Sodium–Lithium Phase Diagram: Redetermination of the Liquid Immiscibility System by Resistance Measurement

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The sodium–lithium phase diagram has been determined over the entire composition range by a combination of resistance and thermal methods. Each method is especially effective for specific parts of the phase diagram. Two liquid phases separate below 305 ± 1 °C; this temperature is variously reported between 303 and 442 °C in the literature. The consolute composition is 63 mol % Li. The immiscibility boundary extends from 10.1 to 97.0 mol % Li at the monotectic temperature 170.75 ± 0.05 °C. A eutectic occurs at 3.0 mol % Li and 92.10 ± 0.05 °C. Positive deviation from ideality has been observed for both sodium- and lithium-rich solutions.

THE sodium–lithium phase diagram is relatively simple. A region of two immiscible liquids dominates the system. A eutectic occurs near the sodium end and a monotectic is adjacent to the lithium axis. Our interest originally centred on the minimum temperature at which the two metals are miscible in all proportions. This was required in kinetic studies of the solutions with nitrogen [1] and for electrical-resistivity measurements.[2] The published data on the miscibility are shown in Table 1 and fall into two categories. Those which give temperatures of 442 and 380 °C (both interpolated), and those which give much lower temperatures of 306 and 303 °C. Significantly the high temperatures were obtained by thermal and chemical analysis whereas lower values were provided by densitometry or resistance changes. The discrepancy is so great that it was necessary to redetermine the phase boundary and it seemed judicious to employ more than one technique. The investigation developed to cover all features of the phase diagram since it was clear that there were other inconsistencies as shown in Table 1, *e.g.* consolute composition and width of immiscibility.

TABLE 1

Comparison of the salient features in the published data on the sodium–lithium phase diagram

		a	*b*	*c*	*d*	*e*	*f*
Consolute point	θ_c/°C	442	380	306	303		
	mol % Li	59.7	65.0	66.0	62.5		
Monotectic	θ_c/°C	170.6	171	170		162	166
	mol % Li	8.4—96.6	13.1—96.2	12.1—96.6		98	
Eutectic	θ_c/°C	92.2	93.4			93	91
	mol % Li	3.8	3.7				
M.p. of Li	θ_c/°C	180.54	179.4	180.5		179	
Method		t.a.	t.a.–c.a.	d	r	t.a.	t.a.

t.a. = Thermal analysis, c.a. = chemical analysis, d = density, and r = resistance. [a] Ref. 6. [b] Ref. 7. [c] Ref. 8. [d] Ref. 9. [e] G. Masing and G. Tammann, *Z. anorg. Chem.*, 1910, **67**, 187. [f] B. Böhm and W. Klemm, *Z. anorg. Chem.*, 1939, **243**, 69.

EXPERIMENTAL

Apparatus for determining phase changes in metallic mixtures by thermal and resistance methods has been described previously.[3] Liquid metal from a steel reservoir was drawn by a miniature electromagnetic pump through a capillary loop. The resistance of the liquid in the capillary was measured using a Kelvin–Wheatstone bridge. The temperature (±0.05 °C) of both reservoir and capillary was measured by thermocouples. Argon was used to protect the metals and alloys were prepared *in situ* by weighing. Sodium [4] and lithium [5] were purified as before. Temperatures between 60 and 450 °C were investigated. For

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

[2] M. G. Down, P. Hubberstey, and R. J. Pulham, *J.C.S. Faraday I*, 1975, **71**, 1378.

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

[4] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.*, 1961, 1482.

[5] G. K. Creffield, M. G. Down, and R. J. Pulham, *J.C.S. Dalton*, 1974, 2325.

temperature–time analysis solutions were cooled at rates between 0.021 and 0.0033 °C s^{-1} at 300 and 100 °C respectively. Temperatures were measured by the reservoir thermocouple. For resistance–temperature analysis resistances were determined at constant temperatures every 10 °C. Near the phase boundaries smaller temperature intervals were employed.

