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Ultrasonic spectroscopy in nonionic micellar solutions far from and near to T_c

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The absorption spectra and velocity of ultrasonic longitudinal waves are reported for some aqueous solutions of the triethylene glycol monohexyl ether (C_6E_3) nonionic surfactant, with special emphasis on the region near the consolute point. The excess ultrasonic absorption spectra from 5 to 160 MHz are satisfactorily fitted by an equation with two relaxation times. Samples near the consolute point did not show the absorption and velocity anomalies as expected in binary critical mixtures. The sound absorption behavior in both micellar and critical samples is discussed from the point of view of the existing aggregate equilibria and of the current theories for critical sound propagation, respectively. The peculiar concentration dependence of the sound velocity at different temperatures is explained as being due to a competition between the compressibility of water and the apparent compressibility of the surfactant.

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I. INTRODUCTION

Aqueous solutions with amphiphilic solutes usually display molecular aggregations. It has been proved that the type and the size of molecular aggregates depend on many factors, mainly on the number and location of the hydrophilic groups as well as on the size of the hydrophobic alkyl chain of the amphiphilic molecule.

Ultrasonic spectroscopy represents a useful tool to get information either on static (compressibility) or dynamic properties of these systems since their characteristic relaxation times are usually located in the frequency range of typical ultrasonic techniques. In previous papers [1–4] we reported detailed ultrasonic absorption and velocity measurements in water solutions with ethanol and alkoxyethanols (ethoxyethanol and 2-butoxyethanol). These compounds are of type $C_nH_{2n+1}(OCH_2CH_2)_mOH$ (denoted briefly as C_nE_m) where $n=2$, $m=0$ for ethanol, $n=2$, $m=1$ for ethoxyethanol, and $n=4$, $m=1$ for butoxyethanol. Thus these compounds can be regarded as homologous, differing from each other both in the length of the hydrophobic chain and in the number of hydrogen bonds they can form with water or similar molecules. The length of the alkyl chain seems to have an important role not only in the formation of aggregates but also in creating demixing regions and critical points. In this regard, the behavior of butoxyethanol looks quite similar to that exhibited by micelle-forming nonionic surfactants of type C_nE_m ($m \geq 6$) so that C_4E_1 seems to possess the minimal hydrophobic length for the formation of micellar aggregates.

In this paper we present detailed measurements of sound absorption coefficient (α) and velocity (c) in C_6E_3 aqueous solutions as functions of temperature, concentration, and frequency. From the comparison of these data with those obtained in the previously investigated shorter homologous systems, we will try to characterize similarities and differences related to the aggregates formed. In particular, we will analyze the behavior near the critical point since previous experiments in C_4E_1 solutions showed a lack of critical contributions.

Apart from experiments with other techniques such as light [5] and neutron scattering [6], our investigated system has been previously studied by ultrasonic techniques in Ref. [7]. However, this study was limited only to the sound absorption behavior and in a rather restricted frequency range (4–12 MHz).

II. EXPERIMENTAL SECTION

The phase diagram of $C_6E_3+H_20$ solutions exhibits a demixing curve separating a (low T) homogeneous region from a (high T) two-phase one. The reported LCST (lower critical solution temperature) is $T_c=44.7\,^{\circ}C$ at the critical concentration (wt %) $w_c=13$ wt % [5]. The system shows a temperature-dependent CMC (critical micellar concentration) line ranging from 1% at 63 °C to 3% at 25 °C [5].

Four samples are investigated in the present work and they are denoted as B1 (2.5 wt %), B4 (8 wt %), B2 (13 wt %), and B3 (20 wt %). Three of them (B1, B2, and B3) correspond to those previously studied by neutron scattering techniques in Ref. [6]. B1 is below the CMC line, while B4, B2, and B3 lie in the isotropic micellar region. In particular, B2 corresponds to the critical concentration reported in Ref. [5]. However, this sample separated at a critical temperature lying between 41.652 and 41.800 °C.

