Sodium–Strontium Phase Diagram: Redetermination of the Solubility of Strontium in Liquid Sodium

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The sodium–strontium phase diagram has been redetermined up to 37.9 mol % Sr (439 °C). Considerable differences from existing data have been found; the solubility of Sr is less than previously reported and the eutectic point is located at 0.65 mol % Sr and 94.80 °C. The solubility is compared with those of the other Group 2A metals in sodium; whereas Be, Mg, and Ca are virtually insoluble, Sr is quite soluble but not to the extent shown by Ba.

IN earlier papers we have described the ability of solutions of barium in liquid sodium to react with and dissolve nitrogen even though pure Na does not have either of these capabilities.[1,2] In extending these investigations to strontium solutions, we found it necessary to redetermine the phase relations between strontium and sodium, since we were troubled repeatedly by precipitation of Sr from the binary metal solutions at far higher temperatures than expected.

The phase diagram has been studied twice before and, although the results show general agreement, there are considerable differences in detail.[3,4] Complete miscibility exists in the liquid, but there is restricted mutual solid solubility. No intermetallic compounds have been observed by *X*-ray or thermal analysis or even by electrodiffusion experiments.[5] The eutectic point was reported at considerably different locations: 3.2 (at 92.5) [4] and 1.3 mol % Sr (at 94 °C).[3] Two peritectic reactions, attributed to phase transformations of strontium terminal solid solutions, occur at 192 and 635 °C; these correspond to those of pure Sr at 232 and 620 °C,[3] respectively.

EXPERIMENTAL

Both resistivity–temperature and thermal analyses were used to examine sodium–strontium phase equilibria, in the manner described for sodium–lithium solutions.[6] Sodium was purified as before,[7] and strontium (Koch-Light, 99.8%) was mechanically cleaned of surface film under argon in a glove-box. Solutions were prepared *in situ* by weighing in the appropriate quantities (typically 92.02 g of Sr and 39.58 g of Na) of pure components. The entire apparatus was enclosed in an air-oven and homogeneity achieved at 500 °C by prolonged circulation of the liquid through a steel resistivity capillary loop by means of an electromagnetic pump. The resistivity of the solutions was determined at 15 °C intervals from 500 to 100 °C. The temperature at which strontium precipitation commenced was clearly defined, even at low concentration, by the breaks in the typical curves shown in Figure 1. These arose because the temperature dependence of the resistivity of the unsaturated solution (region AB) differed considerably from that of the saturated solution (region BC) which, on cooling, was continually depleted of Sr. The difference in resistivity between the mixtures and pure sodium, $\Delta\rho$, is plotted, rather than resistivity, ρ, in order to clarify the precipitation temperature. The discontinuity moved to higher temperatures and became more pronounced as the solubility of strontium increased. These data provide the hypereutectic liquidus of the sodium–strontium phase diagram.

Cooling curves were also obtained from 120 to 80 °C. A slow cooling rate of 0.006 °C s^{-1} was maintained which provided thermal arrests ($\pm$0.02 °C) lasting between 1 500 and 600 s for Na and for a solution containing 37.9 mol % Sr, respectively. The thermal arrests provided the hypoeutectic liquidus and the eutectic horizontal components of the phase diagram. Attempts to determine the hypereutectic liquidus by thermal means were unsuccessful; this could only be established from resistivity changes.

