

CRITICAL SOUND ABSORPTION IN BINARY LIQUID
MIXTURE OF TRIETHYLAMINE-WATER SYSTEM

$$\begin{aligned}
 &= -\frac{k_B T}{D} \sum_{\mathbf{k}} k_x k_y \chi_{\mathbf{k}} \\
 &\simeq \frac{-8}{15\pi^2 - 40} \eta^* \log(k_c \xi_0) \quad (12)
 \end{aligned}$$

これは温度もしくは ξ によらない。 ξ_0 はマイクロな長さである。流れがあるときの熱伝導率 $\kappa(\lambda)$ については、

$$\kappa(\lambda) = \sum_{\mathbf{k}} \frac{1}{k^2} \chi_{\mathbf{k}} \simeq k_c^{-1} \sum_{\mathbf{l}} \frac{1}{l^2} \chi^*(l, \infty), \quad (13)$$

これは発散せず k_c^{-1} に比例している。

以上の結果の解釈は容易である。即ち、 $\lambda = (k_c \xi)^3 > 1$ のとき、 k_c^{-1} が correlation length となるのである。 $\Gamma_{k_c} = D$ であるので、 $k < k_c$ のゆらぎは Shear D でこわれ、 $k > k_c$ のゆらぎは熱的にこわれて平衡のときと大差ない。 k_c^{-1} より大きなゆらぎは熱的にこわれるより前に Shear で変形されこわされるわけである。同時に大きなゆらぎは(すぐこわされるので)できにくくなる。最後に、光散乱の実験で、 $\chi_{\mathbf{k}}$ や $\Gamma_{\mathbf{k}}$ の shear 依存性は十分観測されることに注意する。今だこのような実験はなされてはいない。(6)で $\varepsilon = 10^{-5}$, $D = 10^3$ とすれば $\lambda = 0.34 \times 10^5$ である!

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Ultrasonic attenuation in triethylamine-water has been measured over the frequencies range 15-95MHz and temperatures 12.5-18.0°C. The experimental data have been analyzed by

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including the universal critical relaxation part $\Psi_1(\epsilon, \omega)$, on the basis of Kawasaki's mode-mode coupling theory, and non-universal background relaxation part $\Psi_2(\epsilon, \omega)$. As a result, the total sound absorption $\Psi(\epsilon, \omega)$ can be written as the sum of three terms,

$$\Psi(\epsilon, \omega) = \Psi_1(\epsilon, \omega) + \Psi_2(\epsilon, \omega) + \sigma(T),$$

where ϵ is a reduced temperature, $\epsilon = (T_c - T)/T_c$, and $\sigma(T)$ is a classical contribution. At high frequency ($\omega^* > 1$), the behavior of the sound absorption is quite different from the case of liquid-gas phase transition that is observed in Xe. In particular, the Kawasaki prediction, which is confirmed by the experimental results in Xe, is clearly not verified for the mixture TEA/W examined here.

Introduction

For recent years, the study on the critical dynamics of classical liquids has been developed extensively both in experimental and theoretical aspects. In particular, the critical divergence of ultrasonic absorption near the critical points has attracted an increasing amount of attention for the understanding of the dynamics of order-parameter fluctuations. The theory of ultrasonic absorption and dispersion near the critical points, which is proposed by Kawasaki on the basis of the mode-mode coupling theory,¹ has been successfully used to explain the experimental results of liquid-gas phase transition and critical binary mixtures. As a system approaches a critical point the order parameter fluctuations become very large as a consequence of the divergence of the generalized susceptibility for the system. In the Kawasaki theory the macroscopic normal modes are the solutions to the linearized hydrodynamic equations and the divergences in the transport coefficients are calculated by considering the breakup on one hydrodynamic mode into a multiplicity of other modes, with coupling constants that are obtained by an involved projection operator technique.^{1,2} D'Arrigo et al.³ have explained their ultrasonic absorption measurements for the critical binary mixtures of aniline-cyclohexane and of nitrobenzen-n-hexane using the Kawasaki theory. The most essential point in their results is that the reduced critical sound absorption per wavelength, $(\alpha\lambda)^*$, depends only on a single reduced variable $\omega^* = \omega/\omega_D$, with the characteristic frequency defined by $\omega_D \equiv 2D\xi^{-2}$, where D is the diffusion coefficient and ξ is the correlation length of the order-

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parameter fluctuations. They also show experimentally that within the experimental uncertainty the data for the dimensionless quantity, $(\alpha\lambda)^*$, are all described by the same universal function of the variable ω^* .

