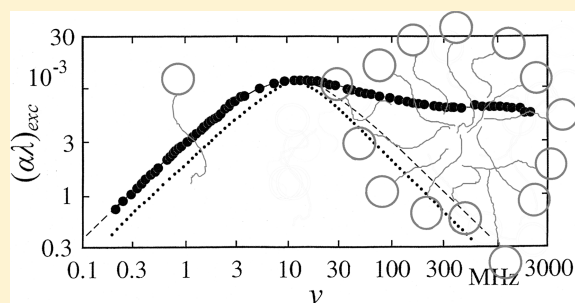


Anomalous Dynamics of Solutions of Nonionic Micelles in Water

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ABSTRACT: In addition to a previous theory on the coupling between noncritical concentration fluctuations and elementary chemical processes, an alternative treatment is presented which allows for a closed-form solution of ultrasonic attenuation spectra. This analytical form is first compared to a previous model and also to experimental spectra of binary liquid mixtures. The broadening of the spectra is briefly discussed in terms of molecular interactions and of the ratio of the relaxation times of the chemical equilibrium and of the diffusion of fluctuations. Extension of the theoretical model to apply to nonionic micelle solutions reveals that a flat contribution in the experimental spectra of such quasi-ternary systems may be simply due to different structure factors of the monomers and the micelles. Some exceptional findings for polyethylene glycol monoalkyl ether/water mixtures are discussed in light of the theory.



1. INTRODUCTION

Ultrasonic spectroscopy has become a valuable tool for the study of liquids. As sonic signals couple to a liquid via fundamental parameters, such as density, viscosity, and heat capacity, ultrasonic spectroscopy allows us to investigate a wide range of elementary processes which still today are only incompletely understood. Due to the presently available measurement frequency range from almost 10 kHz to 10 GHz, ultrasonic spectrometry provides direct monitoring of dynamic processes with relaxation times in the range of 20 ps to 20 μ s. It thus has the potential to elucidate liquid properties which are difficult to study by other methods.

In the frequency range under consideration ultrasonic relaxation phenomena of solutions or liquid mixtures are discussed in light of three different mechanisms involving sound attenuation and, consequently, sound velocity dispersion. Pressure variations in a sonic field may cause scattering, associated with deformation and oscillation of particles in suspensions and emulsions,^{1,2} perturbations of chemical equilibria,^{3–6} and interferences of fluctuations in the local concentrations. Such fluctuations may be critical,^{7–10} associated with a demixing point, or noncritical, controlled by diffusion.^{11–15}

Elementary chemical equilibria contribute Debye-type terms with discrete relaxation times to the ultrasonic spectra, whereas relaxations due to concentration fluctuations extend over a broader frequency range, thus reflecting a distribution of relaxation times. An example is shown in Figure 1, where the excess attenuation per wavelength

$$(\alpha\lambda)_{\text{exc}} = \alpha\lambda - B\nu \quad (1)$$

predicted by the Romanov–Solov'ev theory^{11,12} of noncritical fluctuations, $(\alpha\lambda)_{\text{exc,RS}} \equiv R_{\text{RS}}(\nu)$, is contrasted with a Debye

relaxation term

$$R_{\text{D}}(\nu) \equiv (\alpha\lambda)_{\text{exc,D}} = A_{\text{D}} \frac{\omega\tau_{\text{D}}}{1 + (\omega\tau_{\text{D}})^2} \quad (2)$$

with discrete relaxation time τ_{D} . In these relations, α is the sonic attenuation coefficient, $\lambda = c_{\text{s}}/\nu$ is the wavelength at frequency ν , c_{s} is the sound velocity, and B is the coefficient of the asymptotic high-frequency term that contains the Stokes–Kirchhoff damping^{16,17} due to viscous friction and thermal conductivity. In eq 2, A_{D} is an amplitude and $\omega = 2\pi\nu$.

In this context broad-band ultrasonic attenuation spectra of aqueous solutions of nonionic surfactants reveal an interesting and inexplicable behavior. At surfactant concentrations above the critical micelle concentration (cmc), the $(\alpha\lambda)_{\text{exc}}$ data establish a reasonable flat spectrum over several decades of frequency. As an example, the excess attenuation spectrum for a mixture of triethylene glycol monohexyl ether (C_6E_3) with water is also displayed in Figure 1. Such flat spectra are characteristic of binary liquids near a critical demixing point.¹⁰ The spectrum of the mixture of critical composition shown in Figure 1, however, refers to a temperature far below the lower critical temperature of the system. At that temperature any critical fluctuations are absent.

