CONTRIBUTION TO THE THERMODYNAMICS OF SODIUM AMALGAMS

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Basing on the assumption that considerable negative deviations from ideal behaviour of sodium amalgams are due to the formation of an intermetallic compound $NaHg_4$, the up to now published data on equilibrium potentials of sodium amalgams of different concentrations were used to calculate the values of the apparent equilibrium constant of the formation of the mentioned compound. Its extrapolation to the state of infinitely diluted solution yielded its true value, referred to the standard state of infinitely diluted amalgam ($K = 6.608 . 10^{12}$ at 25°C). Concentration dependence of the apparent equilibrium constant made it possible to calculate the activity coefficients of the individual components of the system.

Dilute liquid sodium amalgams containing less than 1 mass % of the alkali metal are of considerable technical importance, *e.g.* in amalgam process of the electrolytic production of chlorine and sodium hydroxide, for amalgam fuel cells, *etc.* Consequently, also their equilibrium potential is an important quantity, governing the reversible voltage of systems which work with amalgam electrodes. Their value can be determined by means of the Nernst equation either using the standard equilibrium potential of pure metallic sodium[1] $E^0_{Na(s)/Na+}$ (-2.71424 V at 25°C) or the standard equilibrium potential of sodium amalgam, derived from the infinitely diluted amalgam[1] ($E^0_{Na(am)/Na+} = -1.95584$ V at 25°C) as the reference state. In the first case it is possible to calculate the true activity of free sodium in the amalgam, as related to the activity of pure metallic sodium, from the known value of the equilibrium potential of the sodium amalgam of a given composition, provided that the relation between the activity and the concentration of sodium in the amalgam[2] is known. In the second case[1,3,4], the activity of sodium in the amalgam of a given composition is referred to the activity of a hypothetical state of pure sodium, derived from the reference state of infinitely diluted amalgam in which $\gamma_{Na(am)} \to 1$ for $x_{Na(am)} \to 0$. Both calculations must, of course, yield the same value of the equilibrium potential $E_{Na(am)}$ for the same composition of the system. However, in both procedures the system is regarded as a binary one, irrespective of what it is really.

ANALYSIS OF THE PROBLEM

The phase diagram of the system Na–Hg clearly shows[5] (Fig. 1) that chemical reactions between both components take place yielding intermetallic compounds of a definite composition which are formed at the respective temperatures as a solid phase from the amalgam of the given composition. Of a number of these compounds only the compound $NaHg_2$ is thermally stable and melts congruently at 353°C. The region of diluted amalgams containing less than 1 mass% Na, which is the most interesting one in the field of technical electrochemistry, is at the same time a system with sufficient thermal stability, since the compound $NaHg_4$, coexisting with saturated liquid amalgams in this concentration region, melts incongruently only at 157°C under dissociation to the stable $NaHg_2$ and Hg. Consequently, from the standpoint of the phase diagram in Fig. 1, sodium amalgams with less than 1 mass% Na at temperatures lower than 100°C can be considered to be solutions of the intermetallic compound $NaHg_4$ in mercury.

