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Pseudo-Critical Dynamics in Binary Fluids*

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Recent advances in a new type of critical phenomena, in which response functions diverge near the 1st-order phase transition that is not a thermodynamic singular point, have been reviewed from experimental and theoretical standpoints. These phenomena are now referred to as “pseudo-critical phenomena” (PCP) which are for the first time introduced by us from ultrasonic studies on binary fluids. The Ikeda’s theoretical classification of PCP based on molecular field theories is discussed. We have proposed a general concept of “three-circle model”, in which more general critical phenomena such as nonequilibrium, nonlinear open systems can be included. Finally, our experimental results of ultrasonic absorptions on PCP in binary fluid systems are presented. It is shown that the hypercritical state of a multicomponent system of n-BuOH/H₂O/Ca(SCN)₂ is equivalent to the pseudo-critical state of a binary system of t-BuOH/H₂O, in which the 2nd-order-like 1st-order phase transition occurs.

I. INTRODUCTION

Over the past two decades, remarkable progress has been achieved on the studies of phase transitions and critical phenomena of various systems of gases, fluids, and solids.¹⁾ In general critical phenomena various physical quantities show anomalies near the 2nd-order phase transition point which is a thermodynamic singular point and response functions such as transport coefficients diverge at this point.

On the other hand, quite recently another type of critical phenomena has been found, in which response functions diverge even near the 1st-order phase transition point that is not a thermodynamic singular point. These phenomena are now referred to as “pseudo-critical phenomena” (PCP), which are for the first time introduced by us from the studies of sound absorptions in binary fluids.²⁾ Recently, similar phenomena have been observed in a variety of material systems, such as liquid

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crystals,³⁾ binary intermetallic compounds,⁴⁾ ferroelectrics,⁵⁾ and metal-nonmetal transitions.⁶⁾ Theoretical studies on PCP are first presented by Saito;⁷⁾ he treated static PCP problems in terms of renormalization-group theories. More recently, Ikeda has attempted to define the concept of PCP and developed the unified theories on PCP within the framework of molecular-field theory.⁸⁾ According to him, PCP is defined as the critical phenomena, in which “various physical quantities diverge at the point where “spinodals”, or the second derivatives of free energy with respect to order parameters, vanish”.

In this review paper, we shall first show some of typical examples of PCP observed experimentally thus far, and shall review the Ikeda classification of PCP. Then more general classification is proposed, which we call “Three-circle model”, including nonequilibrium, nonlinear open systems. Finally, our sound absorption studies on PCP in binary fluids will be shown in some detail.

II. EXAMPLES OF PSEUDO-CRITICAL PHENOMENA

(1) Supercooling or metastability limit in liquid gallium

Figure 1. shows the results of neutron scattering experiments by Bosio and Windsor for dispersed emulsions of supercooled Ga.⁹⁾ The frequency distributions become narrowed as the temperature is lowered. This indicates that as the metastability limit is approached from above, there is an approximately logarithmic divergence of the time-averaged fluctuation density $S(Q_0, \omega = 0)$ reminiscent of the approach to a 2nd-order phase transition.

(2) Pretransition in isotropic phases of liquid crystals in relation to nematic-isotropic phase transition.

As shown in Fig. 2, the reciprocal of the intensity of light scattering in the isotropic phase of MBBA depends on temperature linearly. The intensity of scattering varies as $(T-T^*)^{-1}$, where T^* is the 1st-order transition point, according to Stinson et al.¹⁰⁾ Also Bhattacharya et al. have shown that strong anomalies in the velocity and attenuation of longitudinal sound absorption and dispersion in the MHz range are observed near the nematic-smectic A phase transition in a liquid crystal. ³⁾ For the nematic-smectic A phase transition, the possibility of 2nd-order transition has been predicted theoretically, such as mean field like transition by de Gennes,³⁾ λ -like transition by Taylor et al.,¹¹⁾ and Hoshino et al.³⁾

(3) Metal-nonmetal transition in NiS

The metal-nonmetal transition in NiS displays the characteristics of the 1st-order transition, as found by Trahan and Goodrich.⁶⁾ Figure 3 is the temperature dependence of the heat capacity at constant pressure C_p , where the lattice contribution is subtracted for both heating and cooling runs.

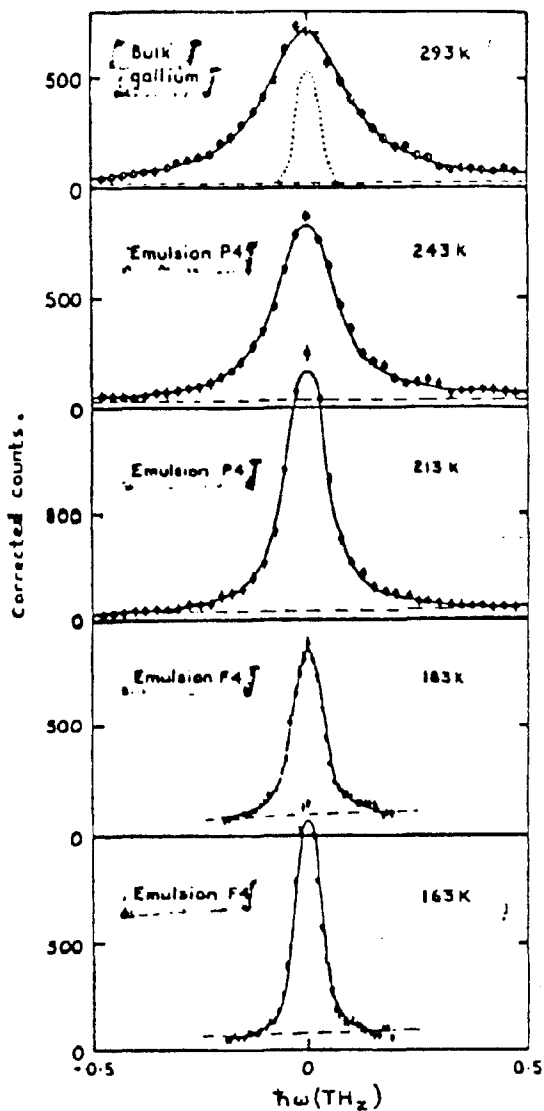


Fig. 1. Constant- Q scans at $Q_0 = 2.5 \text{ \AA}^{-1}$ (corresponding to the peak in the structure factor) in bulk and dispersed liquid gallium. The solid lines represent the best-fit Lorentzians, convoluted with the experimental resolution function (shown dotted). The fitted background is shown dashed.

