RESEARCH ON GALVANIC CIRCUITS IN TOLUENE

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In our preceding paper [1] we described our research on the electromotive forces in benzene solutions of $AlBr_3$ to which the halides of various metals had been added.

In the present paper we report on analogous research on toluene solutions. The method of measurement was somewhat different from that employed earlier. Formerly, we used the customary method of eliminating or reducing the diffusion potential by means of the so-called intermediate electrolyte. Inasmuch as a series of preliminary tests had shown that the value of the e.m.f. remains almost unchanged in the medium under investigation if no intermediate electrolyte is used, we also made a series of tests without an intermediate electrolyte. Eliminating the intermediate electrolyte is desirable, owing to the high resistance of the solution caused by the electrolyte, which makes it hard to measure the e.m.f.

In the present research we made a series of tests to investigate the electrode potential of such metals as aluminum, bismuth, silver, antimony, copper, and arsenic.

The feasibility of measuring electrode potentials in toluene was settled by a number of papers by V.A.Plotnikov and his associates [3] on the conductivity and the decomposition potentials of toluene solutions of aluminum bromide when halides of the foregoing metals are added to the solution.

A solution of $AlBr_3$ in toluene is almost a non-conductor, but silver, copper, bismuth, antimony, and arsenic bromides are readily soluble in this solution, which then becomes a conductor.

When toluene solutions of $AlBr_3 - KBr$, $AlBr_3 - AgBr$, $AlBr_3 - CuBr$, $AlBr_3 - Sb - Br_3$, and $AlBr_3 - BiBr_3$ are electrolyzed, Al, Ag, Cu, Sb, and Bi are deposited, respectively at the cathode, in accordance with the data in the literature.

Measurements of the decomposition potentials in the foregoing binary systems of salts in benzene and toluene solutions indicate that in many cases the decomposition potentials in toluene solutions are different from those in benzene solutions.

EXPERIMENTAL METHODS AND RESULTS OF MEASUREMENT

The toluene was purified by shaking it up with sulfuric acid. The toluene was then separated from the sulfuric acid and washed free of acid, first with a solution of NaOH and then with water; after the water had been removed, the toluene was desiccated with metallic sodium. The desiccated toluene was then distilled over metallic sodium. The product was redistilled at a fixed temperature and then sealed in ampoules. The purification of the salts used (with the sole exception of the $AsBr_3$) was described in the preceding paper. Chemically

pure arsenic bromide was distilled and sealed into ampoules. For our tests we used a preparation that was completely colorless and had been refined by double distillation. Rods of solid cast metal or electrolytically deposited metals were used as the electrodes. The silver electrode was prepared by depositing silver electrolytically upon a silver wire in a cyanide bath.

The aluminum electrode was a thin plate of chemically pure sheet aluminum. The copper electrode was a wire of chemically pure copper.

The bismuth and antimony electrodes were rods of cast metal. The arsenic electrode was prepared by depositing arsenic electrolytically from a 10% solution of $AsBr_3$ in ether.

In all our tests the solvent used was a solution of aluminum bromide in toluene, with an $\frac{AlBr_3}{toluene}$ ratio of 0.25. This solution was prepared immediately before the beginning of a run, owing to the undesirability of keeping it for any length of time (possible hydrolysis). Then the requisite amount of halide of the metal whose potential was to be determined was poured into a small flask containing the solvent.

The weight of metallic halide was so chosen as to make the $\frac{MeHal}{AlBr_3}$ ratio equal 0.1

The comparison electrode used, as in the previous paper, was silver, immersed in a standard electrolyte, i.e., a solution whose $\frac{AgBr}{AlBr_3}$ ratio equaled 0.1.

This electrode was freshly prepared anew for each circuit.

As the stability of the e.m.f. in such media is less than in aqueous solutions, the tests with each galvanic circuit were repeated several times until the results corresponded closely.

The initial value of the e.m.f. was measured 15 minutes after the cell had been set up; it took an hour for the value of the e.m.f. to become steady. In some cases this value of the e.m.f. remained unchanged for twenty-four hours. this was the case for Cu and Bi. The Al, As, and Sb potentials were less steady, the precision of measurement of these potentials not exceeding a hundredth of a volt.

