167. The Behaviour of Ion-exchange Resins with Mixed Solvents. Part II.[1] Aqueous Ammonia Solutions.

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Measurements have been made of the uptake of water and ammonia from aqueous solutions by a commercial ion-exchange resin in a number of cationic forms. The silver resin forms a very stable diammine, and a column of the resin removes the whole of the ammonia from a dilute aqueous solution. The sodium and the potassium resin show no evidence of complex formation, but the lithium form absorbs ammonia more freely. The cupric tetrammine form is very stable, but nickel, especially in a highly cross-linked resin, forms complexes with ammonia to a smaller extent than in aqueous solution, and the difference is attributed to the restrictive effect of the stretched resin framework.

IN continuation of earlier work,[1] this paper describes the uptake of ammonia and water by a commercial ion-exchange resin in various cationic forms.

EXPERIMENTAL

Materials.—ZeoKarb 225, of 14—52 mesh, was used in the 8%, 12%, and 20% cross-linked forms. After preliminary washings with dilute hydrochloric acid to remove traces of iron and colloidally dispersed material the resin was converted into the required cationic form by column treatment with an appropriate reagent, exhaustively washed with de-ionised water, and dried in the air. The moisture content of the hydrogen form was determined by heating small samples to constant weight at 120°; for the ammonium and the silver form the moisture content was determined by quantitative conversion into the hydrogen form, followed by oven-drying. The capacity of the hydrogen resin was determined by the complete conversion of a weighed sample into the sodium form and titration of the acid released with standard sodium hydroxide. For the alkali-metal forms the procedure was reversed, the sample in a small column being treated with an excess of hydrochloric acid. The capacity of the ammonium form was found by distillation from sodium hydroxide, and for the other forms the metal was released by treatment with an excess of hydrochloric acid and determined by standard methods.

Procedure.—A 1-g. sample of air-dried resin was weighed into a dry filter-tube which was placed in a stoppered bottle containing a known weight (about 16 g.) of standard ammonia solution. The bottle was tilted several times during equilibration so that the ammonia solution could percolate through the resin bed, and under these conditions preliminary experiments showed that 24 hr. sufficed for attainment of equilibrium. The filter-tube was then removed, covered with a rubber cap, and supported in a centrifuge-tube by rubber rings. It was centrifuged at 2000 r.p.m. for 30 min. and then transferred quickly to a stoppered bottle and weighed. The concentration of the equilibrium ammonia solution was found by running a weighed sample into a known weight of standard hydrochloric acid and then titrating the excess of acid with dilute sodium hydroxide solution. From the known weight of the swollen resin, the weight of water originally contained in it, and the composition of the solvent before and after equilibration, it was possible to calculate the weights of water and ammonia taken up by the resin.

RESULTS AND DISCUSSION

Univalent Cations.—The results obtained with the 8% cross-linked resin are given in Table 1. Each is the mean of duplicate experiments. The first four rows of figures (the fifth will be discussed below) for each resin show successively: M, the concentration of ammonia at equilibrium in the outer solution, in moles per kg. of solution; W, the total weight of solvent absorbed by one equivalent of the resin; and the weights of water and ammonia contained in this.

Table 2 presents in the same way the results obtained with the 12% cross-linked resin.

[1] Part I, Davies and Owen, *J.*, 1956, 1676.

TABLE 1.

8% Cross-linked resin.

	Ammonium resin. Equiv. wt. 208.					Lithium resin. Equiv. wt. 203.3.				
M	0	0.72	1.66	2.46	3.31	0	0.87	1.78	3.05	3.88
W	175.8	172.8	171.3	170.4	169.7	211.3	209.2	206.5	204.4	202.6
H_2O	175.8	170.6	165.9	162.8	159.4	211.3	204.8	198.0	190.5	185.8
NH_3	0	2.18	5.41	7.61	10.34	0	4.42	8.51	13.86	16.82
V	176.4	174.2	174.2	174.1	174.6	211.9	211.5	210.8	211.0	210.5

	Sodium resin. Equiv. wt. 217.4.					Potassium resin. Equiv. wt. 230.8.				
M	0	0.90	1.82	3.11	3.94	0	0.90	1.83	3.12	3.96
W	192.2	187.9	186.2	184.0	181.5	164.5	162.1	159.0	154.6	153.1
H_2O	192.2	185.1	180.8	174.8	170.0	164.5	159.9	154.5	147.4	143.9
NH_3	0	2.79	5.40	9.22	11.53	0	2.19	4.53	7.16	9.17
V	192.7	192.4	194.4	197.7	198.5	165.0	165.7	165.9	165.3	166.6

Silver resin. Equiv. wt. 307.2.