As ultrasonic attenuation spectra containing a flat contribution with relaxation characteristics have emerged for a variety of critical as well as noncritical polyethylene glycol monoalkyl ether/water mixtures, they have been generally described by an empirical sum of relaxation terms $R(\nu)$ including a critical term $R_{\text{c}}(\nu)$ even if the systems were not critical.²⁰ In this paper we put forward an idea of a coupling between noncritical fluctuations

Received: January 31, 2011

Revised: March 7, 2011

Published: April 21, 2011

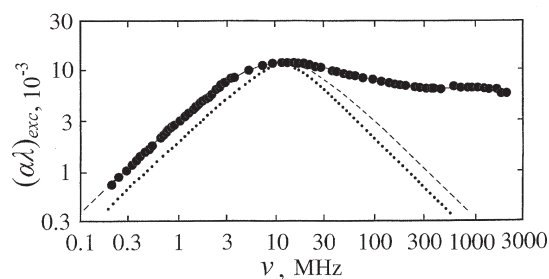


Figure 1. Ultrasonic excess attenuation spectrum for a triethylene glycol monohexyl ether/water mixture with mass fraction $Y = Y_{\text{crit}} = 0.146$ of surfactant at 25 °C.¹⁸ The critical demixing temperature of this mixture of critical composition is $T_{\text{crit}} = 44.7$ °C.¹⁹ Also shown are the graphs of a Debye relaxation term (dotted line, eq 2) and a Romanov–Solov'ev term (dashed line). The amplitude and relaxation frequency of the latter term have been adjusted to fit to the low-frequency part of the experimental spectra. Parameters of the Debye term have been chosen so that its relative maximum agrees with both that of the Romanov–Solov'ev term and the experimental spectrum.

and elementary chemical equilibria which is capable of featuring a flat spectrum without resorting to critical behavior and which is thus able to well account for the experimental results on a physical basis.

2. THEORETICAL MODEL

2.1. Binary Systems. Let us start with a description of the ultrasonic attenuation in noncritical mixtures using the bulk viscosity and the equation of state for fluids. The frequency-dependent complex bulk viscosity $\zeta(\nu)$ is related to the sonic excess attenuation per wavelength^{10,21} according to

$$(\alpha\lambda)_{\text{exc}}(\nu) = \frac{\pi\omega}{\rho c_s^2} (\text{Re})\zeta(\nu) \quad (3)$$

The Kubo formula^{22,23} yields the frequency-dependent complex bulk viscosity as^{21,24,25}

$$\zeta(\nu) = \frac{V}{k_B T} \int_0^\infty \langle \delta P(t_1) \delta P(t_2) \rangle \exp(i\omega t_{12}) dt_{12} \quad (4)$$

where k_B is Boltzmann's constant and δP is the pressure variation caused by a harmonically alternating sonic field. Virial expansion^{26,27} gives the equilibrium pressure as

$$P_{\text{eq}} = nk_B T - \frac{n^2}{6} \int_0^\infty h(r) g(\vec{r}) d^3r \quad (5)$$

In this equation, n is the sum of concentrations of the constituents, $h(r) = [r d\Phi(r)]/dr$, with Φ denoting the interaction potential between two molecules or particles of the liquid, assumed to be spherically symmetric. Furthermore, $g(\vec{r})$ is the correlation function, given by

$$g(\vec{r}) = \frac{1}{V} \int_0^\infty \langle n(\vec{x}) n(\vec{x} + \vec{r}) \rangle d^3x \quad (6)$$

with angular brackets denoting the equilibrium average. To allow for variations due to the sonic field, eq 5 is generalized to read

$$P(t) = nk_B T - \frac{n^2}{6} \int_0^\infty h(r) g(\vec{r}, t) d^3r \quad (7)$$

From this equation the pressure fluctuations follow as

$$\delta P(t) = nk_B \delta T(t) - \frac{n^2}{6V} \int_0^\infty h(r) \delta n(\vec{x}, t) \delta n(\vec{x} + \vec{r}, t) d^3x d^3r \quad (8)$$

and the instantaneous correlation function reads

$$g(\vec{r}, t) = \frac{1}{V} \int_0^\infty n(\vec{x}, t) n(\vec{x} + \vec{r}, t) d^3x \quad (9)$$

Because of conservation of energy

$$E = \frac{3}{2} nk_B T(t) + \frac{n^2}{6} \int_0^\infty h(r) g(\vec{r}, t) d^3r \quad (10)$$

the time dependence $T(t)$ of temperature is related to that of the correlation function, so that

$$\delta P(t) = (\text{const}) \int_0^\infty h(r) \delta n(\vec{x}, t) \delta n(\vec{x} + \vec{r}, t) d^3x d^3r \quad (11)$$

results in coordinate space and

$$\delta P(t) = (\text{const}) \int_0^\infty \hat{h}(\vec{q}) \delta \hat{n}(\vec{q}, t) \delta \hat{n}(-\vec{q}, t) d^3q \quad (12)$$

in momentum space. Here \hat{h} and \hat{n} denote the spatial Fourier transforms of h and n , respectively. Let us assume the dynamics to be controlled by a differential equation^{28–30}

$$\frac{d\delta n(\vec{r}, t)}{dt} = D \nabla^2 \delta n(\vec{r}, t) - \frac{1}{\tau_0} \delta n(\vec{r}, t) \quad (13)$$

