

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

## Critical Opalescence of a Fluorocarbon-Hydrocarbon Liquid Mixture. Normal Perfluoroheptane-Normal Heptane

BY B. CHU

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Experiments are reported on the angular dissymmetry of visible light as well as on the temperature dependence of the scattered intensity for a fluorocarbon-hydrocarbon system,  $n$ -C<sub>7</sub>F<sub>16</sub> and  $n$ -C<sub>7</sub>H<sub>16</sub>, at the critical solution concentration over a range of temperatures near the critical solution temperature in the one-phase region. According to the Debye theory [*J. Chem. Phys.*, **31**, 690 (1959)], the system behaves normally, and it has an average molecular interaction range ( $l$ ) of 11.6 Å. Alternate interpretations for the anomalous behavior of other liquid mixtures are presented. The molecular interaction range of Debye is discussed in terms of the solubility parameter theory of Hildebrand and Scatchard. The results substantiate Scott's proposal on the breakdown of the geometric mean law for fluorocarbon-aliphatic hydrocarbon systems.

The outstanding and inspiring works of Debye<sup>1</sup> on critical opalescence have kindled the interests of many investigators to re-examine this fundamental phenomenon, both theoretically and experimentally. Recent literature on critical phenomena has become extensive. However, several papers have raised doubt in the Debye theory. This paper provides additional evidence that the Debye theory is in good agreement with experimental facts and tries to point out possible experimental errors which may lead some theorists astray.

Theoretical developments given by Fixman,<sup>2</sup> Münster,<sup>3</sup> and Hart<sup>4</sup> have equivalent or nearly equivalent results to those of Debye, Ornstein, and Zernike.<sup>5</sup> In the meantime, Debye<sup>6</sup> has generalized the theory applicable to density fluctuations without using the Taylor development. The same approach was further substantiated by a rigorous treatment of the one-dimensional van der Waals model<sup>7</sup> which indicated that the pair correlation function decays exponentially with distance away from the critical point, in agreement with the Ornstein-Zernike-Debye (OZD) theory, while the behavior is complicated at the critical point. Green<sup>8</sup> criticized the Ornstein-Zernike-Debye theory and derived a different scattering formula which leads to strongly divergent predictions concerning the low angle light scattering behavior. Developments based on some extensions of the Ising Model yield various forms of correlation functions whereby the corresponding intensity functions are quite different from one another.<sup>9</sup> In addition, the extrapolated zero-angle scattered intensity varies with  $(T - T_c)^{-1}$  for the van der Waals model; but with  $(T - T_c)^{-1/4}$  according to the Ising Model.<sup>10</sup> One important fact remains: all those theories depend on experimental verifications.

Although a number of experimental light- and X-ray scattering studies of critical opalescence have been published, theoretical reappraisals as a result of observed anomalies according to the Debye theory often become doubtful in view of the experimental uncertainties. Recent results on a binary critical mixture of  $n$ -decane and  $\beta,\beta'$ -dichlorodiethyl ether<sup>11</sup> and the results of this investigation of  $n$ -heptane and  $n$ -perfluoroheptane further suggest the questionable validity of several of those observed "anomalies."

Careful measurements on fluorocarbon-hydrocarbon liquid mixtures were first discussed by Hildebrand and Scott.<sup>12</sup> The solubilities, critical solution temperatures, and critical solution compositions of many binary liquid mixtures with a fluorocarbon as one of its two components were found to be in excellent agreement with the solubility parameter theory of Hildebrand<sup>13</sup> and Scatchard.<sup>14</sup> On the other hand, studies of solutions of fluorocarbons with aliphatic hydrocarbons, such as  $n$ -C<sub>7</sub>H<sub>16</sub>- $n$ -C<sub>7</sub>F<sub>16</sub>,<sup>15</sup>  $n$ -C<sub>6</sub>H<sub>12</sub>- $n$ -C<sub>6</sub>F<sub>12</sub>,<sup>16</sup> and  $n$ -C<sub>4</sub>H<sub>10</sub>- $n$ -C<sub>4</sub>F<sub>10</sub>,<sup>17</sup> demonstrated deviations from the solubility parameter theory. However, the "anomalies" were not confined to only fluorocarbon-aliphatic hydrocarbon systems.<sup>18</sup> In 1958, Scott<sup>19</sup> reviewed and criticized various explanations for the anomalous behavior and judged that the anomaly must be attributed to a failure of the geometric mean law. Opalescence studies, being related to molecular interactions, could give additional information on fluorocarbon solutions. So, the choice of a fluorocarbon-aliphatic hydrocarbon system was indeed twofold.

