761. *Liquid Metals. Part VI.*[1] *The Surface Tension of Solutions of Barium and Calcium in Liquid Sodium.*

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Barium has a high solubility in liquid sodium. The surface tension of solutions containing up to 29 atom % (71 wt. %) of barium at 100—400° has been measured by the vertical-plate method. The preparations, analysis, and manipulation of these solutions are described. Addition of barium to liquid sodium causes an initial decrease in surface tension, which passes through a minimum at 4 atom % of barium; this can be correlated with the barium–sodium phase diagram. At higher concentrations the tensions move towards the arithmetic mean value. Calcium has a low solubility in liquid sodium (6 atom % at 700°) and the surface properties of the calcium solutions are abnormal. Surface tensions of solutions containing up to 1·45 atom % (2·5 wt. %) of calcium have been measured in the temperature range 100—450°. Addition of calcium increases the surface tension of liquid sodium, to an extent which is greatest at low temperatures.

The measurements described in this paper form part of a wider study of the use of liquid sodium as a solvent. Despite the importance of this liquid as a reactor coolant, relatively little is yet known of the physical properties of solutions in liquid sodium, the species present in such solutions, or the nature of reactions in the liquid. Only a limited number of elements have appreciable solubilities in liquid sodium; the solubility of the non-metals is low, though the small quantities which do dissolve have considerable influence on the utility of liquid sodium as a coolant. Some metals, *e.g.*, the metals of the copper and the zinc group, form stoicheiometric intermetallic compounds when brought into contact with liquid sodium, but most transition metals (*e.g.*, metals of the titanium, the vanadium, and the chromium group) neither react with, nor dissolve in, liquid sodium.[2]

Solutions of barium and calcium are of special interest since these solutes have a marked influence on the wetting properties of liquid sodium. The solutions are stable; their surface tensions give some measure of the ideal nature (or otherwise) of the solutions, and from a knowledge of these values it is possible to assess the extent to which the surface tensions of the solutions are responsible for the wetting properties described in Part V.[1] Solubility values for the Group II metals are collected in Table 1; the solubilities of calcium and barium are widely different, and the physical natures of the solutions bear little resemblance. This is illustrated by comparison of the phase diagrams [3,4] which are directly relevant to the present work and are reproduced in Fig. 1. Addition of barium initially lowers the freezing point of sodium, and the liquidus curve is typical of a binary

Table 1.

Solubility of the Group II metals in liquid sodium.

Metal	Solubility (atom %) at 150°	200°	300°	400°
Be[2]	0	0	0	0
Mg[3]	0·14	0·27	0·53	0·80
Ca[4]	0·045	0·11	0·42	1·07
Sr	Not known			
Ba[3]	15·77	17·80	54·87	62·30

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[1] Part V, Addison, Iberson, and Manning, *J.*, 1962, 2699.

[2] Liquid Metals Handbook, 2nd edn., NAVEXOS—P. 733, U.S. Govt. Printing Office, Washington, 1952.

[3] Liquid Metals Handbook, Na–K Supplement, TID-5277, pp. 16, 18, U.S. Govt. Printing Office, Washington, 1955.

[4] Rinck, *Compt. rend.*, 1930, **191**, 404; 1931, **192**, 1378.

system in which there is some weak association between the components. In contrast, addition of calcium raises the freezing point of sodium. The data on which Rinck's phase diagram[4] was based gave the solubility of calcium in sodium as 7·0 wt. % at 700°. More recent work shows this value to be 9·42%,[3] or even 10·0% (equiv. to 6·0 atom % of calcium).[5] This part of Rinck's diagram is therefore redrawn in Fig. 1, on the basis of the last value. Homogeneous solutions are obtained up to a concentration of 6·0 atom % of calcium at 700°; thereafter, two immiscible liquid phases are obtained, and this wide immiscibility gap extends over the range 6—78 atom % calcium (*i.e.*, between lines A and B in Fig. 1). Pronounced differences are also observed in the surface properties of barium and calcium solutions in sodium.

