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Light Scattering Measurements near the Lower Critical Solution Temperature of the 2,6-Dimethylpyridine–Water System[1]

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The light scattering of the 2,6-dimethylpyridine–water system near the critical solution temperature of 33.93° and at the critical composition, 29.94 w/o of 2,6-dimethylpyridine, has been measured and can be represented by the Ornstein–Zernike–Debye theory, yielding an average Debye l-parameter of 8.7 ± 1.0 Å. Deviations from the predicted behavior, however, suggest that this theory is a good approximation to the actual phenomena only over a sufficiently small range of sin $(\theta/2)/\lambda$.

Recent theoretical treatments of critical phenomena[2-5] have prompted us to undertake precise light- and small-angle X-ray scattering measurements[6,7] in the critical region of a number of binary systems.

Since few reliable data of this nature are available for systems with a *lower* critical solution temperature (LCST), it was of interest to investigate an example of such a system, the 2,6-dimethylpyridine–water binary. The measured critical temperature and composition, after careful purification of the components by distillation, were 33.93 ± 0.005° at 29.94 w/o of 2,6-dimethylpyridine (DMP).
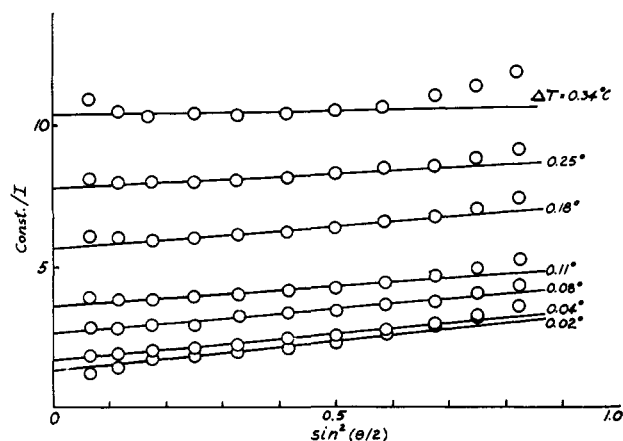

Fig. 1.—Ornstein–Zernike plot of $I^{-1}(\theta)$ *vs.* sin² $(\theta/2)$ for several temperature distances from the critical solution temperature.

Light scattering experiments were made with a Brice–Phoenix photometer modified by the insertion of two-slit collimators between light source and sample cell, and between the latter and the detector. Provision was made for monitoring and controlling the constancy of the source. The sample cell permitted precise temperature control of the sample; water from a constant-temperature bath was circulated rapidly through an immersion coil situated in the fluid of the cell jacket surrounding the sample cell itself. The jacket fluid was chosen to have nearly the same refractive index as the glass of which the cell was constructed. Temperature control to ±0.005° or better was maintained for the duration of each run. Temperature measurements were made with a Beckmann thermometer calibrated against a certified platinum resistance thermometer in the appropriate range.

The sample cell was tested with fluorescein. All DMP–water samples were thermally equilibrated before each run; freshly prepared mixtures were used for each temperature series.

Experiments were performed with sample cells of 8- and 4-mm. diameter, at wave lengths of 4360 Å. and 5460 Å. (*in vacuo*), and at two compositions in addition to the critical one. It was observed that the results for the shorter wave length were considerably more erratic, possibly due to multiple scattering effects. Consequently, the data obtained at 5460 Å. are reported here. The intensity of opalescence near the separation temperature was observed to diminish rapidly at compositions away from the critical. Results for the two cell sizes were similar in all respects; all the results quoted here are for the 4-mm. cell, which should minimize secondary scattering effects.

