Reactions in Mixed Non-aqueous Solutions containing Sulphur Dioxide. Part 8.[1] Phase Studies of Sulphur Dioxide–Dimethyl Sulphoxide and Sulphur Dioxide–Dimethylformamide Mixtures

J. Bernard Gill,* David C. Goodall, and Brian Jeffreys
Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

Phase diagrams are given for the complete range of compositions of sulphur dioxide–dimethyl sulphoxide (dmso) and sulphur dioxide–dimethylformamide (dmf). SO_2–dmso mixtures contain compounds of compositions $2SO_2$•dmso and SO_2•dmso, identifiable as solids with melting points −74 and −39 °C, but no compound of composition SO_2•2dmso was found which was stable as a solid. SO_2–dmf mixtures contain three stable solid species: $2SO_2$•dmf, SO_2•dmf, and SO_2•2dmf, with melting points −65, −60, and −40 °C.

The results reported in this paper were obtained to support the Raman spectroscopic studies on the sulphur dioxide–dimethyl sulphoxide (dmso) mixtures described in the preceding paper.[1]

A preliminary and semi-quantitative melting point study indicated the formation of an adduct of 1:1 stoicheiometry with a melting point near −40 °C.[2] Qualitative evidence of adduct or compound formation is provided by the large release of enthalpy observed when SO_2 gas is bubbled into dmso; the temperature of a 10 cm^3 sample rapidly rises to *ca.* 100 °C.

Because the experiments were limited to semi-quantitative melting point measurements our earlier work proved the existence of only one adduct. At the time we were severely limited by our apparatus and able to make measurements only at temperatures higher than −65 °C. Thus melting point determinations were restricted to the dmso-rich mixtures and examination of mixtures rich in SO_2 was precluded.

The Raman spectra of SO_2–dmso mixtures are very complex. Changes in the spectra with both the composition and the temperature of the medium indicate the existence of equilibria between a number of constituent species, and it is apparent that the mixtures are much more complex than had originally been supposed. Accordingly apparatus has been constructed and experimental techniques have been established to obtain a low-temperature phase diagram of the mixtures.

We also report the results of a phase study of SO_2–dimethylformamide (dmf) mixtures.

Experimental

Samples were prepared, as for Raman spectroscopy,[1,3,4] in sealed medium-walled Pyrex tubes (12 mm outside diameter, 185 mm length) with a concave thin breakseal in the base of each tube. Care was needed after the tubes had been filled and sealed to avoid fracture of the breakseal whilst the frozen mixtures were being thawed. The compositions (quoted throughout as mol fraction SO_2) of the samples were determined by weight before the filled sample tubes G were inserted into the apparatus (Figure 1). This device was constructed to fit snugly into an Oxford Instruments top-loading DN704 cryostat with its thin-walled measuring finger D horizontally in line with the four radial windows of the cryostat. Into the tip D was blown a small recess to hold a chromel–alumel thermocouple to monitor the sample temperature. The thermocouple output, compared with ice-point, was read into a Hewlett Packard 3490A multimeter and a chart recorder.

After loading the sample tube the measuring device was closed with the stopper F, evacuated, and flushed through tap E with dry N_2 while inverted. The sample tube was opened by rotating the complete assembly and cracking the breakseal on the sharp glass point C whilst the sample was still frozen. On warming, the liquid ran into the thin-walled neck and the apparatus was positioned within the cryostat.

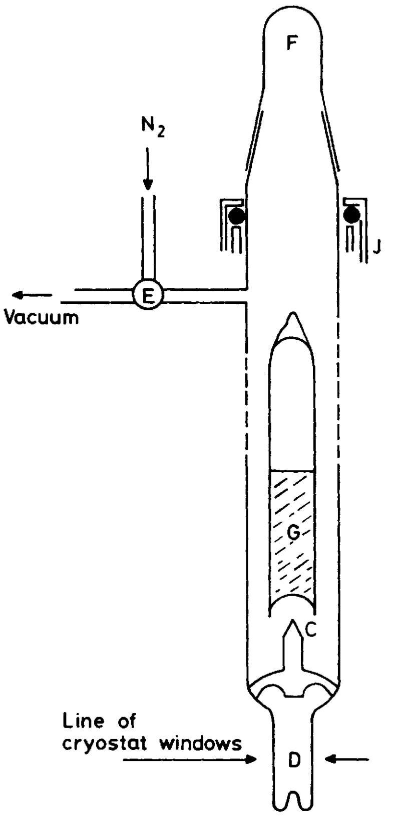

Figure 1. Apparatus for determination of melting and eutectic temperature points at sub-ambient temperatures: C, glass needle to break ampoule; D, thin-walled glass measuring finger; E, two-way tap to N_2 supply or vacuum; F, coned stopper; G, sealed ampoule with breakseal; J, top of cryostat

