Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1938. Volume XIX, № 9

CHEMISTRY

NON-AQUEOUS SOLUTIONS

By V. A. PLOTNIKOV, Member of the Ukrainian Academy, Corresponding Member of the Academy of Sciences of the USSR

1. Introduction. During recent years a considerable animation in the field of non-aqueous solution investigations has become noticeable. What may be the explanation of the increasing interest in this but little studied section of physical chemistry? The Arrhenius' theory of electrolytic dissociation underlies the industrial electrochemistry, but, owing to the impetuous development of electrochemical industry and the actual wide use of electrochemical methods in diverse branches of industry, this old theory has become already insufficient, although the latest attempts to widen and change the ancient ideas of the electrolytic dissociation have not yet given any positive results. There are used in industry chiefly aqueous solutions, but the enormous, by its volume, material obtained in the field of aqueous solutions suffers of one-sidedness, therefore the necessity arose of studying different solvents in order to explain the nature of electrolytic dissociation.

Another reason of the animation in the domain of non-aqueous solutions consists in the revolution that occurred during the last years in our views on the nature of liquid state. Not very long ago there existed the assumption that the properties of the liquid were due to the action of the forces that displayed themselves at the interaction of gas molecules, and the crystallization was considered to be a phenomenon of a quite different character. At the present time, though, it can be taken for granted that liquids possess a crystalline-like structure; therefore numerous investigators have directed their attention to the elucidation of the nature of liquid state from a new point of view and the non-aqueous solutions proved in this case to be a particularly precious material.

2. Forecrystallization. Potassium bromide is insoluble in benzene. But should aluminium bromide be dissolved in benzene beforehand, potassium bromide would also dissolve in this solution. At the addition of potassium bromide the freezing temperature of the benzene solution does not fall but rises(1). Since there is no reason to expect the formation of solid solution, the rise of the crystallization temperature should be explained by the formation of associated molecules of the complex compound of aluminium bromide with potassium bromide and may be also with benzene. The molecules of the complex contain about four molecules $AlBr_3$. The composition of such complicate molecular aggregates is difficult to be expressed by Werner's co-ordination formulae. Supposing that the formation of

these complicate aggregates in the solution resembles crystallization, I have proposed to call this phenomenon «forecrystallization»(2). We have observed the formation of similar large molecular aggregates in many other cases(3). The structure of these «forecrystals» may be expressed by formulae similar to those expressing the structure of crystals according to roentgenograms, as, for instance, the structure of sodium chloride crystals may be expressed by the formula $NaCl_6$—$ClNa_6$. But, because of the small size of the «forecrystals», the formulae have an intermediary character between usual and roentgenographical formulae. At the present time the majority of investigators have come to the conclusion that the formation of such «forecrystals» takes really place in liquids. This phenomenon is also called «quasi-crystallization».

3. Dissociating Power of the Solvent. Nernst and Walden attribute a «dissociating power» or «ionizing tendency» to the solvents. The greater the dielectric constant of the solvent, the greater its dissociating power. Even nowadays in most of our manuals the parts dealing with non-aqueous solutions are exposed almost solely from the viewpoint of the dissociating power of the solvent. Electrochemical investigations of solutions in bromine and benzene display a considerable electroconductance, although these solvents are numbered among the «non-ionizing», because they possess a weak «dissociating power». For example, the 3% solution of pyridine in bromine (dielectric constant 3) had the same conductance as the aqueous solution of potassium chloride at the same percentage (dielectric constant of water 81). Besides there ought to be considered that the viscosity of bromine solutions is stronger than of aqueous solutions. Such cases have been stated in our investigations frequently enough.

According to Walden's opinion, the considerable conductance that we have found in solvents with a small dielectric constant does not depend upon a notable dissociation, but on a greater mobility of ions. Yet the viscosity of investigated solutions is very strong and cryoscopic measurements and observations of transference numbers indicate the formation of very large complex ions that cannot possess a great mobility in a strongly viscous medium. Hence, Walden's attempt ought to be acknowledged as unsuccessful and it would be high time to abandon the metaphysical ideas about «dissociating power» and «ionizing tendencies».

It is quite another matter with the two also out-of-date terms: «solvent» and «solute». Both components of a solution are equivalent. The properties of a solution are determined by its concentration and the interaction of both components. This statement becomes particularly obvious at the investigation of non-aqueous solutions, while in aqueous solutions water is always considered to be a solvent, even for a 90% sulphuric acid. The practical meaning of these terms is obvious and cannot be excluded from the spoken language, but from a theoretical standpoint the division on solvent and solute is groundless and can lead towards false conceptions as the «dissociating power» of the solvent.

