MECHANISM FOR HYDROGEN EVOLUTION FROM ALKALINE SOLUTIONS AT ALKALI METAL AMALGAM ELECTRODES CONTAINING INDIUM

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It was shown in [1] that the decomposition rate of amalgams (Am) of alkali metals (Me) in aqueous solutions with pH > 10 is basically fixed by the rate of the chemical interaction of the Me atoms with H_2O molecules. It was of interest to study the decomposition mechanism in the case when a third, less active component is introduced into the Am.

According to [2], the addition of Cd dislodged the Me from the Am | vacuum interface. It was found in [3] that additions of Tl to Li, Na, and K amalgams caused a shift ΔE in the equilibrium potential E of these Am in the negative direction; assuming that the increase in the chemical potential of Me_2 with the introduction of Me_3 is associated primarily with the increase in the concentration of electrons which appear during the dissociation of Me_2 and Me_3 atoms, the following thermodynamic relation was derived:

$$\frac{\partial \ln f_2}{\partial x_3} = \sqrt{\frac{\partial \ln f_2}{\partial x_2} \cdot \frac{\partial \ln f_3}{\partial x_3}}, \qquad x_2, x_3 \to 0 \tag{1}$$

(where f is the activity coefficient of the metal dissolved in the Hg, x is its mole fraction, "2" denotes the alkali metal, and "3" denotes the added metal). If for not too large x_3 the right side of Eq. (1) is a constant (K) for a given Am mixture, we obtain by integration and substitution into the Nernst equation

$$\Delta E = -K\frac{RT}{nF}x_3. \tag{2}$$

The existence of a shift in E should change the reactive capability of the Am.

We studied the decomposition kinetics of amalgams of Li, Na, K, and Cs at 20°C in aqueous solutions of 2 N MeOH after addition to the Am of 99.999% pure In (x_3 = 0.00-0.68) as the Me which dissolves best in Hg. An equilibrium method was used for the study [4, 5]: the Hg or indium Am was cathodically polarized in the test solution at i = const or at E = const until the system's E reached a maximum (or i reached a minimum) and no longer changed in value; when such a steady state was achieved, the current corresponded to the Am decomposition. The analytic concentration c_{Am} of the alkali Me in the mixed Am forming was also determined (by titration) for several values of i and x_3. All solutions were cleansed at a Hg cathode.

The polarization curves (PC) of E vs. log i (Fig. 1) at an Am saturated with indium (x_3 = 0.68) in MeOH solutions, with i not too large, are Tafel dependences (TD) with slopes b equal to 0.118-0.122 V, close to 2.3 2RT/F, and coincide for all the alkali metals except CsOH; in 2 N CsOH the TD are displaced in the positive direction by 0.05 V (all values of E are against the N.C.E.). The path of the PC is the same for both glass and polystyrene vessels and for Pt, Cu, and In contacts with the Am. A break is observed with increase of i in the PC for the NaOH and KOH solutions; after the break the curves continue to be rectilinear, but b decrease to a value of 0.058-0.068 V, close to 2.3 RT/F. A further lowering of x_3 shifts the region of the PC with the larger b toward smaller i (in NaOH and KOH this shift can be followed up to $x_3 \sim 0.5$; the rapid increase in c_{Am} at constant i with a further decrease in i = const causes the equilibrium method to lose its applicability); the break in the PC is clearly visible in all solutions. The regions of the curves with the higher slopes (the curve for x_3 = 0 among them) are continuations of each other, being line segments of the type

