LETTERS TO THE EDITOR

THE ELECTRIC DOUBLE LAYER ON MERCURY IN HEXAMETHYLPHOSPHORAMIDE

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The kinetics of the electrochemical generation of solvated electrons in hexamethylphosphoramide (HMPA) began to be studied recently [1]. It was interesting in this connection to study the structure of the electric double layer on mercury in this solvent. Differential-capacity and electrocapillary curves were measured therefore, and in addition polarization curves in order to determine the potential range where there are no electrochemical reactions occurring. All measurements were done relative to an aqueous normal calomel electrode which was connected to the test solution via a salt bridge containing saturated potassium chloride solution. The capacity curve in sodium or lithium perchlorate can be recorded over the potential range from −0.2 to +1.7 V (n.c.e.). The minimum value of capacity in 0.2 N $NaClO_4$ solution is 3.7 $\mu F/cm^2$. From $\sigma - \varphi$ curves measured in the same solution it was seen that a reproducible electrocapillary curve can only be obtained after carefully freeing the solution from oxygen. One then observes that the measured $\sigma - \varphi$ curve coincides with the one calculated by double integration of the differential-capacity curve. The point of zero charge was determined by the method of mean chord diameters, and was −0.140 V.

The nature of the cations influences the value of electric double-layer capacity in HMPA solutions. Thus, when going from lithium to sodium salt one observes a small increase in capacity, and this only at sufficiently cathodic potentials, but when going to Cs^+ salt the capacity rise occurs over a wider potential range, and amounts to 6 $\mu F/cm^2$ at $\varphi = -1.5$ V. When this potential region is compared to the $I - \varphi$ curve it is seen that this increase is not due to an electrode reaction. A tenfold decrease in the electrolyte concentration produces a small decrease in capacity over the entire potential range. At −0.3 V one observes a small anodic "hump" which vanishes completely when small quantities of water are introduced into the solution. The chloride ion is more surface active than ClO_4^- at the mercury-HMPA interface. Measurements in 0.2 N LiCl solution have shown that the curves recorded at 10, 25, and 50°C completely coincide.

LITERATURE CITED

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