with diffusion coefficient D of fluctuations and relaxation time τ_0 characteristic of the elementary chemical process. We then get

$$\begin{aligned} & \int_0^\infty \langle \delta P(t_2) \delta P(t_1) \rangle \exp(i\omega t_{12}) dt_{12} \\ &= (\text{const}) \int_0^\infty \hat{h}(\vec{q}) \hat{h}(\vec{p}) \langle \delta \hat{n}(\vec{q}, t_2) \delta \hat{n}(-\vec{q}, t_2) \\ & \quad \delta \hat{n}(\vec{p}, t_1) \delta \hat{n}(-\vec{p}, t_1) \rangle d^3p d^3q \\ &= (\text{const}) \int_0^\infty \hat{h}^2(p) S^2(p) \frac{d^3p}{-i\omega + Dp^2 + \tau_0^{-1}} \end{aligned} \quad (14)$$

$S(p)$ is the structure factor, which may be taken according to Ornstein–Zernike,^{31,32} and $\hat{h}(p)$ may be assumed to be flat, corresponding with very short range interactions in coordinate space. On those conditions, the bulk viscosity results as

$$\zeta = \zeta_0 \int_0^\infty \frac{1}{(p^2 + \xi^{-2})^2} \frac{d^3p}{-i\omega + Dp^2 + \tau_0^{-1}} \quad (15)$$

and the sonic excess attenuation per wavelength as^{10,21}

$$\begin{aligned} (\alpha\lambda)_{\text{exc}} &= \frac{\pi\omega}{\rho c_s^2} (\text{Re})\zeta \\ &= \zeta_0 \int_0^\infty \frac{1}{(p^2 + \xi^{-2})^2} \frac{\omega(Dp^2 + \tau_0^{-1})}{\omega^2 + (Dp^2 + \tau_0^{-1})^2} d^3p \end{aligned} \quad (16)$$

where ξ is the correlation length of the Ornstein–Zernike ansatz and ζ_0 is a frequency-independent amplitude factor. Equation 16

can be exactly integrated to yield

$$(\alpha\lambda)_{\text{exc}} = \tilde{R}(\nu) \\ \equiv (\text{const}) \frac{\omega\tau_0 \left[1 + \sqrt{2} \left(\frac{1}{\omega_0\tau_0} \right)^{1/2} \left(1 + \sqrt{1 + \omega^2\tau_0^2} \right)^{1/2} + \frac{1}{\omega_0\tau_0} \right]}{\left[1 + \sqrt{2} \left(\frac{1}{\omega_0\tau_0} \right)^{1/2} \left(1 + \sqrt{1 + \omega^2\tau_0^2} \right)^{1/2} + \frac{1}{\omega_0\tau_0} (1 + \omega^2\tau_0^2)^{1/2} \right]^2} \quad (17)$$

where $\omega_0 = D/\xi^2$. This form is particularly simple when an elementary chemical process does not contribute to the dynamics ($\omega_0\tau_0 \rightarrow \infty$). In terms of $\Omega = \omega/\omega_0$, we then have

$$\tilde{R}(\nu) \equiv \tilde{R}(\nu, \{\omega_0\tau_0\}^{-1} = 0) \\ = (\text{const}) \frac{\Omega(1 + \sqrt{2\Omega})}{(1 + \sqrt{2\Omega} + \Omega)^2} \quad (18)$$

2.2. Ternary Fluids. It is obvious that surfactant solutions at concentrations below the cmc belong to the type of fluids that has been considered before, because monomers are basically the only solute. At surfactant concentrations above the cmc, however, the picture changes since monomers as well as micelles exist. Micelles are subject to a size distribution which is normally assumed to be Gaussian.³³ Here we neglect the size distribution and characterize the micelles by only one species with aggregation number equal to the mean \bar{m} of the Gaussian distribution. Fluctuations in the concentration of the surfactant are then considered by

$$\delta n = \delta n_1 + \delta n_{\bar{m}} \quad (19)$$

where δn_1 represents the fluctuations of the monomer and $\delta n_{\bar{m}}$ those of the micelle concentrations. We insert relation 19 into eq 11 and focus on the mixed part

$$\delta P(t) = (\text{const}) \int_0^\infty h(r) \delta n_1(\vec{x}, t) \delta n_{\bar{m}}(\vec{x} + \vec{r}, t) d^3x d^3r \\ = (\text{const}) \int_0^\infty \hat{h}(q) \delta \hat{n}_1(\vec{q}, t) \delta \hat{n}_{\bar{m}}(-\vec{q}) d^3q \quad (20)$$

since the $\delta \hat{n}_1 \delta \hat{n}_1$ part has already been considered above and the $\delta \hat{n}_{\bar{m}} \delta \hat{n}_{\bar{m}}$ part is significantly smaller than the others. The quantities \hat{h} , \hat{n}_1 , and $\hat{n}_{\bar{m}}$ are the spatial Fourier transforms of h , n_1 , and $n_{\bar{m}}$, respectively. For sinusoidal sonic fields the mixed part under consideration leads to an additional contribution to the bulk viscosity at surfactant concentrations above the cmc, namely

