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ELECTROCAPILLARY PHENOMENA ON GALLIUM*

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Abstract—The electrocapillary curves and the differential capacitance of liquid gallium have been determined in solutions containing H^+, Li^+, Na^+, K^+ and Ca^+ cations, ClO_4^-, SO_4^{2-}, Cl^-, Br^-, I^- and CNS^- anions, and in the presence of aliphatic alcohols. Conclusions concerning the structure of the gallium/aqueous-solution interface as compared with that of the mercury/solution interface are drawn.

Résumé—Les courbes électrocapillaires et la capacité différentielle ont été déterminées dans les solutions contenant les cations H^+, Li^+, Na^+, K^+ et Cs^+ et les anions ClO_4^-, SO_4^{2-}, Cl^-, Br^-, I^- et CNS^-, ainsi qu'en presénce des alcohols aliphatiques. La structure de l'interface gallium/solution aqueuse a été comparée à la structure dans le cas du mercure.

Zusammenfassung—Die Elektrokapillarkurven und die differentielle Kapazität einer flüssigen Ga-Elektrode wurden bestimmt in Lösungen, welche die H^+, Li^+, Na^+, K^+ und Cs^+ Kationen, die ClO_4^-, SO_4^{2-}, Cl^-, Br^-, I^- und CNS^- Anionen, sowie aliphatische Alkohole enthielten. Der Bau der Grenzflächenschicht an der Trennfläche Gallium-wässerige Lösung wurde mit dem an der Trennfläche Quecksilber-wässerige Lösung verglichen.

UNTIL now accurate quantitative data on the structure of the electric double layer in aqueous solutions have been available only for mercury and amalgam electrodes. Some studies on the electrocapillary properties and capacitance measurements of a gallium electrode[1–3] were made using gallium of insufficient purity, which greatly affects its surface properties. Most of the results of the present investigation were obtained using gallium with the 99·9998 per cent purity, purified by the method of the Institute of Rare Metals, Moscow. Some measurements were made with gallium from Eagle Picher, U.S.A., designated in the text as gallium.[1]

EXPERIMENTAL TECHNIQUE AND RESULTS

We have measured differential capacitance curves for a dropping gallium electrode in Na_2SO_4, $NaClO_4$, LiCl, NaCl, KCl, CsCl, KI, KCNS solutions at 30°C over the frequency range from 318 c/s to 80 Kc/s. To prevent the formation of an oxide film on gallium, on the one hand, and to obtain the maximum shift of the region where hydrogen evolution starts in the direction of more negative potentials on the other, different sections of the capacitance curve were measured in solutions with different pH, as previously.[1] In the potential range from $-1·9$ to $-1·2$ V (nce) the measurements were carried out in neutral solutions of salts; in the range from $-1·3$ to $-1·1$ V, in solutions acidified to 0·01 N; and from $-1·15$ V and more positive potentials, in solutions acidified to 0·1 N. Acidification was carried out using the acid with the same anion, except in the case of KI and KCNS solutions, which were acidified with HCl. The overall concentration of the electrolyte was 1 N. To plot the total differential capacitance curve from its sections those values of C were used, which within the pH range of the solutions employed did not depend upon pH. The maximum shift in the direction of positive potentials was limited by the beginning of

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oxide-film formation, which was accompanied by a sharp decrease in the capacitance. The formation of an adsorption layer of oxygen, preceding that of the phase oxide, should have been accompanied by a capacitance increase, but we failed to observe this effect. Other experimental details are given elsewhere.[4] The results of the measurements are given in Figs. 1 and 2 (potentials against nce). It is seen from Fig. 1 that at

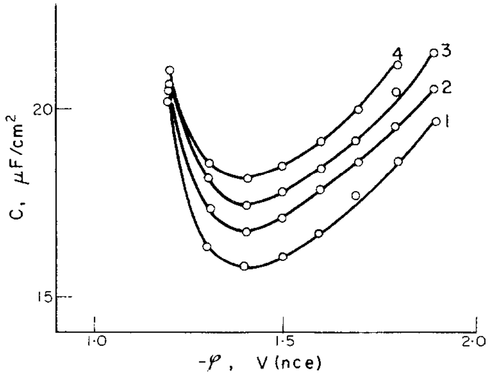

FIG. 1. Dependence of the differential capacitance of gallium upon potential at negative potentials in 1 N solutions.
1, LiCl; 2, NaCl; 3, KCl; 4, CsCl.

