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Note

COMMENT ON "ENTROPIES OF DIPHENYLGLYOXAL SOLUTIONS IN NON-POLAR SOLVENTS"

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Solubilities are reported for diphenylglyoxal in benzene, toluene, carbon tetrachloride, n-hexane and n-heptane at 25.0 ° C. Results of these measurements are used to resolve discrepancies in the published literature.

Recently, Jimenez and Ordoñez [1] reported experimental solubilities for diphenylglyoxal (also called benzil) in eight nonpolar solvents at temperatures between 15 and 45 ° C. The authors failed to mention that their measured values differed appreciably from literature values as is shown in Table 1. To resolve these discrepancies we have remeasured benzil solubilities in high purity HPLC grade solvents.

Benzil (Aldrich) was recrystallized several times from methanol giving a melting point of 95.0 ± 0.5 ° C. Carbon tetrachloride (Aldrich, HPLC), benzene (Aldrich, HPLC), n-hexane (Aldrich, 99%), n-heptane (Aldrich, HPLC) and toluene (Aldrich, HPLC) were used as received. Excess benzil and solvent were placed in amber glass bottles and allowed to equilibrate in a constant temperature shaker bath at 25.0 ± 0.1 ° C for several days. Attainment of equilibrium was verified by repeat measurements after several additional days and in all cases by approaching equilibrium from supersaturation by pre-equilibrating the solution at a higher temperature. Aliquots of saturated benzil solutions were transferred through a coarse filter into a tared volumetric flask to determine the amount of sample and diluted quantitatively with methanol. Concentrations were determined spectrophotometrically at 390 nm on a Bausch and Lomb Spectronic 2000. Experimental solubilities of benzil in the five solvents studied are listed in the final column of Table 1, and are in excellent agreement with the earlier values of Acree and coworkers [2,3]. Numerical values represent the average of between four and six independent determinations, the reproducibility being about ± 1%. An upper solubility limit was obtained through preparation of solutions in sealed ampoules having a known 10% excess of benzil based on

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TABLE 1

Mole fraction solubilities of benzil in various organic solvents at 25 ° C

Solvent	Ref. 1	Ref. 2 and 3	This work
Benzene [a]	0.3421	0.1804	0.1791
Carbon tetrachloride	0.1078	0.0804, 0.0808	0.0790
Toluene	0.1762	0.1504	0.1486
n-Hexane	0.0070	0.00570	0.00573
n-Heptane	0.0085	0.00654, 0.00659	0.00657

[a] Carroll et al. [5] reported a benzil mole fraction solubility of 0.179 in benzene at 25.0 ° C.

the measured saturation solubilities. Benzil completely dissolved at 35 ° C, whereas crystals formed upon cooling to 25 ° C.

Solvent impurities perhaps led to some of the differences in measured solubilities. We strongly suspect, however, that Jimenez and Ordoñez tried to measure spectroscopically benzil concentrations in the UV region near the wavelength of maximum absorbance. The experimental method of Jimenez and Ordoñez, as referenced to an earlier publication in Spanish [4], states

> La muestras se diluyen y se ensayan mediante espectrofotometría ultravioleta. En experimentos previos se estableció la longitud de onda de máxima absorción y el cumplimiento de la ley de Beer.

Unfortunately, benzene, toluene and carbon tetrachloride absorb in the UV spectral region, as would possible trace aromatic hydrocarbon impurities in the alkane solvents. For this reason, we elected to work in the visible spectral region where solvent interferences are eliminated.

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