

## REDETERMINATION OF SOLIDUS-LIQUIDUS CURVES FOR THE Na-Hg SYSTEM IN THE CRYSTALLIZATION REGION OF PURE MERCURY

Jan BALEJ and JAN BIROŠ

*Institute of Inorganic Chemistry,  
Czechoslovak Academy of Sciences, 160 00 Prague 6, and  
Institute of Macromolecular Chemistry,  
Czechoslovak Academy of Sciences, 162 06 Prague 6*

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*Dedicated to Professor F. Čižka on the occasion of his 80th birthday.*

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The solidus-liquidus curves for the Na-Hg system in the crystallization region of pure mercury were reinvestigated with the aid of a differential scanning calorimeter of the type DSC-2 (Perkin-Elmer). The composition of the eutectic mixture was found to correspond to a mole fraction of sodium of  $0.02552$  at a temperature of  $225.6 \pm 0.3$  K.

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A thermodynamic analysis<sup>1</sup> of published data about the phase diagram of the Na-Hg system in the low sodium concentration region (up to about 18 mol % Na) revealed considerable discrepancies among the data of different authors, hence no definite conclusions about the composition of liquid amalgams were possible. A comparison of the data for the liquidus curve in the crystallization region of pure mercury with theoretical curves calculated for various composition of the possible intermetallic compounds  $\text{NaHg}_m$  in liquid amalgams showed that the data of Tammann<sup>2</sup> and Schüller<sup>3</sup> are in accord with the possible existence of the compound  $\text{NaHg}_{16}$ ; this has been assumed also to explain large negative deviations of this system in the vapour phase from the ideal behaviour<sup>4</sup> at temperatures above  $200^\circ\text{C}$ . The data of Vanstone<sup>5</sup> show a considerable scatter especially at the crystallization temperature of the eutectic mixture and lie between the theoretical curves for  $m = 0$  (i.e., no intermetallic compounds) and  $m = 16$  (i.e., for  $\text{NaHg}_{16}$ ). The latest data of Inoue and Osugi<sup>6</sup> seem to be not reliable for the considered concentration range, since one point lies still higher than the highest theoretical curve for  $m = 0$ , whereas the other one lies below the theoretical curve for  $\text{NaHg}_{16}$ , a compound with the highest mercury content considered as yet. Also the characteristic data for the position of the eutectic point differ somewhat: according to Schüller<sup>3</sup>,  $T_E = 224.95$  K ( $-48.2^\circ\text{C}$ ) and the total mole fraction of sodium  $x'_{\text{Na},E} = 0.028$ , whereas Vanstone<sup>5</sup> gives  $T_E = 226.35$  K ( $-46.8^\circ\text{C}$ ) and  $x'_{\text{Na},E} = 0.027$ ; in reality he found the com-

position of three alloys which solidified at the eutectic temperature to be in the range 2.38–3.30 mol % Na.

The aim of the present work was to reinvestigate the solidus–liquidus equilibrium of the Na–Hg system in the crystallization region of pure mercury.