Samples under test were cooled and heated at steady rates. Melting points and eutectic temperatures were obtained from the inflexions in the cooling and heating curves. Cooling was continued to 50—60 °C below the melting points. Samples which formed glasses were recycled through their glass transition temperatures several times to ensure that melting points were not obscured by problems of supercooling. Heating rates of 5 °C min^{-1} gave clear results with a chart speed of 500 mm h^{-1} and a full scale deflection of either 2.5 or 5 mV. Cooling rates

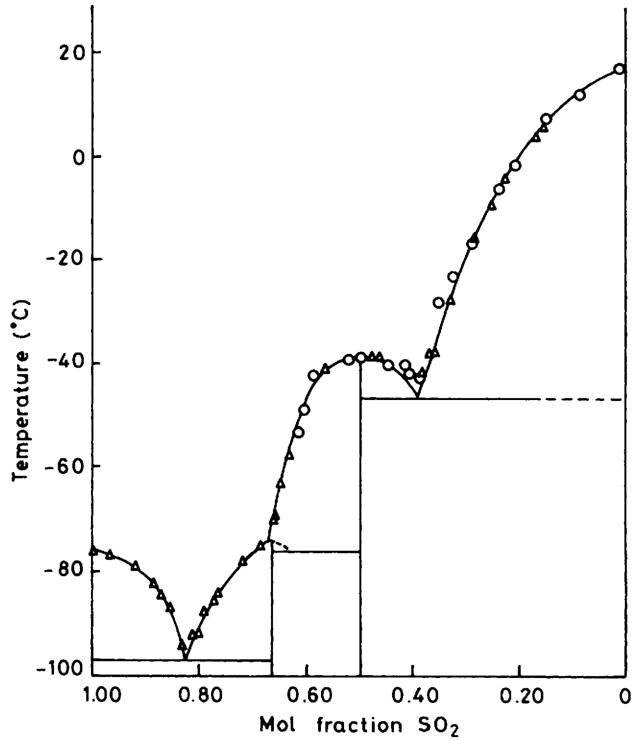

Figure 2. Phase diagram for mixtures of sulphur dioxide with dimethyl sulphoxide

were made identical to achieve comparability, and each sample was run through its thaw–melt cycle three or four times to ensure reproducible results.

The apparatus was calibrated using a set of pure liquids with melting points covering the range of the SO_2–dmso system. Observed melting points (°C literature values[5] in parentheses) were: dmso, 18.5 (18.55); CCl_4, −22.9 (−22.9); dmf, −60.8 (−60.4); $CHCl_3$, −63.7 (−63.4); SO_2, −75.7 (−75.47); diethyl ether, −117.3 (−116.3). Above −75 °C temperatures were measured to ±0.2 °C, and below −75 °C, in the determination of eutectic temperatures, to ±0.5 °C.

Results

The phase diagrams for the SO_2–dmso and SO_2–dmf systems are shown in Figures 2 and 3. For reasons of clarity details of the individual measurements of eutectic melting temperatures have not been included but have been presented as horizontal lines to ±0.5 °C.

Sulphur Dioxide–Dimethyl Sulphoxide Mixtures.—All samples showed some tendency to supercool especially those in the region 0.7—0.8 mol fraction SO_2. These were repeatedly cycled through the glass transition temperature until they were observed as opaque beads growing in the sample finger.

Two eutectic points, at −97 and −46.5 °C, occur at 0.82 and 0.39 mol fraction SO_2 respectively, and the experiments indicate a third eutectic melting temperature at *ca.* −76 °C between 0.50 and 0.67 mol fraction SO_2. The maximum melting point of −39.2 °C at 0.50 mol fraction SO_2, indicating the formation of a 1:1 adduct, confirms our earlier observations.[2] A maximum melting point at 0.67 mol fraction SO_2 corresponding to a 2:1 adduct is obscured on the melting point curve by peritectic behaviour: an incongruent melting point of *ca.* −74 °C at 0.68 mol fraction SO_2, very close to the probable metastable point at *ca.* −73 °C, is suggested.