Supercooling and subsequent self-heating of the sample occur, giving negative values in addition to double-valued positive specific heats. It can be seen that the cooling curve exhibits a sharp discontinuity in C_p due to supercooling. On the heating run such is not the case

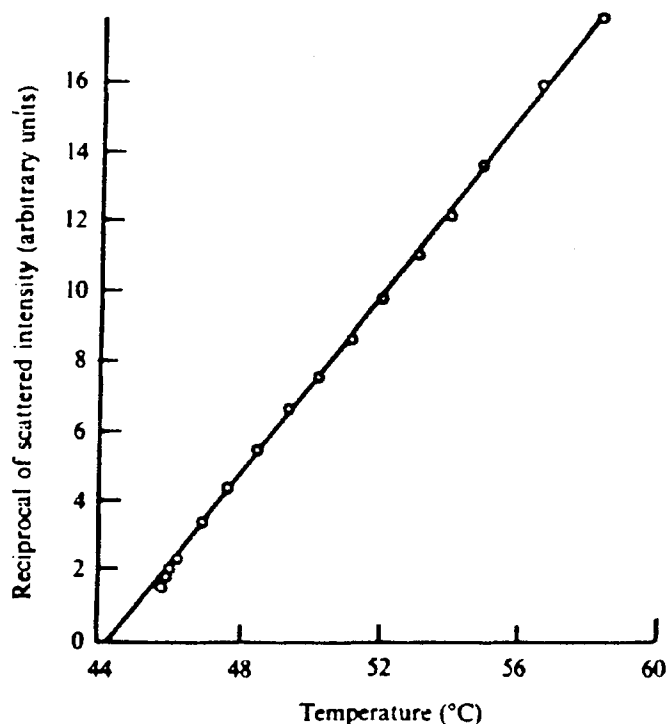


Fig. 2. Reciprocal of the intensity of light scattering in the isotropic phase of MBBA vs temperature, after Stinson et al.¹⁰⁾

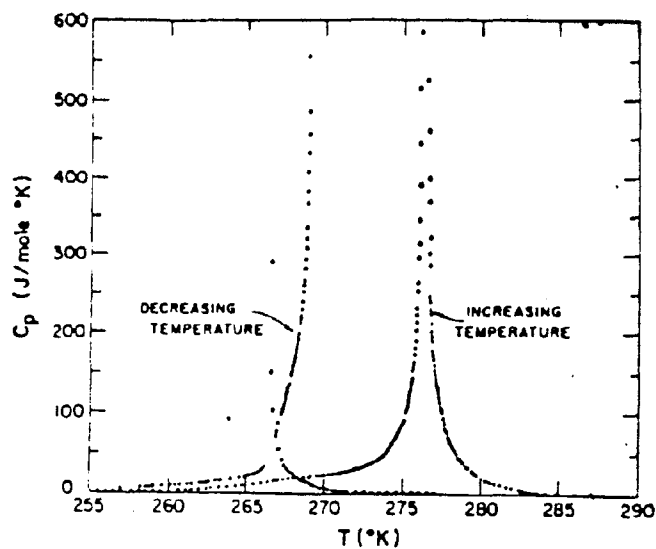


Fig. 3. Heat capacity near the MNM transition in hexagonal NIS, sample No. 1. The transition temperature for the cooling curve has been chosen as the maximum temperature reached after supercooling.

and there are no infinities associated with the heating curve. Broadening of the peak is considered to be due to inhomogeneity in the sample used.

(4) Order-disorder transition in Ni-Mn alloys

According to Collins and Teh,¹²⁾ the rate of disordering of a Ni-Mn alloy shows a “critical slowing down”, as if the transition were of higher order than 1st-order.

(5) Intermetallic compound Cu_3Au

Hashimoto et al. investigated the transitional process in the Cu_3Au alloy from the disordered to the ordered state and the relaxation process in the phase change by measuring the time dependence of the X-ray superstructure linewidth and the electrical resistivity.⁴⁾ The first kind phase transition of Cu_3Au occurs at $T_t = 664.2\text{K}$. In their experiments, the samples were quenched from the disordered state to the ordered state very near the phase transition point. Figure 4 shows the relaxation times, $\tau_{D \rightarrow O}$ for disorder-order transition and $\tau_{O \rightarrow D}$ for the reverse, as a function of temperature. The relaxation time becomes longer as the temperature approaches the phase transition temperature of the 1st-order T_t , and this is considered to be a sort of critical slowing down phenomena. Their experiments seem to be the first to show one of the typical examples of transient phenomena. Furthermore, they found that the average cluster size increases in proportion to the square root of the aging time t , in good agreement with theoretical predictions by Kawasaki et al.¹³⁾ which are based on the TDGL model.

(6) Pseudo-spinodal in phase separation of binary mixture

As studied by Chu et al.,¹⁴⁾ the concentration of one component is taken as the conserved order parameter. In Fig. 5 are shown the inverse intensity for light scattering I_{c0} and the diffusion coefficient a of isobutyric acid/water mixtures as a function of temperature. By extrapolation of these data to zero scattering angle and then to unrealized states below the phase separation temperature, they obtained a common “pseudo-spinodal curve”.

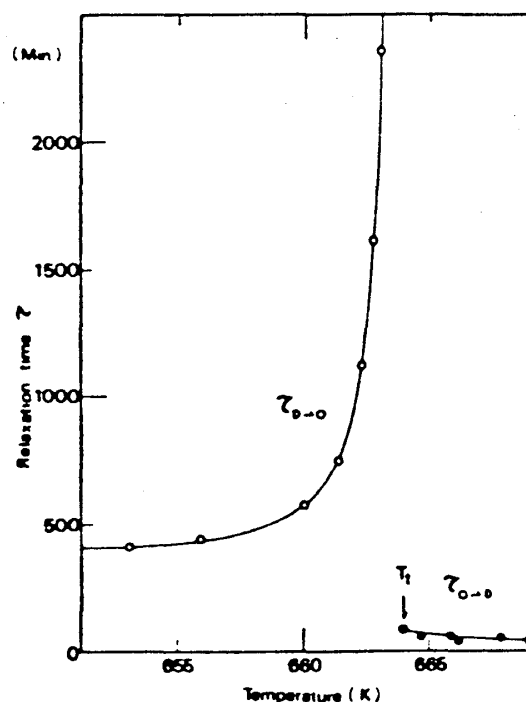


Fig. 4 The temperature dependences of the relaxation time $\tau_{D \rightarrow O}$ and $\tau_{O \rightarrow D}$, $\tau_{D \rightarrow O}$ and $\tau_{O \rightarrow D}$ are shown by the open and the closed circles, respectively.

