Slowing Down in Chemical Reactions. The Isobutyric Acid/Water System in the Critical Region

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Ultrasonic attenuation spectra (30 kHz $\leq \nu \leq$ 400 MHz) of the isobutyric acid/water mixture of critical composition and also of the acid itself (50 kHz $\leq \nu \leq$ 1100 MHz) are discussed at different temperatures. Quasielastic light scattering data from photon correlation spectrometry of the critical system are evaluated to yield the amplitude D_0 of the mutual diffusion coefficient in the homogeneous phase. Using literature values for the amplitude of the fluctuation correlation length, the background and critical part of the heat capacity, and the linear coefficient in the pressure dependence of the critical temperature T_C, the sonic attenuation spectrum as predicted by the Bhattacharjee−Ferrell model has been calculated for the critical mixture at T_C. Following again this theoretical model, the contribution due to concentration fluctuations at the temperatures of measurement and also the high-frequency asymptotic background contribution has been subtracted from the experimental spectra. The resulting excess attenuation spectra of the isobutyric acid/water mixture reveal two relaxation processes, both characterized by a discrete relaxation time. These Debye-type relaxations are discussed in terms of the monomer/linear dimer and linear dimer/cyclic dimer equilibria of the carboxylic acid. The relaxation times of the mixture of critical composition exhibit slowing characteristics in the chemical reactions near the critical temperature ($T - T_C < 5$ K) which cannot be explained by the critical behavior of the viscosity. Rather there seems to be an intrinsic effect that slows down near the critical point.

1. Introduction

During the past decades there has been considerable interest in binary liquids near their consolute points, particularly because of their fascinating feature to display order parameter fluctuations of equal importance over a wide range of sizes.[1−8] Much attention has been directed toward universality, renormalization, and scaling. Additionally, Procaccia et al. pointed to effects of critical slowing of chemical reactions which might occur between the constituents of a binary fluid when the system approaches a critical demixing point.[9,10] However, little has been done to elucidate the interrelations between specific molecular interactions and the existence of critical concentration fluctuations.

Because of their periodic variations of temperature and pressure, acoustic fields couple to the spatial Fourier components of the fluctuations. Unique sonic spectra result from the retarded heat transfer within a microheterogeneous liquid. Ultrasonic attenuation and sound velocity measurements, therefore, provide important information upon the molecular dynamics of binary liquids near a critical point. For this reason, there has been considerable activity, both theoretical[11−31] and experimental, in the field of acoustic properties of critical binary liquids. However, most experimental studies, of which we mention only some more recent ones,[32−41] suffer from a too limited frequency range of measurements. Small band measurements are inadequate for several reason. First of all, critical contributions to the sonic spectrum, due to the many scales of the fluctuation correlation length ξ and all the more so of the relaxation rate[7]

$$\omega_D = k_B T/(3\pi\eta_s\xi^3) \tag{1}$$

of the order parameter fluctuations, extend over a very broad frequency range. Hence theoretical models of the critical molecular dynamics can be undoubtedly verified only by broadband acoustical spectrometry. In eq 1 η_s is the shear viscosity of the liquid, k_B denotes the Boltzmann constant, and T is the temperature.

On the basis of the scaling hypothesis,[42−44] the critical part $\alpha_\lambda{}^c$ in the sonic attenuation per wavelength α_λ (=$\alpha\lambda$, α is the total attenuation coefficient, $\lambda = c_s/\nu$ is the wavelength, and c_s is the sound velocity) is assumed to be given by the relation

$$\alpha_\lambda{}^c(\nu,T) = A(T)F(\Omega) \tag{2}$$

Here $A(T)$ denotes a frequency independent amplitude and $F(\Omega)$ the scaling function. The reduced frequency Ω, according to

$$\Omega = 2\pi\nu/\omega_D = 2\pi\nu/(\omega_0\hat{t}^{Z_0\tilde{\nu}}) \tag{3}$$

in strongly dependent upon the reduced temperature

$$\hat{t} = \frac{|T - T_C|}{T_C} \tag{4}$$

Measurements at fixed frequency ν and varying temperature T are thus frequently used to measure the scaling function. This procedure may be questioned because (noncritical) background

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contributions $\alpha_\lambda{}^b$ to the sonic attenuation per wavelength

$$\alpha_\lambda(\nu,T) = \alpha_\lambda{}^c(\nu,T) + \alpha_\lambda{}^b(\nu,T) \tag{5}$$

may remain undiscovered and thus lead to severely incorrect results.[45] In the above relations, T_c is the critical temperature, ω_0 is the amplitude of ω_D, Z_0 denotes the dynamical critical exponent, and $\tilde{\nu}$ is the exponent of the fluctuation correlation length, following power law behavior

$$\xi = \xi_0 \hat{t}^{-\tilde{\nu}} \tag{6}$$

Using eq 6, it is tacitly assumed that background contribution ξ_b to ξ can be neglected.

We recently performed a broadband ultrasonic attenuation study of the critical system ethanol/dodecane[46,47] which, in the frequency range of measurements (0.2 MHz $\leq \nu \leq$ 500 MHz), displays a simple background term only, proportional to the frequency

$$\alpha_\lambda{}^b(\nu,T) = B(T)\nu \tag{7}$$

It was found that for this simple system with unusually small coupling constant g, the experimental scaling function can be well represented by the Folk−Moser scaling function $F_{FM}(\Omega)$[29,30] and, with some reservations, also by the empirical Ferrell−Bhattacharjee scaling function $F_{FB}(\Omega)$[21,23]. At $\Omega < 1$, F_{FB} somewhat exceeds the measured data while F_{FM} remains somewhat below the experimental data, a result to which attention has to be given in future work. We nevertheless feel that theoretical models are so well established that attempts can be made to calculate the critical contribution $\alpha_\lambda{}^c(\nu)$ to complete ultrasonic spectra and to properly extract the noncritical background contributions thereby. From a clear separation of the critical part from noncritical background contributions with relaxation characteristics, we expect valuable insights into the correlations between the fluctuations in concentration and the elementary chemical processes occurring in the binary liquid. In this paper we focus on the system isobutyric acid/water, the critical solution behavior of which has been intensively studied in the past[48−60] applying a variety of experimental methods. In addition to the protolysis reaction, association equilibria exist in carboxylic acid/ water mixtures. It is well established now that preferably single hydrogen-bonded linear dimers (“chain-like”, D_{ch}) and double bonded cyclic dimers (D_{cy}) are formed with the higher homologues of formic acid.[60] Here we inspect the prospective effects of critical concentration fluctuations on the coupled dimerization reactions.

