EFFECTS OF TEMPERATURE AND NATURE OF MOLTEN SALT ON THE PROPERTIES OF A DOUBLE ELECTRICAL LAYER

(UDC 541.135.3)

E. A. Ukshe and N. G. Bukun

Bereznikova Branch, All-Union Aluminum-Magnesium Institute
Translated from Élektrokhimiya, Vol. 1, No. 1,
pp. 113-115, January, 1965
Original article submitted February 12, 1964

Capacitance measurements on double layers in fused salts have thrown some light on the structure of the interface between a metal and an ionic liquid [1-3]. Here we present some fresh results on these layers near the electrocapillarity zero.

The electrode was molten lead; the design has already been described [2]. The capacitance was measured at 20,000 cps by a bridge method in an argon atmosphere; for details see [1, 2]. Repeated measurements have shown that the minimum capacitance C_m (that for electrocapillarity zero) can be measured to about 2% if the salts are carefully purified, except for iodides, which give rather larger errors, on account of thermal decomposition.

Figure 1 shows C_m derived from the capacitance-potential curves for various temperatures; $C_m(T)$ is nearly exponential, and the salts are very clearly divided into two groups, namely the halides of lithium and sodium (curves 1-5) and those of potassium and cerium (curves 6-10). A notable feature is that difference between the groups increases with the temperature.

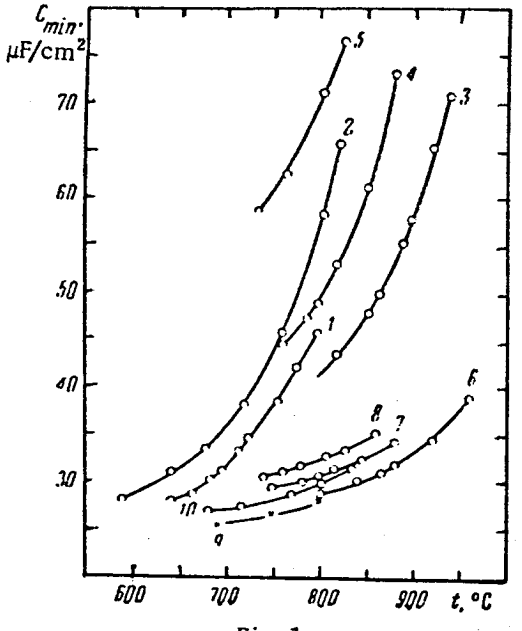


Fig. 1

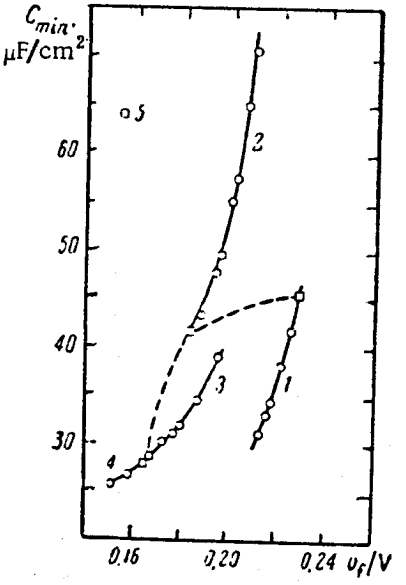


Fig. 2

Fig. 1. Minimal capacitance of a lead electrode as a function of temperature for the following salts: 1) LiCl; 2) LiBr; 3) NaCl; 4) NaBr; 5) NaI; 6) KCl; 7) KBr; 8) KI; 9) CsCl; 10) CsI.

Fig. 2. Minimal capacitance of a lead electrode as a function of the free volume for: 1) LiCl; 2) NaCl; 3) KCl; 4) CsCl; 5) points corresponding to 800°C.

Relative Free Volumes v_f/V for Various Fused Salts

Salt	700°	800°	900°	1000° C	Salt	700°	800°	900°	1000° C
LiCl	0,215	0,229	0,249	0,271	KCl	—	0,167	0,183	0,204
LiBr	0,230	0,245	0,265	0,288	KBr	—	0,159	0,174	0,192
NaCl	—	0,184	0,202	0,220	KI	0,155	0,171	0,189	0,210
NaBr	—	0,175	0,188	0,202	CsCl	0,152	0,167	0,184	0,205
NaI	0,171	0,188	0,204	0,224	CsBr	0,150	0,168	0,190	0,212

The presently available evidence cannot be explained in terms of the dense and diffusion layers envisaged for dilute electrolyte solutions; in fact a diffusion structure is not compatible with the high capacitance (C_m of 25-75 $\mu F/cm^2$) and with the positive temperature coefficient.

These difficulties are largely overcome if we suppose that the layer has the sign-varying structure first proposed by Esin [5] and latterly extended by others [5], which has been confirmed by studies [6] on models for ionic liquids. This layer should have several novel properties, especially very high (in principle, unlimited) capacitance, relation of capacitance to coordination numbers of the ions, and positive temperature coefficient of capacitance.

The evidence (Fig. 1) receives a general explanation if we relate the capacitance to the free volume, the latter being given [7] by

$$v_f = R\beta / \alpha, \tag{1}$$

in which R =8.317 J/deg-mole, β is compressibility, and α is thermal expansion coefficient. We have shown [7] that the v_f of (1) agree closely with the volume change on melting, so $(1-v_f/V)$, in which V is the molar volume at the working temperature, defines the deviation of the coordination number from the value for the crystal lattice (i.e., determines the density of the melt). The relative free volume v_f/V increases with temperature, so the melt becomes of more open structure and the distance out to which the particles remain ordered is reduced. Chizmadzhev and Dogonadze have shown that the latter necessarily leads to increased capacitance.

The table gives v_f/V for some fused salts as calculated from (1) by reference to the data of [8] for β and of [9] for α and V.

This shows that vf/V increases from potassium or cesium to sodium or lithium, which agrees with the capacitance results. The vf/V and the C_m for potassium salts are much the same as those for cesium ones and do not vary much, whereas sodium and lithium have rapidly increasing v_f/V and C_m. Figure 2 shows C_m as a function of v_f/V for the chlorides, together with points for isothermal conditions (800°C), which also lie on a smooth curve. There is clearly a functional relation between the capacitance and the free volume, though C_m is probably also dependent on the sizes of the ions.

LITERATURE CITED

1. E. A. Ukshe, N. G. Bukun, and D. I. Leikis, Izv. AN SSSR, Otd. khim. n., 1, 31 (1963).
2. E. Ukshe, N. Bukun, D. Leikis, and A. Frumkin, Electrochim. Acta, 9, 431 (1964)
3. N. G. Bukun and E. A. Ukshe, Zh. prikl. khim., 36, 1965 (1963).
4. O. A. Esin, Zh. fiz. khimii, 30, 3 (1956).
5. Yu. A. Chizmadzhev and R. R. Dogonadze, Summaries of Papers at the Conference on the Physical Chemistry and Electrochemistry of Fused Salts [in Russian], Kiev, Izd. AN USSR, 44 (1963).
6. E. A. Ukshe and N. G. Bukun, Ibid, 25.
7. E. A. Ukshe and Yu. M. Ryabukhin, Izv. AN SSR, Metallurgiya i gornoe delo, 5, 84 (1963).
8. J. O'M. Bockris and N. E. Richards, Proc. Roy. Soc., 241, 44 (1957).
9. E. R. van Artsdalen and J. S. Yaffe, J. phys. Chem., 60, 1125 (1956).