Thus, the experimental data confirm the hypothesis that the reduction of $PtCl_6^{2-}$ takes place in two stages, with $PtCl_4^{2-}$ as the intermediate. The reduction of $PtBr_6^{2-}$ is also retarded at strongly negative potentials, and the retardation decreases with increasing concentration of the supporting electrolyte. However, polarisation curves for the reduction of $PtBr_6^{2-}$ in electrolyte solutions are complicated by chemical reactions in the bulk of the solution[12].

We thank academician A.N. Frumkin for his advice and interest in this work.

SUMMARY

1. The effect of various electrolytes on the reduction of halide complexes of platinum at a dropping mercury electrode has been investigated and it has been shown that the retardation of the reaction observed at potentials more negative than the zero-charge potential of mercury may be explained as due to repulsion of anions from the negatively charged electrode surface causing a decrease of their concentration in the double layer.
2. Investigation of the rate of reduction as a function of the concentration of the supporting electrolyte and the charge and radius of its cation, together with the observed difference in the effects of surface-active organic cations on the reduction of $PtCl_6^{2-}$, $PtCl_4^{2-}$, and $PtBr_4^{2-}$, showed that the varying sensitivity of the reduction to the additives may be due to the geometry of the anions.
3. The data for the dependence of the rates of reduction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ on the composition of the solution show that the reduction of $PtCl_6^{2-}$ takes place in two stages, *via* $PtCl_4^{2-}$ as the intermediate.

1. H. Laitinen and E. Onstott, J. Amer. Chem. Soc., 72, 7565 (1950).
2. A. N. Frumkin and G. M. Florianovich, Dokl. Akad. Nauk SSSR, 80, 907 (1951); Zhur. Fiz. Khim., 29, 1829 (1955).
3. T. A. Kryukova, Dokl. Akad. Nauk SSSR, 65, 517 (1949).
4. P. Kivalo and H. Laitinen, J. Amer. Chem. Soc., 77, 5205 (1955).
5. P. Kivalo, Suomen Kem., 30B, 209 (1957).
6. A. N. Frumkin and N. V. Nikolajeva, J. Chem. Phys., 26, 1552 (1957).
7. N. V. Nikolaeva-Fedorovich, L. A. Fokina, and O. A. Petrii, Dokl. Akad. Nauk SSSR, 122, 639 (1958).
8. L. Gierst, "Cinétique d'Approche et Réactions d'Electrodes Irréversibles", Bruxelles, 1958.
9. L. Gierst, Enlarged Abstracts of Papers Presented at the Session of the Theoretical Division, Amer. Chem. Soc. Spring Meeting, Philadelphia, May, 1959.
10. A. N. Frumkin, Trans. Faraday Soc., 55, 156 (1959).
11. Z. A. Iofa and A. N. Kolychev, Zhur. Fiz. Khim., 14, 58 (1940).
12. N. V. Nikolaeva and V. N. Presnyakova, Dokl. Akad. Nauk SSSR, 87, 61 (1952).
13. S. Siekierski, Roczniki Chem., 30, 1083 (1956).
14. B. B. Damaskin, Thesis, Moscow State University, 1959.
15. A. N. Frumkin, Uspekhi Khim., 24, 933 (1955).
16. A. N. Frumkin, O. A. Petrii, and N. V. Nikolaeva-Fedorovich, Dokl. Akad. Nauk SSSR, 128, 1006 (1959).

Lomonosov Moscow State University

Received 19th September 1959

ADSORPTION OF TETRA-ALKYLAMMONIUM CATIONS ON MERCURY

B. B. Damaskin and
N. V. Nikolaeva-Fedorovich

Many organic substances are adsorbed at the metal-solution boundary. Early work on the electrocapillary phenomena revealed that the extent of adsorption of neutral organic substances depends on the potential difference between the electrode and the solution and that at high surface charges the organic molecules are desorbed[1,2]. A quantitative theory of the effect of the electric field on the adsorption of neutral molecules was developed by Frumkin[3], who showed that when allowance is made for the force of attraction among the adsorbed molecules, the degree of surface coverage θ and the concentration of the surface-active substance c are related by the following expression:

$$Bc = \frac{\theta}{1-\theta} e^{-2a\theta}, \qquad (1)$$

where a and B are constants at constant electrode potential; a is a measure of the mutual attraction of the adsorbed molecules. When $a = 0$, Eqn. (1) reduces to the Langmuir isotherm. If the adsorbed substance has a high molecular weight, $a > 0$ and the adsorption isotherm is S-shaped. When the interaction among the adsorbed species is very strong, there may be an abrupt change in the degree of coverage as the concentration of the adsorbed substance increases.