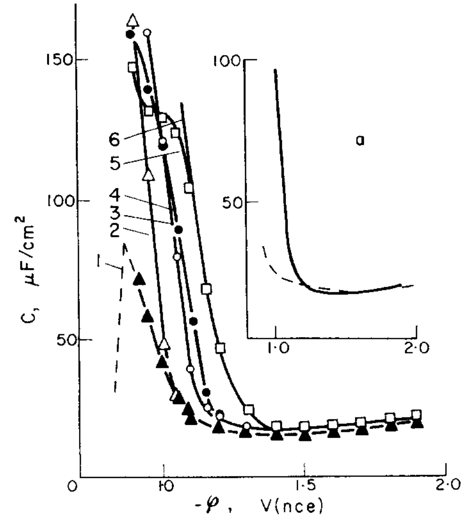

FIG. 2. Dependence of the differential capacitance of gallium upon the potential in 1 N solutions.
1, $NaClO_4$; 2, Na_2SO_4; 3, KCl; 4, KBr; 5, KI, 6, KCNS.
- - -, Grahame's data for 0·1 N KCl.

negative potentials, corresponding to the region of adsorption of cations, the differential capacitance increases with the transition from Li^+ to Cs^+. In solutions containing different anions but the same cation (Fig. 2), at negative potentials the differential capacitance curves practically merge. At potentials corresponding to the beginning of the adsorption of anions, the capacitance starts rapidly to increase; the sequence $ClO_4^- < SO_4^{2-} < Cl^- < Br^- < I^- < CNS^-$ is observed. The capacitance measured did not depend upon the frequency within the frequency range used, and consequently was a true measure of the electric double layer capacitance. The absence of capacitance dispersion points to the irreversibility of the process of gallium dissolution, which is indeed observed in the region of more positive potentials.

At still more positive potentials, the differential capacitance curve for KI solution shows an arrest, similar to the "hump" observed on the differential capacitance curves for mercury near the potential of zero charge. The same arrest is observed also in the case of 4 N LiCl; a hump appears with 8 N LiCl. The decrease in the capacitance in a $NaClO_4$ solution, shown in Fig. 2, seems to be due to the formation of a phase oxide film on the electrode surface.[1] A similar capacitance decrease was observed in all the solutions investigated. In the vicinity of the potentials corresponding to the decrease, the capacitance measured begins to depend upon the frequency, which is probably due to the appearance at these potentials of the pseudocapacitance of the process of gallium dissolution.

The C/φ curves for Ga in 0·1 N KCl obtained in the present paper (solid line) and those obtained previously[3] (dotted line) are compared in Fig. 2(a). At negative potentials there is a satisfactory coincidence between the values of C, but at more positive potentials the capacitance measured by us was much larger. At present it is impossible to suggest the reason of this discrepancy.

By the integration of the differential capacitance curves, we obtain plots for the dependence of the charge density on gallium upon the potential in solution of different composition. The constant of integration was determined from the charging current flowing to the gallium dropping electrode in 1 N KCl solution, thoroughly freed of O_2, at the potential $-1{\cdot}45$ (nce), at which gallium practically behaves as an ideally polarizable electrode. As is clear from Fig. 2, at this potential the capacitance of the gallium electrode does not depend on the nature of the anion in the solution. The results of this calculation are presented in Fig. 3. In the same figure we also see the ε/φ curve (shown with a dotted line) for the mercury electrode in 1 N Na_2SO_4 solution.

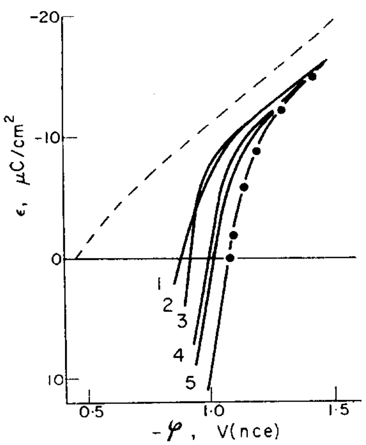

FIG. 3. Dependence of the charge density ε of gallium upon the potential in 1 N solutions.