2. Experimental Section

Samples. Various samples of the isobutyric acid/water mixture of critical composition have been prepared using isobutyric acid, $(CH_3)_2CHCOOH$, from Fluka (puriss. p.a., ≥99.5%) without additional purification. Water was deionized, distilled, and UV sterilized. The mass fraction of the critical mixture was $Y_c = 0.392 \pm 0.01$ due to the equal volume criterion. The visually determined critical temperature T_c of the individual samples varied between 26.28 ± 0.02 °C and 26.42 ± 0.02 °C, in conforming with the scatter of literature data (e.g., 26.202,[73] 26.28,[53] 26.38,[55] and 26.393 °C[57]). Pure isobutyric acid was also measured as delivered by the manufacturer.

Ultrasonic Spectrometry. At frequencies between 200 kHz and 400 MHz, the ultrasonic attenuation spectra for the samples of critical composition had been measured previously at the Drittes Physikalisches Institut (DPI) using three methods.[58] Below 1 MHz, utilizing a biplanar cavity cell, a resonator method had been applied.[74] At high frequencies, pulse modulated travelling wave transmission methods had been used in a fixed path (5 MHz $\leq \nu \leq$ 30 MHz) and a variable path length (30 MHz $\leq \nu \leq$ 400 MHz) mode of operation.[75] The spectra for the mixture of critical composition were complemented at the Heat Physics Department (HPD) by reverberation measurements between 30 and 60 kHz.[76] The previous measurements on pure isobutyric acid at 25 °C[58] were completed by spectrometry at 10, 20, 30, and 40 °C (HPD). In these measurements, in addition to the reverberation method,[76] a cavity resonator method ($\nu \leq$ 1 MHz)[76,77] and also further developed versions of a pulse-modulated wave transmission technique was applied.[78] The cavity resonator measurements involved a cell with convexo-concave piezoelectric lenses.[77] The error in the attenuation coefficient data was 20% at $\nu <$ 200 kHz and 5% at $\nu =$ 200 kHz. The error in the values of the measuring frequency was negligibly small. The temperature of the various specimen cells was controlled and measured to within 0.03 K.

Dynamic Light Scattering. In order to determine the mutual diffusion coefficient D, which according to the Kawasaki−Ferrell relation[14,79]

$$D = k_B T/(6\pi\eta_s\xi) \tag{8}$$

is related to the fluctuation correlation length ξ, we used a self-beating digital photon-correlation spectrometer[47] to measure the decay rate Γ of the time autocorrelation function

$$S(q,T) = \exp(-t\Gamma(q,T)) \tag{9}$$

of the light quasielastically scattered from the sample.[80−83] Here

$$q = (4\pi n/\lambda_0)\sin(\theta/2) \tag{10}$$

is the amount of the wave vector selected by the scattering geometry, λ_0 denotes the wavelength of the incident light, n the refractive index of the sample liquid, and θ the scattering angle. In the hydrodynamic limit

$$D(T) = \lim_{q=0}(\Gamma(q,T)/q^2) \tag{11}$$

To enable careful measurements of Γ/q^2 at 30° $\leq \theta \leq$ 145° a specially designed cell[47] was precisely positioned on a goniometer system. The autocorrelation function of the scattered light at each selected scattering angle was determined with the aid of a commercial digital correlation board (ALV Laser, Langen, FRG). It was provided with 288 channels that allow for real time measurements with a characteristic time scale between 2×10^{-7} and 3.4×10^3 s.[84,85] We used a 632.8 nm light source (He−Ne laser, 8 mW) and the usual setup to reach high spatial resolution, to exclude fluorescent light from detection, and to avoid contributions from orientation correlations within the liquid.[86] The temperature of the sample was controlled to within 0.02 K and was measured with an error of less than 0.01 K.

3. Results and Treatment of Data

Isobutyric Acid Ultrasonic Spectra. In Figure 1 a bilogarithmic plot of an ultrasonic excess attenuation spectrum

$$\alpha_\lambda{}^{exc}(\nu) = \alpha_\lambda(\nu) - \alpha_\lambda{}^{asy}(\nu) \tag{12}$$

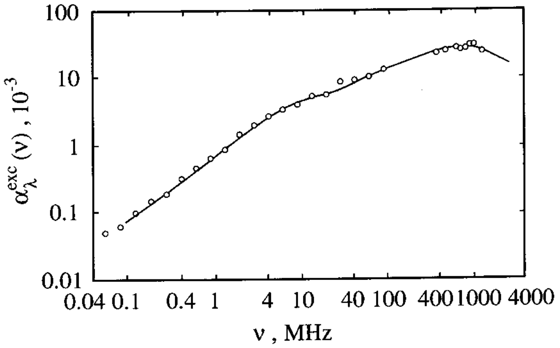

Figure 1. Ultrasonic excess attenuation per wavelength bilogarithmically plotted versus frequency for isobutyric acid at 40 °C. The curve is the graph of the relaxation spectral funcion defined by eq 14 with the parameter values given in Table 1.