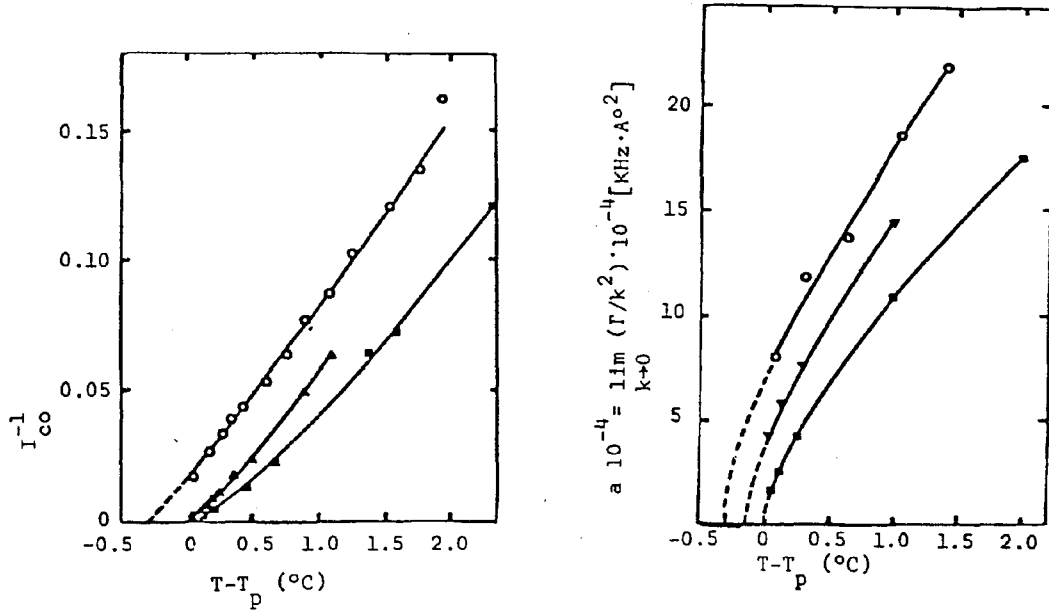


Fig. 5 The temperature dependences of the inverse intensity for light scattering I_{co} and the diffusion coefficient a of isobutyric acid/water mixtures, after Chu et al. (ref. 14).

III. IKEDA'S CLASSIFICATION OF PCP

As mentioned in the introduction, Ikeda has developed a molecular field approach to PCP. His theory is based on earlier works such as Landau's phenomenological theory of phase transitions, extension of "cluster model" developed by Fisher and Domb, and series expansion method (Pada approximation). Thus he obtained "pseudo-critical exponents" and "pseudo-scaling relations" and further discussed "linear and nonlinear relaxations". Now according to the Ikeda theory, the PCP can be classified into two main systems, as shown in Table I: (a) the conserved order parameter system and (b) the non-conserved order parameter system. The latter is associated with the 1st-order phase transition and can be further divided into (b-1) disordered phase and (b-2) ordered

Table I. Ikeda's classification of PCP.

		Examples		
PCP	{	(a) Conserved OP	{ Pseudo-spinodal in phase separation of binary mixture	
		(b) Nonconserved OP	(b-1) Disordered phase	{ Liquid crystals Aqueous solution Metastability limit of supercooling
			(b-2) Ordered phase	{ Binary alloy Ferroelectrics Metal-nonmetal transition Binary fluids

OP: Order parameter.

phase. Some of the experimentally observed examples for each case are also shown in Table I.

The characteristic differences between usual critical phenomena and PCP are summarized in Table II. Usual order parameters correspond to the pseudo-order parameters. The corresponding pseudo-scaling relations are obtained quite similar to the usual scaling relations. Furthermore, additional relations are predicted to exist, such as

$$\alpha_s = \gamma_s, \quad \gamma_s + \beta_s = 1, \quad \beta_s \delta_s = 1,$$

and the values of pseudo-critical exponents are also derived.

Table II. Characteristic differences between usual critical phenomena and pseudo-critical phenomena by the Ikeda theories.

Usual critical phenomena	Pseudo-critical phenomena
Order parameter	Pseudo-order parameter
Scaling relation	Pseudo-scaling relation
$\alpha + 2\beta + \gamma = 2$	$\alpha_s + 2\beta_s + \gamma_s = 2$
$dv = 2 - \alpha$	$dv_s = 2 - \alpha_s$
	$\alpha_s = \gamma_s, \gamma_s + \beta_s = 1, \beta_s \delta_s = 1$
Critical exponents	Pseudo-critical exponents
$\alpha = \alpha' = 0$	$\alpha_s = 1/2$
$\beta = 1/2$	$\beta_s = 1/2$
$\gamma = \gamma' = 1$	$\gamma_s = 1/2$
$\delta = 3$	$\delta_s = 2$

The Ikeda theory on PCP has been constructed within the framework of molecular field theory and to some extent successfully applied to various systems. However, we should note the followings: For the studies of dynamic critical phenomena it is important to establish relations between singular transport coefficients or relaxation times and the singularities of static properties. Although mean field theories and related "conventional theories of critical slowing down" are not very satisfactory near the critical point, more successful treatments have been based on, such as hydrodynamic approaches and scaling arguments, mode-mode coupling approximations, and renormalization group expansions. By taking account of these aspects, more generalized and unified theories will be required.

Moreover, PCP are considered to have a close relationship with other fields of physics, including problems of nonlinear and non-equilibrium open systems which have been developed along with the studies of critical dynamics. Basing on these points, we have tried to classify the field of general critical phenomena.

IV. THREE CIRCLE MODEL

Our classification is shown schematically in Fig. 6, which we tentatively call “three circle model”. The region I of critical phenomena means a whole set of usual critical phenomena at thermo-dynamic equilibrium state. The region II of PCP means the phenomena which show the 2nd-order like 1st-order phase transition and includes the stability limit at metastable state. The region III is the nonequilibrium phase transition phenomena, or nonlinear, nonequilibrium open systems. The overlapping or crossover regions A, B, C, and D are described as follows:

The overlapping region (A) is the phenomena which occur at metastable state of nearly homogeneous systems and at very close to thermal equilibrium state. In this case, anomalies in various transport coefficients associated with the 1st-order phase transition are observed. Typical examples are liquid crystals and binary mixtures. The region (B) is found in non-equilibrium critical phenomena. The examples of this category are critical phenomena in the presence of velocity fields and thermal flux under external disturbances near the critical point at nonequilibrium steady state, as theoretically predicated by Onuki and Kawasaki.¹⁵⁾ Also nonequilibrium super-conductivity of current interest may be included in this region.

The crossover region (C) includes transient phenomena which occur when a thermodynamically stable state is changed suddenly to an unstable state. Typical phenomena are, for example, the order-disorder phase transition of Cu_3Au alloy and spinodal decomposition of binary critical fluids. Finally, the region (D) is seen in transient phenomena which occur from the regions (A), (B), (C) under action of external disturbances. That is, in this region, nonlinear relaxation process near an unstable point is observed. In this sense this region is different from the region (C). For example, the transition from region (A) to (D) is a sort of collapsing process of metastable state in solution systems. The transition from (C) to (D) is likely to be transient phenomena of order-disorder transition observed in Cu_3Au . The transition from (B) to (D) is, for example, a nonlinear relaxation process occurring from near-critical point to an unstable point, or transient phenomena which occur from a stable point to an unstable point near “spinodal”.

