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ARTICLE · JANUARY 1996

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Islamic unviersity Journal Vol. 4, No. 2, July 1996

The Critical Behavior of the Ultrasonic Attenuation for the Binary Mixture of Cyclohexane and Aniline

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ملخص البحث

تم قياس معامل الامتصاص فوق الصوتي (α) كداله في درجة الحراره والتردّد للخليط الثنائي المكوّن من الهيكسان الحلقي والأنيلين . واستخدمت نظرية القياس التحريكي (الديناميّ) في تحليل هذا المعامل عند تردّدات مقدارها ٥،١٠، ١٥، ٢٥، ٣٥ ميغاهيرتز وفوق درجة الحرارة الحرجة T_c . وقيس ايضا ثابت الكظيم (الادياباتيّ) g. كذلك قورنت القيم التجريبية ل $\frac{\alpha}{\alpha_c}$ (حيث α_c قيمة معامل الامتصاص فوق الصوتي عند درجة الحراره الحرجه) للخليط الحرج بدالّة القياس $F(w^*)$ النظرية فلوحظ توافق جيد بين القيم التجريبيّة والنظرية.

Abstract

Ultrasonic absorption measurements were made as a function of temperature and frequency for the binary mixture of cyclohexane and aniline . Ultrasonic absorption at 5,10,15,25 and 35MHz, above T_c , is analyzed using the dynamic scaling theory. The adiabatic coupling constant g is calculated. The experimental values of $\frac{\alpha}{\alpha_c}$ for the critical mixture are compared to the scaling function $F(w^*)$. Good agreement with the theory is obtained.

1. Introduction :

In the literature, there are two papers with ultrasonic measurements of the binary mixture of cyclohexane and aniline[1,2] However, the absorption results in these papers do not cover a wide range of frequencies ; in particular these results are not extensive enough to allow analysis using the dynamic scaling theory by Ferrell and Bhattacharjee. Accordingly, in the present work further absorption coefficients are measured for an extended frequency range of 5-35MHz. Since the necessary collateral data exist for this system, the experimental results are compared to the prediction of the dynamic scaling theory[3,4]. The critical amplitudes of the thermal expansion and specific heat of the mixture have been calculated using the two-scaling-factor universality relation[5-9].

2.Theoretical Considerations :

The measured absorption $\frac{\alpha_{meas}}{f^2}$ near the critical temperature can be expressed as the sum of two terms[10,11],

$$\frac{\alpha_{meas}}{f^2} = \frac{\alpha_{crit}}{f^2} + \frac{\alpha_{back}}{f^2} \quad (1)$$

where $\frac{\alpha_{back}}{f^2}$ is the background term which includes absorption due to the Navier Stokes term, the radiation and the diffusion near the boiling point. In the dynamic scaling theory, the critical term can be expressed in terms of the reduced frequency

$w^* = \frac{w}{w_D}$, w_D being a characteristic temperature-dependent relaxation rate given by the Stokes-Einstein expression[10]:

$$w_D = \frac{k_B T_c}{3\pi\eta\xi^3} \quad (2)$$

Here the correlation length ξ and the shear viscosity η are given by :

$\xi = \xi_0 t^{-\gamma}$ and $\eta = \eta_0 t^{-x_\eta \gamma}$,

where $t = \frac{T - T_c}{T_c}$ is the reduced temperature[12], and k_B designates Boltzmann's constant. Note that γ and x_η are critical exponents.

The temperature - dependent relaxation rate can be written simply as

$w_D = w_0 t^{z\gamma}$ (3)

where $z\gamma = 1.9$.

The critical attenuation coefficient in the dynamic scaling theory can be written as [9,10]:

$$\frac{\alpha_{crit}}{f^2} = \left(\frac{\pi^2 C_{pc}\, \bar{\alpha}}{2Z\gamma} \frac{U_c g^2}{T_c C_p^2 (t_f)} \left(\frac{a w_0}{2\pi} \right)^{\frac{\bar{\pi}}{Z\gamma}} \right) f^{-\left(1+\frac{\bar{\alpha}}{Z\gamma}\right)} \quad (4)$$

Here α and Cpc are the critical exponent and critical amplitude in the following expression for the heat capacity per gram (i.e., the specific heat) :

$C_p = C_{pc} t^{-\bar{\alpha}} + C_{pb}$; C_{pb} is the background specific heat, $a = \frac{w}{w_0} t_f^{-\gamma}$ is a dimensionlless scaling factor of the order unity[13], U_c is the adiabatic sound velocity at T_c, g is the adiabatic coupling constant, and Cp(tf) is the specific heat at a characteristic reduced temperature tf, which can be approximated by the t value at which $\frac{\alpha_{(crit,conc)}}{f^2}$ for a given frequency is one-half its value at T_c[10].