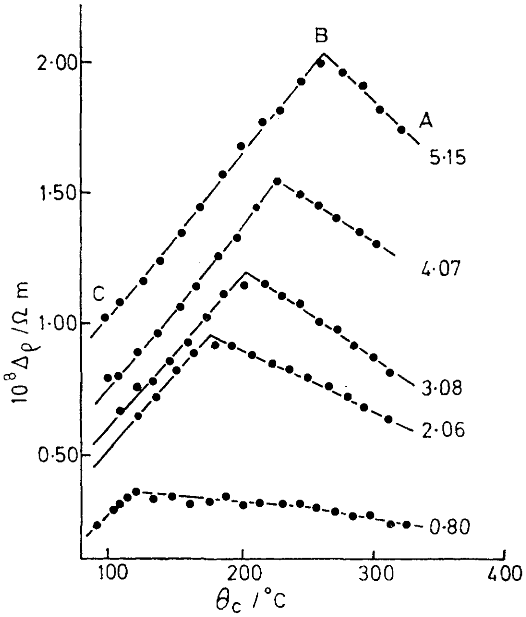

FIGURE 1 Determination of the precipitation temperatures of sodium–strontium solutions (compositions in mol % Sr given on curves) by means of resistivity changes

Two further determinations of the solubility of Sr in liquid Na were made using a filtration and analysis technique. A Pyrex-glass filtration tube was charged with the two metals and held at constant temperature, measured by a thermocouple, for 18 000 s. A lower sample chamber was evacuated thereby forcing liquid metal through the filter

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[1] C. C. Addison, R. J. Pulham, and E. A. Trevillion, *J.C.S. Dalton*, 1975, 2082.

[2] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J.C.S. Dalton*, 1976, 1105.

[3] W. O. Roberts, U.S.A.E.C. Report TID-20639, 1964.

[4] H. Remy, G. Wolfrum, and H. W. Haase, *Naturwiss.*, 1957, **44**, 534.

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[6] M. G. Down, P. Hubberstey, and R. J. Pulham, *J.C.S. Dalton*, 1975, 1491.

[7] P. Hubberstey and R. J. Pulham, *J.C.S. Dalton*, 1972, 819.

and into the chamber. The residue on the filter was identified as α-Sr by *X*-ray diffraction, and the filtrate was analysed for Sr by dissolution in dilute acid followed by precipitation as strontium sulphate.

RESULTS AND DISCUSSION

Twenty-eight solutions were investigated at concentrations up to 37.9 mol % Sr. The liquidus data are presented in the Table; the eutectic horizontal was consistently located at 94.80 ± 0.05 °C. The hypereutectic-liquidus points, derived from the resistivity results, rose smoothly from the eutectic point except for a single inflexion, which we attribute to the peritectic reaction (1), at 192 °C. The filtration experiments confirm this liquidus. It is in this dilute-solution region

$$\text{liquid} + \beta\ (\alpha\text{-Sr saturated with Na}) \rightleftharpoons \text{liquid} + \gamma(\beta\text{-Sr saturated with Na}) \quad (1)$$

that our results differ from previous work. Two other sets of data exist; although Remy *et al.*[4] did not report sufficient results in this composition range for comparison to be made, our findings may be compared to those of Roberts.[3]

Liquidus temperatures for sodium–strontium solutions

Composition (mol % Sr)	Temperature (θ_c/°C)	Composition (mol % Sr)	Temperature (θ_c/°C)	Composition (mol % Sr)	Temperature (θ_c/°C)
0.00	97.8 [a]	3.08	199	11.3	338
0.10	97.8 [a]	3.58	211	12.1	348
0.19	97.4 [a]	4.01	223	13.3	351
0.29	97.1 [a]	4.07	225	16.4	373
0.53	95.8 [a]	4.13	224 [b]	20.0	391
0.80	116	5.15	247	23.4	406
1.03	136 [b]	6.42	267	28.1	417
1.56	154	7.95	302	32.4	426
2.06	168	9.25	316	37.9	439
2.28	173				

[a] From thermal analysis. [b] From filtration and analysis; all the other values were obtained from resistivity changes.