TABLE 1: Sound Velocity c_S and Parameters of the Low-Frequency (1) and High-Frequency (2) Debye Term as Well as the Asymptotic High-Frequency Term (B) of the Model Spectral Function R_m (Eq 14) for Isobutyric Acid at Four Temperatures T

T (°C)	c_S (m/s) ±0.5%	$10^{-3}A_1$ ±10%	τ_1 (ns) ±20%	$10^{-3}A_2$ ±10%	τ_2 (ns) ±20%	B (ps) ±5%
10	1192	4.6	26	54	0.47	66.6
20	1156	5.8	18	55	0.37	63.4
30	1118	5.2	14	51	0.33	53.5
40	1082	6.6	10	57	0.25	46.6

is shown for pure isobutyric acid. The asymptotic high-frequency part (eq 7)

$$\alpha_\lambda^{asy}(\nu) = B(T)\nu \tag{13}$$

with B independent of ν has been subtracted from the total attenuation per wavelength α_λ in order to accentuate the two relaxation regions in the spectrum. These relaxations with relaxation frequencies ν_1 and ν_2 around 10^7 and 10^9 Hz, respectively, can be analytically represented by Debye-type relaxation terms with discrete relaxation times $\tau_i = (2\pi\nu_i)^{-1}$, $i = 1, 2$. We thus fitted the model relaxation function ($\omega = 2\pi\nu$)

$$R_m(\nu) = A_1\omega\tau_1/(1 + \omega^2\tau_1^2) + A_2\omega\tau_2/(1 + \omega^2\tau_2^2) + B\nu \tag{14}$$

to the measured spectra using a nonlinear least-squares regression analysis.[87] The values for the parameters of R_m are displayed in Table 1.

Mixture of Critical Composition. In Figure 2 the excess attenuation spectrum for the mixture of critical composition is shown for two temperatures distinctly above the upper critical demixing temperature T_c. Again two relaxation regimes emerge. The relaxation frequencies, however, are shifted to somewhat smaller frequencies and the relative magnitude of the relaxation amplitude changed. The spectra can no longer be described by a sum of two Debye-type relaxation terms only. Particularly at low frequencies, where a Debye term displays a simple linear log α_λ vs log ν behavior with slope

$$\lim_{\nu\to 0}[\mathrm{d}(\log \alpha_\lambda^{\mathrm{Debye}})/\mathrm{d}(\log \nu)] = 1 \tag{15}$$

smaller slopes are found for the spectra of the mixture of critical composition. Moreover, the slope noticeably decreases when approaching the critical point, as characteristic for critical contributions $\alpha_\lambda^c(\nu)$ to the ultrasonic spectrum. Since no reliable subdivision of the measured spectra into two Debye terms, the asymptotic high-frequency term and a critical term due to concentration fluctuations, is possible without any restrictions in the parameter values,[58] we shall fix the critical contribution in the following.

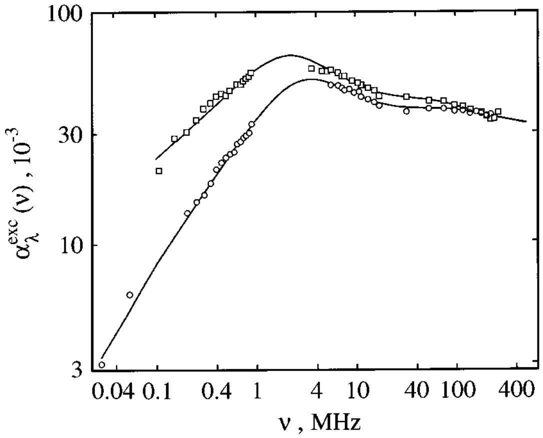

Figure 2. Ultrasonic excess attenuation spectra for the isobutyric acid/water mixture of critical composition at 35 °C (□, $T - T_C = 8.58$ K) and at 30 °C (○, $T - T_C = 3.58$ K).

In a broadband ultrasonic study of the system ethanol/dodecane,[46] we found the Folk–Moser scaling function F_{FM} to be somewhat superior to the Ferrell–Bhattacharjee scaling function F_{FB}, as mentioned in the Introduction. We shall nevertheless use the FB model here to calculate the critical contribution to the sonic attenuation because all necessary parameters are available. Following this procedure we tacitly assume that the different contributions superimpose linearly in the acoustic spectra.

Ferrell and Bhattacharjee have presented the empirical relation[23]

$$F_{FB}(\Omega) = \Omega(1 + \Omega^{1/2})^{-2} \tag{16}$$

for the scaling function. Hence using eq 3 the F_{FB} function can be calculated provided the amplitude ω_0 of the relaxation rate of the order parameter fluctuations is known. If eqs 1 and 8 are analogously applied, the amplitude

$$\omega_0 = 2D_0/\xi_0^2 \tag{17}$$

can be obtained from the amplitudes of the diffusion coefficient and the fluctuation correlation length. We used our light scattering data to determine the mutual diffusion coefficient (eq 11) as a function of temperature. The D vs T relation as measured in the homogeneous phase close to the critical temperature is displayed in Figure 3. When fitted to the power law

$$D(T) = D_0\hat{t}^{\nu^*} \tag{18}$$

these data yield $D_0 = 5.9 \times 10^{-10}$ m^2 s^{-1} if the exponent is fixed at $\nu^* = 0.664$, as predicted by mode coupling theory.[14] Using $\xi_0 = 3.6 \times 10^{-10}$ m from the literature,[88] $\omega_0 = 9.1 \times 10^9$ s^{-1} follows, and with the aid of this value $F_{FB}(\Omega)$ can be calculated.

The critical concentration $\alpha_\lambda^c(\nu,T)$ to the ultrasonic spectrum at a temperature T, according to[23]

$$\alpha_\lambda^c(\nu,T) = \alpha_\lambda^c(\nu,T_c)F_{FB}(\Omega) \tag{19}$$

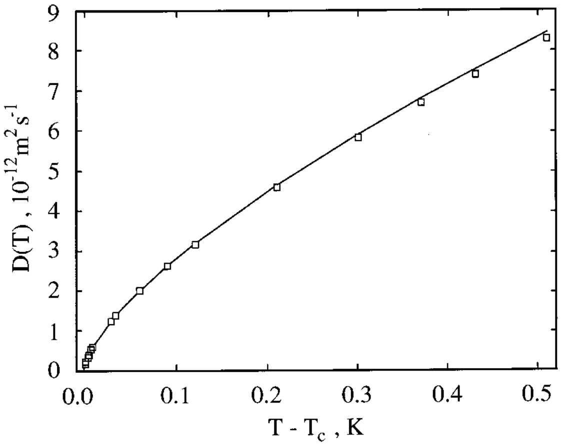

Figure 3. Mutual diffusion coefficient D of the isobutyric acid/water/ mixture of critical composition displayed versus $T - T_C$. The curve shows the power law behavior predicted by the theory (eq 18) with the critical exponent $\nu^* = 0.664$ and the amplitude $D_0 = 5.9 \times 10^{-10}$ m^2 s^{-1}.