### Experimental

**Materials.**—Both  $n$ -heptane (research grade) and  $n$ -perfluoroheptane were dried over sodium and purified by preparative gas chromatography on an Aerograph Model A-700 Autoprep vapor fractometer (Wilkins Instrument and Research, Inc.). For  $n$ -perfluoroheptane, a 20-ft. long  $\times$  3/8-in. o.d. column packed with 20% Carbowax 20 M (or with 30% SE-30 for  $n$ -heptane) on 40/60 chromosorb P, operated at 40° (or at 90° for  $n$ -heptane) and 40

(1) P. Debye, "Scattering of Radiation by Non-Crystalline Media" in "Conference on Non-Crystalline Solids," V. D. Frechette, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 1-25; *J. Chem. Phys.*, **31**, 680 (1959).

(2) M. Fixman, *J. Chem. Phys.*, **33**, 1357 (1960).

(3) A. Münster, *J. chim. phys.*, **57**, 492 (1960).

(4) E. W. Hart, *J. Chem. Phys.*, **34**, 1471 (1961).

(5) F. Zernike, Thesis, *Proc. Acad. Sci. Amsterdam*, **17**, 793 (1916); *Arch. Néerl. sci.*, Ser. III A, **4**, 74 (1917); L. S. Ornstein and F. Zernike, *Physik. Z.*, **19**, 134 (1918); **27**, 761 (1926).

(6) P. Debye, "Proceedings of the Interdisciplinary Conference on Electromagnetic Scattering," Pergamon Press, London, 1963, p. 393. It is also clear how the formula has to be generalized for concentration fluctuations.

(7) M. Kac, *Phys. Fluids*, **2**, 8 (1959); M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.*, **4**, 216 (1963).

(8) M. S. Green, *J. Chem. Phys.*, **33**, 1403 (1960).

(9) F. H. Stillinger, Jr., and H. L. Frisch, *Physica*, **27**, 751 (1961); H. L. Frisch and G. W. Brady, *J. Chem. Phys.*, **37**, 1514 (1962); M. E. Fisher, *Physica*, **28**, 172 (1962); *J. Math. Phys.*, **4**, 278 (1963).

(10) B. Widom, *J. Chem. Phys.*, **37**, 2703 (1962).

(11) B. Chu, *ibid.*, in press.

(12) J. H. Hildebrand and R. L. Scott, *Ann. Rev. Phys. Chem.*, **1**, 75 (1950).

(13) J. H. Hildebrand and R. L. Scott: (a) "The Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950; (b) "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.

(14) G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).

(15) J. H. Hildebrand, B. B. Fisher, and H. A. Benesi, *J. Am. Chem. Soc.*, **72**, 4348 (1950).

(16) J. H. Simmons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

(17) J. H. Simmons and J. W. Mausteller, *ibid.*, **20**, 1516 (1952).

(18) N. Thorp and R. L. Scott, *J. Phys. Chem.*, **60**, 670 (1956).

(19) R. L. Scott, *ibid.*, **62**, 136 (1958); also J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, Chapters 7 and 10.

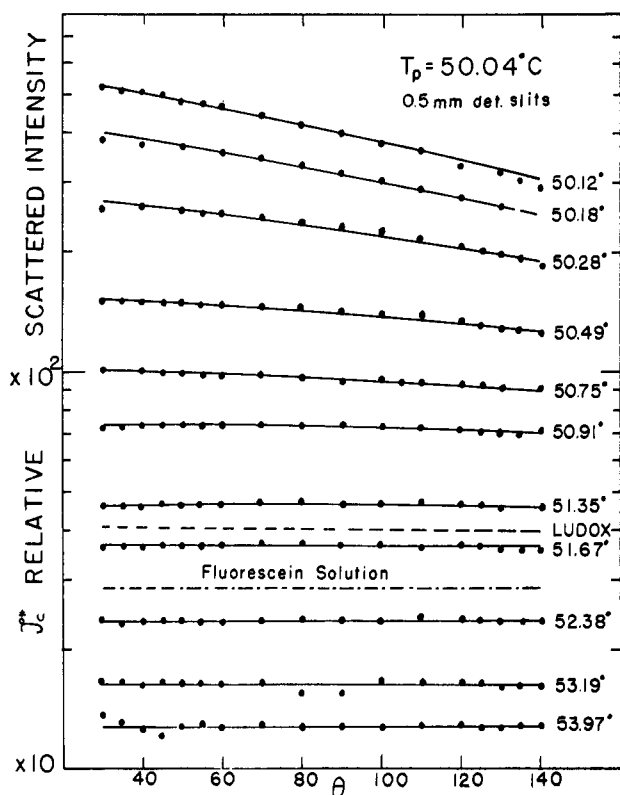


Fig. 1.—A typical set of intensity curves measured as the temperature is lowered. Critical solution concentration 31.71 wt. %  $n\text{-C}_7\text{H}_{16}$  in  $n\text{-C}_7\text{F}_{16}$ . Wave length *in vacuo* ( $\lambda_0$ ) 436  $\mu\text{m}$ .

p.s.i.g. was used. Flow rates of helium carrier gas were around 200 ml./min. The injection volume was limited to 0.1 ml. each time for  $n$ -perfluoroheptane and to about 1 ml. each time for  $n$ -heptane. Organic impurities of the purified  $n$ -perfluoroheptane and  $n$ -heptane were estimated at less than 0.05% and 0.01%, respectively.

