LXVII.—*Note on Partially Miscible Aqueous Inorganic Solutions.*

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THE phenomena accompanying the partial miscibility of water with various organic liquids, and of organic liquids among themselves, have been studied by various observers and are quite familiar. With simple aqueous solutions of inorganic substances this is not the case, so that the following short note may be of interest.

When ordinary strong aqueous ammonia is shaken with a saturated solution of potassium carbonate and the mixture allowed to stand, two distinct liquids will be seen to separate out. Calling the two original liquids A and B, then one layer is a saturated solution of B in A while the other is a saturated solution of A in B. If A is the potassium carbonate solution, then at the ordinary temperature, after shaking together, solution A will have dissolved about 37 per cent. by volume of solution B, while solution B (the upper ammoniacal liquid) will contain about 6 per cent. of solution A.

The solubility of these two liquids in each other increases with rise of temperature, so that the composition of the two saturated layers or phases will gradually approximate until they are both identical, at which point the two liquids are miscible in all proportions.

Thus if we plot temperatures upon the vertical axis, and the percentage composition along the horizontal axis, the two curves representing the solubility of each liquid in the other will be seen to meet at a temperature of 43° , above which the two separate phases cease to exist and the liquids are miscible in all proportions.

For the experiments, the results of which are tabulated on these curves, A was a solution of potassium carbonate saturated (in contact with the solid) at the ordinary temperature. This solution was found to contain 57.2 grams of potassium carbonate in 100 c.c. Solution B was the so-called 0.880 ammonia. The sp. gr. of the sample actually used was 0.885 at 16° , corresponding to about 33 per cent. ammonia.

In order to determine the solubility of, say, solution B in A, a measured volume of the latter was first cooled to the required temperature. The potassium carbonate under these circumstances does not deposit crystals, but merely becomes supersaturated. Ammonia at the same temperature was added, and the mixture thoroughly shaken up in a tube closed by a cork; the ammonia being added until the mixture just began to show opalescence due to incipient separation of the two phases at the particular temperature.

At temperatures above 30° , the mixtures were confined in sealed tubes. The following figures were obtained:

Temp.	Solubility of A in B.		Solubility of B in A.	
	100 c.c. B dissolve A.	Mixture contains of solution A.	100 c.c. A dissolve B.	Mixture contains of solution A.
1°	2.0 c.c.	2 per cent.	37.5 c.c.	72.7 per cent.
6	3.0	3	47.5	67.6
11	5.0	4.7	52.5	65.0
16	6.5	6.1	60.0	63.1
21	8.5	8.0	77.5	56.3
26	10.5	9.5	105.0	49.0
31	12.5	11.1	152.5	39.0
38	20.0	16.6	195	33.0
39	21.0	17	220	31.0
42	25.0	20	250	28.5
43	35.0	26	285	26.0

Not only is the mutual solubility of these two liquids promoted by rise of temperature, but it is greatly influenced by the addition of small quantities of water. The second pair of curves shows the solubility of A in B when to B has been added 10 per cent. of its volume of water, and the solubility of B in A when to the latter 10 per cent. of its volume of water has been introduced. These two curves are seen to meet at a temperature of 25° . At this point, the mixture contains 6.9 per cent. of added water, which has had the effect of lowering the temperature above which complete miscibility takes place (that is, the critical temperature of solution) from 43° to 25° .

By the further addition of water, the point of intersection of the two solubility curves is still further lowered. Thus, when the added water amounts to 12.9 per cent. of the whole, the two phases cannot exist at temperatures above 10° ; whilst with 18.1 per cent. of added water the curves intersect at 0° , so that the liquids are now miscible in all proportions at all temperatures above the melting point of ice. These points are shown at C_1 , C_2 , and C_3 in the figure (p. 777).

It will be seen therefore that mixtures of solutions of potassium carbonate and ammonia can be produced which are critical for any desired temperature between certain pretty wide limits. Above the particular temperature, the solution remains clear; at the critical temperature, it becomes turbid owing to the separation of the mixture into the two phases.

In view of the considerable quantity of water originally present in the saturated potassium carbonate solution and in the ammonia, it seems suprising that the comparatively small addition of water should

When anhydrous potassium carbonate is added to strong ammonia, the solid first becomes pasty and gradually dissolves, forming a heavy liquid layer beneath the ammonia; at the same time, ammonia gas is disengaged. The carbonate appears to dissolve in the water at the expense, as it were, of some of the ammonia, for if the materials are confined in a sealed tube so that the ammonia cannot escape, very little

A number of experiments have been made in the hope of finding other aqueous inorganic solutions which exhibited a similar behaviour,

but so far without success. Saturated and supersaturated solutions have been used, and in many cases where they were completely miscible at the ordinary temperature the mixtures have been cooled to -60° , when in the majority of instances solidification set in.

When the obvious substitution of saturated sodium carbonate for the potassium salt is made, it is found that the addition of ammonia results in the precipitation of a crystalline salt, presumably one of the hydrated carbonates. It may be mentioned that strong aqueous solutions of trimethyl- and triethyl-amine behave with potassium carbonate precisely as ammonia does, and they also throw down the same precipitate from saturated sodium carbonate.

Addendum.—Since the above was communicated to the Society, it has been brought to my notice that the observation had previously been made by Mr. B. S. Proctor (*Chem. News*, 1864, 9, 25), that when strong aqueous ammonia is added to a strong solution of potassium carbonate, two liquid layers are obtained. The conditions determining the separation of these liquids, and their mutual solubility, were not ascertained, and, moreover, some of the observations recorded are not confirmed by my experiments. Thus Mr. Proctor found that the two liquids became miscible on standing 24 hours, and that a heavy, crystalline precipitate was deposited, which, he concluded, was potassium carbonate. I have kept the solutions in contact for *two years* without the slightest indication of mixing taking place, and under no conditions does any precipitation of solid occur. G. S. N.

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