Based on this “three circle model”, we shall explain more in detail the crossover and nonlinear

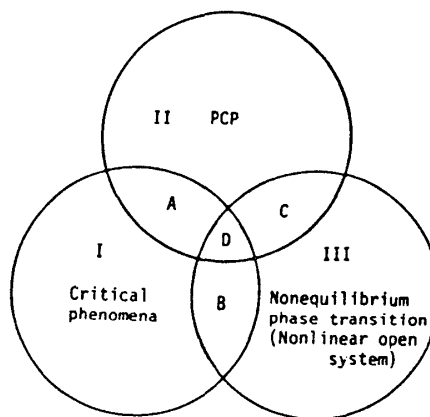


Fig. 6. Three circle model representing schematically a whole set of general critical phenomena, including nonlinear nonequilibrium open systems.

relaxation problems which are so far studied experimentally and theoretically by many workers, and then we shall try to correlate these studies with our model. For crossover phenomena, Ikeda theories treat the transition from the region (I) to (A) as a static problem and from (II) to (C) as a dynamic problem. The Onuki and Kawasaki theory of velocity field of binary mixtures is considered to correspond to the problem of the transition from (B) to (D). Our ultrasonic studies of binary fluids treat the phenomena from (I) to (A) and from (II) to (D). On the other hand, Tomita and Murakami¹⁶⁾ discussed metastability in a system with short-range forces from unified viewpoints of statics and dynamics. Their studies correspond to the transition from (I) to (A) and from (II) to (C). Hashimoto et al. studied Cu₃Au problems which correspond to the transition from (II) to (C). Finally, it is to be noted that the Suzuki scaling theories¹⁷⁾ treat globally nonlinear relaxation problems.

V. ULTRASONIC STUDIES ON PCP IN AQUEOUS SOLUTIONS OF ALCOHOLS

Finally, we shall show our studies on pseudo-critical dynamics in aqueous solutions of aliphatic alcohols using ultrasonic techniques²⁾. Fig. 7 shows a general aspect of criticality in aqueous solutions of aliphatic alcohols. Alcohol molecules are expressed by $C_nH_{2n+1}OH$ (R_n-OH), where the alcohols with $n=1$ are metanol, $n=2$ ethanol, $n=3$ two isomers of normal- and iso-propanol, and $n=4$ four isomers of ter-, secondary-, iso-, and normal-butanol. Their structures are schematically shown here. With the increase of n , the alcohol molecules becomes longer. Aqueous solutions of these alcohols with $n=1$ to 3 and t-BuOH are "noncritical solutions." But only three isomers of sec-, iso-, and n-BuOH with $n=4$ become critical solutions. Thus with increasing n the criticality increases. As is shown, t-BuOH has a structure with high symmetry and so it is soluble in water.

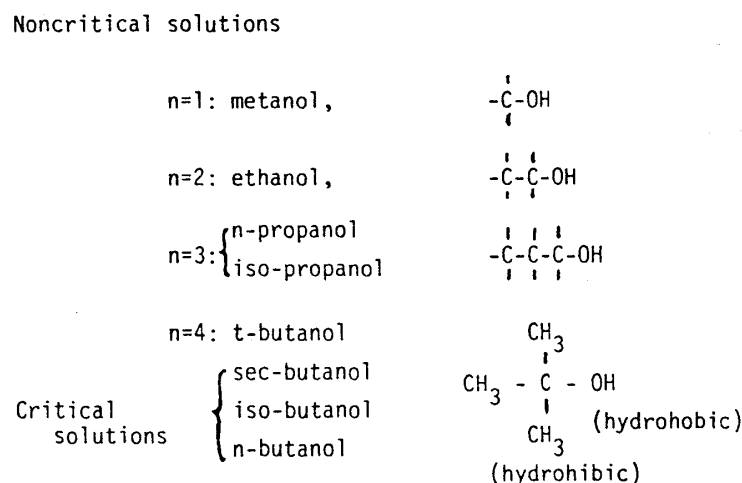


Fig. 7 Criticality in aqueous solutions of aliphatic alcohols $C_nH_{2n+1}OH$ (R_n-OH).

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In aqueous solutions of t-BuOH, the CH₃-chain has a *hydrohobic* interaction with water, while the OH-molecule has a *hydrohobic* interaction.

Typical sound absorptions α/f^2 vs alcohol fraction are shown in Fig. 8¹⁸⁾ With increasing n , the absorption peak increases and the PSAC shifts to a lower alcohol concentration. As shown later, the t-BuOH/water system which is a noncritical solution shows the PCP, in which a 2nd-order like 1st-order phase transition has been observed for the first time by us.

On the other hand, usual critical mixtures possess an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST) and in some cases a closed solubility loop with both, as shown in Fig. 9. Now it is known that a multicomponent system exhibits a multicritical state, forming a projection surface which is made up of temperature T -pressure P -component concentration x space; thermodynamical variables such as pressure, or chemical potential are suitably used. This multicritical point is a thermodynamical singular point characteristic of aqueous solutions and called the "hypercritical point" (HCP). The variable P can be replaced by adding a salt into the solution as the third component and thus the T - P - x space becomes equivalent to the T - μ - x phase space.

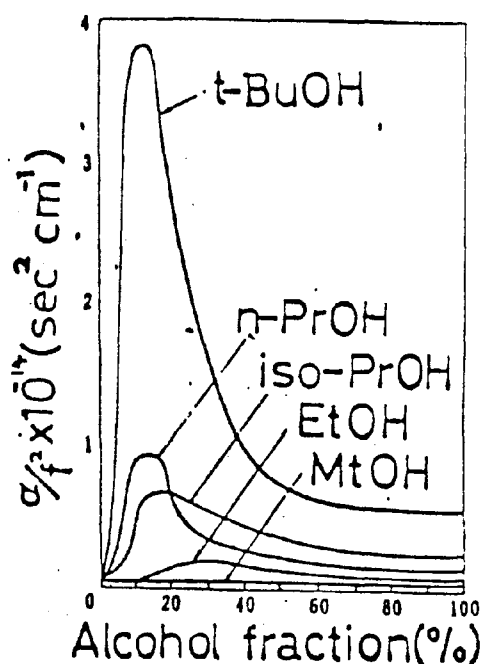


Fig. 8. Sound absorptions vs alcohol fraction, after ref. 18.

The n -BuOH/water/calcium thiocyanate, $\text{Ca}(\text{SCN})_2$, system is one of the typical examples of such multicomponent systems. One of the main conclusions of our work is that the hypercritical state of this solution system is equivalent to the pseudo-critical state of the binary system of t-BuOH/water.

