Electrocapillary Curves of Alloys in Fused Salts

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The theory of electrocapillary phenomena for binary alloys was developed by Frumkin[1]. But in aqueous solutions Frumkin and A. Gorodetzkaja could only investigate dilute amalgams and certain low-melting alloys.

To extend the scope of experimental investigation we undertook a study of electrocapillary phenomena for binary alloys in fused salts.

Investigation of the Sn — Zn alloy

At first we investigated the Sn — Zn alloy in two fused electrolytes: the KCl — LiCl eutectic and a KJ — LiJ mixture with 70 molal percent of LiJ. The experimental method was the same as in our investigation of pure metals[2]. In the present case, however, we expressed the interfacial tension not in arbitrary units, but in dynes/cm. The interfacial tension, γ, was calculated by the equation:

$$\gamma = \frac{g}{2} \frac{1}{1/r_1 + 1/r_2} [p - (h_1 - h_2)\,\delta],$$

where g is the acceleration of gravity; r — the radius of the capillary (to determine this radius the capillaries were calibrated with mercury); r_2 — the radius of the wide parts of both limbs of the vessel; p — the pressure of the inert gas in the limb with the metal alloy; h_1 — the height of the electrolyte column over the meniscus of the metal in the capillary; h_2 — the height of the electrolyte column over the surface of the metal in the other limb of the vessel; δ — the specific gravity of the fused electrolyte at 430° C. The specific gravity was determined in the usual way.

[1] A. Frumkin and A. Gorodetzkaja, Z. physik. Chem., 136, 451 (1928).

[2] S. Karpatschoff and A. Stromberg, Z. physik. Chem., (A) 176, 182 (1936).

All experiments were carried out at 430° C. The values of the ohmic potential drop in the capillary at the maxima of the electrocapillary curves are given in Table 1.

From Table 1 it is clear that the ohmic potential drop in the capillary may in most cases be safely neglected. The results of the experiments are represented in Tables 2 and 3. From Tables 2 and 3 it becomes evident that in the KCl — LiCl electrolyte the derivative $\frac{d\gamma}{d\mu_{Tl}}$ (where μ_{Zn} is the thermodynamic potential of Zn in the alloy) changes its sign with the variation of the alloy composition at constant potential of the capillary electrode.

Table 1

Molal percent of Zn	Ohmic potential drop in the capillary in volts	
	Electrolyte KCl — LiCl	Electrolyte KJ — LiJ
0	0.001	0.017
5	—	0.016
10	0.004	0.041
25	0.006	—
50	0.016	—
75	0.002	—
90	0.005	0.027
95	0.004	—

In the case of thallium amalgams in aqueous solutions the derivative $\frac{d\gamma}{d\mu_{Zn}}$ also changes its sign, but only with the variation of the potential.

In connection with the above results it was very interesting to investigate the thallium amalgams in fused KCl—LiCl electrolyte.

Investigation of thallium amalgams

This investigation was carried out at 420° C. At this temperature we were able to study the thallium amalgams in fused KCl — LiCl eutectic from 0 to 100% Tl.

It is clear that at 420° C we had to work with a sealed vessel. This vessel is represented in Fig. 1 in which *1* denotes the capillary; *2* — an iron cylinder with a glass casing. When necessary we immersed this cylinder in the fused metal by means of the magnetic field of a solenoid and thus pressed out the metal from the capillary. We thus could eliminate the breaks in the metal column in the capillary; *3* is a tungsten wire to create contact between the liquid metal in the vessel and the source of e. m. f.; *4* — an iron wire

Table 2

Potential of the capillary electrode in volts	Electrolyte KCl — LiCl. Interfacial tension in dynes/cm.								
	0 mol. % Zn	5 mol. % Zn	10 mol. % Zn	25 mol. % Zn	50 mol. % Zn	75 mol. % Zn	90 mol. % Zn	95 mol. % Zn	100 mol. % Zn
0.0	492	451	438	494	521	522	524	528	700
0.1	507	455	441	499	523	525	527	531	703
0.2	511	457	442	500	524	526	530	533	706
0.3	511	456	442	501	527	528	531	535	714
0.4	501	456	442	501	529	532	532	536	725
0.5	491	454	434	494	526	532	532	538	730
0.6	477	443	422	482	518	523	532	533	730
0.7	468	435	410	471	506	506	514	522	728
0.8	450	429	392	448	487	490	500	503	722
0.9	426	412	375	439	465	486	489	484	707
1.0	413	401	357	425	445	457	465	462	691
1.1	379	391	337	408	436	430	455	454	675
1.2	362	377	321	382	420	414	439	446	661
1.3	342	366	314	—	410	398	433	434	646
1.4	326	361	304	—	406	385	416	415	626
1.5	311	350	—	—	396	375	—	407	617
1.6	299	343	—	—	387	366	—	395	612
1.7	—	—	—	—	—	—	—	388	607
1.8	—	—	—	—	—	—	—	377	607
1.9	—	—	—	—	—	—	—	—	590
2.0	—	—	—	—	—	—	—	388	576

which effected contact between the liquid lead (the auxiliary electrode) and the source of e. m. f.; *5* — the glass capillary which was used to prevent contact between the iron wire and the fused electrolyte.

