Phase diagram of the system Na—Hg in the region of dilute sodium amalgams*

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A new set of experimental data relevant to the phase diagram of the system Na—Hg in the region of dilute sodium amalgams (up to *ca.* 17 at. % Na) is given. The results are discussed from the point of view of the possible composition of structural species in the liquid amalgams as well as of the composition of solid intermetallic compounds coexisting with the saturated liquid sodium amalgams in the studied temperature and concentration region.

Предложен новый ряд экспериментальных данных для построения диаграммы состояния системы Na—Hg в области разбавленных амальгам натрия (до 17 ат. % Na). Полученные результаты обсуждены с точки зрения возможного состава частиц в жидкой амальгаме и твердых интерметаллических соединениях сосуществующих с насыщенными жидкими амальгамами натрия в изучаемой области температур и концентраций.

In the previous paper [1] a thermodynamic analysis of the hitherto published data on the liquidus curves of the phase diagram of the system Na—Hg has been given in order to make some conclusions on the real composition of individual species present in the liquid amalgams. It is known that a series of solid intermetallic compounds is formed in the system, however, the data concerning the concentration range from 0 to 18 at. % Na are rather controversial. According to the phase diagram presented in [2], the dilute liquid amalgams below 18 at. % Na may be considered to be solutions of the intermetallic compound $NaHg_4$ in an excess of mercury. On the other hand, however, in this concentration range also the existence of other intermetallic compounds, *viz.* $NaHg_5$ [3—5], $NaHg_6$ [4, 5], $NaHg_7$, $NaHg_8$, $NaHg_{10}$, $NaHg_{12}$, and $NaHg_{14}$ [6], has been suggested. For explanation of great deviations of this system from an ideal behaviour in the

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gaseous phase at temperatures above 200°C even the existence of $NaHg_{16}$ dissolved in the liquid phase was assumed [7]. X-ray diffraction measurements [8] have again proved a considerable degree of organization in the liquid phase even at temperatures above 200°C, when the intermetallic compounds, stable at lower temperatures (in the solid state) must have necessarily undergone the respective peritectic decompositions (Fig. 1). On the other hand, another group of authors considers the liquid sodium amalgams only to be solutions of sodium in mercury with great negative deviations from ideality and rules out any possibility of existence of intermetallic compounds in the liquid phase (for review see Ref. [9—11]).

A critical review of all solidus—liquidus data in the mentioned region [1] which are of great importance with respect to the theory of chlorine production by the mercury process as well as to other applications of sodium amalgams has shown that the discrepancies between the reported data make it impossible to carry out an exact thermodynamic analysis which might give information on the composition of species present in the liquid dilute sodium amalgams.

In the present paper a new set of equilibrium data for the phase diagram of the system Na—Hg in the region of diluted amalgams (up to *ca.* 17 at. % Na) is given.

Experimental

The presented data were obtained by means of two independent experimental methods:

a) Direct thermal analysis of individual amalgams of various composition using the differential scanning calorimeter DSC-2 (Perkin—Elmer) [12];

b) Electrochemical measurement of the reversible potential difference of concentration cell Na/Na(Hg) at various amalgam concentrations and temperatures [13].

The direct method of thermal analysis made it possible to determine the primary as well as the secondary temperatures of crystallization (T_{PC} and T_{SC}, respectively) and was used preferentially for analysis of very diluted amalgams in the crystallization region of pure mercury. The measurements were carried out in the atmosphere of purified and dried nitrogen. Other details of this technique are given in [12].

The applicability of EMF measurements [13] is based on the fact that the equilibrium potential difference of concentration cell Na/Na(Hg) decreases with increasing sodium concentration in the liquid amalgam at given temperature till the sodium concentration reaches the saturation value. Any further increase in the total sodium content in the system results only in an increase of the amount of the coexisting solid phase (intermetallic compound $NaHg_m$), the equilibrium potential difference of the cell, $E_{r,cell}$, remaining unchanged as the degree of freedom of such system becomes zero.

The equilibrium potential differences of concentration cells Na/Na(Hg) were measured using two different types of nonaqueous electrolytes containing sodium cations:

a) Solution of 0.1 M-$NaClO_4$ in highly dry propylene—carbonate (PC) [14];

b) Solid β-alumina ($Na_2O \cdot 11Al_2O_3$ doped with 2% MgO) [15].

