337. *The Activity of Ammonia in Ammonium Chloride Solutions.*

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THE effect of added salts upon the behaviour of a non-electrolyte in solution can be studied by vapour-pressure measurements, if the non-electrolyte is sufficiently volatile, or by solubility measurements if its solubility is conveniently small. Both methods are of limited application, and suffer from the disadvantage that the concentration of the non-electrolyte must be fairly high, from practical considerations, in the first method, and is fixed by its solubility in the second. We have used distribution measurements to study the effect of ammonium chloride on the activity of ammonia in aqueous solution, and by varying the concentration of ammonia over a wide range it has been possible to study the effect of the salt on the base in infinitely dilute aqueous solution as well as at finite concentrations. The results show that the more common methods of studying such systems, owing to the limitations already mentioned, lead to a picture which is incomplete and may sometimes be misleading.

EXPERIMENTAL.

The experimental procedure was designed to prevent any contamination of the solutions by atmospheric impurities. The water used throughout was of conductivity less than 0·5 gemmho, and the air stream needed for manipulating the solutions was purified by passage through two towers containing pumice stone moistened respectively with fresh caustic soda and Nessler's solution, and through a spray trap consisting of glass wool followed by a filter-paper diaphragm. The distribution bulbs were of the Brown and Bury type (J., **1923**, **123**, **2430**), but the sample of the upper layer was withdrawn through a separate outlet tube that passed through the rubber bung closing the neck of the bulb. The distribution bulbs were supported in a thermostat adjusted to 25° ± 0·02°.

The chloroform consisted of B.P. samples that had been shaken with 0·01*N*-sodium hydroxide, washed with conductivity water, separated, and fractionally distilled in a current of pure air. It was collected and stored in a yellow bottle fitted with syphon and guard tubes, and was periodically tested for acidity. The stock solution of ammonia was prepared by distilling A.R. solution (*d* 0·88) to which a little baryta solution had been added, and was collected in a waxed bottle containing conductivity water.

For each experiment, the bulb was washed out with conductivity water and pure air, and suitable amounts of chloroform, ammonia, and water syphoned in under pressure of pure air. The bulb was left in the thermostat for several hours with frequent vigorous shakings, and was then left undisturbed for 18 hours, after which separation into two clear layers was always complete. It is essential that samples of the two layers should be taken without withdrawing the bulb from the thermostat, and this was done by forcing them through the appropriate syphon tubes into weighed flasks containing indicator, the first few c.c. being always rejected. After the solution had been weighed, a slight excess of standard acid was weighed in, and the solution back-titrated with dilute alkali. Further samples were treated in the same way after the distribution bulb had remained for several hours longer in the thermostat.

Four standard solutions were used in the work, approx. 0·7*N*-sulphuric acid and 0·02*N*-sodium hydroxide for analysing the aqueous layer, and 0·03*N*-acid and 0·002*N*-alkali for the chloroform layer. These were prepared as nearly as possible carbon dioxide-free, and the alkaline solutions were stored in wax vessels. The four were frequently intercompared, and as ultimate standard sodium carbonate was used, prepared in the usual way from A.R. sodium hydrogen carbonate. All titrations were by weight. Moore and Winmill (J., **1912**, **101**, **1635**) encountered difficulties in using methyl-red as indicator owing to its solubility in chloroform. We avoided this by using bromocresol-purple in all distribution measurements (and acid–alkali intercomparisons); this indicator is not extracted by the solvent and is sufficiently sensitive for use with very dilute alkali.

In the experiments with ammonium chloride, salt of A.R. quality was used, and the same precautions as before were taken against ingress of carbon dioxide in the making up and handling of solutions.

DISCUSSION OF RESULTS.

