

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF OREGON]

Acetamide as a Solvent

BY O. F. STAFFORD

Assuming a measure of validity for the doctrine that a substance dissolves other substances of its own kind, a most interesting case should be presented by acetamide as a solvent. This substance melts at about 80° to form a fairly mobile liquid. The fact that it contains a methyl group should give it solvent powers for hydrocarbons; its carbonyl group relates it to ketones, esters and acids; its tautomeric hydroxyl group gives it kinship to water and the alcohols; its amino group brings it into line with ammonia and its derivatives, while the ease with which it yields nitrile suggests a relationship to cyanogen compounds. In the field of inorganic chemistry the above considerations are supplemented by the fact that acetamide outranks all but a half dozen substances in the magnitude of its dielectric constant (59.2).

To test these assumptions the approximate solubilities of some 400 organic compounds and about half that number of inorganic compounds have been ascertained. The procedure, in general, was merely to add the substance to fused acetamide (at about 100°) and to note whether much or little would dissolve. Where in any instance the solubility thus appeared to be slight, the influence of higher temperatures was investigated. Sparingly soluble inorganic compounds were not only tested directly, but in most cases were precipitated by suitable double substitution reactions. It is interesting to note that these precipitation reactions occur with the same readiness as in water or ammonia as solvent.

The general results may be summarized by saying that of the 400 organic substances the only one showing no indications of solubility was cellulose. Asparagine, barbituric acid, oxamide and uric acid are sparingly soluble at low temperatures (*i. e.*, below 100°). It is significant that these same substances are but slightly soluble in water and are rated as insoluble in alcohol and ether. The solubilities of the inorganic compounds are strikingly analogous to those in water. Exceptions are presented by potassium perchlorate, the halides of mercury and lead, and the phosphate and oxide of mercury, all of which are more soluble in acetamide than in water.

More specifically, it was found that among organic compounds sixty-five ammonia-nitrogen derivatives (except uric acid), seventeen carbohydrates (excepting cellulose but including starch), sixty-eight dyestuffs, forty-four alcohols, eleven nitro and nitroso compounds and a number of miscellaneous nitrogen derivatives, all dissolve readily. Of the twenty hydrocarbons tested, anthracene, phenanthrene and triphenylmethane are quite soluble. The others are soluble at higher temperatures, but

separate out to form two-phase systems at lower temperatures (80 to 120°). Forty-five acids tested are all soluble, but those with very long hydrocarbon chains are less soluble than the others.

Some twenty oxygen compounds were tested, in this class the ethers appearing to be somewhat less soluble than the others.

Among inorganic compounds bismuth nitrate gives a white insoluble compound similar to that formed by hydrolysis or ammonolysis. Mercurous nitrate undergoes some transformation in contact with the solvent. A similar action appears to take place with mercurous halides. Chromates are slowly reduced in acetamide solutions, although even the solution of chromium trioxide (which in color exactly resembles solutions of chromates) is stable for quite a while. The brown silver carbonate precipitate is presumably in the form of silver oxide, as in the case of precipitation from water.

The close analogy between acetamide and water as solvent is proved not only by the close correspondence which is shown by solubilities of inorganic compounds in these two substances but also by the chemical behaviors of dissolved substances. Mention has already been made of the fact that double substitution reactions occur with the same readiness in acetamide solution as in water solution. In such cases the precipitates in acetamide are even similar in appearance to those formed in water, colored sulfides, for example, appearing precisely as when precipitated from water. A search of the literature reveals that conductivity curves for a considerable number of salts in acetamide solution have been determined and that these curves resemble those obtained in water solutions. Furthermore, it has been shown that electrodeposition occurs readily in acetamide solutions with metals not more active than zinc. Numerous instances are described in which acetamide seems to function analogously to water of crystallization.

It follows, therefore, that the expectations enumerated in the opening paragraph of this article are surprisingly substantiated by experiment. Seemingly acetamide has a wider range of solvent powers than any other substance which has been reported.

EUGENE, OREGON

RECEIVED MAY 29, 1933
PUBLISHED OCTOBER 6, 1933