So far, no uniformly accepted opinion is available on the real form in which sodium is present in liquid, more diluted amalgams of the mentioned composition (for review see refs[3,6-8]). At present, the existence both of well-defined intermetallic compounds and of solvated (mercuriated) sodium atoms or ions or even of other particles is accepted. A number of the hitherto obtained experimental data support either one or the other alternative, however, a consistent interpretation of all observed data has failed as yet. X-ray diffraction measurements[8] which should have proved the existence of intermetallic compounds in liquid amalgams, have in fact proved a considerable degree of organisation in the liquid phase, eventhough the measurements were carried out at relatively high temperatures (200°C min), when the compounds, stable at lower temperatures (in the solid phase) must have necessarily undergone the respective peritectic reactions (Fig. 1). However the method of Kozlovskij, Zebreva and Gladyšev[9] cannot be accepted, who, attempting to join the expression for the equilibrium potential of metal amalgams under the formation of intermetallic compounds, as derived by Jangg and Kirchmayr[10] with
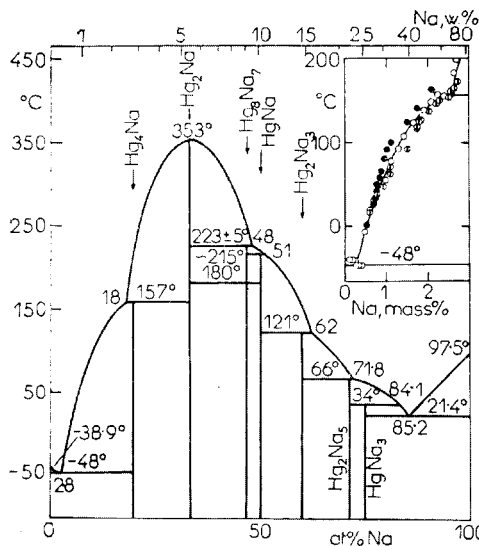

FIG. 1

Phase Diagram of the System Na–Hg (ref.[5])

the concepts of the less probable existence of an intermetallic compound, assume its total dissociation in the liquid amalgam to its initial components. According to this assumption the inter- metallic compound is in fact not formed in liquid amalgams and consequently the value of its free enthalpy of formation cannot be taken into account. If the mentioned authors obtain formally the same expression as Jangg and Kirchmayr, it is due to the fact that the activities of sodium and mercury in their expressions do not represent the activities of all sodium and mercury present in the amalgam, but only the activities of the remaining parts of these components which are not bound in the form of an intermetallic compound.

Since the so far obtained data on equilibrium electrode potentials in the system Na–Hg (for review see[1]) were treated only regarding this system as a binary one, *i.e.* without the formation of intermetallic compounds (a detailed explanation of such thermodynamical treatment was given in paper[11], published after this study had been finished), I attempted in the present study to interpret the up to now published data on equilibrium potentials of diluted liquid sodium amalgams in terms of the formation of the intermetallic compound $NaHg_4$ also in the liquid phase. I was led to this assumption by the results of the shape of phase diagram of this system in the respective concentration range (Fig. 1) as well as by the extraordinarily low values of activity coefficients of sodium (of the order 10^{-12} and less) referred (in the scale of mole fractions) to the unit activity of pure metallic sodium. Such low values unambiguously indicate a strong interaction between both components and prove that the prevailing part of the total sodium content in the amalgam is present in a form, different from that of a physical solution of metal, whose real content is, of course, only responsible for the establishing of the measured equilibrium potential of the reaction $Na \rightarrow Na^+ + e$.

RESULTS AND DISCUSSIONS

According to the above mentioned considerations the equilibrium state of the system Na–Hg is given by the equilibrium of the chemical reaction

$$Na + 4\,Hg \rightleftarrows NaHg_4, \qquad (A)$$
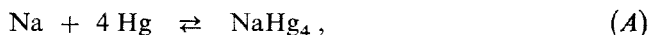
whose equilibrium constant is defined by the expression

$$K = a_{NaHg_4}/(a_{Na} \cdot a_{Hg}^4) = [x_{NaHg_4}/(a_{Na} \cdot x_{Hg}^4)]\,(\gamma_{NaHg_4}/\gamma_{Hg}^4) = K' \cdot K_\gamma, \qquad (1)$$

where the unknown activities of the intermetallic compound as well as of the un- reacted mercury are substituted by the product of their mole fraction x_i and activity coefficient γ_i. Activity of the remaining unreacted sodium in the amalgam a_{Na} can be calculated from the values of the equilibrium voltage of the concentration cell, con- sisting of pure metallic sodium and sodium amalgam of the given composition, immersed into a solution of sodium salt. Since the equilibrium potentials of sodium amalgams in the whole concentration range from very diluted up to saturated with intermetallic compound $NaHg_4$ are known with a sufficient accuracy only for 25°C (see ref.[1]), all further calculations were carried out only for this temperature. Calcula- tion of the activity of the remaining sodium dissolved in the amalgam of the given total composition was performed using the relation

$$\log a_{\text{Na}} = (F/2 \cdot 3\, RT)\left(E^0_{\text{Na(s)/Na}^+} - E_{\text{Na(am)/Na}^+}\right) \qquad (2)$$

in which the value of the equilibrium potentials of sodium amalgam of the given total composition, $E_{\text{Na(am)/Na}^+}$ were calculated using the correlation equation derived recently on the basis of a critical analysis of the hitherto published data[1].