$$E = A - b \lg i \tag{3}$$

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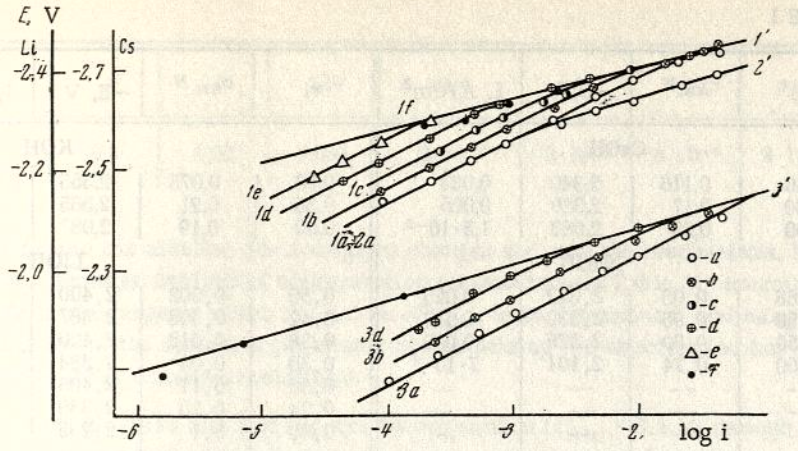

Fig. 1. Polarization curves in 2 N MeOH solutions (1,1'-LiOH; 2,2'-NaOH and KOH; 3,3'-CsOH) on In amalgams: a) x_3 = 0.68; b) 0.50; c) 0.42; d) 0.30; e) 0.15; f) 0.00.

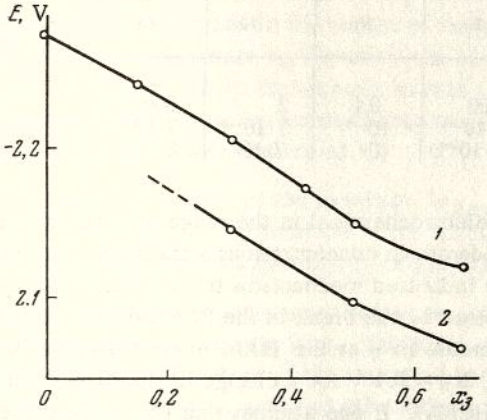

Fig. 2

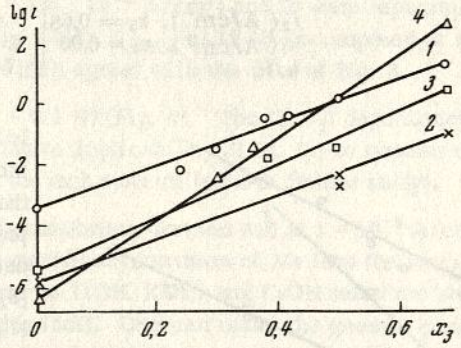

Fig. 3

Fig. 2. E, x_3 dependence for i = 10^{-4} A/cm^2 in: 1) LiOH and 2) CsOH.

Fig. 3. Dependence of the logarithm of the decomposition rate of a 0.1 N amalgam (expressed in A/cm^2) on the magnitude of x_3 in: 1) LiOH; 2) NaOH; 3) KOH; 4) CsOH solutions.

with A and b values of −2.496 and 0.059 (LiOH), −2.447 and 0.067 V (NaOH), −2.458 and 0.068 V (KOH), and −2.476 and 0.063 V (CsOH). The path of the PC after the break point depends somewhat on the nature of the Me.

The following explanation of the shape of the PC can be given: in the range of i where the curves have the greater slopes, the Am decomposition mechanism is electrochemical; the rate of H_2 evolution is limited by the rate of H_2O molecule discharge on the Am, and is fixed by the value of the H_2 overvoltage, η, on the Am. The shift of the PC in the positive direction in CsOH is further confirmation of this conclusion. It is known [6] that Cs^+ cations are surface active; according to slow discharge theory, their specific adsorption should lead to increased η in an acidic medium (experimentally confirmed in [7] on a Hg cathode) and to a decrease of this quantity in an alkaline medium (a lowering of η by 0.04 V on a Ga electrode in a 0.5 N CsOH solution has been observed by I. A. Bagotskaya). In the range of i where the PC have the smaller slopes, the Am decomposition apparently occurs by a chemical mechanism, following the kinetic equation

$$i = ka_{\text{Am}}, \tag{4}$$

where a_{Am} is the activity of the alkali Me in the Am. An actual dependence i = kc_{Am} was assumed instead of Eq. (4) in [1]; since the range of c_{Am} and thus of i, studied in [1] was extremely narrow and the scatter in the data rather large, the process under consideration probably did not actually follow the indicated dependence.