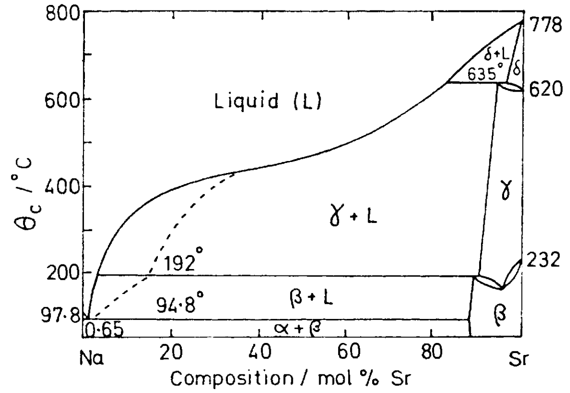

FIGURE 2 The sodium–strontium phase diagram; the continuous lines represent a composite diagram based on present sodium-rich (0—38 mol % Sr) and previous strontium-rich data (38—100 mol % Sr)[3]; the broken lines represent previous sodium-rich data (0—38 mol % Sr)[3], included for comparison

The comparison is made in Figure 2 which depicts the composite phase diagram produced by combination of our sodium-rich data with the strontium-rich data of Roberts. Roberts' solubilities (<38 mol % Sr), depicted as a broken line (Figure 2), are considerably greater than we find, the temperature difference amounting to as much as 150 °C at 15 mol % Sr. There is no obvious reason for this discrepancy except that Roberts encountered considerable difficulty, as we did, in detecting thermal arrests for the hypereutectic liquidus. For this reason, we believe our solubility values, which were determined from equilibrium resistivities and filtration followed by analysis, to be more reliable than his thermal-analysis results in this concentration range. The current knowledge of the phase diagram is depicted, therefore, by the continuous lines in Figure 2.

The eutectic composition was located at 0.65 mol % Sr at 94.80 °C; this is less than the value (1.3 mol % Sr at 94.65 °C) reported by Roberts. That part of the eutectic horizontal lying beneath the hypoeutectic liquidus was not detected by either resistivity or thermal methods, so that no direct measurement of the solid solubility of Sr in Na was possible. This was calculated, however, to be 0.04 mol % Sr at the eutectic temperature from the depression of the freezing point, $T_m - T$, using the ideal-solution equation (2), where ΔH_f, x_l, and x_s are the enthalpy of fusion of sodium (2.603 kJ mol^{-1}),[8] and the liquid and solid solubilities, respectively.

$$T_m - T = (RT_mT/\Delta H_f)(x_l - x_s) \qquad (2)$$

The solubilities of the Group 2A solutes fall into two groups; one, comprising the low solubilities of Be,[9] Mg,[9] and Ca,[9] and the other the much higher solubilities of Sr and Ba.[10,11] Whereas a near vertical hypereutectic liquidus adjacent to the sodium axis is exhibited for each of the lighter solutes, the solubility at 150 °C, for example, is 1.5 mol % for Sr and increases to 11.7 mol % for Ba. Together with their high solubilities, strontium and barium [10] cause a measurable depression of the freezing point of sodium. Moreover, the hypoeutectic liquidus shows a common gradient as might be expected for solutes giving the same number of particles in solution.

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For the reasons outlined earlier, we are more interested in the solubilities of the Group 2A elements in liquid Na, than in any other phase relations. The solubilities are inextricably linked, however, to the extent of miscibility between the elements. The Na–Sr phase diagram shows a near horizontal liquidus over a large composition range (Figure 2), a feature which is characteristic of incipient liquid immiscibility. This system falls, therefore, between the largely immiscible systems, Na–Be, Na–Mg, and Na–Ca, and the miscible system, Na–Ba. The reasons for immiscibility, and hence low solubilities, have been extensively investigated. In this context, the Hildebrand relation,[12] which attributes immiscibility to the magnitude of the enthalpy of vaporization of the components and to their atomic volumes, correctly predicts that Na–Be and Na–Mg should exhibit liquid immiscibility but that Na–Ca, as well as Na–Sr and Na–Ba, should be miscible. Contrary to prediction, however, the Na–Ca phase diagram shows distinct immiscibility. Modifications [13,14] designed to take account of electronegativity differences fare no better at predictions for Na–Ca. The change from immiscibility in Na–Ca to miscibility in Na–Sr must be attributable to some other parameter.

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