The tungsten wire *3* was not protected with a glass capillary because the corresponding limb of the vessel contained no fused electrolyte. In the course of the polarization of the capillary electrode we observed the position of the meniscus of the metal in the capillary by means of a cathetometer and in this way determined the variation of the interfacial tension. The diameter of the capillary

Table 3

Potential of the capillary electrode in volts	Electrolytes KJ + LiJ. Interfacial tension in dynes/cm.								
	0 mol. % Zn	5 mol. % Zn	10 mol. % Zn	25 mol. % Zn	50 mol. % Zn	75 mol. % Zn	90 mol. % Zn	95 mol. % Zn	100 mol. % Zn
0.0	391	414	429	438	436	438	453	—	542
0.1	410	419	434	444	439	440	455	—	547
0.2	417	421	435	446	441	441	459	—	553
0.3	425	427	436	455	447	443	464	—	563
0.4	423	429	440	455	458	453	475	—	590
0.5	418	425	439	455	454	464	477	—	604
0.6	412	419	435	444	449	457	474	—	609
0.7	402	412	428	435	445	452	465	—	605
0.8	393	405	424	426	—	431	457	—	594
0.9	388	398	417	414	—	423	444	—	581
1.0	384	393	412	403	—	—	—	—	—
1.1	378	388	—	—	—	—	—	—	—
1.2	374	382	—	—	—	—	—	—	—

was ~ 1 mm. The constancy of the diameter in different points of the capillary was checked.

In these experiments we determined only the change of interfacial tension with polarization. The absolute value of the interfacial tension in the absence of polarization was determined from other experiments in a vessel of the same type but without electrodes. The angle of contact of the amalgam drops with glass in the atmosphere of the mercury vapour considerably exceeds the zero value. Therefore, a layer of fused electrolyte was placed over the metal in the right-hand limb of the vessel. We thus could simplify the experiments and the calculations.

The surface tension γ was calculated by the equation

$$\gamma = \frac{1}{2\,(1/r_1 + 1/r_2)}\left[h_1 g\,(\delta_1 - \delta_2) - h_2 g\delta_2 - 2\gamma_1\left(\frac{1}{r_1} - \frac{1}{r_3}\right)\right],$$

where r_1 is the radius of the capillary; r_2 — radius of the wide limb with the metal; r_3 — radius of the wide part of the limb with the electrolyte; h_1 — difference between the metal levels in the wide

tube and in the capillary; h_2 — difference between the electrolyte levels in the capillary and in the wide part of the same limb; $\gamma = 128.3$ dynes/cm. — the surface tension at the boundary between the fused electrolyte and its vapour; δ_2 — the specific gravity of the electrolyte; δ_1 — the specific gravity of the amalgam, which was calculated on the basis of our experiments according to the law of additivity.

Before each experiment the absorbed gases were removed from the amalgam by boiling it in vacuum at 330° C in a special apparatus with a return cooler. To this apparatus the above-mentioned vessel (Fig. 1) was sealed. After the removal of the absorbed gases, the amalgam, by tilting the whole apparatus, was poured into the above vessel. This vessel was then sealed off from the apparatus. Now the vessel with the electrodes and electrolyte was ready for the experiment, which we carried out in a special electric furnace. The results of the experiments are given in Table 4.

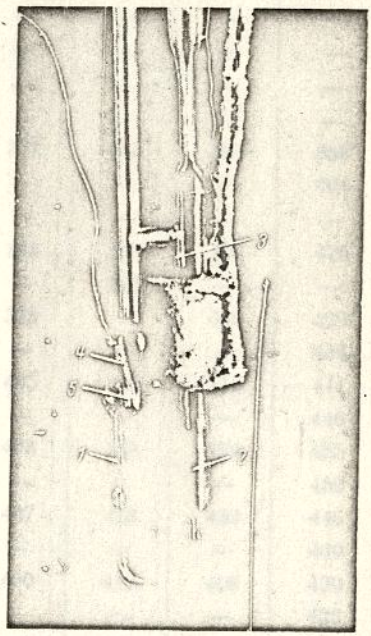

Fig. 1.

The electrocapillary curves for the different amalgams are represented in Fig. 2. The position of the electrocapillary curves in Fig. 2 is the same as with aqueous solutions. All curves practically intersect at one point. On increasing the thallium content the potential for the maximum of the curves is shifted to more negative values. It is very interesting that this displacement is, within the limits of experimental error, the same as that observed by A. Frumkin and A. Gorodetzkaja in aqueous solutions. This fact confirms A. Frumkin's point of view according to which the