## EXPERIMENTAL

The solidus–liquids curves for the Na–Hg system in the region of crystallization of pure mercury were studied with the use of a DSC-2 type differential scanning calorimeter (Perkin–Elmer, USA). Samples of amalgams and pure mercury (all liquid at normal temperature) in the form of droplets at most 1 mm in diameter were taken in an atmosphere of pure dry nitrogen on a small dish of a preheated carbon of spectral purity and placed into the measuring head of the apparatus. After it was closed, the temperature was lowered several degrees under the assumed eutectic temperature, *i.e.*, to 220 K, so that the sample solidified. Then it was relatively rapidly heated to estimate the temperature ranges at which the main phase changes in the amalgam take place, *i.e.*, melting of the eutectic mixture and of the mercury that crystallized from the amalgam during its cooling. After the sample had been completely melted, a slow cooling rate of 0.62 K/min was adjusted and the sample slowly crystallized under practically equilibrium conditions. Nevertheless, it was apparent from the recorded curve of the heat input ( $dQ/dt$ ) against temperature that the eutectic mixture solidified only after the sample had been undercooled by several degrees, which followed by comparison with the value of  $T_E$  of the same sample obtained during heating, when neither undercooling nor overheating took place. Hence, after the temperature drop by several degrees under  $T_E$  (complete solidification) the sample was heated at a rate of 0.62 K/min to a temperature by several tenths of a degree lower than the melting point of pure mercury, whose solid traces coexisted with the liquid portion of the amalgam. The residual solid mercury played the role of nuclei for crystallization during the subsequent slow cooling regime (0.62 K/min), whereby undercooling was efficiently prevented and the solidification proceeded at nearly equilibrium conditions. The final record of the temperature changes of the sample, serving for the evaluation of the primary and secondary crystallization temperatures ( $T'_{PC}$  and  $T'_{SC}$ ), was made during subsequent equally slow heating up to temperatures by several degrees higher than necessary for the melting of last traces of mercury in the amalgam.

## RESULTS AND DISCUSSION

A record of the heat input rate in dependence on the temperature corresponding to an amalgam with  $x'_{Na} = 0.00843$  is shown in Fig. 1. The melting of the eutectic mixture is manifested by a marked narrow peak, which is followed by a broader region of gradual melting of pure mercury which crystallized from the amalgam at temperatures above the eutectic point. In the diagram is also shown how the noncorrected primary and secondary crystallization temperatures  $T'_{PC}$  and  $T'_{SC}$  were determined. The found value of  $T'_{PC}$  for pure mercury was compared with its tabulated melting point (234.28 K) to find the total correction of the apparatus, by which found values of  $T'_{PC}$  and  $T'_{SC}$  were corrected to give the true values,  $T_{PC}$  and  $T_{SC}$ . These are summarized in Table I.

It is seen from this Table that the amalgam for which  $x'_{\text{Na}} = 0.02552$  just corresponds to the eutectic mixture, since in this case  $T_{\text{PC}} = T_{\text{SC}} = T_{\text{E}} = 225.4 \text{ K}$  ( $-47.75^\circ\text{C}$ ). A more concentrated amalgam with  $x'_{\text{Na}} = 0.02829$  has both characteristic temperatures different from one another and at  $T_{\text{PC}}$  an intermetallic compound  $\text{NaHg}_m$  separates from it (according to most authors<sup>7</sup>,  $m = 4$ ). By comparison of our results with the theoretical curves of liquidus for various  $m$  values in the crystallization region of pure mercury (Fig. 2) it follows, however, that a close agreement exists with the theoretical curve for  $m = 16$ . This is in accord with the results of Tammann<sup>2</sup> and — to a certain extent — also of Schüller<sup>3</sup>, whose value of  $T_{\text{E}}$  is somewhat lower than our.

Since according to the above analysis an evidence was obtained for the possible existence of an intermetallic compound with a larger  $m$  value than the commonly

TABLE I

Values of  $T_{\text{PC}}$  and  $T_{\text{SC}}$  for Diluted Sodium Amalgams in Crystallization Region of Pure Mercury

| $x'_{\text{Na}}$ | $T_{\text{PC}}$ , K | $T_{\text{SC}}$ , K | Solid phase          |
|------------------|---------------------|---------------------|----------------------|
| 0.000            | 234.28              | —                   | Hg                   |
| 0.00843          | 232.0               | 225.6               | Hg                   |
| 0.01483          | 230.0               | 225.8               | Hg                   |
| 0.02552          | 225.4               | 225.4               | Hg + $\text{NaHg}_m$ |
| 0.02829          | 227.4               | 225.6               | $\text{NaHg}_m$      |