It was shown later[5] that differential-capacity measurements constitute a more sensitive method for the study of adsorption of organic substances than electrocapillary measurements. Up to the present much work has been done on the structure of the adsorption layer and also on the kinetics of the adsorption of organic substances on the electrode surface[4-13]. When the adsorption of surface-active organic molecules and ions is not complicated by the formation of multilayers or micellar films, differential-capacity curves may be satisfactorily interpreted on the basis of Frumkin's theory[3], at least for the adsorption of saturated aliphatic compounds. The theory was further developed by Hansen *et al.*[4] who applied it to establish the relation between differential capacity and polarisation and adsorption.

In the present work the differential-capacity method was applied to the adsorption of tetramethylammonium, tetrabutylammonium, and tetraethylammonium cations on a mercury electrode.

EXPERIMENTAL

The differential-capacity measurements were made by means of the previously described impedance bridge[14] on a pendant mercury drop electrode. The auxiliary electrode was a platinum cylinder symmetrically surrounding the mercury drop and the reference electrode was a normal calomel half-cell. All values of the potentials quoted are in volts with respect to the normal calomel electrode. The temperature was 25° ± 0.1°.

The sulphates of the organic cations were prepared as follows. The initial tetra-alkylammonium iodide or

bromide was several times recrystallised from twice-distilled water, and then its solution was stirred for 2 h with freshly prepared silver oxide which had been washed six times with hot twice-distilled water (Ag_2O was prepared by adding 0.1 *N* $AgNO_3$ to 0.2 *N* KOH). The tetra-alkylammonium base obtained was decanted off, titrated, and then neutralised with a solution of twice-distilled H_2SO_4. The neutral solution was kept over mercury for 24 h in order to remove residual Ag^+ ions and only then was employed for the measurements. The other salts used were twice recrystallised from twice-distilled water and ignited.

RESULTS AND DISCUSSION

Fig. 1 shows capacity curves based on measurements in 0.1 *N* tetramethylammonium sulphate and iodide. Comparison with the capacity curves obtained in the presence of inorganic cations[15] shows that adsorption of the $[(CH_3)_4N]^+$ cation leads to a marked lowering of the double-layer capacity. Thus in the tetramethylammonium sulphate solution at a potential ϕ = -1.3 V the differential capacity is 13.2 $\mu F\,cm^{-2}$. When the negative polarisation is increased, the capacity begins to rise slowly, apparently as a result of slight deformation of the tetramethylammonium cations. From Fig. 1 it is evident that when the potentials are sufficiently negative, iodide anions are expelled from the double layer and the differential-capacity curves for tetramethylammonium iodide and sulphate solutions merge. In this respect they resemble analogous capacity curves for solutions of the fluorides and iodides of sodium and caesium[15]. However, the potential, ϕ, at which the I^- ion ceases to affect the differential-capacity curves is much more negative for the tetramethylammonium cation than for the inorganic cations. Thus, in 0.1 *N* solutions in the presence of Na^+, ϕ = -1.2 V; for Cs^+, ϕ = -1.45 V; and for $[(CH_3)_4N]^+$, ϕ = -1.70 V. This result indicates an increase in the preferential adsorption on going from the tetramethylammonium cation to the caesium cation.

By analogy with the tetramethylammonium cation, it might have been expected that the enhanced capacity due to the iodide anion in the presence of the tetraethylammonium cation would persist at even more negative potentials. However, this is not so. The $C-\phi$ curves obtained for 0.1 *N* tetraethylammonium sulphate, bromide, and iodide solutions are plotted in Fig. 2, from which it is evident that the introduction of the more strongly adsorbed anion is accompanied in this case by an initial lowering of the capacity which increases again only at more negative potential, so that the capacity curves for the various anions intersect twice. This result indicates that within a certain potential range the tetraethylammonium cations in the double layer are closer to the mercury surface than the I^- anions. The preferential adsorption of the iodide anions increases the specific adsorption of the tetraethylammonium cations which lowers the differential capacity. At more negative potentials the anions are expelled from the dense part of the double layer and the electrical state of the mercury surface, determined by its charge, becomes the same for all the solutions. Thus desorption of iodide anions is accompanied by the desorption of part of the tetraethylammonium cations. This process should lead to the appearance of pseudocapacity, which is in fact responsible for the increase in the differential capacity at very negative polarisations.

