The Reaction between Barium and Nitrogen in Liquid Sodium: Resistivity Studies

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The reaction of nitrogen with solutions of barium (between 0.34 and 6.89 mol % Ba) in liquid sodium at 573 K has been followed by changes in the electrical resistivity of the liquid. The capillary method has been employed, continuous sampling during reaction being achieved by electromagnetic pumping. The initial solution of nitrogen in the metal, followed by precipitation of barium and nitrogen from sodium as the nitride Ba_2N, are reflected in the resistivity changes. The solubility of nitrogen in the alloy is a linear function of the barium concentration: S(mol % N) = $x/4$ ($0 \leqslant x \leqslant 6.89$ mol % Ba). This, and the decrease in resistivity which invariably occurs during the solution process, provides additional information on the nature of solvation of nitrogen in solution in the liquid metal.

PREVIOUSLY,[1] we have shown by a filtration and analysis technique that although nitrogen is inert towards liquid sodium, addition of barium promotes reaction and solution. Thus the solubility of nitrogen in a 4.4 mol % solution of barium in sodium is 1.08 mol % at 573 K, corresponding to a Ba : N ratio of 4 : 1 which also persisted in the solution throughout precipitation of Ba_2N. The process has now been investigated by means of resistivity changes of the liquid. This technique is particularly suitable for studying reaction, solution, and precipitation because both barium and nitrogen cause relatively large changes in the resistivity.

EXPERIMENTAL

The apparatus used was essentially that described previously for the determination of the resistivity of solutions of liquid alkali metals.[2] Liquid metal was drawn continuously through a steel capillary loop (bore 1.5 mm, length 500 mm) by means of a d.c. electromagnetic pump and returned to a reservoir where nitrogen was metered in from a vacuum frame. The returning liquid metal was injected into the gas as a jet, thereby facilitating rapid reaction and dissolution of products. The resistance of the liquid metal thread was measured by a Kelvin–Wheatstone bridge. Sodium (*ca.* 70 g) and barium (up to 10 g) were purified as before,[2] and nitrogen (up to 650 cm^3) (Air Products Ltd., 99.99%) was further purified by passage through liquid NaK and over manganese(II) oxide to remove trace amounts of moisture and oxygen, respectively.

The procedure involved (*i*) calibration of the empty capillary by measuring the resistance over a few degrees either side of the operating temperature, 573 K, (*ii*) repeating the measurements with the capillary full of sodium and alloy, respectively, (*iii*) determining the resistance changes occurring when nitrogen reacted with the alloy, and (*iv*) calculating the resistivity of the liquid thread in all cases from the resistances and dimensions of the capillary as before.[2]

RESULTS AND DISCUSSION

Sodium–Barium Solutions.—The resistivities of solutions of barium in liquid sodium at 573 K are shown in the upper part of Figure 1. At this temperature, the resistivity of sodium is $17.32 \times 10^{-8}\,\Omega$ m and rises steeply with increasing barium concentration. This has the advantage that removal of even small amounts of barium from the solution by reaction results in a relatively large decrease in resistivity. Over this composition range, resistivity rises almost linearly with barium concentration, and the unit increase in resistivity over that of sodium, $\Delta\rho/x$, is $2.96 \times 10^{-8}\ \Omega$ m (mol % Ba)$^{-1}$. Controls were set so that all experiments would run at 573 K, but the constant temperature achieved sometimes

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

[2] (*a*) C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1393; (*b*) M. N. Arnol'dov, M. N. Ivanovskii, V. I. Subbotin, and B. A. Shmatko, *Teplofizika Vysokikh Temperatur*, 1967, **5**, 812.

varied from this by a few degrees. The resistivity of the alloys was therefore determined over a small temperature range to allow correction to 573 K. The same resistivity–temperature relation (shown for a 3.46 mol % solution of barium in the lower part of Figure 1) was also applicable to the dilute ternary solutions.

