ELECTROCHEMICAL INVESTIGATION OF SOME BINARY SYSTEMS IN NITROMETHANE

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Solutions of aluminum and antimony halides and their complexes in nitro derivatives of hydrocarbons have interesting electrochemical properties. Such solutions were studied in greatest detail in nitrobenzene, in an investigation in which Plotnikov and his coworkers were engaged. A solution of aluminum bromide in nitrobenzene is a good conductor and as shown by Plotnikov [1], and later by Plotnikov and Bendetsky [2], its specific electrical conductivity passes through a maximum.

It was found that nitrobenzene solutions of aluminum bromide and aluminum chloride have the power to dissolve the alkali metal halides, which do not dissolve in nitrobenzene by themselves.

It is interesting to note that during electrolysis of these ternary systems the alkali metal is deposited at the cathode, whereas during electrolysis of the benzene and toluene solutions of these same complexes, aluminum is deposited at the cathode. Here the specific effect of the solvent on the process of electrolytic dissociation appears. It is obvious that the process of complex formation underlies this.

An electrochemical investigation of solutions of the antimony halides and their complexes in nitrobenzene was made by Vaisberg [3]. In much less detail he investigated solutions of aluminum and antimony halides in nitromethane. In general the small number of inorganic salts soluble in nitromethane should be noted, about which there is an indication by Brunner [4]. A small number of works on the electrical conductivity of solutions of inorganic salts in nitromethane was cited in Walden's [5] monograph. Solutions of aluminum bromide and some of its complexes in nitromethane were studied by Mezhennyi [6]. He studied the binary system, $AlBr_3$—nitromethane, and of the ternary systems, $AlBr_3$—$LiCl$—CH_3NO_2 and $AlBr_3$—KCl—CH_3NO_2, were studied. It was found that, during the electrolysis of these ternary systems, alkali metal deposits at the cathode. We also studied the binary systems $AlBr_3$—$NaCl$, $AlBr_3$—KBr, $AlCl_3$—$NaCl$, $SbBr_3$—KBr, in this solvent, for the purpose of broadening our knowledge of the nitromethane solutions.

EXPERIMENTAL

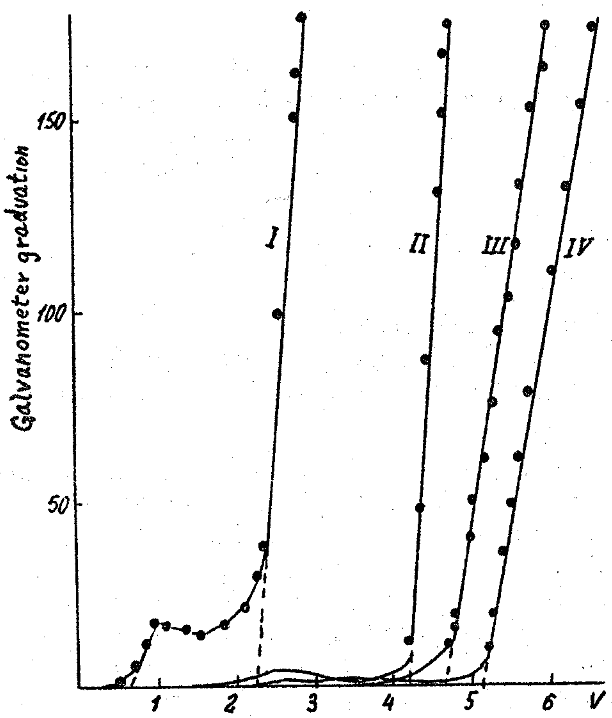
Nitromethane was synthesized from chloroacetic acid and sodium nitrite. The resulting product was distilled, dried with fused calcium chloride, then the nitromethane was distilled over mercuric oxide. The final product was distilled directly into an ampoule and sealed up. The specific electrical conductivity of the nitromethane at 20° was $5.3 \cdot 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

Chemically pure anhydrous preparations of the salts were used for the investigation. A vessel with a ground-glass stopper and platinized platinum electrodes was used for the measurements of the electrical conductivity. The electrical conductivity was measured in a water thermostat at 20° by means of a tube oscillator. The solutions were prepared in the following way. Into a previously weighed vessel for measurement of the electrical conductivity, we poured a certain quantity of fused aluminum bromide from an ampoule. After cooling, the vessel was weighed, the nitromethane was added, and it was reweighed. The electrical conductivity of the initial solution was determined, and then a constantly increasing quantity of alkali metal halide was added. After each addition, the electrical conductivity was measured. Thus, at a constant ratio of aluminum bromide and nitromethane, solutions with different ratios of aluminum bromide and alkali metal halide were obtained.

Similar experiments were also carried out with other ternary systems containing aluminum chloride and antimony bromide. An evolution of heat was observed during the dissolving of $AlBr_3$ and $AlCl_3$ in nitromethane. The electrical conductivity of the solutions of the aluminum and antimony halides in nitromethane increased (Tables 1, 2, 3, 4, 5) on addition of the alkali metal halides.

