EQUILIBRIUM POTENTIAL DIFFERENCE OF CONCENTRATION CELLS Na/Na$^+$-β-ALUMINA/Na(Hg) IN THE REGION OF DILUTED AMALGAMS

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The equilibrium potential difference of concentration cells Na/Na$^+$-β-alumina/Na (Hg), where Na$^+$-β-alumina doped with 2% MgO served as a solid electrolyte with purely cationic (Na$^+$) conductivity, was measured at $25-150°C$ and with the most concentrated amalgam up to 165°C. The mole fraction of the amalgams was in the range $0.000924-0.171$ so that the amalgams were in the considered temperature range either nonsaturated single-phase solutions or they formed a mixture of a saturated amalgam with the coexisting solid phase (intermetallic compound NaHg$_m$). With the single-phase amalgams, the equilibrium potential difference was found to depend on the temperature and mole fraction of amalgam according to $E_{cell,T} = 0.84855 - 3.0326 . 10^{-4}T - (2.3026RT/F) [\log x'_{Na} + (20.8369 - 1.5737 . 10^{-2}T) x'_{Na}]$ with a mean relative deviation of 0.54%. The measured potentials are in very good agreement with previous data for an analogous system with a nonaqueous electrolyte 0.01M-NaClO$_4$ in very dry propylene carbonate.

In the previous work[1], we presented the measured equilibrium potential differences of concentration cells Na/Na(Hg) in the region of diluted liquid amalgams with 0.1M-NaClO$_4$ in very dry propylene carbonate as a nonaqueous electrolyte. The measuring cell enabled to work at temperatures below the melting point of sodium and with sodium amalgams attaining saturation at normal temperature. The measurements were therefore restricted to the temperature range $15-90°C$ and mole fractions of sodium in amalgam up to $x'_{Na} = 0.054$ (*i.e.*, saturated at 25°C).

To measure equilibrium potential differences of the mentioned system at higher temperatures and with more concentrated amalgams, which are at normal temperature mixtures of a saturated liquid amalgam with a solid intermetallic compound NaHg$_m$ (for $x'_{Na} \leq 0.17$ this was found[2] to be NaHg$_4$), a modified measuring cell was used enabling a perfect mixing of the amalgam to attain its equilibrium with the solid intermetallic compound NaHg$_m$. β-Alumina was used as a solid electrolyte containing sodium cations (in substance Na$_2$O·11 Al$_2$O$_3$), whose conductivity is purely cationic[3] ($t_{Na} = 1.00$), which makes this material suitable for galvanic cells with a sodium anode[4-8]. The results of these measurements are presented below.

EXPERIMENTAL

Measuring cell. The scheme of the measuring cell is shown in Fig. 1. The whole cell was made of Sial glass and consisted of a cylindrical vessel **1** of about 50 cm^3 holding capacity provided with a vacuum-tight stopper **2** (Sovirel, France) through which a sodium electrode **3** was inserted reaching almost to the bottom; this is shown in detail in Fig. 1. The sodium electrode was formed by a tube made of sintered corundum **4** with a top **5** from the same material. Its bottom was from a plate **6** of β-alumina $+2\%$ MgO. All parts were cemented together with a ceramic enamel. A niobium tube **7** passed through the top nearly to the bottom; it was partly longitudinally cut off and through the resulting orifice it was filled in an inert atmosphere with pure melted sodium. The tube was then evacuated and the niobium tube was pressed, welded and provided with a long molybdenum wire **8** serving as electrical contact and simultaneously as a holder of the sodium electrode. This wire was above the electrode sealed into a glass tube **9** passing through a vacuum-tight stopper **2**. The latter enabled to use the sodium electrode in the described form for mixing the amalgam in the measuring cell. Evacuated ampoule **10** containing a sodium amalgam of a known concentration was sealed above the nickel cylinder **11** to the inlet tube leading into the measuring cell **1**. From **10**, the liquid amalgam was transferred into the measuring cell, rinsed thoroughly with purified dry argon and evacuated by an oil vacuum pump, analogously as in the preceding work[1]. The quantity of the sodium amalgam was chosen so that the melted amalgam formed on the bottom of the measuring cell an at least 1 cm thick layer into which the sodium electrode was dipped to a depth of several mm. Tubes with vacuum stopcocks **13—15** served for inlet and outlet of pure dry argon and evacuation of the measuring cell. This was maintained at the chosen temperature with a thermostated liquid (petroleum, silicon oil) passing through the cell mantle; its temperature was measured just at the inlet and the outlet of the cell mantle **16**. The difference of these temperatures did not exceed 0·3°C and their arithmetic mean was taken as the system's temperature. Electric contact to the sodium amalgam on the bottom of the cell was provided by a "Kovar" wire **17**. The electromotive force of the concentration cells was measured with a digital voltmeter of the type IDV 1 200 (Aritma, Prague).
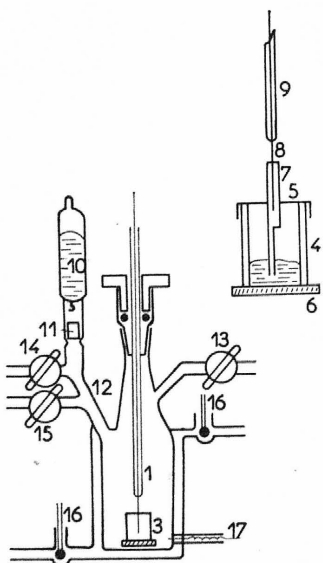

