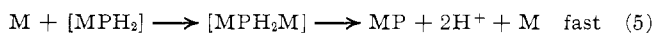
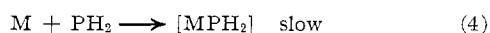


portance in that, while a metal ion can attack a porphyrin molecule from both above and below, the *N*-methyl group completely blocks to metal ion attack one of the axial positions of an *N*-methylporphyrin. Studies with systems in which "sitting-atop" species are formed in aqueous solution<sup>5,7</sup> show rate laws which are second order in metal ions and presumably involve one ion on each side of the porphyrin plane. Therefore in systems showing simple first-order metal ion kinetics, it cannot be ruled out that a second faster metal ion dependent step follows the slower rate-determining step, in a scheme such as



Since *N*-MeEtio obeys the same rate law as Etio, the implication is that such a second step does not occur with most porphyrins.

Etio and *N*-MeEtio each incorporate Cd(II) about twice as rapidly as Zn(II) in DMF (Tables I and II). In aqueous solutions<sup>5</sup> and in acetic acid solvents,<sup>4</sup> the reverse situation is found; that is, zinc inserts hundreds of times faster than cadmium ions. Such solvent-dependent rate reversals are also shown by Cu and Zn: in acetic acid<sup>13</sup> Zn > Cu, while in 8.3% acetic acid-water<sup>4</sup> and water<sup>5</sup> Cu > Zn. For both Etio and *N*-MeEtio, although the zinc reactions have lower energies of activation by about 4 kcal than those of cadmium, the cadmium reactions have higher entropies of activation (*ca.* 14 eu) than zinc. The higher charge: radius ratio of zinc compared to cadmium would favor a stronger zinc to porphyrin bond in the activation complex in line with the low zinc activation energy. The same factor would tend to increase solvent orientation in the activated complex more with zinc than with cadmium. Such ordering is expected to be important in the low dielectric solvent DMF.<sup>25</sup> There thus appears to be no *intrinsic* order of metal ion formation rates with porphyrins.

Tables I and II show that metal ion incorporation rates are about 10<sup>5</sup> faster into *N*-MeEtio than Etio. It is known that *N*-methylporphyrins are stronger bases toward protons than are porphyrins.<sup>15,17</sup> This is presumably due to the extremely nonplanar nature of *N*-methyl species, with the bulky methyl group preventing porphyrin planarity and thereby causing the central nitrogen atoms to tilt in a direction away from the porphyrin center and more toward the solvent environment. In terms of the free base-monocation equilibria



corprophyrin<sup>26</sup> has  $pK_3 = 7.16$  and *N*-methylcorprophyrin shows  $pK_3 = 11.3$ . The differences in  $pK$  should be similar for Etio and *N*-MeEtio. Studies with 2,4-disubstituted deuteroporphyrins<sup>23</sup> show that the rates of Cu(II) incorporation increase with porphyrin basicity. Thus meso-, proto-, and diacetylporphyrins having  $pK_3$  values of 5.8, 4.8, and 3.3, respectively, give relative incorporation rates of 7.0, 2.5, and 1.0. On this basis, the *N*-MeEtio reactions should be no more than 200-fold faster than those of Etio, since Etio has two sides vacant for attack whereas

*N*-MeEtio has only one. Thus basicity and statistical factors alone cannot account for the marked rate differences.

One model for metal ion incorporation<sup>27</sup> would involve a transition state with the porphyrin bent such that the two opposite pyrrole lone pairs are coordinated to the metal ion with the other two pyrrole groups bent in the opposite direction to facilitate proton dissociation. The inherent nonplanarity of *N*-MeEtio compared to Etio indicates that less energy would be expended to form such a bent activated complex with the *N*-methyl species, thus favoring a faster metal ion incorporation. Another factor favoring the *N*-MeEtio rate is the amount of partial positive charge formed as a result of the incipient dissociation of two protons in Etio and one in *N*-MeEtio in the transition state. Insofar as this charge will order the surrounding solvent, the entropy increase should be in favor of the *N*-MeEtio system. Similarly the amount of solvent reorganization about the metal ion should be less stringent with *N*-MeEtio than Etio, since a three- rather than four-coordinate (with respect to porphyrin) species is to be formed.

**Acknowledgments.**—We thank Miss Yasmin Majid for technical assistance and the USAEC, Contract No. AT-(40-1)-4047, for financial support.