M	0	0.47	1.38	2.75	3.57
W	165.5	183.1	185.6	176.5	175.5
H_2O	165.5	148.7	148.9	137.2	133.4
NH_3	0	34.43	36.71	39.31	42.08
V	166.0	233.0	238.7	233.3	236.3

TABLE 2.

12% Cross-linked resin.

	Ammonium resin. Equiv. wt. 213.5.					Silver resin. Equiv. wt. 310.3.				
M	0	0.73	1.67	2.50	3.27	0	0.46	1.45	2.67	3.60
W	121.4	120.6	118.3	118.6	118.5	113.6	127.7	127.2	125.5	125.6
H_2O	121.4	118.8	114.1	112.8	110.4	113.6	93.7	92.0	88.4	87.1
NH_3	0	1.84	4.20	5.76	8.12	0	34.01	35.19	37.05	38.45
V	121.8	123.6	124.7	128.6	130.5	114.0	142.7	142.7	141.8	142.4

Fig. 1 shows the number of grams of ammonia absorbed by 1 equivalent of resin, plotted against the equilibrium concentration of ammonia in the outer solution. The most striking feature is the very direct demonstration by these measurements of the
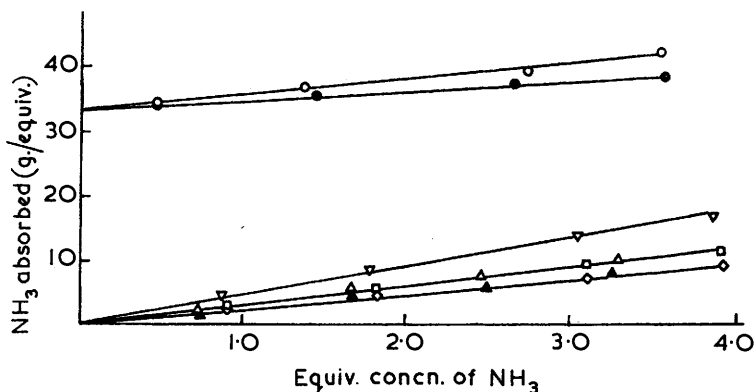

FIG. 1. 8% Cross-linked resins: O, silver; ▽, lithium; □, sodium; △, ammonium; ◊, potassium. 12% Cross-linked resins: ●, silver; ▲, ammonium.

formation of a diamminesilver ion, $Ag(NH_3)_2{}^+$, which is very stable in the resin, as it is in an ordinary aqueous solution. The plot of ammonia absorbed is linear for both 8% and 12% cross-linked resin, and the lines both extrapolate to a limiting value of 33.5 g. of ammonia absorbed per equivalent. The small discrepancy between this and the theoretical value, 34.0, for the diammine draws attention to a possible source of error in all these measurements, namely, the possibility of exchange between the cation of the resin and

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ammonium ion from the solution. The concentration of the latter, as calculated from the known basic dissociation constant of ammonia, never reached 0·01N, even in the most concentrated ammonia solutions used, and it is thought that cation exchange could not have caused significant errors in the results for the alkali-metal resins where the ammonia absorption differs little from that of the ammonium resin itself. Nevertheless, in the silver resin experiments the silver ion could be qualitatively detected in the outer solution, although quantitative estimations failed to give consistent results, and cation exchange probably accounts, therefore, for the slightly low result.

Table 3 contains some results for the 8% cross-linked silver resin at low ammonia concentrations. For these measurements a complete swelling analysis was unnecessary, since the earlier results had shown that swelling alone would not produce significant changes in the composition of the outer solution. Various weights of air-dried silver resin were therefore brought to equilibrium with 100 ml. (200 ml. for the most dilute point) of dilute ammonia solution, and the uptake of ammonia was calculated from the original and the final concentration of the solution.

TABLE 3.

8% Cross-linked silver resin.

