

Critical behavior of the ultrasonic attenuation and velocity and shear viscosity for the binary mixture of carbon tetrachloride and coconut oil

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Measurements of the ultrasonic velocity and absorption at the critical concentration were made as a function of temperature and frequency for the binary mixture of carbon tetrachloride and coconut oil. In addition, viscosity measurements were made. Ultrasonic absorption at 5, 7, 10, 15, 21, 25, 30, and 35 MHz above T_c is analyzed by the dynamic scaling theory of Ferrell and Bhattacharjee [Phys. Rev. A **31**, 1788 (1985)]. The values of α_c/f^2 vs $f^{-1.06}$ show a good agreement with the theory. Also, the experimental values of α/α_c for carbon tetrachloride and coconut oil are compared to the scaling function $F(\omega^*)$. The temperature and frequency dependence of the velocity are also determined. The coefficient of viscosity of the critical mixture shows a different temperature dependence from that of the pure components.

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INTRODUCTION

In this article, the dynamic scaling theory of Ferrell and Bhattacharjee¹ is applied to analyze the absorption and velocity data for the critical mixture of carbon tetrachloride and coconut oil above the critical temperature ($T_c = 22.2^\circ\text{C}$). The sound velocity at low frequency provides information on equilibrium thermodynamical properties of the system. On the other hand, the increased absorption and the velocity as the frequency is changed, are connected with the dynamic behavior of the system.²

The theory indicates that α/α_c [see Eq. (1) for definitions of α and α_c] should be a function of the reduced frequency ω^* , and should scale with the scaling function $F(\omega^*)$. According to the theory, α_c/f^2 vs $f^{-1.06}$ should give a straight line at the critical temperature and concentration. The ultrasonic attenuation data of Bhattacharya and Deo³ for the frequency range 1–5 MHz, and our data extending the frequency range to 5–35 MHz will be evaluated using the dynamic scaling theory. In our work, the shear viscosity of the carbon tetrachloride and coconut oil as a function of temperature and concentration has also been studied in order to determine the value of ω_0 in Eq. (3). Note ω_0 depends on the viscosity.

I. EXPERIMENTAL METHOD

The absorption and velocity measurements were made with a Matec pulse-echo system that generates a train of ultrasonic pulses through the temperature-controlled test cell. The setup and operational procedures are discussed in our previous papers.^{4–6} The shear viscosity was measured by using a Brookfield digital viscometer. To control the temperature of the sample cell, a water jacket is provided with inlet and outlet attached with a thermostatic device consisting of a constant temperature water bath and a water-pump circulating system. The thermostatic control error was $\pm 0.01^\circ\text{C}$. The coconut oil was from Frey Scientific and of a

pure labgrade. The purified carbon tetrachloride was from Fisher Scientific. The chemicals were used without any further purification. The sample was carefully weighed with an analytical balance.

In general, attention must be paid to maintaining a steady temperature. Difficulties are due mainly to irregularities in peak structure arising from the temperature fluctuations near critical temperature. These were minimized and the diffraction effects were not a problem in our measurements.^{7,8}

II. RESULTS AND ANALYSIS

The estimated critical temperature T_c for the system is approximately equal to 22.2°C corresponding to the critical concentration x_c of 0.732 by weight of carbon tetrachloride.³ In Fig. 1(a) and (b), the temperature dependence of the absorption for the critical mixture of carbon tetrachloride and coconut oil at 5, 7, 10, 15, 21, 25, 30, and 35 MHz is shown. The error in the absorption measurements was less than 5%. It is observed that α/f^2 decreases with temperature at all frequencies, studied. Figure 2 indicates the frequency dependence of α/f^2 at various temperatures.

The temperature and frequency dependence of ultrasonic velocity are shown in Fig. 3. The velocity decreases with increasing temperature above T_c and increases with the frequency increase. Figure 3 shows a velocity dispersion in critical mixtures. The error in the velocity measurements was less than 0.3%.

