The Phase Diagram
Li$_2$SO$_4$—Na$_2$SO$_4$

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The system Li$_2$SO$_4$—Na$_2$SO$_4$ has been investigated by differential thermal analysis (DTA) and microscopic study of equilibrated quenched samples as well as by high temperature microscopy. A detailed account of the techniques and a thorough description of the system will be published shortly elsewhere. The system has previously been investigated among others by Le Chatelier,1 Nacken,2 and by Schroeder and Kvist.3 As the phase diagrams presented on several points are conflicting and in many respects open to doubt a reinvestigation was undertaken.

Experimental. Anhydrous Li$_2$SO$_4$ was prepared from Analar Reagent Li$_2$SO$_4$·H$_2$O (Mallinkrodt). The water was removed by heating in vacuum. The salt was slowly heated to about 280°C and left for 3 days at this temperature. Anhydrous Na$_2$SO$_4$ was obtained from Merck (quality p.a.) and was dried in a similar way as the Li$_2$SO$_4$. The dehydrated salts were kept in closed capsules in a desiccator when not in use. The DTA was carried out in a Mettler thermoanalyser. Samples of 20 mg were held in a platinum crucible under an argon atmosphere. Heating and cooling rates of 8°C/min were employed. In some cases, however, rates of 2°C/min were also used for comparison. The reference substance was Al$_2$O$_3$ powder. The liquidus lines were obtained on cooling curves and the solidus lines on heating curves.

Result and discussion. The system consists of

(1) a peritectic at 636°C where a liquid of 60.0 mol % Na$_2$SO$_4$ is in equilibrium with two solid phases with 62.0 and 67.5 mol % Na$_2$SO$_4$, respectively;

(2) a eutectic at 585°C where a liquid of 37.5 mol % Na$_2$SO$_4$ is in equilibrium with two solid phases of 33.8 and 38.8 mol % Na$_2$SO$_4$, respectively;

(3) a peritectoid at 515°C where the intermediate compound LiNaSO$_4$ decomposes incongruently giving rise to two solid phases with 49.5 and 53.5 mol % Na$_2$SO$_4$, respectively;

(4) a eutectoid at 508°C where a b.c.c. phase with 40.5 mol % Na$_2$SO$_4$ is in equilibrium with a f.c.c. phase with 34.5 mol % Na$_2$SO$_4$ and the compound LiNaSO$_4$;

(5) a eutectoid at 465°C where a solid f.c.c. phase is in equilibrium with pure Li$_2$SO$_4$ and the compound LiNaSO$_4$;

(6) a eutectoid at 230°C where a hexagonal phase with 97.0 mol % Na$_2$SO$_4$ is in equilibrium with the intermediate compound LiNaSO$_4$ and pure Na$_2$SO$_4$;

(7) transformations in pure Na$_2$SO$_4$ at 237 and 228°C.

At about 480°C and around 75 mol % Na$_2$SO$_4$ the boundary curve, separating the hexagonal phase from the two-phase region for LiNaSO$_4$ and this hexagonal phase, has a point of inflexion. Because of the sudden change in solubility in this region the heat of mixing will give rise to heat effects on the DTA curve. These points have also been included in Fig. 1 but they should not be interpreted as a three-phase line.

A reinvestigation of this system by Kvist4 has recently been carried out and his values confirm to a large extent the diagram obtained in the present work.

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13C—15N Spin-Spin Coupling Constants in [15N]-Aniline from 13C NMR Spectra

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In connection with current 13C NMR studies on signs and magnitudes of 13C—13P spin-spin coupling constants involving sp2 hybridized carbon atoms in aromatic and heteroaromatic phosphine derivatives, a comparison with corresponding 13C—15N coupling constants would be of interest. However, in only a very few cases the signs and magnitudes of 13C—15N couplings have been obtained. This note reports on the 13C—15N coupling constants in [15N]-aniline as determined from noise-modulated and single-frequency proton decoupled 13C NMR spectra. The noise-modulated proton decoupled 13C spectrum of [15N]-aniline in acetone-d6 is shown in Fig. 1. Assignment of the aromatic carbon resonances followed from a series of single-frequency proton decoupling experiments (rH(4) > rH(5)) and is in agreement with that proposed earlier for aniline. Under conditions of higher resolution (sweep width 0.5 Hz/cm) all carbon resonances were observed to show additional splittings due to 13C—15N spin-spin interactions. The J(13C—15N) coupling constants and 13C chemical shifts are collected in Table 1. Information on the signs of the 13C—15N coupling constants could be obtained for J(13C(2)—15N) and J(13C(3)—15N) using off-resonance and selective proton decoupling techniques as recently described. In spite of the very small magnitude expected for J(15N—H(3)) the sign of J(13C(3)—15N) could nevertheless be related to the sign of this coupling constant. As seen from Fig. 2 the sign of the two 13C—15N couplings is found to be the same as for the couplings between 15N and the corresponding ring protons, i.e.

Fig. 1. Natural abundance 13C NMR spectrum (single scan; 1H noise-decoupled) of [15N]-aniline. The ppm scale is downfield from internal TMS. Peak marked with an asterisk is an impurity.

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