The angular distribution of scattered relative intensity (using vertically polarized incident light) corrected for scattering volume is shown in Fig. 1 in the form of an Ornstein–Zernike (OZ) plot of $I^{-1}(\theta)$ *vs.* sin² $(\theta/2)$.[8] A plot of OZ intercepts—*i.e.*, of $I^{-1}(0)$ obtained by extrapolation of the linear portions of Fig. 1 to zero angle—*vs.* ΔT, where $\Delta T = |T - T_c|$, is shown in Fig. 2. It is apparent from Fig. 1 that the dissymmetry increases in the expected fashion as the LCST is approached from below. Certain systematic deviations from OZ behavior are observed, notably an upward curvature at high scattering angles for which multiple scattering may be responsible. A smaller but also systematic upward trend at the smallest angles gradually lessens as T_c is approached and is replaced by a slight downward displacement at the closest temperature to T_c, $\Delta T = 0.02°$. Very similar behavior has been reported for the polystyrene–cyclohexane system by McIntyre, Wims, and Green,[9] and has been observed by us for the nitrobenzene–*n*-heptane system,[6,7] and, using X-ray scattering, for the perfluoroheptane–isooctane system by Frisch and Brady.[10] In view of the diversity of systems and

(1) This paper represents part of the dissertation submitted by Mr. R. Pancirov to the Department of Chemistry at Syracuse University in partial fulfillment of the requirements for the Ph.D. degree.

(2) (a) P. Debye, *J. Chem. Phys.*, **31**, 680 (1959); (b) P. Debye, B. Chu, and H. Kauffman, *ibid.*, **36**, 3378 (1962).

(3) B. Widom, *ibid.*, **37**, 2703 (1962).

(4) M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.*, **4**, 216, 229 (1962); **5**, 60 (1963).

(5) P. C. Hemmer, *ibid.*, **5**, 75 (1963).

(6) H. Brumberger and W. C. Farrar, "Proceedings of the Interdisciplinary Conference on Electromagnetic Scattering," Pergamon Press, London, 1963, pp. 403–416.

(7) H. Brumberger and R. Pancirov, to be published.

(8) Relative intensities have not been corrected for reflection at the air–glass interface, since the corrections are somewhat uncertain in this case. They are, however, small and do not materially alter the features of the OZ plot. The cell jacket was coated with flat black paint.

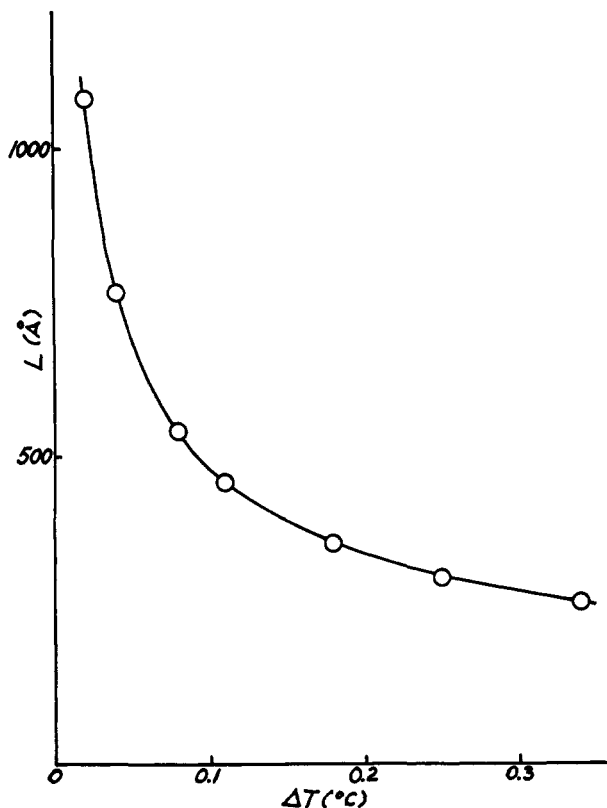(9) D. McIntyre, A. Wims, and M. S. Green, *J. Chem. Phys.*, **37**, 3019 (1962).