On the other hand, several papers have been reported on the anomalous sound absorption near the critical point in triethylamine-water (TEA/W) mixtures,^{4,5,6,7} but the data reported in these works are not conclusive because the experimental points are taken only over the limited frequency ranges and a lot of uncertainty is involved in their analysis. Among them the analysis by Yun⁸ bases on the Fixman theory⁹ seems to be adequate. In order to examine the Fixman's model quantitatively, however, D'Arrigo et al. pointed out that many of the additional assumptions introduced by Fixman lead to a breakdown of the theory close to a critical temperature T_c or alternatively at high frequency. Therefore, the critical sound absorption analysis by Yun may not be conclusive and not always accurate. In the present works, we have measured the critical sound absorption in TEA/W system over a wide frequency range and in order to examine the universality hypothesis we have analyzed¹⁰ the data according to the same procedure reported by Garland et al., which is based on the Kawasaki's mode-mode coupling theory for critical dynamics. It has become clear from our data analysis that the universality hypothesis is not valid if background corrections are not made which reflect directly the characteristics of the system. Furthermore, it is shown that the superposition of a universal relaxation $\Psi_1(\epsilon, \omega)$ and a non-universal relaxation $\Psi_2(\epsilon, \omega)$ must be satisfactorily included in all the data of anomalous critical sound absorption for TEA/W system¹⁰, where ϵ is the reduced temperature $\epsilon = (T_c - T)/T_c$. The purpose of this paper is to show that the clear understanding of the background corrections is essential to give a more excellent explanation of the anomalous critical sound attenuation in TEA/W system.

Experimental Procedure

The TEA of special grade was obtained from Wako Chemical Co. Ltd. and used without further purification. Water used was prepared by distilling deionized water in an all pyrex still of special design.¹⁰ The TEA/W system has a lower critical solution temperature of 18.3°C, at a critical concentration of 44.9 wt.%. The sound absorption measurements were carried out over the temperature range from 12.5°C to 18.0°C by controlling the temperature of the sample cell within the accuracy of $\pm 0.03^\circ\text{C}$. The absorption coefficients were measured using a standard pulse transmission technique over the frequency range 15-95MHz with 5MHz X-cut quartz transducers.

Experimental results and discussion

The temperature dependence of the absorption coefficient, α/f^2 , in the single phase of the TEA/W solution for nine different frequencies is shown in Fig. 1. What is important in this