is controlled by the scaling function F_{FB} and the critical contribution $\alpha_\lambda{}^c(\nu,T_c)$ at the critical temperature. Following again the Ferrell–Bhattacharjee model[83]

$$\alpha_\lambda{}^c(\nu,T_c) = S c_s \nu^{-\delta} \tag{20}$$

where $\delta = \alpha_0/(Z_0\tilde{\nu}) = 0.06$ and

$$S = \frac{\pi^2 \delta C_0^c}{2T_c}\left(\frac{\Omega_{1/2}\omega_0}{2\pi}\right)^{\delta}\frac{c_s(T_c)g^2}{C_p{}^2} \tag{21}$$

In these equations α_0 is the critical exponent of the specific heat

$$C_p = C_0^c \hat{t}^{-\alpha_0} + C_0^b \tag{22}$$

$\Omega_{1/2} = (\omega/\omega_0)t^{-Z_0\tilde{\nu}}$ (= 2.67) is the dimensionless half-attenuation frequency[23] and g is the coupling constant, given by

$$g = \rho(T_c)C_p\left(\frac{dT_c}{dp} + \frac{T\alpha_p^c}{\rho C_p}\right) \tag{23}$$

with the thermal expansion coefficient α_p^c for the mixture of critical composition. Using $\rho(T_c) = 0.99$ g m^{-3},[53] $dT_c/dP = -5.5 \times 10^{-7}$ K/Pa,[89] $C_0^b = 3.5$ J g^{-1} K^{-1},[53] and $C_0^c = 3.5 \times 10^{-2}$ J g^{-1} K^{-1},[53] $g = 2.1$, and $S = 6.5 \times 10^{-5}$ m^{-1} s$^{0.94}$ follows. With these values and with the sound velocities obtained as a byproduct from our ultrasonic attenuation measurements (Table 2), we are able to calculate the critical contribution

$$\alpha_\lambda{}^c(\nu,T) = c_s S \nu^{-0.06} F_{FB}(\Omega) \tag{24}$$

to the measured ultrasonic attenuation spectra. In doing so we also used the alternative form of the scaling function

$$F_{FB}(\Omega) = [1 + 0.414(\Omega_{1/2}/\Omega)^{1/2}]^{-2} \tag{25}$$

given by Ferrell and Bhattacharjee.[23]

Two ultrasonic excess attenuation spectra from which the critical part, due to concentration fluctuations, has been subtracted, are displayed in Figure 4. The remaining contributions to the frequency-dependent sonic attenuation again can be well described by a sum of two Debye type relaxations. This correspondence with the pure isobutyric acid spectra may be taken to indicate that the $\alpha_\lambda{}^c(\nu,T)$ part has been appropriately considered. Hence we fitted the relaxation spectral function $R_m(\nu)$ also to the $\alpha_\lambda(\nu,T) - \alpha_\lambda{}^c(\nu,T)$ spectra for the mixture of critical composition. The parameter values obtained thereby are presented in Table 2. Also given in that compilation of data are the values for the relaxation rate ω_D as following from the power law behavior (eq 3) and $\omega_0 = 9.1 \times 10^9$ s^{-1}.

TABLE 2: Sound Velocity c_S, Relaxation Rate ω_D of Concentration Fluctuations, and Parameters of the Relaxation Spectral Function Defined by Eq 14 for the Isobutyric Acid/Water Mixture of Critical Composition with $T_C = 26.46$ °C

T (°C)	$10^{-3}\hat{t}$	c_S (m/s) ±0.2%	$10^3\omega_D$ (s^{-1})	$10^{-3}A_1$ ±10%	τ_1 (ns) ±10%	$10^{-3}A_2$ ±10%	τ_1 (ns) ±20%	B (ps) ±10%
26.46	0.1335	1411.3	0.3	74	180	31	6.6	66
26.57	0.5005	1411.3	3.9	82	156	30	4.5	66
26.68	0.8672	1411.2	11.2	94	124	27	2.7	63
26.90	1.600	1411.2	36.7	99	112	25	1.9	60
27.0	1.932	1411.1	52.8	99	108	25	1.7	61
28.0	5.246	1410.4	365	99	99	21	1.7	60
30.0	11.81	1410.1	1770	93	85	18	1.7	59
35.0	27.84	1405.7	9570	72	58	17	1.6	58

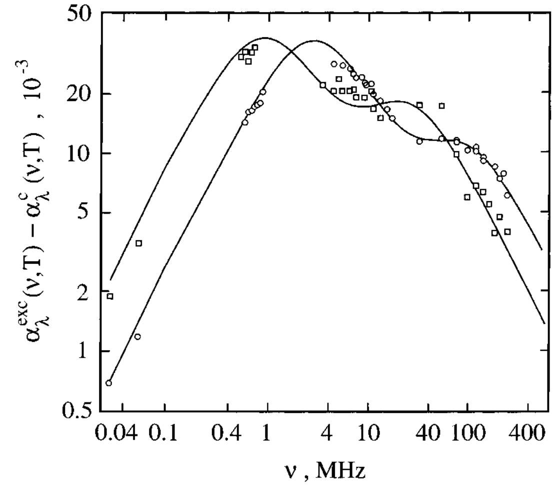

Figure 4. Ultrasonic excess attenuation without the critical contribution as calculated according to the Bhattacharjee–Ferrell theory, displayed at 35 °C (□, $T - T_C = 8.58$ K) and at 26.46 °C (○, $T - T_C = 0.04$ K). The curves are graphs of the double-Debye-term relaxation spectral function (eq 14) with the parameters given in Table 2.

