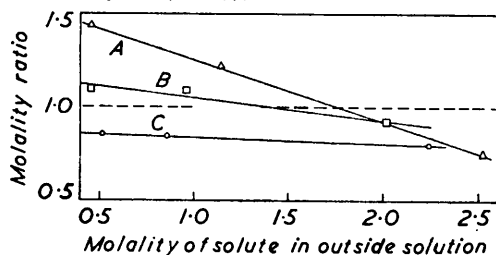


FIG. 8. Molality ratios for the absorption of (A) acetic, (B) propionic, and (C) *n*-butyric acid by the H-form of a 5½% DVB resin.



objection may not be conclusive since, as will be shown below, with the alcohols powerful polar interactions occur and these may mask the co-volume effect.

The effect of cross-linking may now be considered in more detail. Samuelson^{2b} showed that with a resin of very low cross-linking (*i.e.*, very high swelling) the molality of acetic or *n*-butyric acid inside the resin phase was the same as in the outside solution. This might be expected since, relatively to the amount of water present, the amounts of both the polar groups and the hydrocarbon matrix of the resin are too small for salting-out effects, London dispersion interactions, or salting-in effects to be appreciable. In this discussion, therefore, it will be assumed that, for all solutes at all concentrations, the molality ratio is unity at extremely low degrees of cross-linking. As the cross-linking is increased, in some cases (acetic acid may be an example—see above), the molality ratio decreases immediately to values below unity for all concentrations. In other cases (*e.g.*, *n*-butyric acid and *n*-butyl alcohol) the molality ratio increases to values above unity (at least at low concentrations). This is clearly due to predominance of salting-in over the salting-out effects. At higher degrees of cross-linking, salting-out effects always predominate and (in this range) further increase of cross-linking always decreases the molality ratio. Certainly in some and probably in all cases, increase of cross-linking eventually reduces the molality ratio to below unity. Concentration also plays a part since, with a given solute and a resin of a given degree of cross-linking in a particular cationic form, increasing the concentration may alter the molality ratio from a value above unity to one below unity.

So for each solute at a given concentration there is an optimum degree of cross-linking at which the molality ratio is a maximum, provided, of course, that it can rise above unity at all.

The explanation of the very considerable increase in absorption of the alcohols on changing from the Na- to the H-form of the resin appears to lie in one or more of three possibilities: (1) The difference is due to the fact that the hydrogen forms of the resins swell more, *i.e.*, absorb more water. However, this difference of swelling is relatively small and it is difficult to see how it could cause the large difference in molality ratio by any direct effect. Further, the difference in swelling is probably due entirely to the difference in the hydration of the sodium and the hydrogen ions,^{3,9} in which case the sodium

FIG. 9. Molality ratios for the absorption of (A) ethyl, (B) n-propyl, and (C) n-butyl alcohol by the H-form of a 5½% DVB resin.

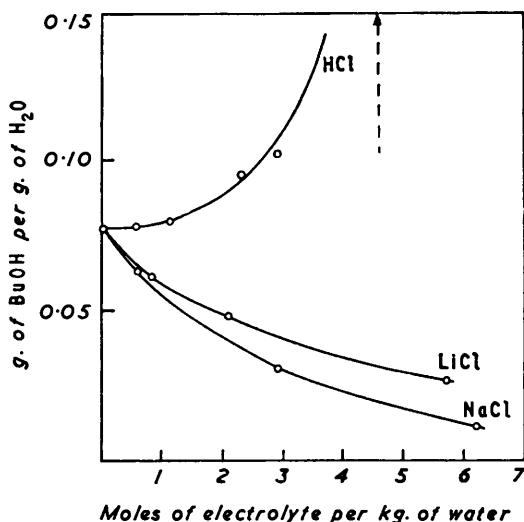
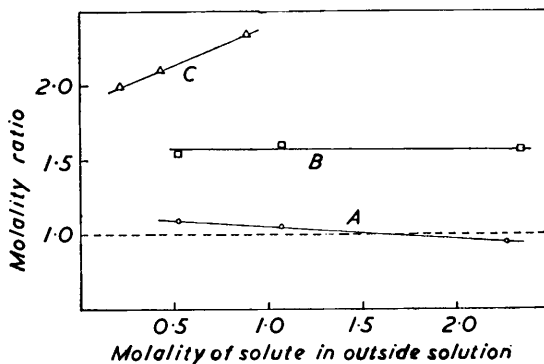


FIG. 10. Effects of NaCl, LiCl, and HCl on the solubility of n-butyl alcohol in water at 20°.

Aqueous solutions of HCl of molality 4.6 and higher are miscible in all proportions with n-butyl alcohol at 20°.

form of a resin would contain *more* "free" water than the hydrogen form. (2) If the sodium forms of the resins were completely ionized but the hydrogen forms only partly ionized, differences between the properties of the un-ionized SO_3H groups and the ionized SO_3^-Na^+ groups might be responsible for the effect. Thus there might be some form of polar interaction between the un-ionized SO_3H groups and the alcohol molecules. Or the un-ionized SO_3H groups might be incapable of salting-out the solute from the resin to the same extent as the ionized SO_3^-H^+ or SO_3^-Na^+ groups. This hypothesis is not implausible since, although sulphonic acids are generally regarded as "strong" acids, they are known to be not as strong as sulphuric acid, which in turn is not as strong as perchloric acid.¹⁰

⁹ Reichenberg, *Research*, 1953, 6, 9s.

