1940 ACTA PHYSICOCHIMICA U.R.S.S. VOL. XII. No. 2

Electrocapillary Curves in Liquid Ammonia. II[1].

Inorganic electrolytes

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Owing to the poor solubility of electrolytes in non-aqueous solvents, it is difficult to make electrocapillary measurements in such solutions. Consequently, the electrocapillary curves hitherto measured for non-aqueous solvents are confined mostly to those obtained by A. Frumkin[2] for a few solvents.

In this respect, however, liquid ammonia as a solvent is an exception, since many inorganic substances dissolve in it very well. Furthermore, in spite of the fact that its dielectric constant is one-fourth that of water, the electrical conductivity of solutions of salts in liquid ammonia in a number of cases attains even higher values than that of the same salts in aqueous solutions. This is explained by the greater mobility of the ions due to the very low viscosity of liquid ammonia. This circumstance also markedly distinguishes liquid ammonia from many other non-aqueous solvents, while, for an investigation of the electrocapillary curves in the presence of some organic substances, liquid ammonia even presents a certain advantage over water as a solvent. It is known that certain substances, *viz.*, hydrocarbons, dissolve very well in liquid ammonia and only slightly in water.

The first problem with which we were faced was the development of a satisfactory method for carrying out measurements in liquid ammonia. Owing to the fact that the solubility of many organic

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[1] A. Murtazayev and M. Abramov, J. Phys. Chem., 13, 350 (1939).

[2] A. Frumkin, "Electrocapillary Curves and Electrode Potentials", Odessa, 1919.

and inorganic substances in liquid ammonia markedly decreases with a decrease in temperature, we set ourselves the task of designing an apparatus in which measurements might be made at temperatures in the neighbourhood of room temperature.

For advice in designing and constructing the apparatus, we turned to the Laboratory of Liquefied Gases of the Karpov Institute of Physical Chemistry, which had had many years of experience in this field. We wish to express our deep gratitude to A. I. Schattenstein of this laboratory for suggesting the design of the apparatus and actively assisting us in its construction.

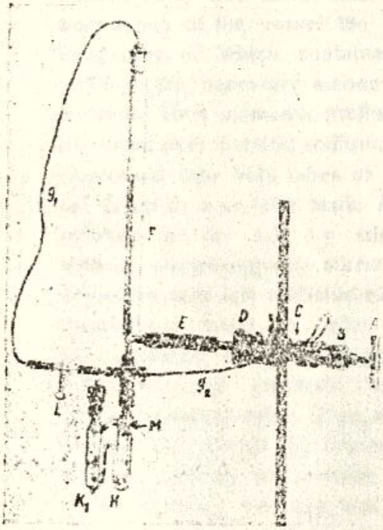

Fig. 1. *A* — piston-rod, *B* — stuffing box, *C* — cylinder filled with mercury, *D*—cap, *E*—vacuum tubing, *F*—glass tube, g_1 and g_2 — copper capillary tubes, *L* — trap, *H* — vessel with liquid ammonia, K_1—platinum contacts, *M*—capillary,

Owing to the fact that liquid ammonia has a high vapor pressure at room temperature (6 — 7 atm.), the apparatus in which the measurements are made must be absolutely hermetic. Furthermore, during an experiment, pressure changes and evaporation of ammonia in the vessel should not occur. Our apparatus shown in Fig. 1 meets all these requirements (modified Lippmann electrometer).

Vessel *H*, of Jena glass, is composed of two tubes each of which has a volume of 10—12 $cm.^3$. The tubes are connected with one another by means of a U-shaped tube with a fine glass filter in the center. Threaded joints of chrome-nickel rustless steel (all metallic parts of the apparatus were made of this steel) were fastened to both tubes of vessel *H* with the aid of Wood's alloy so that metal caps could be screwed on to both tubes. The right-hand tube served as a container for the solution under investigation, whilst the left-hand one contained a non-polarizable electrode. Mercury in a 1 *N* solution of NH_4NO_3 in liquid ammonia served as the non-polarizable electrode in all the experiments. The potential of such an electrode became sufficiently constant a few hours after condensation of ammonia into the vessel.