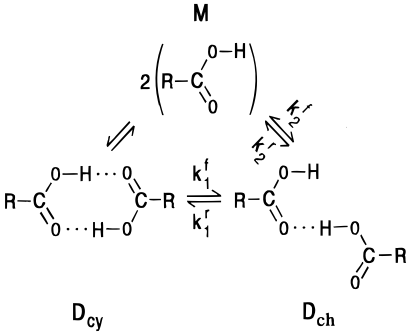

Figure 5. Scheme of coupled reactions for the formation of single-H-bonded chainlike dimers D_{ch} and double-H-bonded cyclic dimers D_{cy} from carboxylic acid monomers M.

4. Discussion

It is now well established[60,63,66,72,90−92] that in pure carboxylic acids and also in carboxylic acid/water mixtures association equilibria exist as depicted in Figure 5. It is also accepted that the high-frequency relaxation term ("2") in the ultrasonic spectra reflects the monomer/chainlike dimer equilibrium

$$2\mathrm{M} \underset{k_2^{\mathrm{r}}}{\overset{k_2^{\mathrm{f}}}{\longleftrightarrow}} \mathrm{D}_{\mathrm{ch}} \tag{26}$$

and the low-frequency relaxation ("1") the equilibrium between both types of dimers

$$\mathrm{D}_{\mathrm{cy}} \underset{k_1^{\mathrm{r}}}{\overset{k_1^{\mathrm{f}}}{\longleftrightarrow}} \mathrm{D}_{\mathrm{ch}} \tag{27}$$

Since the relaxation times τ_1 and τ_2 differ by about 2 orders of magnitude, both steps of the total reaction 2M ⇔ D_{cy} are assumed to be largely decoupled from one another. The dimer/dimer reaction has been found to be significantly promoted by catalytic action from hydronium ions ("A", acid) and carboxylate ions ("B", base) so that eq 27 has to be completed[90−92]

$$\mathrm{A} + \mathrm{D}_{\mathrm{cy}} \underset{k_{\mathrm{a}}^{\mathrm{r}}}{\overset{k_{\mathrm{a}}^{\mathrm{f}}}{\longleftrightarrow}} \mathrm{D}_{\mathrm{ch}} + \mathrm{A} \tag{27a}$$

$$\mathrm{B} + \mathrm{D}_{\mathrm{cy}} \underset{k_{\mathrm{b}}^{\mathrm{r}}}{\overset{k_{\mathrm{b}}^{\mathrm{f}}}{\longleftrightarrow}} \mathrm{D}_{\mathrm{ch}} + \mathrm{B} \tag{27b}$$

The relaxation rate τ_1^{-1} related to the cyclic dimer/chainlike dimer reaction is then given by the relation

$$1/\tau_1 = k_1^{\mathrm{f}} + k_1^{\mathrm{r}} + (k_{\mathrm{a}}^{\mathrm{f}} + k_{\mathrm{a}}^{\mathrm{r}})c(\mathrm{A}) + (k_{\mathrm{b}}^{\mathrm{f}} + k_{\mathrm{b}}^{\mathrm{r}})c(\mathrm{B}) \tag{28}$$

where $c(\mathrm{A})$ and $c(\mathrm{B})$ denote the concentrations of the hydronium ions and carboxylate ions, respectively. The forward and reverse rate constants are independent of concentrations. The rate constants for the reverse reaction (formation of a double hydrogen-bonded cyclic dimer from a single-bonded chainlike dimer), however, are inversionaly proportional to the viscosity η_{s} of the solution, due to the molecular rotation around the direction of the existing hydrogen bond involved in this step. Following Corsaro and Atkinson[66]

$$k_i^{\mathrm{r}} = k_{i0}^{\mathrm{r}} \frac{\eta_{\mathrm{s}}(Y{=}1)}{\eta_{\mathrm{s}}(Y)} \qquad i = 1, a, b \tag{29}$$

in eq 28.

The relaxation rate of the monomer/chainlike dimer reaction step, according to[93]

$$1/\tau_1 = 4k_2^{\mathrm{f}} c(\mathrm{M}) + k_2^{\mathrm{r}} \tag{30}$$

is related to the rate constants k_2^{f} and k_2^{r} and to the monomer concentration $c(\mathrm{M})$. Let us assume the formation/disruption of the hydrogen bond itself to be very fast as compared to τ_2. The bonding strength of the hydrogen bonds in pure water, for example, fluctuates very rapidly, with correlation times on the order of 0.1−1 ps.[94,95] Hence it may be justified to consider the dimerization reaction to be diffusion-controlled so that[93]

$$k_2^{\mathrm{f}} = k_{20}^{\mathrm{f}} D_{\mathrm{M}} \qquad k_2^{\mathrm{r}} = k_{20}^{\mathrm{r}} D_{\mathrm{M}} \tag{31}$$

with D_{M} denoting the diffusion coefficient of carboxylic acid monomers.

Let us now inspect the relaxation times τ_1 and τ_2 as extracted from the ultrasonic attenuation spectra. In Figure 6 the relaxation times for pure isobutyric acid are logarithmically plotted as a function of $1/T$. This plot has been chosen because the formation of the hydrogen-bonded chainlike dimer from monomers and also the single-bonded/double-bonded dimers reaction are assumed to be governed by activation barriers. Hence the temperature dependence of the relaxation times is assumed to be controlled by Eyring relations[96]

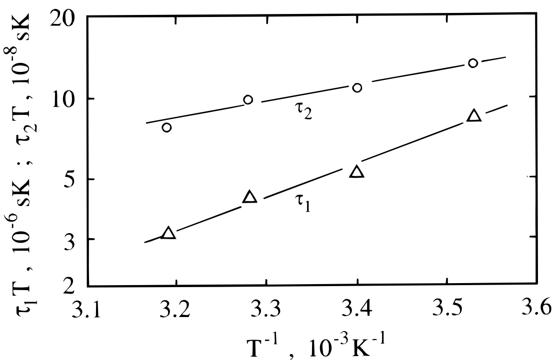

Figure 6. Eyring plot of the relaxation times of the low-frequency (τ_1) and the high-frequency (τ_2) Debye term in the isobutyric acid excess attenuation spectra.