The solutions were prepared by weighting bidistilled water and >97% purity C_6E_3 purchased from Fluka Biochemika and used without further purification.

The ultrasonic measurements were performed by using a variable path cell with two 5 MHz fundamental frequency quartz transducers. In particular, α was measured in the range 5–155 MHz by using a standard pulse echo technique while c was determined in the range 5–55 MHz by a superposition method [1,2].

III. RESULTS AND TREATMENT OF DATA

The temperature and concentration dependence of the sound velocity in pure components and in the investigat-

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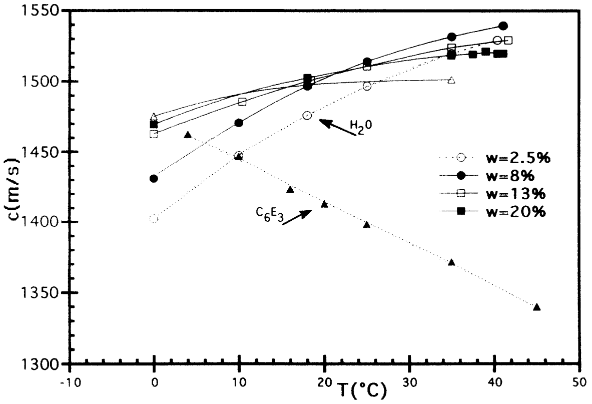

FIG. 1. Sound velocity (5 MHz) as a function of temperature in the investigated $C_6E_3+H_2O$ samples (w is the concentration by weight) and in pure components.

ed samples are shown in Figs. 1 and 2 where curves through the experimental points are smoothed lines. A negligible dependence of the sound velocity on the frequency was observed in samples B1 and B4 but it was detectable in samples B2 and B3, especially at the lower temperatures. Dispersion behaviors are shown in Figs. 3(a)–3(c) where lines are fitting curves as explained below.

Figures 4(a)–4(c) and 5(a)–5(c) are plots of the sound attenuation (as expressed by α/f^2) at $f=5,15,45$ MHz, respectively, as a function of temperature and concentration. The overall investigated ultrasonic spectra are collected in Figs. 6(a)–6(c).

With the same criterion utilized in butoxyethanol plus water solutions [3], we analyzed the ultrasonic absorption spectra α/f^2 by checking them against the six following relaxational behaviors: (a) $A/[1+(\omega\tau)^2]$ (single relaxation time equation, SR); (b) $A_1/[1+(\omega\tau_1)^2]+A_2/[1+(\omega\tau_2)^2]$ (two relaxation times equation, TR); (c) $A_{RS}F_{RS}(\omega\tau)$ (Romanov-Solovjev distribution, RS); this equation has been proposed to explain the ultrasonic attenuation in binary mixtures as due to concentration fluctuations. A_{RS} is an amplitude related to several thermodynamic parameters and F_{RS} a known [3] scaling function of a continuum distribution of diffusive relaxation times with a minimum $\tau=(2Dq^2_{\max})^{-1}$. (d) $A_{CC}/[1+(\omega\tau)^{2(1-\alpha)}]$ (stretched form, approximate Cole-Cole distribution, CC); (e) $A_{CD}\cos(\beta\theta)\sin(\beta\theta)/\omega$ (Cole-Davidson distribution, CD) where $\theta=\arctan(\omega\tau)$ and β and τ are parameters characterizing the width and the maximum relaxation time in the asymmetrical Cole-Davidson distribution; (f) $A_{FB}F_{FB}(\omega\tau)$ (Ferrell-Bhattacharjee form for attenuation in critical mixtures, FB). Expressions for A_{FB}, F_{FB}, and τ are given in Sec. IV.