Upon standing, some solutions resinified, separating into layers, probably because of the formation of a Gustavson coordination compound.

The slow establishment of the potential may be due to the slow rate of formation of the coordination compound. The slow rate of formation of the coordination compound in the $AlBr_3 - AsBr_3$ system was established by Plotnikov and Yakobson [3], who observed the change in conductivity with time.

In the more stable systems, with copper and bismuth bromides, the deviations in individual e.m.f. measurements did not exceed 1 to 2 millivolts.

A summary table of the e.m.f's in the investigated circuits is given below:

$$\text{Me} \left| \begin{array}{l} \frac{AlBr_3}{\text{toluene}} = 0.25 \\ \frac{MeHal}{AlBr_3} = 0.1 \end{array} \right\| \left| \begin{array}{l} \frac{AlBr_3}{\text{toluene}} = 0.25 \\ \frac{AgBr}{AlBr_3} = 0.1 \end{array} \right| \text{Ag}$$

The potential of the silver electrode is taken as zero.

As seen in the table, the potential sequence of the metals investigated

has a quite different order from that of the normal potentials of the same metals in aqueous solutions.

Whereas in water the sequence of normal potentials is as follows: Al, Bi, Sb, As, Cu, Ag, the potential sequence in the $AlBr_3$ – MeBr – toluene system is as follows: Al, Cu, Ag, Bi, Sb, As.

The shift of silver in the potential sequence is found in both the benzene and toluene solutions. This shift of silver in the potential sequence was also found by Izbekov [4], who used fused $AlBr_3$ as his solvent.

Electrode	Electrode potential, volts		Sequence of normal potentials in aqueous solution, taking the potential of silver as zero.
	In a toluene solution of $AlBr_3$ - MeHal	In a benzene solution of $AlBr_3$ - MeHal	
Al/Al^{+++}	-0.075	-0.306	-2.728
Cu/Cu^{+}	-0.026	-0.023	-0.268
Ag/Ag^{+}	0.000	-0.000	0.000
Bi/Bi^{+++}	+0.309	+0.393	+0.608
Sb/Sb^{+++}	+0.470	+0.497	-0.608
As/As^{+++}	+0.590	–	-0.508

The order of potentials established by measuring the e.m.f. was confirmed by experiments on the direct displacement of the metals. Though the sequence is the same in the potential series for benzene and toluene solutions, the absolute magnitudes of the electrode potentials differ.

The greatest difference is found in the potential of aluminum, which may be related, evidently, to the different values of the decomposition potential of $AlBr_3$ – KBr in benzene and toluene solutions, as established in the research done by Plotnikov and his associates.

We find that the two values almost coincide for copper, with only a slight difference being observed, toward a lowering of the potential, in the cases of bismuth and antimony.

For the sake of comparison, we cite below the series of potentials found by other authors in their work on various nonaqueous media:

Pyridine: Al, Cu, Sb, Bi, Hg, Ag (Kahlenberg [5]).
Acetone: Zn, Cd, Co, Bi, Hg, Cu (Skobets [6]).
Fused $AlBr_3$: Al, Zn, Cd, Ag, Hg, Sb, Bi (Izbekov [4]).

Hence, it may be stated that the considerable formation of coordination compounds in these media greatly affects the sequence of the potentials of the metals investigated.

SUMMARY

1. Research has been done on the e.m.f. of galvinic circuits in these toluene solutions: $AlBr_3$-AgBr, $AlBr_3$ - KBr, $AlBr_3$ - CuBr, $AlBr_3$ - $SbBr_3$, $AlBr_3$ - $BiBr_3$, $AlBr_3$ - $AsBr_3$.

2. Measurements were made of the following metals: Al, Bi, Cu, Sb, and As, paired with a silver electrode.

3. The sequence of potentials for these metals is arranged in the following order: Al, Cu, Ag, Bi, Sb, As.

4. This potential sequence differs from that of the same metals in aqueous solutions, but coincides with the sequence found in benzene solutions.

LITERATURE CITED

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