According to Refs. 2, 9–11,

$$\alpha/\alpha_c = \alpha(\text{crit}, \omega, T)/\alpha(\text{crit}, \omega, T_c) = F(\omega^*), \quad (1)$$

where $\alpha(\text{crit}, \omega, T)$ is the critical term at temperature T and $\alpha(\text{crit}, \omega, T_c)$ is the critical term at the critical temperature T_c and

$$F(\omega^*) = (1 + \omega^{*-1/2})^{-2} \quad (2)$$

is the predicted scaling function. The dimensionless reduced

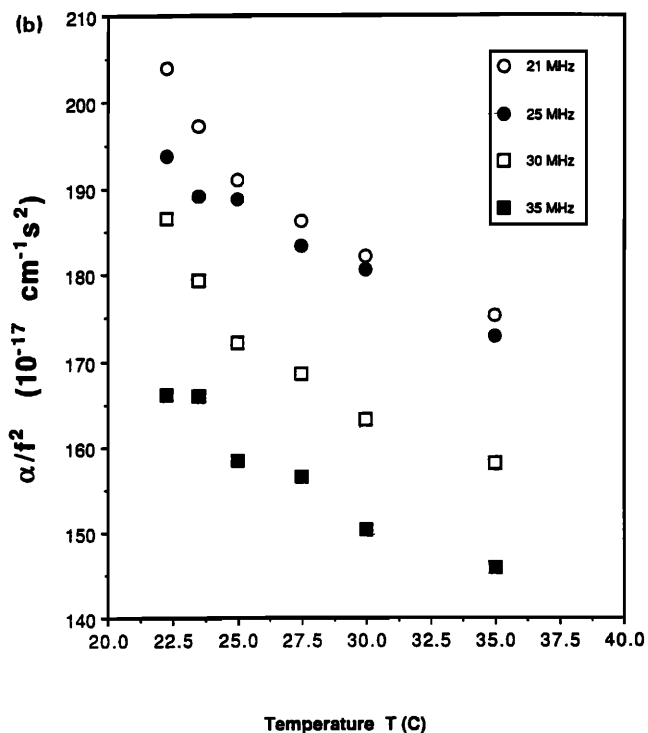
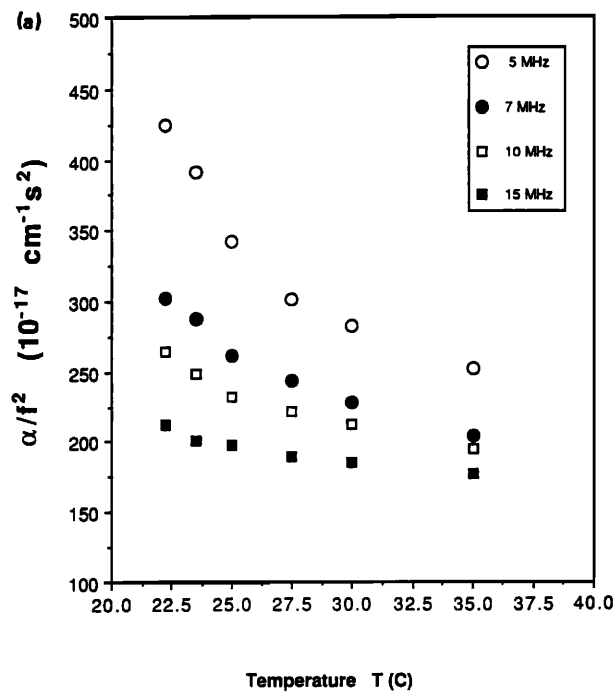


FIG. 1. (a) and (b) Temperature dependence of α/f^2 for the critical binary mixture of carbon tetrachloride and coconut oil.

frequency ω^* is defined by $\omega^* = \omega/\omega_D$, where the characteristic temperature-dependent relaxation rate ω_D is given by^{9,12}

$$\omega_D = \omega_0 t^{1.93}, \quad (3)$$

where $t = (T - T_c)/T_c$ is the reduced temperature and ω_0 is

$$\omega_0 = 2D_0\xi_0^{-2}, \quad (4)$$

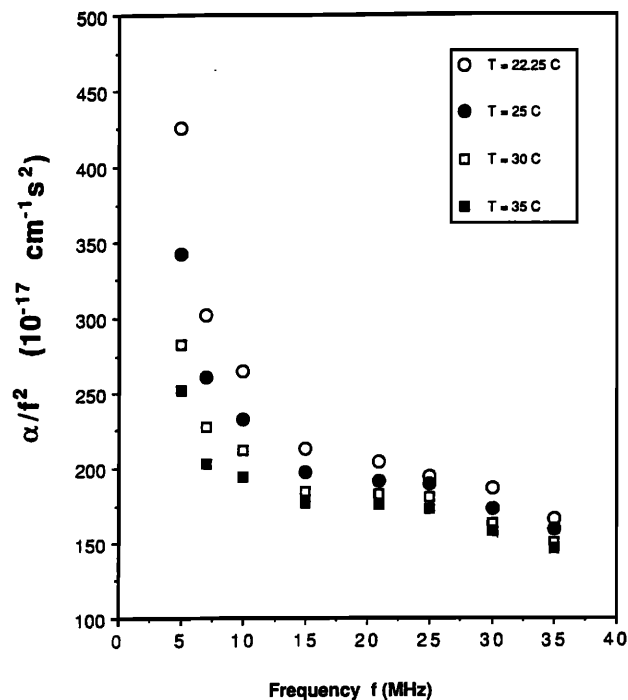


FIG. 2. Frequency dependence of α/f^2 for the critical binary mixture at various temperatures.