The total attenuation term of $\frac{\alpha_{meas}}{f^2}$ yields ;

$\frac{\alpha_{meas}}{f^2} = Sf^{-1.06} + b$, (5)

Where S is the term in parentheses in equation (4) and b represents the frequency- independent background term of $\frac{\alpha_{meas}}{f^2}$ at T_C

The prediction for the variation in α(crit,w,T) as a function of the reduced frequency is given in the form[3]

$$\frac{\alpha_{(crit.,w,T)}}{\alpha_{(crit.,w,T_c)}} = \frac{\alpha}{\alpha_c} = F(w^*) = \frac{1}{(1 + w^{*\frac{1}{2}})^2} \quad (6)$$

Here α(crit.,w,T) is the critical term at temperature T and critical concentration and

α(crit.,w,Tc) is the critical term at critical temperature T_C and critical concentration.

The adiabatic coupling constant g was introduced by the FB theory which is given by [9,14]

$$g = \rho_c C_p \left[\frac{dT_c}{dp} - \left(\frac{\partial T}{\partial p} \right)_s \right] \cong \frac{C_{pb}\, \alpha_{pc}\, T_c}{C_{pc}} - \alpha_{pb} T \quad . \quad (7)$$

Note that $\alpha p \equiv$ the isobaric thermal expansion coefficient ; αpc and α pb being the critical and background parts of the thermal expansion coefficient.

3. Experimental :

Measurements of absorption were made using the matec pulse-echo technique that generates pulses through the temperature-controlled test cell. The setup and procedures are discussed in our previous papers[15-19]. The chemicals were used without any further purification.

4. Results and Analysis:

Measurements were made in one region starting at 60 °C and taking successive reading as the temperature was lowered step by step toward T_C=30.20 °C. The critical concentration was taken to be

47.0% aniline in weight. The ultrasonic absorption was measured for frequencies 5,10,15,25 , and 35 MHz. The temperature of the sample was controlled within ±0.01 °C.

Fig. 1 shows the temperature dependence of the absorption $\frac{\alpha}{f^2}$ for the critical binary mixture of aniline-cyclohexane at five different frequencies. The error in the absorption measurements was less than 4%. It is observed that $\frac{\alpha}{f^2}$ decreases with temperature above T_c at all frequencies studied.

Fig. 2 shows the absorption coefficient at a given frequency (15 MHz) and three different concentrations plotted versus temperature. For the noncritical mixtures of aniline and cyclohexane some critical behavior in the absorption is still evident.

Tanaka and Wada[1] have measured the ultrasonic absorption in a critical aniline and cyclohexane solution. (47.0% by weight of aniline, T_c=30.20 °C) . Their frequency range is from 18Hz to 8.93MHz. Our data show good agreement with their data. For example , at T=30.40 °C and frequency f = 8.93 MHz their measurement of absorption is $894\text{x}10^{-17}\frac{s^2}{cm}$, and our measurement at the same temperature and at frequency f = 10MHz is $45\text{x}10^{-17}\frac{s^2}{cm}$.

In Fig. 3, the experimental values of $\frac{\alpha}{\alpha_c}$ at different frequencies are shown along with the theoretical function $F(w^*)$. The data were fit to the theoretical curve using a value of w_0 of $.82\text{x}10^{10}$ Hz, which was calculated with the correlation length $\xi_0 = 2.2 \pm 0.1$ Å and the measured shear viscosity $\eta_0 = 1.01$cp shown in Fig.4.

The error in the viscosity measurements was less than 0.4%. Tanaka and Wada[1] assumed in their paper that $w_0 = 2.5\text{x}10^{10}$ Hz.

Fig. 5 shows a plot of absorption $\frac{\alpha_c}{f^2}$ at critical mixture and temperature T_c versus $^{-1.06}$. A least squar fit yields an experimental slope S of $2.38\times10^{-7}\,cm^{-1}S^{0.94}$ and the an intercept of $27\times10^{-17}cm^{-1}S^2$ The calculated value of S using equation (4) and the calculated value of g = -0.13, is $.1\times10^{-7}\,cm^{-1}S^{0.94}$. Using the values of $\frac{dT_c}{dp}$, $\left(\frac{\partial T}{\partial p}\right)_s$, and the asymptotic behavior of α_p and C_p which can be represented by power laws of the form[1]:

$$\alpha_p = \alpha_{pc} t^{-0.11} + \alpha_{pb}$$

$$C_p = C_{pc} t^{-0.11} + C_{pb} ,$$

one can find the background parts of the thermal expansion α_{pb} and specific heat C_{pb}, The critical amplitudes of the thermal expansion α_{pc} andspecific heat C_{pc} can be calculated usthe two-scale-factor universality[9]

$$\xi_0\left(\frac{\bar{\alpha}\rho_c c_{pc}}{k_B}\right)^{\frac{1}{3}} = \xi_0\left(\frac{\bar{\alpha} T_c \alpha_{pc}}{k_B T_c'}\right)^{\frac{1}{3}} = 0.270 .$$