**Procedure.**—Detailed descriptions of the light scattering photometer,<sup>11,20</sup> preparation of solutions, phase separation temperature determinations, and attenuation corrections due to critical opalescence are discussed elsewhere.<sup>11</sup> The scattering envelope of a dilute solution of fluorescein, using a sharp cut-off filter (Corning Glass Works, CS-375), 364- $\mu\text{m}$  incident wave length, and no Nicol prism, was found to be spherically symmetrical after volume corrections ( $\sin \theta$ ). The entry of extraneous light into the receiver was checked by examining the scattering envelope of a dilute solution of carefully filtered colloidal silica (LUDOX) using 436- $\mu\text{m}$  incident wave length and vertically polarized light (see Fig. 1).

The temperature of the insulated tank bath was controlled to  $\pm 0.002^\circ$ . Two Leeds and Northrup 8163 platinum resistance thermometers (both NBS calibrated), a Leeds and Northrup 8069 Type G-2 Mueller bridge, and a Leeds and Northrup 2285 B Type HS galvanometer were used for temperature measurements. The critical solution concentration ( $\phi_{2c}$ ) was taken from the literature. In our case, we have arbitrarily taken  $n$ -perfluoroheptane as the second component.  $\phi_{2c}$  ( $n\text{-C}_7\text{F}_{16}$ - $n\text{-C}_7\text{H}_{16}$ ) = 46 vol. %  $n$ -perfluoroheptane.<sup>15,21</sup> The phase separation temperatures were determined by visual observation: (a) in a separate constant temperature bath, and (b) directly in the light scattering photometer by means of a telescope. It was found necessary to insulate the metallic light scattering sample cell holder and the detector slits (both immersed in the constant temperature bath inside a light-tight compartment) before the two phase separation temperatures ((a) and (b)) could coincide. Evidently heat loss of the immersed cell holder and detector slits due to partial metallic contact with ambient temperature produced a temperature gradient for the sample cell. Without further insulation, regions of various shades of opalescence for the system  $n\text{-C}_7\text{F}_{16}$ - $n\text{-C}_7\text{H}_{16}$  could be observed before the phase separation temperature was reached.

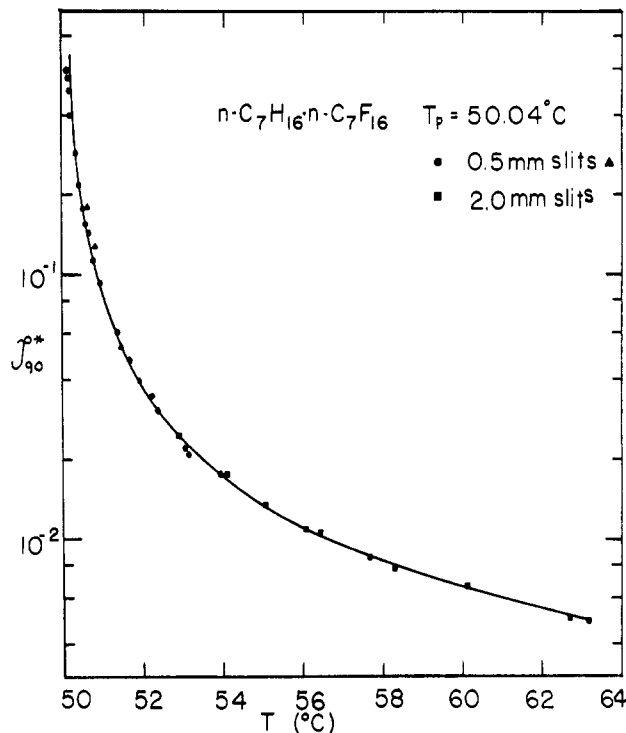


Fig. 2.—Plot of relative scattered intensity at  $90^\circ$  ( $I_{90}^*$ ) vs. temperature. The solid curve is of the form  $I_{90}^* = A(T - T_c)^{-1}$  where  $A = 6.73 \times 10^{-2}$ .

$\text{C}_7\text{H}_{16}$  could be observed before the phase separation temperature was reached. Furthermore, if the light scattering cell was allowed to maintain direct contact with a piece of metallic wire which emerged partially from the thermostated bath oil, then the temperature gradient of the sample cell, produced by its contact with the metallic wire, caused the mixture to produce visible (magnified by a telescope) macroscopic "colloidal" fluctuations without phase separation into two distinct layers for periods of many hours at even a few tenths of a degree above the phase separation temperature. A similar effect consisting of regions in the form of layers of different shades of opalescence without phase separation could be observed if the homogeneous mixture was cooled toward the phase separation temperature too rapidly. Such phenomena are evidently artifacts depending on whether the critical liquid mixture is truly under isothermal conditions. The scattering curves reported here were reproducible. The rate of cooling was always very slow.<sup>11</sup> Visual observation of the sample by means of a telescope showed that the scattering measurements were indeed performed in the homogeneous one-phase region. Both the light scattering cell and the detector slit systems were virtually suspended in the oil bath with glass supports to ensure uniform temperature for the sample under observation. Two sets of detector nose piece, one set consisting of two slits with dimensions  $10 \times 2$  mm. and 20 mm. apart, and the other  $10 \times 0.5$  mm., and 20 mm. apart, were used.