Each method was especially effective for specific parts of the phase diagram. This is illustrated in Figure 1. The left-hand side shows experimental superimposed curves for θ_c against R (*a*) and θ_c against t (*b*) for a 44.5 mol % Li solution. Breaks in these curves are correlated (by broken lines) with boundaries in the schematic phase diagram on the right-hand side. The θ_c against R curve plainly shows a break at 295 °C which is absent in the θ_c against t curve. Thus the $l_1 + l_2$ boundary is only located (±1 °C) by resistance changes. The hypereutectic liquidus (between 171 and 92 °C) is similarly located. Resistance is effective because it monitors the change in composition of the sampled liquid as separation into two liquids occurs. The expected inflexion was not observed in the thermal curve (*b*) as the enthalpy change for separation is too small. The monotectic horizontal reaction at 171 °C was detected by both methods but was far more accurately located (±0.05 °C) by thermal arrests. The latter can be accentuated by using larger quantities of metal; resistance is insensitive to quantity. The eutectic horizontal at 92.1 °C could be located by both techniques but was more accurately defined (±0.05 °C) by thermal analysis. The m.p.s of the pure metals and their depressions were also better determined by thermal analysis.

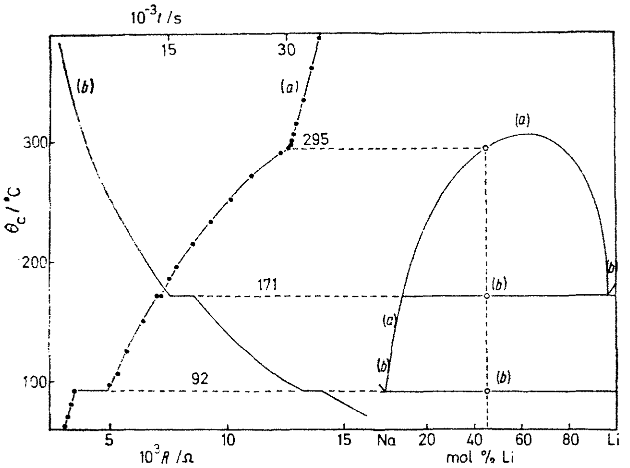

FIGURE 1 Plots of θ_c against R (*a*) and θ_c against t (*b*) and schematic-phase diagram showing the sections determined by each technique

RESULTS AND DISCUSSION

Features of the Phase Diagram.—The phase diagram is shown in Figure 2 and is derived from data on 30 solutions. The miscibility gap is not symmetrical; lithium is more soluble in sodium than is sodium in lithium. The consolute point occurs at 305 ± 1 °C and 63 mol % Li. This is 137 and 75 °C below that reported by Howland and Epstein[6] and Salmon and Ahmann[7] respectively (Table 1). These were both interpolated temperatures but whereas the experimental points (by chemical analysis) of Salmon and Ahmann fall close to our curve and only the interpolation differs, those of Howland and Epstein (by thermal analysis) differ considerably from ours. We were unable to detect this boundary by thermal analysis (see above). In view of the present results and the corroboration provided by certain other studies,[8-10] we believe that the interpolated curve of Salmon and Ahmann and the entire curve of Howland and Epstein are in considerable error. To add to the confusion these misleading data are propagated in the reference volumes of Hansen[11] and Elliott[12] respectively.

The immiscibility boundary extends from 10.1 to 97.0 mol % Li at the monotectic temperature 170.75 ± 0.05 °C. The m.p., 180.50 ± 0.05 °C, of lithium is thus depressed by 9.75 °C. The monotectic reaction extends at least to 99.36 mol % Li, *i.e.* the maximum solid solubility of Na in Li is below 0.64 mol % Na. The eutectic horizontal was observed at 92.10 ± 0.05 °C and between 1.90 and 99.36 mol % Li which is consistent with the absence of intermetallic compounds. The solid solubility of Li in Na, therefore, is no more than 1.90 mol % Li and may be much less since the terminal