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CONTRIBUTION NO. 2908 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA 50010

### Miscibility in the Systems Sodium Iodide-Trisodium Bismuthide and Sodium Iodide-Trisodium Antimonide<sup>1</sup>

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Received December 10, 1970

An earlier study<sup>3</sup> revealed that the intermetallic phases Na<sub>3</sub>Bi and Na<sub>3</sub>Sb exhibited sizable solubilities in molten sodium halides. For example, the NaI-NaCl eutectic composition was found to dissolve up to 26 mol % Na<sub>3</sub>Bi at 1000° and ~20 mol % Na<sub>3</sub>Sb at 700°. The principal technique employed earlier involved equilibration in sealed tantalum containers followed by rapid quenching and then analysis of the separated salt phase. The question was raised at the time<sup>4</sup> as to whether some segregation and recombination of the once-dissolved intermetallic phase might have taken place even during rapid cooling, thereby giving solubility data lower than equilibrium values. The occurrence of such errors has been well documented in studies of some binary systems in which samples have

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) Summer research participants supported by the Division of Nuclear Education and Training, USAEC.

(3) M. Okada, R. A. Guidotti, and J. D. Corbett, *Inorg. Chem.*, **7**, 2118 (1968).

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been quenched from well above the melting point of the solute phase.<sup>5</sup>

The present article reports the results of an examination of the systems of NaI–Na<sub>3</sub>Bi and NaI–Na<sub>3</sub>Sb by thermal analysis techniques. These results demonstrate that complete miscibility of the components occurs in both systems at the melting point of the intermetallic phase, an event which has been previously known only in systems involving the metal halides with the pure metals themselves.<sup>5–7</sup> Appreciably higher solubility data than obtained earlier with the NaI–NaCl mixture are found at higher temperatures with Na<sub>3</sub>Bi in NaI.

#### Experimental Section

The materials, syntheses, and many of the techniques were as previously described.<sup>3</sup> Sodium metal was purified either by vacuum distillation or by melting and pouring under vacuum, the oxide wetting the glass container in the latter step and thereby remaining behind. All preparations and subsequent studies were carried out in sealed tantalum containers. The sodium was weighed within the drybox on a balance calibrated to the nearest 10 mg (<±0.5%). Generally a small excess of sodium (Na/Y = 3.01–3.03) was used in the direct syntheses of the Na<sub>3</sub>Y components to allow for its adventitious oxidation in later stages; no evidence of excess sodium was ever noted, however. As before,<sup>5,9</sup> the welded containers used for thermal analysis were constructed so as to allow repetitive additions of a component through a port which could be cut open and then resealed each time. The component NaI, mp 660°,<sup>5</sup> was used as a calibration standard at the start of each thermal analysis run.

#### Results and Discussion

**NaI–Na<sub>3</sub>Bi.**—The phase data obtained are shown in Figure 1. The system showed evidence of slow

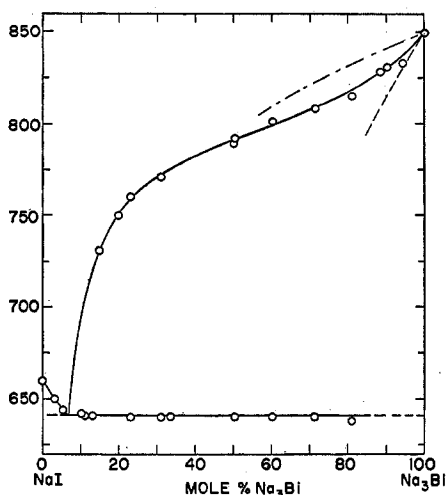


Figure 1.—The NaI–Na<sub>3</sub>Bi system: O, cooling data; ---, calculated for I<sup>-</sup> solute (see text); - - - -, liquidus curve for Na solute.<sup>10</sup>

equilibration in that several hours at 950° was necessary in order to get reproducible (rather than decreasing) liquidus temperatures on repeated cooling. In spite of several attempts no liquidus data could be found in the region 8–12 mol % Na<sub>3</sub>Bi, evidently because of the small change of composition with temperature. Missing eutectic points generally mean the transition was not looked for, although in the bismuth system

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 (7) M. A. Bredig, H. R. Bronstein, and W. T. Smith, *J. Amer. Chem. Soc.*, **77**, 1454 (1955).  
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 (9) P. E. Caro and J. D. Corbett, *J. Less-Common Metals*, **18**, 1 (1969).

specifically these could not be located for compositions richer in NaI than the eutectic. Some solid solution effects may be responsible.