Refractive indices of the critical liquid mixture ( $n\text{-C}_7\text{F}_{16}$ - $n\text{-C}_7\text{H}_{16}$ ) near the critical solution temperature at different wave lengths ( $\lambda_0$  364, 436, and 575  $\mu\text{m}$ ) were calculated from an empirical mixture rule<sup>22</sup> with the aid of known dispersion curves<sup>23</sup> and densities.<sup>23,24</sup> The calculated corresponding wave lengths in the medium are  $\lambda$  273, 329, and 437  $\mu\text{m}$ , respectively.

## Results

Figure 1 shows a typical set of intensity curves measured as the temperature is lowered. The scale for the scattered intensity has been made logarithmic in order

(22) B. Chu, *J. Phys. Chem.*, **67**, 1969 (1963).

(23) G. D. Oliver, S. Blumkin, and C. W. Cunningham, *J. Am. Chem. Soc.*, **73**, 5722 (1951) ( $n\text{-C}_7\text{F}_{16}$ ); J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1959 ( $n\text{-C}_7\text{H}_{16}$ ).

(24) American Petroleum Institute Research Project 44; "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Government Printing Office, Washington, D. C., 1950.

(20) B. Chu, *Rev. Sci. Instr.*, in press.

(21) B. G. Kyle and T. M. Reed, III, *J. Am. Chem. Soc.*, **80**, 6170 (1958).

TABLE I  
 SUMMARY OF RECENTLY PUBLISHED EXPERIMENTAL RESULTS<sup>a</sup>

Systems	$\Delta n$	$\frac{1}{\xi^*} \text{ vs. } \sin^2 \frac{\theta}{2}$	$\left(\frac{1}{\xi^*}\right)_0^b \text{ vs. } (T - T_c)$	$l, \text{ \AA.}$	Scattering technique and ref.
Perfluoromethylcyclohexane-carbon tetrachloride	0.176	Linear	Linear <sup>c</sup>	14.7	Light 28
Ethylene; ethane <sup>d</sup>	...	...	...	...	Light <sup>e</sup>
Aniline-cyclohexane <sup>f</sup> (1)	.157	Maximum at about 90° when $T - T_c < 0.3$	Linear	...	Light <sup>g</sup>
Aniline-cyclohexane (2)		No maximum; some upward curvature at large angles	Curved <sup>h</sup>	(Small) <sup>h</sup>	Light 26
Aniline-1-hexene	.204	Upward curvature	...	...	Light <sup>i</sup>
Methanol-cyclohexane	.098	Linear	Linear	13.7 <sup>j</sup>	Light 26
<i>n</i> -Decane- $\beta, \beta$ -dichlorodiethyl ether	.05	Linear	Linear	13.4	Light 11
Polystyrene-cyclohexane (1)	.17	Linear (detectable upward curvature)	Linear	26-66	Light <sup>k</sup>
Polystyrene-cyclohexane (2)		Downward bend at small angles and upward curvature at large angles when $(T - T_p)$ is small	Curved	...	Light 27
Polystyrene-cyclohexane (3)		Downward bend at small angles	(Linear)	...	Light <sup>l</sup>
Polystyrene-ethylcyclohexane	> .17	Upward curvature	Curved slightly	28-47	Light 25
<i>n</i> -Perfluoroheptane- <i>n</i> -heptane	.124	A qualified linear (see Fig. 3)	Linear	11.6	Light (This article)
<i>n</i> -Perfluoroheptane-isooctane	.13	Constant intensity persists over a temperature range of 1.0°	Disagrees with the OZD theory		X-Ray 32
Nitrobenzene- <i>n</i> -heptane	.166	Linear but with a changing slope	Bent at small $(T - T_c)$	(2.6)	X Ray 30
Argon	...	Linear	Linear	5.3	X-Ray <sup>m</sup>
Aluminum-zinc	...	...	...	...	X-Ray <sup>n</sup>