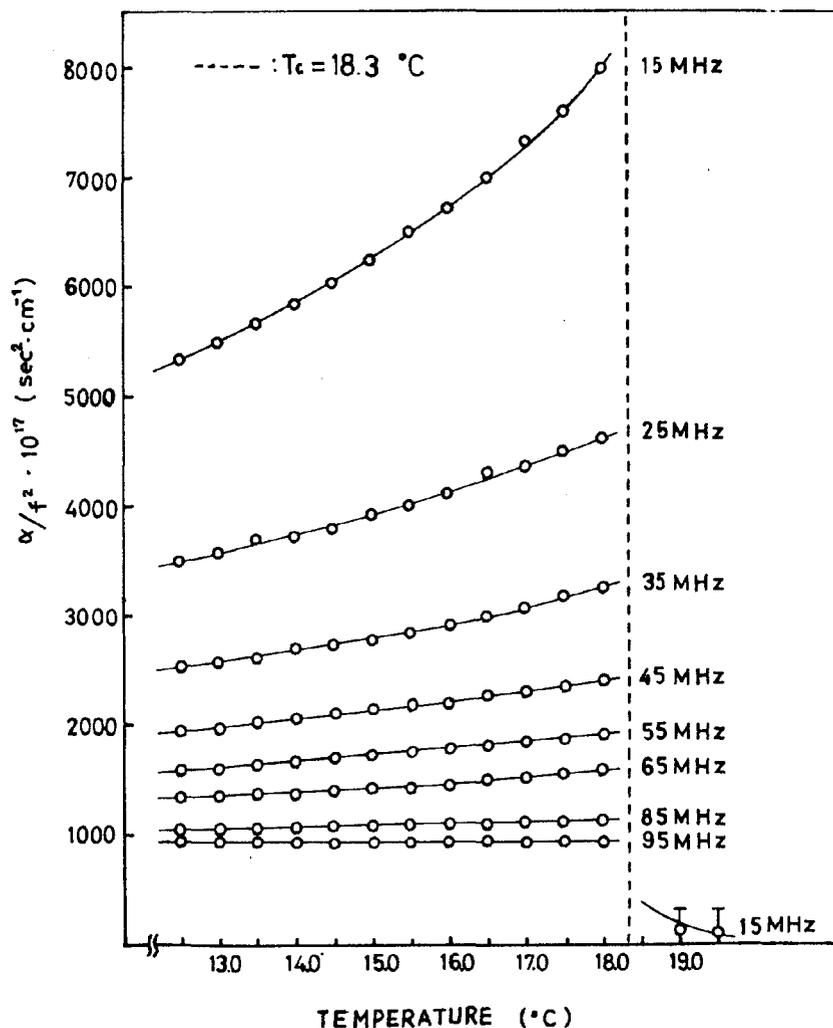


Fig. 1. Temperature dependence of ultrasonic absorption in triethylamine-water as a function of frequency.

figure is that in the low frequency region the absorption coefficients increase asymptotically as the temperature approaches from upward to the critical temperature, while in the high frequency region this behavior does not occur. The value of α/f^2 in the high frequency region seems to approach to a constant value independent of temperature. Such a high value of α/f^2 ($= 1000 \times 10^{-17}$ neper/cm) at 95MHz suggests the presence of an residual relaxation absorption. The data obtained were analyzed with the same procedure of D'Arrigo et al. The results are

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summarized as follows:

- [1] The Characteristic frequency f_D of the order-parameter fluctuations becomes extremely high compared with the decay rate of order-parameter fluctuations.
- [2] The experimental spectral pattern does not agree with the theoretical one over a wide frequency range.
- [3] The experimental plot of $(\alpha\lambda)^*$ versus ω^* in Fig. 3 does not fit to the curve of the universal function.

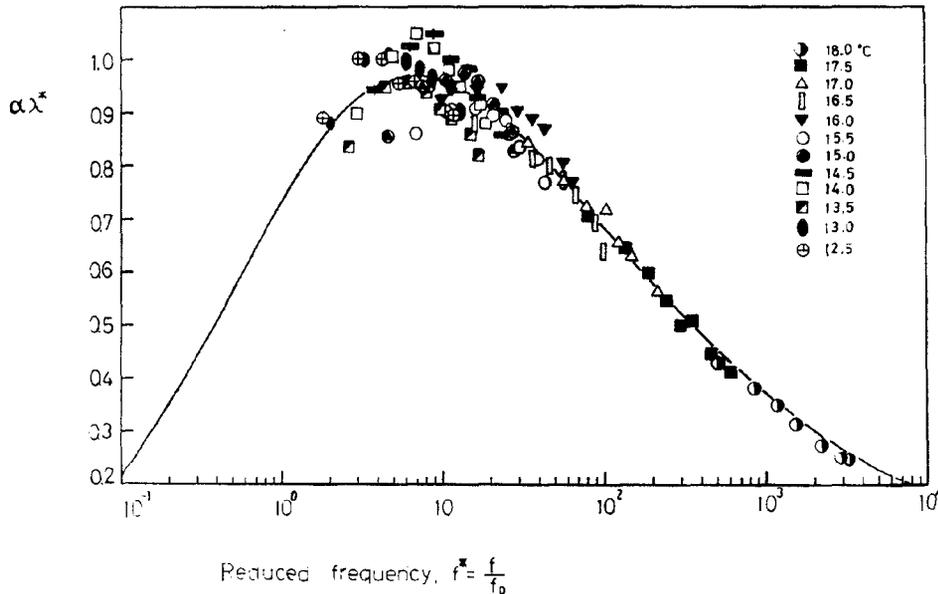


Fig. 3. Reduced critical sound absorption per wavelength $(\alpha\lambda)^*$ in triethylamine-water as a function of the reduced frequency f^* .

These discrepancies may suggest a serious question as to whether the universality hypothesis is practically applicable to the present TEA/W system, which has been believed to be valid in critical dynamics for other systems. The background and critical parts in the transport coefficients play an important role for the data analysis in any experimental investigation of the dynamics of a system near the critical point. In the analysis of the Rayleigh linewidth measurements, it is well known that the universality hypothesis becomes valid when one takes into account the background corrections.

