

The Phase Diagram $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4$

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The system $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4$ 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_2SO_4 was prepared from Analar Reagent $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ (Mallinckrodt). 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_2SO_4 was obtained from Merck (quality *p.a.*) and was dried in a similar way as the Li_2SO_4 . The dehydrated salts were kept in closed capsules in a desiccator when not in use. The DTA was carried out in a Mettler thermoanalyzer. Samples of 20 mg were held in a platinum crucible under an argon atmosphere. Heating and cooling rates of 6°C/min were employed. In some cases, however, rates of 2°C/min were also used for comparison. The reference substance was Al_2O_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_2SO_4 is in equilibrium with two solid phases with 62.0 and 67.5 mol % Na_2SO_4 , respectively;

(2) a eutectic at 585°C where a liquid of 37.5 mol % Na_2SO_4 is in equilibrium with two solid phases of 33.8 and 38.8 mol % Na_2SO_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_2SO_4 , respectively;

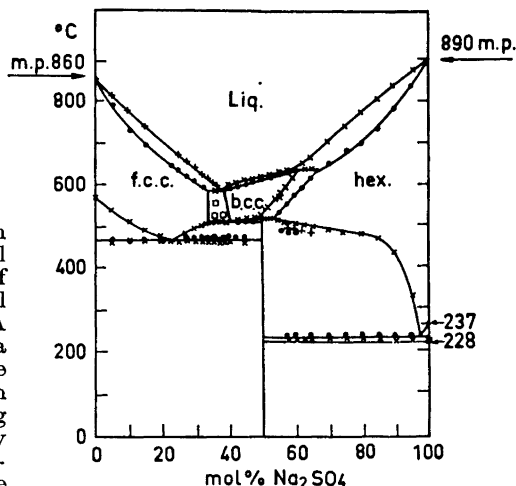


Fig. 1. The phase diagram $\text{Li}_2\text{SO}_4\text{—Na}_2\text{SO}_4$.
× Cooling curve data; ● Heating curve data;
□ Equilibration data.

(4) a eutectoid at 508°C where a b.c.c. phase with 40.5 mol % Na_2SO_4 is in equilibrium with a f.c.c. phase with 34.5 mol % Na_2SO_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_2SO_4 and the compound LiNaSO_4 ;

(6) a eutectoid at 230°C where a hexagonal phase with 97.0 mol % Na_2SO_4 is in equilibrium with the intermediate compound LiNaSO_4 and pure Na_2SO_4 ;

(7) transformations in pure Na_2SO_4 at 237 and 228°C.

At about 480°C and around 75 mol % Na_2SO_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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^{13}C — ^{15}N Spin-Spin Coupling Constants in [^{15}N]-Aniline from ^{13}C NMR Spectra

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In connection with current ^{13}C NMR studies on signs and magnitudes of ^{13}C — ^{31}P spin-spin coupling constants involving sp^2 hybridized carbon atoms in aromatic and heteroaromatic phosphine derivatives,^{1a-c} a comparison with corresponding ^{13}C — ^{15}N coupling constants

would be of interest. However, in only a very few cases the signs and magnitudes of ^{13}C — ^{15}N couplings have been obtained.^{2a-d} This note reports on the ^{13}C — ^{15}N coupling constants in [^{15}N]-aniline as determined from noise-modulated and single-frequency proton decoupled ^{13}C NMR spectra.

The noise-modulated proton decoupled ^{13}C spectrum of [^{15}N]-aniline in acetone- d_6 is shown in Fig. 1. Assignment of the aromatic carbon resonances followed from a series of single-frequency proton decoupling experiments ($\nu_{\text{H}(3)} > \nu_{\text{H}(4)} > \nu_{\text{H}(2)}$)³ and is in agreement with that proposed earlier for aniline.⁴ Under conditions of higher resolution (sweep width 0.5 Hz/cm) all carbon resonances were observed to show additional splittings due to ^{13}C — ^{15}N spin-spin interactions. The $J(^{13}\text{C}$ — $^{15}\text{N})$ coupling constants and ^{13}C chemical shifts are collected in Table 1.

Information on the signs of the ^{13}C — ^{15}N coupling constants could be obtained for $^2J(^{13}\text{C}(2)$ — $^{15}\text{N})$ and $^3J(^{13}\text{C}(3)$ — $^{15}\text{N})$ using off-resonance and selective proton decoupling techniques as recently described.^{1a} In spite of the very small magnitude expected for $^4J(^{15}\text{N}$ — $\text{H}(3))$ ⁵ the sign of $^3J(^{13}\text{C}(3)$ — $^{15}\text{N})$ could nevertheless be related to the sign of this coupling constant. As seen from Fig. 2 the sign of the two ^{13}C — ^{15}N couplings is found to be the same as for the couplings between ^{15}N and the corresponding ring protons, *i.e.*

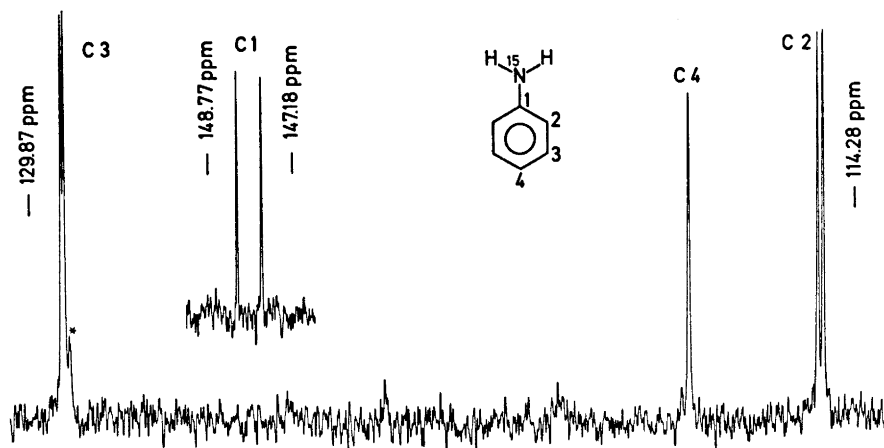


Fig. 1. Natural abundance ^{13}C NMR spectrum (single scan; ^1H noise-decoupled) of [^{15}N]-aniline. The ppm scale is downfield from internal TMS. Peak marked with an asterisk is an impurity.