<sup>a</sup> Data after 1950 and only those directly related to the Debye theory are summarized. Therefore, many Russian studies have been omitted. <sup>b</sup> Reciprocal scattered intensity extrapolated to zero scattering angle from the OZD plot. <sup>c</sup> See B. Chu, ref. 11, footnote 41. <sup>d</sup> A region of large and erratic scattering was observed at small temperature distances from the critical temperature. <sup>e</sup> H. A. Cataldi and H. G. Drickamer, *J. Chem. Phys.*, **18**, 650 (1950); A. L. Babb and H. G. Drickamer, *ibid.*, **18**, 655 (1950). <sup>f</sup> A "class I" liquid mixture. Several binary liquid mixtures were reported. <sup>g</sup> Q. Chow, *Proc. Roy. Soc. (London)*, **A224**, 90 (1954). <sup>h</sup> The horizontal curves in ref. 26, Fig. 3, may result from an over correction on the alignment of the light scattering photometer as indicated by the slightly negative slope of LUDOX in the same figure. <sup>i</sup> P. Debye, H. Kaufmann, K. Kleboth, and B. Chu, *Trans. Kansas Acad. Sci.*, **66**, 260 (1963). <sup>j</sup> The reported  $l = 12.7 \text{ \AA.}$  was based on  $\lambda = \lambda_0/1.5$ , whereas  $\lambda = \lambda_0/1.3944$  should actually be used. <sup>k</sup> P. Debye, H. Coll, and D. Woermann, *J. Chem. Phys.*, **32**, 939 (1960); **33**, 1746 (1960); P. Debye, B. Chu, and D. Woermann, *ibid.*, **36**, 851, 1803 (1962). <sup>l</sup> V. E. Eskin, *Vysokomolekul. Soedin.*, **2**, 1049 (1960); V. N. Tsvetkov, V. E. Eskin, and V. S. Skazka, *Ukr. Fiz. Zh.*, **7**, 923 (1962); they found that Debye's theory was satisfied for some polymers, but not for others. <sup>m</sup> J. E. Thomas and P. W. Schmidt, *J. Chem. Phys.*, **39**, 2506 (1963). <sup>n</sup> A. Münster and K. Sagel, *Mol. Phys.*, **1**, 23 (1958).

to bring the low intensity regions into prominence. Figure 2 shows a plot of relative scattered intensity at 90° ( $\xi_{90}^*$ ) vs. temperature. The solid curve is of the form  $\xi_{90}^* = A(T - T_c)^{-1}$  where  $A$  is a constant chosen to give the best fit of the data. Corrections for density fluctuations and attenuation have been neglected. Since the experimental scattered intensity  $\xi_{90}^*$  is lower than the theoretical curve at small temperature distances from the critical mixing point ( $T - T_c = \Delta T < 0.2^\circ$ ), and, at  $\Delta T \sim 10^\circ$ , the absolute scattered intensity of the critical liquid mixture is still relatively high when compared with that due to density fluctuations of the pure components, the scattered intensity extrapolated to zero angle is expected to follow a  $(T - T_c)^{-1}$ , rather than a  $(T - T_c)^{-3/2}$ , dependence over the temperature range of our measurements ( $\Delta T \sim 0.06-13^\circ$ ).

The treatment of data according to the original Debye theory is described elsewhere<sup>11,25,26</sup>

$$\begin{aligned}
 (\xi_c^*)^{-1} &= F(T)(T_c/T) \left[ (\Delta T/T_c) + \frac{8\pi^2}{3} (l^2/\lambda^2) \sin^2 \frac{\theta}{2} \right] \\
 &= A + B \sin^2 \frac{\theta}{2} \\
 &= A + B' \left( \frac{s}{\lambda} \right)^2
 \end{aligned}$$

where  $\xi_c^*$  is the relative scattered intensity due to concentration fluctuations;  $F(T)$  is a temperature function for attenuation correction;  $T$  is the temperature in °K.;  $T_c$  is the critical solution temperature;  $\Delta T = T - T_c$ ;  $\lambda$  is the wave length of light in the medium;  $l$  is a molecular interaction range; and  $\theta$  is the scattering angle. The form of  $F(T)$  is unimportant so long as it is not dependent on scattering angles.<sup>11</sup> A plot of  $1/\xi_c^*$  vs.  $(s/\lambda)^2$  at two fixed temperature distances above  $T_c$  is shown in Fig. 3. Each scattering curve constitutes a superimposition of three scattering curves measured at  $\lambda_0$  364, 436, and 575 m $\mu$ . At each wave length, the curve bends slightly upward at higher angles. On the other hand, the forced superimposition of measurements at three different wave lengths indicates that this upward bend is of doubtful nature.

### Discussion

Table I summarized the pertinent experimental results designed to test existing theories. Deviations from the Debye theory are (1) upward curvature at large angles in the OZD plot from light scattering measurements. This could very well be the result of multiple scattering.<sup>27</sup> Only systems with large  $\Delta n$

(25) P. Debye, D. Woermann, and B. Chu, *J. Polymer Sci.*, **A1**, 255 (1963).

(26) P. Debye, B. Chu, and H. Kaufmann, *J. Chem. Phys.*, **36**, 3378 (1962).

(27) D. McIntyre, A. Wims, and M. S. Green, *ibid.*, **37**, 3019 (1962).