As usual, to each of (a)–(f) equations we added a constant background B in order to take into account high-

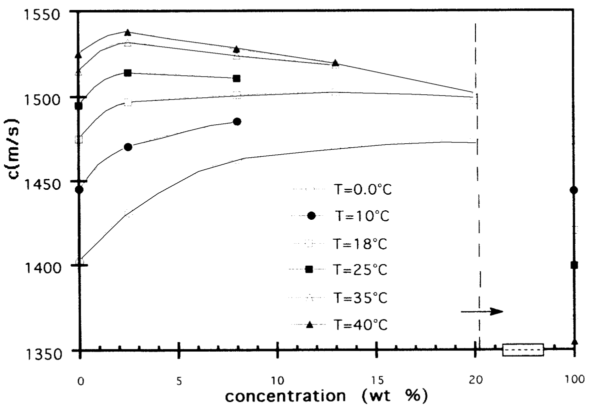

FIG. 2. Sound velocity (5 MHz) as a function of concentration (in wt %) for some temperatures.

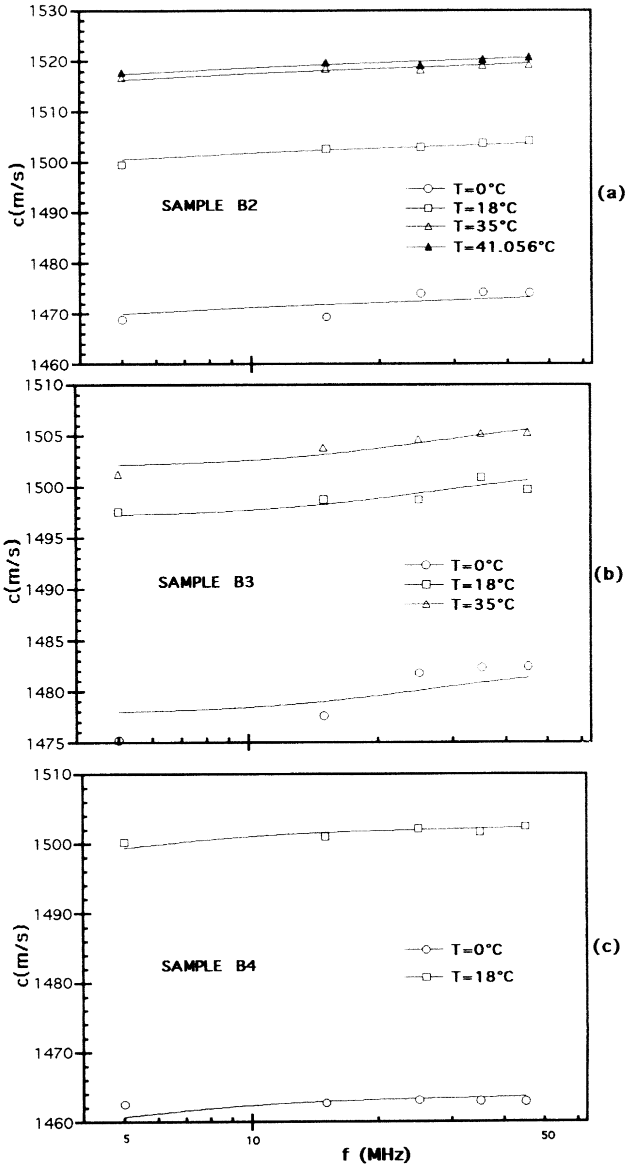

FIG. 3. Sound velocity dispersion in the micellar samples B4 [$w=8$ wt %, plot (a)], B2 [$w=13$ wt % critical, plot (b)], and B3 [$w=20$ wt %, plot (c)] for some temperatures. Lines through the experimental points are two relaxation times fitting curves as explained in the text.

frequency residual contributions to α/f^2. We fitted the six expressions to the measured spectra (9 to 11 points for each spectrum) by using a self-made least squares computer routine choosing the related set of unknown parameters $[B, A_1, f_1 = 1/(2\pi\tau_1), A_2, f_2, \alpha, \beta, \ldots]$ which minimize the χ^2. The reliability of each equation to fit a single spectrum was established by comparing the corresponding χ^2 and taking into account the number of free parameters in each equation (three in SR, RS, and FB; four in CC and CD; five in TR). By adopting this criterion, we reached the following conclusions.