The distribution of ammonia between chloroform and water is shown in Table I. Col. 1 gives the molality (g.-mol./1000 g. of solvent) of ammonia in the aqueous layer and col. 2 that in the chloroform layer; col. 3 shows the ratio of the two. These results require correction for the dissociation of the ammonia in the aqueous layer, and col. 4 shows the degree of dissociation, calculated from Goldschmidt's conductivities (*Z. anorg. Chem.*, 1901, **28**, 97) by the formula $\alpha = \Lambda\eta/\Lambda_x$, where η is the relative viscosity of the solution, and Λ_x is the sum of the mobilities of the ammonium and the hydroxyl ion at the ionic concentration considered, as given by Onsager's equation. The partition coefficient of the undissociated ammonia is shown in col. 5. Each of the values given is the result of at least two determinations; the average deviation between duplicate determinations was 0·14%. When the partition coefficient is plotted against the concentration in the chloroform layer, a smooth curve is obtained which becomes approximately linear in the most dilute solutions, and is fitted by the equation $P = 35{\cdot}637 - 36{\cdot}5M'$, where M' is the molality in the chloroform solution. The deviations of the three most dilute solutions from the requirements of this equation are $-$ 0·003, $\pm$ 0·000, and $+$ 0·004, so the value 35·637 can be accepted as the hypothetical distribution coefficient of undissociated ammonia at infinite dilution. The result agrees satisfactorily with earlier determinations. Most of these are expressed in terms of concentrations in g.-mols. per litre, and on this basis our result becomes $P_0 = 23{\cdot}94$. Previous values (corrected where necessary for the ionisation of the ammonia) are: 24·0 (Moore and Winmill, *loc. cit.*); 24·0 (Dietrich, *J. Physical Chem.*, 1929, **33**, 95); 23·85 (Occleshaw, J., 1931, 1436).

TABLE I.

M.	M'.	M/M'.	α.	P.	$f^w_{NH_3}$.	$f^c_{NH_3}$, exptl.	$f^c_{NH_3}$, calc.
0·12890	0·003587	35·934	0·01186	35·509	1·0059	1·0022	1·0018
0·49757	0·01408	35·333	0·005936	35·123	1·0225	1·0077	1·0072
0·77957	0·02229	34·981	0·00470	34·819	1·0351	1·0113	1·0113
0·95192	0·02735	34·802	0·00418	34·655	1·0427	1·0141	1·0140
1·0264	0·02957	34·707	0·00399	34·567	1·0459	1·0146	1·0150
1·2129	0·03513	34·523	0·00363	34·399	1·0540	1·0172	1·0179
2·2678	0·06762	33·538	0·00235	33·460	(1·1020)	—	1·0345
3·0349	0·09233	32·868	0·00191	32·806	(1·1375)	—	1·0471

The partial vapour pressure of ammonia in dilute aqueous solution at 25° has been measured by de Wijs (*Rec. trav. chim.*, 1925, **44**, 655), and is given, up to $C = 1{\cdot}60$, by the equation: p (mm.) $= 12{\cdot}9C(1 + 0{\cdot}046C)$, where C is the concentration in g.-mols. per litre. From this the activity in aqueous solution has been calculated; on the assumption that it is proportional to the partial pressure and equal to unity at infinite dilution, then $f^w_{NH_3}$, the activity coefficient of ammonia in aqueous solution, is given by $1 + 0{\cdot}046C$. In terms of molalities, using the density data given in Int. Crit. Tables, **3**, 59, this becomes $f^w_{NH_3} = 1 + 0{\cdot}045M$, and the activity coefficients (up to $C = 1{\cdot}6$) obtained from this are shown in col. 6 of Table I. The activity coefficients of ammonia in moist chloroform are now calculated on the assumption that the activity ratio is constant; this leads to the relation $f^c_{NH_3} = f^w_{NH_3}.P/P_0$, where P_0 is the partition coefficient at zero concentration. The values found are given in col. 7. The variations in these values (extending to 0·035 molal) are proportional to the molality, and it seems plausible to suppose that the proportionality will extend to the highest molality studied (0·092). On this basis, $f^w_{NH_3}$ can be calculated for concentrations above those for which vapour-pressure measurements are available, and the values so obtained are included in parentheses in Table I. Col. 8 of the table shows the values of $f^c_{NH_3}$ calculated from the equation $f^c_{NH_3} = 1 + 0{\cdot}510M'$. The close approximation to a linear relationship of the activity coefficients in chloroform as well as in water is rather striking in view of the marked curvature of the P–M' graph from which they were derived. Another point of interest lies in the much more rapid rise of activity coefficient in chloroform than in water. In considering this it must be remembered that the mutual solubility of the two solvents may be affected by the addition of ammonia. The effect is mainly due, however, to the much greater molecular weight of chloroform; if solutions containing equal molar fractions of ammonia are compared, the deviation of the activity coefficient from unity in chloroform is only 1·7 times, instead of being more than 10 times, that in water.