FIG. 1

Scheme of Apparatus for Measurement of Equilibrium Potential Differences of Concentration Cell Na/Na$^+$-β-Alumina/Na(Hg) Description is given in the text.

Method of measurement. Prior to every series of measurements with a given amalgam, the outer surface of the β-alumina plate of the sodium electrode was ground by an emery paper and wipped off with a dry filter paper. After assembling the apparatus, flushing with pure dry argon and evacuating, the cell was tempered to a temperature by about 10°C higher than the highest temperature of measurement with the given amalgam and a liquid or melted amalgam from the ampoule **10** was transferred into the cell. The amalgam was stirred thoroughly with the sodium electrode, which was dipped into it, and the cell was filled with pure argon at atmospheric pressure. The temperature of the tempering liquid was then lowered to the first highest temperature of measurement while the amalgam was frequently mixed by the sodium electrode. At the same time the potential difference of the studied concentration cell and the temperature of the tempering liquid at the inlet and the outlet of the cell mantle were followed. In several cases we measured the stationary voltage of the concentration cell of the same composition at the given temperature after different temperature programs lasting for different times. A very good agreement among the measured data suggested that the measured potential difference corresponded to an equilibrium state. In most cases, we followed the equilibrium potential difference at a steady temperature for about 15—20 min; the measured potential was subject to slight periodical changes due to fluctuations of the temperature around a mean value. From a record of these changes and the corresponding changes of the temperature around a chosen mean value, the corresponding equilibrium potential difference at the corresponding mean temperature was determined. The temperature was then lowered to another chosen value and the measurement continued analogously. With more concentrated amalgams, where with decreasing temperature an intermetallic compound NaHg$_m$ was precipitated, the equilibrium voltage was measured at two or three temperatures at which a part of the amalgam was solid. Reversed runs during increasing temperature were carried out only several times to check the reversibility of the system.

RESULTS AND DISCUSSION

The measured equilibrium potential differences of the concentration cells Na/Na$^+$-
-β-alumina/Na(Hg) are summarized in Table I. The amalgam composition is given by the mole fraction of the total sodium content, x'_{Na}. The amalgams with $x'_{Na} = \leqq 0.054$ correspond to those used in the previous work in measuring the same system in the medium of very dry propylene carbonate[1]. Measurements were carried out up to $x'_{Na} = 0.1713$. The lowest temperature at which sufficiently reliable results were obtained with the mentioned measuring cell was 25°C. At lower temperatures the measurements became unreliable owing apparently to the rapidly increasing internal cell resistance. With less concentrated amalgams, the equilibrium potentials were measured up to 150°C and with the most concentrated amalgam the highest temperature of measurement was 165°C to obtain a sufficient number of data for which the amalgam formed a single-phase system.

It is apparent from the table that the present data obtained with the solid β-alumina electrolyte at 25—90°C are in a very good agreement with the previous measurements[1] for the same amalgam concentrations; the deviations are in some cases positive, in other cases negative, their mean value being ±0.77 mV. This shows that the β-alumina plate in the sodium electrode has practically a purely cationic con-

ductivity and its electronic conductivity is negligible in the range of experimental errors.