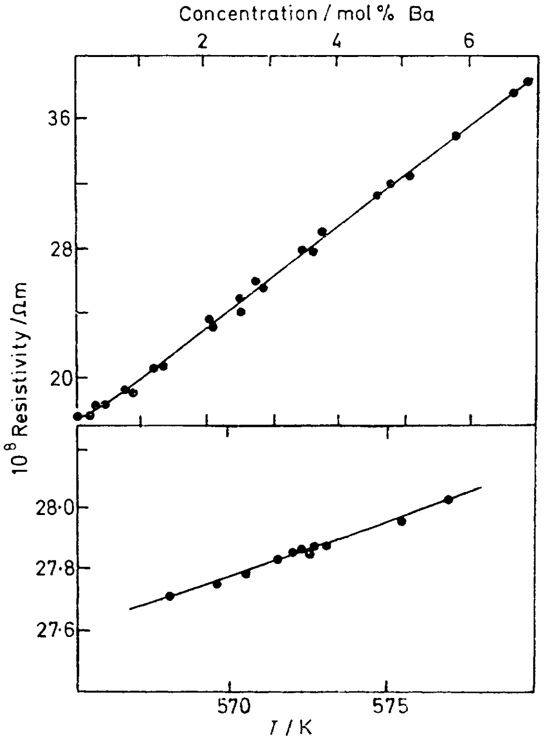

FIGURE 1 Influence of barium concentration and temperature (at 3.46 mol % Ba) on the resistivity of solutions of barium in liquid sodium

Resistivity Changes during Reaction.—Reactions were carried out using six different concentrations of barium (see Table 1) and the resistivity changes followed the same general pattern in each experiment. Since some of the features which arise are new, experiment (2) will be taken as typical, and will be discussed in detail. The interpretations advanced will then be supported by reference to the other experiments.

TABLE 1

Significant data for the reactions of Na–Ba with N_2 at 573 K (for ρ_1, ρ_2, *etc.*, see Figures 2, 3, and 5)

Experiment no.	Barium concentration / mol %	Ba : N at ρ_2	$10^8\Delta\rho/x$ [a] / Ω m (mol % N)$^{-1}$	Solubility of N / mol %	Ba : N at E
(1)	0.34	4.45	8.25	0.08	2.08
(2)	2.04	4.39	9.17	0.46	2.01
(3)	2.51	4.31	9.17	0.58	2.05
(4)	2.85	3.94	9.03	0.72	
(5)	3.46	3.93	8.04	0.87	1.99
b	4.40	4.16		1.08	1.95
(6)	6.89	3.98	8.85	1.70	

[a] $(\rho_2 - \rho_0)/x$. [b] Filtration and analysis experiment.[1]

The resistivity of a 2.04 mol % solution of barium is plotted in Figure 2 against the nitrogen added. The latter is expressed as a N : Ba ratio, to facilitate comparison with other experiments using different barium concentrations. The original resistivity of pure sodium, ρ_0, is shown by the horizontal broken line at 17.32×10^{-8} Ω m, and the barium solution causes this to increase to 23.32×10^{-8} Ω m (ρ_1). On addition of nitrogen, two main processes occur. First, nitrogen dissolves as the N^{3-} ion, and this stage is represented by a linear decrease in resistivity (AC) over the range ρ_1 to ρ_2. Previous work [1] has shown that this stage extends up to a composition near Ba_4N, consistent with the formation in solution of a solvated nitrogen species of this composition. At C(ρ_2), precipitation of Ba_2N commences, and continues until at E the resistivity returns to the value for pure sodium; ρ_2 is readily identified as the point at which departure from the linear decrease in resistivity first occurs.