The differential-capacity curve for a solution of a tetrabutylammonium salt alone, differs sharply from those obtained for the corresponding solutions of tetramethyl- and tetraethyl-ammonium salts. The $C-\phi$ curve for a 0.1 *N* solution of $[(C_4H_9)_4N]Br$ approximately 15–20 sec after formation of a new mercury drop, is plotted in Fig. 3, from which it is clear that over a wide potential range there is a lowering of the capacity of the double layer to values of the order of 5 $\mu F\,cm^{-2}$, due to adsorption of the large organic cation on the mercury surface. At potentials more negative than -1.7 V, the rise of the differential capacity begins and at ϕ = -2.3 V the curve passes through a maximum at which the capacity is about 29 $\mu F\,cm^{-2}$. However, the values of the differential capacity measured in this potential range are not entirely reliable because of their strong dependence on the time elapsed from the moment of formation of a clean mercury surface. Curve *2*

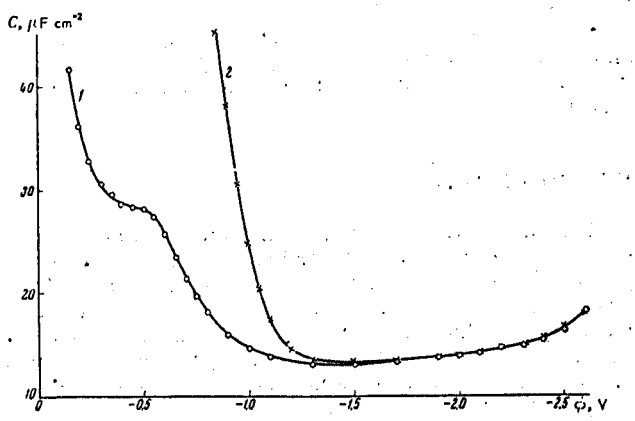

Fig. 1. Differential-capacity curves in 0.1 *N* solutions: 1) $[(CH_3)_4N]_2SO_4$; 2) $[(CH_3)_4N]I$; frequency 1000 c/s.

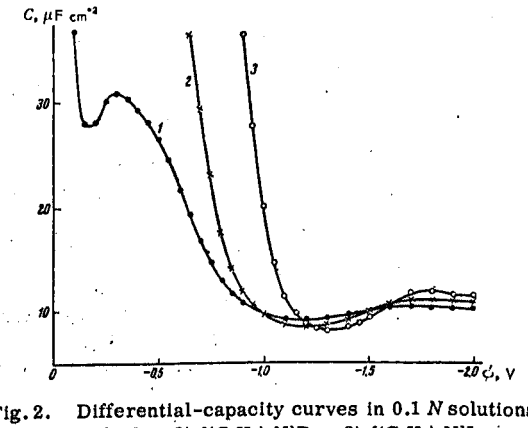

Fig. 2. Differential-capacity curves in 0.1 *N* solutions: 1) $[(C_2H_5)_4N]_2SO_4$; 2) $[(C_2H_5)_4N]Br$; 3) $[(C_2H_5)_4N]I$; frequency 1000 c/s.

in Fig. 3 represents values of the capacity obtained when a mercury drop has been maintained for a long time (30 min) at a given potential. It is seen that at strongly negative polarisation the capacity falls to values of the order of (1–2) $\mu F\,cm^{-2}$. Such low values of the capacity were obtained by Melik-Gaikazyan in the case of multimolecular adsorption of n-hexyl and n-octyl alcohols[7]; he found that the formation of multimolecular layers also required a long time, of the order of tens of minutes. It appears that the sharp lowering of the capacity with time which occurs in pure solutions of tetrabutylammonium salts at strongly negative polarisations is caused by the formation of multimolecular layers on the mercury surface, but the nature of such layers remains obscure and requires further investigation. It is possible that here we have adsorption of products of slow chemical reactions taking place in solutions of tetrabutylammonium salts near the negatively polarised electrode.