where D_0 is the diffusion coefficient and ξ_0 is the correlation length. In Fig. 4, α/α_c vs ω^* is shown along with $F(\omega^*)$. The data were fitted to the theoretical curve using a value of $\omega_0 = 1.36 \times 10^{11} \pm 0.33 \times 10^{11}$ Hz [a least-square fit of the data given by Ref. 3 yields the value of ω_0]. Bhattacharya and Deo³ have also measured the absorption in the frequency range 1 to 5 MHz.

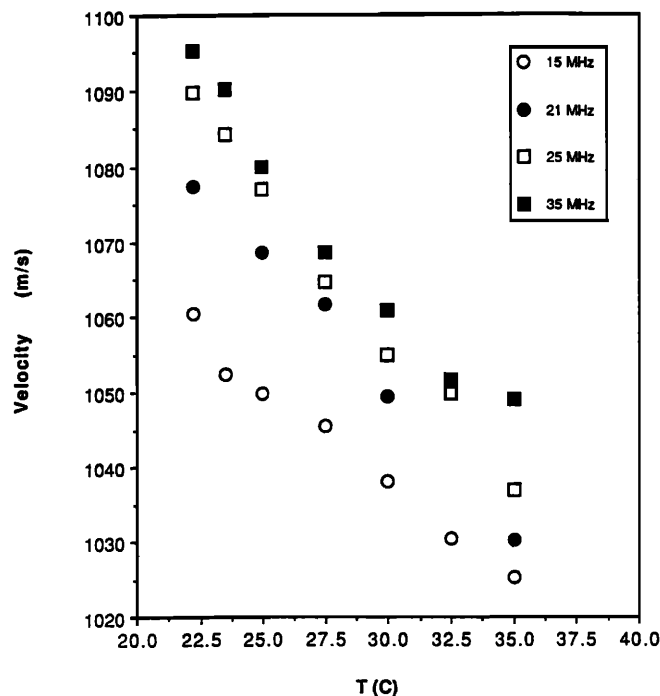


FIG. 3. Temperature dependence of the ultrasonic velocity above T_c for the critical binary mixture.

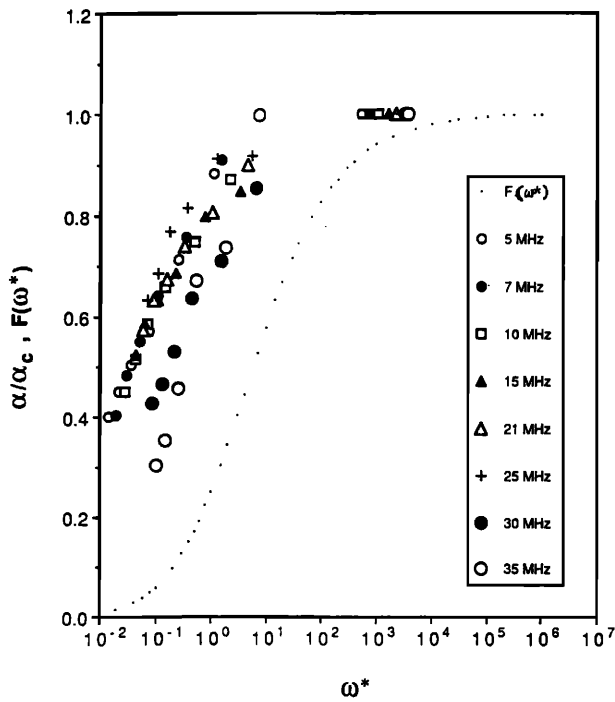


FIG. 4. A plot of α/α_c as a function of the reduced frequency ω^* along with scaling function $F(\omega^*)$.