In the case of the analysis of ultrasonic absorption data, we must examine what kind of background should be corrected. Here we have attempted¹⁰ to separate the total sound absorption $\Psi(\epsilon, \omega) = \alpha/f^2$ into three contributions as

$$\Psi(\epsilon, \omega) = \Psi_1(\epsilon, \omega) + \Psi_2(\epsilon, \omega) + \sigma(T), \quad (1)$$

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where

- $\Psi_1(\epsilon, \omega)$: the critical sound absorption on the basis of the Kawasaki's mode-mode coupling theory,
 $\Psi_2(\epsilon, \omega)$: the background relaxation part,
 $\sigma(T)$: the classical absorption part or the frequency-independent contribution to α/f^2 which is due to a shear viscosity and any excess absorption due to a relaxation process with a relaxation frequency much higher than f_c .

The expression of $\Psi_1(\epsilon, \omega)$ is given by

$$\Psi_1(\epsilon, \omega) = [2\pi Q(\epsilon)/U_0(T)f_D(\epsilon)] I(\omega^*), \quad (2)$$

where $Q(\epsilon)$ is a purely thermodynamic quantity given by

$$Q(\epsilon) = [K_B T^3/2\pi^2\rho^3 U_0^2 C_v^2] (1 - \eta/2)^2 (\partial\kappa/\partial T)^2 \kappa (\partial P/\partial T)_v^2, \quad (3)$$

where K_B is the Boltzmann's constant, C_v the specific heat at constant volume, P the pressure, η the critical exponent arising from the Fisher correction to the Ornstein-Zernike correlation function, $\kappa \equiv \xi^{-1}$ the inverse correlation length, $U(T)$ the zero-frequency sound velocity, and $f_D(\epsilon) = (D/\pi)\xi^{-2}$ the characteristic frequency of the order-parameter fluctuations. $I(\omega^*)$ represents the following integral

$$I(\omega^*) = \int_0^\infty \frac{dx x^2 K(x)}{(1+x^2)^2 K^2(x) + \omega^{*2}}, \quad (x = q\xi) \quad (4)$$

where q is the wave number, $\omega^* = \omega/\omega_D$ is a reduced frequency scaled by ω_D and $K(x)$ is the Kawasaki function

$$K(x) = 3/4 [1 + x^2 + (x^3 - x^{-1})\tan^{-1}x]. \quad (5)$$

The expression of $\Psi_2(\epsilon, \omega)$ is given as

$$\Psi_2(\epsilon, \omega) = \sum_i A_i(\epsilon) / [1 + (f/f_{ci})^2], \quad (6)$$

where f_{ci} is a relaxation frequency associated with the relaxing part of the background adsorption $A_i(\epsilon)$ and i is the integers (1, 2, 3, ...).

Here, $\Psi_2(\epsilon, \omega)$ is treated as a single relaxation ($i=1$). For a binary mixture there are suggestions that $U(T)$, C_v and $(\partial P/\partial T)_v$ are not singular at a consolute point.¹¹ As far as $U(T)$ is concerned, there are experimental verifications of this suggestion.^{13,3} Therefore, the quantity $Q(\epsilon)$ can be estimated from the data of sound velocity and Rayleigh linewidth measurements. The quantities $Q(\epsilon)$, $U(T)$, $f_D(\epsilon)$ and $\sigma(T)$ appearing in Eq. (1) are adjustable parameters to be

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determined from a best fitting of the experimental data. In order to determine the frequency dependence of α/f^2 , the experimental data at a temperature $T=18.0^\circ\text{C}$ were first fitted to Eq. (1). Then the theoretical values of α/f^2 were calculated using Eq. (1) and the results are shown in Fig. 2.¹⁰ Before discussing detailed analysis of critical relaxation we would like to