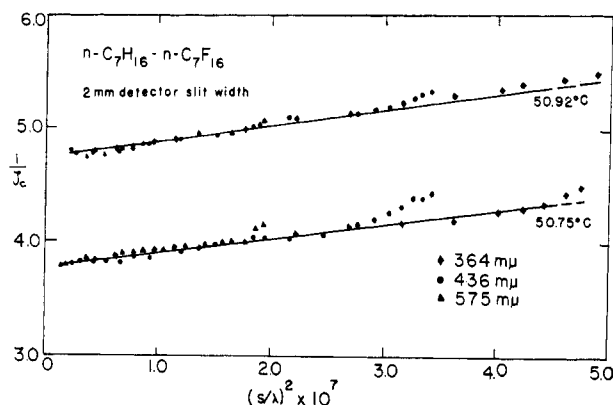


Fig. 3.—Plot of reciprocal relative scattered intensity after correction for attenuation and density scattering  $1/\xi_c$  vs.  $(s/\lambda)^2$ .  $s = 2 \sin \theta/2$ ,  $\lambda$  = wave length in the medium. Each curve constitutes a superimposition of three scattering curves measured at  $\lambda_0$  364, 436, and 575  $m\mu$  and at a fixed temperature distance above the critical solution temperature ( $T_c = 50.04^\circ$ ).

and high turbidities show this behavior and Fig. 3 clearly argues against this upward curvature. The only exception is Zimm's results<sup>28</sup> in which a different geometry for his photometer was used. Furthermore, small angle X-ray scattering studies of polystyrene-cyclohexane<sup>6,29</sup> show a downward curvature in the OZD plot signifying a breakdown of the approximate Debye theory, but the curvature is in the opposite direction. (2) Downward bend at small angles in the OZD plot: Eskin found a downward bend at large temperature distances from the phase separation temperature ( $T_p$ ) for the system polystyrene-cyclohexane not at the critical solution concentration, while McIntyre, *et al.*, found a downward bend only at very small temperature distances from  $T_p$ . The sharp downward bends at small angles indicate the presence of very large fluctuations. In view of our visual observations of the critical mixture, *n*-perfluoroheptane-*n*-heptane, it is probable that a slight temperature gradient may produce some form of "localized" phase separation, resulting in the downward bend. Very long range correlations were definitely absent from measurements of the system *n*-decane- $\beta,\beta'$ -dichlorodiethyl ether<sup>11</sup> over a range of  $s/\lambda$  which varied from  $1.29 \times 10^{-4}$  to  $7.46 \times 10^{-4} \text{ \AA}^{-1}$ . This deviation may be true but should be examined with caution. (3) Curvature at small  $T - T_c$  in a plot of extrapolated reciprocal scattered intensity (from an OZD plot) vs. temperature: deviations became appreciable for most systems where turbidities were high; yet in most cases, attenuation corrections were neglected. In the case of small angle X-ray scattering, the validity of extrapolation of the scattered intensity to zero scattering angle from an OZD plot is very questionable for liquid mixtures since the first two terms in the Taylor development of the approximate Debye theory may no longer be sufficient. The initial slope of the OZD curves is not known as indicated by an abnormally small  $l$  ( $\sim 2.6 \text{ \AA}$ ) calculated for the system nitrobenzene-*n*-heptane.<sup>30</sup> (4) The system *n*-perfluoroheptane-*n*-heptane<sup>31</sup> clearly con-

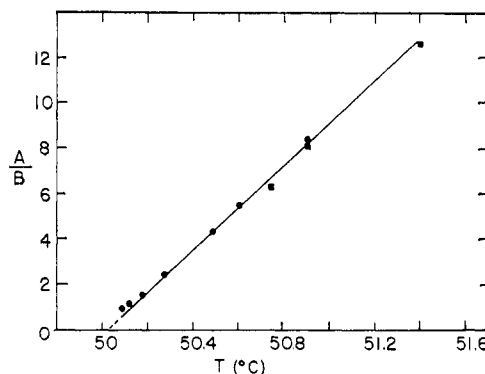


Fig. 4.—Plot of  $A/B$  vs. temperature.  $A/B = (3\lambda^2/8\pi^2 l^2 T_c)(T - T_c)$  with  $T_c = -\text{intercept/slope}$  of the resulting straight line.

tradicts the *constant* intensity results of Brady and Frisch.<sup>32</sup>

Figure 4 shows a plot of  $A/B$  vs.  $T$ , where  $A/B = (3\lambda^2/8\pi^2 l^2 T_c)(T - T_c)$ .  $T_p = T_c = 50.04^\circ$  which agrees well with  $T_p = 50.0^\circ$  from the literature<sup>15,21</sup>  $l = 11.6 \pm 0.5 \text{ \AA}$ . This "smaller than usual" value of  $l$  reveals an interesting aspect in molecular interaction studies if we discuss it in terms of both the Debye theory of critical opalescence<sup>1</sup> and the solubility parameter theory of Hildebrand<sup>13</sup> and Scatchard.<sup>14</sup> In view of the semiempirical approach of Hildebrand and the approximate Debye theory, it is within reason to identify the Debye cohesive energy density with the square of the Hildebrand solubility parameter

