Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1963

SovietRxiv

Fig. 1. Quartz capillary electrometer.

Figure 1: Fig. 1. Quartz capillary electrometer.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1963. Volume 150, No. 2

PHYSICAL CHEMISTRY

E. A. UKSHE, I. V. TOMSKIKH

THE INFLUENCE OF THE NATURE OF THE ELECTROLYTE ON THE ELECTROCAPILLARY CURVES OF LEAD IN MOLTEN SALTS

(Presented by Academician A. N. Frumkin on February 1, 1963)

A study of the capacitance of the electrical double layer on a lead electrode in molten salts showed ([1]) that the structure of the double layer depends substantially on the nature of the electrolyte. In particular, a noticeable difference exists between the capacitance curves of lead in melts of potassium and sodium halides. In this connection it was of interest to compare the previously obtained capacitance curves with electrocapillary curves determined under identical conditions.

For measuring the electrocapillary curves of a liquid lead electrode we used a procedure similar to that described in ([2,3]). Certain changes in the procedure were connected with the high temperatures at which the measurements were carried out (800–820°). We used a capillary electrometer made of quartz glass (Fig. 1). A rod of spectrally pure graphite served as the auxiliary electrode for polarization by direct current. The current leads to the metal and graphite were molybdenum, in quartz sheaths. As the reference electrode we used an electrode Pb/2.5 mol.%—$PbCl_2$—electrolyte, enclosed in a separate test tube with a capillary opening.

Fig. 1. Quartz capillary electrometer.

The apparatus was placed in a vertical tubular furnace equipped with two glazed windows, through which the meniscus of lead in the capillary could be observed. Observations of the metal meniscus were made with a precision cathetometer KM-6, whose optical system was located 35-40 cm from the capillary. The cathetometer made it possible to determine vertical displacements of the meniscus with an accuracy of up to 0.001 mm.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

We did not set ourselves the task of determining the absolute value of the surface tension at the metal-salt phase boundary, since we were interested only in the change in surface tension relative to its value at the maximum of the electrocapillary curve. In this case, as is known (4),

$$\Delta\sigma = \sigma_{\text{max}} - \sigma = \frac{9.81(\rho_{\text{Pb}} - \rho_{\text{el}})}{2} \cdot r_m \Delta h, \qquad (1)$$

where ρ_{Pb}, ρ_{el} are the densities of liquid lead and of the electrolyte at the given temperature; Δh is the distance between the position of the meniscus at the maximum of the e.c. curve and at the given value of the potential; r_m is the radius of curvature of the meniscus.

The radius of curvature of the meniscus was calculated from tables (4), with the surface tension at the maximum taken to be $398 \cdot 10^{-5}$ N/cm, i.e., 2.5% less than the surface tension of lead in vacuum at 800°.* In view of the fact that the diameter of the capillary of the electrometer could vary

* The closeness of these values was established in the works of V. A. Kuznetsov (3).

in height by 3-4%, some scatter of points was observed in repeated measurements. The absolute fluctuations of the values of σ on the side branches of the electrocapillary curves, where the surface tension strongly depends on the potential, reached $(1—3) \cdot 10^{-5}$ N/cm when $\Delta\sigma$ changed over the investigated potential interval by $(20—30) \cdot 10^{-5}$ N/cm.

The electrocapillary curves for the same conditions were also calculated by double graphical integration of the capacitance curves presented in work (1). The results of such calculations are shown in Figs. 2 and 3 by solid curves. The points plotted there are the results of direct measurements. It is not difficult to see that in this case there is complete agreement between the capacitance and electrocapillary (e.c.) measurements. In particular, the e.c. curves of lead in KCl and KBr melts are flatter than in NaCl and NaBr melts. The values of the potentials of the maxima of the electrocapillary curves, within the accuracy of the measurements, coincide with the values of the potentials corresponding to the minima of the capacitance curves in the corresponding melts.

Fig. 2. E.c. curves of a lead electrode at 820°: 1 –NaCl; 2 –KCl. Points are experimental data; the solid line was calculated from the capacitance curve (1)

Fig. 3. E.c. curves of a lead electrode at 800°: 1 –NaBr; 2 –KBr. Points are experimental data; the solid line was calculated from the capacitance curve (^{1})

The agreement between the calculated and experimental e.c. curves is an indisputable confirmation of the previously developed method for measuring the capacitance of the double layer in molten salts (^{1}). It is also clear that the influence of the salt cation on the character of the capacitance curves is due to the behavior of these cations in the electrical double layer and is not connected with any extraneous circumstances, for example, with the appearance of pseudocapacitances. The different character of the electrocapillary curves in melts of sodium and potassium salts is probably due to the fact that Na^+ ions have a smaller radius and can penetrate to the metal surface between the anions. This leads to a greater interaction of the ions in the double layer and to a stronger decrease in surface tension. In other words, in sodium halides the electrical double layer is deformed more easily than in potassium halides. This may be connected with the fact that the structure of molten salts with a small cation is less loose and the structural changes in the field of the double layer are more substantial in them than in molten salts with a large cation.

The authors express their deep gratitude to Acad. A. N. Frumkin, and also to B. N. Kabanov and D. I. Leikis for discussion of the results obtained.

Bereznikov Branch
of the All-Union Aluminum-Magnesium Institute

Received
31 I 1963

CITED LITERATURE

1. E. A. Ukshe, N. G. Bukun, D. I. Leikis, *Izv. AN SSSR, OKhN*, 1963, No. 1, 2.
2. S. V. Karpachev, A. G. Stromberg, *ZhFKh*, **13**, 1831 (1939).
3. V. A. Kuznetsov, T. D. Dyakova, V. P. Maltseva, *ZhFKh*, **33**, 1551 (1959).
4. N. K. Adam, *Physics and Chemistry of Surfaces*, Moscow–Leningrad, 1947.

Note: Figure translations are in progress. See original paper for figures.