Both tubes of vessel *H* were filled with solution in the following manner. First a weighed amount of NH_4NO_3, which served as the basic electrolyte in all the experiments, was introduced into both tubes of the vessel the left-hand tube of which contained in addition the necessary amount of mercury. Then ammonia, preliminarily dried over metallic sodium, was condensed into both tubes of vessel *H* up to a definite mark. After solution of the salt by stirring with an electromagnetic stirrer, the apparatus was left undisturbed for twenty-four hours in order that the potential of the non-polarizable mercury electrode could attain a constant value. Then, while cooling the vessel by immersing it in a mixture of acetone and carbon dioxide, the cap was unscrewed from the right-hand tube and the upper part of the apparatus was screwed down. Finally, after testing for leakage the vessel *H* was immersed in ice and an experiment began (all measurements were carried out at 0° C).

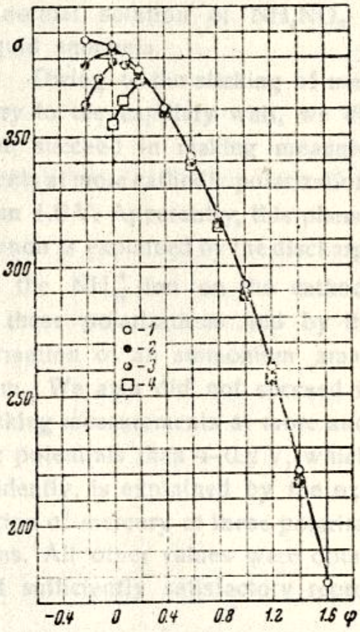

Fig. 2. Electrocapillary curves for mercury in liquid ammonia solutions: *1*—*1N* NH_4NO_3, *2* — *1N* NH_4NO_3 + 0.5 *N* NaCl, *3* — *1N* NH_4NO_3 + 0.5 *N* NaBr, 4 —1 *N* NH_4NO_3 + 1 *N* KJ.

The experiment was carried out as follows: The piston-rod *A* is connected with a piston which moves in the cylinder *C*. The latter, as well as the tube *F*, is filled with distilled mercury. Thus, by turning the rod *A* one could change the level of the mercury in the tube *F*. The copper capillary tubes g_1 and g_2 served to equalize the pressure throughout the system. The trap *L* was included in the system to condense any of the ammonia solution contaminated with copper from the upper part of the capillary g_1.

Electrocapillary curves were obtained for the following solutions: $1\,N$ NH_4NO_3; $1\,N$ $NH_4NO_3 + 0.5\,N$ $NaCl$; $1\,N$ $NH_4NO_3 + 0.5\,N \cdot NaBr$; and $1\,N$ $NH_4NO_3 + 1\,N$ KJ. The curves are shown in Fig. 2, where σ is the surface tension in dynes/cm. and φ is the cathodic polarization in volts against a mercury electrode in a normal solution of NH_4NO_3 in liquid ammonia.

Owing to the sticking of mercury to the capillary wall, we did not succeed in making measurements at more cathodic polarizations than 1.6 V. Apparently, this phenomenon is explained by the discharge of the NH_4^+-ion on the cathode at these polarizations and by the formation of an ammonium amalgam. We also did not succeed in making measurements at more anodic potentials than $+0.2$ V, which, evidently, is explained by the oxidation of mercury at these polarizations. All other values were obtained quite easily and gave results of sufficiently satisfactory reproducibility.