The Nature of the Solute.—The increase $\rho_1 - \rho_0$ in the resistivity of pure sodium on addition of barium is caused essentially by the increased scattering of conduction electrons in the medium. Usually, dissolved N^{3-} ions also scatter strongly, as shown by the increase in resistivity of liquid lithium on solution of nitrogen.[3] Assuming the same value of $\Delta\rho/x$ for nitrogen in the sodium–barium solutions as in liquid lithium, the resistivity of the Na–Ba solutions would move along the broken line AB (Figure 2) on addition of nitrogen, in the absence of any interaction between solutes. But the resistivity actually decreases from ρ_1, so that addition of nitrogen reduces the ability of dissolved barium atoms to act as scattering centres. Since no precipitation occurs during this stage, we deduce that the scattering ability of dissolved barium is greatly reduced when it is incorporated with N^{3-} in solution to form the strongly bonded Ba_4N

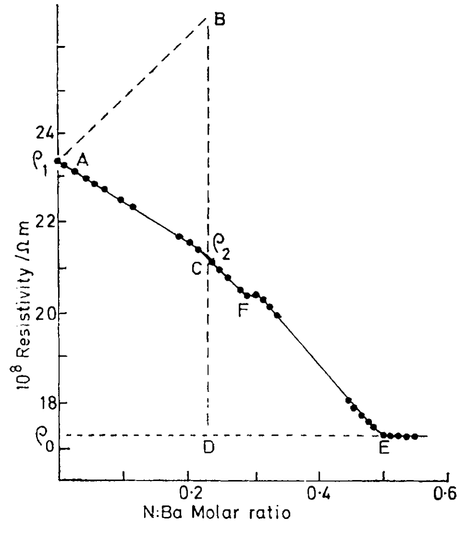

FIGURE 2 Resistivity changes during absorption of nitrogen by a 2.04 mol % solution of barium in liquid sodium at 573 K

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[3] P. F. Adams, M. G. Down, P. Hubberstey, and R. J. Pulham, *J. Less-common Metals*, 1975, **42**, 325.

unit. The region ρ_1 to ρ_2 is linear, so that each dissolving N^{3-} ion takes up the same number of barium atoms in its solvation shell throughout the solution process. In effect, therefore, at point C, five ($4Ba^{2+} + N^{3-}$) scattering centres have been replaced by one.

The term ' Ba_4N unit ' is used because attempts to define this cluster of atoms or ions with greater precision would be unjustified, and depend on the concept of the metallic state which is employed. Thus, if a solution of barium in sodium is regarded as a mixture of atoms, then barium atoms would be the solvating species and the unit would be written as $[Ba_4N]^{3-}$. However, in all our work we have chosen to consider metals in terms of the free-electron theory, which applies most closely to the strongly electropositive metals. The alkali metals and the heavier Group 2 metals are then regarded as consisting entirely of metal ions and free electrons, and the Ba_4N unit would be written $(Ba^{2+})_4N^{3-}$, *i.e.* $[Ba_4N]^{5+}$. The difference is not a real one, and depends only on whether the unit is viewed against an atomic or an ionic background.

At point C (Figure 2) the solution is saturated with nitrogen and the solute consists entirely of Ba_4N units; the difference BC, therefore, represents the extent to which the scattering of electrons by the five ions ($4Ba^{2+}$ and N^{3-}) is reduced in the formation of the single Ba_4N unit, and CD represents the change in resistivity of sodium which is characteristic of electron scattering by Ba_4N units in solution. In this experiment the resistivity increase for the Ba_4N unit, $\Delta\rho/x$ [*i.e.* $(\rho_2 - \rho_0)/x$] is $9.17 \times 10^{-8}\ \Omega$ m (mol % N)$^{-1}$.

Precipitation.—This commences at point C. On addition of further nitrogen beyond this point there is insufficient barium in solution to solvate each nitride ion as a Ba_4N unit. A solvation shell consisting of sodium and barium atoms does not provide sufficient solvation energy to stabilise N^{3-} in solution,[4] and precipitation therefore occurs. The N : Ba ratio at C corresponds to the precipitation point already found by filtration and analysis.[1] Between C and E, precipitation continues according to $(Ba_4N) + \frac{1}{2}N_2 \longrightarrow 2Ba_2N$. The barium and nitrogen contents of the solution are progressively depleted, until at E only a mixture of solid Ba_2N and sodium remains. The resistivity, therefore, decreases to the sodium value.

A plateau, F, occurs soon after precipitation commences. This is a feature of the apparatus which has no theoretical significance, and is due to the presence of nitride precipitate in the capillary tube. The precipitated nitride has a higher resistivity than the metal, but in its formation barium and nitrogen are removed from solution. The plateau represents the balance between these effects, and the length of the plateau is possibly related to the rate of coagulation of the precipitate.