[NH$_3$]	0·0292	0·0237	0·0138	0·0115
G. absorbed	32·52	32·45	31·98	30·96
NH$_3$/Ag, moles	2·00	1·99	1·95	1·91

The first row of figures gives the equilibrium concentration of the ammonia solution in moles per kg. of solution, and the second the number of grams of ammonia absorbed by one equivalent of the resin. It might appear from these figures that the silver diammine complex is appreciably dissociated at these low ammonia concentrations; however, exchange with the ammonium ion is much more important in these than in the earlier experiments because greater volumes of solutions were used, and the ammonia is relatively more highly dissociated at these dilutions. A correction for exchange was calculated as follows. The selectivity coefficient, $[\overline{Ag(NH_3)_2}^+][NH_4^+]/[\overline{NH_4}^+][Ag(NH_3)_2^+]$, is 3·0, according to a preliminary determination of our own (barred symbols refer to the resin phase). Let n be the milliequivalents of silver resin originally taken, and x be the milliequivalents exchanged for ammonium ion. $[\overline{Ag(NH_3)_2}^+]/[\overline{NH_4}^+]$ is therefore $(n - x)/x$, and $[Ag(NH_3)_2^+]$ is x/v, where v is the volume in ml. of equilibrium solution. The concentration of ammonium ion in the solution can be calculated from the concentration of the ammonia (with allowance for ammine formation) and the known dissociation constant, and the selectivity coefficient equation can thus be solved for x. The true number of moles of ammonia bound by an equivalent of silver is now given by (mequiv. absorbed − x)/$(n - x)$, and values obtained in this way are given in the third row of Table 3.

In an ordinary aqueous solution, the known stability constants [2] indicate that at the two lower ammonia concentrations more than 1% of a diamminesilver complex will be dissociated to the monoammine. We think that the remaining discrepancy between this and our figures may be no greater than the experimental error.

The stability of the amminesilver resin was demonstrated in another way. A 0·008N-ammonia solution was allowed to pass at a rate of 40 drops a minute through an 8-cm. column containing 5 g. of the air-dried, 8% cross-linked, silver resin. Ammonia could not be detected by Nessler's solution in the first 1·5 l. of effluent. At this stage, when the column was 83% exhausted, ammonia appeared in the effluent at a concentration of approximately 3×10^{-4}M; but this premature break-through was undoubtedly due to channelling, as could clearly be seen from the darker colour of the resin.

For the ammonium, sodium, and potassium forms of the resin, straight lines are obtained when the concentration of ammonia in the outer solution is plotted against the concentration of ammonia in the liquid taken up by the resin. The results can therefore be described by distribution coefficients, where $p = [\overline{NH_3}]/[NH_3]$ is 1·08 for the ammonium

resin, and 0·87 and 0·94, respectively, for the potassium and the sodium form. The results provide no evidence for the weak ammine complexes that have been suggested in the past for the sodium and potassium ions.[2]

For the lithium resin the ammonia absorption is markedly higher, and J. Bjerrum has reported a monoammine (as well as higher complexes) with a stability constant $K = 0.5$. If this value could be applied to the interior of the swollen resin, calculation shows that for the four concentrations given in Table 1 the number of grams of ammonia that would be bound in this way by the lithium ion would be 6·52, 9·31, 11·32, and 12·06. The first two figures are greater than the total absorbed ammonia; so, if the lithium resin forms a complex at all, it is certainly far less stable than would correspond to Bjerrum's value for aqueous solution.

Since the other cationic forms show little preferential absorption either of water or of ammonia, it would not be expected that the presence of ammonia would have a marked effect on the swelling pressure, or on the volume of the swollen resin. This is not directly borne out by the figures in Table 1, for it will be seen that, apart from the initial increase due to ammine formation in the case of the silver resin, there is a regular decrease in the values of W, as the ammonia concentration in the solution is increased, amounting to about 5% over the concentration range studied. However, the densities[3] of aqueous ammonia at 25° can be represented, up to 16% ammonia, by the straight line: $1/d = 1.003 + 0.0043P$, where P is the weight % of ammonia. This leads to a constant partial molar volume of 24·36 ml. for ammonia in aqueous solution. It may be doubted if this value is strictly applicable to the liquid in the swollen resin, owing to changes in the water structure, but it will be approximately correct. The values of V in Tables 1 and 2 represent the total volume of the swelling liquid in the resin, on the assumption that water and ammonia occupy, respectively, 18·05 and 24·36 ml. per mole, respectively. Apart from an unexplained tendency to rise in two cases, the values, including those for silver where ammine formation occurs, are satisfactorily constant.

Bivalent Cations.—The copper(II) resin forms a very stable tetrammine, as is shown by the results in Table 4. The points fall on a good straight line when the amount of

TABLE 4.

