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ELECTRODEPOSITION OF ALUMINUM FROM THE SOLUTION SYSTEMS OF ANILINE AND ITS SEVERAL DERIVATIVES

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Aniline and its several derivatives, belonging to primary, secondary, or tertiary amines, are shown to be the effective solvents of aluminum bromide for the electrodeposition of metallic aluminum. The secondary and tertiary amine systems showed an intricate conductometric behavior in the dilute region of aluminum bromide. The correspondence of behavior between electrodeposition and conductivity was observed.

Previous work[1)] on the electrodeposition of aluminum was carried out with N,N-dimethylaniline as the solvent. The present letter shows that aniline and its several derivatives are also effective solvents for the purpose. These are aniline and m-toluidine (primary amines), N-methylaniline (secondary amine), N,N-diethylaniline and N,N-dimethyl p-toluidine (tertiary amines). From every solution of aluminum bromide in these solvents, metallic aluminum was electrodeposited under suitable conditions. The behavior that seemed to characterize, to some extent, the individual solvents was observed only in the dilute region of the bromide below 50 mol%.

Electrodeposition of aluminum. So far as the concentration of $AlBr_3$ was above 50 mol%, metallic aluminum was electrodeposited without fail from all of these systems with a current efficiency of 80-90 % under optimum conditions. Fig. 1 illustrates the change of the cathode current efficiency with current density. The deposits were usually smooth and light grey, but took a metallic luster when they were rubbed.

In the dilute region, on the contrary, the electrodeposition took place only in the systems of diethylaniline and dimethyl p-toluidine, though the current efficiency and the properties of the deposits were not satisfactory. This feature is quite similar to that of the dimethylaniline system reported previously.

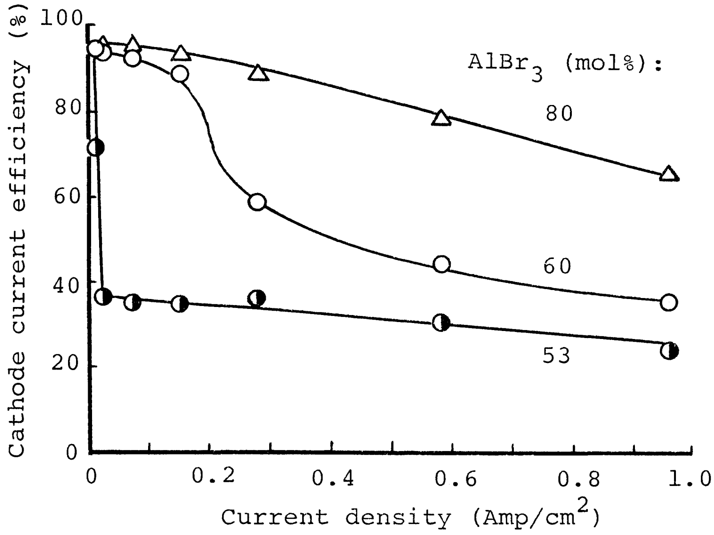

Fig.1. Change in cathode current efficiency with current density. Aniline system at 130°C.

Correspondence of behavior between electrodeposition and conductivity. As described above, in the concentrated region all these amines can indiscriminately afford the electrodeposits of aluminum, whereas in the dilute region the primary and secondary amines, which have one and two N-hydrogen atoms respectively in each of their molecules, can not. This behavior of all these amines seems to correspond with the conductometric behavior of their solution systems.

In the concentrated region, the specific conductivity of every system changed with temperature in such a manner as is illustrated in Fig. 2. The conductivity rapidly changed as the temperature was increased or decreased, and this change was reversible.

In the dilute region, however, the conductivity changed in a different manner, except for the primary amine systems of aniline and m-toluidine. An example is shown in Fig. 3, which is for the N-methylaniline system. Within the temperature range from A to B, the change of conductivity was in the same manner as that in the concentrated region, i.e., the change was reversible. On the contrary, the change became irreversible at any temperatures above B; the conductivity no longer returned to its former value when the temperature was reduced, but changed along an another path, e.g., the curve CD, along which the change was again rapid and reversible. This critical temperature B differed in its value with the concentration and the solvent species of solutions. At any temperature above this, the time, taken for the conductivity to attain a next stationary value when the temperature was raised, was unusually long, i.e., 10-20 hours. This peculiar behavior was common to all of the secondary and tertiary amine systems. Moreover, the N-hydrogen atoms were liberated as gaseous hydrogen when metallic aluminum

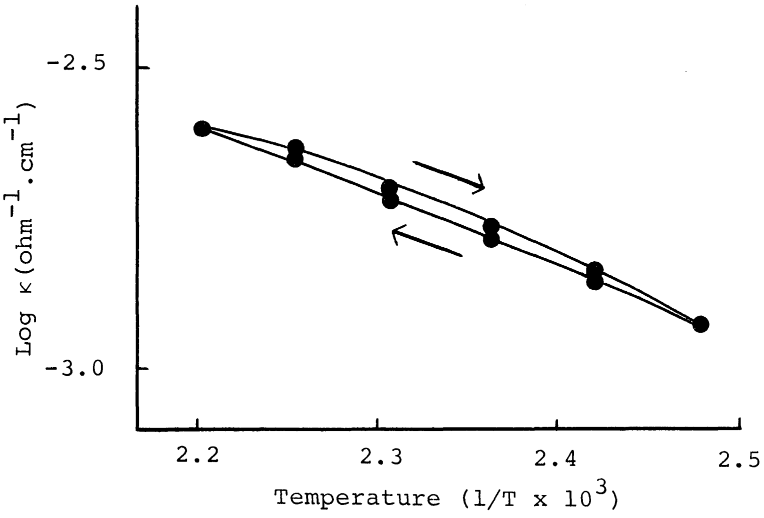

Fig.2. Change in specific conductivity with temperature in concentrated region. N,N-dimethyl p-toluidine system. $AlBr_3$, 65.1 mol%.