Because the activity coefficient of the intermetallic compound γ_{NaHg_4} and of the remaining unreacted mercury, γ_{Hg} are not known, the first step was to calculate the values of the apparent equilibrium constant K' from the known total composition of amalgams and from the corresponding activities of free sodium, determined according to Eq. (2). In this calculation the mole fraction of the intermetallic compound x_{NaHg_4} and of the remaining unreacted mercury x_{Hg} were expressed in terms of the mole fraction of total sodium content in the amalgam, x'_{Na}, and of the mole fraction of total mercury content $x'_{\text{Hg}} = 1 - x'_{\text{Na}}$. According to this, the amount of substance of the individual components, really present in the system, n_i, formed from the total amount of substance of sodium, x'_{Na}, and that of mercury, x'_{Hg}, equals

$$n_{\text{Na}} = a'_{\text{Na}}, \qquad (3a)$$

$$n_{\text{NaHg}_4} = x'_{\text{Na}} - a'_{\text{Na}}, \qquad (3b)$$

$$n_{\text{Hg}} = x'_{\text{Hg}} - 4n_{\text{NaHg}_4} = 1 - 5x'_{\text{Na}} + 4a'_{\text{Na}} \qquad (3c)$$

and the total amount of substance of all components considered is

$$n_i = 1 - 4x'_{\text{Na}} + 4a'_{\text{Na}}. \qquad (3d)$$

The activities of the unreacted, physically dissolved sodium, as determined from Eq. (2) lie in the range of $10^{-14} - 10^{-16}$ (Table I) for the concentration range $x'_{\text{Na}} = 0 \cdot 001 - 0 \cdot 0538$ (*i.e.* up to the saturated amalgam at 25°C (see[12]), and therefore it is evident that $a'_{\text{Na}} \approx a_{\text{Na}} \lll x'_{\text{Na}}$. Consequently, the mole fractions of the considered components of the system can be expressed as

$$x_{\text{Na}} = a_{\text{Na}}, \qquad (4a)$$

$$x_{\text{NaHg}_4} = x'_{\text{Na}}/(1 - 4x'_{\text{Na}}), \qquad (4b)$$

$$x_{\text{Hg}} = (1 - 5x'_{\text{Na}})/(1 - 4x'_{\text{Na}}). \qquad (4c)$$

The values of the apparent equilibrium constant K', calculated in this way for different compositions of liquid sodium amalgams in the whole concentration range at 25°C are presented in Table I. As can be seen, the value of this quantity varies, over

the whole concentration range, within the limits of the order of magnitude of 10^{12}, decreasing slowly with increasing concentration of the amalgam.

This concentration dependence of K' can be caused first of all by the fact that the activity quotient $K_\gamma \neq 1$. Choosing pure metal as the standard state of mercury $(\gamma_{Hg} \rightarrow 1$ for $x_{Hg} \rightarrow 1)$ and the standard state of the intermetallic compound derived from infinitely diluted solution $(\gamma_{NaHg_4} \rightarrow 1$ for $x_{NaHg_4} \rightarrow 0)$ then it is obvious that in an infinitely diluted sodium amalgam it holds $K_\gamma = 1.0$, so that in this case $K = K'$. Therefore, the true thermodynamic equilibrium constant of the formation of the inter-metallic compound $NaHg_4$ in liquid sodium amalgam can be determined by extrapolating the dependence of the apparent equilibrium constant K' to zero concentration of sodium in the amalgam. The value of K obtained in this way was $6.608 \cdot 10^{12}$.