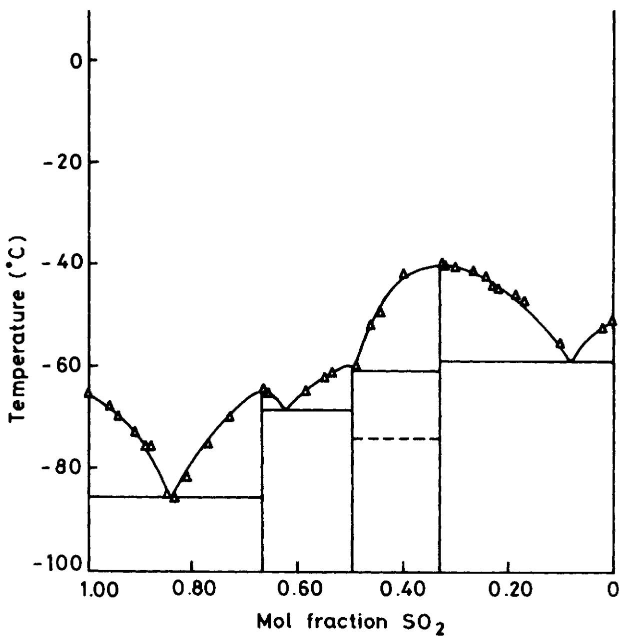

Figure 3. Phase diagram for mixtures of sulphur dioxide with dimethylformamide

The rather flat melting point maximum near 1:1 stoicheiometry, and the incongruent melting point in the 2:1 region, lead us to believe that the compounds between the two solvents are relatively unstable. The peritectic behaviour near 2:1 stoicheiometry shows that the adduct of this composition essentially decomposes as it melts (rather than before or after), and presumably when the solution is at its melting temperature the solid adduct is in equilibrium with both its decomposition products and the 2:1 species.

Much time was spent in attempts to detect a 1:2 adduct. In the $\nu(SO)_{dmso}$ region of the Raman spectra of these solutions a component band, which we have assigned to $SO_2 \cdot 2dmso$, appears at *ca.* 1 013 cm^{-1}. However, cooling and heating curves showed that the eutectic melting point at −46.5 °C persists to 0.15 mol fraction SO_2. The experimental results at lower mol fractions SO_2 were poorly defined, and no evidence for the 1:2 adduct could be obtained from the phase diagram. Thus it must be concluded that, although there is good evidence from the spectra for the existence of a 1:2 species, this adduct is unstable as a solid and does not contribute to the phase diagram.

Sulphur Dioxide–Dimethylformamide Mixtures.—The temperature–composition profile differs from that of the SO_2–dmso system. Three adducts, of stoicheiometries 2:1, 1:1, and 1:2, are identified with melting points of −65, −60, and −40 °C, respectively.

Between 1.00 and 0.66 mol fraction SO_2 there is a eutectic melting temperature at −85.5 °C with a eutectic composition point close to 0.84 mol fraction SO_2. As with the SO_2–dmso system mixtures near 0.80 mol fraction SO_2 show a marked tendency to supercool. From 0.66 to 0.50 mol fraction SO_2 the eutectic melting temperature is at −68.5 °C with an invariant point at 0.62 mol fraction SO_2. Between 0.33 and 0.00 mol fraction SO_2 the eutectic temperature is −59 °C with a eutectic composition point close to 0.08 mol fraction SO_2.

Between 0.50 and 0.33 mol fraction SO_2 a eutectic melting temperature of −61 °C was established. In the region around 0.50 mol fraction SO_2 (and slightly below) it was difficult to assess whether there is an invariant eutectic melting temperature with a composition close to 0.49 mol fraction SO_2, or whether the melting point curve indicates a peritectic point at about this composition. We are inclined to the view that there is normal congruent melting point behaviour with a maximum of -60 °C at 0.50 mol fraction SO_2 indicating a 1:1 adduct.

All measurements of the thaw–melt profiles between 0.50 and 0.33 mol fraction SO_2 showed inflexions at -74 °C, generally followed by fracture of the glassware. The inflexions imply crystal modification involving a volume expansion near this temperature. Experimental data were difficult to obtain because of the damage sustained by the apparatus, and the situation in this part of the phase diagram is somewhat unclear; this is indicated by the dotted line shown in Figure 3. However, a phase change occurs between enantiomorphic crystalline forms which may relate, either to a change in adduct structure, or to a variation in the packing mode of one particular form of SO_2·dmf adduct.

Acknowledgements

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