According to dynamic scaling theory^{9,10}

$$\alpha_c/f^2 = Sf^{-1.06} + b, \quad (5)$$

where the quantity b is the frequency-independent value of

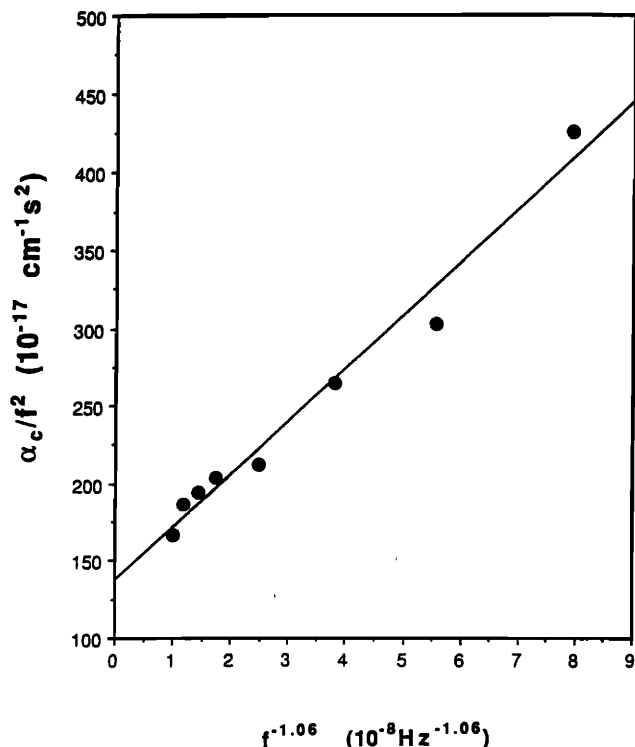


FIG. 5. α_c/f^2 versus $f^{-1.06}$ at T_c and critical mixture for this work.

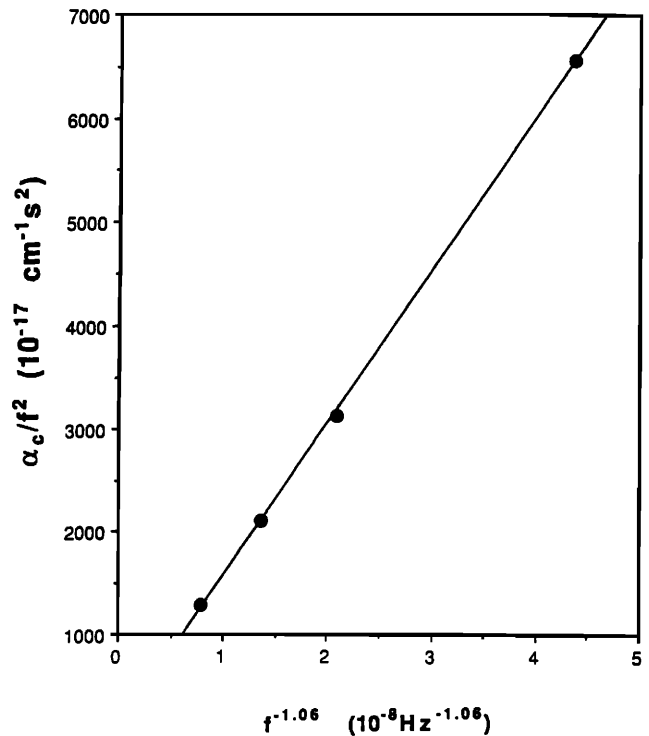


FIG. 6. α_c/f^2 versus $f^{-1.06}$ at T_c and critical mixture for Bhattacharya and Deo's³ data.

Navier-Stokes term,^{9,13} or $\alpha(\text{background})/f^2$, and S is a constant independent of frequency. The value of S can be predicted theoretically. Figure 5 shows a plot of absorption α_c/f^2 at critical mixture and temperature T_c vs $f^{-1.06}$. A least-square fit yields a slope of $0.341 \times 10^{-7} \text{ cm}^{-1} \text{ s}^{0.94}$ and an intercept of $137.1 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2$. Bhattacharya and Deo's data were plotted in Fig. 6. A least-square fit yields a slope of $1.477 \times 10^{-7} \text{ cm}^{-1} \text{ s}^{0.94}$ and an intercept of $88.8 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2$.

In Tables I and II the shear viscosity data as a function of temperature and concentration are shown. Plots of the logarithms of the viscosity versus the reciprocal of the absolute temperature at the concentration extremes and at the critical composition for the system, carbon tetrachloride and coconut oil, are shown in Fig. 7 (a) and (b). From our data, the background viscosity for the pure components obeys the equation, $\log \eta = A + B/T$, where $A = -5.6$ and $B = 1568.8 \text{ K}$ for coconut oil and $A = -3.57$ and $B = 471.4 \text{ K}$ for carbon tetrachloride.^{14,15} The error in the viscosity measurements was less than 0.5%.