$$\Delta\zeta = (\text{const}) \int_0^\infty \hat{h}(q) \hat{h}(p) \langle \delta \hat{n}_1(\vec{q}, t_2) \delta \hat{n}_1(\vec{p}, t_1) \\ \times \delta \hat{n}_{\bar{m}}(-\vec{q}, t_2) \delta \hat{n}_{\bar{m}}(-\vec{p}, t_1) \rangle \exp(i\omega t_{12}) d^3p d^3q dt_{12} \\ = (\text{const}) \int_0^\infty \hat{h}(p) \hat{h}(p) \langle \delta \hat{n}_1(\vec{p}, t_2) \delta \hat{n}_1(-\vec{p}, t_1) \rangle \\ \times \langle \delta \hat{n}_{\bar{m}}(\vec{p}, t_2) \delta \hat{n}_{\bar{m}}(-\vec{p}, t_1) \rangle \exp(i\omega t_{12}) d^3p dt_{12} \quad (21)$$

The dynamics of concentration fluctuations are assumed to be controlled by diffusion relations corresponding with eq 13:

$$\frac{d\delta n_1(\vec{r}, t)}{dt} = D_1 \nabla^2 \delta n_1(\vec{r}, t) - \frac{1}{\tau_1} \delta n_1(\vec{r}, t) \quad (22)$$

and

$$\frac{d\delta n_{\bar{m}}(\vec{r}, t)}{dt} = D_{\bar{m}} \nabla^2 \delta n_{\bar{m}}(\vec{r}, t) - \frac{1}{\tau_{\bar{m}}} \delta n_{\bar{m}}(\vec{r}, t) \quad (23)$$

where D_1 and $D_{\bar{m}}$ denote the diffusion coefficients of the monomers and the micelles, respectively. Relaxation times τ_1 and $\tau_{\bar{m}}$ are characteristic of a monomer–monomer (dimerization) reaction and a monomer–micelle (monomer exchange) reaction, respectively. Leaving the setting of structure factors $S_1(p)$ and $S_{\bar{m}}(p)$, eq 21 now becomes ($i^2 = -1$)

$$\Delta\zeta = (\text{const}) \int_0^\infty \hat{h}^2(p) S_1(p) S_{\bar{m}}(p) \frac{d^3p}{-i\omega + D_1 p^2 + D_{\bar{m}} p^2 + \tau_1^{-1} + \tau_{\bar{m}}^{-1}} \quad (24)$$

The widely accepted primary Aniansson–Wall–Teubner–Kahlweit theory of micelle formation^{33–35} proceeds from the assumption of a Gaussian distribution of micelle sizes, which leads to two Debye-type relaxation processes with discrete relaxation time in the ultrasonic spectra. The fast process is due to the monomer exchange, and the slower one, with relaxation frequency well below the frequency range under consideration, represents the redistribution of micelle sizes.^{34,35} Hence, consideration of the size distribution of micelles cannot account for the flat contributions to the experimental spectra. For this reason we argue that there might be an effect of structure as the structure factors $S_1(p)$ and $S_{\bar{m}}(p)$ of monomers and micelles, respectively, cannot have the same form.

Structure factors are not given by genuine principles, so there is some ambiguity in selecting suitable forms of these factors.³⁶ The monomers may reveal Ornstein–Zernike^{31,32} behavior, $S_1(p) = (\text{const})(p^2 + \xi_1^{-2})^{-1}$, corresponding to the position correlation

$$S_1(r) = (\text{const}) \exp(-r/\xi_1)/r \quad (25)$$

with characteristic length ξ_1 . For the micelles we presume a faster structure factor falloff at large r and a stronger correlation of micelle positions at small r . We therefore postulate the form

$$S_{\bar{m}}(r) = (\text{const}) \exp(-r/\xi_{\bar{m}})/r^2 \quad (26)$$

with characteristic length $\xi_{\bar{m}}$ in the position space. If $1/\xi_{\bar{m}} = 0$, the Fourier transform $\hat{S}_{\bar{m}}$ of $S_{\bar{m}}$ is $1/p$, and if p is very small, then the Fourier transform is $\xi_{\bar{m}}$. Accordingly, we propose a simple momentum–space form

$$\hat{S}_{\bar{m}}(p) = (\text{const})(p^2 + \gamma^2/\xi_{\bar{m}}^2)^{-1/2} \quad (27)$$

in which γ is a parameter that can be adjusted into a redefinition of $\xi_{\bar{m}}$. Again we approximate $\hat{h}(p)$ by a constant, and the additional contribution to the bulk viscosity becomes

$$\Delta\zeta = (\text{const}) \int_0^\infty \frac{d^3p}{(p^2 + \xi_1^{-2})(p^2 + \xi_{\bar{m}}^{-2})^{1/2}} \frac{1}{-i\omega + D_{\text{eff}} p^2 + \tau_{\text{eff}}^{-1}} \quad (28)$$

where $D_{\text{eff}} = D_1 + D_{\bar{m}}$ and $\tau_{\text{eff}}^{-1} = \tau_1^{-1} + \tau_{\bar{m}}^{-1}$. The contribution to the excess attenuation per wavelength finally