1, $NaClO_4$; 2, Na_2SO_4; 3, KCl; 4, KBr; 5, KI.

— · — · —, KCNS, - - - , ε/φ curve for mercury in 1 N Na_2SO_4.

Upon transition from Li^+ to Cs^+, the capacitance on gallium increases in the same sequence as on mercury: $C_{Li^+} < C_{Na^+} < C_{K^-} < C_{Cs^+}$. At more positive potentials than $-1 \cdot 2$ V (nce), the increase in the capacitance on gallium in all the solutions investigated is much greater than in the case of mercury. Thus, at the point of zero charge the differential capacitance in 1 N Na_2SO_4 is $C_{Ga} = 135\ \mu F/cm^2$, compared with $C_{Hg} = 29 \cdot 5\ \mu F/cm^2$.

It is clear from the ε/φ curve that on Ga in all solutions investigated, ε in the vicinity of the point of zero charge increases with the electrode potential much more rapidly than on Hg. The increase in ε slows down with the distance from the point of zero charge and becomes the same as on Hg. The distance between parallel sections of the ε/φ curves on Ga and Hg is *ca* 0·17 V.

In the presence of aliphatic alcohols, the C/φ curves of Ga show a cathodic desorption peak, as first observed by Leikis.[5] In Fig. 4 are given the C/φ curves for

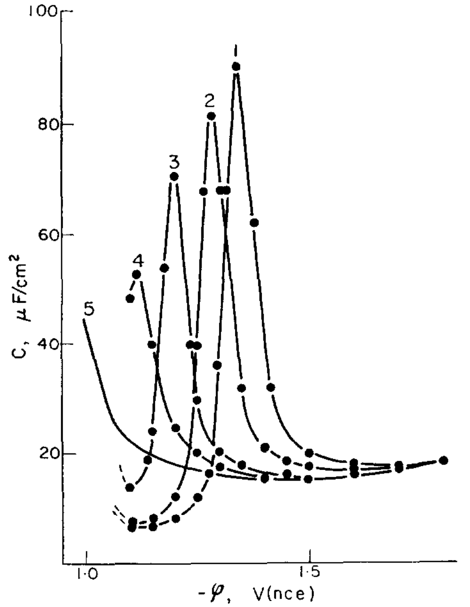

FIG. 4. Dependence of the differential capacitance of gallium upon the potential in 1 N Na_2SO_4 + tert. $C_5H_{11}OH$ solutions.
Concentration of t-$C_5H_{11}OH$: 1, 0·3 m; 2, 0·2 m; 3, 0·1 m; 4, 0·05 m; 5, 0.
Ac frequency 318 Hz.

tert. amyl alcohol with N Na_2SO_4 a supporting electrolyte. The differential capacitance curves have a shape characteristic of the C/φ curves on mercury. We could not measure the anodic desorption peaks owing to the oxidation of gallium at the relevant potentials. At the potentials of maximum adsorption, the capacitance values are higher than in the case of mercury. Thus, the minimum capacitance on gallium for n-propyl alcohol is 9 $\mu F/cm^2$, and on mercury[6] 5 $\mu F/cm^2$.

The region of adsorption on gallium is much narrower and sharply asymmetrical relative to the potential of maximum adsorption, which is accounted for by a much faster increase in the positive charge on gallium with rising φ, as compared to that on mercury.

It is interesting that at the potential of maximum adsorption, the capacitance of gallium for not very large alcohol concentrations depends on the ac frequency.

The measurements of the electrocapillary curves were performed with a small size Gouy capillary electrometer at 36°C. This technique is described in more detail elsewhere.[7]

A number of electrocapillary curves are shown in Fig. 5. To avoid difficulties in measurements due to the formation of the oxide film, which is formed at the more negative potentials the more alkaline is the solution,[1] and to the hydrogen evolution caused by cathodic polarization, the curves were measured consecutively, just as in the case of capacitance measurements, in three or four solutions of different acidity:

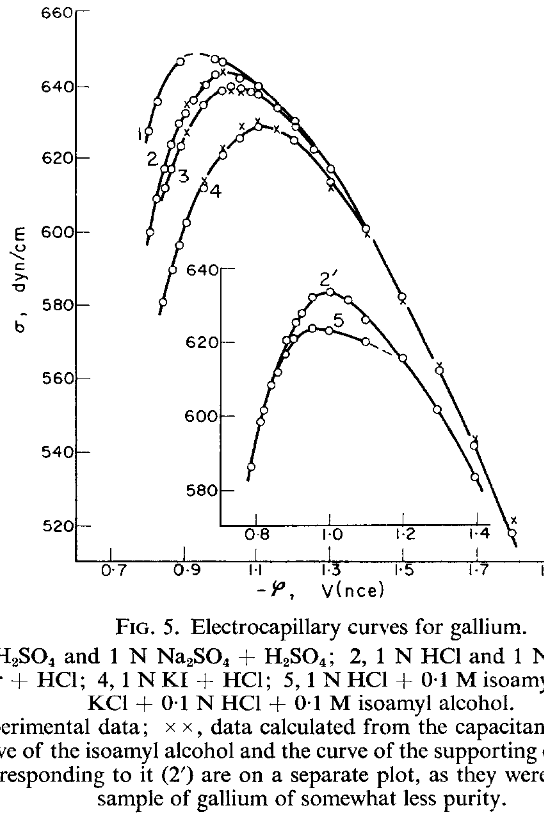

FIG. 5. Electrocapillary curves for gallium.
1, 1 N H_2SO_4 and 1 N Na_2SO_4 + H_2SO_4; 2, 1 N HCl and 1 N KCl + HCl; 3, 1 N KBr + HCl; 4, 1 N KI + HCl; 5, 1 N HCl + 0·1 M isoamyl alcohol and 1 N KCl + 0·1 N HCl + 0·1 M isoamyl alcohol.
○○, experimental data; ××, data calculated from the capacitance measurements. The curve of the isoamyl alcohol and the curve of the supporting electrolyte KCl + HCl corresponding to it (2′) are on a separate plot, as they were obtained with a sample of gallium of somewhat less purity.

from −0·80 to −0·95 V in 1 N acid (only curves 1, and 2, Fig. 5); from −0·86 to −1·1 V in a salt solution in the presence of 0·1 N acid; from −1·0 to −1·6 V in a salt solution in the presence of 0·001 N acid; from −1·5 V to −1·8 V, in a salt solution in the presence of 0·01 N alkali. The values of σ obtained in the overlapping potential ranges coincided well, which points to the absence of the effect of adsorption of hydroxyl and hydrogen on the anodic and cathodic ends of each section of the curve, respectively, which would have resulted in the dependence of σ upon pH of the solution. However it proved impossible to join the sections of the curve measured in 1 N H_2SO_4 and 1 N Na_2SO_4 + 0·1 N H_2SO_4 (Curve 1): there was a difference of 4 dyn/cm between the curves of these two solutions at −0·95 V. Therefore, the intermediate section on the curve is shown with a dotted line. The measurements at more positive potentials than eg $-0{\cdot}95$ in 1 N KCl + 0·1 N HCl were performed under anodic polarization of the meniscus in the capillary (the normal potential of a gallium electrode is $-0{\cdot}81$ V); which, however, did not seem to lead to any difficulties.

We have made a comparison between the experimental electrocapillary curves and the σ/φ curves, calculated by the double integration method from the data on the dependence of the differential capacitance C upon the potential. The integration constants for KCl + HCl were chosen in such a way that the observed curve should coincide with the calculated one at the electrocapillary maximum; for the other solutions they were chosen on the basis of the assumption that the descending branches of the electrocapillary curves of different anions coincide at sufficiently negative φ. As is evident from Fig. 5, in all cases there is a good coincidence between the results obtained by the two different methods, which is a proof of the reliability of the present electrocapillary measurements. On the contrary, the capacitance values given before[3] are greatly at variance with the electrocapillary measurements.

TABLE 1. POTENTIALS OF ZERO CHARGE OF GALLIUM

Electrolyte	$NaClO_4$ + + $HClO_4$	Na_2SO_4 + + H_2SO_4	KCl–HCl	KBr–HCl	KI–HCl
φ_0 (I), V(nhe)	−0·90	−0·93	−1·01	−1·04	−1·11
φ_0 (II), V(nhe)	−0·89	−0·925	−1·00	−1·03	−1·10
σ_{max}dyn/cm	653·9	648·9	644·0	640·3	628·9

In Table 1 are listed the potentials of the zero charge of gallium, φ_0, in various solutions, determined from the electrocapillary curves (I) and from the dependence of the charge density upon the potential (II), as well as the values of the maximum interfacial tension σ_{max}.