Results in Ammonium Chloride Solutions.—These are in Table II. Cols. 1 and 2 show the molalities in the aqueous and the chloroform layer, respectively. Col. 3 shows the approximate degree of dissociation in the ammonium chloride solution, calculated from the dissociation constant $K = 1{\cdot}80 \times 10^{-5}$, and col. 4 gives the corrected partition coefficient. Col. 5 gives the activity coefficient in the aqueous layer, calculated on the same basis as before, with the assumption that the chloroform layer is unaffected by the ammonium chloride, *i.e.*, from the equation $f^w_{NH_3} = (1 + 0{\cdot}510M')P_0/P$. Col. 6 gives the value of $f^w_{NH_3}$ calculated from the equation shown at the head of the section, M here referring to the molality of ammonia in the aqueous layer.

TABLE II.

M.	M'.	a.	P.	$f^w_{NH_3}$.	$f^w_{NH_3}$, calc.
Solvent : $0{\cdot}02N$-NH_4Cl. $f^w_{NH_3} = 0{\cdot}9976 + 0{\cdot}0435M$.					
0·47363	0·01343	0·00088	35·235	1·0182	1·0182
0·52575	0·01493	0·00088	35·182	1·0205	1·0205
1·2506	0·03620	0·00085	34·516	1·0514	1·0520
2·6100	0·07820	0·00081	33·349	1·1113	1·1112
Solvent : $0{\cdot}05N$-NH_4Cl.					
2·4921	0·07419	0·00034	33·580	1·1015	—
Solvent : $0{\cdot}2N$-NH_4Cl. ${}^w_{NH_3} = 1{\cdot}0063 + 0{\cdot}0398M$.					
0·58555	0·01678	0·00009	34·901	1·0296	1·0296
1·2537	0·03641	0·00009	34·428	1·0543	1·0562
2·4973	0·07463	0·00009	33·462	1·1057	1·1057
Solvent : $1{\cdot}0N$-NH_4Cl.					
2·6810	0·07633	0·00002	35·124	1·0545	—

For two series the results can be extrapolated to infinite dilution of ammonia. A comparison may also be made at a constant concentration of ammonia of $2{\cdot}681M$; for this purpose the results for $0{\cdot}02N$- and $0{\cdot}2N$-ammonium chloride were extrapolated according to the equations given, and, by analogy with these, the short extrapolation for the measurement in $0{\cdot}05N$-salt was made according to the equation $f = f_0 + 0{\cdot}042M$. The results are shown in Table III, in which the last figure given has been calculated from some distribution measurements of Bell and Field (*J. Amer. Chem. Soc.*, 1911, **33**, 940), using $3N$-ammonium chloride.

TABLE III.

Activity coefficients of ammonia in ammonium chloride solution.

Zero concentration of ammonia.

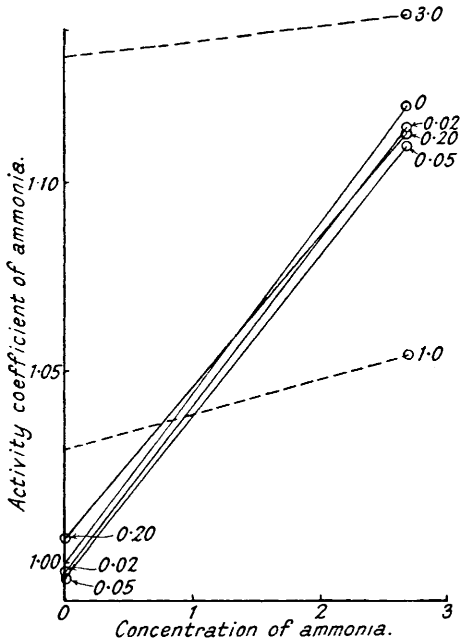
Concn. of NH_4Cl	0	0·02	0·2
f	1·0000	0·9976	1·0063

Concn. of ammonia : 2·681 g.-mol. per 1000 g. water.