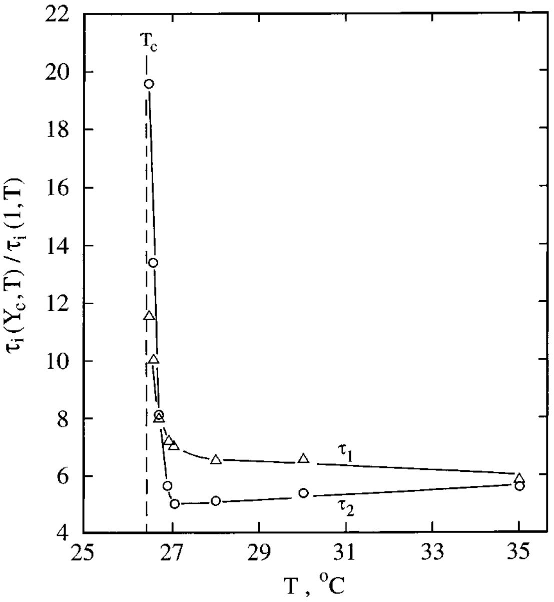

Figure 7. Relaxation time ratio $\tau_i(Y{=}Y_c,T)/\tau_i(Y{=}1,T)$, $i = 1$,2 versus temperature. The curves are drawn just to guide the eye. The $\tau_i(Y{=}1,T)$ values have been interpolated due to the Eyring type behavior (eq 32; Figure 6).

$$\tau_i = \frac{h}{k_{\mathrm{B}}T} C_{\mathrm{f}i} \exp\left(\frac{\Delta G_i^{\ddagger}}{k_{\mathrm{B}}T}\right), \quad i = 1, 2 \tag{32}$$

In this equation $C_{\mathrm{f}i}$, $i = 1$,2 denote configurational factors almost independent of T and $\Delta G_i^{\ddagger} = \Delta H_i^{\ddagger} - T\Delta S_i^{\ddagger}$ are the Gibbs free energies of activation. The relaxation times τ_1 and τ_2 for isobutyric acid follow an Eyring behavior as predicted by eq 32. The plots in Figure 6 yield $\Delta H_1^{\ddagger} = 26.5 \pm 5$ and $\Delta H_2^{\ddagger}$ 11.7 ± 2 kJ/mol. Both values are in the order of hydrogen bond energies. The finding of $\Delta H_1^{\ddagger} > \Delta H_2^{\ddagger}$ may in parts be due to the viscosity effect in the τ_1 data which tends to enhance the variation of the relaxation time with temperature.

In order to demonstrate the particular temperature effect in the relaxation times of the isobutyric acid/water mixture of critical composition, a plot of the ratios $\tau_i(Y{=}Y_{\mathrm{C}},T)/\tau_i(Y{=}1,T)$ as a function of T is given in Figure 7. At 27 °C ≤ T ≤ 35 °C these ratios reveal almost identical temperature dependences in the relaxation times of the mixture and of the pure acid, recpectively. At $T - T_{\mathrm{c}} < 0.5$ K, however, the relaxation times

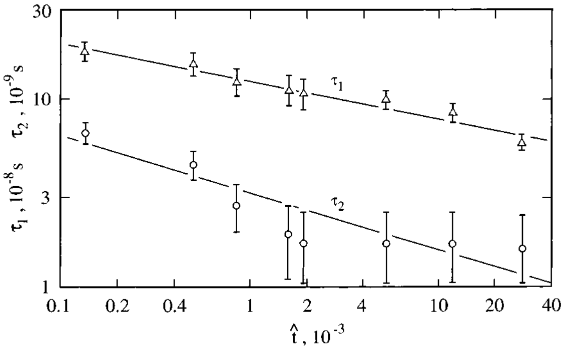

Figure 8. Bilogarithmic plot of the relaxation times τ_i, $i = 1$, 2 of the isobutyric acid/water mixture of critical composition versus the reduced temperature $\hat{t}$. The lines indicate power law behavior (eq 33).

of the mixture of critical composition substantially increase when approaching the critical temperature.

The high-frequency relaxation term is located at the upper limit of our frequency range of measurements (Figures 2,4) where it interferes with the asymptotic high-frequency contribution α_λ^{asy}. The τ_2 values, therefore, are subject to considerable errors, not shown in Figure 7 for reasons of clearness of the plot. Nevertheless, our spectra seem to reveal a noticeable effect of critical slowing in the monomer/chainlike dimer reaction and there exists clearly a substantial effect of slowing down in the single-bonded/double-bonded dimer reaction. In Figure 8 a bilogarithmic plot of τ_1 and τ_2 as a function of reduced temperature $\hat{t}$ is given. Within the limits of experimental error, the temperature dependence of both relaxation times can be represented by a power law

$$\tau_i = \tau_{i0}\hat{t}^{-\gamma_i}, \quad i = 1, 2 \tag{33}$$

For τ_2 there are indications of a background contribution τ_{2b} with small dependence upon temperature, $\tau_2 = \tau_{2c} + \tau_{2b}$, where τ_{2c} follows a power law (eq 33). A clear-cut conclusion upon the existence of a background contribution in the relaxation time of the monomer/chainlike dimer reaction requires precise attenuation data at even higher frequencies. Applying the relation defined in eq 33 yields $\gamma_1 = 0.2 \pm 0.05$ and $\gamma_2 = 0.3 \pm 0.2$. Since the viscosity of the isobutyric acid/water mixture of critical composition varies near T_c[97] as $\eta_S = \eta_{S0}\hat{t}^{-0.04}$ only, the power law behavior in the relaxation time of the low-frequency single-bonded/double-bonded dimer reaction cannot be solely due to an effect of viscosity (eq 29). Hence there must exist an intrinsic mechanism that slows down near the critical demixing point. On the contrary, due to the exponent $\nu^* = 0.664$ in the power law behavior of the mutual diffusion coefficient (eq 18), it appears to be likely that the diffusion-controlled monomer chainlike dimer reaction (eq 31) near T_c is largely governed by the critical slowing of the diffusion coefficient D_M of monomers.