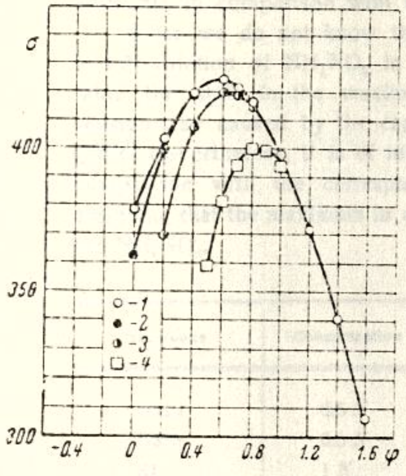

Fig. 3. Electrocapillary curves for mercury in aqueous solutions. 1 — 1 N NH_4NO_3, 2—1 N $NH_4NO_3 + 0.5\,N$ NaCl, 3—1 N $NH_4NO_3 + 0.5\,N$ NaBr, 4—1 N $NH_4NO_3 + 1\,N$ KJ.

For comparison, we also obtained the electrocapillary curves for aqueous solutions of the same substances at the same concentrations and temperature. The curves obtained are given in Fig. 3.

On the basis of the values of σ obtained for a $1\,N$ NH_4NO_3 solution, the capacity of the electric double layer in liquid ammonia was calculated by the method of least squares making use of the following equation:

$$\sigma = A + B\varphi - \frac{1}{2} C\varphi^2,$$

where C is the capacity of the electric double layer. In the calculation of C, the value of σ corresponding to the value $\varphi = -0.1$ V was taken as the beginning of the descending branch of the curve.

The capacity of the electric double layer on mercury in a 1 *N* NH_4NO_3 solution in liquid ammonia, calculated in such a manner, was found to be equal to 11 μF/cm.[2]. This value differs from the capacity of mercury in an aqueous solution (17—18 μF/cm.[2]) — a fact which is undoubtedly connected with the smaller dielectric constant of ammonia in comparison with that of water[3].

Since we do not know the exact position of the maximum in a 1 *N* solution of NH_4NO_3 in ammonia, we cannot accurately determine the shift in the maximum $\Delta\varphi$[4] and the decrease in surface tension $\Delta\sigma$[5] caused by the capillary-active anions which we investigated. Nevertheless, it is of interest to make at least an approximate comparison with the corresponding values for aqueous solutions, assuming that the maximum in an ammoniacal solution lies at $+0.2$ V for NH_4NO_3.

Substance	Concentration	$\Delta\varphi NH_3$	$\Delta\varphi H_2O$	$\Delta\sigma NH_3$	$\Delta\sigma H_2O$
NaCl	0.5 *N*	0.15	0.02	4.14	0.29
NaBr	0.5 *N*	0.20	0.11	8.38	4.56
KI	1 *N*	0.43	0.30	15.60	24.13

From an examination of the accompanying table it is evident that the shift in the maximum and the decrease in the surface tension for all the substances studied (with the exception of $\Delta\sigma$ for KJ) is considerably greater for an ammoniacal solution than it is for an aqueous solution. This is, apparently, explained by the fact that the anion is less highly solvated in ammonia than it is in water.

A similar effect of a larger shift in the maximum was found by Frumkin[6] for solutions in acetone and pyridine.

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[3] A. Frumkin, *l. c.*, p. 187.

[4] The difference between the positions of the maximum for a NH_4NO_3 solution and the given solution.

[5] The difference between the value of σ_{max} for a NH_4NO_3 solution and σ_{max} for the given solution.

[6] A. Frumkin, *l. c.*, p. 182.

Summary

1. A method for measuring electrocapillary curves in liquid ammonia at ordinary temperatures has been elaborated.

2. The electrocapillary curve obtained for mercury in liquid ammonia in a normal solution of NH_4NO_3 was used to calculate the capacity of the electric double layer on mercury which proved equal to 11 μ F/cm.^{2}.

3. It is shown that Cl-, Br- and J-ions, which are adsorbed at the mercury/solution interface and cause a shift of the maximum of the electrocapillary curve in aqueous solutions, exhibit a similar behaviour in liquid ammonia.

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Received
October 15, 1939.