The measurements with the solution of $NaClO_4$ in PC were used for determining the saturation concentrations of sodium amalgams at temperatures 15 and 25°C. The concentration cells with β-alumina as solid electrolyte with almost pure sodium cation transference ($t_{Na^+} = 1.0$) [16] were used for measurements both at room and elevated temperatures. For details on experimental techniques see Ref. [14, 15].

Results and discussion

The values of T_{PC} and T_{SC} of very diluted sodium amalgams for the crystallization region of pure mercury [14] are given in Table 1. The concentration is expressed in mole fraction of the total amount of sodium in the amalgam, x'_{Na}. The melting point of pure mercury ($T^f_{Hg} = 234.28$ K) served as the calibration point of the temperature measuring. The coordinates of the eutectic point were found to be: $T_E = 225.4 \pm 0.5$ K (-47.75 ± 0.5°C), $x'_{Na,E} = 0.0255$.

From a comparison of the experimental results in the crystallization region of pure mercury with the liquidus curves calculated on the assumption of existence of intermetallic compounds $NaHg_m$ of various composition ($m = 0$, 4, 6, and 16) in dilute liquid amalgams with ideal behaviour (Fig. 1) it is evident that the

Table 1

Experimental data of T_{PC} and T_{SC} of the system Na—Hg in the region of diluted amalgams

x'_{Na}	T_{PC}		T_{SC}		Method of determination	Ref.
	K	°C	K	°C		
0.000	234.28	−38.87	—	—		
0.008435	232.0	−41.15	226.6	−46.55	DSC-2	[12]
0.014830	229.82	−43.33	225.9	−47.25	DSC-2	This paper
0.025524	225.4	−47.75	225.4	−47.75	DSC-2	This paper
0.043955	278.15	5.0	—	—	EMF	[23]
0.04870	288.15	15.0	—	—	EMF isoth.	[23] and this paper
0.0538	298.15	25.0	—	—	EMF	[23]
0.0540	298.15	25.0	—	—	EMF isoth.	This paper
0.05763	306.65	33.5	—	—	EMF polyth.	This paper
0.0625	313.15	40.0	—	—	EMF isoth.	This paper
0.06534	320.95	47.8	—	—	EMF polyth.	This paper
0.0765	338.15	65.0	—	—	EMF isoth.	This paper
0.0942	363.15	90.0	—	—	EMF isoth.	This paper
0.09766	368.15	95.0	—	—	EMF polyth.	This paper
0.11002	382.35	109.2	225.9	−47.25	EMF polyth. + DSC-2	This paper
0.1205	393.15	120.0	—	—	EMF isoth.	This paper
0.12473	397.35	124.2	—	—	EMF polyth.	This paper
0.17134	421.65	148.5	—	—	EMF polyth.	This paper

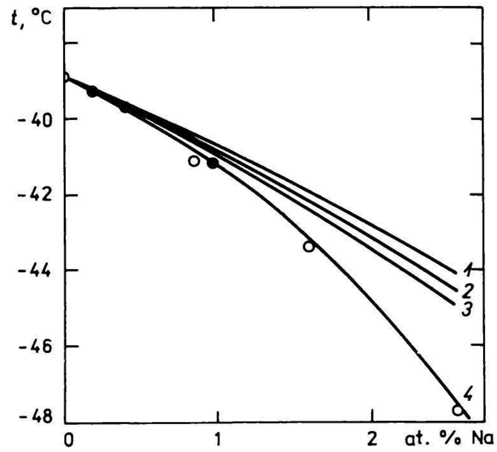

Fig. 1. Phase diagram of the system Na—Hg in the crystallization region of pure mercury.
○ This paper; ● Ref. [17].
Full lines: theoretical liquidus curves for assumed values of the stoichiometric coefficient $m = 0, 4, 6$, and 16 (curves *1*, *2*, *3*, and *4*, resp.).

experimental data are almost identical with those calculated assuming the presence of $NaHg_{16}$ in the amalgam as well as with the values reported by *Tammann* [17] for very low sodium concentrations. Considering the large discrepancies with the data presented by other authors [6, 18, 19] for this concentration range, however, no final conclusion could be done.