Figures 10 and 11 show the results of sound absorptions for these two solution systems as a

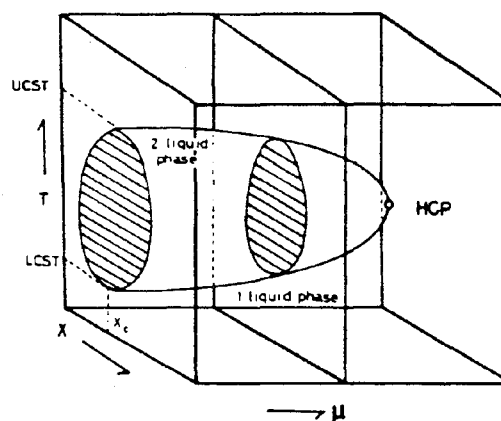


Fig. 9 Schematic phase diagram in T - μ - x space of n -BuOH/ $\text{H}_2\text{O}/\text{Ca}(\text{SCN})_2$ system; HCP is a hypercritical point.

function of each alcohol mole fraction. In each case the absorption peak decreases with increasing the sound frequency, from which we can obtain the relaxation curve as shown later. It should be emphasized that the behavior of noncritical solution of *t*-BuOH/water system is very similar to that of the critical solution of *n*-BuOH/water/Ca(SCN)₂ system observed near the hypercritical state.

The phase diagram of *n*-BuOH/water/Ca(SCN)₂ system was measured in the T - μ cut plane, where μ is the concentration of Ca(SCN)₂ in units of wt. %. Figure 12 shows the result. The shaded region is the critical region. Thus we have determined the hypercritical temperature T_{HC} to be 61°C and the hypercritical concentration μ_{HC} of calcium thiocyanate to be 11.93 wt. %. Sound absorption measurements were carried out along the critical line; and the results are shown in Fig. 13.

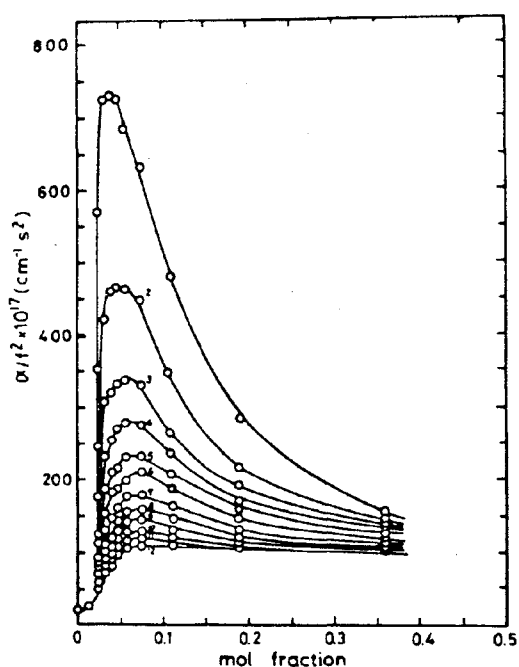


Fig. 10. α/f^2 vs *n*-BuOH concentration of the solution with $\mu=9.8$ wt% at $T=33.0$ C and at various frequencies in MHz units (1) 16.4, (2) 27, (3) 38, (4) 48, (5) 58, (6) 69, (7) 79, (8) 89, (9) 101, (10) 110, (11) 121, (12) 133.

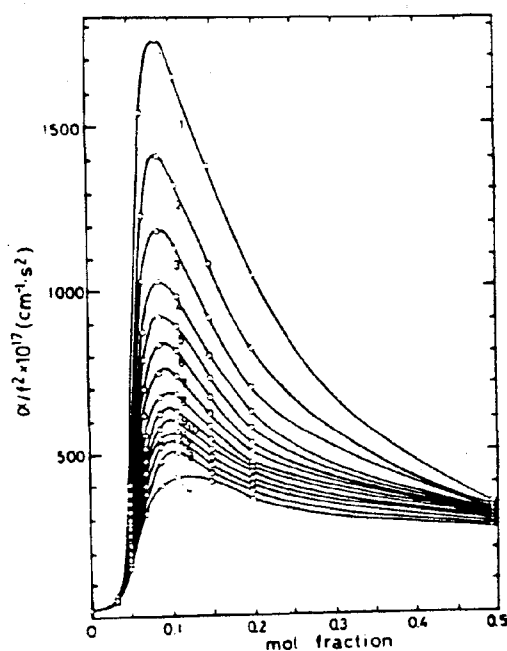


Fig. 11. α/f^2 vs *t*-BuOH concentration of *t*-BuOH H₂O system at 20°C and at various frequencies in MHz units: (1) 15, (2) 25, (3) 35, (4) 45, (5) 55, (6) 65, (7) 75, (8) 85, (9) 95, (10) 105, (11) 115, (12) 125, (13) 135, (14) 165.

We note the following characteristic features:

The critical amplitude and critical region of the divergence in the sound absorptions observed near T_c are rather small and narrow compared with those found in usual critical binary mixtures. As the system approaches the hypercritical point, this divergence decreases appreciably and almost disappears and flattens out at this point. Even though the critical divergence disappears, a nonlinear relaxation spectrum due to order-parameter fluctuations was observed in the frequency dependence

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of sound absorptions near HCP, as will be shown later. The sound absorption increases drastically near the 1st-order transition temperature or the freezing point. Such a behavior is also observed in *t*-BuOH/water system which is due to the 1st-order phase transition very similar to the 2nd-order phase transition.

In this way we have obtained the relaxation spectra at various temperatures for the system with different concentrations, as shown in Figs. 14–16. The first two figures are obtained along the critical line and the last is taken near the HCP. It is of

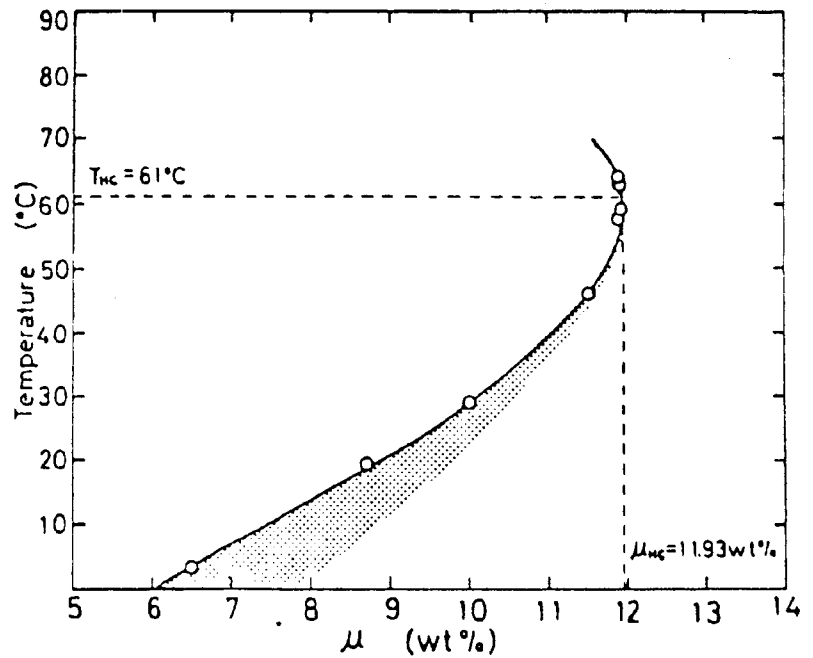


Fig. 12 The T - μ diagram of the *n*-BuOH/water/ $\text{Ca}(\text{SCN})_2$ system. μ is the concentration of calcium thiocyanate in units of wt. %. The shaded region is the critical region.