Here ξ_0 is the amplitude of the correlation length ξ, $\alpha = 0.11$ is the critical exponent and $T_c' = \frac{dT_c}{dp}$.

The values of the thermal expansion and specific heat are calculated to be :

$$\alpha_p = 0.49\times10^{-4} t^{-0.11} + 7.96\times10^{-4} K^{-1} ;$$

$$C_p = 0.27\times10^{7} t^{-0.11} + 2.04\times10^{7} \frac{erg}{gK} .$$

The thermodynamic quantities , Cpb, Cpc, α_{pb}, α_{pc}, and T_c enable us to determine the adiabatic coupling constant g for anilineand cyclohexane critical mixture. From equation (7) one obg -

0.13. Table (1) shows the measured and the calculated values both in this work and other references.

5. Discussion and Conclusion :

The absorption coefficient for the critical concentration increases as the critical temperature is approached from the high-temperature region for all frequencies. It can be seen that the experimental values of $\frac{\alpha}{\alpha_c}$ at critical mixture are compared to the scaling function $F(w^*)$ and show good agreement above $w^* = 1$ with the FB theory.

The measured absorption of the $\frac{\alpha_c}{f^2}$ versus $f^{-1.06}$ yields a straight line , as predicted by the FB theory.

For the aniline-cyclohexane binary mixture the adiabatic constant g is a negative value, which implies that phase separation can be induced by a sudden pressure decrease.

References

. H. Tanaka, Y. Wada, and H. Nakajima, Chem. Phys. 68, 223 (1982).
2. S. V. Krivokhizha, L. Sabirov, and Ya. Turakulov, Sov. Phys. JETP 51(4) 793 (1980)
3. R. A. Ferrell and J. K. Bhattacharjee, Phys. Rev . A31, 1788 (1985).
4. J. K. Bhattacharjee and R. A. Ferrell, Phys. Rev. A24, 1643 (1981).
. M. Pelger, H. Klein, and D. Woermann, J. Chem. Phys. 67, 5362 (1977).
6. C. Bervillier and Godreche, Phys. Rev. B21,5427 (1980).
7. D. Stauffer, M. Ferer, and M. Wortis, Phys. Rev. Lett. 29,345 (1972).
8. S. J. Fast and S. S. Yun, J. Chem. Phys. 86(1), 497 (1987).
. E. A. Clerke, J. V. Sengers, R. A. Ferrell, and J. K. Bhattacheriee, Phys. Rev A27, 2140 (1983).
10. C. W. Garland and G. Sanchez, J. Chem. Phys. 79(6), 3090 (1983).
11. S. J. Fast and S. S. Yun, J. Chem. Phys. 83(11), 5888 (1985).
12. P. Calmettes, Phys. Rev Lett. 39,1151 (1977).
13. J. K. Bhattacharjee and R. A. Ferrell, Phys. Lett. A88, 77 (1982).
14. H. Tanaka and Y. Wada , Chem. Phys. 78, 143 (1983).
15. S. Fast and S. S. Yun, J. Acoust. Soc. Am.83, 1384 (1988).
. I. Abdelraziq, S. S. Yun , and F. Stumpf, J. Acoust. Soc. Am , 88, 183 (1990).
. P. Spickler. I. Abdelraziq, S. S. Yun, and F. B. Stumpf, J. Acoust. Soc. Am. 85, 1363 (1989).
. R. Esqivel-sirvent, B. Tan , I. Abdelraziq, S. S. Yun, and F. B. Stumpf, J. Acoust. Soc. Am. 93, 819 (1993).
19. I. R. Abdelraziq, S.S. Yun, and F. B. Stumpf, J. Acoust. Soc Am. 91, 844 (1992).
20. C. C. Lai and S. H. Chen, Phys. Lett. A41, 259 (1972).
. H. Chaar, M. R. Moldover, and J. W. Schmidt, J. Chem. Phys. 85(1), 418(1986).
22. H. C. Burstyn and J. V Sengers, Phys. Rev. A25, 448 (1982).