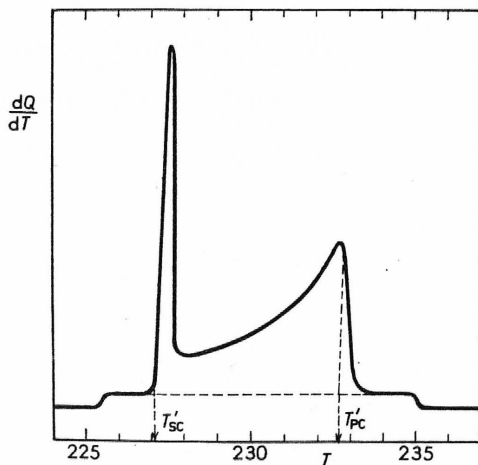


FIG. 1

Recorded Curve of  $dQ/dT$  against  $T$  (K) for Sodium Amalgam of Total Mole Fraction  $x'_{\text{Na}} = 0.00843$  and Method of Evaluation of Noncorrected Values of  $T'_{\text{PC}}$  and  $T'_{\text{SC}}$

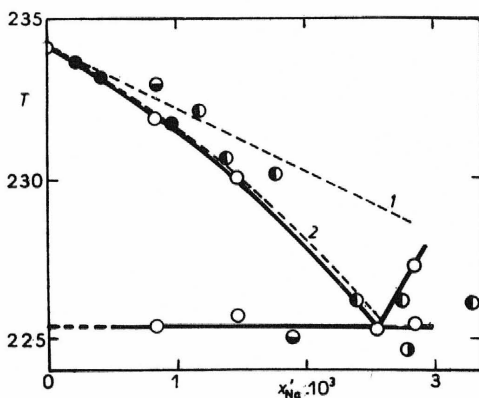
accepted  $m = 4$ , we carried out a calorimetric analysis also of an amalgam with  $x'_{\text{Na}} = 0.1100$ . From the measurements of the equilibrium potential differences of Na/Na(Hg) concentration cells the value of  $T_{\text{PC}} = 382.35 \text{ K}$  ( $109.2^\circ\text{C}$ ) was determined for this amalgam<sup>8,9</sup>. Its sodium content however, is lower than corresponds to the intermetallic compound  $\text{NaHg}_6$  considered by some older authors<sup>10-12</sup>. Its calorimetric analysis on the DSC-2 apparatus revealed  $T_{\text{SC}} = 225.9 \text{ K}$  ( $-47.25^\circ\text{C}$ ), which is practically equal to the solidification point of the eutectic mixture,  $T_{\text{E}}$ . Another characteristic temperature could not be recorded with the mentioned sample since a large difference between  $T_{\text{SC}}$  and  $T_{\text{PC}}$  together with the small quantity of the sample makes the determination of  $T_{\text{PC}}$  by our method impossible. Nevertheless, it can be concluded from the values of  $T_{\text{SC}}$  thus found that in the concentration interval  $x'_{\text{Na,E}} < x'_{\text{Na}} \leq 0.11$  only a single intermetallic compound  $\text{NaHg}_m$  with  $m < 6$  crystallizes after the temperature dropped below  $T_{\text{PC}}$ .

A comparison of the obtained solidus-liquidus curves for the Na-Hg system in the crystallization region of pure mercury with those of other authors revealed a good agreement with the work of Tamman<sup>2</sup> for diluted amalgam and – to a certain extent – of Schüller<sup>3</sup> for the position of the eutectic point. Deviations of the data of other authors may be attributed to their less perfect experimental techniques available at the beginning of this century, when most of the studies were carried out. However, the last published results of Inoue and Osugi<sup>6</sup> were not confirmed either.

An analysis of our data in view of the phase diagram of the Na-Hg system and the possible composition of intermetallic compounds in diluted sodium amalgams will be given in a further communication<sup>9</sup>.

FIG. 2  
Liquidus-Solidus Curves for Na-Hg System  
in Crystallization Region of Pure Mercury

○ Present results; comparison with data for the liquidus curve of: ● Tamman<sup>2</sup>, ⊙ Schüller<sup>3</sup>, ⊙ Vanstone<sup>5</sup>, ⊙ Inoue and Osugi<sup>6</sup>; 1 theoretical curve of liquidus for  $m = 0$ , 2 for  $m = 16$ .



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