Thus the decomposition rate of simple Am of active Me in an alkaline medium is governed by the rate of interaction of Me atoms with H_2O molecules; when In is introduced (before saturation) the process becomes primari-

TABLE 1

x_3	c_{Am}, N	−E, V	i, A/cm²	x_3	c_{Am}, N	−E, V	i, A/cm²
CsOH				KOH			
0,36	0,116	2,340	0,033	0,50	0,075	2,355	0,02
0,30	0,17	2,329	0,005	0,38	0,21	2,365	0,026
0,00	0,55	2,083	$1,5\cdot10^{-6}$	0,00	0,19	2,087	$5\cdot10^{-6}$
NaOH				LiOH			
0,68	0,03	2,342	0,025	0,50	0,002	2,400	0,026
0,50	0,95	2,332	0,012	0,42	0,008	2,387	0,025
0,50	0,30	2,325	0,009	0,38	0,012	2,420	0,04
0,00	0,74	2,101	$7\cdot10^{-6}$	0,30	0,03	2,384	0,01
—	—	—	—	0,30	0,11	2,405	0,033
—	—	—	—	0,24	0,20	2,389	0,01
—	—	—	—	0,00	0,1	2,255	$3\cdot10^{-4}$

TABLE 2

Me	Li	Na	K	Cs
i_2(A/cm²), $x_3 = 0,68$	20	0,1	2	500
i_1(A/cm²), $x_3 = 0.00$	$3\cdot10^{-4}$	10^{-6}	$3\cdot10^{-6}$	$3\cdot10^{-7}$
i_2/i_1	$7\cdot10^{+4}$	10^5	$7\cdot10^5$	$2\cdot10^8$

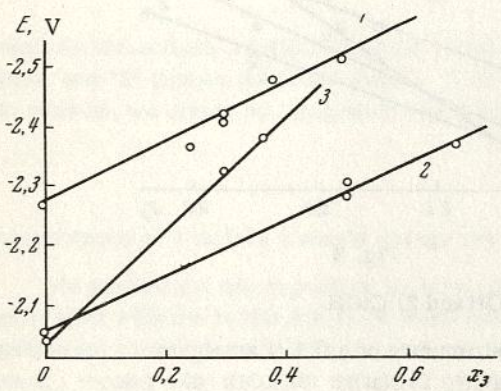

Fig. 4. E, x_3 dependence for c_{Am} in: 1) LiOH; 2) NaOH; and 3) KOH solutions.

ly electrochemical in the range of i studied. In the range of moderate In concentrations a transition can occur from one of the indicated mechanisms to the other. Such a transition (expressed by the break in the PC) becomes feasible because of the decrease in η at the InAm in comparison with Hg (according to [8], $\Delta\eta \sim 0.1$ V for a change in the In x_3 from 0 to 0.68 in 0.1 N $HClO_4$). If one assumes that the PC described by Eq. (3), characterized by a value of b = 2.3 RT/F, reflecting a chemical decomposition, and obtained by combining Eq. (4) and the Nernst equation, suffers no change for a given Me with variation in x_3 (which is experimentally confirmed), i.e., if the addition of In charges only a_{Am}, and not the constant k in Eq. (4), the mentioned PC and the electrochemical TD for the discharge of H_2O molecules at the corresponding Am must intersect because of the different slopes. In the case of Hg (more accurately, of a dilute Am of an active Me), the intersection is a such small i (corresponding to very small values of c_{Am}) that it cannot be determined experimentally. The introduction of In, accompanied by a shift in the TD toward larger i, makes such a determination feasible.