The experimental determination of the liquidus curve for $x'_{Na} > x'_{Na,E}$ in the crystallization region of intermetallic compound $NaHg_m$ (EMF measurements of concentration cells Na/Na(Hg)) consisted in finding the concentrations of saturated sodium amalgams at various temperatures. These values were obtained by two methods [13]:

a) At a given temperature: from the crossing point of the dependence of $E_{r,cell}$ on the concentration of unsaturated amalgams with that for supersaturated amalgams. The determination may be performed graphically either from the usual Nernstian form of the dependence of $E_{r,cell}$ on log x'_{Na} (Fig. 2) or, preferably, from the correlation $E'_{r,cell}$ *vs.* x'_{Na}, where $E'_{r,cell} = E_{r,cell} + (RT/F) \ln x'_{Na}$ (Fig. 3) which has been tested for the system under study [8, 20, 21] and the applicability of which also for systems with a possible existence of intermetallic compounds A_xB_y in the liquid phase has been proved [22];

b) At a given concentration: from the crossing point of the dependence of $E_{r,cell}$ on temperature for unsaturated solutions ($T > T_{PC}$) with that for supersaturated amalgams ($T < T_{PC}$) which have different courses for both temperature regions (Fig. 4).

The values of composition of saturated amalgams at various temperatures determined by such treatment of experimental data [12, 14, 15] are summarized in Table 1, including the results of *Bent* and *Swift* [23] obtained by a similar

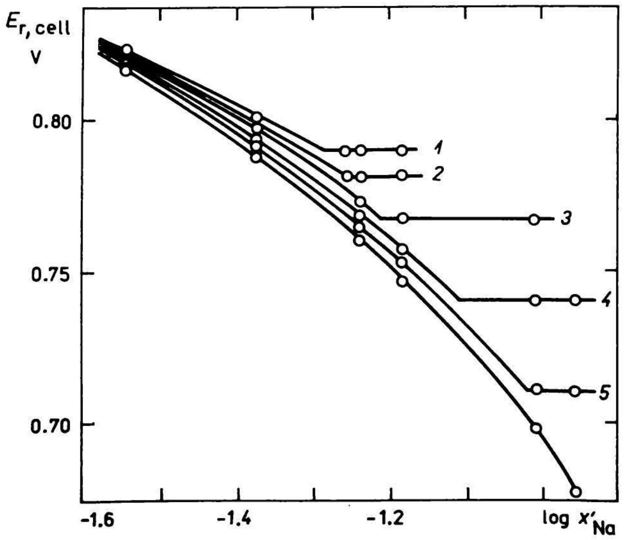

Fig. 2. Dependence of equilibrium potential difference $E_{r,cell}$ on $\log x'_{Na}$ for concentration cells Na/Na(Hg) at various temperatures.
1. 15°C; *2.* 25°C; *3.* 40°C; *4.* 65°C; *5.* 90°C.

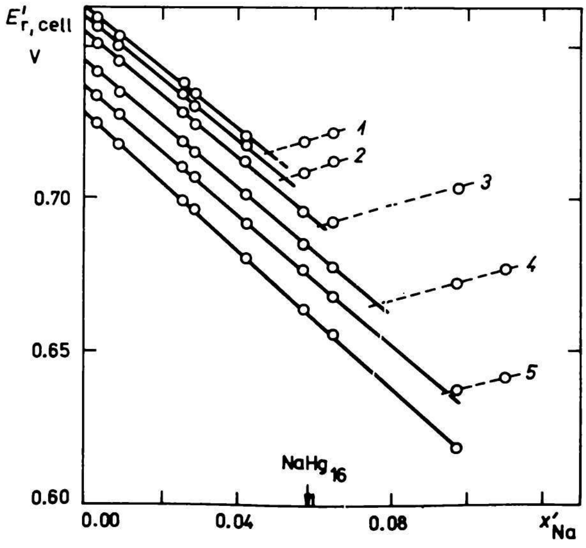

Fig. 3. Dependence of the quantity $E'_{r,cell}$ on x'_{Na} for concentration cells Na/Na(Hg) at various temperatures.
1. 15°C; *2.* 25°C; *3.* 40°C; *4.* 65°C; *5.* 90°C.

