

Anomalous solubility behaviour of C₆₀

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SOLUBILITIES of solids in liquids exhibit a temperature dependence that is correlated with the energetics of dissolution. For organic solutes in organic solvents the common experience is that solubility increases on warming (that is, dissolution is normally endothermic), forming the basis for purification by crystallization by slow cooling of hot solutions¹. Interactions between inorganic compounds and water are often more energetic, and may lead to complicated temperature-dependent solubilities, often associated with the formation of hydrated solid phases². We have investigated the temperature-dependent solubility of C₆₀ in hexane, toluene and CS₂. We observe a solubility maximum near room temperature (around 280 K) for all three solvents. Although the solubility of C₆₀ in these three solvents differs by several orders of magnitude, the temperature dependence of the relative solubilities is much the same in each case. We conclude that dissolution is endothermic below room temperature and exothermic above. We interpret this change as being due to a phase change in solid C₆₀, presumably the phase change observed previously in the absence of a solvent³⁻⁵, modified by solvent wetting. A solubility maximum (or minimum) for organic compounds in non-electrolytes is highly unusual, and may be unprecedented. The effect may have consequences for solvent-extraction techniques of fullerene purification.

Our aim was to find more efficient procedures for extracting and separating fullerenes, prompted in part by the observation⁶ that chromatographic retention times for C₆₀ and C₇₀, on a Regis (R)-*N*-(3,5-dinitrobenzoyl)-phenylglycine column using 10% dichloromethane in hexane as the mobile phase increased when the temperature was raised from ambient to 90 °C.

The apparatus used to determine the solubilities consists of a pyrex U-tube with a fine sintered-glass frit (4 μm) in one of the arms. The apparatus is immersed in an insulated glass bath. For our initial experiments we placed constant-temperature slushes in the bath; for subsequent experiments we used refriger-

ated fluids circulated through a copper tube in the bath. Excess C₆₀ and solvent are placed in the arm without the frit to make saturated solutions. After stirring in the dark for a minimum of 12 hours, the saturated solution is forced through the frit by pressurizing the arm with argon. The solution is forced in and out of the filter arm four or five times to condition the filter in case it absorbs some C₆₀. An aliquot of 1–2 ml is removed with a pipette from the filter arm for analysis by high-performance liquid chromatography (HPLC) either with further dilution (as in the case of toluene and CS₂) or without (hexane).

To keep the solution at constant temperature, the bath is stirred, and the U-tube is positioned such that about 5 cm³ of bath liquid is above the frit. Calibrated thermometers are placed in the bath and the arm containing C₆₀, and always read (to within 0.2 °C) the same temperature. The highest temperatures achieved for each solvent were the atmospheric-pressure boiling points: 46 °C for CS₂, 68 °C for hexanes, 110 °C for toluene. A reflux condenser was fitted to the U-tube for the boiling solutions.

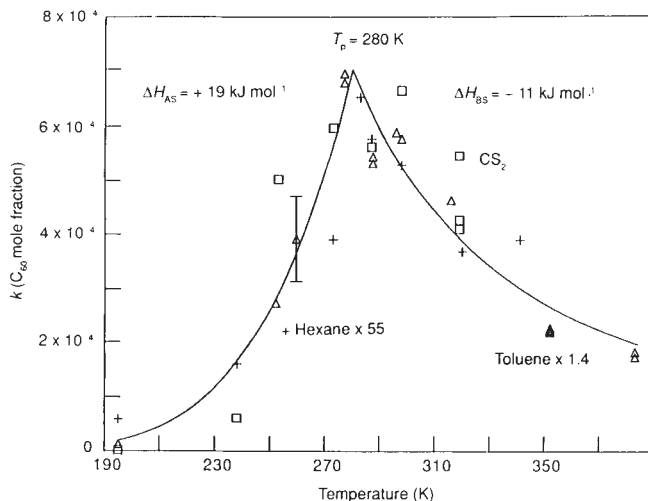
The solubility of C₆₀ at room temperature in hexane, toluene and CS₂ was determined to be 0.04, 2.8 and 7.9 mg ml⁻¹ respectively. Expressed in mole fractions, the room temperature solubility is 0.073 × 10⁻⁴ in hexane, 4.1 × 10⁻⁴ in toluene and 6.6 × 10⁻⁴ in CS₂. The temperature dependence of the solubilities (mole fractions) is shown in Fig. 1. From replicate determinations, we estimate the reported solubilities (*k*) to be within 20% of the true values. In all three solvents, the solubility of C₆₀ is minimal at -78 °C. Warming increases the solubility of all three solvents, albeit to different extents. The trend continues up to ~10 °C, above which it is roughly flat till 25 °C and then decreases by a factor of about 2–3 from 25 °C to the normal boiling point of each solvent.