If we compare the electrocapillary curves obtained on gallium with those for mercury in solutions containing the same anions (Fig. 6), as well as the corresponding ε/φ curves, we see that the surface activity of the SO_4^{2-} (or HSO_4^-), Cl^-, Br^-, I^-

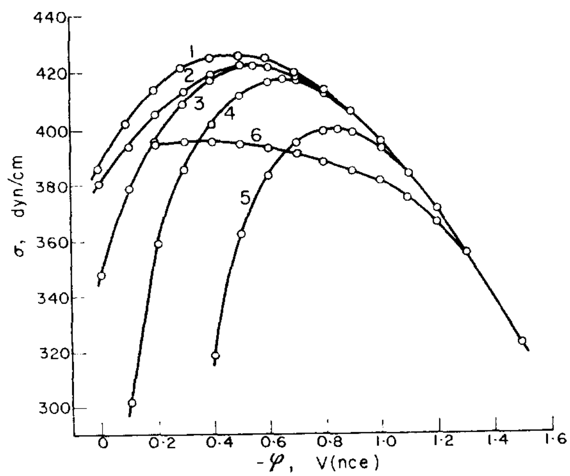

FIG. 6. Electrocapillary curves for mercury.
1, 1 N Na_2SO_4 + 0·1 N H_2SO_4; 2, 1 N $NaClO_4$ + 0·1 N $HClO_4$; 3, 1 N KCl + 0·1 N HCl; 4, 1 N KBr + 0·1 N HCl; 5, 1 N KI + 0·1 N HCl, 6, 1 N KCl + 0·1 N HCl + 0·1 M isoamyl alcohol.

anions changes in the same sequence as on mercury, but is less pronounced. This affects especially the value of the shift of φ_0. Thus, upon transition from sulphate to iodide solution, the decrease in σ_{max} and the shift of φ_0 are 20 dyn/cm and $-0{\cdot}18$ V, respectively, for gallium and 26·5 dyn/cm and $-0{\cdot}37$ V for mercury. Other characteristic differences in the behaviour of anions at the gallium/solution interface, as compared with those at the mercury/solution interface, are: closely similar adsorptivity of Cl^- and Br^- ions, no surface activity of the ClO_4^- ion and more pronounced surface activity in the case of the SO_4^{2-} (or HSO_4^-) ion.

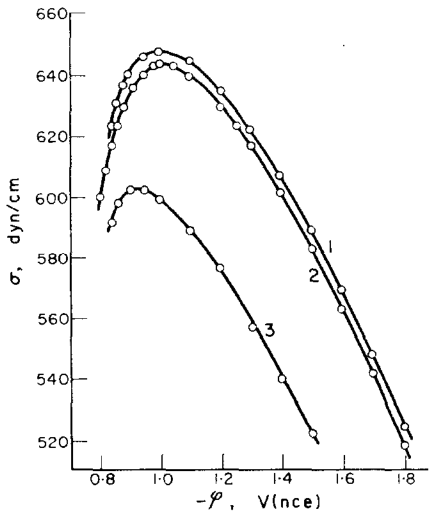

FIG. 7. Electrocapillary curves in solutions of 1 N HCl and 1 N KCl + HCl for gallium (1) and gallium with purity (1), 99·9998% (2), 99·996% (3).

A considerable decrease in the adsorptivity on the transition from mercury to gallium is observed in the case of the organic substance iso-amyl alcohol (Figs. 5 and 6), although the electrocapillary curves retain the shape characteristic of aliphatic alcohols on mercury.

The purity of gallium greatly affects the electrocapillary curve. Figure 7 shows that in the case of gallium of 99·996 per cent purity the maximum of interfacial tension lies at $-0{\cdot}92$ V in KCl, which coincides with the data given in earlier works. The value of σ_{max} is less by 41 dyn/cm than on curve 2. Curve 1, Fig. 7 was obtained with gallium (1), a sample of which we received by the courtesy of Prof. J. O'M. Bockris. In this case σ_{max} is still somewhat higher (by 4–6 units) than on curve 2; φ_0 has the same value.

