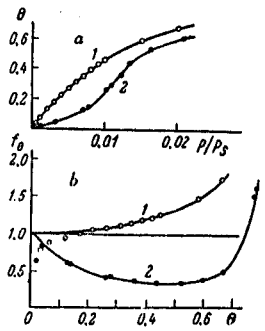

Curves calculated from appropriate equations to adsorption isotherms and experimental points representing:
a) initial portions of isotherms;
b) activity coefficients of adsorbate:
1) benzene; 2) carbon tetrachloride.

has been calculated by means of Eqn. (5) for benzene[10], and by means of Eqn. (6) for carbon tetrachloride[11]. At low θ the experimental points diverge from the calculated curves as a result of the residual non-uniformity of the graphitised black surface [which increases the value of θ in Eqn. (14) at low p/p_s]. Since the adsorption isotherm of benzene is concave to the pressure axis over the whole range of θ, it follows that $f_{(\theta)} > 1$; whereas for the adsorption isotherm of carbon tetrachloride, which at $\theta < 0.5$ is convex to the pressure axis, $f_{(\theta)} < 1$.

SUMMARY

1. Standard thermodynamic functions have been evaluated for adsorption of the vapours of benzene (weak adsorbate–adsorbate interaction), n-hexane, and carbon tetrachloride (strong adsorbate–adsorbate interaction) on a graphitised thermal black having an extremely uniform surface. By means of equations to adsorption isotherms which take into account adsorbate–adsorbate interaction, standard values have been calucated for zero coverage (only adsorbate–adsorbent interaction) and 50% coverage (both adsorbate–adsorbent and adsorbate–adsorbate interaction).
2. The dependence on surface coverage of activity coefficients of the adsorbate in the adsorbed layer has been calculated.

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BRIEF COMMUNICATIONS

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BEHAVIOUR OF DROPPING GALLIUM ELECTRODE IN THE HYDROGEN OVERPOTENTIAL RANGE IN ALKALINE SOLUTIONS

K.Sabo, I.A.Bagotskaya, and N.B.Grigor'ev

The principal quantitative data on the influence of solution composition (of pH at constant electrolyte concentration[1] and of total electrolyte concentration at constant pH[2]) on the hydrogen overpotential have been obtained at a mercury electrode, whose surface is uniform and reproducible. A dropping mercury electrode has been widely used in these investigations, for it allows concentration polarisation to be taken into account and measurements to be made on a continuously renewed surface. In alkaline solutions, however, alkali metals are reversibly deposited on mercury with subsequent formation of an amalgam. In the study of hydrogen overpotential in solutions of alkalis, therefore, the rate of evolution of hydrogen must be determined by measuring its volume, or determinations must be made on the establishment of the stationary content of alkali metal in the amalgam corresponding to a given potential[3,4].

It was of interest to choose a different metal for the electrode, on which the variation of hydrogen potential could be studied quantitatively by direct measurements of $\eta = f(\log i)$ uncomplicated by simultaneous deposition of an alkali metal. We have investigated as such an electrode liquid gallium at 32°. The design of the dropping gallium electrode used and the measurement technique have been described previously[5]. The purity of the gallium was 99.996%. The solution was prepared by decomposing sodium amalgam in twice distilled water, and freed from traces of mercury ions by cathodic polarisation at a platinum electrode.

The resulting sodium hydroxide solution was stored in a polystyrene vessel to avoid contamination with products extracted from glass. Organic impurities which may enter aqueous alkali on storage in polystyrene are not

adsorbed on a gallium electrode in the hydrogen overpotential range owing to the high negative potentials, as capacitance measurements in our laboratory have shown. Sodium sulphate and potassium iodide were recrystallised twice, the former being further roasted at 700°. Tetramethylammonium iodide was recrystallised twice at a temperature not exceeding 50°, and was dried at 50° with continuous evacuation.

Fig. 1 shows polarisation curves obtained in aqueous NaOH of different concentrations. Their slopes of 0.125–0.135 V indicate that reversible deposition of sodium on the gallium does not occur. On mercury the slope of the polarisation curves in aqueous alkali is 58 mV, and is determined by reversible deposition of sodium with subsequent amalgamation. We have confirmed the absence of reversible deposition of sodium on gallium also by capacitance measurements on the dropping gallium electrode in a solution containing 1 N Na_2SO_4 + 0.01 N NaOH (Fig. 2), using an a.c. bridge. The maximum cathodic polarisation of the electrode corresponded to -1.9 V (relative to the saturated calomel electrode, s.c.e.). Measurements at more negative potentials were hindered by vigorous hydrogen evolution. It is seen from Fig. 2 that the capacitance is close to that of the double layer at potentials between -1.55 and -1.9 V, which indicates the absence of reversible sodium deposition in this potential range. The rapid increase in capacitance at potentials more positive than -1.55 V is probably associated with dissolution of gallium.