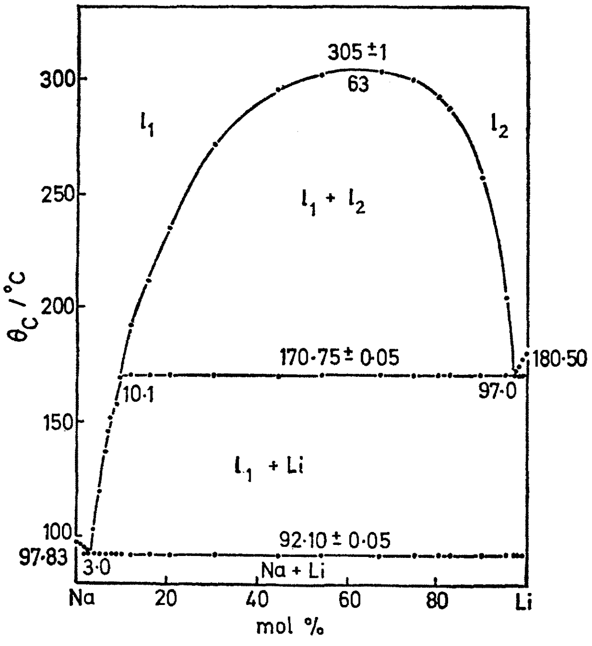

FIGURE 2 The sodium–lithium phase diagram

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[6] W. H. Howland and L. F. Epstein, *Adv. Chem. Ser.*, 1957, **19**, 34.

[7] O. N. Salmon and D. H. Ahmann, *J. Phys. Chem.*, 1956, **60**, 13.

[8] F. A. Kanda, R. C. Faxon, and D. V. Keller, *J. Phys. and Chem. Liquids*, 1968, **1**, 61.

[9] H. K. Schürmann and R. D. Parks, *Phys. Rev. Letters*, 1971, **27**, 1790.

[10] W. van der Lugt, personal communication.

[11] M. Hansen, 'Constitution of Binary Alloys,' McGraw-Hill, 1958, p. 899.

[12] R. P. Elliott, 'Constitution of Binary Alloys,' McGraw-Hill, 1965, p. 583.

solid solubility is reported to be very small in this system.[13] The m.p., 97.83 °C, of sodium is depressed by 5.73 °C as the hypoeutectic liquidus falls to the eutectic at 3.0 mol % Li.

Deviation from Ideality.—The depression in freezing point ($T_m - T$) can be used to determine the activity coefficient of the solvent by using equation (1), where

$$\ln \gamma_l x_l/\gamma_s x_s = -H_f(T_m - T)/RT_mT \qquad (1)$$

γ_l and γ_s are the activity coefficients of the solvent in the liquid and solid phases respectively in equilibrium at temperature T, x_l and x_s the corresponding mol fractions, H_f the latent heat of fusion (2.603 and 3.000 kJ mol^{-1} for Na [14] and Li [15] respectively as solvents), and R is the gas constant. For dilute solution γ_s and x_s are assumed unity since there is negligible solid solubility. The activity coefficients so calculated for Na and Li at $x_l =$ 0.99 for each are 1.0058 and 1.0045 respectively. These are both significantly greater than unity and show that for dilute solutions there is large positive deviation from ideality. That this persists to higher concentrations is evidenced by the extensive immiscibility seen over the rest of the phase diagram.

The activity coefficient for sodium in other mixtures is also greater than unity as shown in Table 2. Ideality is approached most closely in Na–K. γ_{Na} Increases in the order K < Rb < Cs < Li. The relative sizes of the atoms appear partly responsible for this trend, though electronegativity and cohesive forces are also recognised as influential factors. The solutes K, Rb, and Cs are larger than Na and progressively increase in size and there is a corresponding increase in non-ideal behaviour. As expected, this manifests itself as an increasing immiscibility tendency in the phase diagrams. Lithium, being smaller than sodium and with a larger cohesive force, causes a disproportionately large deviation.

TABLE 2

Activity coefficient of sodium, γ_{Na}, in sodium–alkali metal mixtures

System	γ_{Na}
Na–Li	1.0058
Na–K *	1.0004
Na–Rb *	1.0030
Na–Cs *	1.0054

* Data were derived from phase diagrams in 'Sodium-NaK Engineering Handbook,' ed. O. J. Foust, Gordon and Brecch, London, vol. 1, 1972.

Comparable activity coefficients for lithium are not available because the metal is completely immiscible with K, Rb, and Cs at reasonable temperatures. These larger atoms, therefore, presumably create even greater deviations from ideality than that seen for sodium in lithium.

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[13] W. B. Pearson, *Internat. Ser. Monographs Metallurgical Physics and Phys. Metallurgy*, 1964, **4**, 717.

[14] G. W. Thomson and E. Garelis, 'Physical and Thermodynamic Properties of Sodium,' 2nd edn., Ethyl Corporation, Detroit, 1955.

[15] R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelley, 'Selected Values of Thermodynamic Properties of Metals and Alloys,' Wiley, London, 1963, p. 154.