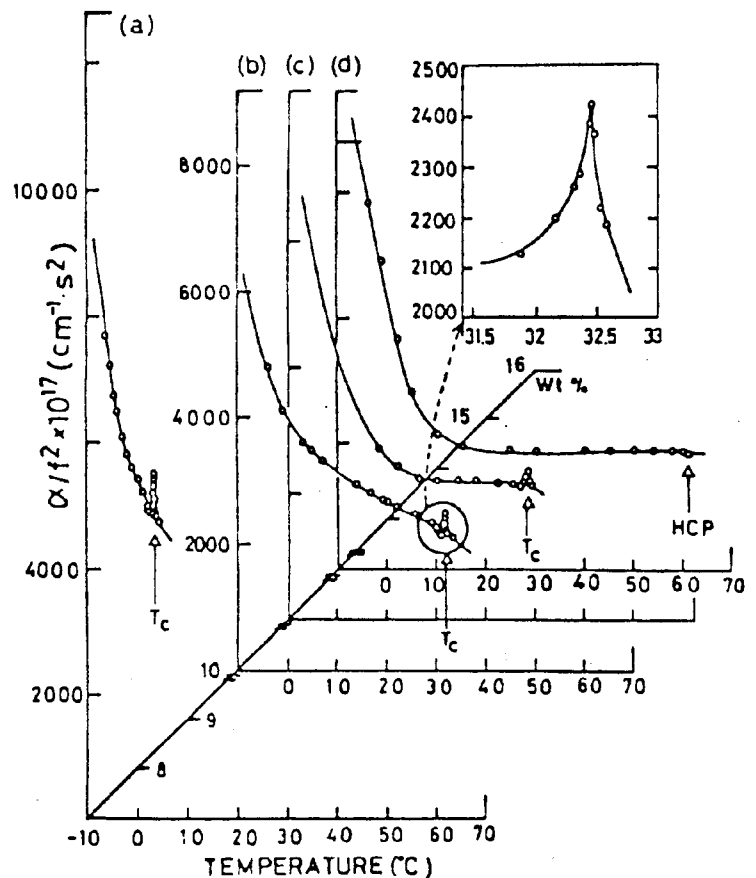


Fig. 13 Temperature dependence of sound absorptions at 4.5 MHz for *n*-BuOH/water/ $\text{Ca}(\text{SCN})_2$ system with different $\text{Ca}(\text{SCN})_2$ concentrations in units of wt. %: (a) 6.5, (b) 9.8, (c) 10.8, and (d) 11.93. The inset shows the extended figure near T_c for the case of (b).

interest to note that these curves do not fit a linear relaxation spectrum of a Debye type, but rather a nonlinear relaxation spectrum of a critical fluctuation type.

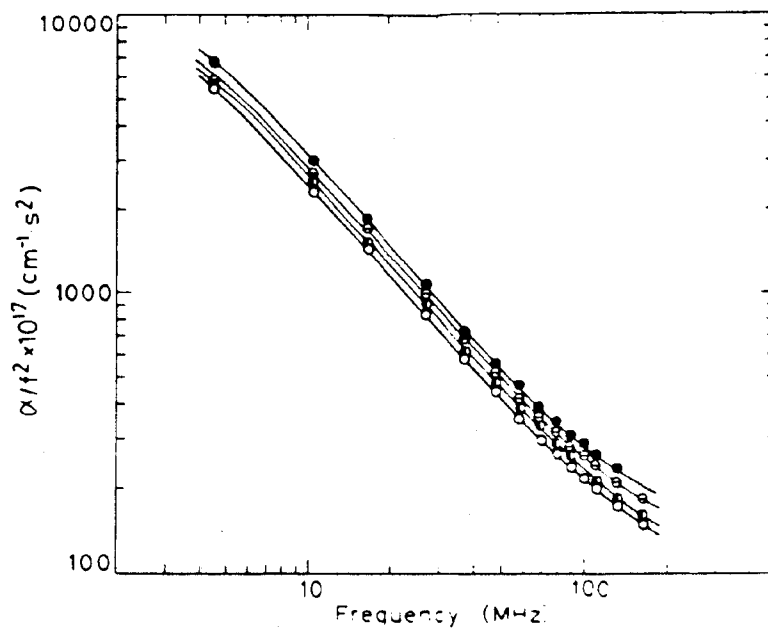


Fig. 14. α/f^2 vs frequency for the sample with $\mu = 6.5$ wt% and $x = 20$ wt% at various temperatures: (●) $T = -4.631$ C, (⊖) $T = -1.991$ C, (⊙) $T = -0.838$ C, (○) $T = 3.350$ C.

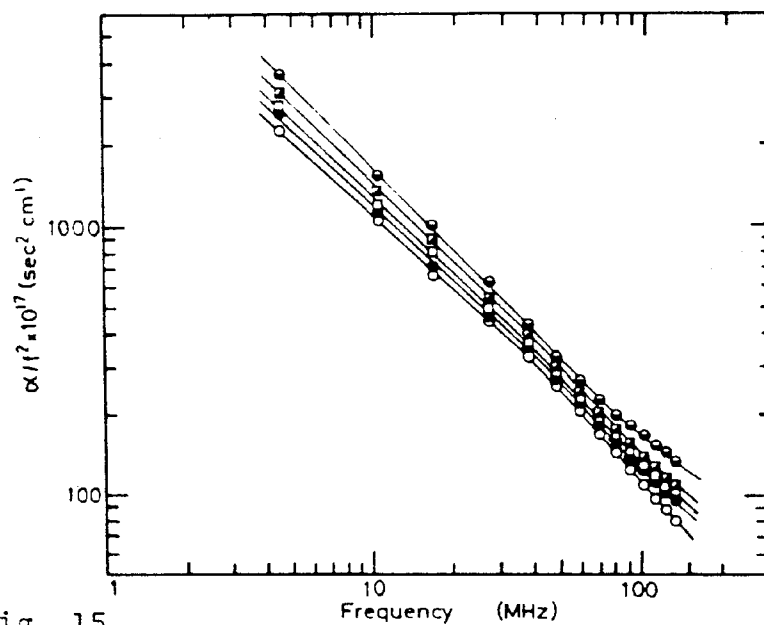


Fig. 15. α/f^2 vs frequency for the sample with $\mu = 9.8$ wt% and $x = 15$ wt% at various temperatures: (⊖) $T = 4.0$ C, (■) $T = 11.0$ C, (□) $T = 17.3$ C, (●) $T = 27.4$ C, (○) $T = 30.9$ C.