The melting point of Na<sub>3</sub>Bi found, 849°, compares favorably with the value of 848.1° recently reported by Johnson and Fischer.<sup>10</sup> The shape of the liquidus curve is of course characteristic of many metal–metal halide systems and others which exhibit large positive deviations and hence a tendency toward demixing. Data reported earlier<sup>3</sup> for the solubility of Na<sub>3</sub>Bi in NaI–NaCl eutectic mixture (63 mol % NaI) are lower, particularly at higher temperature. As discussed at that time, a moderate decrease in Na<sub>3</sub>Bi solubility when NaI is diluted by NaCl is reasonable, but the earlier data may be suspect in that they do not show any indication of the rapidly increasing solubility found here above ~750°. Thermal analysis of a mixture of 20 mol % Na<sub>3</sub>Bi in the NaI–NaCl eutectic composition gave a liquidus of 746°, which is comparable to the value shown with NaI rather than *ca.* 900° expected on the basis of the earlier quench data with the mixed salt. On the other hand the previous results for Na<sub>3</sub>Bi at the lower temperatures or for the higher melting Na<sub>3</sub>Sb (*vide infra*) do not seem to be in serious error.

**NaI–Na<sub>3</sub>Sb.**—This system exhibits a comparable phase relationship but it contains another surprise, an intermediate phase. The results are shown in Figure 2. The melting point of 1010 (±3)° found for

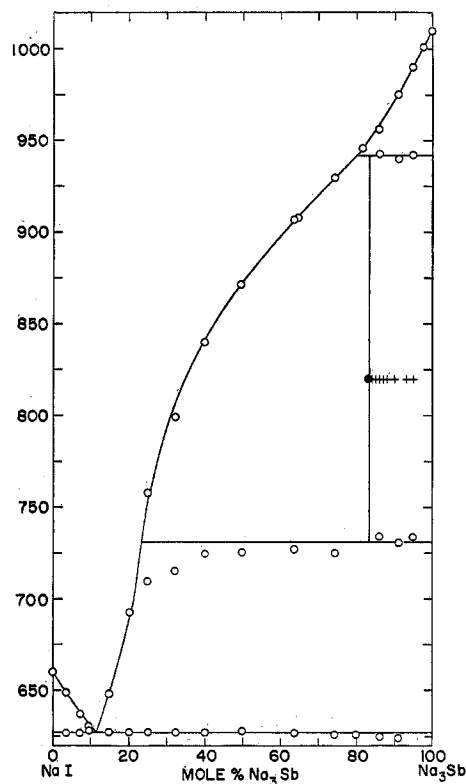


Figure 2.—The NaI–Na<sub>3</sub>Sb system: O, cooling data; +, solid; ●, partially liquid at temperature.

Na<sub>3</sub>Sb compares with 856° reported by Mathewson<sup>11</sup> 65 years ago when adequate materials and precautions were difficult to come by. Reported solubility data for Na<sub>3</sub>Sb in the NaI–NaCl eutectic<sup>3</sup> are quite comparable

- (10) C. E. Johnson and A. K. Fischer, *ibid.*, **20**, 339 (1970).  
 (11) C. H. Mathewson, *Z. Anorg. Allg. Chem.*, **50**, 192 (1906).

to those found here in the common range, 700° and below. The shape of the liquidus curve in the present system suggests a more nearly ideal mixing than was seen with Na<sub>3</sub>Bi.

The occurrence of two additional thermal arrests at 942 ± 1 and 731 ± 3° was unexpected, and these appeared more unusual when no X-ray evidence whatsoever could be found for any new phase. Powder patterns which were indistinguishable from the appropriate mixture of the NaI and Na<sub>3</sub>Sb components were also obtained from a 90% composition equilibrated at either 1050 or 920° for 12 hr or a 80% composition held at 700° for 12 hr, each of these then being quenched by dropping the container into room-temperature silicone oil within the vacuum system. Similarly, equilibration of a 70% mixture 12 hr just above or below 731° made no difference in the relative magnitude of the eutectic arrest on subsequent cooling, contrary to expectation and experience when the cooling halt in question arises from the peritectic formation of an intermediate phase. The only explanation apparently left is that the lower (731°) transition on cooling must result from the inverse peritectic decomposition of an intermediate phase formed at 942° back into the original components NaI and Na<sub>3</sub>Sb. The trends in the data obtained for the presumed decomposition (Figure 2) suggest that the presence of Na<sub>3</sub>Sb(s) prevents supercooling or, more likely, that the intermediate phase exhibits some variable composition.