Apart from the adsorption of tetra-alkylammonium cations from pure solutions of their salts, we have also investigated their adsorption on mercury from mixtures with various electrolytes. Fig. 4 shows differential-capacity curves for 0.01 N sodium sulphate solution alone and also in the presence of 0.001 and 0.01 N tetramethylammonium sulphate. The results show that addition of the tetramethylammonium cation increases the capacity at the minimum in the $C-\phi$ curve near the zero-charge point, and also at the maximum at somewhat more negative potentials. Thus the capacity at the minimum in 0.01 N Na_2SO_4 alone and with 0.001 N and 0.01 N $[(CH_3)_4N]_2SO_4$ added is 14.4, 16.2, and 20.0 $\mu F\,cm^{-2}$ respectively. The increase in the capacity at the minimum of the $C-\phi$ curve is due to a decrease in the diffuseness of the double layer as a result of the marked specific adsorption of the tetramethylammonium ions. Such increase in the differential capacity at the minimum near the zero-charge point under the influence of the specific adsorption of chloride, bromide, and iodide anions was first observed by Vorsina and Frumkin[16]. They found that the capacity increased on going from Cl^- to I^-, the minimum itself being displaced towards more negative

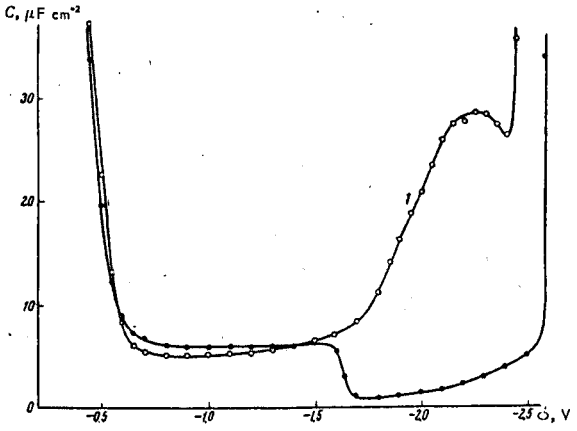

Fig. 3. Differential-capacity curves in 0.1 $N[(C_4H_9)_4N]Br$:
1) 15–20 sec after formation of a new mercury drop;
2) 30 min after formation of a new mercury drop;
frequency 1000 c/s.

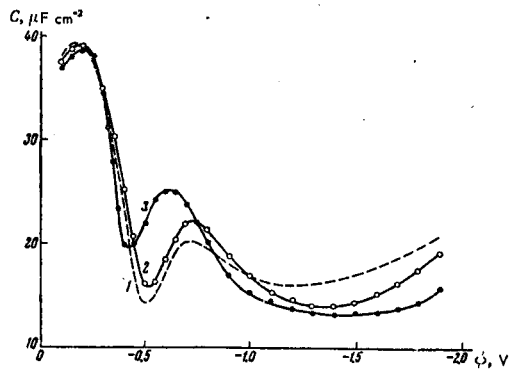

Fig. 4. Differential-capacity curves:
1) in 0.01 N Na_2SO_4;
2) in 0.01 N Na_2SO_4 + 0.001 N $[(CH_3)_4N]_2SO_4$;
3) in 0.01 N Na_2SO_4 + 0.01 N $[(CH_3)_4N]_2SO_4$;
frequency 400 c/s.

potentials. It was to be expected that adsorption of tetramethylammonium cations would cause a positive shift in the capacity minimum, and in fact in the presence of 0.01 N tetramethylammonium sulphate the minimum in the capacity curve near the zero-charge point is at a potential approximately 70 mV more positive than for a pure solution of Na_2SO_4 (Fig. 4).

Fig. 4 shows that at negative potentials the addition of tetramethylammonium sulphate lowers the measured capacity. Thus at ϕ = -1.4 V in a 0.01 N Na_2SO_4 + 0.01 N $[(CH_3)_4N]_2SO_4$ solution the capacity is 13.35 $\mu F\,cm^{-2}$. The lowering of the capacity at negative potentials is due to increasing coverage of the surface by $[(CH_3)_4N]^+$ ions, because in a pure 0.1 N tetramethylammonium sulphate solution the capacity at these potentials is about 13.2 $\mu F\,cm^{-2}$ (Fig. 1). The subsequent increase in the capacity at strongly negative polarisations is due to partial desorption of the tetramethylammonium cations from the mercury surface and their replacement by sodium cations.