Room-temperature solubilities were also independently determined by filtration with a 0.45-μm polytetrafluoroethylene (PTFE) filter (Gelman Acrodisc)⁷; the measured solubilities were identical to those determined with the U-tube apparatus used here. This agreement confirms that the glass filter (~4-μm) was fine enough to preclude small particles from contributing to the measured solubilities.

Several additional tests were done to verify the unusual solubility behaviour of C₆₀ in each solvent and to rule out experimental artefacts. A room-temperature saturated toluene solution was filtered with a 0.45-μm PTFE filter, and subsequently placed

FIG. 1 Temperature dependent solubility of C₆₀ in hexane (+, ×55), toluene (Δ, ×1.4), and CS₂ (□). The phase-transition model is represented by the solid line, with a transition temperature of 280 K and enthalpy change of 30 kJ mol⁻¹.

METHODS. Pure C₆₀ (99.5%) was obtained by extraction from Krätschmer-Huffman soot followed by column chromatography on neutral alumina with hexane eluent, and drying for 24 hours in a vacuum oven at 100 °C. A separate U-tube was used for each of the three solvents: hexanes (Mallinckrodt HPLC grade, 98% *n*-hexane, boiling range 68.3–68.9 °C), toluene (Mallinckrodt HPLC grade, 99.9%, boiling range 110.5–110.6 °C), and CS₂ (Baker analysed reagent grade, 99% by GC, boiling point 46.3 °C). HPLC analyses were conducted using a Waters System 6000 Chromatography equipped with a DNAP column (9 mm × 250 mm; E. S. Industries), an ultraviolet detector set at 340 nm, and an integrator. A solution of toluene (20% by volume) in hexane was used as the eluant. Under these conditions, better than baseline separation between C₆₀, C₇₀, and higher fullerenes is achieved to permit quantitative analysis. Detector response for C₆₀ was calibrated using several standard solutions in the range of 0.01 to 0.20 mg ml⁻¹. A representative error bar is shown for the solubility of C₆₀ in toluene at 260 K. Saturated solutions of C₆₀ in toluene and in CS₂, which are generally much more concentrated than the highest concentration used for calibration were diluted (typically, 20- to 100-fold) before analysis. In the case of hexane, an aliquot of the solution at temperature was removed and later, when the solution was at room temperature, 20 μl were injected into the chromatograph. Corrections for density changes are therefore warranted only in the case of hexane. The concentrations reported here have been corrected using 0.095% per °C as the volumetric coefficient of expansion for hexane⁹.



in a bath at 80 °C. A solid precipitated out, and the intensity of the saturated solution in the vial had visibly diminished: we could see through the vial quite easily. The saturated solution with solid precipitate was then cooled to room temperature, and placed in an ultrasound bath for ~20 s. All of the solid precipitate returned to solution. The cycle was repeated several times, with the same results.

A second test to ensure equilibration was to determine the solubility at room temperature over different time intervals of stirring: 12 hours, 2 days, 7 days. The solubilities in hexane, for each time interval, were in agreement within 5% as determined with calibrated HPLC. Because the solubility is close to a maximum at room temperature, we believe that equilibration should have occurred on the 12-hour timescale used at all other temperatures; we have approached both higher and lower temperatures starting with solutions equilibrated at room temperature.

The unusual temperature dependence is likely to be caused by the changes in the solid phase. We arrived at this hypothesis as a result of recognizing the nearly identical temperature dependence of k in three different solvents, although the absolute value of k in these solvents varies by about two orders of magnitude. Crystalline C_{60} has a phase transition at about 260 K, and the temperature width of the transition is influenced by the degree of crystallinity present. Differential scanning calorimetry has been used to obtain ΔH for this first-order phase transition. Two experimental values for ΔH are 6.6 and 7.0 kJ mol⁻¹ (refs 4, 5). First-order phase transitions in the solid phase cause a change in slope of $k(T)$ at T_p , the phase transition temperature. Thus, one might think that the observed $k(T)$ can be rationalized if $H_A < H_s < H_B$, where H_A , H_B and H_s are respectively the enthalpies of the low-temperature phase (A), the high-temperature phase (B), and the solution (s). We find, however, that the first-order phase transition of pure C_{60} cannot by itself explain the observed solubility behaviour.