Concn. of NH_4Cl	0	0·02	0·05	0·2	1·0	3
f	1·1204	1·1142	1·1095	1·1130	1·0545	1·144

In both series the activity coefficient goes through a marked minimum in the neighbourhood of $0{\cdot}1N$-ammonium chloride. The results at high concentrations of ammonia seem curious, since this minimum is followed by a maximum, after which the activity coefficient must fall rapidly; at some concentration above $1{\cdot}0N$ a second minimum occurs, and at still higher concentrations the ammonium chloride exerts a markedly positive salting-out effect. These results find their explanation in the figures given in Table II. The activity coefficient of ammonia in aqueous solution increases with its concentration, but does so the more slowly the more ammonium chloride is present. The effect is illustrated in the figure. The numbers by the curves refer to the concentration of ammonium chloride. The curves cross, and the result of this is to produce a second minimum which lies at a higher ammonia concentration the more ammonium chloride is present. The true slopes of the broken lines in the figure are quite unknown, and may be negative.

Our results therefore suggest the presence of at least three effects: (1) ammonium chloride tends to reduce the activity coefficient of ammonia in aqueous solution, and the fall in activity coefficient depends on some fractional power of the salt concentration. This effect governs the results at low salt concentrations. (2) At higher concentrations of ammonium chloride an effect in the opposite direction predominates, the increase in the activity coefficient of the ammonia being roughly proportional to the concentration of added salt. Measurements by Abegg and Riesenfeld (*Z. physikal. Chem.*, 1902, **40**, 84) and by de Wijs (*loc. cit.*) of the vapour pressure of ammonia over salt solutions show this effect, but do not extend over a wide enough concentration range to show our other two effects. (3) The increase in the activity coefficient of ammonia with increase in its concentration is the less the more ammonium chloride is present.



Of these, the second is the normal salting-out effect, which is common to all non-electrolyte–salt mixtures, and has had adequate attention. An effect similar to the first has been reported by Rørdam (" Studies on Activity," Copenhagen, 1925) for phenylthiourea in various salt solutions. He also finds the effect in solubility measurements with some weak acids, but here the evidence is more doubtful, since allowance was not made for the presence of the hydrogen sulphate ion and other possible products of interaction between the weak acid and the added salt. Rørdam attributes the effect to the electric moment of the non-electrolyte and proposes the use of the equation $\log f = -aC^{\frac{1}{2}} + bC$ for both ions and non-electrolytes, where *a*, for most of the latter, will have a value far smaller than the Debye–Hückel value for a univalent ion, but is zero only for non-polar molecules, while *b* includes the ordinary salting-out ratio. On the other hand, Butler and Thomson (*Proc. Roy. Soc.*, 1933, *A*, **141**, 86) have derived equations which show how the activity of either constituent of a binary mixture is lowered on the addition of a salt. When allowance is made in this derivation for the change in the activity coefficient of the salt with its concentration (Butler, privately communicated), the resulting expression predicts an effect similar to that which we have found, in that the activity coefficient of the non-electrolyte will be depressed by the salt to an extent which is relatively the greater the lower the concentration of the salt. The depressions we have observed seem many times too great to be wholly accounted for in this way, but it will be evident that much more work is needed at small salt concentrations before an interpretation of these low activity coefficients can safely be undertaken.

The third effect is probably a general one; it is shown in Shaw and Butler's measurements with lithium chloride in alcohol–water mixtures (*Proc. Roy. Soc.*, 1930, *A*, **129**, 519), but by workers in dilute aqueous solutions its existence and consequences have been generally overlooked. It suggests that in studies of this kind conditions should be chosen such that the concentration of the non-electrolyte as well as that of salt can be varied. The effect shows that the salting-out ratios ordinarily determined, and possibly the salting-out order of ions, are dependent on the concentration of non-electrolyte, and that comparisons are only valid where extrapolation to zero concentration of the non-electrolyte is possible. In recent studies on the activity of benzoic acid, Larsson (*Z. physikal. Chem.*, 1931, **153**, 466) has determined the salting-out ratio for sodium benzoate at 0° as well as at 18°. In view of our results it seems possible that a large part of the " temperature effect " recorded may be attributed to the change in concentration, since benzoic acid is almost twice as soluble at 18° as at the lower temperature.

SUMMARY.

Precise distribution measurements are used to study the effect of ammonium chloride on the activity of ammonia in aqueous solution. Three separate effects exerted by the salt on the non-electrolyte are distinguishable, and the possible bearing of this on other work is discussed.

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