The alkali metal halides ceased to dissolve as the ratio between them and the Al and Sb halides approached unity. Since the increase of the electrical conductivity was related to the dissolving of the alkali metal salts, it is natural that, as the ratio between the alkali metal halides and the aluminum and antimony salts approached unity, the electrical conductivity ceased to increase. A study was made of the system, $AlBr_3$—$NaCl$—nitromethane, for two ratios of $AlBr_3$:nitromethane. It is obvious that the solution with the larger $AlBr_3$ content had the higher electrical conductivity, although the forms of the curves for both were identical. There is a similar type of curve for the three remaining systems.

The increase of the electrical conductivity on addition of alkali metal halides, and the fact that the dissolving ceased when the ratio between the alkali metal halides and the aluminum or antimony halides approached unity, enabled us to assume that in the solutions complexes are formed which contain one molecule of alkali metal halide, of such compositions as: $NaCl \cdot AlCl_3$, $NaCl \cdot AlBr_3$, $KBr \cdot AlBr_3$ and $SbBr_3 \cdot KBr$. We did not exclude the possibility that molecules of solvent enter into the composition of a complex.



Decomposition voltage of nitromethane solutions. I) $SbBr_3-KBr$; II) $AlCl_3-NaCl$; III) $AlBr_3-NaCl$; IV) $AlBr_3-KBr$.

The solutions of $AlBr_3-NaCl$ and $AlBr_3-KBr$ thickened during storage, and after several days they were transformed to gels. At first these gels were transparent, straw-yellow colored masses, which after several days were converted to opaque white gels. After a series of measurements was made, the solution was not poured from the vessel used for measuring the electrical conductivity, but remained in it, where from time to time the electrical conductivity was checked. It was found that the electrical conductivity of the ternary systems had not changed during 7-10 days, and only after this did it begin to decrease.

Solutions of $AlCl_3-NaCl$ and $SbBr_3-KBr$ did not gel completely on storage. Thus, experiments showed that gelation was characteristic only for solutions containing aluminum bromide. Experiments were also carried out on solutions of $AlBr_3$ in nitromethane without the addition of alkali metal salts. Our experiments confirmed Mezhennyi's observation that solutions of $AlBr_3$ in nitromethane gel. Simultaneously, we observed a phenomenon not described in the work of Mezhennyi, namely – it was found that the electrical conductivity of solutions of $AlBr_3$ in nitromethane decreases strongly with time, and it decreased more rapidly in the more concentrated solutions. It is possible to assume here that gel formation is related to the continuous process of chemical reaction of aluminum bromide with the solvent. The fact that the electrical conductivity remains constant in the ternary systems over a long period of time is an additional indication that the alkali metal halides bind $AlBr_3$ into complexes, and therefore, the activity of its interaction with the solvent diminishes.

TABLE 1

Change of the Specific Electrical Conductivity of the System $AlBr_3-NaCl-$Nitromethane with a Change of the Ratio $\frac{NaCl^*}{AlBr_3}$. $AlBr_3$: nitromethane = 1:8.64.

Molecular ratio $\frac{NaCl}{AlBr_3}$	0	0.169	0.355	0.506	0.727	0.95	1.2
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	16.85	20.1	25.5	30.0	36.0	41.5	42

TABLE 2

Change of the Specific Electrical Conductivity of the System $AlBr_3-NaCl-$Nitromethane with a Change of the Ratio $\frac{NaCl}{AlBr_3}$. $AlBr_3$: nitromethane = 1:30.13

Molecular ratio $\frac{NaCl}{AlBr_3}$	0.089	0.235	0.349	0.409	0.522	0.653	0.780	0.864	0.996	1.27
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	10.63	12.19	16.0	18.58	19.30	20.66	22.72	26.45	28.52	28.5

* In Tables 1-5, where the ratio between the alkali metal halides and the corresponding halides of aluminum or antimony is larger than unity, deposits of undissolved salts were found at the bottom of the vessel.

TABLE 3

Change of the Specific Electrical Conductivity of the System $AlBr_3$—KBr—Nitromethane with a Change of the Ratio $\frac{KBr}{AlBr_3}$. $AlBr_3$: nitromethane = 1 : 20.5

Molecular ratio $\frac{KBr}{AlBr_3}$	0	0.214	0.392	0.615	0.750	1	1.2
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	16.8	21.7	26.0	32.0	36.0	42.1	42.1

TABLE 4

Change of the Specific Electrical Conductivity of the System $AlCl_3$—NaCl—Nitromethane with a Change of the Ratio $\frac{NaCl}{AlCl_3}$*. $AlCl_3$: nitromethane = 1 : 7.43

Molecular ratio $\frac{NaCl}{AlCl_3}$	0	0.053	0.163	0.253	0.505	0.59	0.70	0.91	1.05
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	6.8	8.2	20.7	24.5	29.5	37.4	40	48	50

The decomposition voltage of the ternary system was also studied. We used the usual system for determining the decomposition voltage. The value of a voltmeter graduation was 0.04 V and the sensitivity of the galvanometer was $1 \cdot 10^{-4}$ amp. Measurement was made at room temperature in a vessel with platinum point electrodes. The results of the measurements are presented in Table 6.