¹⁰ Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 261.

However, it is difficult to obtain reliably even an estimate of the dissociation constants of sulphonic acids in water. King and King¹¹ showed that, while the sulphonic acid group in sulphamic acid has a dissociation constant of only 0.1, in taurine the value is probably somewhat greater than unity. Taking this value of unity and neglecting activity coefficients, one calculates that only about 40% of the sulphonic acid groups would be ionized in the 5½% divinylbenzene resin and less in the resins of higher cross-linking. The calculation is crude and further discussion of this possibility is inhibited by lack of relevant data. (3) The most attractive hypothesis is that the difference in absorption is due mainly or entirely to the difference between the properties of sodium and hydrogen ions. Evidence for this is provided by the fact that hydrochloric and other strong acids markedly increase the solubility of alcohols in water and may ultimately make them completely miscible.¹² Fig. 10 shows the effect of hydrogen chloride and of lithium and sodium chloride on the solubility of *n*-butyl alcohol in water at 20°. Both salts salt-out markedly while the acid (particularly at molalities above unity) salts-in equally markedly (Fig. 10 is based on measurements by the authors; for the acid, these agree fairly well with those of Reburn and Shearer,¹² considering that the latter measurements were carried out at 25°).

If we assume the correctness of the third hypothesis, the question of the detailed mechanism arises. The most obvious possibility is the direct co-ordination of a proton with an alcohol molecule, $H^+ + ROH \rightleftharpoons ROH_2^+$. This mechanism is commonly accepted as necessary to explain the conductivity of solutions of hydrogen chloride in anhydrous alcohols.¹³ It is more open to question whether, in systems containing large amounts of water (such as the resin systems and the system *n*-butyl alcohol-water-hydrogen chloride), this protonation occurs to any appreciable extent. The relative basicity of water and alcohols has been a point of controversy for some years (see Remick¹⁴). However, the most reliable recent work¹⁵ indicates that the intrinsic basicity of water considerably exceeds that of ethyl alcohol. *E.g.*, Braude and Stern showed that in a 0.1M-solution of hydrogen chloride in aqueous ethanol, containing only 1% (by volume) of water, hydroxonium ions exceeded protonated alcohol ions by a factor of over 7. In the presence of large amounts of water, therefore, it appears that very little protonation would occur.

Two comments may be made on this apparent objection: (a) Most (if not all) of the evidence that water is more strongly basic than ethyl alcohol is based on solutions with a hydrogen chloride concentration of 1 molar or less; it may be significant that this acid only shows a salting-in effect on *n*-butyl alcohol at molalities above unity (Fig. 10) and the effect increases markedly with increasing concentration of the acid. (b) The foregoing discussion and objection have been based on the assumption that the interaction involves protonated alcohol ions which can only be formed at the expense of hydroxonium ions. However, there is the alternative possibility that in solutions containing large amounts of water (or inside the resins) the hydroxonium ion may remain intact and the alcohol molecule may enter its solvation shell, displacing one or more water molecules (the values of G_0 in Table 4 support this view, being lower with alcohols than with acids). While it is not easy to see why this should occur more with the hydroxonium ion than with other cations, there is some evidence that it does. Thus the conductance measurements by Bezman and Verhoek¹⁵ indicate that the interionic separation of hydrogen chloride is much greater in ethanol solutions containing 2 moles of water per l. than in either water or ethanol solutions, whereas the interionic separation of ammonium chloride varies very little over the whole range of water-ethanol compositions. It is quite possible that, for some reason, alcohol molecules interact more strongly with hydroxonium ions than with other cations.

¹¹ E. J. King and G. W. King, *J. Amer. Chem. Soc.*, 1952, **74**, 1212; E. J. King, *ibid.*, 1953, **75**, 2204.

¹² Lieben and Rossi, *Annalen*, 1871, **158**, 137; Orton and Jones, *J.*, 1919, **115**, 1194; Reburn and Shearer, *J. Amer. Chem. Soc.*, 1933, **55**, 1774.

¹³ Glasstone, "Introduction to Electrochemistry," Van Nostrand, New York, 1942, p. 13.

¹⁴ Remick, "Electronic Interpretations of Organic Chemistry," John Wiley, New York, 2nd Edn., 1949, pp. 252-259.

¹⁵ Braude, *J.*, 1948, 1971; Braude and Stern, *J.*, 1948, 1976; Bezman and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1330.

It is of interest that polar interactions of a positive kind (as opposed to salting-out effects) are not confined to the alcohols. Thus Wheaton and Bauman^{2a} showed that the hydrogen form of a sulphonic acid resin cross-linked with 8% of divinylbenzene absorbed acetone about twice as strongly as formaldehyde. The sulphate form of a strong-base anion-exchange resin of the same cross-linking (8%) absorbed formaldehyde nearly twice as strongly as acetone, while the chloride form of a similar anion-exchange resin (of 7.5% divinylbenzene) absorbed formaldehyde and acetone to nearly the same extent.

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