

NON-AQUEOUS SOLVENTS AS MEDIA FOR
CHEMICAL REACTIONS

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Chemists have become so accustomed to the idea of water as the universal solvent that it may seem almost unbelievable that other media may be used effectively for carrying out chemical reactions. There is no question but that our slavish devotion to water as the medium for chemical reactions has obscured much important chemistry and has somewhat retarded the advance of our knowledge along certain lines. During the last few years such solvents as liquid ammonia, hydrogen fluoride, glacial acetic acid, the alcohols, and many others have been studied by numerous investigators. These researches have brought to light not only many new and interesting facts, but they have shown very definitely that in some instances it is of decided advantage to use solvents other than water.

The writers of this paper have been interested in the use of non-aqueous solvents in a variety of reactions. The experimental results summarized briefly in the following paragraphs give ample proof of the applicability of non-aqueous solvents to specific problems and for special reactions which could not have been carried out in water.

Electrodeposition of Arsenic, Antimony, and Bismuth from Solutions of their Salts in Glacial Acetic Acid.—The chlorides of these three fifth-group elements are characterized by their high solubility in anhydrous acetic acid, and by the fact that they undergo no solvolysis in this medium, because of the *acidic* nature of the solvent. In water, on the other hand, these chlorides undergo hydrolysis with the precipitation of basic compounds. Electrolysis of acetic acid solutions of these substances under varying conditions of concentration, temperature, and current density results in the cathodic deposition of these metals.

Preliminary results led to the hope that a method might be worked out for plating objects with antimony. Antimony is very resistant to corrosion by hydrochloric acid, and antimony plated apparatus would find wide application in industry. The metal is, however, characterized by its brittleness under ordinary conditions which means that it must

be deposited in a very finely crystalline form and must be prevented from changing to a more coarsely crystalline state.

The original deposits on copper and brass were smooth and adherent, but were found after a time to scale off and break when sample plates were subjected to stresses and strains. X-ray investigations of these deposits by Dr. C. W. Stillwell brought out the fact that an unstable, monotropic, amorphous form of the metal was deposited under ordinary conditions which tended to revert to the more stable crystalline form. Investigation of arsenic deposits showed that these, too, were plated out in the amorphous state, whereas bismuth was found to come out in the crystalline form. This problem is still under investigation.

Preparation of Rare Earth Metal Amalgams by Electrolysis of Solutions of the Halides in Absolute Ethanol.—Many attempts have been made to deposit the metals of the rare earth family from solutions of their salts in various non-aqueous solvents, but have not met with any success. The preparation of the rare earth metals presents a problem of extraordinary scientific interest, in view of the fact that only six of the sixteen elements of this group have ever been obtained in the free form (Yt, Ce, La, Nd, Sm, Eu) and only two in a high state of purity (Ce, La).

Amalgams of many active metals have been prepared by the electrolysis of concentrated aqueous salt solutions using a mercury cathode. In several instances it has been found that amalgams of higher concentration can be prepared very much more readily and with less attendant decomposition by the use of non-aqueous ionizing media. Thus, Hevesy¹ prepared a 30 per cent barium amalgam by the electrolysis of a concentrated solution of the iodide in pyridine using a mercury cathode. Laszynski² prepared concentrated amalgams of potassium and sodium by electrolysis of the corresponding thiocyanates in acetone under similar conditions. Kettenbeil³ also studied the preparation of amalgams of various elements, but was not able to prepare those "of the rare earth metals by electrolysis of their salt solutions at a mercury cathode." He reported negative results in his attempts to prepare amalgams of Ce, Yt, Di, Zr, and Th electrolytically using water, pyridine and alcohol as solvents.

However, amalgams of Yt, Ce, and La have been prepared by thermal methods and their properties studied. The decomposition of cerium amalgam has been suggested as a method for the purification of the metal.⁴ In view of these facts it was decided to study the elec-

¹ Z. Elektrochem., vol. 16, p. 672, 1910.