(i) The ultrasonic spectra in samples B4, B2, and B3 (micellar solutions) over the entire temperature range cannot be described by SR, RS, or FB equations (for the spectra in B2 near T_c see also Sec. IV). Rather, they are, in general, better accounted for by a two relaxation equation TR. Even if the quality of the CC, CD, or FB fits is comparable to that of TR for some temperatures, this finding seems casual and not as systematic as the TR results.

(ii) Attenuations in the B1 sample are very small and flat in the range 15–155 MHz with higher values at 5 MHz. This finding indicates the presence of relaxation processes at lower frequencies. However, the isolated points at 5 MHz (and their accuracy) do not allow reliable fits over the entire frequency range.

The significant quantities obtained in the best fittings of the TR equation to the measured ultrasonic spectra in

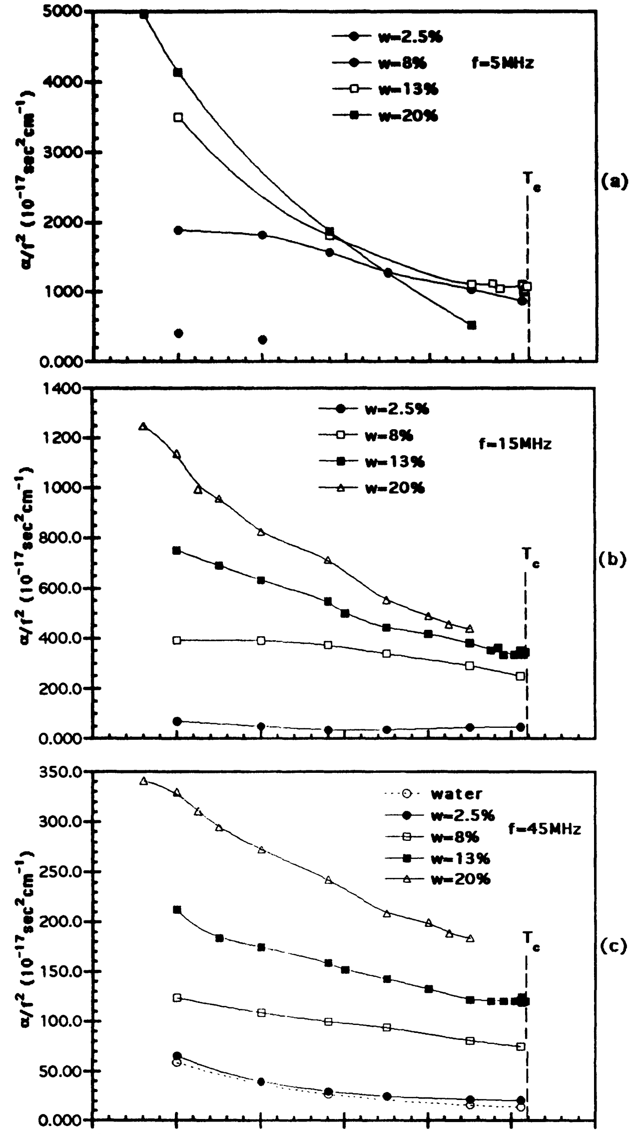

FIG. 4. The temperature dependence of the sound attenuation α/f^2 at $f = 5$ (a), 15 (b), and 45 MHz (c) in the investigated samples. Lines through the experimental points are smoothed curves. Note the absence of critical anomalies in the critical sample $w = 13$ wt %.