The correlation length ξ_0 and diffusion coefficient D_0 were calculated using the value of ω_0 and the measured shear viscosity coefficient η_0 . The measured data of the viscosity for carbon tetrachloride and coconut oil were fit to the power law $\eta = \eta_0 t^{-x_\eta \nu}$, where η_0 is the shear viscosity coefficient and x_η, ν are critical exponents, $x_\eta \nu = 0.04$. A least-square fit yields a value of $\eta_0 = 2.59 \text{ cp}$.¹⁶ The values of ξ_0 and D_0 are 1.1 \AA and $0.78 \times 10^{-5} \text{ cm}^2/\text{s}$, respectively. Some measured and calculated quantities are given in Table III.

TABLE I. Viscosity data (in cp) for the noncritical mixture ($X_{\text{carb}} = 0.0, 0.268, 0.50, 0.60, 0.65, 0.70,$ and 0.725 by weight of carbon tetrachloride).

T (°C)	$X_{\text{carb}} = 0.00$	0.268	0.50	0.60	0.65	0.70	0.725
22.25	51.03	23.35	9.18	6.18	5.10	4.25	3.70
23.50	48.46	22.27	8.95	6.00	4.95	4.15	3.70
25.00	45.88	20.95	8.48	5.83	4.85	4.05	3.60
30.00	37.12	17.65	7.38	5.25	4.40	3.70	3.33
35.00	30.33	14.90	6.52	4.72	4.00	3.35	3.08
40.00	25.22	12.70	5.83	4.25	3.65	3.13	2.83
45.00	21.37	10.90	5.20	3.82	3.35	2.95	2.70
50.00	17.84	9.40	4.67	3.58	3.10	2.90	2.55
55.00	15.07	8.15	4.30	3.25	2.95	2.85	2.43

TABLE II. Viscosity data (in cp) for the mixture ($X_{\text{carb}} = 0.732, 0.74, 0.77, 0.80, 0.85, 0.90,$ and 1.0 by weight of carbon tetrachloride).

T (°C)	$X_{\text{carb}} = 0.732$	0.74	0.77	0.80	0.85	0.90	1.0
22.25	3.75	3.40	3.08	2.68	2.15	1.70	1.08
23.00	3.63
23.50	...	3.35	3.03	2.63	2.13	1.68	1.05
25.00	3.38	3.25	2.93	2.55	2.08	1.65	1.03
26.00	3.30
28.00	3.15
30.00	3.03	3.00	2.68	2.38	1.93	1.58	0.97
32.00	2.86
35.00	2.73	2.75	2.48	2.23	1.83	1.48	0.91
40.00	...	2.58	2.28	2.08	1.73	1.40	0.86
45.00	...	2.55	2.15	1.98	1.63	1.35	0.84
50.00	...	2.43	2.03	1.93	1.58	1.28	0.79
55.00	...	2.20	1.93	1.90	1.48	1.25	0.73