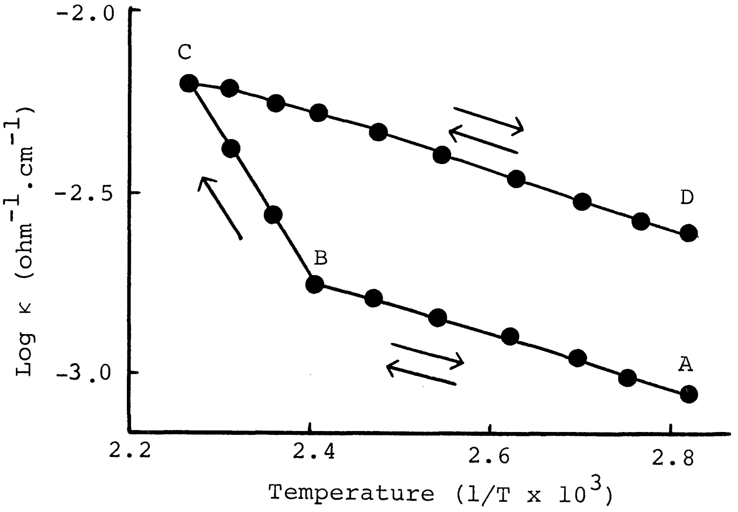

Fig.3. Change in specific conductivity with temperature in dilute region. N-methylaniline system. $AlBr_3$, 20.0 mol%.

was immersed in a dilute solution of aluminum bromide in any of these secondary and primary amines. It has already been found that,[1)] though the current efficiency of aluminum deposition was low in a dilute solution of aluminum bromide in dimethylaniline at a low temperature, it became remarkably higher even at the same temperature after the solution was once heated to a higher temperature for a long time. The conductometric peculiar behavior of the secondary and tertiary amine systems in the dilute region, when considered in connection with those foundings described above, is likely to be due to cleavage of the bond(s) between the amino nitrogen atom and alkyl group(s) in the molecule of these solvents, with the results that a new conductive species is irreversibly formed, and only the species from any of the tertiary amines is able to give metallic aluminum at cathode.

The change in specific conductivity of all systems with the concentration of aluminum bromide is typically shown in Fig. 4, which is for the system of di-

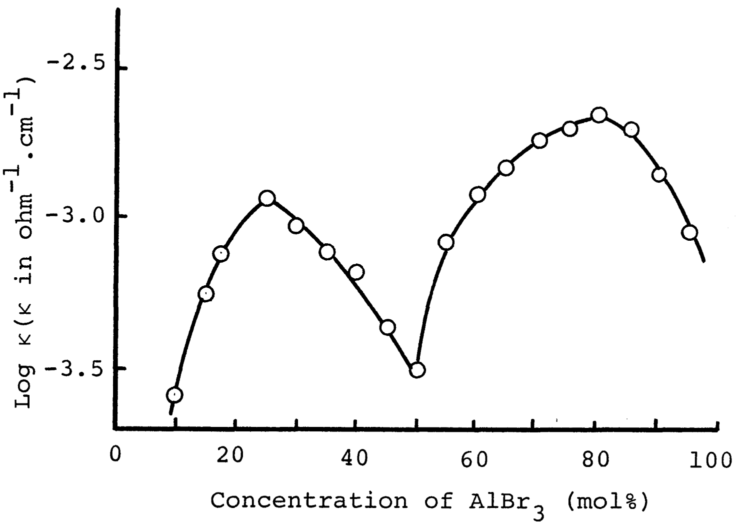

Fig.4. Change in specific conductivity with composition. N,N-dimethyl p-toluidine system at 140°C.

methyl p-toluidine at 140°C. The conductivity curve for any of these systems passes through two peaks in the dilute and concentrated regions, and through a minimum at the equimolar composition. This minimum of conductivity indicates the occurrence of a molecular complex which is composed of equimolecular amounts of aluminum bromide and any of these solvent species. In the case of aniline, such a complex, $C_6H_5NH_2 \cdot AlBr_3$ was actually isolated as a solid.

Anodic dissolution of aluminum. As described above, aluminum dissolved non-electrolytically in a dilute solution of aluminum bromide in the primary (aniline or m-toluidine) or secondary amine (N-methylaniline) with the evolution of hydrogen. However, in the concentrated region of all these systems, an aluminum anode dissolved electrochemically with a current efficiency (estimated on the basis of the reaction $Al \rightarrow Al^{3+}$) of about 100 % under optimum conditions, and the dissolved aluminum was able to be deposited at the cathode. As the efficiency was 103 % at the best, the dissolution of the metal as univalent ions was unlikely to occur.

References

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