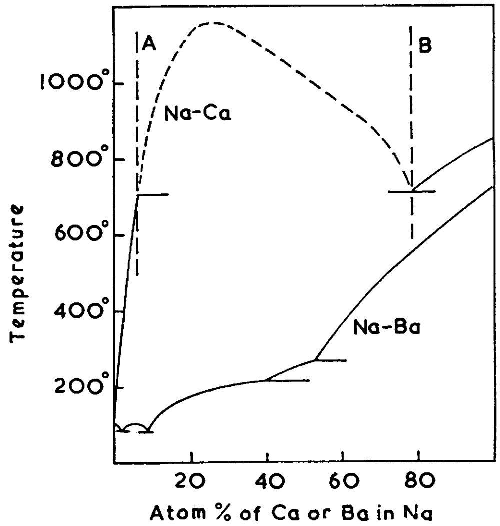

FIG. 1. Phase diagrams for the barium–sodium and the calcium–sodium system.

EXPERIMENTAL

Surface tensions were measured by the vertical-plate method. The apparatus used was that described in Part I,[6] modified as described in Part V.[1] The plates used were made from pure nickel or pure iron sheet. In all cases the plates were wetted immediately on contact with the calcium or barium solutions, so that the receding contact angle could be assumed to be zero. The values used for the density (*d*) of the solutions were those obtained in a parallel study of volumes of mixing of liquid metals which will be described in a later paper.[7] The treatment of results, and the necessary calibrations, have been described in Part I.[6] Each value quoted (Tables 2 and 3) is the mean of several measurements which were reproducible within ±2 dynes/cm. For example, for a 22·8 wt. % solution of barium in sodium at 250°, five measurements gave values of 170·0, 171·0, 172·0, 169·5, and 173·5 dynes/cm.

Preparation of Solutions.—Sodium and argon were purified as already described.[2, 6] Barium metal (B.D.H. Ltd.; 99·99%) and calcium metal (Hopkin and Williams Ltd.; 99%) were cleaned as follows. The metals (10-g. pieces) were first washed with ether to remove adhering paraffin. They were then filed in an argon-filled glove-box, and washed with ethanol containing 2% of concentrated hydrochloric acid solution. When the metal was bright, it was washed with dry ethanol, dried in a vacuum, and stored under pure argon. Two methods were used to prepare solutions in sodium. (*a*) To reduce oxide content to a minimum, sodium was invariably filtered into the apparatus through sintered-glass plates at a temperature near 105°. Barium has a high solubility in sodium at this temperature (Fig. 1); solutions could therefore be made in a separate vessel and filtered directly into the apparatus at 105°. Sodium

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[5] Imperial Chemical Industries Limited, General Chemicals Division, personal communication.
[6] Addison, Kerridge, and Lewis, *J.*, 1954, 2861.
[7] Addison, Coldrey, and Pulham, unpublished work.

(previously purified) was filtered into a glass vessel containing barium metal in an atmosphere of argon. The solution was heated at 10^{-5} cm. at 300° for 12 hr. to remove traces of organic impurity, then filtered directly into the surface-tension apparatus at 105°. Barium concentration could be decreased at will by dilution with further pure sodium. (*b*) The above method was unsuitable for the preparation of solutions containing more barium than is soluble at 105°, or for calcium solutions. In these cases, the solute metal was added directly to sodium contained in the steel beaker in the tension apparatus (Fig. 1 of Part V [1]), through a side-arm and against a counter-flow of argon. Temperature was then raised to the required level, and the solution stirred intermittently by a stainless-steel stirrer. Dissolution of calcium or barium was usually complete within an hour.

Measurements could not be carried out above 450°. At this temperature the vapour pressure of sodium is high; even when a counter-flow of argon was maintained from the torsion wire and suspension towards the liquid metal, there was a danger that sodium vapour might condense on the suspension wire. The attack of sodium vapour on glass is also rapid at this temperature.

The surfaces of both the barium and the calcium solutions remained bright throughout the experiments. The behaviour of the suspended plate when immersed in the barium solutions was quite normal, but a number of abnormal effects were observed in the calcium solutions. Plates of the same dimensions as used with the barium solutions showed a marked tendency to pull to the side of the containing vessel, and increasing the diameter of the liquid surface up to 5·5 cm. did not alter this. The effect was one which might have been expected for liquids of very high density or very high surface tension. However, the density of the calcium solutions was little different from that of pure sodium, and although the surface tension of sodium is increased by addition of calcium, this increase is relatively small. This experimental complication is best overcome by the use of smaller plates. Again, the calcium solutions showed the type of " creep " phenomenon which is well-known for alcoholic solutions in glass vessels. When the plate had been withdrawn sufficiently far through the surface to expose a length (say, 1 cm.) of wetted plate, the solution " crept " up this film to form a ridge of solution at the top of the wetted area of the plate. This ridge slowly solidified, which may perhaps be associated with an increase in calcium concentration to a value at which separation into two phases occurs (Fig. 1). It was possible to allow for this effect by withdrawing the plate completely and weighing the solid adhering to the plate, but the effect was never observed with the barium solutions.