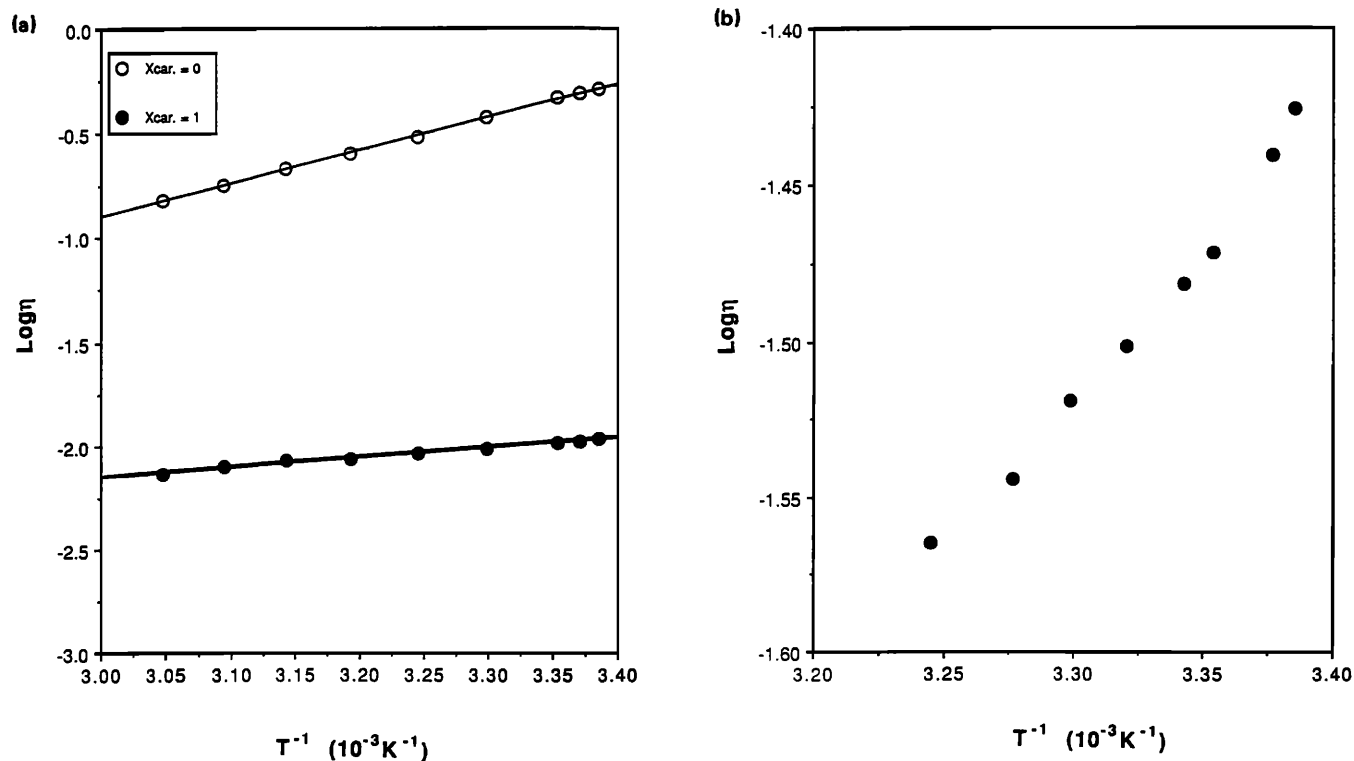


FIG. 7. (a) and (b) Plots of the logarithms of the viscosity versus the reciprocal of the absolute temperature at $x = 0$, $x = 1$, and $x_c = 0.732$ Wt carbon tetrachloride.

TABLE III. Measured and calculated values for carbon tetrachloride and coconut oil.

Quantity	Measured	Calculated	From references
T_c (°C)			22.2 ^a
α_c (critical exponent for C_p)			0.11 ^b
zv			1.9 ^c
ω_0 (Hz)/ 2π		1.36×10^{11}	
D_0 (cm ² /s)		0.78×10^{-5}	
η_0 (cp)	2.59		
ξ_0 (Å)		1.1	
u (m/s) at 15 MHz ($T = 22.25$ °C)	1060.5		
u (m/s) at 5 MHz ($T = 22.5$ °C)			1079 ^a

^a Reference 3.

^b References 5 and 17.

^c Reference 18.

III. DISCUSSION AND CONCLUSIONS

It can be seen from Figs. 1 and 2 that the absorption coefficient for the critical concentration increases as the critical temperature is approached from the high-temperature region for all frequencies. The absorption coefficient at the critical temperature and concentration decreases with increasing frequency. The velocity (see Fig. 3) for the critical mixture increases with increasing frequency. This indicates the dispersion is observed, although the pure components have no dispersion. It may be due to noncritical effects as reported previously.³ The experimental values of α/α_c in Fig. 4 are displaced relative to the FB theory perhaps because of ω_0 which depends on the correlation length ξ_0 , vis-

cosity η_0 , and T_c . In Fig. 5 the values of α_c/f^2 vs $f^{-1.06}$ show a good agreement with the theory. The plot of absorption α_c/f^2 at T_c versus $f^{-1.06}$ in Fig. 6 for Bhattacharya shows a similar relationship for the lower frequency range. As the concentration, $x = m_{\text{carbon}}/(m_{\text{carbon}} + m_{\text{oil}})$, increases from 0.0 to 1.0, the viscosity decreases. The viscosity in Table I also decreased at each concentration as the temperature increased. In Fig. 7(b) the critical binary mixture of carbon tetrachloride and coconut oil seems to indicate a weak anomaly in the shear viscosities near the critical temperature. The collateral data are not available in the literature to do a complete analysis using dynamic scaling theory.

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