² Ibid., vol. 4, p. 292, 1897.

³ Z. anorg. Chem., vol. 38, p. 213, 1904.

⁴ Hirsch. Trans. Am. Electrochem. Soc., vol. 29, p. 57, 1911; Ind. Eng. Chem., vol. 3, p. 880, 1911.

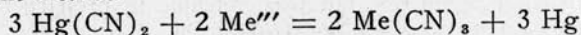
trolytic preparation of the amalgams of lanthanum and neodymium, a problem which was only recently brought to a successful conclusion⁵ at the Chemical Laboratory of the University of Illinois.

Electrolysis of anhydrous neodymium chloride and of the monohydrated bromide in absolute ethanol, using a 110 direct current and with a current density of 0.06 to 0.15 amperes per square centimeter at a mercury cathode, results in the formation of pasty amalgams containing from 2 to 3 per cent of the metal. Such amalgams are quite reactive towards air, water, and alcohol and are best preserved in a vacuum or under a saturated solution of the electrolyte. Lanthanum amalgams are obtainable in a similar manner. Much of the mercury in these amalgams may be removed by distillation in vacuo, but not completely even at the temperature at which pyrex begins to melt. The products so obtained are extremely pyrophoric, black powders which take fire in air. By heating to a still higher temperature in specially constructed furnaces the free metals can be obtained.

The electrolytic preparation of these rare earth metal amalgams from non-aqueous solutions thus offers a method for obtaining at least these two metals in a high state of purity.

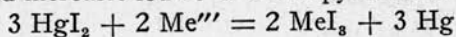
Metathetical Reactions in Non-Aqueous Solvents.—It is well-known that ordinary ionic reactions can be carried out in solvents other than water. These are particularly useful where hydrates are to be avoided, or where the preparation of compounds, not capable of existence in aqueous solutions, is involved. Several typical reactions are presented below.

Third-group cyanides and thiocyanates are immediately hydrolyzed by water, but are stable in liquid ammonia solution. If it is desired to prepare aluminum or rare earth metal cyanides, the interaction of the free metal with mercuric cyanide in liquid ammonia affords a very convenient method.



Thus, "misch-metal" displaces mercury from mercuric cyanide in liquid ammonia to give a mixture of the rare earth metal cyanides. This reaction is best carried out in a closed tube at room temperatures.

It is difficult to prepare anhydrous rare earth metal iodides, and here again use can be made of several non-aqueous solvents, acetone or pyridine, and a reaction similar to the one above. Thus, a mixture of rare earth metal iodides can be obtained by the interaction of misch-metal and mercuric iodide in either pyridine or acetone solution.



⁵ Audrieth, Jukkola, Meints, and Hopkins, *J. Am. Chem. Soc.*, vol. 53, 1931.

An interesting series of reactions has been carried out involving the direct interaction of halogens with misch-metal in various solvents. Free bromine and misch-metal shavings were allowed to react together in ether, in carbon tetrachloride, carbon disulfide and in ethyl bromide. Only in ether was an appreciable reaction noticeable, after shaking for 24 hours, with separation of copious quantities of a yellow solid. This product was found to be very soluble in acetone, in absolute alcohol, and in pyridine. As the misch-metal employed was composed largely of cerium, it was shown that the metal had been oxidized to the ceric state and that the yellow solid consisted mainly of ceric bromide.

Interesting directional experiments carried out recently indicate that mercury diethyl and misch-metal react, presumably with formation of the rare earth metal alkyls. Lead tetraethyl and anhydrous neodymium chloride also react in ether solution with formation of triethyl lead chloride and the mono-ethyl neodymium dichloride.

CONCLUSION

As has been shown briefly in this paper, non-aqueous solvents find application in a variety of metathetical and electrolytic reactions. It is suggested that many solvents are available for carrying out reactions similar to those described above, where the presence of water would be decidedly detrimental.