Sampling.—The concentration of barium or calcium was determined by analysis of samples drawn from the apparatus at the temperature of the experiment. A glass tube (0·3—0·4 cm. internal diameter) blown out to a series of small (0·5 ml.) bulbs was inserted into the apparatus through a side-arm (Fig. 1 of Part V [1]) against a current of argon. The solution was drawn up into the tube, where it quickly solidified. Any metal adhering to the outside of the tube was oxidised by placing the tube in an atmosphere of argon containing a little oxygen. The oxide could then be removed by wiping, and this technique prevented the samples catching fire. The sample-tube was then transferred to an argon glove-box where it was broken into its separate bulbs. The exposed ends of the tubes were guarded by Polythene " policemen."

Analysis of Samples.—The contents of a weighed sample-tube were dissolved in distilled water in an open flask. The risk of explosion was minimised by the fact that the sample-tubes were restricted at each end, so that the reaction area was small. Provided that the original sample-tubes were of sufficiently narrow bore, explosion could be prevented by continual removal of the hydrogen generated, by passing a rapid flow of argon through the flask. Samples containing a high concentration of barium could be dissolved safely by this means in dilute hydrochloric acid. Empty sample-tubes were undamaged and could be reweighed. Barium in the solution was determined gravimetrically as sulphate, and calcium volumetrically by means of EDTA.

RESULTS AND DISCUSSION

Solutions of Barium in Sodium.—The results for pure sodium [6] and for solutions of barium are given in Table 2.

Some measure of the extent to which these solutions conform to ideality may be obtained by reference to Fig. 2. The broken lines join surface-tension values for pure

TABLE 2.

Surface tensions of solutions of barium in liquid sodium.

	Surface tension (dynes/cm.)						
Atom % of Ba	100°	150°	200°	250°	300°	350°	400°
0·00	194·8	189·8	184·8	179·8	174·8	169·8	164·8
2·0	—	—	177	—	167	—	—
4·6	187	182	177	172	167	163	—
8·2	—	187	182	177	172	167	—
14·6	—	—	191	186	181	175	—
29·0	—	—	—	201	196	192	187

sodium and pure barium, and the arrows represent the solubility limits of barium in sodium at each temperature. The surface tension of liquid barium has been determined over a temperature range of 720—1000° and will be described in a later paper.[7] These values were extrapolated below the melting point of pure barium (720°) to obtain the 100% barium axis values shown in Fig. 2. This degree of extrapolation may introduce some error, but is inevitable because of the high melting point of barium. Experimental values for the surface tension of the solutions lie only a few dynes/cm. below the broken lines, and the curve representing ideal behaviour will also lie a little below the broken lines in Fig. 2. Guggenheim[8] has expressed the surface tension of an ideal 1 : 1 mixture of two liquids A and B by the equation

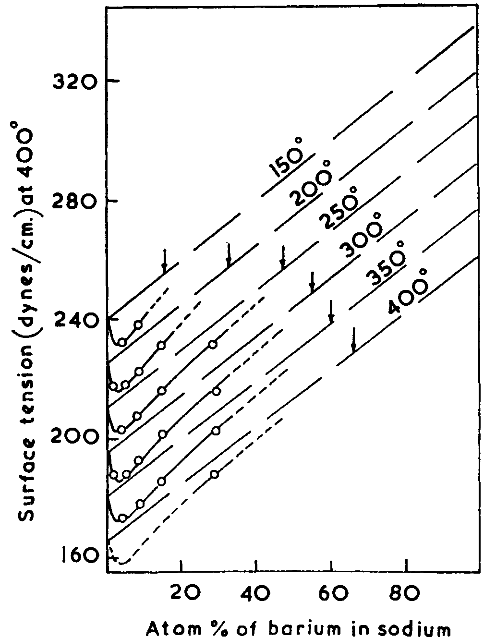

FIG. 2. Surface tensions of solutions of barium in sodium.