(10) H. L. Frisch and G. W. Brady, *ibid.*, **37**, 1514 (1962).
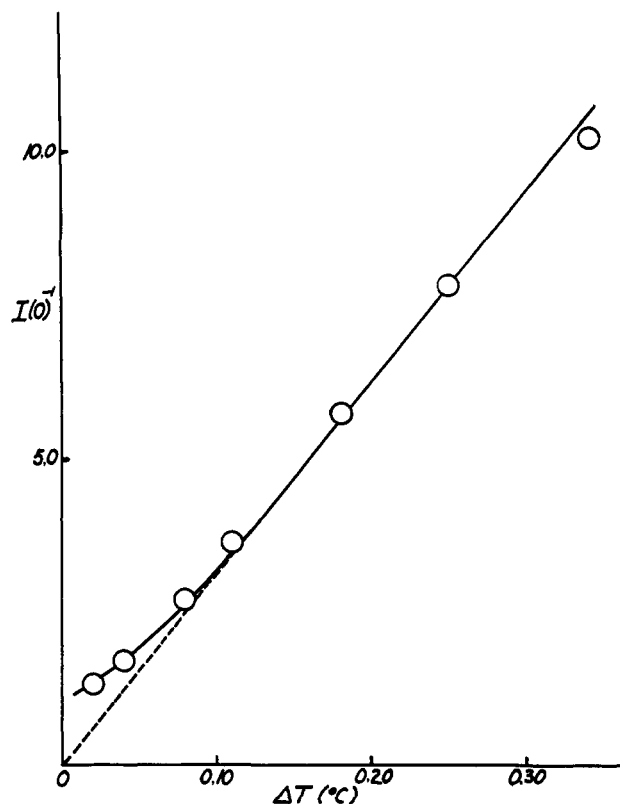
Fig. 2.—Plot of the OZ intercepts $I^{-1}(0)$ vs. ΔT.

Fig. 3.—Plot of the correlation length L vs. ΔT.

techniques used in these experiments, we feel that the deviations are real and throw some doubt on the universal validity of the OZ and Debye theories. This conclusion stands in contrast to that of Münster and Schneeweiss,[11] who feel that a general conclusion as to the failure of the OZ theory cannot be drawn from the available evidence.

In spite of the observed deviations, the Debye theory furnishes a very good approximation, and allows the calculation of meaningful parameters, namely the "radius of action of intermolecular forces" l and the correlation length L. The former may be calculated from eq. 1. of ref. 2b, and the latter from

$$L^2 = \frac{l^2 T_c}{\Delta T} \tag{1}$$

(11) A. Münster and Ch. Schneeweiss, Z. physik. Chem., 37, 369 (1963).

An average l value of 8.7 ± 1.0 Å. is obtained from the seven temperature runs of Fig. 1. L is shown as a function of ΔT in Fig. 3.

The suggestion that the deviations from the Debye and OZ theories occur for systems with abnormally flat consolute curves does not seem to hold.[11] A more likely situation is that the OZ curves are not in fact linear except over a relatively narrow range of sin $(\theta/2)/\lambda$; this is supported by our X-ray and light scattering observation for the nitrobenzene–n-heptane system,[6,7] and also by observations reported by Debye.[12]

(12) P. Debye, ref. 6, pp. 393–401

COMMUNICATIONS TO THE EDITOR

Thermodynamic Properties of Nonpolar Mixtures of Small Molecules

Sir:

The treatment of n-paraffin hydrocarbons and their mixtures presented elsewhere in this issue[1,2] (these papers will be referred to as I and II, respectively) can be recast in a form[3] which appears to be generally

(1) P. J. Flory, R. A. Orwoll, and A. Vrij, J. Am. Chem. Soc., 86, 3507 (1964).
(2) P. J. Flory, R. A. Orwoll, and A. Vrij, ibid., 86, 3515 (1964).
(3) P. J. Flory, to be published.

applicable to liquid solutions, irrespective of the size and shape of the molecular species, provided that they are not hydrogen bonded or highly polar. Here we present a preliminary comparison of theory with experiment for several representative binary mixtures of small, approximately spherical molecules.

The enthalpy of mixing can be expressed as follows

$$H^E = N_1 p_1^* v_1^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + N_2 p_2^* v_2^* (\tilde{v}_2^{-1} - \tilde{v}^{-1}) +$$

$$(N_1 v_1^* \varphi_2 / \tilde{v}) X_{12} \tag{1}$$