The data obtained allow an estimate of the values of the constants a in the Tafel equation for the case of electrochemical evolution of H_2 on Hg in an alkaline medium under the hypothetical condition of the absence of a Me^+ ion discharge. The increase of E ($i = 10^{-4}$ A/cm²) with decrease of x_3 in the LiOH solution can be extrapolated to $x_3 = 0$ (Fig. 2). The change in η during the transition from a cathode of saturated InAm to Hg is equal to 0.16 V. Using this value and the TD characteristics of saturated InAm in 2 N LiOH, we find that the constant a for Hg in 1 N MeOH is equal to approximately 1.7 V. The reality of the extrapolation made is confirmed by the evolution of H_2 in 0.2 N $(CH_3)_4NI$ recorded on Hg and In Am ($x_3 = 0.68$). The indicated curves are parallel with a slope of 0.12 V, but the Hg PC is displaced by 0.155 V in the negative direction. The value of a found is almost 0.2 V higher than that determined in [9] from the study of the Am decomposition kinetics in rather pure solutions, but approximately 0.1 V lower than the value obtained in $(CH_3)_4NOH$ solutions [10]; the latter is apparently associated with the different energetic barriers during H_2O discharge because of the different dimensions of the Me^+ and $(CH_3)_4 + N^+$ ions. We note that the difference in the values of a on Hg in 1 N MeOH and 1 N HA (~0.3 V) is close to the analogous difference on the Ca electrode [11, 12].

TABLE 3

x_3	0	0,24	0,30	0,38	0,42	0,50	0.68
c_{eq} (N) 2 N LiOH	0,3	0,02	0,003	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	$3 \cdot 10^{-6}$

The introduction of In into the alkaline Me amalgams changes not only the mechanisms, but also the rate of the decomposition reaction. From an analysis of concentration measurements (Table 1), assuming that the slope of the PC is close to 2.3 RT/F in the range in which the values of c_{Am} were determined and using the Nernst equation and Eq. (3), a rough calculation of the several dependences characterizing the acceleration has been made (further study is required to obtain the strict numerical relations).

a) Effect of the In addition on the rate i of the Am decomposition (c_{Am} = 0.1 N) through the chemical mechanisms (Fig. 3). The log i, x_3 dependence is approximately linear and an extrapolation to x_3 = 0.68 allows an estimate of the increase in i during the transition from a simple Am to one saturated with In (Table 2). The decomposition rate of the simple Am does not depend in a regular manner on the radius R of the alkali Me atom [1], and the accelerating effect of the introduction of In clearly increases with growth of R. Experimental checks of these accelerations evidently cannot be made in the region of large x_3; they will be hindered by diffusion limitations on the alkali Me. In the range of moderate x_3, however, the acceleration effect could be illustrated in the following manner: amalgams of K (c_{Am} = 0.5 N, decomposition rate $i = 1.5 \cdot 10^{-5}$ A/cm^2) and In were separately prepared and known volumes were mixed. The Am mixture obtained (x_3 = 0.4; c_{Am} = 0.17 N) decomposed at a rate (found gasometrically) of $i = 2.2 \cdot 10^{-2}$ (acceleration of $1.5 \cdot 10^{-3}$) which agrees with the data of Fig. 3.

b) Effect of In addition on the E of the amalgam (c_{Am} = 0.1 N) (Fig. 4). The (E, x_3) dependence in this case is also approximately linear, permitting assertion of the qualitative applicability of Eq. (2) to systems concentrated in a 3-rd component (the quantitative applicability of Eq. (1) for such systems requires further study).

c) Effect of the In addition on the concentration c_{eq} of equilibrium-formed Am at $i = 10^{-3}$ A/cm^2. The value of c_{eq} drops sharply with an increase in x_3 (Table 3); a significant intrusion of Me into the Am is therefore not observed during cathodic polarization of the saturated InAm in LiOH, KOH, and CsOH solutions (study of the fall of E of the Am after the current is switched off confirms this fact). One can make the general conclusion that there is a definite similarity between the electrode properties of saturated InAm and liquid Ga [12]; the introduction of In into the Hg allows a smooth transition from Hg to Ga for the H_2 evolution process from alkaline solutions.

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