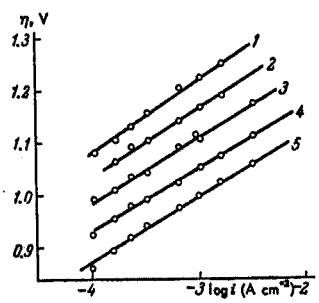

Fig. 1. Polarisation curves on gallium in different concentrations (N) of NaOH: 1) 0.01; 2) 0.03; 3) 0.1; 4) 0.33; 5) 1.

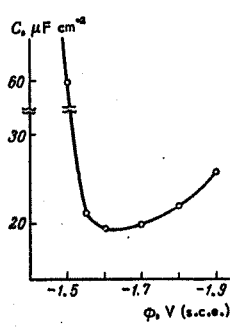

Fig. 2. Differential capacitance curve obtained at a frequency of 318 c/s on a dropping gallium electrode in a solution of 1 N Na_2SO_4 + 0.01 N NaOH.

In order to ascertain whether alkali-metal ions could be discharged in the hydrogen overpotential range on liquid gallium in alkaline solutions, and accumulate in appreciable amounts on the electrode surface, current–time curves were recorded, on a TsLA-02 oscillographic polarograph, during application of an anodic pulse to a cathodically polarised gallium drop (Fig. 3a). The initial potential of the drop in 0.33 N NaOH solution lay between -2.1 and -2.2 V (s.c.e.), and corresponded to the hydrogen overpotential range. The drop time was about 2.5 s. Fig. 3b shows for comparison a photograph of the corresponding curve obtained at a dropping mercury electrode under the same conditions. Fig. 3a shows that no appreciable amount of dissolved alkali metal is present in the liquid gallium. In the case of mercury (Fig. 3b) the cathodic current flowing to the electrode actually falls rapidly on application of an anodic pulse, and after some time changes into an anodic current, indicating ionisation of a mercury-soluble alkali metal. Such a phenomenon is not observed in the case of the gallium electrode.

In order to calculate the capacitance of the electrode, current–time curves were recorded at different rates of application of the anodic pulse $\partial\varphi/\partial t$ = 1, 2.4, and 8 V s^{-1}. At these rates the change in surface of the drop due to its growth could be neglected, since the time of application of the pulse did not exceed 0.7 s. The anodic pulse was applied to the drop at an instant close to detachment of the latter, and its surface area was taken to be the maximum value. The above curves were used to plot a curve representing the variation of current I (at some selected constant potential φ) with $\partial\varphi/\partial t$. The current I is made up of a capacitive current I_C and the current I_{H_2} involved in hydrogen evolution at the given potential: $I = I_C + I_{H_2}$. The currents I_C and I_{H_2} differ in sign. The latter current was found by extrapolating to $\partial\varphi/\partial t \to 0$, and the capacitance $C = (I - I_{H_2})/(\partial\varphi/\partial t)$ was calculated as 20–25 $\mu F \times \times cm^{-2}$, corresponding to the capacitance of the electrical double layer.

In order to confirm that discharge of alkali metal does not occur at a dropping gallium electrode in alkaline solutions, we have determined φ–log$i$ polarisation curves in solutions of the same concentration (0.33 N) of electrolytes containing different cations — Na_2SO_4, KI, and $(CH_3)_4NI$ — the last of which is able to form an amalgam only at very

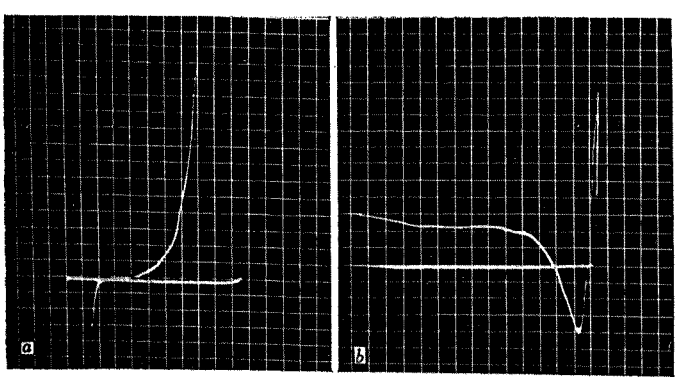

Fig. 3. Variation in current with time of application of anodic pulse to cathodically polarised drops in 0.33 N NaOH solution with $I_{Init} \simeq 1.82$ V (s.c.e.) and $\partial\varphi/\partial t = 0.5$ V s^{-1}: a) gallium; b) mercury.