Table 4

Potential of the capillary electrode in volts	Interfacial tension in dynes/cm.						
	0 mol. % Tl	2 mol. % Tl	5 mol. % Tl	20 mol. % Tl	40 mol. % Tl	80 mol. % Tl	100 mol. % Tl
+0.60	321	—	—	—	—	—	—
+0.50	347	—	—	—	—	—	—
+0.40	377	—	—	—	—	—	—
+014	386	—	—	—	—	—	—
0.00	387	378	380	377	385	385	388
—0.10	—	—	—	—	—	—	404
—0.14	—	386	389	—	—	—	—
—0.20	387	386	391	388	390	404	416
—0.25	—	—	—	—	393	—	—
—0.30	—	—	—	398	—	416	429
—0.35	—	—	—	—	—	—	436
—0.40	380	383	402	405	412	414	441
—0.50	—	—	—	—	—	—	446
—0.60	373	372	397	408	429	434	455
—0.70	—	—	—	—	—	—	450
—0.80	355	356	—	407	418	433	446
—0.90	—	—	—	—	—	—	440
—1.00	—	339	—	400	412	416	430
—1.10	—	—	—	—	—	—	423
—1.20	—	320	—	388	407	404	—

displacement of the maximum of the electrocapillary curves in this case is caused by the adsorption of thallium on the mercury-electrolyte interface. With Tl-concentrations exceeding 20% the position of the maximum becomes nearly constant. On the basis of the results obtained we calculated the composition of the surface layer of the amalgams for the maxima of the electrocapillary curves. This calculation was carried out as follows:

The values of the derivative $\frac{d\gamma}{d\mu_{Tl}}$ for the maxima of the electrocapillary curves were determined from the $\gamma - \mu_{Tl}$ curves.

The values of the thermodynamic potential of thallium were taken from a paper by Hildebrand and Eastmann[3].

In our case, at a comparatively high temperature, the relation between μ_{Tl} and the amalgam composition is described fairly well

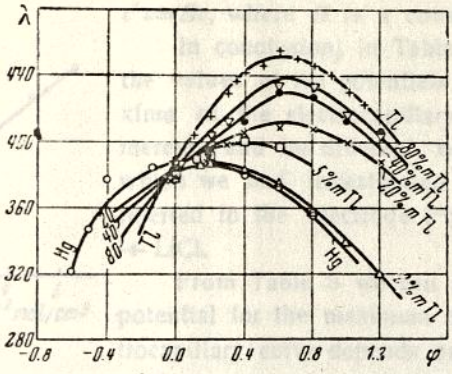

Fig. 2.

by the equation $\mu_{Tl} = \text{const} + b \ln c$, where c is the concentration of thallium in gm. at./cm.[3]. The numerical value of the coefficient b differs little from RT.

The curve in Fig. 3 gives the relation between the Gibbs' surface concentration of thallium, Γ_{Tl}, and its content c in the amalgam, calculated with the help of Gibbs' equation.

Using the numerical value of Γ_{Tl} we calculated the concentration c' of thallium in the surface layer of the amalgam.

The corresponding equation is $\Gamma_{Tl} = (c' - c)\delta$, where δ is the thickness of the surface layer. We took the value of δ from the above-mentioned paper by Frumkin and Gorodetzkaja: $\delta = 6.1 \times 10^{-8}$ cm.

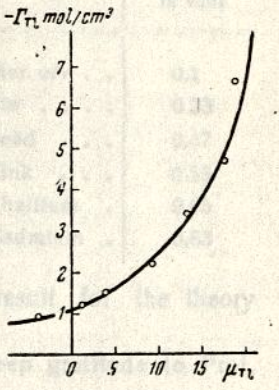

Fig. 3.

[3] Hildebrand and Eastmann, J. Am. Chem. Soc., 37, 2452 (1915).

The dependence of c' on the thallium concentration c in amalgam can be seen in Fig. 4.

It is interesting that over the range of comparatively concentrated amalgams the relation between c' and c closely fits the equation $c' = Bc$, where B is a constant.

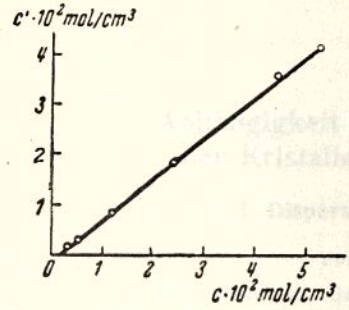

Fig. 4.

In conclusion, in Table 5 we give the values of the potentials for the maxima of the electrocapillary curves for mercury and for different other metals which we had investigated previously, referred to the electrode Pb in KCl + + LiCl.

From Table 5 we can see that the potential for the maximum of the electrocapillary curve depends on the nature of the metal and cannot, therefore, correspond to an absolute zero value.

Table 5

Metals	Potentials for the maxima in volts
Mercury . .	0.1
Tin	0.23
Lead . . .	0.47
Zink . . .	0.55
Thallium .	0.65
Cadmium .	0.63

Summary

The electrocapillary curves for Sn—Zn and Mg—Tl alloys in fused electrolytes were investigated. The interfacial tension as a function of the concentration in the Sn—Zn system shows a minimum.

The electrocapillary curves of Tl-amalgams are very similar to those obtained in aqueous solutions by Frumkin and Gorodetzkaja. The significance of this result for the theory of electrocapillarity is discussed.

In conclusion we wish to express our deep gratitude to Prof. A. Frumkin for his valuable advice.

Sverdlovsk.

Received
February 1, 1940.