Problems of reactivity and containment have discouraged the verification of the existence of the new phase at temperature with X-rays. However, the flow properties of the system near the middle of the apparent 731–942° range of existence substantiate the presence of an all-solid system from Na<sub>3</sub>Sb down to about the composition NaI·5Na<sub>3</sub>Sb (83.3 mol % Na<sub>3</sub>Sb). For this examination containers were constructed of 3-in. lengths of 0.25-in. diameter tantalum tubing welded to the center of the bottom of a 6-in. length of a 0.5-in. diameter tube. The inner tube was filled with a mixture of the desired composition and the top of the outer was capped and welded. The components were then fused at 1010° for 1 hr, rapidly quenched upright in silicone oil, and then inserted into a preheated furnace and held at 820–840° for 3 hr. (This procedure was designed to give a uniform, intimate mixture which would readily reach equilibrium at temperature.) The crucible within the containing furnace was then tipped past the horizontal position for 3–5 hr, after which it was cooled in an upright position and opened in the drybox to look for evidence of flow. As denoted on Figure 2 by a cross no flow was evident for compositions containing 95, 93, 90, 88, 87, 86, and 85 mol % Na<sub>3</sub>Sb. Flow was slight and questionable at 84% with two samples which had already received repetitive additions of NaI; however cumulative compositional errors or a slight oxidation had probably occurred during the run as another sample made up directly to 84 mol % did not flow but did so readily when the composition was reduced to 83 mol %. A control showed a partially liquid system was present at 680° with an 86 mol % Na<sub>3</sub>Sb composition, consistent with the diagram shown.

The results for these two systems obviously raise questions concerning the nature of these solutions, particularly as to whether they may be considered akin to those (1) of the heavy alkali metals and their

halides<sup>6,7</sup> or (2) of two salts of rather different melting points and properties. Present evidence suggests the latter may be somewhat more appropriate although the classification is by no means completely satisfactory.

The intermetallic phases used both have the Na<sub>3</sub>As structure, which is the antitype of the tysonite structure common with the rare earth metal and actinide trifluorides. Neither phase exhibits any transition between room temperature and the ranges studied. The Na<sub>3</sub>Sb is a semiconductor with a gap of *ca.* 1.1 eV,<sup>12</sup> while solid Na<sub>3</sub>Bi is evidently metallic. Cryoscopic data for these compounds in dilute solution in sodium halides were earlier shown to be consistent with the formation of Sb<sup>3-</sup> or Bi<sup>3-</sup> anions therein.<sup>3</sup> A similar consideration of the solution of salt in metal is limited by the fact that an enthalpy of fusion is available only for Na<sub>3</sub>Bi.<sup>13</sup> The lower dashed curve shown in Figure 1 is the depression therewith calculated for an ideal solution of a one-particle depressant (*i.e.*, I<sup>-</sup> in Bi<sup>3-</sup> or a molecular mixture). (The upper interrupted curve in this figure illustrates the relative effect of sodium metal.<sup>10</sup>) Only a limiting description seems at all feasible for the saltlike model, although the very applicability of this consideration may be questionable. On the other hand, use of the same entropy of fusion for Na<sub>3</sub>Sb (6.32 eu) gives an *excellent* description of the observed liquidus curve in terms of an ideal solution up to about 12 mol % NaI.

The Na<sub>3</sub>Sb and Na<sub>3</sub>Bi phases themselves have large cohesive energies. This property is in considerable contrast with the low values considered important in the solution of the heavier alkali metals in their halides.<sup>7</sup> Although partial ionization of Y<sup>3-</sup> to electrons and polymeric anions of the heavy metal cannot be eliminated in the more concentrated solutions of Na<sub>3</sub>Y, the stability of the phases and the negligible tendency of the solutions to lose sodium make this seem unreasonable. Accordingly we are somewhat more inclined to view the liquid systems as a somewhat novel mixture of two saltlike materials, or at least phases which are potentially saltlike on dilution. This does not preclude some appreciable electronic conduction which seems particularly probable in the concentrated solutions of Na<sub>3</sub>Bi. Some similarity to the conceptual problems of the solution of LaI<sub>3</sub> in the metallic La<sup>3+</sup>(I<sup>-</sup>)<sub>2</sub>e<sup>-</sup>, and *vice versa*,<sup>14</sup> is apparent.

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## Synthesis of a Two-Metal Macrocyclic System

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Received January 4, 1971

The preparation and investigation of macrocyclic metal complexes has been an area of intense study in

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