8% Cross-linked resin.

M	0	0·571	1·442	2·722	3·559
W	194·5	142·0	140·5	139·7	138·6
H_2O	194·5	106·4	102·1	97·6	93·7
NH_3	0	35·62	38·39	42·11	44·90
V	195·0	157·7	157·4	158·3	158·3

ammonia absorbed is plotted against the equilibrium concentration of ammonia, and the extrapolated value for $M = 0$ is 34·0 g. The slope of the line is steeper than those shown in Fig. 1, however. If the ammonia absorbed in excess of 34·0 is regarded as forming part of the swelling solvent, the distribution coefficients of ammonia between the cuprammine resin and water are: 1·55, 1·68, 1·66, and 1·72, respectively, for the four concentrations shown in the Table. The values are much higher than the distribution coefficients of the univalent cation resins, and tend to rise with increasing concentration. They are consistent, therefore, with Bjerrum's finding[2] that copper has a feeble tendency to form a higher ammine.

The amminenickel complexes are less stable than those of copper, and it was thought of interest to study both dilute ammonia solutions and a resin of high cross-linking. The results are in Table 5.

The ammonia absorbed by the 8% resin is plotted in curve 1 of Fig. 2, and it is evident that ammine formation is not complete at the concentrations studied. Curve 2 shows the

[2] " Stability Constants," Bjerrum, Schwarzenbach, and Sillén, Part II, p. 49 (*Chem. Soc. Special Publ.* No. 12, 1958).
[3] *Internat. Crit. Tables,* Vol. III, p. 59.

results in the 20% cross-linked resin, where the ammonia absorption is markedly less. Curve 3 gives the water absorption for the 20% resin, and it will be seen that for this resin, with its more limited swelling power, it is only below 0·6N-ammonia that the absorption of water exceeds that of ammonia, the total swelling being again approximately constant.

J. Bjerrum[2] has given the successive stability constants, K_1 to K_6, for nickel ammine

TABLE 5.

8% Cross-linked nickel resin.   Equiv. wt. 239·2.

M	0	0·0218	0·0503	0·148	0·516	1·356	2·625	3·466
W	180·6				133·5	133·7	133·7	132·6
H₂O	180·6				93·1	88·1	83·4	80·1
NH₃	0	21·33	27·14	34·16	40·42	45·64	50·28	52·53
V	181·1				151·3	153·7	155·7	155·6

20% Cross-linked nickel resin.   Equiv. wt. 247·0.

M	0	0·0241	0·0561	0·155	0·341	0·513	1·396	2·660	3·488
W	88·8					76·8	75·8	74·4	73·9
H₂O	88·8					40·3	34·6	29·7	26·1
NH₃	0	18·32	24·01	29·69	34·43	36·51	41·22	44·72	47·76
V	89·1					92·7	93·8	93·9	94·6

formation at 30°. His results are not strictly comparable with ours, partly because of the temperature difference, and partly because of differences in ionic strength. Bjerrum quotes constants in 2N-ammonium nitrate and also values extrapolated to zero ionic
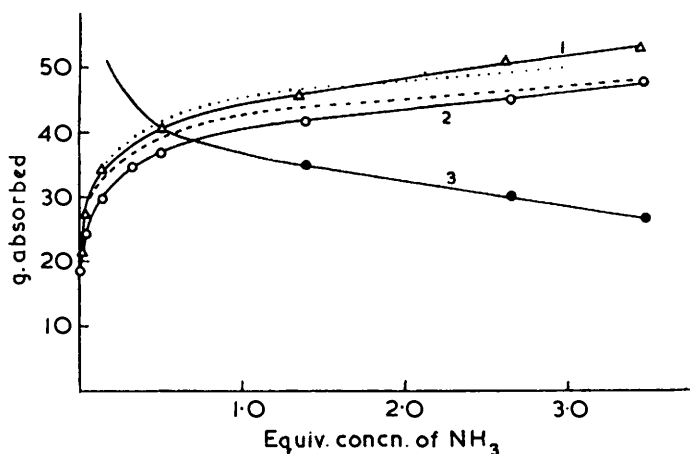

FIG. 2.   (1), Absorption of ammonia by 8% cross-linked nickel resin; (2), (3), absorption of ammonia and water, respectively, by 12% cross-linked nickel resin.   For explanation of broken and dotted curves see the text.