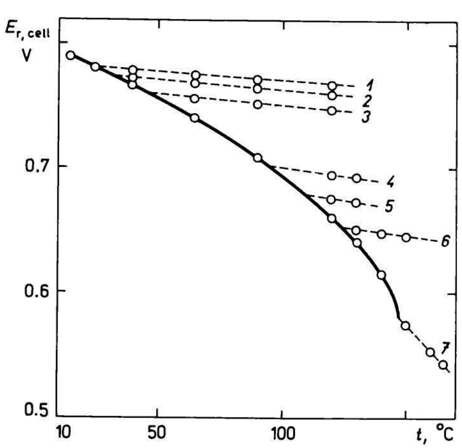

Fig. 4. Dependence of $E_{r,cell}$ on temperature for various concentrations of sodium amalgams x'_{Na}.
1. 0.05400; *2.* 0.05763; *3.* 0.06534;
4. 0.09766; *5.* 0.1100; *6.* 0.1247; *7.* 0.1713.
The full line connects $E_{r,cell}$ for saturated amalgams.

experimental method. From Fig. 5 constructed on the basis of those data it may be seen that all experimental points in this concentration and temperature range ($0.17 > x'_{Na} > x'_{Na,E}$) lie on a single curve headed towards the eutectic point, without any abrupt change in its course. This would indicate that only one solid intermetallic compound of the same composition $NaHg_m$ probably coexists with the saturated liquid amalgams in the whole temperature range from $T_E = 225.4$ K up to *ca.* 420 K. This conclusion is supported by the EMF measurements of concentration cells with liquid sodium amalgams of various concentrations at constant temperatures, for which the same correlation equation in the form $E'_{r,cell} = E^0_{r,cell} - (2.3RT/F)\,k_T x'_{Na}$ has been found for all measured concentrations from very diluted amalgams up to the saturated ones [14, 15] (Fig. 3). In the given correlation equation, $E^0_{r,cell}$ and k_T are temperature dependent constants. As, however, the investigated concentration range at higher temperatures was greater than the one corresponding to the composition of $NaHg_{16}$ (for such case $x'_{Na} = 0.0588$), it may be concluded that the stoichiometric coefficient m of the coexisting intermetallic compound must be lower than 16. That means that the conclusion on the possibility of existence of $NaHg_{16}$ in dilute liquid amalgams following from the course of the liquidus curve in the crystallization region of pure mercury (Fig. 1) is not valid for the concentration and temperature conditions when the solid intermetallic compound coexists with saturated liquid amalgams. This conclusion was further supported by the thermal analysis of amalgam with $x'_{Na} = 0.110$ for which only the value $T_{SC} = 225.9$ K was determined without any other thermal effect at higher temperatures. As the given T_{SC} is almost the same as the eutectic temperature $T_E = 225.4$ K (± 0.5 K), it is evident that in the whole concentration range ($x'_{Na} \leqq 0.110$) only one type of solid intermetallic compound $NaHg_m$ with $m < 16$ would exist with saturated liquid sodium amalgams at all the

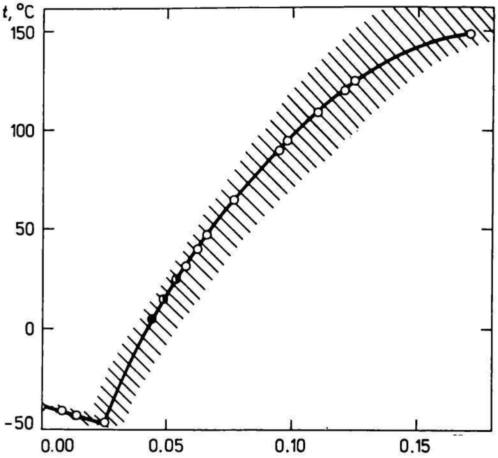

Fig. 5. Phase diagram of the system Na—Hg for dilute sodium amalgams.
○ This paper; ● Ref. [23]; hatched region indicates the range of hitherto published data.

respective temperatures. According to that the deviation of experimentally determined liquidus curve for the crystallization of pure mercury from that one for $m < 16$ might be explained by a nonideal behaviour of diluted liquid amalgams. On the basis of the obtained experimental data, however, no final conclusion on the real value of the stoichiometric coefficient m for the dissolved intermetallic compound in liquid amalgam may be done.

From the comparison of the experimental data in the crystallization region of intermetallic compound $NaHg_m$ with the results reported by other authors [1] it is evident that there is an excellent agreement with the data of *Bent* and *Swift* [23] at 5, 15, and 25°C obtained by a similar EMF method using NaI in dimethylamine as nonaqueous electrolyte, while the data presented by other authors are open to criticism. The reliability of the EMF method used is very good, as the reproducibility of $E_{r,cell}$ for saturated amalgams has been proved to be very high in both directions of the temperature changes. From this point of view especially the results of *Inoue* and *Osugi* [6] must be disapproved as entirely incorrect, not only with respect to the reported values, but especially owing to their interpretation.