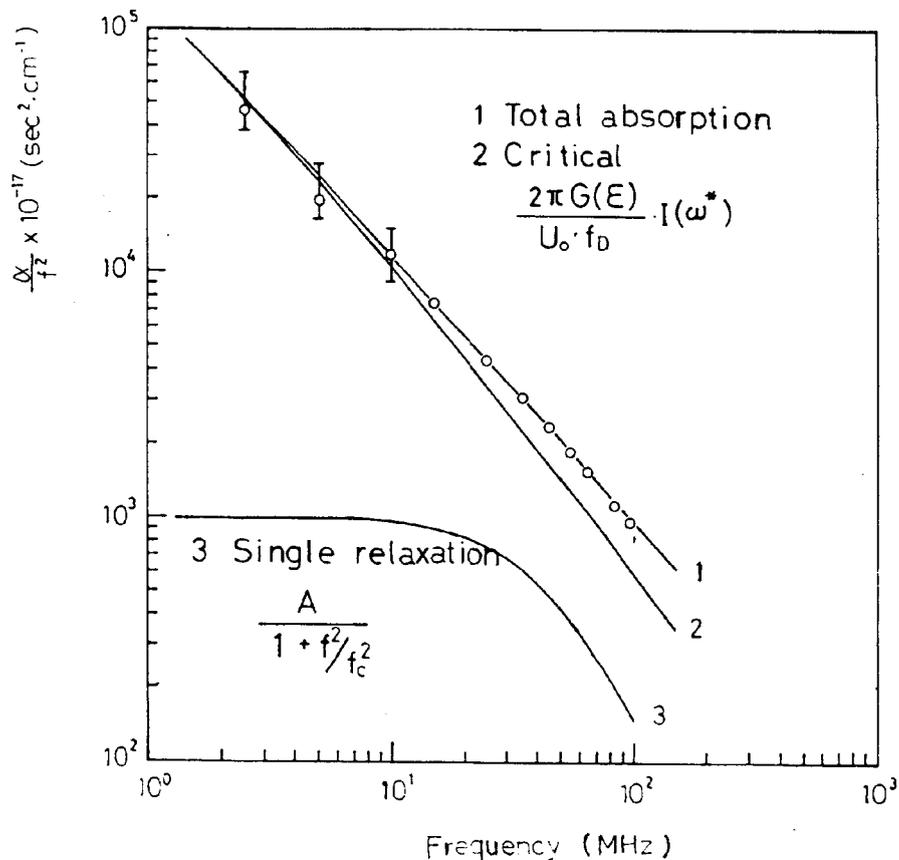


Fig. 2. Critical sound attenuation in triethylamine-water as a function of frequency. The experimental attenuation curve (1) is the sum of a singular term (2) and a background relaxation term (3).

point out the origin of the mechanism of background relaxation. It is well known the fact that there are three different rotational isomers in triethylamine. The ultrasonic absorption of triethylamine has been studied by Heasell and Lamb¹⁴ over a temperature range from 25°C to 70°C and its relaxation process has been attributed to the perturbation of an equilibrium system between these rotational isomers; the characteristic frequency is 89.3 MHz and the maximum value of the absorption per wavelength at the frequency $f=f_c$, μ_{max} , is equal to 0.0209 at 25°C . The original mode of rotational isomers is transformed into new deformed rotational mode by through the molecular interactions between triethylamine and water in the form of a

hydrogen-bonding. The excess sound absorption at high frequency region can be attributed to this new deformed rotational mode. We consider that the concentration fluctuations are enhanced to a great extent by the mixed mode which is made up of the local molecular motion of the deformed rotational isomers and the viscous mode of critical fluctuations with long wavelength. As is known from the sound velocity measurement in TEA/W by Yun,⁸ the temperature dependence of the sound velocity is different from that in other critical binary mixtures such as nitrobenzen-n-hexane and aniline-cyclohexane. The shape of the temperature dependence is cusp-like in TEA/W system weakly diverges. This marked characteristic could be reasonably explained in terms of the formation of the mixed mode as mentioned above. In Eq. (1) we have included the contribution of this new deformed mode $\Psi_2(\epsilon, \omega)$ due to a single relaxation to the excess sound absorption; the nonuniversal relaxation term which directly reflects the characteristics of the system. Thus, it is necessary to take account of the nonuniversal background relaxation for the validity of the universality hypothesis and to give a reasonable explanation of the experimental results within the framework of the Kawasaki's mode-mode coupling theory.

From Eq. (1) we can derive¹⁰ the reduced absorption per wavelength, $(\alpha\lambda^*)$;

$$(\alpha\lambda^*) = [\Psi(\epsilon, \omega) - \Psi_2(\epsilon, \omega) - \sigma(T)] U_O(T)/fQ(\epsilon) = 2\pi f^* I(\omega^*). \quad (7)$$