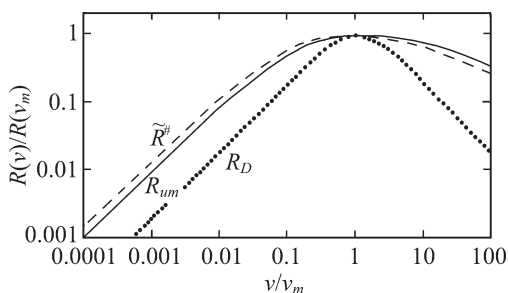


Figure 2. Graphs of the relaxation spectral function $\tilde{R}^{\#}(\nu)$ at the vanishing elementary chemical process (dashed line, eq 18), of the relaxation function $R_{\text{um}}(\nu)$ of the unifying model (full line, eq 30), and of a Debye relaxation term $R_D(\nu)$ (dotted line, eq 2), shown in the normalized format $R(\nu)/R(\nu_m)$ versus ν/ν_m .

follows as

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \int_0^{\infty} \frac{\omega d^3 p}{(p^2 + \xi_1^{-2})(p^2 + \xi_m^{-2})^{1/2}} \frac{D_{\text{eff}} p^2 + \tau_{\text{eff}}^{-1}}{(D_{\text{eff}} p^2 + \tau_{\text{eff}}^{-1})^2 + \omega^2} \quad (29)$$

3. DISCUSSION

3.1. Analogy to the Previous Relaxation Model. Experimental spectra of binary liquids exhibiting noncritical concentration fluctuations and elementary chemical reactions have been well represented by a “unifying” model²⁹ that combines aspects of prior theories.^{11,12,14,15,28,36,37} We first inspect how the function $\tilde{R}(\nu)$, defined by eq 17, fits the relaxation function $R_{\text{um}}(\nu)$ of the unifying model. The latter is given by the integral relation

$$R_{\text{um}}(\nu) = (\text{const}) \int_0^{\infty} \frac{q^2 dq}{(1 + 0.164q\xi + 0.25q^2\xi^2)^2} \frac{\omega\tau_g}{1 + \omega^2\tau_g^2} \quad (30)$$

where $\tau_g^{-1} = Dq^2 + \tau_0^{-1}$. Let us first restrict to the limiting situation in which no elementary chemical processes exist. For the limiting forms the spectra should be broadest because the dynamics is just governed by diffusion. In Figure 2 the graphs of functions $\tilde{R}^{\#}(\nu)$, as defined by eq 18, and $R_{\text{um}}(\nu)$ at $\tau_g = D^{-1}q^{-2}$ are displayed along with that of a Debye term $R_D(\nu)$. Here and in the following we are predominantly interested in the shapes of the functions, which, for reasons of easy comparison, are thus shown in a normalized format.

$\tilde{R}^{\#}(\nu)$ and $R_{\text{um}}(\nu)$ both extend over a significantly broader frequency range than $R_D(\nu)$. However, a small deviation between both former functions exists. It is due to the different modeling of the interaction forces between molecules. Whereas very short-range interactions and a structure factor featuring Ornstein–Zernike behavior have been presumed throughout when deducing $\tilde{R}(\nu)$, in deriving $R_{\text{um}}(\nu)$ an Ornstein–Zernike ansatz has been used to represent the long-range correlations ($r \geq \xi$) only. Short-range correlations ($r < \xi$) have been considered by a nearly exponential decay, as originally proposed by Montrose and Litovitz.³⁶ A suitable choice of $\hat{h}(p)$, which has just been taken to be flat here, will result in a closer agreement between $\tilde{R}^{\#}(\nu)$ and $R_{\text{um}}(\nu)$. Here we do without a more sophisticated interaction potential because we are predominantly interested in ternary systems.

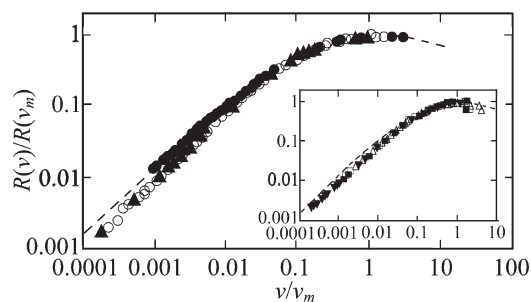


Figure 3. Ultrasonic excess-attenuation-per-wavelength spectra in the normalized format $R(\nu)/R(\nu_m)$ versus ν/ν_m for mixtures of water with 1-propanol³⁸ (●, $X = 0.12$; X = mole fraction of the nonaqueous constituent), 2-isopropoxyethanol³⁹ (▲, $X = 0.15$), and *n*-ethylurea⁴⁰ (○, $X = 0.1$). In the inset results for aqueous solutions of 1,2-diethylurea⁴⁰ (■, $X = 0.02$; □, $X = 0.036$; △, $X = 0.041$) and a solution of 1,1-diethylurea⁴⁰ (▼, $X = 0.041$) are given. Attenuation data between 100 kHz and 5 GHz were measured at 25 °C. The dashed lines are graphs of the relaxation spectral function $\tilde{R}^{\#}(\nu)$ as defined by eq 18.

