ZERO POINTS OF DILUTE SODIUM AMALGAMS

![Fig. 1. Apparatus for determining the zero points of amalgams by the dropping-weight method](image)

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Abstract

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ZERO POINTS OF DILUTE SODIUM AMALGAMS

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Over the last decade, the important role played by the zero-charge potential, or zero point, of a metal $\left({}_{\mathrm{Me}}E_{q=0}\right)$ in various electrochemical processes has become especially clearly evident (1–6). In this connection, the determination of the zero points of dilute amalgams, many of which have found application in the reduction of inorganic and organic substances (7–9), is of considerable interest. Up to the present, from this point of view, only thallium (10) and cadmium (11) amalgams have been investigated in aqueous solutions. Here the results are presented for the determination of the zero points of dilute sodium amalgams.

(Figure: Fig. 1. Apparatus for determining the zero points of amalgams by the dropping-weight method)

Fig. 1. Apparatus for determining the zero points of amalgams by the dropping-weight method

The determination of the zero points of alkali-metal amalgams is complicated by their comparatively easy oxidizability and rather rapid decomposition by aqueous electrolyte solutions. In addition, the exchange currents between amalgams and solutions containing ions of the corresponding metal are usually large. Therefore, in order to produce a noticeable displacement of the potential from its equilibrium or stationary value, the use of considerable currents is required, which may lead to a change in the composition of the surface layer of the amalgam and to distortion of the results.

In carrying out the present investigations, the amalgams, immediately after their preparation, were transferred, in order to reduce possible oxidation, into a special vessel filled with hydrogen*; the portion of amalgam necessary for the experiment was taken immediately before the measurement.

To reduce errors associated with the influence of self-dissolution and concentration polarization, the dropping-weight method of recording electrocapillary curves was chosen, ensuring constant renewal of the amalgam surface. Some changes were introduced into the usual procedure for dropping-weight measurements (12), and the apparatus shown in Fig. 1 was used. To carry out each measurement rapidly, the weighing–

* The amalgams and hydrogen were obtained electrolytically.

The weighing of the drops was carried out directly in the solution by means of a torsion balance. The required rate of dropping was achieved by using capillaries with different orifice diameters and by selecting the appropriate pressure, monitored with a mercury manometer. The capillary and the reservoir above it, with a total capacity of about 10 ml, were filled with the amalgam under study. Before the measurements were carried out, electrolytic hydrogen was passed for 3-4 hours through the solution of the electrolyte used. Then the current was switched on; mercury poured onto the bottom of the electrolytic cell served as the second electrode*.

After a definite value of the potential of the dropping electrode had been established, the weight of a known number of drops, collected in a glass cup suspended by a glass thread from the arm of the torsion balance, was determined. The discrepancy between individual experiments carried out under the specified conditions did not exceed 0.5%. Control curves recorded for mercury in 1.0 *n* NaOH and 1.0 *n* H_2SO_4 did not differ from ordinary electrocapillary curves and confirmed the reliability of the method.

(Figure: Fig. 2. Electrocapillary curves of sodium amalgams. Mole fraction of sodium: 1 –0.000126; 2 –0.000783; 3 –0.0174)

Fig. 2. Electrocapillary curves of sodium amalgams. Mole fraction of sodium: 1 –0.000126; 2 –0.000783; 3 –0.0174

The electrocapillary curves recorded for sodium amalgams in 1.0 *n* NaOH solution are shown in Fig. 2. They have a clearly expressed maximum, which must correspond to the potential of zero charge of the amalgam of the given composition**. The position of the amalgam maximum shifts regularly when its composition is changed.

Table 1

	Mole fraction of Na in the amalgam						
	0.00	0.000126	0.000783	0.00587	0.0174	0.0558	1.00
$E_{q=0}$, V	−0.21	−1.69	−1.73	−1.78	−1.81	−1.82	−2.25–−2.15
$\frac{P_{\text{Na(Hg)}}}{P_{\text{Hg}}}$	1.0	0.60	0.48	0.39	0.40	0.48	–

Table 1 gives the values of the zero points for all the amalgams studied and the values of the zero points of pure sodium, calculated from the electron work functions ([13], [14]), as well as the magnitudes of the relative decrease in the surface tension of the amalgams in comparison with mercury, calculated from the ratio of the weights of the same number of drops of amalgams and mercury.