The experimental values of $(\alpha\lambda^*)$ shown in Fig. 3. have been evaluated from this Eq. (7). The solid line represents the same quantity according to the theory using the Kawasaki theory. The most striking feature of this curve is that all the points, taken over a wide range of temperature and frequency, fall on a single universal curve. From such a background correction we find that the value of exponent ν in the characteristic frequency of the order-parameter fluctuations in Fig. 4, $f_D = f_O \epsilon^{3\nu}$, becomes 0.65 which is nearly equal to theoretical values reported ($\nu = 0.625 \sim 0.66$). However, when the value of $Q(\epsilon)$ is plotted against ϵ by appropriately re-scaling the theoretical value, the part in the bracket of Eq. (2), we find that the exponent α in $Q = Q_O \epsilon^{-\alpha}$ is 0.084 for $\epsilon > 6 \times 10^{-3}$ and 0.48 for $\epsilon < 6 \times 10^{-3}$, which does not satisfy the well-known hyperscaling relation $\alpha = 2 - 3\nu$, but rather an inequality $\alpha > 2 - 3\nu$. Furthermore, we have calculated the value of $Q(\epsilon)$ from Eq. (3) using the observed diffusion coefficients by Haase and Siry¹⁵ and found a single value of $\alpha (= 0.084)$ over the entire ranges of ϵ . However, a difficulty is encountered that the calculated value of α/f^2 from Eq. (2) with $\alpha = 0.084$ ceases to diverge and shows a rapid decrease in the vicinity of T_c . With regard to such a difficulty, we should note the following features: First, in the calculation of critical relaxation $\Psi_1(\epsilon, \omega)$ we should take into account the effect¹⁶ of the departure from the Ornstein-Zernike correlation function. Second,¹⁹ we note that a variety of asymptotic forms of correlation function for large

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value of $q\xi$ have been proposed thus far because of the lack of scaling function $g(x)$ of sufficient accuracy. As pointed out by Chang et al.¹⁷ this deficiency may be remedied by Bray and reproduces to high accuracy the theoretically known Ising-model correlation functions in two and $4-\epsilon$ dimensions. Third, according to Kawasaki,¹ $\alpha\lambda$ must be independent of frequency and practically independent of temperature for $\omega^* > 1$. This prediction is confirmed experimentally for a liquid-gas phase transition of xenon, although this is not the case for two binary mixtures

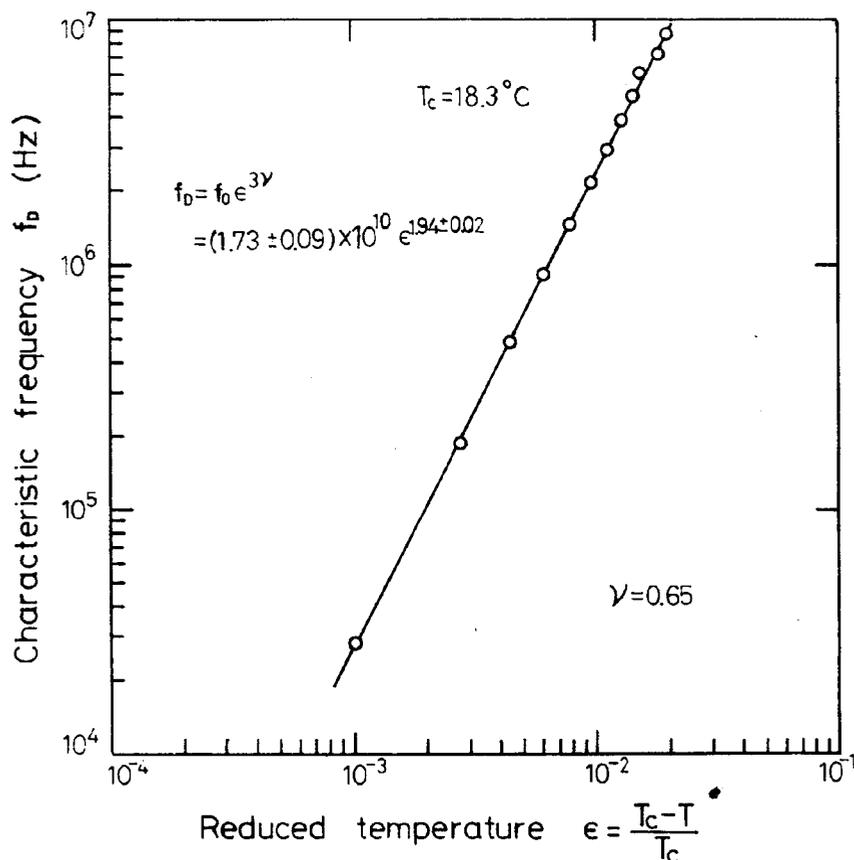


Fig. 4. The characteristic frequency of order-parameter fluctuations plotted against reduced temperature.

(nitrobenzen-n-hexane and aniline-cyclohexane) by D'Arrigo et al.³ and for the mixture studied in this work. By taking account of all these factors, we are now reanalyzing our data and the results will be reported later.

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