Nitrogen Absorption beyond Ba_2N.—Further slow absorption of nitrogen beyond the point E occurs, due to reaction of Ba_2N to produce the normal nitride Ba_3N_2. Precipitation of Ba_2N occurs at the gas–liquid interface in the main reaction vessel, and most of the crystals collect in a ring around the meniscus. This is fortunate, as they might otherwise collect in the capillary and prevent measurement of resistivity. The crystals are wetted by sodium, which reduces reaction rate much below that expected in the absence of the sodium film. Rates of reaction (mm^3 s^{-1} at s.t.p. and 59 kN m^{-2}) decreased from 6 (region AC) to 1 (region CE) to 0.6 beyond E.

Reactions at Other Barium Concentrations.—The various clearly defined stages in the nitrogen–barium reaction have been discussed above in terms of a single solution of barium. In all, six experiments were carried out using the barium concentrations listed in column 2 of Table 1, and the general concepts and interpretations outlined above are applicable to all the solutions. Figure 3 shows the initial (solution) stage for six concentrations. In all the cases the variation of resistivity with nitrogen concentration is precisely linear, and the point ρ_2 at which precipitation commences (marked by arrows in Figure 3) is clearly defined even in the most dilute (0.34 mol % Ba) solution. The N : Ba ratios at the precipitation point (listed in column 3 of Table 1) show no significant variation with concentration, confirming that the same Ba_4N unit is formed in solution in every experiment. It follows from this that the solubility of nitrogen in the barium solutions should depend only on the quantity of barium present. Figure 4 shows the solubility values (listed in column 5 of Table 1) as a function of barium concentration; all the points lie close to the line shown, represented by equation (1), where x is the concentration

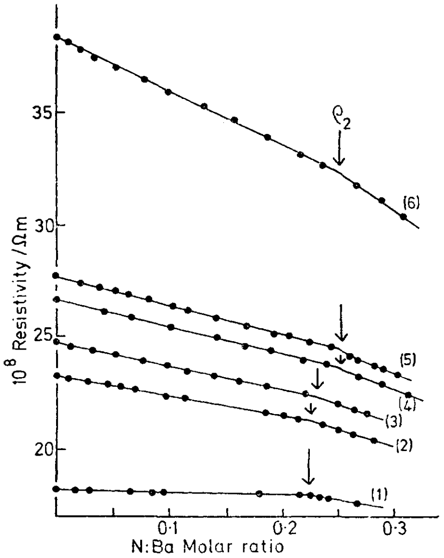

FIGURE 3 Linear change in resistivity with concentration of nitrogen dissolved in barium–sodium mixtures (The numbers refer to the experiments in Table 1.)

$$S(\text{mol \% N}) = x/4 \qquad (1)$$

of barium in solution, and there is also excellent agreement with the value (open circle, Figure 4) obtained by filtration and analysis.[1]

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[4] C. C. Addison, *Sci. Progr.*, 1972, **60**, 385.

From the positions of the precipitation points (Figure 3), it is possible also to derive values for the unit resistivity increase, $\Delta\rho/x$, characteristic of the Ba_4N unit in liquid sodium. These are listed in column 4 of Table 1, with a mean value of 8.8. This is compared with some related values in Table 2. The general trend of the results in the two solvents lithium and sodium is very similar. Oxygen and hydrogen dissolve in both the pure solvents, and their ions are no doubt solvated in each case. Nitrogen dissolves in pure lithium, and has a high $\Delta\rho/x$ value, and it is reasonable to consider that the N^{3-} ion in lithium is strongly solvated by Li^+ ions. Other experiments[5] suggest that the co-ordination number is greater than four.