The values of the activity quotient $K_\gamma = \gamma_{NaHg_4}/\gamma_{Hg}^4$ were determined from the values of $K/K' = K_\gamma$. With respect to the very low values of the free physically dissolved sodium in these amalgams, this system was taken as quasibinary in further calculations of the activity coefficients of the intermetallic compound and of the remaining mercury from the calculated value of K_γ. First, the system was assumed to behave as a purely regular one, so that according to Hildebrand[13] the dependence of the

TABLE I

Calculated Values of Apparent Equilibrium Constant K' of the Formation of Intermetallic Compound $NaHg_4$ in Liquid Sodium Amalgams of Varying Composition at 25°C

x'_{Na}	x_{NaHg_4}	$-\log a_{Na}$	$\log K'$	$\log K_\gamma$	$\log K_\gamma$ (calc. from Eq. (10))
0·001	0·00100402	15·7913	12·7948	0·01296	0·01261
0·002	0·00201613	15·4744	12·7818	0·02588	0·02525
0·004	0·00406504	15·1416	12·7563	0·05145	
0·006	0·00614754	14·9338	12·7306	0·07711	0·07607
0·008	0·00826446	14·7771	12·7051	0·1026	
0·010	0·0104167	14·6485	12·6768	0·1310	0·1273
0·015	0·0159574	14·3931	12·6166	0·1911	
0·020	0·021739	14·1888	12·5542	0·2535	0·2561
0·025	0·027778	14·0125	12·4916	0·3161	
0·030	0·0340909	13·8540	12·4318	0·3760	0·3842
0·035	0·040698	13·7077	12·3717	0·4360	
0·040	0·047619	13·5704	12·3125	0·4952	0·5083
0·045	0·054878	13·4399	12·2542	0·5535	
0·050	0·062500	13·3148	12·1971	0·6106	0·6234
0·0538[a]	0·068553	13·2227	12·1544	0·6534	0·6633

[a] Saturated amalgam at 25°C, coexisting with the solid compound $NaHg_4$.

activity coefficient of mercury (as solvent) on the content of the intermetallic compound was calculated using the relation

$$-\ln \gamma_{Hg} = B \cdot x_{NaHg_4}^2 \, . \tag{5}$$

Application of the Gibbs–Duhem equation to a binary system and its integration yields an expression for the dependence of the activity coefficient of the intermetallic compound on composition

$$\ln \gamma_{NaHg_4} = 2B \cdot x_{NaHg_4} - B \cdot x_{NaHg_4}^2 \, . \tag{6}$$

Substituting expressions (5) and (6) into the logarithmized relation for K_γ and by rearrangement we obtain

$$\log K_\gamma / (2 + 3x_{NaHg_4}) = B \cdot x_{NaHg_4} / 2 \cdot 303 \, , \tag{7}$$

from which it follows that the left-hand side of Eq. (7) should be a linear function of x_{NaHg_4} with the slope $B/2 \cdot 303$. However, as can be seen from Fig. 2, this condition, denoted by dashed line, is fulfilled only for very low values of $x_{NaHg_4} \leqq 0 \cdot 01$; for higher amalgam concentrations the course of this dependence is non-linear. This means that the system does not behave as a purely regular one over the whole concentration range.

In the second approximation the following relation was chosen to describe the dependence of the activity coefficient of mercury on composition

$$-\ln \gamma_{Hg} = B \cdot x_{NaHg_4}^2 + C \cdot x_{NaHg_4}^3 \, , \tag{8}$$

from which the expression for the dependence of the activity coefficient γ_{NaHg_4} on composition could be determined by means of the Gibbs–Duhem equation

$$\ln \gamma_{NaHg_4} = 2B \cdot x_{NaHg_4} - (B - 1 \cdot 5C) \cdot x_{NaHg_4}^2 - C \cdot x_{NaHg_4}^3 \, . \tag{9}$$