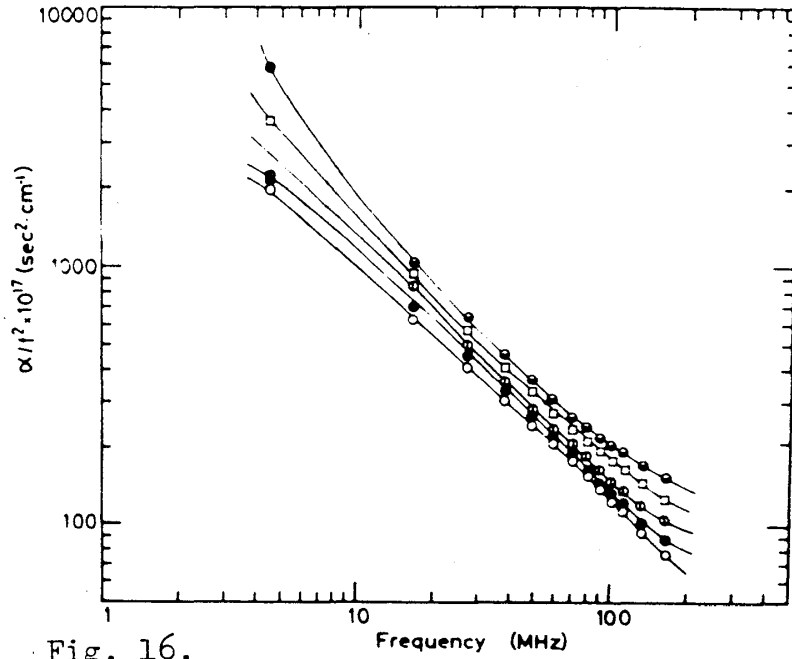


Fig. 16.
 αf^2 vs frequency for the sample with $\mu = 11.93$ wt% and $x = 17$ wt% at various temperatures: (\ominus) $T = -3.73$ C, (\square) $T = 2.07$ C, (\oplus) $T = 10.42$ C, (\bullet) $T = 20.72$ C, (\circ) $T = 61.0$ C.

Now the transition at the HCP takes place from the liquid phase of the 2nd-order transition in binary critical mixtures to the liquid phase of the 1st-order transition. Therefore, in view of the static critical phenomena, we have attempted to apply to this system the expression of “generalized surface critical exponent” on the semi-infinite surface, developed by Bray and Moore.¹⁹⁾ As a model of phase transition, they use a Hamiltonian of the Ginzburg-Landau-Wilson type, containing arbitrary quartic term (e.g., cubic or other anisotropies may or may not be present). The effect of the surface is modeled by the inclusion of an extra “surface” term in the Hamiltonian:

$$H_s = \frac{1}{2} g \int d^d x \delta(z) \sum_i^n \phi_i(x)^2 \quad (1)$$

Here $\phi_i(x)$ is the i -th Cartesian component of the n -component order parameter. The “surface” perturbation, which destroys the translational invariance, is restricted to the plane $z=0$ and the integration in eq. (1) is over all space, not just over the half space $z > 0$. They assume that such a model belongs to the same universality class as a semi-infinite system. The parameter g is proportional to the reduction of the local mean field transition temperature in the surface plane. Then the transition temperature $T_c(g)$ for the formation of a surface phase is related to g by the crossover exponent ϕ_s through the relation

$$T_c(g) - T_c(0) \propto |g|^{1/\phi_s} \quad (2)$$

The bulk-surface crossover exponent is $\phi_s = \nu\lambda_s = 1 - \nu$. To extend this idea to the $T-\mu-x$ field space of the actual system of $n\text{-BuOH}/\text{water}/\text{Ca}(\text{SCN})_2$, we introduce a new expression

$$t' = a\delta^b \text{ with } b = 1/\phi, \quad (3)$$

where $t' = |T_c(g) - T_{\text{HC}}(0)|/T_{\text{HC}}(0)$ and $\delta = |\mu_c(g) - \mu_{\text{HC}}(0)|/\mu_{\text{HC}}(0)$. The least square analysis of the t' vs δ plot yields the value $b = 0.54 \pm 0.02$, as shown in Fig. 17. In conclusion, the HCP is the

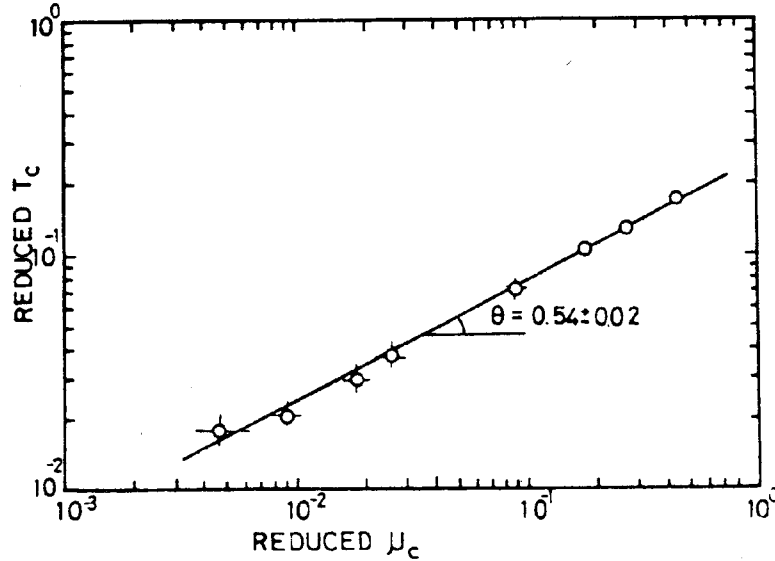


Fig. 17. The reduced T_c vs reduced μ_c or the t' vs δ relation of Eq. (3) for the $n\text{-BuOH}\cdot\text{H}_2\text{O}/\text{Ca}(\text{SCN})_2$ system. The slope θ or $b = 1/\phi$ is 0.54 ± 0.02 .

transition point from the 2nd-order phase transition to the pseudo-critical state, and the transition point corresponds to the crossover point from the critical line to the pseudo-critical state.

In the following we shall discuss the dynamical scaling for PCP. For our solution system the total sound absorption $\psi(\epsilon, \omega)$ can be expressed by three terms,

$$\psi(\epsilon, \omega) = \psi_{\text{pc}}(\epsilon, \omega) + \psi_{\text{bg}}(\epsilon, \omega)f^2 + \sigma(T)f^2, \quad (3)$$

where $\epsilon = |T_{\text{pc}} - T|/T_{\text{pc}}$ is the reduced temperature, ω the angular frequency of the sound, and T_{pc} the pseudo-critical point:

$\psi(\epsilon, \omega)$ = total sound absorption α ,

$\psi_{\text{pc}}(\epsilon, \omega)$ = pseudo-critical sound absorption α_p ,

$\psi_{\text{bg}}(\epsilon, \omega) = \Sigma A_i(\epsilon) / [1 + f/f_{ci}]$, background absorption,

$\sigma(T)$ = classical sound absorption.