Analogous results were obtained when tetramethylammonium sulphate was added to 0.01 N Na_2SO_4 solution (Fig. 5). Here, too, there is a decrease in the capacity at the minimum near the zero-charge point and a positive shift of the minimum. It is notable that the effect of the additive is appreciable at much lower concentrations of $[(C_2H_5)_4N]_2SO_4$ (10^{-4} N); The influence of the tetraethylammonium cation on the capacity is much stronger than that of the tetramethylammonium cation at the same concentration. The capacity at the minimum in the presence of 0.001 N tetraethylammonium sulphate is 21.4 $\mu F\,cm^{-2}$ and when the concentration of the additive is 0.01 N the minimum is virtually absent. The results indicate a greater specific adsorbability of the tetraethylammonium cation compared with the tetramethylammonium cation. On the other hand, with tetraethylammonium salts the organic cation is desorbed from the mercury surface to a greater extent at strongly negative polarisation. When the concentration of the additive is 10^{-4} N at ϕ = -1.9 V, the differential-capacity curve coincides with that obtained for pure Na_2SO_4 solution, which indicates complete replacement of the organic cations by sodium cations in the double layer. In the presence of

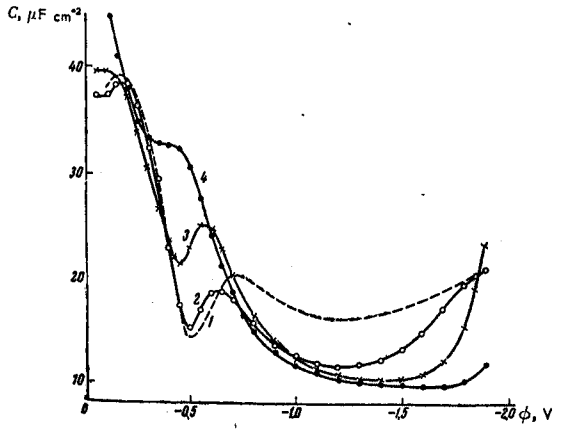

Fig. 5. Differential capacity curves:
1) in 0.01 N Na_2SO_4;
2) in 0.01 N Na_2SO_4 + 0.0001 N $[(C_2H_5)_4N]_2SO_4$;
3) in 0.01 N Na_2SO_4 + 0.001 N $[(C_2H_5)_4N]_2SO_4$;
4) in 0.01 N Na_2SO_4 + 0.01 N $[(C_2H_5)_4N]_2SO_4$;
frequency 400 c/s.

0.001 N additive the differential-capacity curve has a characteristic desorption peak; however, the descending branch of the peak cannot be realised, since at more negative potentials there is a sharp rise in the capacity due to the discharge of the sodium cations.

In the presence of the tetrabutylammonium cation the differential-capacity curve assumes a form characteristic of solutions containing small quantities of neutral organic compounds. There is a section on the curve corresponding to the adsorption of the large organic cation, characterised by low values of the capacity of the order of 5 $\mu F\,cm^{-2}$, bounded on either side by desorption peaks (see Fig. 5 in ref. 12). An interesting peculiarity of the capacity curves obtained for 0.01 N Na_2SO_4 solution containing tetrabutylammonium sulphate is the presence of a small maximum at negative potentials immediately before the desorption of the organic cations from the mercury surface. The height of the maximum grows with the increase in the concentration of the additive and the maximum itself is displaced towards negative potentials (see Fig. 5c in ref. 12). Fig. 6*a* shows the negative branch of the capacity curve at 400, 1000, and 10000 c/s in a 0.01 N Na_2SO_4 + 0.001 N $[(C_4H_9)_4N)]_2SO_4$ solution. It is evident that the differential capacity depends on the frequency not only at the desorption peak but also at potentials corresponding to the capacity maximum mentioned above. The lowering of the capacity at the maximum when the frequency is changed from 400 to 10000 c/s amounts to 1.20 $\mu F\,cm^{-2}$. This result indicates that the maximum in the $C-\phi$ curves is due to the pseudocapacity caused by a process in the electrical double layer at the given potentials. Such a process may be a change in the nature of the adsorption of tetrabutylammonium cations on the mercury surface, apparently, as a result of their deformation. Only at potentials at which there is an increase in the capacity in the $C-\phi$ curves does the tetrabutylammonium cation increase the rate of the electrochemical reduction of the $PtCl_4^{2-}$ anion[17]. Before the potential corresponding to the capacity maximum the positive charge of the cation is situated at a considerable distance from the electrode surface and does not influence the rate of reduction of $PtCl_4^{2-}$, because the anion has a planar configuration and approaches close to the electrode. To increase the rate of its reduction, it is necessary that the centre of the positive charge on the tetrabutylammonium cation should come closer to the electrode surface. For this reason, the observed increase in the current in the $I-\phi$ curves for the reduction of $PtCl_4^{2-}$ at potentials corresponding to the capacity maximum confirms the hypothesis that the tetrabutylammonium cation is deformed under the action of the strong electric field.