Substituting expressions (8) and (9) into the relation for K_γ and after rearrangement we obtain

$$\log K_\gamma = 2B' \cdot x_{NaHg_4} + (3B' + 1 \cdot 5C') x_{NaHg_4}^2 + 3C' \cdot x_{NaHg_4}^3 \, . \tag{10}$$

This equation may serve to calculate, for known compositions of the amalgams and the corresponding values of K_γ, the values of constants $B' = B/2 \cdot 3026$ and $C' = C/2 \cdot 3026$. The values of B' and C' calculated in this way from the data in Table I are $B' = 6 \cdot 511$ and $C' = -36 \cdot 026$. Thus it is possible to express the dependence of the activity coefficients γ_{NaHg_4} and of the unreacted mercury γ_{Hg} on composition in the

whole concentration range up to the saturated solution in the form of following relations

$$\log \gamma_{\text{NaHg}_4} = 13\cdot021 x_{\text{NaHg}_4} - 60\cdot549 x^2_{\text{NaHg}_4} - 108\cdot077 x^3_{\text{NaHg}_4}, \qquad (11)$$

and

$$\log \gamma_{\text{Hg}} = -6\cdot051 x^2_{\text{NaHg}_4} + 36\cdot026 x^3_{\text{NaHg}_4}. \qquad (12)$$

The course of the dependence of K_γ on composition as taken from the tabellated data (Table I) and that determined according to Eq. (10) using the coefficients B' and C' are presented in Fig. 3. As can be seen, the agreement is very good.

The value of the true equilibrium constant K may be used to calculate the change of the standard free enthalpy of the formation of the infinitely diluted intermetallic compound NaHg_4 according to the relation $-\Delta G° = 2\cdot3026 \, RT \log K$. By substituting the respective values the found value of $-\Delta G° = 17489$ cal/mol. This quantity equals, as to its numerical value, to the change of the standard free enthalpy of the amalgamation reaction, calculated from the value of the standard voltage of the concentration cell metallic sodium–sodium amalgam in which the standard state of sodium amalgam was obtained by extrapolation from infinitely diluted amalgam[1]. According to this, the standard equilibrium potential of sodium amalgam $E^0_{\text{Na(am)/Na}^+}$, referred in the papers of Yeager and coworkers[3] and Mussini and coworkers[4],
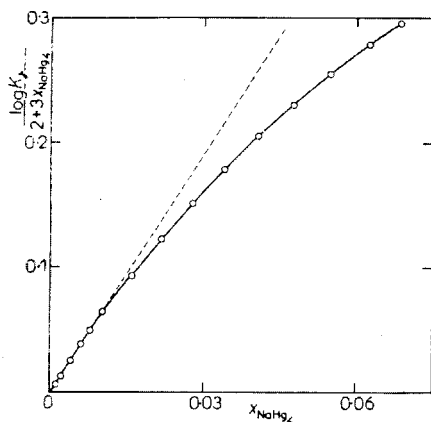

FIG. 2

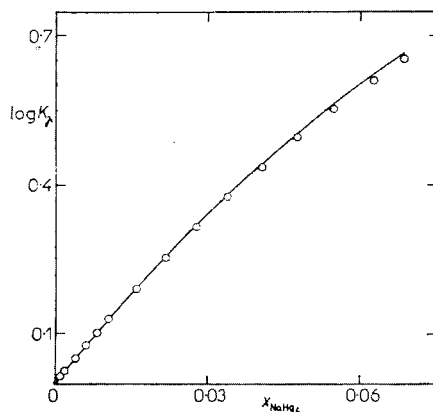Dependence of the Expression $\log K_\gamma / (2 + 3x_{\text{NaHg}_4})$ on Mole Fraction x_{NaHg_4}

FIG. 3

Dependence of the Activity Quotient K_γ on Mole Fraction x_{NaHg_4}
○ Tabellated data (Table I), ——— calculated according to Eq. (10).

as well as in our preceding work[1], is given by the relation

$$E^0_{Na(am)/Na^+} = E^0_{Na(s)/Na^+} - \Delta G^0_{f,NaHg_4(merc)}/nF . \tag{13}$$