The correlation of the measured values of $E_{cell,T}$ with the amalgam composition at constant temperature was expressed by the equation[1]

$$E'_{cell,T} = E_{cell,T} + (2 \cdot 3026 RT/F) \log x'_{Na} = E^0_{cell,T} - (2 \cdot 3026 RT/F) k_T x'_{Na}, \quad (1)$$

where $E^0_{cell,T}$ denotes standard equilibrium potential of the cell Na/Na (Hg); the standard state of the sodium amalgam is given by extrapolation to the infinitely dilute amalgam, k_T is a temperature-dependent constant. The values of both constants, calculated from the measured data and Eq. (1) by the least squares method, are for different temperatures given in Table II. Their average relative deviation is less than 0·1%, only at 150°C, where greater fluctuations of the temperature of the tempering liquid were observed, the average relative deviation attains 0·23%. In an analogous way, the temperature dependence of both constants was calculated. The standard equilibrium potential difference $E^0_{cell,T}$ can be expressed by a second-order polynomial similarly as in the previous work[1]

$$E^0_{cell,T} = 0 \cdot 87697 - 4 \cdot 6288 \cdot 10^{-4} T + 2 \cdot 2060 \cdot 10^{-7} T^2. \quad (2)$$

TABLE I

Measured Equilibrium Potential Differences of Concentration Cell Na/Na$^+$-β-Alumina/Na(Hg) at 25—165°C

The data denoted by a cross $+$ correspond to cases where the amalgam was just saturated or was formed by a mixture of the saturated solution and coexisting solid phase (NaHg$_m$). For $x'_{Na} = 0 \cdot 1713$ were measured the values 0·5540 and 0·5435 V at 433·15 and 438·15 K, respectively.

x'_{Na}	$E_{cell,T}$, V, at temperature, K							
	298·15	313·15	338·15	363·15	393·15	493·15	413·15	423·15
0·000924	0·9377	0·9412	0·9492	0·9568	0·9656	0·9677	0·9716	0·9748
0·002698	0·9076	0·9104	0·9144	0·9200	0·9358	0·9278	0·9298	0·9317
0·008435	0·8737	0·8741	0·8756	0·8782	0·8803	0·8811	0·8820	0·8828
0·002555	0·8288	0·8272	0·8256	0·8251	0·8240	0·8236	0·8231	0·8227
0·02828	0·8222	0·8209	0·8194	0·8190	0·8174	0·8172	0·8167	0·8162
0·04209	0·7998	0·7978	0·7943	0·7919	0·7888	0·7875	0·7862	0·7849
0·05400	0·7818$^+$	0·7790	0·7747	0·7732	0·7690	0·7676	0·7662	0·7648
0·05763	0·7819$^+$	0·7733	0·7687	0·7651	0·7603	0·7587	0·7571	0·7556
0·06534	0·7817$^+$	0·7670$^+$	0·7572	0·7528	0·7477	0·7456	0·7443	0·7426
0·09766	—	0·7670$^+$	0·7409$^+$	0·7097$^+$	0·6960	0·6940	0·6919	0·6899
0·1100	—	—	0·7409$^+$	0·7096$^+$	0·6773	0·6751	0·6729	0·6707
0·1247	—	—	—	0·7097$^+$	0·6618$^+$	0·6518	0·6496	0·6473
0·1713	—	—	—	—	0·6617$^+$	0·6417$^+$	0·6160$^+$	0·5750

Thus, the values obtained from isothermal measurements and Eq. (*1*) are fitted with an average relative deviation $2·52 . 10^{-2}\%$. This dependence can, however, be expressed in more simplified form

$$E^0_{cell,T} = 0·84855 - 3·0326 . 10^{-4}T \tag{3}$$

with a quite same average relative deviation $3·8 . 10^{-2}\%$. The temperature dependence of the coefficient k_T can be linearized as in the previous work[1] to give

$$k_T = 20·8369 - 1·5737 . 10^{-2}T. \tag{4}$$

Thus, the obtained values of k_T (Table II) are fitted with an average relative deviation of $0·54\%$.

Hence, with the use of Eqs (*2*) and (*4*) we can express the dependence of the equilibrium potential difference of the cell Na/Na$^+$-β-alumina/Na(Hg) on the concentration and temperature as

$$E_{cell,T} = 0·87697 - 4·6288 . 10^{-4}T + 2·2060 . 10^{-7}T^2 -$$
$$-(2·3026RT/F)\left[\log x'_{Na} + (20·8369 - 1·5737 . 10^{-2}T) x'_{Na}\right] \tag{5}$$

TABLE II

Thermodynamic Quantities Calculated from Measured Equilibrium Potential Differences of Concentration Cell Na/Na$^+$-β-Alumina/Na(Hg)

Quantities calculated from *1*) measured data (Table I) correlated with Eq. (*1*); *2*) data of the first line with the use of Eq. (*2*); *3*) data of the first line with the use of Eq. (*3*); *4*) measured data (Table I) correlated with Eq. (*1*); *5*) data of the fourth line with the use of Eq. (*4*); *6*) data of the first line with the use of Eq. (*7*); *7*, data of the third line with the use of Eq. (*7*).