Fig. 6*b* represents the negative branches of differential-capacity curves for 0.01 N solutions of KCl, KBr, and KI in the presence of 0.001 N tetrabutylammonium sulphate. It is evident that the height and position of the capacity maximum depend on the nature of the anion, and that on going from Cl^- to I^- the capacity at the maximum increases and the maximum undergoes a negative displacement. This shows that the tetrabutylammonium cations specifically adsorbed at very negative potentials entrain surface-active anions in the double layer which in turn induces further adsorption of the tetrabutylammonium cations. The higher the surface activity of the anion, the greater the additional adsorption of the tetrabutylammonium cation. For this

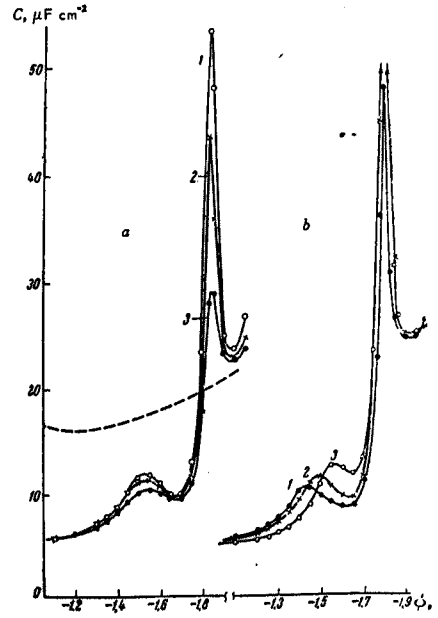

Fig. 6. Differential-capacity curves:
a) in 0.01 N Na_2SO_4 + 0.001 N $[(C_4H_9)_4N]_2SO_4$ at various frequencies:
1) 400 c/s;
2) 1000 c/s;
3) 10000 c/s; broken curve — 0.01 N Na_2SO_4;
b) in 0.001 N $[(C_4H_9)_4N]_2SO_4$ + 0.01 N halide:
1) KCl;
2) KBr;
3) KI; frequency 400 c/s.

reason, on going from Cl^- to I^- the changes in the differential-capacity curve correspond qualitatively to the increase in the concentration of the tetrabutylammonium cations; there is an increase in the capacity at the maximum and a negative shift of the maximum itself.

The entrainment of the anions in the electrical double layer under the influence of the strong specific adsorption of the tetrabutylammonium cations is also evidenced by the differential capacity in 1 *N* solutions of K_2SO_4, KCl, KBr, and KI in the presence of 0.001 *N* $[(C_4H_9)_4N]_2SO_4$. The negative branches of the capacity curves are shown in Fig. 7. The form and the frequency dependence of the desorption

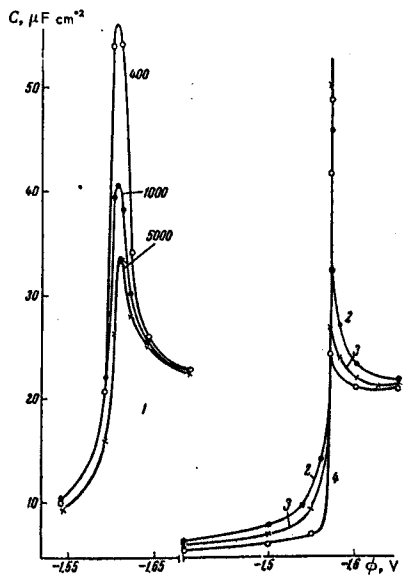

Fig. 7. Differential-capacity curves in 0.001 *N* $[(C_4H_9)_4N]_2SO_4$ and 1 *N* supporting electrolyte:
1) K_2SO_4 (400, 1000, and 5000 c/s);
2) KCl;
3) KBr;
4) KI; frequency 1000 c/s.