3.2. Comparison with Spectra for Binary Liquids. In Figure 3, as an example, experimental excess-attenuation-per-wavelength data are presented for mixtures of water with an alcohol, for aqueous solutions of some derivatives of urea, and for mixtures of water with an ethylene glycol monoalkyl ether. Again the spectra are shown in a normalized format, throwing information on the frequencies ν_m of the relative maximum in the spectra and also the maximum values $R(\nu_m)$ themselves away. We only mention that useful pieces of information, such as a correlation between ν_m and the hydrophobic character of the organic constituent, had been derived from the original relaxation function of the unifying model.²⁹

Except for 1-propanol/water the data in Figure 3, within the limits of their experimental uncertainty, condense on one curve. This “master curve” agrees perfectly with $R_{\text{um}}(\nu)$. Hence, it slightly deviates from $\tilde{R}^{\#}(\nu)$. Only at lower frequencies ($\nu/\nu_m < 0.1$) do the 1-propanol/water data tend toward the latter function (eq 18). As mentioned before, the deviations of the majority of the data from the $\tilde{R}^{\#}(\nu)$ function can be simply accounted for by an appropriate choice of $\hat{h}(p)$.

A narrowing of the relaxation spectral function follows not just from a suitable choice of the structure factor but also from consideration of an additional chemical equilibrium, i.e., from taking the original $R(\nu)$ function (eq 17) with finite τ_0 . The effect of a finite τ_0 is illustrated by the inset in Figure 4, where, in addition to the limiting version $\tilde{R}^{\#}(\nu)$, the function $\tilde{R}(\nu)$ is shown at $(\omega_0\tau_0)^{-1} = 1/4$ and $(\omega_0\tau_0)^{-1} = 4$. This is the range of parameter values that covers the presently available experimental spectra, especially those for aqueous solutions of derivatives of urea,^{29,40} for which some spectra are given in the main part of Figure 4. Obviously, spectral function $\tilde{R}(\nu)$ fits well to the experimental data. We mention that at $(\omega_0\tau_0)^{-1} = 4$ this function almost agrees well with the often empirically applied restricted Hill function^{41–43}

$$R_H^*(\nu) = (\text{const}) \frac{\omega\tau_H}{(1 + \{\omega\tau_H\}^{2s_H})^{3/(4s_H)}} \quad (31)$$

If $s_H = 1$

$$R_H(\nu) = R_H^*(\nu, s_H = 1) = (\text{const}) \frac{\nu/\nu_m}{(1 + 2\{\nu/\nu_m\}^2)^{3/4}} \quad (32)$$

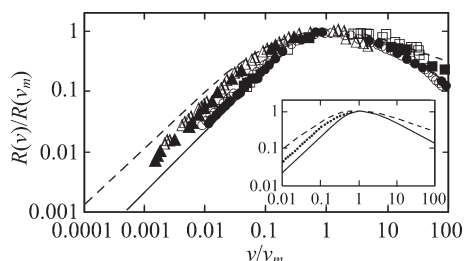


Figure 4. Ultrasonic excess-attenuation-per-wavelength data plotted in the normalized format $R(\nu)/R(\nu_m)$ versus ν/ν_m for aqueous solutions of *n*-butylurea⁴⁰ at 25 °C (▲, $X = 0.0095$; △, $X = 0.0156$; □, $X = 0.0178$; ■, $X = 0.0199$; ○, $X = 0.0234$; ●, $X = 0.0257$). Dashed lines show the limiting relaxation function $\tilde{R}(\nu)$ at the vanishing chemical process ($\omega_0\tau_0 \rightarrow \infty$, eq 18), the full lines are graphs of the function $R(\nu)$ at $\omega_0\tau_0 = 4$, and the dotted line shows the same function (eq 17) at $\omega_0\tau_0 = 1/4$.

In such events $\tilde{R}(\nu)$ may thus be favorably used to discuss experiments within the framework of a physical model rather than a simple description in terms of an empirical relaxation function.