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References and Notes

(1) Fisher, M. E. *The Nature of Critical Points*; University of Colorado Press: Boulder, 1965.

(2) Stanley, H. E. *Introduction to Phase Transitions and Critical Phenomena*; Clarendon Press: Oxford, UK, 1971.

(3) Ma, S. K. *Modern Theory of Critical Phenomena*; Benjamin: Reading, MA, 1976.

(4) Sengers, J. V. In *Progress in Liquid Physics*; Croxton, C. A., Ed.; Wiley: Chichester, UK, 1978. p 103.

(5) Patashinskii, A. Z.; Pokrovckii, V. L. *Fluctuation Theory of Phase Transitions*; Pergamon Press: Oxford, UK, 1979.

(6) Wilson, K. G. *Sci. Am.* **1979**, *241*, 140.

(7) Anisimov, M. A. *Critical Phenomena in Liquids and Liquid Crystals*; Gordon and Breach: Philadelphia, PA, 1991.

(8) Brown, L. M. *Renormalization*; Springer: Berlin, 1993.

(9) Procaccia, I.; Gittermann, M. *Phys. Rev. Lett.* **1981**, *46*, 1163.

(10) Hentschel, H. G. E.; Procaccia, I. *J. Chem. Phys.* **1982**, *76*, 666.

(11) Fixman, M. *J. Chem. Phys.* **1960**, *33*, 1363.

(12) Fixman, M. *Adv. Chem. Phys.* **1964**, *4*, 175.

(13) Kawasaki, K. *Phys. Rev.* **1966**, *150*, 291.

(14) Kawasaki, K. *Ann. Phys.* **1970**, *61*, 1.

(15) Khabibullaev, P. K.; Aliev, S. S.; Shakhparanov, M. I.; Kvasova, L. E. In *Fizika i Fizika-Khimiya Zhidkostey*; Shakhparonov, M. I., Ed.; Moscow State University: Moscow, 1972.

(16) Mistura, L. *J. Chem. Phys.* **1972**, *57*, 2311.

(17) Chaban, L. A. *Sov. Phys. Acoust.* **1975**, *21*, 64; 177.

(18) Kroll, D. H.; Ruhland, J. H. *Phys. Lett.* **1980**, *80A*, 45.

(19) Kroll, D. H.; Ruhland, J. H. *Phys. Rev. A* **1981**, *23*, 371.

(20) Shiwa, Y.; Kawasaki, K. *Prog. Theor. Phys.* **1981**, *66*, 118; 406.

(21) Bhattacharjee, J. K.; Ferrell, R. A. *Phys. Rev. A* **1981**, *24*, 1643.

(22) Kawasaki, K.; Shiwa, Y. *Physica A* **1982**, *113*, 27.

(23) Ferrell, R. A.; Bhattacharjee, J. K. *Phys. Rev. A* **1985**, *31*, 1788.

(24) Tanaka, H.; Wada, Y. *Phys. Rev. A* **1985**, *32*, 512.

(25) Drossel, B.; Schwabl, F. *Z. Phys. B* **1993**, *91*, 93.

(26) Dengler, R.; Schwabl, F. *Europhys. Lett.* **1993**, *24*, 533.

(27) Onuki, A. *Phys. Rev. E* **1997**, *55*, 403.

(28) Onuki, A. *J. Phys. Soc. Jpn.* **1997**, *66*, 511.

(29) Folk, R.; Moser, G. *Phys. Rev. E* **1998**, *57*, 705; *58*, 6246.

(30) Folk, R.; Moser, G. *Int. J. Thermophys.* **1998**, *19*, 1003.

(31) Bhattacharjee, J. K.; Ferrell, R. A. *Physica A* **1998**, *250*, 83.

(32) Hornowski, T.; Labowski, M. *Arch. Acoust.* **1990**, *3/4*, 301.

(33) Davidovich, L. A.; Karabaev, M. K.; Shinder, I. I. *Sov. Phys. Acoust.* **1990**, *36*, 205.

(34) Hornowski, T.; Labowski, M. *Acustica* **1990**, *72*, 96.

(35) Inoue, N.; Marakami, Y.; Kato, M.; Hasagawa, T.; Matsuzawa, K. *Jpn. J. Appl. Phys.* **1992**, *31*, Suppl.1, 66.

(36) Hornowski, T. *Acta Phys. Pol. A* **1992**, *82*, 961.

(37) Subrahmayam, T. V. S.; Viswanadha Sarma, A. *Acustica* **1994**, *80*, 198.

(38) Bittmann, E.; Alig, I.; Woermann, D. *Ber. Bunsen-Ges.Phys. Chem.* **1994**, *98*, 189.

(39) Zielesny, A.; Woermann, D. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3889.

(40) Khabibullaev, P. K.; Mirzaev, S. Z.; Saidov, A. A.; Shinder, I. I. *Phys. Dokl.* **1995**, *40*, 627.

(41) Hornowski, T.; Labowski, M. *Arch. Acoust.* **1996**, *21*, 53.

(42) Fisher, M. E. *Rep. Prog.Phys.* **1967**, *30*, 615.

(43) Kadanoff, L. P.; Swift, J. *Phys. Rev. E* **1968**, *166*, 89.

(44) Halperin, B. I.; Hohenberg, P. C. *Phys. Rev.* **1969**, *177*, 952.

(45) Mirzaev, S. Z.; Kaatze, U. *Chem. Phys. Lett.*, submitted for publication.

(46) Mirzaev, S. Z.; Telgmann, T.; Kaatze, U. *Phys. Rev. E* **2000**, *61*, 542.

(47) Dürr, U.; Mirzaev, S. Z.; Kaatze, U. *J. Phys. Chem.*, submitted for publication.