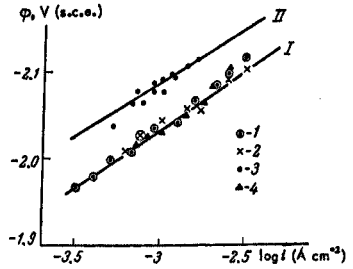

Fig. 4. Curves of φ as function of $\log i$ at a dropping gallium electrode in 0.33 N solutions of:
1) Na_2SO_4; 2) KI; 3) $(CH_3)_4NI$; 4) NaOH.

negative potentials. Fig. 4 includes also comparable results for 0.33 N NaOH solution. It is seen that, in conformity with the slow discharge thecry in alkaline solutions, values of φ as a function of $\log i$ in 0.33 N Na_2SO_4, 0.33 N KI, and 0.33 N NaOH lie close to a single straight line I of slope 0.13†. The results for 0.33 N $(CH_3)_4NI$ lie at potentials about 40–50 mV higher (straight line II). A similar phenomenon has been observed previously on a mercury electrode, and is explained by a different distribution of the force field in the double layer in solutions containing alkali-metal cations and the $(CH_3)_4N^+$ cation, caused by the difference in their size and resulting in different mean values of the ψ' potential. The above result also confirms the absence of appreciable deposition of alkali metal on gallium. Quantitative data on the influence of solution pH and total electrolyte concentration on the hydrogen overpotential of gallium in alkaline solutions have been published previously [5,7]. Deposition of alkali metals in the hydrogen overpotential range from solutions of alkalis, with formation of intermetallic surface compounds, has been found [8] to occur on several metals — lead, zinc, cadmium, and silver — and produces an appreciable change in their electrochemical properties, the hydrogen overpotential usually increasing.

Thus the low affinity of gallium for alkali metals is of considerable interest, for it enables the kinetics of electrochemical processes at a liquid metal in solutions of high pH to be studied without the complication of simultaneous deposition of an alkali metal.

We are deeply grateful to Academician A. N. Frumkin for valuable advice in carrying out the present work and discussing the results.

SUMMARY

No appreciable deposition of alkali metal is observed in the hydrogen overpotential range on liquid gallium in solutions of an alkali.

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† In the KI and Na_2SO_4 solutions, hydrogen evolution actually takes place from alkaline solutions of variable pH.

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RELATIVE DIFFERENCE IN THE MOBILITIES OF THE IONS OF POTASSIUM-39 AND POTASSIUM-41

V. P. Troshin

The separation of the potassium-39 and potassium-41 isotopes by countercurrent electromigration was first carried out by Brewer and Madorsky [1]. The use of a sand filler in the separating column made it possible to avoid convective mixing. Another improvement was the application of a hydrodynamic countercurrent. The isotopic analysis was carried out in a mass-spectrometer. The values of the relative difference ϵ between the mobilities of the isotopic potassium ions ranged from 0.15 to 0.38%. In view of the considerable scatter of the experimental data, Brewer and Madorsky [1] were unable to determine the variation of ϵ with concentration and with the chemical nature of the electrolyte solutions.

Fiks [2] used the countercurrent electromigration method to separate potassium-39 and potassium-41 isotopes in 1 and 3 N KCl solutions. The relative differences between the mobilities were found to be ϵ = 0.21% for 1 N KCl and ϵ = 0.25% for 3 N KCl.

In the present work this method was used to determine the relative difference between the mobilities of the ions of potassium-39 and potassium-41 in solutions of KCl, K_2SO_4, and KNO_3. The experimental technique differed little from that used in the separation of lithium isotopes [3].

The experiments were carried out as follows. The separating tube packed with quartz sand was filled with solutions in the order of increasing mobilities of the cations H^+, K^+, and Cu^{2+}, which form the boundaries between the electrolyte solutions; the test potassium salt solution (for example KCl) was "squeezed" between the two indicator solutions — an HCl solution in the front and a $CuCl_2$ in the rear (upper Figure). The current was then passed through the solution, and the difference in the mobilities of the potassium-39 and potassium-41 ions resulted in a change of the isotope concentration during the time of the experiment in the column of solution. Because of diffusion, the distribution of the light isotope along the length of the column is non-uniform (lower Figure). Consider a cross-section of the separating tube aa' for a column of solution of length l, in which the isotope concentration has not as yet