TABLE 5

Change of the Electrical Conductivity of the System $SbBr_3$—KBr—Nitromethane with a Change of the Ratio $\frac{KBr}{SbBr_3}$. $SbBr_3$: nitromethane = 1:1.96

Molecular ratio $\frac{KBr}{SbBr_3}$	0	0.311	0.45	0.55	0.67	0.83	1.05	1.19
$\kappa \cdot 10^3\ \Omega^{-1}\ cm^{-1}$	1.89	11..9	15.7	18.7	20.7	21.7	22	22

It should be pointed out that for the system KBr—$SbBr_3$ only one discontinuity was observed on the curve in the region of 0.6 V; it is possible that this decomposition voltage corresponds to the decomposition of HBr, which might be formed in small quantities as a result of hydrolysis. The high values of the decomposition voltage for systems containing an aluminum halide enabled us to assume that alkali metal deposited during electrolysis of the first three systems. The electrolysis experiments confirmed this.

TABLE 6

Decomposition Voltage of the Ternary Systems

Composition of the solution	Decomposition voltage (V)	Remarks
$\frac{AlBr_3}{\text{nitromethane}} = \frac{1}{9.5}$; $\frac{NaCl}{AlBr_3} = 1$	4.6	Solutions had deposits of insoluble alkali metal salts.
$\frac{AlCl_3}{\text{nitromethane}} = \frac{1}{7.43}$; $\frac{NaCl}{AlCl_3} = 1$	4.2	
$\frac{AlBr_3}{\text{nitromethane}} = \frac{1}{1.40}$; $\frac{KBr}{AlBr_3} = 1$	5.1	
$\frac{SbBr_3}{\text{nitromethane}} = \frac{1}{1.96}$; $\frac{KBr}{SbBr_3} = 1$	2.2	

The electrolysis was carried out in a U-shaped, curved tube with an internal diameter of 9 mm. A small plug of glass wool was placed in the bottom of the tube as a diaphragm. Platinum wires embedded in stoppers, sealed in glass tubes, served as the electrodes. The voltage of the battery was 12 V, and the current strength was 15 mA. During electrolysis of the systems $AlBr_3$—NaCl and $AlBr_3$—KBr, the liquid around the anode turned brown as a result of the bromide formed, and the cathode was covered with a dense deposit of antimony. A series of experiments on the electrolysis of the systems $AlBr_3$—NaCl and $AlCl_3$—NaCl was carried out, and the duration of the

* A. Ilchenko participated in the study of the electrical conductivities of the systems $AlCl_3$—NaCl and $AlBr_3$—KBr.

experiments varied from 1 to 3 hours. After completion of the electrolysis the cathode was removed and washed with dry gasoline, and after this it was immersed in a beaker of water. Phenolphthalein was added to the water and the alkali which formed was titrated. In some experiments, the current efficiency for sodium was 20-25%. During electrolysis of the systems of $AlBr_3$—KBr we also observed the deposition of metallic potassium, but we were unable to determine the current efficiency, since an explosion occurred during the removal of the electrode from the solution, and a large portion of the metallic potassium was discarded with the electrode. The electrode was washed with benzene and submerged in a beaker of water containing phenolphthalein. Thus, the deposition of potassium during the electrolysis was demonstrated qualitatively. The electrolysis of systems of $SbBr_3$—KBr was carried out in small beakers. Platinum wire served as the anode, as in previous experiments, and a plate of stainless steel with a surface of 1.5 cm^2 served as the cathode. The battery voltage was 4 V, and the current strength was 15 mA; the cathode was covered with a black deposit of antimony. The electrolysis was carried out for 1 hour. The current efficiency for antimony was 80%.

SUMMARY

1. An electrochemical investigation of nitromethane solutions was carried out for the systems $AlBr_3$—NaCl, $AlBr_3$—KBr, $AlCl_3$—NaCl, $SbBr_3$—KBr.

2. The solubility of the alkali metal halides in nitromethane solutions of the corresponding aluminum and antimony halides was investigated. The electrical conductivity, decomposition voltage and electrolysis were also studied.

3. On addition of alkali metal halides to solutions of the corresponding halides of aluminum and antimony in nitromethane, the specific electrical conductivity of the solutions increased.

4. The alkali metal halide ceased to dissolve when the ratio between the alkali metal halide and the corresponding halides of aluminum or antimony became equal to unity.

5. The investigation of the electrical conductivity and the solubility indicated the formation in the nitromethane solutions of complexes such as: $NaCl \cdot AlCl_3$, $NaCl \cdot AlBf_3$, $KbR \cdot AlBr_3$, $KBr \cdot SbBr_3$.

6. During electrolysis of solutions containing $AlBr_3$—NaCl, $AlCl_3$—NaCl, sodium deposited at the cathode; during the electrolysis of solutions of $AlBr_3$—KBr metallic potassium deposited at the cathode; and during electrolysis of solutions of $SbBr_3$—KBr antimony deposited at the cathode.

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