The advantage of this expression is that it contains only further standard thermodynamic quantities which can be, with respect to the choice of standard states, determined with high precision. An analogous general expression, derived by Jangg and Kirchmayr[10] for the formation of an intermetallic compound MHg_y in the amalgam in the form

$$E^{0'}_{M(am)/M^{z+}} = E^0_{M(s)/M^{z+}} - (\Delta G^{0'}/zF) + (RT/zF)\ln a^{*y}_{Hg} \tag{14}$$

is not quite suitable just because it contains mostly unknown or not sufficiently known quantities, $viz.$ the change of the free enthalpy of formation of a pure solid intermetallic compound, $\Delta G^{0'}$, and the activity of the remaining unreacted mercury, a^*_{Hg}, in an amalgam saturated with intermetallic compound MHg_y at the given temperature.

The so far presented interpretation of the equilibrium data in liquid amalgams was based on the assumption that an equilibrium is taking place under the formation of the intermetallic compound $NaHg_4$. The concentration dependence of the apparent equilibrium constant was explained by the non-unity values of activity coefficients γ_{NaHg_4} and γ_{Hg}. Besides this interpretation, another attempt to explain the found thermodynamic behaviour of this system was made, considering the possibility of further chemical reactions of the primarily formed compound $NaHg_4$. Up to now the following reactions were supposed to proceed simultaneously: $NaHg_4 + Na = 2 NaHg_2$ (B), $NaHg_4 = NaHg_2 + 2 Hg$ (C) and $2 NaHg_4 = (NaHg_4)_2$ (D). However, calculations of these more complex equilibria, carried out under simplifying assumptions, that in an infinitely diluted amalgam practically only $NaHg_4$ is formed, resulted in non-realistic values of the degree of transformation of the primarily formed compound $NaHg_4$ in the sense of some of the mentioned consecutive reactions $(B)-(D)$.

An analogous calculation of the apparent equilibrium constants was also performed, assuming the formation of only one of the further compounds $NaHg_2$, $NaHg_6$ or $NaHg_{16}$ in liquid amalgams of the given total composition. $E.g.$, the existence of only $NaHg_2$ in liquid sodium amalgams at all temperatures is supposed by Angus and Hucke[14], on the basis of the incongruent melting of the solid compound $NaHg_4$ at $157°C$ under the formation of solid $NaHg_2$ and liquid mercury. The compounds $NaHg_6$ and $NaHg_{16}$, although they were not firmly proved by measurements of the phase diagrams of the system Na–Hg, are supposed to exist by Bent and Hildebrand[15], because they can explain the strongly negative deviations of the vapour tension of this system in the concentration range $x'_{Na} \leqq 0.1$ at temperatures higher than $300°C$. However, the assumption of the formation of only $NaHg_2$ in liquid sodium amalgams

leads to a still more expressive concentration dependence of the respective apparent equilibrium constant K', the assumed formation of $NaHg_6$ results in an only slightly lower concentration dependence than in the case of $NaHg_4$ and the supposed formation of $NaHg_{16}$ yields even the concentration dependence with a minimum at $x'_{Na} = = 0{\cdot}004$ and then the apparent equilibrium constant increases steeply by up to two orders of magnitude. From all this it follows that these further intermetallic compounds $NaHg_y$, no matter whether their existence was proved or not, do not yield a concentration independent equilibrium constant, as it was calculated under the simplifying assumption of unit activity coefficients of all components of the system.

Thus, the concentration dependence of the apparent equilibrium constant of the formation of $NaHg_4$ as the most probable product existing at normal temperatures in diluted sodium amalgams, seems to be due either to the non-ideal behaviour of this compound in a mercury solution (as it follows from the results of the present paper) or to further, so far not proved chemical transformations of the primarily formed compound $NaHg_4$ which lead to particles of another species (possibly also ionized), as it is indicated in the hitherto published reviews on the nature of alkali metals amalgams[3,6−8].

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