alcohol as shown in Table I. This work checks closely with that of Timofeiew in so far as the data are comparable, whereas the results of Speyers differ considerably.

Summary

1. The composition of an alcoholated form of urea has been established and found to be $CO(NH_2)_2.CH_3OH$.
2. A study of its solubility together with that of non-solvated urea has been made.
3. The transition point of these two forms of urea was found to be $+19.25°$.

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IODINE AS AN EMULSIFYING AGENT

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To illustrate the Nernst distribution law some ether was shaken with water to which had been added iodine and potassium iodide.[1] An emulsion formed and slowly creamed. The cream, which was very viscous, lasted for several days. Since the cream rose it represented an emulsion of ether in water or, to be exact, of wet ether in ethereal water.

No emulsion could be prepared from ether and water alone so it was evident that the emulsifying agent was iodine, potassium iodide or potassium tri-iodide. We failed to secure an emulsion on shaking ether with a freshly prepared aqueous solution of potassium iodide, yet an old solution enabled us to make a very poor emulsion. Probably a very little iodine was released by the action of light or by the action of the carbon dioxide and oxygen of the air. This led us to try iodine alone as the emulsifying agent for the system ether-in-water. Good emulsions were obtained, improving as the concentration of iodine in the wet ether was increased up to 1%.

In attempting to prepare emulsions of 75% by volume, we found very little value in a 0.05% solution of iodine in wet ether. A very unstable 50% emulsion was, however, prepared with this concentration of iodine. At a 0.1% concentration of iodine a fair 75% emulsion was made while a 1.0% iodine solution showed the maximum emulsifying power in this system.

That potassium tri-iodide could not be held responsible for emulsification was shown by trying to emulsify ether in an aqueous solution of iodine and potassium iodide containing an excess of the iodide. This gave us a much poorer emulsion than a similar solution containing a good deal less

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[1] W. H. Chapin in this Laboratory.

potassium iodide: $KI + I_2 \rightleftarrows KI_3$. Increasing the amount of potassium iodide present drives the equilibrium to the right, making *more* tri-iodide and *less* free iodine. Consequently, iodine alone must be the emulsifying agent. To confirm this view we repeated the above experiment using an equivalent amount of potassium chloride instead of the potassium iodide. The emulsion was very nearly as good as one obtained in the absence of salts. Neither bromine nor chlorine showed any such emulsifying properties, nor did such salts as sodium iodide, calcium iodide sodium bromide, potassium chloride and sodium sulfate.

J. von Amann[2] observed that the red-brown solutions of iodine in carbon disulfide, carbon tetrachloride, chloroform and in petroleum showed practically no ultramicroscopic particles. He found some of these colloidal aggregates in amyl acetate solutions of iodine and many in an amyl alcohol solution. It is noteworthy that we failed to secure good emulsions of carbon disulfide, carbon tetrachloride and chloroform in water using iodine as the emulsifying agent, while good emulsions were made by dispersing amyl alcohol, amyl acetate, or ethyl acetate in water with the aid of iodine.

Evidently a film of colloidal aggregates of iodine[3] formed at the liquid-liquid interface. This must be an adsorption film rather than a mere precipitation film for we were able to saturate ether with water and water with ether and proceed to make good emulsions after iodine had been added to either or both of the solutions.

To prove that iodine did concentrate at the liquid-liquid interface we saturated 20 cc. of water with iodine and added, in small amounts, 10 cc. of ether, shaking the mixture vigorously after each addition. In this way a good emulsion was built up, creaming overnight. The water layer underneath no longer gave the starch test for free iodine. Obviously the iodine had all gone into the cream where we had the greatest area of interface. The Nernst distribution law held, as expected, when we cautiously poured a layer of 10 cc. of ether onto 20 cc. of water saturated with iodine (no shaking and no emulsifying) and allowed it to stand for several hours. Iodine was found distributed in both layers.

All the emulsions were of the oil-in-water type. When the dispersed liquid was the lighter the cream rose and when the dispersed liquid was the heavier the cream sank. Drop dilution tests confirmed this conclusion. It is difficult to account for this type of emulsion considering that the emulsifying agent, iodine, is more soluble in the dispersed phase than in the continuous phase. By the usual rule the opposite type, water-in-oil,

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[2] von Amann, *Kolloid Z.*, **6**, 235 (1910); **7**, 67 (1910).

[3] Hildebrand and Glascock [THIS JOURNAL, **31**, 26 (1909)] held that the brown color of certain iodine solutions is due to a combination of iodine with the solvent. In such an event the brown compound must concentrate in an interfacial film.

should be obtained. Nor can we readily suggest polarity of the emulsifying agent when this agent is an element.

It may be that the aggregates of iodine in the film receive some sort of wedge shape due to penetration of ether between aggregates on one side of the film and of water between aggregates on the other side.

That the drops were negatively charged was shown by the greatly superior precipitating power of positive polyvalent aluminum ion as compared with univalent positive ions or with any negative ion.

As might be expected, it is easier to make an emulsion (using iodine as the emulsifier) with a pair of liquids showing considerable but not complete miscibility than with two much less miscible liquids. This is merely another way of stating that the lower the interfacial tension between the two liquids, the more easily emulsification is secured. In the case of iodine this influence is modified by the von Amann phenomenon previously mentioned.

The use of iodine as agent enabled us to prepare 75 to 80% (by volume) emulsions of ether, ethyl acetate, amyl acetate, or amyl alcohol in water. These creamed to richer emulsions and broke after a few days. Hand shaking was used and, in fact, seemed preferable to other types of agitation.

As a good example of one of these emulsions we suggest the preparation of an ether-in-water emulsion. To 10 cc. of water (saturated with ether) add slowly 30 cc. of a 1% solution of iodine in ether (saturated with water) with intermittent shaking. When this is carefully prepared the emulsion is almost jelly-like.

Summary

1. Emulsions of ether, ethyl acetate, amyl acetate and of amyl alcohol in water were prepared using iodine as the emulsifying agent.

2. The existence of adsorption films of iodine at the liquid-liquid interface was demonstrated by analysis of the liquid below the cream. A marked change in concentration of iodine was observed.

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