peak for the SO_4^{2-} anion differ little from those obtained in the adsorption of neutral organic compounds on mercury[7], although the capacity peak itself is at much more negative potentials for the adsorption of the organic cation. On going from Cl^- to Br^- and I^-, the form of the peak alters substantially: the higher the surface activity of the anion, the sharper the peak. Thus a definite value of the differential capacity at the peak potential cannot be obtained in the presence of iodide, even when very low amplitudes of the alternating currents (0.1 mV) are employed. This result may be explained as follows. It is seen from the right-hand part of Fig. 7 that at potentials both more positive and more negative than that corresponding to the desorption peak, the differential capacity in the presence of I^- is lower than in the presence of Cl^- and Br^- †. This means that even at concentrations as low as 0.001 *N* the specifically adsorbed tetrabutylammonium cations entrain the surface-active anions in the double layer, inducing additional adsorption of the tetrabutylammonium cations, the latter increasing in the same order as the surface activity: $Cl^- < Br^- < I^-$. As a result there is an increase in the interaction among the adsorbed tetrabutylammonium cations which are now more firmly bound together by the entrained anions. For this reason instead of desorption in some, albeit narrow, potential range, in the presence of iodide there is a sudden breakdown of the adsorption layer at a well-defined potential (ϕ = -1.57 V)[18]. According to Frumkin[3], in such a case a sudden change in the degree of surface coverage is to be expected when the concentration of the adsorbed substance increases [see Eqn. (1)]. In fact isotherms of this form were obtained by Frumkin and Damaskin[19] for the adsorption of the tetrabutylammonium cation from 1 *N* solutions of KI.

We express our gratitude to Academician A. N. Frumkin for a thorough examination of the manuscript and for valuable advice.

SUMMARY

1. Differential-capacity curves have been obtained for solutions containing tetramethylammonium, tetraethylammonium, and tetrabutylammonium cations. Replacement of an inorganic cation by a large organic cation lowers the capacity of the double layer, which for the tetramethylammonium cation is ~13 μF cm^{-2}, for tetraethylammonium ~10 μF cm^{-2}, and for tetrabutylammonium ~5 μF cm^{-2}.
2. All the cations investigated possess marked specific adsorbability on the mercury surface, which grows with increase in the number of carbon atoms.
3. In dilute solutions containing tetrabutylammonium cations the capacity curve has, at negative potentials, a small maximum before the desorption peak. The presence of the maximum has been explained by pseudocapacity due to the deformation of the tetrabutylammonium cation.
4. At strongly negative potentials the tetrabutylammonium cations entrain surface-active anions in the double layer. This enhances the attractive interaction among the adsorbed cations.

† Since at more negative potentials the electrical state of the mercury surface, determined by its charge, becomes the same for all the solutions, the height of the peak in KI solution should be much greater than in KCl and KBr solutions. However, it is impossible to measure these high values of the capacity, because the desorption peak degenerates to a vertical line and even small amplitudes of the alternating current (0.1 mV) cause undesirable averaging of the capacity with respect to the potential.

1. G. Gouy, Ann. Chim. Phys., 8, 291 (1906); 9, 75 (1906).
2. A. N. Frumkin, "Elektrokapillyarnye Krivye i Elektrodnye Potentsialy" (Electrocapillary Curves and Electrode Potentials), Odessa, 1919.
3. A. N. Frumkin, Trudy Inst. im. Karpova, No. 5, 3 (1926); No. 4, 56 (1925); Z. Physik, 35, 792 (1926).
4. R.S. Hansen, R.E. Minturn, and D.A. Hickson, J. Phys. Chem., 60, 1185 (1956); 61, 953 (1957).
5. M. A. Proskurnin and A. N. Frumkin, Trans. Faraday Soc., 31, 110 (1935).
6. A. Ksenofontov, M. Proskurnin, and A. Gorodetskaya, Zhur. Fiz. Khim., 12, 408 (1938).
7. V. I. Melik-Gaikazyan, Zhur. Fiz. Khim., 26, 560, 1184 (1952).
8. V. L. Kheifets, B. S. Krasikov, V. V. Sysoeva, and I. V. Guseva, Vestnik Leningrad. Gos. Univ., Ser. Fiz. Khim., No. 22, 128 (1956); No. 4, 127, 148 (1957).
9. J. R. Miller and D. C. Grahame, J. Amer. Chem. Soc., 78, 3577 (1956); 79, 3006 (1957).
10. W. Lorenz and F. Möckel, Z. Elektrochem., 60, 507 (1956); W. Lorenz, Z. Elektrochem., 62, 192 (1958); Z. phys. Chem. (BRD), 18, 1 (1958).
11. H. A. Laitinen and B. Mosier, J. Amer. Chem. Soc., 80, 2363 (1958).
12. N. V. Nikolaeva-Fedorovich and B. B. Damaskin, "Trudy Soveshchaniya po Voprose Vliyaniya Poverkhnostno-Aktivnykh Veshchestv na Elektroosazhdenie Metallov" (Proceedings of the Conference on the Effect of Surface-Active Substances on the Electrodeposition of Metals), Vilna, 1957, p. 33.
13. P. Delahay and P. Trachtenberg, J. Amer. Chem. Soc., 79, 2355 (1957).
14. B. B. Damaskin, Zhur. Fiz. Khim., 32, 2199 (1958).
15. B. B. Damaskin, N. V. Nikolaeva-Fedorovich, and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 121, 129 (1958).
16. M. A. Vorsina and A. N. Frumkin, Zhur. Fiz. Khim., 19, 171 (1945).
17. N. V. Nikolaeva-Fedorovich, L. A. Fokina, and O. A. Petrii, Dokl. Akad. Nauk SSSR, 121, 639 (1958).
18. A. N. Frumkin, B. B. Damaskin, and N. V. Nikolaeva-Fedorovich, Dokl. Akad. Nauk SSSR, 115, 751 (1957).
19. A. N. Frumkin and B. B. Damaskin, Dokl. Akad. Nauk SSSR, 129, 862 (1959).