Quantity	Temperature, K								Note
	298·15	313·15	338·15	363·15	393·15	403·15	413·15	423·15	
E^0_{cell}, V	0·75775	0·75347	0·74545	0·73818	0·72930	0·72618	0·72317	0·72073	*1*)
	0·75857	0·75365	0·74567	0·73797	0·72908	0·72621	0·72338	0·72060	*2*)
	0·75813	0·75358	0·74600	0·73842	0·72932	0·72629	0·72326	0·72022	*3*)
k	16·2796	15·9169	15·4620	14·9069	14·6429	14·5160	14·2859	14·337	*4*)
	16·1450	15·9089	15·5155	15·1221	14·6500	14·4926	14·3353	14·1779	*5*)
$\log K$	12·82598	12·12655	11·11024	10·24478	9·34917	9·07832	8·82057	8·58426	*6*)
	12·81693	12·12943	11·11913	10·24794	9·34875	9·07876	8·82185	8·57707	*7*)

or more simply with the use of Eqs (3) and (4) as

$$E_{\text{cell,T}} = 0{\cdot}84855 - 3{\cdot}0326 . 10^{-4}T - (2{\cdot}3026\,RT/F) .$$
$$. \left[\log x'_{\text{Na}} + (20{\cdot}8369 - 1{\cdot}5737 . 10^{-2}T)\, x'_{\text{Na}}\right] . \tag{6}$$

Eqs (5) and (6) apply naturally only if the sodium amalgam of the mole fraction x'_{Na} forms a single liquid phase.

On the basis of the equation

$$nFE^0_{\text{cell,T}} = 2{\cdot}302RT \log K , \tag{7}$$

where K is the equilibrium constant of the formation of the intermetallic compound $NaHg_m$ whose standard state is derived from the reference state of an infinitely diluted amalgam, we can express the dependence of K on the temperature. From Eq. (2) we obtain

$$\log K = 4419{\cdot}87/T - 2{\cdot}33288 + 1{\cdot}1118 . 10^{-3}T, \tag{8}$$

or with the use of Eq. (3)

$$\log K = 4276{\cdot}64/T - 1{\cdot}52840 . \tag{9}$$

Since the simpler Eq. (3) is practically as accurate as Eq. (2) it is possible to calculate from Eq. (9) with a sufficient accuracy the standard enthalpy of formation of the intermetallic compound $NaHg_m$ as $\Delta H^0 = -35557\ \text{J/mol}$, which is practically equal to the value found previously[1]. With regard to the linear Eq. (9), the value of ΔH^0 is in the considered temperature range practically independent of the temperature.

Our measurements proved that the behaviour of liquid sodium amalgams in the whole concentration range can be in the studied temperature region expressed by a simple equation giving the formal activity coefficient of sodium as a function of the mole fraction of the amalgam:

$$\log \gamma_{\text{Na(Hg)}} = k_{\text{T}} x'_{\text{Na}} . \tag{10}$$

This equation follows from the application of the theory of regular solutions on the Na–Hg system considered either as a purely binary one[9,10] or taking into account the possible formation of the intermetallic compound $NaHg_m$ in the liquid phase[11].

A very good agreement of the present data at 25°C follows also by their comparison with other authors' data reviewed earlier[10], where the following values were derived: $E^0_{\text{cell}} = 0{\cdot}7584\ \text{V}$, $k = 16{\cdot}393$. The results of Hsueh and Bennion[12] were not taken

for the comparison since, as was shown by Galli and coworkers[3], the basic condition of purely cationic conductivity of the β-alumina was not fulfilled in the cited work[12]. A very good agreement of the present data with the analogous results measured in the medium of very dry propylene carbonate[1] is an evidence that a suitably prepared β-alumina as a part of a sodium electrode can be used in concentration cells Na/Na$^+$-β-alumina/Na(Hg) that respond reversibly to the amalgam concentration even at the laboratory temperature, provided that the amalgam forms a single liquid phase.

The present results of measurements of the equilibrium potential difference of amalgam concentration cells up to the region of two-phase amalgams (containing the solid compound NaHg$_m$) were used to determine the solubility of sodium in mercury in the studied temperature range and to make more accurate the corresponding part of the phase diagram of the Na–Hg system[13]. The described method of measurement of the equilibrium cell potentials as function of the composition and temperature can be used generally in determining precise solubility data of liquidus curves of phase diagrams of condensed systems[14].

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