Assuming that within the whole investigated temperature range from $T_E = 225.4$ K up to 420 K the saturated liquid amalgams coexist with the same solid intermetallic compound $NaHg_m$ it should be possible to express the solubility of this compound in mercury (or in other words to express the course of the liquidus curve of the phase diagram in the crystallization region of intermetallic compound $NaHg_m$) using the general simple form of the van't Hoff (or LeChatelier—Shreder) equation

$$\log x_{\mathrm{NaHg}_m} = \frac{\Delta \overline{H}^{\mathrm{s/l}}_{\mathrm{NaHg}_m}}{2.303R} \left(\frac{1}{T^{\mathrm{f}}_{\mathrm{NaHg}_m}} - \frac{1}{T} \right) \qquad (1)$$

in which $\Delta \overline{H}^{\mathrm{s/l}}_{\mathrm{NaHg}_m}$ represents the differential molar heat of solution of the appropriate intermetallic compound in a saturated amalgam with mole fraction x_{NaHg_m} at temperature T, $T^{\mathrm{f}}_{\mathrm{NaHg}_m}$ is the hypothetical temperature of fusion of this compound which, in reality, undergoes the peritectic decomposition at *ca.* 430 K (157°C). From Fig. 6, where the dependence of log x_{NaHg_m} on $1/T$ for various values of the stoichiometric coefficient m (0, 4, and 6, respectively) is given, it may be seen that in no case this dependence is linear.

On the basis of the obtained results it may be concluded that the temperature dependence of the hitherto published data for liquidus curve in the range of primary crystallization of the intermetallic compound NaHg_m cannot be interpreted in the form shown in Fig. 3 of the previous paper [1] with two linear parts of the dependence of log x *vs*. $1/T$, as this dependence exhibits a continuous course without any abrupt break for all assumed values of the stoichiometric coefficient m (Fig. 6).

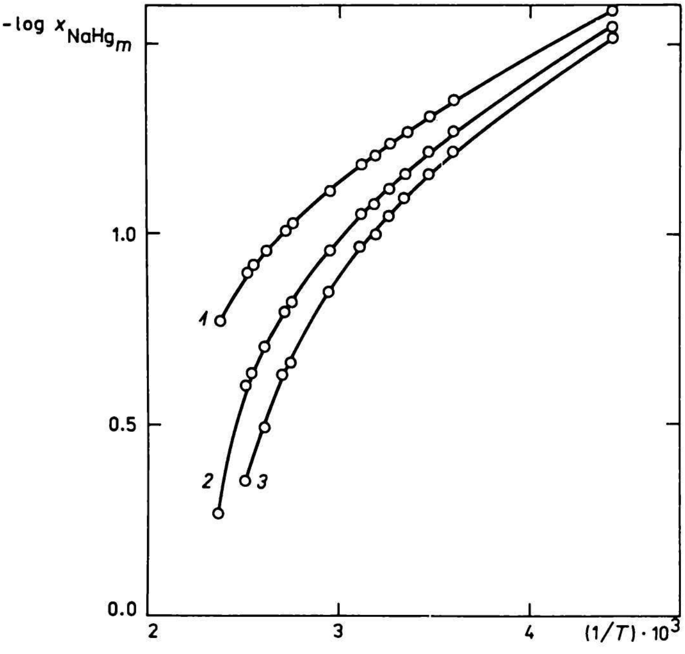

Fig. 6. Dependence of log x_{NaHg_m} on $1/T$ for various assumed values of the stoichiometric coefficient $m = 0, 4$, and 6, resp. (curves *1, 2,* and *3,* resp.).

The nonlinear course of the temperature dependence shown in Fig. 6 indicates that $\Delta\overline{H}^{s/l}_{\mathrm{NaHg}_m}$ shows a great dependence on the composition of liquid amalgam. Such an explanation is also supported by the dependence of $E_{\mathrm{r,cell}}$ on T for various concentrations of liquid amalgams the slopes of which vary with varying amalgam concentrations (Fig. 4). This does not exclude, however, the possibility of existence of several intermetallic compounds which might be present in various amounts depending upon the concentration of the amalgam so that the heat of solution of the investigated system might vary following the relative concentration of the respective intermetallic compounds in liquid amalgams. The treatment of experimental data from this aspect will be the subject of the subsequent contribution.

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