Lomonosov Moscow State University

Received 19th September 1959

EXPERIMENTAL

The structure of specimens, which had previously been subjected to homogenisation and plastic deformation with high degree of annealing was investigated by X-ray diffraction. The controversial concentration range was especially thoroughly investigated.

The alloys, prepared from aluminium of A00 grade and zinc of TsV grade, contained 10.0, 20.0, 30.0, 40.0, 50.0, 55.0, 58.0, 60.0, 64.0, 66.0, 69.0% Zn, and then at 0.5% intervals up to 80.0% of zinc. The specimens were cast in a graphite mould, homogenised at 350° for 168 h, cold worked to 50% deformation, annealed at 350° for 2 h, and cooled in the furnace.

The X-ray investigation was carried out by the back-reflection method without rotation at 25°, 100°, 200°, 250°, 275°, 300°, 320°, 340°, 360°, and 380°, and in some cases also at 345°, 348°, 353°, 358°, and 400°. The temperature was controlled to ±2° by means of an EPD-12 valve potentiometer.

The maximum error in the determination of the lattice parameters was ±0.0004 kX, *i.e.* about ten times smaller than in the experiments of Petrov and Badaeva[10] who employed the Debye–Scherrer method. Copper $K\alpha$ radiation was used; the current intensity was 15 μA [mA? (Ed. of Translation)] and the voltage 40 kV.

In the present article only data relevant to the concentration range in which we are interested are reported. The results are shown in Figs. 1–3.

Fig. 1 shows plasticity isotherms from 320° to 400° for the alloys containing from 60 to 76% Zn. They reveal the presence of a monotectoid dome with a maximum at about 60% Zn. However, even at concentrations near 70% Zn there is a break in the solubility and the lattice parameter changes suddenly on passing from the alloy containing 69.5% Zn to one containing 70.0% Zn. The change in the parameter is 0.0012 kX, *i.e.* much larger than the maximum experimental error. In addition, a considerable difference in the concentration dependence of the lattice parameters (the slope of the curves) is observed.

THE ALUMINIUM–ZINC PHASE DIAGRAM

A. A. Presnyakov, Yu. A. Gorban',
and V. V. Chervyakova

At present there are two versions of the aluminium–zinc phase diagram, which differ from one another in the zinc concentration range 50–85% at temperatures higher than 275°. The phase diagram has been discussed by many authors[1–11]. The data obtained in the study of the hyperplasticity of the aluminium–zinc eutectoid constitute indirect evidence that the phase diagram includes a peritectic reaction[12]. In the present work we have made a thorough study of aluminium–zinc alloys.

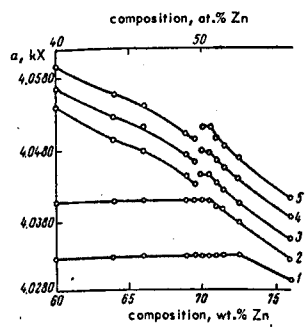

Fig. 1. Composition dependence of the lattice parameter of aluminium–zinc alloys at various temperatures: 1) 320°; 2) 340°; 3) 360°; 4) 380°; 5) 400°.