DISCUSSION

The adsorption of anions on gallium, as follows from the position of the points of zero charge and especially from the values of the interfacial tension, is rather less pronounced than on mercury. However, a sharp asymmetry of the electrocapillary curves, observed on mercury only in the case of most surface-active anions, such as I^-, is a general occurrence in the case of gallium. Thus, the increase in capacitance on gallium with φ shifting to less negative values cannot be accounted for by the adsorption of anions. As the values of C do not depend on pH, the increase in capacitance also cannot be due to the appearance of adsorbed O atoms or OH groups on the surface (initial stage of oxidation). At any rate, this effect is eliminated in the method of plotting the C/φ curve. It could be also supposed that the increase in capacitance is caused by the quantity of gallium ions present in the interfacial layer, since according to the thermodynamical theory of electrocapillarity,[8] the charge on these ions influences the effective capacitance of the electrode in the same way as the charge of the metal surface. To check this supposition, we measured the differential capacitance in 1 N (relative to SO_4^{2-}) $KAl(SO_4)_2$. The aluminium ions present in a high concentration should have replaced the gallium ions in the interfacial layer. But the dependence of capacitance upon potential observed in 1 N Na_2SO_4 is completely retained in this solution also. We can only suppose that the peculiarities in the electrocapillary behaviour of gallium are due to the chemisorption of water molecules.

It has been pointed out earlier that the gain in the free energy in the case of wetting of the uncharged gallium surface with water is greater than with mercury (125 erg/cm²).[9] Unfortunately, it is difficult to calculate this value accurately because the interfacial tension measurements at the gallium/water and gallium/vacuum interfaces have been made with gallium of different purity. The results of measurements[10] with the same sample in H_2 and CO_2, and in 0·1–0·2 N HCl, give the value 170 erg/cm². The increase in the differential capacitance seems to occur because, with the shift of the potential in the less negative direction, the water dipoles turn with their negative, *ie* oxygen, ends towards the gallium surface. A stronger bond of gallium with water accounts for the decrease in the adsorptivity of the ClO_4^- ion and of aliphatic alcohols as compared with that on mercury. The adsorptivity of the ClO_4^- ion and of aliphatic compounds is determined primarily by their displacement from the bulk of the solution due to the interaction between the water molecules. The presence of a strongly bound water layer at the interface should hinder their adsorption.[13]

The orientation of water dipoles with their negative ends towards the metal should have an adverse effect upon the adsorptivity of anions, because of electrostatic interaction. Probably, this interaction is responsible for the fact that at the anodic end of the electrocapillary curve, the capacitance of gallium in solutions of iodides is not larger, but even somewhat smaller, than in solutions of other anions. The change in water orientation with polarization is also evidenced by the difference in the values of φ_0 for mercury and for gallium in the absence of the anion adsorption (0·42 V) being much greater than that between the potential values corresponding to an equal value of the charge ε at negative surface charge (0·17 V). It is at negative potentials that the structure of the interfacial layer on gallium is comparable to that on mercury, because under these conditions the ε/φ curves of both metals become parallel (Fig. 3). This becomes even more evident in comparing the dependence of C upon ε for various cations on mercury and gallium (Fig. 8).

The concept of the re-orientation of adsorbed water dipoles with changing potential has been used lately[11–13] in considering the electrocapillary behaviour of water on mercury. Apparently, these phenomena are more pronounced in the case of gallium.

An essential difference in the structure of the interfacial layer in the region of the anion adsorption is evidenced by the effect of the adsorbed I^- anion upon the hydrogen overvoltage η. Whereas on mercury the adsorption of I^- results in a decrease in η,[14] in the case of high purity gallium η somewhat increases[16] (Fig. 9).* Evidently, the change in the potential distribution in the interfacial layer

* Earlier a small decrease in η on Ga was observed in the presence of I^-.[15] This result, however was obtained with an insufficiently pure sample.