3.3. Application to Surfactant Solutions. It is important to notice that in the above treatment no critical contribution to D_{eff} has been taken into account. Also reaction diffusion mechanisms, which sometimes produce particular dynamical behavior,⁴⁴ are completely absent for reactions of the form $A + A \leftrightarrow A_2$ and $A + B \leftrightarrow C$.⁴⁵ Nevertheless, contribution $\Delta(\alpha\lambda)_{\text{exc}}$ is able to feature the flatness in the high-frequency part of the ultrasonic attenuation spectra of noncritical polyethylene glycol monoalkyl ether (C₆E)/water mixtures (Figures 1 and 5), which appears to be particularly distinctive at surfactant concentrations close to the cmc (Figure 5). The high-frequency limit of eq 29 is given by

$$\begin{aligned}\Delta(\alpha\lambda)_{\text{exc}}(\nu \rightarrow \infty) &= (\text{const}) \int_0^\infty \frac{\omega}{p} \frac{dp}{\omega^2 + D_{\text{eff}}p^4} \\ &= (\text{const}) \int_0^\infty \frac{\omega p}{\omega^2 + D_{\text{eff}}p^4} dp \\ &= (\text{const}) \int_0^\infty \frac{\omega}{\omega^2 + Q^2} dQ \\ &= \text{const}\end{aligned}\quad (33)$$

Hence, the additional contribution to $(\alpha\lambda)_{\text{exc}}$, resulting from the mixed part $\delta\hat{n}_1 \delta\hat{n}_m$ in the pressure fluctuations (eq 20), clearly reveals frequency-independent high-frequency behavior. Normally this contribution will not dominate the input from the monomer fluctuations, coupled to the micelle formation/disintegration kinetics, but since the latter decrease toward high frequencies, $\Delta(\alpha\lambda)_{\text{exc}}$ may prevail in that frequency range.

We now address the finding of the especially distinctive flatness of excess attenuation spectra near the cmc (Figure 5). Aiming at an exact performance of the integral in eq 29, we first focus on the limiting situation in which the elementary chemical reactions are absent ($1/\tau_{\text{eff}} \ll \omega$) so that eq 29 reads

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \int_0^\infty \frac{\omega d^3p}{(p^2 + \xi_1^{-2})(p^2 + \xi_m^{-2})^{1/2}} \frac{D_{\text{eff}}p^2}{D_{\text{eff}}^2p^4 + \omega^2} \quad (34)$$

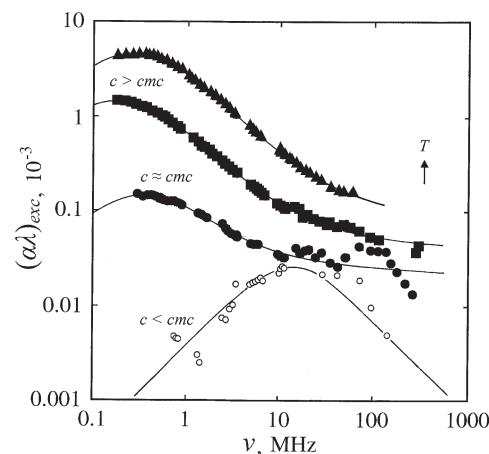


Figure 5. Ultrasonic excess attenuation spectra for a C₆E₃/H₂O mixture with mass fraction $Y = 0.02$ at four temperatures (○, 17.5 °C; ●, 25 °C; ■, 32.5 °C; ▲, 40 °C¹⁸). At 17.5 °C $< T < 25$ °C the mixture composition corresponds with the cmc.⁴⁶ At $T = 17.5$ °C the spectrum is analytically represented by a Debye term with a discrete relaxation time. Passing over the cmc, the spectra reveal a broad low-frequency relaxation term and a flat high-frequency contribution.

Substituting p by q/ξ_m we get

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \int_0^\infty \frac{\omega q^2 dq}{(q^2 + 1)^{1/2} (q^2 + \{\xi_m/\xi_1\}^2)} \frac{q^2}{q^4 + \{\omega/D_{\text{eff}}\}^2 \xi^4} \quad (35)$$

which, assuming a shorter range of interaction for micelles than for monomers ($\xi_m \ll \xi_1$), leads to

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \int_0^\infty \frac{\Omega q^2 dq}{(q^2 + 1)^{1/2}} \frac{1}{q^4 + \Omega^2} \quad (36)$$

where $\Omega = \omega \xi_m^2/D_{\text{eff}}$ denotes a scaled frequency. Looking at high Ω , we find

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \left[1 - \frac{2}{\pi} \frac{\ln \Omega}{\Omega} + \dots \right] \quad (37)$$

Assuming, on the other hand, a large characteristic length for the micelle structure factor ($\xi_m \gg \xi_1$), a closed-form relation follows immediately as

$$\Delta(\alpha\lambda)_{\text{exc}} = (\text{const}) \left[1 - \frac{2}{\pi} \frac{\Omega \ln \Omega + \pi/2}{1 + \Omega^2} \right] \quad (38)$$

The high-frequency limit of this function obviously agrees with eq 37. Hence, in the high-frequency limit, the solution to eq 29 is independent of whether $\xi_m \ll \xi_1$ or $\xi_m \gg \xi_1$.