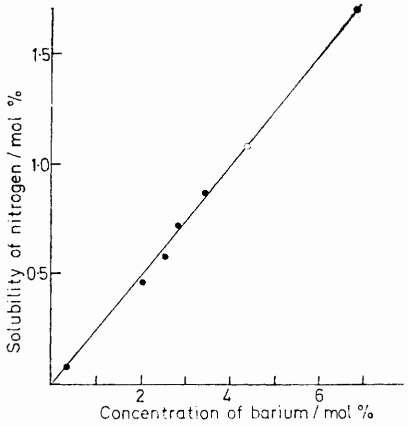

FIGURE 4 Solubility of nitrogen at 573 K in solutions of barium in liquid sodium

TABLE 2

Values for the unit resistivity increase $10^8\Delta\rho$ (Ω m) caused by 1 mol of solute in liquid lithium and in liquid sodium

Liquid metal solvent	Solute	Δρ	Solute radius [a]/Å
Li	O^{2-} [b]	2.3	1.40
	H^-	3.7	1.53
	N^{3-}	7.2	1.71
Na	O^{2-} [b]	2.0	1.40
	H^- [b]	4.3	1.53
	N^{3-} [b] (as $[Ba_4N]^{5+}$)	8.8	

[a] From ionic crystals of corresponding solids. [b] Extrapolated from dilute solution.

For a given solvent, $\Delta\rho/x$ is characteristic of the solute, and is a measure of its ability to scatter electrons. In our study of the nature of the dissolved species we hope to correlate $\Delta\rho/x$ with other properties of the solute species. Values of $\Delta\rho/x$ do not increase in the order H^-, O^{2-}, N^{3-}, so that charge alone is not responsible. The size of the solute species may be relevant under some circumstances (column 4, Table 2); $\Delta\rho/x$ values for the other alkali metals in sodium increase in the order Li, K, Rb, Cs,[6] but for solutes where solvation occurs (*e.g.* ref. 7) the correlation cannot be examined at this time since the charge on the dissolved species, and the co-ordination number, are in most cases unknown.

Complete Reaction.—Four of the experiments [(1)—(3) and (5), Table 1] were taken to completion. The changes in resistivity were similar in all cases, and followed the pattern outlined in Figure 1. Results for experiments (1) and (3) are compared with (2) in Figure 5. In each case, the resistivity decreased more steeply after precipitation commenced, but the length of the plateau depends on the amount of Ba_2N available which can accumulate temporarily in the capillary. Thus, no plateau was observed in the dilute solution (0.34 mol % Ba) used in experiment (1), but was pronounced at 2.51 mol % Ba (3). With these more concentrated solutions, the decrease in resistivity is large after the plateau region, but a small amount of nitride may be retained in the capillary. For example, in experiment (3) the final resistivity value, ρ_3, is a little above that for pure sodium, although the liquid metal consists of sodium only. This was confirmed by determining the resistivity over the temperature range 323—573 K after completion of the experiment; the resistivity–temperature curve was parallel to that for pure sodium, but higher by 0.19×10^{-8} Ω m ($\rho_3 - \rho_0$ in Figure 5) and the metal solidified at the freezing point of pure sodium.

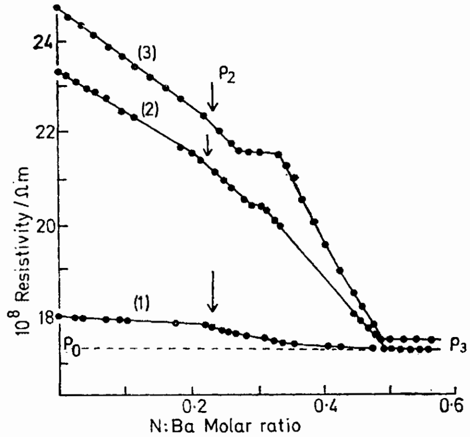

FIGURE 5 Resistivity–composition curves for various barium concentrations. Mol % Ba: (1), 0.34; (2), 2.04; (3), 2.51

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[5] C. C. Addison and B. M. Davies, *J. Chem. Soc. (A)*, 1969, 1827.

[6] J. F. Freedman and D. W. Robertson, *J. Chem. Phys.*, 1961, 34, 769.

[7] P. Hubberstey and R. J. Pulham, *J.C.S. Faraday I*, 1974, 1631.