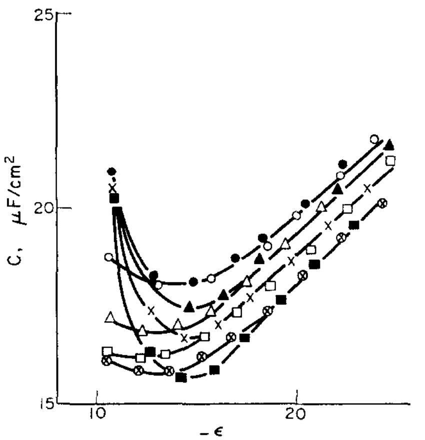

FIG. 8. Dependence of the differential capacitance upon the charge for mercury and gallium at negative charges.
Ga: ■, 1 N LiCl; ×, 1 N NaCl; ▲, 1 N KCl; ◆, 1 N CsCl.
Hg: ⊗, 1 N LiCl; □, 1 N NaCl; △, 1 N KCl; ○, 1 N CsCl.

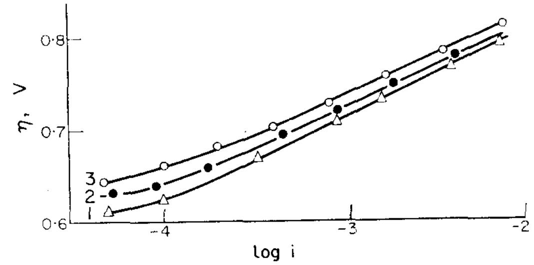

FIG. 9. Effect of anions upon the hydrogen overvoltage η on gallium.
1, 1 N H_2SO_4; 2, 1 N H_2SO_4 + 1 N KCl; 3, 1 N H_2SO_4 + 1 N KJ (according to Preis and Bagotskaya).[16]

caused by the effect of the adsorbed I^- ions upon the orientation of water molecules, in this case exerts a greater influence upon the value of η, than the ψ_1-potential, which directly depends upon the presence of absorbed I^- ions. This problem requires further investigation.

The data presented show that there is an essential discrepancy between the difference of the potentials of zero charge for mercury and gallium, which in the absence of adsorption of anions is equal to 0·42 V, and the difference of the potentials corresponding to equal negative surface charges, which is only 0·17 V. We explain this discrepancy by the difference in the adsorption potentials due to the orientation of the water dipoles at the interface with the uncharged metal.

The possibility of such a discrepancy is of essential importance in the quantitative evaluation of the influence of the position of the point of zero charge upon the kinetics of the electrochemical processes occurring on the electrodes. Therefore, it was of interest to compare the positions of the points of zero charge on mercury and gallium in other media. Ukshe and Bukun[17] determined the position of the point of zero charge of gallium in a melt of LiCl + HCl by two methods, based on the measurements of the electrocapillary curve and of the differential capacitance of a gallium electrode,[17,18] and found at 450°C the mean value −0·62 V against the reference

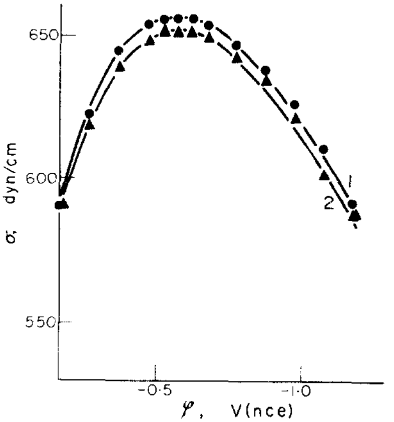

FIG. 10. Electrocapillary curves for gallium in KCl + LiCl melt (according to Kusnetsov). 1, 400°; 2, 450°.

electrode Pb, KCl + LiCl, 10% $PbCl_2$. According to Kusnetsov, the maximum of the electrocapillary curve of gallium (Fig. 10) against the same reference electrode at 400°C lies at —0·57 V[19] and that of Hg at —0·22 V; the difference between the two last values is 0·35 V, close to the value obtained for aqueous solutions. Hence, within the frame of the theory developed, one may draw the conclusion that in a melt, *ie* in the absence of solvating water, the predominant adsorption of anions on gallium is more pronounced than on mercury, a behaviour different from that observed in aqueous solutions. It is impossible, however, to arrive at a final conclusion from the comparison of the positions of the points of zero charge in melts and in aqueous solutions in view of the absence of the data on the temperature dependence of the points of zero charge. Unfortunately also, there are no reliable data available of the electron work-function of gallium; we intend to fill these gaps, in further work.

Note added in proof: Measurements carried out in dilute solutions of HCl and $HClO_4$ show that the difference in the φ_0 values for mercury and for gallium in the absence of the anion absorption is even larger (0·50).

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