$$\frac{W_{ij}}{\omega_i \omega_j} = \delta_{ij}^2$$

where  $W_{ij}/\omega_i \omega_j$  and  $\delta_{ij}$  represent the respective cohesive energy density and solubility parameter of components 1-1, 2-2, and 1-2. The identity is only approximate as the Debye cohesive energy density does not involve a radial distribution function. In a simple-minded way, both theories suggest the use of some form of a van der Waals model. So we shall discuss our results in terms of spheres with hard cores and attractive tails. Such a crude model should certainly break down for coiling molecules (*e.g.*, polystyrene), but may be expected to work in a qualitative way for ordinary liquids. According to the Debye theory,<sup>1</sup> the molecular interaction range  $l$  is defined as

$$l^2 = \frac{(W_{11}/\omega_1^2)l_{11}^2 + (W_{22}/\omega_2^2)l_{22}^2 - 2(W_{12}/\omega_1 \omega_2)l_{12}^2}{(W_{11}/\omega_1^2) + (W_{22}/\omega_2^2) - 2(W_{12}/\omega_1 \omega_2)}$$

Now, with the hard sphere model

$$l_{ii}^2 = \frac{\int_{\sigma_{ii}}^{\infty} \left( -\frac{K}{r^6} \right) r^2 dr}{\int_{\sigma_{ii}}^{\infty} \left( -\frac{K}{r^6} \right) dr} = 3\sigma_{ii}^2$$

where  $\sigma_{ii}$  is a "collision" diameter between two *i* molecules. We shall simply take the cube root of molar volume,  $V^{1/3}$ , as our  $\sigma$ . Furthermore, we shall

(28) B. Zimm, *J. Phys. Colloid Chem.*, **54**, 1306 (1950); see also P. Debye, ref. 1, footnote 6, and M. S. Green, ref. 8, footnote 10.

(29) P. Debye, private communication, and unpublished results of this laboratory.

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

(31) Private communication. The light scattering behavior of the system *n*-perfluoroheptane and isooctane is presently under investigation by J. L. Lundberg, Bell Telephone Laboratories and Brooklyn Polytechnic Institute.

(32) G. W. Brady and H. L. Frisch, *J. Chem. Phys.*, **35**, 2234 (1961); for other results see G. W. Brady, *ibid.*, **32**, 45 (1960); G. W. Brady and J. I. Petz, *ibid.*, **34**, 332 (1961).

TABLE II  
COMPARISON OF OBSERVED AND CALCULATED MOLECULAR INTERACTION RANGE AND SOLUBILITY PARAMETER

Components	$\delta_{11}$ , cal. <sup>1/2</sup> /cm. <sup>3/2</sup>	$\delta_{22}$ , cal. <sup>1/2</sup> /cm. <sup>3/2</sup>	$\sigma_{11}$ , Å.	$\sigma_{22}$ , Å.	$(\delta_1 - \delta_2)$			$l^2_{\text{obsd.}}$ , Å. <sup>2</sup>	$l^2_{\text{calcd.}}$ , Å. <sup>2</sup>
					Obsd.	Calcd. <sup>a</sup>	Eq. 2		
Perfluoromethylcyclohexane (1)	5.8-6.1 <sup>b</sup>		6.88						
Carbon tetrachloride (2)		8.6 <sup>b</sup>		5.44					
System of 1 and 2					2.8	2.84	2.85	216 <sup>c</sup>	227
Cyclohexane (1)	8.2 <sup>b</sup>		5.66						
Methanol (2)		14.5 <sup>d</sup>		4.07					
System of 1 and 2					6.3	5.02	4.1	188 <sup>e</sup>	54.6
<i>n</i> -Decane (1)	7.7 <sup>f</sup>		6.87						
$\beta, \beta'$ -Dichlorodiethyl ether (2)		9.7 <sup>g</sup>		5.79					
System of 1 and 2					2.0	2.78	2.77	182 <sup>h</sup>	544
<i>n</i> Heptane (1)	7.4 <sup>i</sup>		6.27						
<i>n</i> -Perfluoroheptane (2)		5.85 <sup>i</sup>		7.22					
System of 1 and 2					1.58	2.58	Eq. 3 2.61	135	620

<sup>a</sup> Ref. 13b, p. 143

$$RT_c = \frac{2X_1X_2V_1^2V_2^2}{(X_1V_1 + X_2V_2)^3} (\delta_1 - \delta_2)^2 \quad (1)$$

$$= 0.25(V_1 + V_2)(\delta_1 - \delta_2)^2 \quad (2)$$

$$= \frac{2V_1V_2}{(V_1^{1/2} + V_2^{1/2})^2} (\delta_1 - \delta_2)^2 \quad (3)$$

where  $T_c$  and  $X$  are critical solution temperature and mole fraction,  $V$  is the molal volume, and  $\delta$  is the solubility parameter defined as  $(\Delta E^v/V)^{1/2}$ . <sup>b</sup> Values from J. H. Hildebrand, and D. R. F. Cochran, *J. Am. Chem. Soc.*, **71**, 22 (1949). <sup>c</sup> Ref. 28. <sup>d</sup> Calculated from the latent heat of vaporization. Also, F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience Publishers, Inc., New York, N. Y., 1962, p. 26. <sup>e</sup> Ref. 26. <sup>f</sup> Estimated by interpolation of values from other paraffins, ref. 13. <sup>g</sup>  $\Delta H^v$  estimated from Hildebrand's rule:  $\Delta H^v$  (cal./mole) =  $-2950 + 23.7T + 0.020T^2$  where  $T$  is the boiling point. The observed and the calculated values of  $\Delta H^v$  for diethyl ether are in good agreement. <sup>h</sup> Ref. 11. <sup>i</sup> Values from ref. 15.