Using the extended dynamical scaling idea developed by Ferrell et al. and Halperin and Hohenberg,²⁰⁾

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we may write the pseudo-critical absorption α_p in the form

$$\alpha_p = A \omega^\nu H(\omega\tau) \quad (4)$$

Though the pseudo-critical point T_{pc} is expected to lie below the freezing point, we assume here $T_{pc} \sim T_{fp}$. Then relaxation time of the order parameter fluctuations is written by

$$\tau \sim \epsilon^{-\Delta}, \quad \Delta = \nu z, \quad (5)$$

where z is a dimensionality and Δ a pseudo-critical exponent. Then eq. (4) reduces to

$$\psi_{pc}(\epsilon, \omega) = \alpha_p = A \omega^\nu H(\omega\epsilon^{-\Delta}), \quad (6)$$

with $T \rightarrow T_{fp}$, $\epsilon^{-\Delta} \rightarrow \infty$, and hence the scaling function $H(\omega\epsilon^{-\Delta})$ becomes frequency independent. The pseudo-critical sound absorption α_{pc} at T_{fp} is

$$\alpha_{pc} \sim \omega^\nu. \quad (7)$$

Therefore the ratio of α_p to α_{pc} is expressed by

$$\alpha_p/\alpha_{pc} \sim H(\omega\epsilon^{-\Delta}). \quad (8)$$

In Fig. 18 we plot the reduced absorption α_p/α_{pc} as a function of the reduced frequency for n -BuOH/water/Ca(SCN)₂ system with Ca(SCN)₂ concentration $\mu = 11.93$ wt. % and n -BuOH concentration $x = 17$ wt. %. It can be seen that all the experimental points lie on a single universal function and that the interchangeability between frequency and temperature is well established.

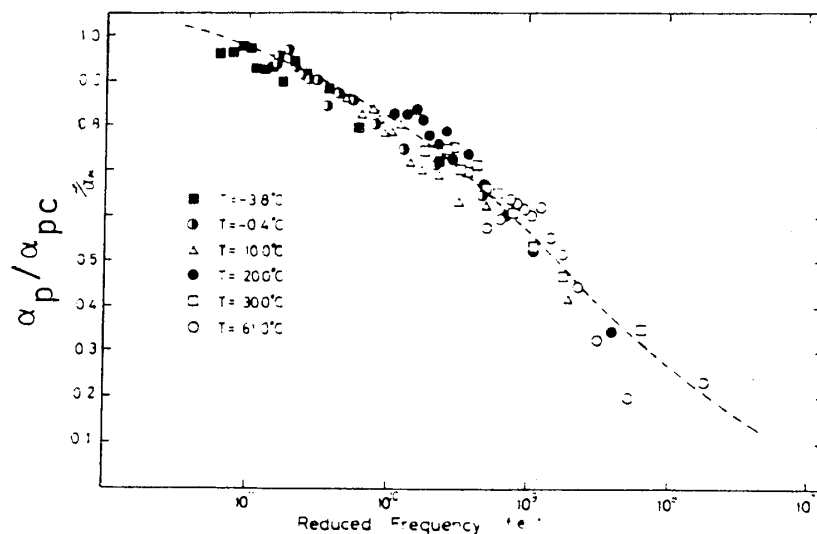


Fig. 18. Reduced absorption vs reduced frequency for the sample with $\mu = 11.93$ wt. % and $x = 17$ wt. % at various temperatures.

On the other hand, in our recent sound absorption experiments for noncritical solution of t-BuOH/water system, we have successfully obtained the temperature dependence of absorptions at various frequencies, as shown in Fig. 19²¹⁾ It is worthy of note that even at the metastable state well below the melting point or freezing point T_{fp} , or in the supercooled state, an anomalous enhancement of the sound absorptions is observed. Furthermore, for this aqueous solution we have confirmed that the dynamical scaling hypothesis for PCP is well established.

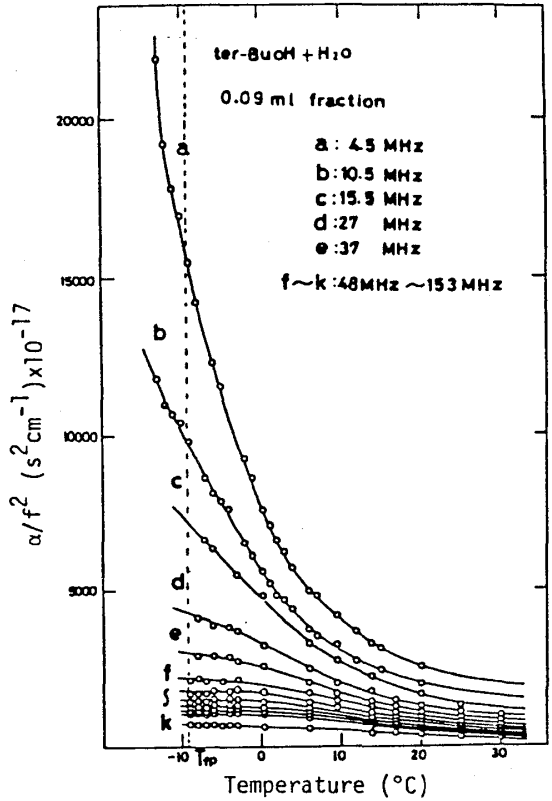


Fig. 19 Temperature dependence of sound absorptions at various frequencies for t-BuOH/water solution.²¹⁾

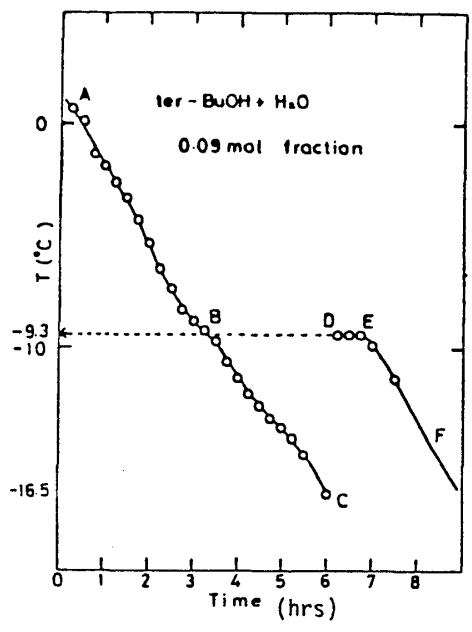


Fig. 20 Supercooling and superheating for t-BuOH/water solution (see text).²¹⁾

Finally, we show the supercooling and superheating experiments for t-BuOH/water system²¹⁾. Figure 20 demonstrates the temperature vs time plot for a solution with 0.09 alcohol mol fraction. The process from A to C is a supercooling curve, while after about 1 minute the system undergoes a superheating from C to D.

In summary, we have clarify the properties of PCP, including dynamical scaling hypothesis. But the discussions given above are rather qualitative. Further theoretical and experimental studies

on PCP will be required, such as the establishment of new scaling argument and universality class for PCP.

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