(48) Friedländer, J. *Z. Phys. Chem.* **1901**, *38*, 385.

(49) Chu, B.; Schoenes, F. J.; Fisher, M. E. *Phys. Rev.* **1969**, *185*, 219.

(50) Stein, A.; Allen, G. T. *Phys. Rev. Lett.* **1972**, *29*, 1236.

(51) Labowski, M. *Acoust. Lett.* **1979**, *3*, 123.

(52) Kaatze, U.; Woermann, D. *Ber. Bunsen-Ges.Phys. Chem.* **1982**, *86*, 81.

(53) Dunker, H.; Woermann, D.; Bhattacharjee, J. K. *Ber. Bunsen-Ges.Phys. Chem.* **1983**, *87*, 591.

(54) Beysens, D.; Gbadamassi, M.; Moncef-Bonanz, B. *Phys. Rev. A* **1983**, *28*, 2491.

(55) Kolb, H. A.; Woermann, D. *J. Chem. Phys.* **1984**, *80*, 3781.

(56) Schwahn, D.; Belkoura, L.; Woermann, D. *Ber. Bunsen-Ges.Phys. Chem.* **1986**, *90*, 339.

(57) Sieber, M.; Woermann, D. *Z. Phys. Chem.* (*München*) **1987**, *153*, 161.

(58) Kaatze, U.; Schreiber, U. *J. Phys. Chem.* **1989**, *43*, 4955.

(59) Belkoura, L.; Calenbuhr, V.; Müller-Kirschbaum, T.; Woermann, D. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1471.

(60) Gailus, T. Dissertation, Georg-August-Universität, Göttingen, 1996.

(61) Freedman, E. *J. Phys. Chem.* **1953**, *21*, 1784.

(62) Zarakhani, N. G.; Vinnik, M. L. *Russ. J. Phys. Chem.* **1964**, *38*, 332.

(63) Tatsumoto, N. *J. Phys. Chem.* **1967**, *47*, 4561.

(64) Haurie, H.; Novak, A. *C. R. Acad. Sci. Paris B* **1967**, *264*, 694.

(65) Bader, F.; Plass, K. G. *Ber. Bunsen-Ges.Phys. Chem.* **1971**, *75*, 553.

(66) Corsaro, R. D.; Atkinson, G. *J. Phys. Chem.* **1971**, *55*, 1971.

(67) Lanshina, L. V.; Lupina, M. I.; Khabibullaev, P. K. *Sov. Phys. Acoust.* **1971**, *16*, 343.

(68) Lupina, H. I. *Russ. J. Phys. Chem*. **1976**, *50*, 345.

(69) Asenbaum, A. *Z. Naturforsch.* **1979**, *34a*, 207.

(70) Semmler, J.; Jrish, D. E. *J. Solution Chem*. **1988**, *17*, 805.

(71) Tanaka, N.; Kitano, H.; Jse, N. *J. Phys. Chem*. **1990**, *94*, 6290.

(72) Rupprecht, A.; Krah, H.; Kühnel, V.; Kaatze, U. In *Proceedings of the 1995 World Congress on Ultrasonics*; Herbertz, J., Ed.; Part 1.

(73) Zielesny, A.; Woermann, D. *J. Chem. Soc., Faraday Trans*. **1994**, *90*, 2215.

(74) Kaatze, U.; Wehrmann, B.; Pottel, R. *J. Phys. E* **1987**, *20*, 1025.

(75) Kaatze, U.; Lautscham, K.; Brai, M. *J. Phys. E* **1988**, *21*, 98.

(76) Davidovich, L. A.; Shinder, I. I.; Kanaki, E. K. *Phys. Rev. A* **1991**, *43*, 1812.

(77) Kononenko, V. S. *Sov. Phys. Acoust*. **1987**, *33*, 401.

(78) Davidovich, L. A.; Makhkamov, S.; Pulatova, L.; Khabibullaev, P. K.; Khaliulin, M. G. *Sov. Phys. Acoust*. **1972**, *18*, 264.

(79) Ferrell, R. A. *Phys. Rev. Lett.* **1970**, *24*, 1969.

(80) Fabelinskii, I. L. *Molecular Scattering of Light*; Plenum: New York, 1968.

(81) Cummins, H. Z.; Pike, E. R., Eds. *Photon Correlation and Light Beating Spectroscopy*; Plenum: New York, 1974.

(82) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley-Interscience: New York, 1976.

(83) Chu, B. *Laser Light Scattering*; Academic Press: New York, 1991.

(84) Schätzel, K. *Appl. Phys. B* **1987**, *42*, 193.

(85) Schätzel, K.; Drewel, M.; Stimac, M. *Modern Opt*. **1988**, *35*, 711.

(86) Trachimow, C.; De Maeyer, L.; Kaatze, U. *J. Phys. Chem. B* **1998**, *102*, 4483.

(87) Marquardt, D. W. *J. Soc. Ind. Appl. Math*. **1963**, *2*, 2.

(88) Chu, B.; Schoenes, F. J. *Phys. Rev. Lett*. **1968**, *21*, 6.

(89) Timmermans, J. *J. Chim. Phys.* **1923**, *20*, 491.

(90) Corsaro, R. D.; Atkinson, G. *J. Chem. Phys*. **1971**, *54*, 4090.

(91) Rupprecht, A. Diploma Thesis, Georg-August-Universität, Göttingen, 1993.

(92) Krah, H. Diploma Thesis, Georg-August-Universität, Göttingen, 1995.

(93) Strehlow, H. *Rapid Reactions in Solution*; VCH Verlagsgesellschaft: Weinheim, Germany, 1992.

(94) Tanaka, H.; Ohmine, I. *J. Chem. Phys*. **1987**, *87*, 6128.

(95) Ohmine, I.; Tanaka, H.; Wolynes, P. G. *J. Chem. Phys*. **1988**, *89*, 5852.

(96) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Clarendon: Oxford, UK, 1969.

(97) Krall, A. H.; Sengers, J. V.; Hamano, K. *Phys. Rev. E* **1993**, *48*, 357.