4. Crystallization. Ethyl bromide does not conduct electricity; aluminium bromide, even fused, shows a poor conductance, but the solution of aluminium bromide in ethyl bromide conducts well. At the crystallization of this solution there precipitates pure aluminium bromide. The bromine solution of acetamide shows the same considerable electroconductance, as aqueous solutions of strong electrolytes do. Evidently, new compounds are formed in this solution, the more so as for some acid amides there have been isolated crystallic compounds with bromine. On the crystallization from the bromine solution, however, precipitates pure acetamine. Among our investigations of non-aqueous solutions may be cited numerous

cases proving that on crystallization other compounds are precipitated than these formed on dissolution. When forecrystallizing proceeds into a definite crystallization, new molecular aggregates are formed. At a final crystallization other complexes may be precipitated than those previously present in the solution and in some cases it may occur that one of the component is entirely displaced from the forecrystallic lattice.

5. New Concentration Galvanic Cells. Among the investigated solutions a particular interest present bromine and iodine solutions where one of the components is an element. In a saturated bromine solution of phosphorus pentabromide the galvanometer shows at the closing of the circuit a considerable deflection, but after some seconds it swiftly recedes to its zero position. The investigation proves that the cathode has been covered with a crystalline film of non-conducting phosphorus pentabromide. After a change of the current direction a new deflection of the galvanometer may be observed, the former cathode that has now become anode gets free from the film and the new cathode becomes covered with phosphorus pentabromide. It is evident that during the electrolysis PBr_5 is carried towards the cathode. This has been confirmed by measurements of the transference numbers. In accordance with these observations has been constructed the concentration cell in which two bromine solutions of different concentrations were divided by a cock with glass wool or asbestos; the electrodes were of platinum or platiniridium (while kept in this solution polished platinum electrode does not change in weight). Our cell differs from other concentration cells firstly because the electrodes do not take here any part in the electrochemical process; secondly, the current flows in the external circuit from a less concentrated solution towards a more concentrated one[4].

6. Electrochemical Resonance. Why occurs the dissociation into ions? This question arose from the beginning of the electrolytic dissociation theory. As the electrostatic theory of electrolytic dissociation progressed, this question lost its actual importance with regard to a series of electrolytes, yet for a whole range of electrolytes and perhaps for all of them at certain moments of their existence it has remained in force, though till now it has had no definite answer. Some authors, as for example Nernst in his «Theoretical Chemistry», Hazlehurst in a paper that has appeared some months ago, express the opinion that the kinetic energy of molecular components participates in the dissociation process[5, 6]. Yet numerous investigations of different non-aqueous solutions performed by us and other authors have shown that the same substance conducting in one solvent does not conduct in another. A considerable value of the dielectric constant does not necessarily involve a considerable conductance. Every solvent has its own group of electrolytes. Many other investigators of non-aqueous solutions have lately come to this conclusion that we had found long ago. Evidently, not every kind of oscillation contributes to the electrolytic dissociation; a definite correspondence between oscillations in molecules can only provoque the dissociation into ions. It is natural to call such electrochemical congruence electrochemical resonance. Wave mechanics and energetic intramolecular levels are to be the foundation of the mathematical theory of electrochemical resonance; further development of the hypothesis depends, therefore, first, upon the development of the wave mechanics that gives as yet an answer to only the simplest systems; secondly, upon an advantageous selection of satisfactory experimental material which in its present state has an one-sided character and as regards its volume is rather poor.

Institute of Chemistry.
Ukrainian Academy of Sciences.

Received
7. IV. 1938.

REFERENCES

[1] Плотников и Якубсон, ЖРФХО, LX, 1588 (1928). [2] Плотников, Тр. I Всесоюзн. конф. по неводным растворам, 29 (1935). [3] Плотников и Бармашенко, Зап. Ин-та химии АН УССР, 177 (1936); Плотников и Чалый, ibid., III, 167 (1936); Плотников и Якубсон, ibid., III, 139 (1936); Плотников и Шека, ЖОХ, III, 214 (1933); Плотников, Шека и Янкелевич, ibid., 481. [4] Плотников и Якубсон, Зап. Ин-та химии АН УССР, 112 (1936). [5] Theoret. Chemie, 438 (1926). [6] Hazlehurst, J. Chem. Educ., 316 (1937).