Under the assumption that there is only a narrow region of coexistence, we can model the observed solubilities by equations of the form

$$k(T) = \exp(\Delta S_{AS}/R - \Delta H_{AS}/RT) \quad \text{for } T \leq T_p \\ = \exp(\Delta S_{BS}/R - \Delta H_{BS}/RT) \quad \text{for } T \geq T_p$$

These equations were used to fit the data shown in Fig. 1, the result being shown by the solid line. The parameters derived are sensitive to the fact that the model requires a sharp maximum in contrast to the observed broad maximum. Reasonable fits can be obtained for $T_p = 280 \pm 10$ K, $\Delta H_{AS} = 19 \pm 3$ kJ mol⁻¹, $\Delta H_{BS} = -11 \pm 2$ kJ mol⁻¹, and $\Delta H_{AB} = 30 \pm 3$ kJ mol⁻¹. The transition temperature is higher, and the transition enthalpy about five times larger, than observed previously in pure C_{60} (refs 3–5). The ΔH for the first-order phase transition of pure C_{60} (~7 kJ mol⁻¹) therefore cannot explain the data. But it is reasonable to conclude from our simple model that a phase change is occurring. A possible interpretation for the substantially larger enthalpy change for the phase transition is that the properties of the solid phase have been modified by solvent wetting. Although it is known empirically from previous studies³ that solvents adhere strongly to C_{60} , leading to difficulty in drying, it is surprising both that the effect would be as large as observed and that hexane, toluene and CS₂ would all show the same influence.

The unusual temperature dependence of the solubility of C_{60} is probably playing a role in a recently reported C_{60} purification procedure⁸. Toluene soxhlet extraction of a primary fullerene soot removes a roughly 80:20 mix of C_{60} : C_{70} . Control of the ratio of primary fullerene soot mass to volume of toluene, and of the extraction time, allows collection of crystals which are 98% pure C_{60} . The collection pot is held at the boiling point of toluene (110.6 °C) during the 10-hour soxhlet extraction⁸. A likely explanation is that the temperature dependence of the

solubility of C_{60} and C_{70} differ, with C_{60} having lower solubility in the boiling toluene.

This simple model explains only the salient features and does not fit the data perfectly. To understand the temperature dependence fully, we need, for example, to characterize the solid phases A and B, and to measure the heat of solution as a function of temperature. □

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Vast Neogene laminated diatom mat deposits from the eastern equatorial Pacific Ocean

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THE eastern equatorial Pacific upwelling region is responsible for up to 50% of global 'new' production¹ and is regarded as a barometer of ocean change. Here we report evidence, from several sediment cores in the region, for repeated episodes of increased equatorial primary production between 15 and 4.4 million years ago, on a scale that is undocumented in the modern ocean. Mats of the diatom *Thalassiothrix* were rapidly deposited as successive laminations at rates exceeding 10 cm per thousand years; mat deposits can be correlated for distances of more than 2,000 km. It is surprising that the laminations were preserved at all: conventional models suggest that bioturbation caused by the benthic sediment community will disrupt such laminations unless there is insufficient oxygen in the water to support the biological activity. In this case, however, the strength of the mats and the scale of their deposition may have overwhelmed the benthos, so that the laminations were preserved by physical means. These remarkable deposits provide a unique window into the Neogene tropical ocean-climate system, and should enable quantification of ancient deep-sea fluxes and the study of short-term (sub-Milankovitch) variability in the ocean.

As a major zone of primary production, the eastern equatorial Pacific continues to be the focus of studies of modern and geological oceanic and climatic processes^{1–5}. Leg 138 of the Ocean Drilling Program (ODP) has provided a high resolution record of the last 15 million years depositional history of the low-latitude Pacific between 90° and 110° W. Intervals of highest biosiliceous phytoplankton abundance are recorded by near monospecific assemblages of the pennate diatom *Thalassiothrix* present in laminated diatom ooze (LDO) at ODP Sites 844, 847, 849, 850, and 851 (Figs 1 and 2). Re-examination of core material from Deep Sea Drilling Project Sites 572–574 confirms the occurrence of similar laminated diatom ooze at least as far as 133° W. Laminated sediment occurs intermittently in the above sites from 15 to 4.4 million years ago (Myr BP) but is concentrated at about 15, 13–12, 10.5–9.5, 6.3–6.1, and 4.4 Myr with a