strength, where log K for each step is approximately 0·12 smaller than the corresponding value at $I = 2$.   Our results, if the resin interior is regarded as a 2 : 1-valent electrolyte dissolved in the swelling liquid, refer to an ionic strength $I = \sim 10$.   Nevertheless, the results for the 8% resin are in quite close agreement with Bjerrum's results for aqueous solutions.   The dotted curve of Fig. 2 was constructed from the latter; each of Bjerrum's constants gives an equation, *e.g.*, $[\text{Ni,NH}_3{}^{2+}]/[\text{Ni}^{2+}] = 468[\text{NH}_3]$, and from these, taken together, the ratio of bound ammonia to nickel was calculated for given concentrations of ammonia.   The curve for the resin includes, not only bound ammonia, but also the free ammonia present in the swelling liquid.   An approximate correction for this can be made if a distribution coefficient, $[\overline{\text{NH}_3}]/[\text{NH}_3]$, of unity is assumed.   A correction on this basis leads to the broken curve of Fig. 2.   The resin results now lie consistently below the curve

for aqueous solutions, and the small remaining discrepancy may be due partly to the difference in ionic strengths but probably mainly to the osmotic effect (see below).

Curve 2 for the 20% cross-linked resin lies well below the results for the 8% resin. In this case, therefore, the restrictive effect of the resin framework on the chemical reaction is unmistakable, and it is of interest to test the hypothesis that the shift in the ammine formation equilibria is wholly due to this. For this purpose the liquid in the interior of the resin with its associated ionised groups is regarded as constituting an ordinary aqueous solution, and it is then reasonable to assume that the normal stability constants for ammine formation will hold good, and that the various activity ratios, $\{Ni(NH_3)_n{}^{2+}\}/\{Ni(NH_3)_{n-1}{}^{2+}\}$, may be replaced by concentration ratios. We may therefore take any ordinate in Fig. 2, representing some definite stage in the ammination of the nickel ion, and compare the corresponding concentration of ammonia for an aqueous solution, as given by the calculated Bjerrum curve, with the concentration of ammonia in the solution in equilibrium with the 20% cross-linked resin. For instance, when 40 g. of ammonia are absorbed per equivalent, the concentration in the outer solution is 1.07M, according to Fig. 2, whilst the concentration of the inner solution, on our hypothesis, is 0.39M.

This comparison is inaccurate, however, partly because the Bjerrum curve refers to concentrations in moles per l., whereas the resin results are in moles per kg. of solution, and partly because the experimental values for the ammonia absorbed by the resin have not yet been corrected for the free ammonia in the swelling liquid. The concentration of this is given by the Bjerrum curve, and the amount associated with the known water uptake can thus be calculated; in this, and in the conversion into molarities, the known density data were used. The results of these calculations for the four concentrations of Table 5 for which complete data were obtained are given in the first three rows of Table 6,

TABLE 6.

[NH$_3$]	0·510	1·378	2·602	3·392
G. absorbed (corr.)	36·36	40·93	44·19	46·40
$\overline{[NH_3]}$	0·211	0·447	0·912	1·549
π (atm.)	890	1130	1050	790

which show the molarity of the outer solution, the bound ammonia in grams per equivalent of resin, and the molarity of the inner solution. Ammonia in water is not subject to large salt effects,[4] and if the whole difference between the values in the first and the third row of the Table is attributed to the restrictive influence of the resin framework, the values can be inserted in the equation for the swelling equilibrium:

$$\log (a_{NH_3}/\overline{a_{NH_3}}) = \log ([NH_3]/[\overline{NH_3}]) = \pi v/2.303RT,$$

where $\overline{a_{NH_3}}$, a_{NH_3} are the activities of ammonia in the inner and the outer solution, respectively, π is the restoring force exerted by the swollen resin framework, v is the partial molar volume of ammonia in aqueous solution, and R is in c.c.-atm. Table 6 gives the values of π obtained in this way; they are probably constant within the errors of experiment and calculation. The values are close to those found by Glueckauf [5] for a 25% cross-linked resin swollen in water, and support the view that the partial suppression of ammine formation in a cation-exchange resin is mainly due to the osmotic term in the equilibrium equation. The same treatment can, of course, be applied, with less accuracy, to the results for the 8% cross-linked resin, and leads, as would be expected, to lower π values which are again of the order predicted by Glueckauf's measurements.

[4] Matthews and Davies, *J.*, 1933 1435.
[5] Glueckauf, *Proc. Roy. Soc.*, 1952, *A*, **214**, 207.