From these data it follows that both the potential of zero charge of the amalgams and their surface tension change most strongly within the range

* All reagents used were purified beforehand: mercury—by the usual chemical method and by double distillation in vacuum; sulfuric acid—by electrolysis between an Hg cathode and a Pt anode; caustic soda was freed from carbonates; solutions were prepared with twice-distilled water.

** A shift of the potential from the zero point of the amalgam into the region of more positive potentials first leads to a decrease in the drop weight, and then to its gradual increase and passage through a second maximum at a potential close to the zero point of mercury.

the concentration of sodium in the amalgam from 0 to 0.0001 mole fractions, while upon a further increase in the sodium concentration up to the composition corresponding to the transition of liquid amalgams to solid ones, they change only insignificantly. A similar regularity was observed earlier by a number of authors for the interfaces amalgam—solution (15) and amalgam—vacuum (16,17).

In the concentration interval investigated, the potential of zero charge varies linearly with the logarithm of the mole fraction of sodium in the amalgam (Fig. 3). This dependence can be expressed by the empirical equation

$$_{\mathrm{Na(Hg)}}E_{q=0} = a + b \lg N_{\mathrm{Na}}. \tag{1}$$

Upon substitution of numerical values, the equation obtained is

$$_{\mathrm{Na(Hg)}}E_{q=0} = -1.90 + 0.053 \lg N_{\mathrm{Na}}. \tag{1a}$$

Fig. 3. Dependence of zero points on the logarithm of the mole fraction of sodium in the amalgam.
1—experimental points; 2—points calculated from the contact potential difference.

Amalgams with lower concentrations were not investigated in the present work; however, the data of O. Chaltykyan and M. Proskurnin on contact potential differences (18), shown in Fig. 3, indicate that in the region of lower concentrations a very sharp increase in the slope of the semilogarithmic curve is observed.

The quantity a represents the zero point at $N_{\mathrm{Na}} = 1$ and, consequently, should correspond to the potential of zero charge of sodium. The numerical value of a differs from the calculated zero point by 0.25-0.35 V. The extrapolated value of $_{\mathrm{Na}}E_{q=0}$ is in this case more positive than the calculated zero points of the pure metal. The reasons for such a discrepancy are not entirely clear, and here it is necessary to confine ourselves to several assumptions. First, it seems unlikely that over the entire concentration range the potential of zero charge varies monotonically in accordance with equation (1), since mercury and sodium form a series of compounds $^{(19)}$. This circumstance is not taken into account by equation (1). In addition, at high sodium contents one should use activities rather than concentrations; the latter, however, are not sufficiently reliable. Secondly, it must be borne in mind that the surface concentration of the metal may differ appreciably from the bulk concentration, in particular because of the impossibility of completely eliminating the concentration gradient associated with the passage of current. Since, in the case of sodium amalgams, the equilibrium or stationary potentials lie more negative than the corresponding zero points, attainment of the latter is possible only upon application of anodic polarization. As a result of depletion of the surface layer of the amalgam, the sodium concentration in it proves to be lower than in the initial amalgam. Obviously, in this case, when extrapolating the dependence ${}_{\mathrm{Na(Hg)}}E_{q=0} - \lg N_{\mathrm{Na}}$ to $\lg N_{\mathrm{Na}} = 0$, the value of ${}_{\mathrm{Na}}E_{q=0}$ is obtained somewhat shifted in the positive direction relative to its true value.

The established change in the zero points of sodium amalgams with their composition has the same character as the change in the equilibrium potentials. In the course of decomposition of the amalgam, the difference between the potential of zero charge and the equilibrium potential therefore remains approximately constant. Since this difference determines the adsorption conditions of organic and inorganic substances on the surface of the amalgam, preservation of its constancy during the decomposition of the amalgam ensures invariability of the surface concentration of the reducible substances. This, probably, is···

···is the reason for obtaining definite final reduction products when using sodium amalgam, despite the change in its composition and potential in the course of decomposition.

The sharp change in the zero point of mercury on passing to dilute sodium amalgams makes it possible to suppose that, in a similar way, during electrolysis in alkaline solutions, the zero points of metals that form surface sodium-metallic compounds (lead, tin, etc.) will change.(20) This circumstance may apparently have a certain influence on the course and direction of electrochemical hydrogenation processes in alkaline solutions.

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