PHYSICAL CHEMISTRY

1957

SovietRxiv

Fig. 1. Surface tension of Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%

Figure 1: Fig. 1. Surface tension of Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%

Abstract

Full Text

PHYSICAL CHEMISTRY

P. P. PUGACHEVICH and V. B. LAZAREV

SURFACE PHENOMENA IN TERNARY METALLIC SOLUTIONS Hg—Cd—K, Hg—Cd—Cs AT 22°

(Presented by Academician I. I. Chernyaev, May 16, 1957)

In our work (1) we showed that, in the case of the ternary metallic solution Hg—Cd—K, in which cadmium and potassium exert opposite effects on the surface tension of mercury, the phenomenon of concentration buffering takes place—an analogous phenomenon to that observed in binary dielectric mixtures in the presence of electrolytes.

At the present time, using a combined apparatus (2), we have studied the surface tension (σ) of 135 Hg—Cd—Cs solutions at 22°, containing from 0 to 6.98 at.% cadmium and from 0 to 0.036 at.% cesium, and in this system likewise found concentration buffering (Figs. 1 and 2).

Fig. 1. Surface tension of Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%.

Comparison of the isotherms of the surface tension of ternary metallic solutions (Fig. 1) with the isotherms of aqueous solutions of alcohols in the presence of electrolytes (Fig. 3) makes it possible to obtain additional confirmation of the main conclusion of the molecular theory of surface phenomena developed by V. K. Semenchenko (4–6): namely, the generality of adsorption regularities in multicomponent solutions belonging to different classes.

Indeed, from Figs. 1 and 3 it is evident that in ternary metallic solutions, just as in aqueous solutions of dielectrics in the presence of surface-inactive components, the buffer point shifts toward lower concentrations as, in the given solution, the

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

surface-active—

component is replaced by a component possessing greater surface activity.

Zeit (^{7}) considered that concentration buffering is associated with hydration or, in the general case, with solvation of the molecules of the surface-inactive substance; he assumed, moreover, that the concentration of the surface-active substance in the surface layer does not depend on the content of the surface-inactive component in the system. This explanation, however, cannot be considered satisfactory (^{6}), and it is certainly inapplicable to metallic solutions.

V. K. Semenchenko ($^{4-6}$) developed a molecular theory of surface phenomena in multicomponent solutions, which makes it possible to make qualitative predictions regarding many surface properties of such solutions and, in particular, to explain the phenomenon of concentration buffering.

Fig. 2. Surface tension of Hg—Cd—Cs solutions at 22°. Cesium concentration: 1—0.00000; 2—0.0000025; 3—0.0000041; 4—0.000055; 5—0.00011; 6—0.00028; 7—0.0011; 8—0.0025 at.%

Fig. 3. Surface tension of aqueous alcohol solutions in the presence of NaBr at 18°, according to V. K. Semenchenko and E. A. Davidovskaya (^{3}). NaBr concentration: 1—1.9; 2—0.5; 3—0.0; 4—1.9; 5—0.95; 6—0.0; 7—1.9; 8—0.5; 9—0.0 mol/l

Indeed, starting from the Gibbs adsorption equation and the Gibbs-Duhem relation for ternary real solutions, as well as V. K. Semenchenko' s expression for adsorption (^{6}), it can be shown (^{8}) that the derivative of the surface tension with respect to the concentration of the surface-inactive substance C_{N2}, expressed in atomic fractions, as the concentration of the surface-active additive C_{N1} is increased, i.e. $(\partial\sigma/\partial C_{N1})_{C_{N1}}$, changes its sign, passing through zero. The concentration of the surface-active substance at which $(\partial\sigma/\partial C_{N2})_{C_{N1}} = 0$ corresponds to the buffering concentration:

$$C_{N1}^{\text{buf}} = -\frac{\left[e^{\frac{\gamma}{kT}(m_0-m_2)} - 1\right]\left(1 + C_{N2}\frac{\partial f_2}{\partial C_{N2}}\right)}{\left[e^{\frac{\gamma}{kT}(m_0-m_1)} - 1\right]\frac{\partial f_1}{\partial C_{N2}}}, \tag{1}$$

where m_0, m_1, and m_2 are the generalized moments of the solvent, the surface-active substance, and the surface-inactive substance; f_1 and f_2 are the activity coefficients of the surface-active and surface-inactive substances.

Fig. 4. Adsorption of potassium and cesium in Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%

Figure 4: Fig. 4. Adsorption of potassium and cesium in Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%

As is seen from equation (1), in a ternary system for which $m_0 - m_2 = \text{const}$, on going to substances with greater surface activity the buffer point shifts into the region of lower concentrations, which is also confirmed by the experimental results (Figs. 1 and 3).

From the theory of V. K. Semenchenko it also follows that in a ternary system, one of whose components is surface-active with respect to the solvent and the other surface-inactive, the adsorption of the former is positive and passes through a maximum. This maximum value of the adsorption increases as the concentration of the surface-inactive substance is increased. The theory also asserts that the adsorption maximum of the surface-active substance in such a system will be the greater, the greater the surface activity of the surface-active substance proves to be, whereas the concentration corresponding to this maximum, on the contrary, will decrease with increasing surface activity of the surface-active additive.

Fig. 4. Adsorption of potassium and cesium in Hg—Cd—K and Hg—Cd—Cs solutions at 22°. Cadmium concentration: 1 —6.98; 2 —3.78; 3 —1.32; 4 —7.13; 5 —5.52; 6 —1.61 at.%

By means of graphical differentiation we calculated the adsorption Γ_1^N of the surface-active components in the ternary metallic solutions Hg—Cd—K, Hg—Cd —Cs studied by us, using the formula proposed by V. K. Semenchenko (^{6}),

$$\Gamma_1^N = \frac{1}{RT}\left[C_{N1}\left(\frac{\partial\sigma}{\partial \ln C_{N2}}\right)_{C_{N1}} - (1 - C_{N1})\left(\frac{\partial\sigma}{\partial \ln C_{N1}}\right)_{C_{N2}}\right] \tag{2}$$

and found (see Fig. 4) that the conclusions of V. K. Semenchenko' s theory ($^{4-6}$) concerning adsorption regularities in multicomponent systems, as applied to ternary metallic solutions, are likewise in complete agreement with the experimental results.

Institute of General and Inorganic Chemistry
Academy of Sciences of the USSR

Received
14 V 1957

CITED LITERATURE

1. P. P. Pugachevich, V. B. Lazarev, DAN, **113**, 127 (1957).

2. P. P. Pugachevich, O. A. Timofeevicheva, Zhurn. neorg. khim., **1**, 1387 (1956).

3. W. Ssementschenko, E. Dawidowskaja, Koll. Zs., **73**, 25 (1935).

4. V. K. Semenchenko, Koll. zhurn., **11**, 109 (1949).

5. V. K. Semenchenko, Izv. sekt. fiz.-khimich. analiza, **21**, 14 (1952).

6. V. K. Semenchenko, *Surface Phenomena in Metals and Alloys*, Moscow, 1957.

7. W. Seith, Zs. phys. Chem., **117**, 257 (1925).

8. V. B. Lazarev, V. K. Semenchenko, Izv. AN SSSR, OKhN, 1957, 1252.

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