base our comparisons on the assumption that the system perfluoromethylcyclohexane-carbon tetrachloride behaves "properly" because the calculated  $(\delta_1 - \delta_2)$  from eq. 1 and 2 (see Table II, footnote *a*) of the solubility parameter theory agrees well with the observed  $(\delta_1 - \delta_2)$ , as shown in Table II.

If we assume  $\delta_1\delta_2 = \delta_{12}^2$ , and let  $\sigma_{12} = [(\sigma_1 + \sigma_2)/2.]$  (1/1.07),<sup>33</sup> then

$$l^2_{\text{calcd}} = 3 \frac{\delta_1^2\sigma_{11}^2 + \delta_2^2\sigma_{22}^2 - \delta_1\delta_2 \frac{(\sigma_1 + \sigma_2)^2}{2.29}}{(\delta_1 - \delta_2)^2}$$

The results, summarized in Table II, show that positive and negative deviations of both theories are in the same direction and of the same magnitude. Figure 5 shows a plot of  $l^2_{\text{calcd}}/l^2_{\text{obsd}}$  vs.  $(\delta_1 - \delta_2)^2_{\text{calcd}}/(\delta_1 - \delta_2)^2_{\text{obsd}}$ . The linearity may be too good to be true, but the correspondence is self-evident. Deviations of ether, alcohol, and hydrocarbon mixtures are as expected and these deviations substantiate Scott's<sup>19</sup> proposal on the breakdown of the geometric mean assumption ( $c_{12} = (c_{11}c_{22})^{1/2}$ ). Considering the narrowness of our theoretical basis, it is surprising that the hard sphere model works so well. Unfortunately only four molecular interaction parameters ( $l^2$ ) for binary critical mixtures are known. Further work on a homologous series of paraffins and  $\beta, \beta'$ -dichlorodiethyl ether and other liquid mixtures with both light and small angle X-ray scattering is in progress.

(33) We assume  $\sigma_{12}$  as only slightly less than  $(\sigma_1 + \sigma_2)/2$  so that, with  $\sigma_{11} = k(\sigma_1 + \sigma_2)/2$  and  $k = (1/107)$ ,  $l^2_{\text{calcd}} \cong l^2_{\text{obsd}}$  for the system perfluoromethylcyclohexane-carbon tetrachloride: S. D. Hamann, J. A. Lambert, and R. B. Thomas, *Australian J. Chem.*, **8**, 149 (1955). They have made a calculation of the interaction between a monatomic molecule and a "quasi-spherical" polyatomic one and have found  $\sigma_{12} \cong (\sigma_1 + \sigma_2)/2$ .

So far, the Debye theory has stood the tests. However, it is expected that the original theory should break down when  $s/\lambda$  is measured over a large range, or when  $\Delta T$

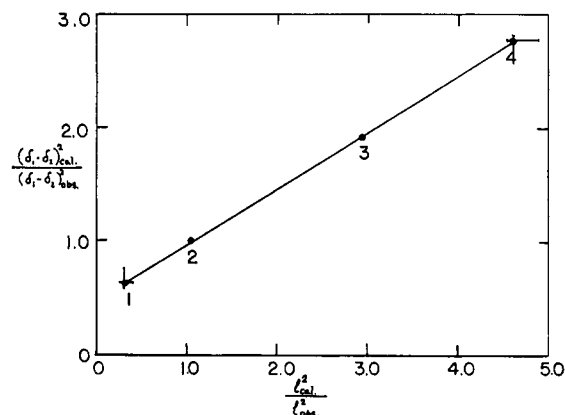


Fig. 5.—Plot of  $(\delta_1 - \delta_2)^2_{\text{calcd}}/(\delta_1 - \delta_2)^2_{\text{obsd}}$  vs.  $l^2_{\text{calcd}}/l^2_{\text{obsd}}$ : (1)  $C_6H_{12}-CH_3OH$ ; (2)  $C_6F_{11}CF_3-CCl_4$ ; (3)  $n-C_{10}H_{22}-\text{Chlorex}$ ; (4)  $n-C_7H_{16}-n-C_7F_{16}$ .

is very small. If  $\Delta T$  is very small, the temperature dependence of the extrapolated zero angle scattered intensity from an OZD plot may deviate from  $(T - T_c)^{-1}$ . Experiments in this region of critical opalescence have certainly been inconclusive.

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