

Polarography in Molten Alkali-metal Acetates

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IN recent years a number of low-melting salts and salt mixtures have been employed as solvents for electrochemical studies; among them, besides nitrates and chlorides, there are bisulphates,¹ perchlorates,² thiocyanates,³ and organic salts such as ammonium formate⁴ and ethylpyridinium bromide.⁵

In this Communication some preliminary results of a study on molten acetates as a solvent are reported. A Li-Na-K acetate mixture (mole ratio 20:35:45, melting point about 460°K) has been used at 470°K. At this temperature the melt is apparently stable, and only after about one day does it begin to darken slightly.

Voltammetric curves on the pure solvent at a dropping mercury electrode ($m = 1.26 \text{ mg. sec.}^{-1}$;

$t = 5.5 \text{ sec.}$) have been obtained with a three-electrode polarograph,⁶ using as reference an Ag/Ag⁺ [0.1 mole kg.⁻¹ in (Li,K)NO₃] electrode enclosed in a thin-walled soft-glass bulb⁷ and, as the counter electrode, a platinum foil. The residual current varies almost linearly between about -0.60 and -1.60v, with a slope of 0.3 $\mu\text{A volt}^{-1}$. Since preliminary experiments showed that the reduction of the solvent on a platinum electrode occurs at more negative potentials, the cathodic reaction on mercury is very probably the reduction of alkali-metal ions to give an amalgam. In order to investigate the anodic reaction, a constant-current electrolysis has been carried out on a mercury pool anode. At the end of the electrolysis the salt in the anode compartment contained finely

divided mercury metal, and only a small amount of dissolved mercury. Separate experiments showed that mercury(I) nitrate reacts with molten acetate to give metallic mercury, while mercury(II) nitrate gives mercury(II) oxide. The most probable anodic process is thus the production of mercury(I) ions which in turn oxidise the solvent.

The polarographic behaviour of some cations was subsequently investigated. Lead(II), cadmium(II), and zinc(II) were introduced into the solution as nitrates; all of them gave well-defined reduction waves in the concentration range 1×10^{-4} — 2×10^{-3} mole kg.⁻¹; the half-wave potentials are approximately 0.95, 1.10, and 1.55 v respectively. For lead and cadmium, the diffusion current is proportional to the concentration within $\pm 3\%$ in the

aforementioned concentration range; the diffusion current constants are 0.85 and 0.75 mA. mole⁻¹ kg. mg.^{-2/3} sec.^{1/2} respectively. The slopes of the E against $\log i/(i_d - i)$ diagram for these cations were respectively 48.0 ± 2.0 and 47.5 ± 2.0 mv; the theoretical value for a reversible two-electron reduction process at 470°K is 46.6 mv.

From these preliminary results, molten alkali-metal acetates appear suitable as solvents for electrochemical investigations; moreover, since it has been found that appreciable quantities of acetic acid dissolve in the molten mixture, and in view of the strongly basic character of the acetate ion, this solvent appears to be a promising one for the study of acid-base reactions.

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