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Fig. 1

Figure 1: Fig. 1

Abstract

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Surface Tension of Ternary Metallic Solutions Hg–Cd–K at 22°

(Presented by Academician N. I. Chernyaev, 31 X 1956)

Apparently many phenomena connected with the influence of impurities on the most diverse properties of multicomponent metallic solutions, both in the liquid and in the solid state, may become understandable through the study of the surface tension of multicomponent melts. However, so far, as far as we know, no systematic investigation has been made of the surface tension (σ) even of ternary metallic systems, let alone multicomponent ones; meanwhile, ternary metallic solutions are of greater practical interest than binary ones, since industrial alloys in the overwhelming majority of cases are multicomponent systems. In the few existing studies of the surface tension of multicomponent metallic solutions, for example iron alloys, the influence, as a rule, of additives (1) or gases (2) was studied under the assumption that the basic composition of the alloy remained unchanged.

Proceeding from the molecular theory of surface phenomena developed by V. K. Semenchenko (3,2) for multicomponent solutions, one may expect that adsorption phenomena in ternary metallic solutions will not differ in character from similar phenomena in ternary solutions of other classes. Of particular interest, both from the practical and from the purely theoretical point of view, is the case when, with respect to a given solvent, one of the dissolved metals is surface-active and the other is surface-inactive. This is connected with the fact that, according to V. K. Semenchenko' s theory, any multicomponent system, with respect to the influence of its components on the surface tension of the solution, may be regarded as a "generalized" ternary system.

Fig. 1. Surface tension of the system water–isopropyl alcohol–sodium chloride at 18° according to the data of V. K. Semenchenko (3). Concentration of sodium chloride in mol/l: 1–0.0; 2–1.0; 3–2.0; 4–3.0; 5–4.0

Here it should be expected, in particular, that at a certain concentration of the surface-active component, called by V. K. Semenchenko (5) the buffer concentration, the surface tension of the ternary metallic solution will not depend on the concentration of the surface-inactive

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

component, i.e., in ternary metallic solutions one may expect in this case the presence of the same regularities in the change of surface tension as were observed by Seith ([6]), Palich ([7]), V. K. Semenchenko ([5], [8], [9], [10]), and others in the study of binary dielectric solutions in the presence of electrolytes.

Fig. 2. Surface tension of the system water—isopropyl alcohol—sodium chloride at 18° according to the data of V. K. Semenchenko ([8]). Concentration of isopropyl alcohol in mol/l: 1—0.0000; 2—0.0033; 3—0.0066; 4—0.0131; 5—0.0263; 6—0.0525; 7—0.105. The dashed line corresponds to the buffer concentration of isopropyl alcohol

For example, V. K. Semenchenko ([8]) found that at 18° the isotherms of the surface tension of the system water—isopropyl alcohol—sodium chloride intersect at one point (Fig. 1), which corresponds to an isopropyl alcohol concentration equal to 0.048 mol/l. If the concentration of the surface-active substance (isopropyl alcohol) is chosen as the parameter, then the buffer point in such a system will correspond to the isotherm, denoted by us in Fig. 2 by a dashed line, parallel to the concentration axis of the surface-inactive substance (electrolyte). As is seen from Fig. 2, the surface tension of the solution up to the buffer concentration of isopropyl alcohol increases if the concentration of electrolyte in the solution is increased; at the buffer point, ( ) of the solution does not depend on the electrolyte concentration, while beyond the buffer point addition of electrolyte to the solution leads to a decrease in the surface tension of the solution. An explanation of this phenomenon was given by V. K. Semenchenko in papers ([5], [8]) and others.

Fig. 3. Surface tension of the system mercury—cadmium—potassium at 22° according to the data of P. P. Pugachevich and V. B. Lazarev. Cadmium concentration in at. %: 1—1.6; 2—5.6; 3—7.1

In order to verify the conclusions of V. K. Semenchenko's theory on the generality of the regularities in the change of surface tension in solutions belonging to different classes, we investigated the surface tension of the system Hg—Cd—K. The choice of components of the system under study

was determined by the fact that potassium, as had been shown by many investigators, is surface-active with respect to mercury, whereas cadmium, according to V. K. Semenchenko’ s rule of generalized moments, should have increased the surface tension of mercury, although work (11) seemingly did not confirm this, and on this basis some authors (12) concluded that the rule of generalized

Figure 4

Figure 4: Figure 4

moments is not fulfilled for Hg–Cd solutions.

If our choice of components was correct, then, proceeding from what was said above, in studying the surface tension of the Hg–Cd–K system it should have been possible to find a concentration buffering.

We measured ( ) of Hg–Cd–K solutions at (22^{ }) in P. P. Pugachevich' s combined apparatus (13); in all, 170 amalgams were studied, containing from 0 to 0.620 at. % K and from 0 to 7.15 at. % Cd. As Fig. 3 shows, at a certain potassium concentration, in our experiments approximately equal to 0.040 at. %, the surface tension of the ternary solution does not depend on the concentration of the surface-inactive substance–cadmium. This potassium content in the solution corresponds to the concentration buffer point. For solutions containing potassium in amounts exceeding the buffer concentration, the effect of cadmium on ( ) of the solution becomes the reverse of its effect up to the buffer point; namely, an increase in the cadmium concentration leads to a decrease in the surface tension of the solution.

Fig. 4. Surface tension of the mercury–cadmium–potassium system at (22^{ }), according to the data of P. P. Pugachevich and V. B. Lazarev. Concentration of K in at. %:
(1)–0.0000; (2)–0.000502;
(3)–0.00116; (4)–0.00250;
(5)–0.00554; (6)–0.0126;
(7)–0.0247; (8)–0.0400;
(9)–0.0615; (10)–0.125;
(11)–0.177; (12)–0.350;
(13)–0.540

This is especially clearly seen from Fig. 4, which shows part of the surface-tension isotherms of the amalgams we studied, when the concentrations of the surface-active substance are taken as the parameter; isotherm 8 in this figure corresponds to the buffer concentration of potassium. It is also evident from the figure (isotherm 1) that cadmium, in accordance with V. K. Semenchenko' s rule of generalized moments, increases the surface tension of mercury, i.e., it is surface-inactive on mercury.

Comparison of Figs. 1 and 2 with Figs. 3 and 4, respectively, confirms the conclusion of the molecular theory of surface phenomena, developed by V. K. Semenchenko, concerning the generality of adsorption processes in multicomponent solutions belonging to different classes.

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