(The axis values for surface tension are correct for 400°; for other temperatures, the following adjustments should be made.

Temp.	150°	200°	250°	300°	350°
Subtract	50	40	30	20	10 dynes/cm.)

$$\gamma = \tfrac{1}{2}(\gamma_A + \gamma_B) - (\boldsymbol{k}T/a) \ln \cosh (\gamma_B - \gamma_A)a/2\boldsymbol{k}T \qquad (1)$$

(where *a* is the mean area occupied by a molecule in the surface), so that the second term represents the extent to which the " ideal " value for the 1 : 1 mixture falls below that indicated by the broken lines in Fig. 2. For liquids to which this equation might be regarded as applicable, *i.e.*, those consisting of covalent molecules, or even molten salts,[9]

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[8] Guggenheim, " Mixtures," Clarendon Press, Oxford, 1952, p. 177.

[9] Dahl and Duke, U.S.A.E.C. Rept. ISC-923.

the difference ($\gamma_B - \gamma_A$) is small; in molten mixtures of sodium nitrate and silver nitrate, for example, the value of the second term amounts to only 2 dynes/cm. in a tension value of 130 dynes/cm.[9] Applied to the sodium–barium system, however, the second " correction " term in equation (1) has the following values:

Temp.	150°	200°	250°	300°	350°	400°
Second term in eqn. (1) (dynes/cm.)	27·7	25·2	22·5	20·4	19·1	18·4

The experimental results (Fig. 2) do not fall below the broken lines by more than 13 dynes/cm., and appear to be approaching the arithmetic mean value with increasing barium concentration. There are two possible reasons why the application of equation (1) to liquid metals may not be feasible. First, $\gamma_{Ba} - \gamma_{Na}$ is often large (in this case near 100 dynes/cm.); secondly, liquid metals differ from all other liquids in that all the atoms are present as cations, with electrons moving freely between the ions, and it is not at present possible to assess quantitatively the influence of these electrons on the surface tension.

On first addition of barium to sodium, the surface tension passes through a minimum at 4 atom % of barium; this is a real effect and may be correlated with the phase diagram. The only true maximum in the liquidus curve (Fig. 1) also occurs at 4 atom % of barium, so that the initial drop in surface tension can be related, to some extent, with attractive forces between sodium and barium atoms. It is probable, however, that it is also brought about by the breakdown of the quasi-crystalline structure of pure liquid sodium on introduction of a foreign (and bivalent) ion.

Solutions of Calcium in Sodium.—The behaviour of these solutions contrasts sharply with that of barium solutions. The solubility of calcium in sodium at 450° is 1·45 atom %, and over this concentration range barium lowers the surface tension of liquid sodium. In spite of the experimental difficulties encountered with the calcium solutions, it was clear that dissolution of calcium in sodium causes an increase in the surface tension. Results are shown in Table 3.

TABLE 3.

Surface tensions of solutions of calcium in liquid sodium.

Atom % of Ca	Temp.	Surface tension of solution (dynes/cm.)	Surface tension of pure sodium (dynes/cm.)
0·23	250°	233, 237	179·8
0·38	300	221, 223	174·8
0·69	350	214, 216 (vertical plate)	169·8
		211, 217 (max. bubble pressure)	,,
0·40	400	171, 174	164·8
0·98	400	199, 203	,,
1·45	450	184, 185, 187	159·8

Where saturated solutions were used, the calcium content (S) was calculated [5] from the formula $\log_{10} S = 2{\cdot}62 - 1580/T$.

The values given in Table 3 were obtained in separate experiments; two values were determined by the maximum bubble pressure method, and the remainder by the vertical-plate method; the influence of calcium is greatest at the lower temperatures. Adsorption of calcium to the stainless-steel orifice is believed to be responsible for the highly unusual behaviour observed during attempts to measure the surface tensions of the solutions by the maximum bubble pressure method. A knife-edge orifice (0·2 cm. diameter) was used, and a technique which gave satisfactory performance and results for pure sodium. With calcium solutions, the argon pressure required for bubble formation increased with time of immersion, and varied continuously with rate of bubble formation. No mechanical blocking occurred, since by raising the orifice above the liquid surface, a reflection of the clean orifice could be seen in the bright surface of the liquid metal. These effects were reduced with increase in the orifice diameter, and the two values quoted in Table **3** were determined with an orifice of 0·4 cm. diameter.

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