Equations 37 and 38 hold for absence of chemical reactions ($1/\tau_{\text{eff}} \rightarrow 0$). Because a vanishing reaction rate of the monomer exchange is predicted at the cmc,³⁴ we thus expect a flat high-frequency contribution to the attenuation-per-wavelength spectra near the critical micelle concentration of the liquid. At higher surfactant concentration, τ_{eff} becomes finite so that, in addition to the diffusion-controlled concentration fluctuations, a second pathway to reach equilibrium after a disturbance is available to the system. In conformity with the results shown in Figure 5, such an additional pathway tends to narrow the relaxation time distribution and, consequently, the spectra.²⁹

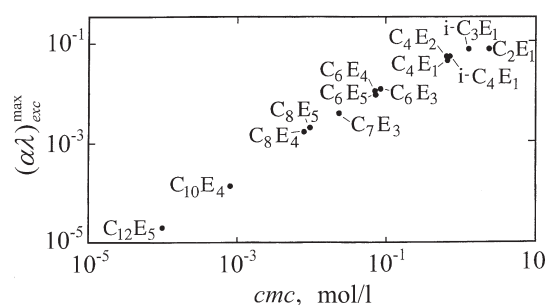


Figure 6. Maximum values $(\alpha\lambda)_{\text{exc}}^{\text{max}}$ in the excess-attenuation-per-wavelength spectra within a series of $\text{C}_i\text{E}_j/\text{H}_2\text{O}$ mixtures of different concentrations for various surfactants displayed versus the cmc. Except for C_7E_3 (22.5 °C) and C_{10}E_4 (18.0 °C), the data refer to 25 °C.²⁰

4. CONCLUSIONS

A theoretical model has been derived that provides a closed-form solution for the ultrasonic attenuation spectra of binary liquid mixtures and solutions exhibiting noncritical concentration fluctuations coupled to an elementary chemical process. Within the framework of a Kubo formalism,^{22,23} the model provides the coupling between the dynamic processes through the cross term in the autocorrelation function of the pressure fluctuations. If, for simplicity, a flat molecular interaction function is assumed in the q space, corresponding with highly short range interactions in the coordinate space, a reasonable limiting form of the spectral function results at the missing chemical process. This limiting function indeed deviates slightly from a previous unifying relaxation model²⁹ and also from the majority of relevant experimental spectra. The small deviations, however, may be avoided by using a more suitable molecular interaction profile.

In correspondence with the unifying model, a chemical process with finite relaxation time tends to reduce the broadness of the spectral function. Available experimental data are predominantly found in the range $1/4 \leq \omega_0\tau_0 \leq 4$, where τ_0 is the relaxation time characterizing the chemical equilibrium, $\omega_0 = D/\xi^2$, D is the diffusion coefficient of concentration fluctuations, and ξ is the correlation length of the structure factor, assumed to follow Ornstein–Zernike behavior.

Extending the above treatment, it is possible to model the flat contributions which have been discovered in the ultrasonic excess-attenuation-per-wavelength spectra of nonionic surfactant/water mixtures at concentrations above the cmc. In our simplified theoretical treatment of surfactant systems, the size distribution of micelles has been neglected. Hence, the micelle formation/disintegration kinetics has just been considered by the dimerization reaction and the monomer exchange with micelles of mean aggregation number. Nevertheless, the model is already capable of featuring a flat high-frequency contribution to the spectra, if different structure factors are assumed for the monomers and the micelles.

The model also accounts reasonably for the experimental result that the excess-attenuation-per-wavelength spectra are particularly flat at surfactant concentrations near the critical micelle concentration. As the relaxation rates of the chemical equilibria are prone to become very small at the cmc, the dynamics of the liquids is largely controlled by diffusion, associated with a broad spectrum. At higher concentrations the spectra narrow because the elementary chemical processes with

nonvanishing relaxation rate offer additional pathways to respond to external disturbances.

Because of the supposed coupling between (noncritical) concentration fluctuations and the micelle formation/disintegration kinetics, the finding of a correlation in a wide range of data between the maximum values $(\alpha\lambda)_{\text{exc}}^{\text{max}}$ in the excess attenuation spectra and the critical micelle concentrations of $\text{C}_i\text{E}_j/\text{water}$ systems (Figure 6) becomes quite understandable. In the frequency range in which the maxima in the spectra are located, the ultrasonic attenuation is dominated by the micelle formation/disintegration kinetics coupled to fluctuations. Only at higher frequencies where contributions due to these processes are already downsized does the additional flat contribution discussed in this paper dominate.

So far the discussion has been restricted to nonionic surfactants since, in solutions of ionic surfactants, an additional coupling between the micelle formation/disintegration and the counterion association/dissociation imposes further complications.^{47,48} Work is in progress to also include ionic surfactant systems.

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ACKNOWLEDGMENT

We are indebted to Andreas Rupprecht, ABS Team, Bovenden, Germany, for inspiring discussions. Financial support by the International Office, Georg-August-Universität Göttingen, is gratefully acknowledged.

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