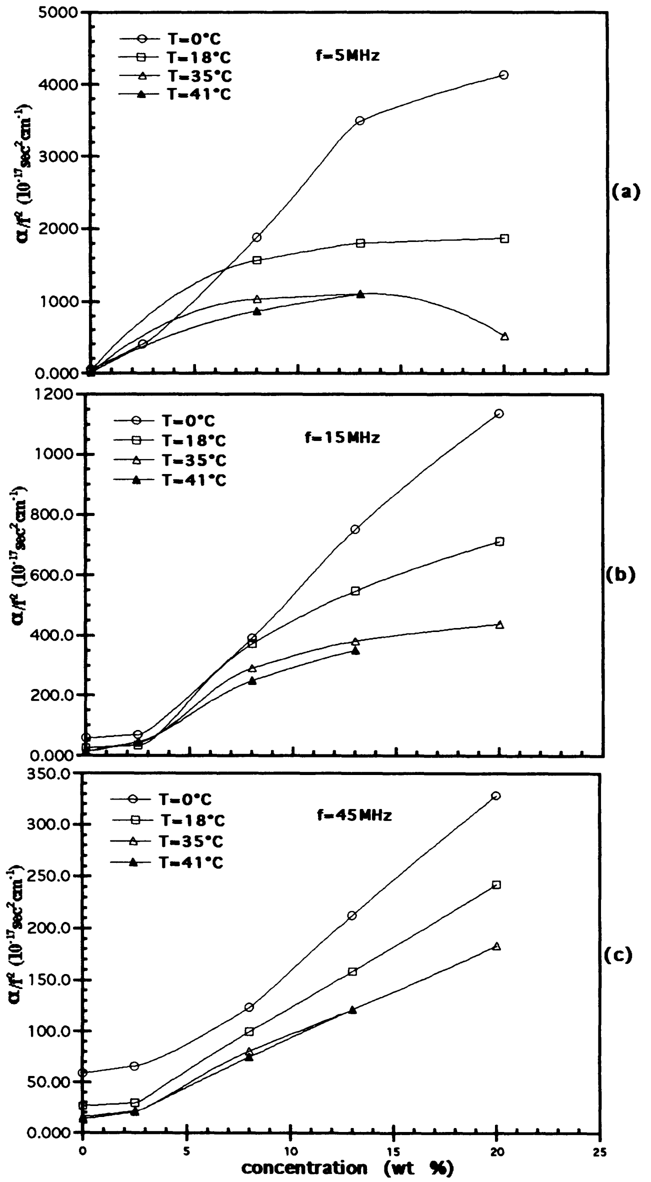

FIG. 5. The concentration dependence of the sound attenuation α/f^2 at $f = 5$ (a), 15 (b), and 45 MHz (c) for some temperatures. Lines through the experimental points are smoothed curves.

the micellar solutions at some temperatures are collected in Table I.

By using sound velocity dispersion data, we also performed a consistency check to test the above-mentioned conclusions. According to a TR equation, the sound velocity frequency dependence is given by

$$c^2(\omega)\cong c_0^2\left\{1+\frac{2}{\pi}\left[\mu_1\frac{\omega^2\tau_1^2}{1+\omega^2\tau_1^2}+\mu_2\frac{\omega^2\tau_2^2}{1+\omega^2\tau_2^2}\right]\right\}, \quad (1)$$

where c_0 is the value in the limit $\omega \rightarrow 0$, and

$$\mu_1=\tfrac{1}{2}A_1f_1c, \mu_2=\tfrac{1}{2}A_2f_2c \quad (2)$$

are the "strengths" (maximum value of the sound absorption coefficient per wavelength, $\mu=\alpha_{\max}\lambda$) associated with the two relaxation processes. In writing Eq. (1), it is assumed that $(c_0^2-c_\infty^2)/c_0^2 \ll 1$. Taking c_0 as a free parameter and using the parameters μ_i and f_i obtained in the TR fits to the absorption spectra, we evaluated $c(\omega)$ through Eq. (1). The good agreement with the experimental behavior is shown in Fig. 3 and it gives a confirmation for a double relaxational behavior.

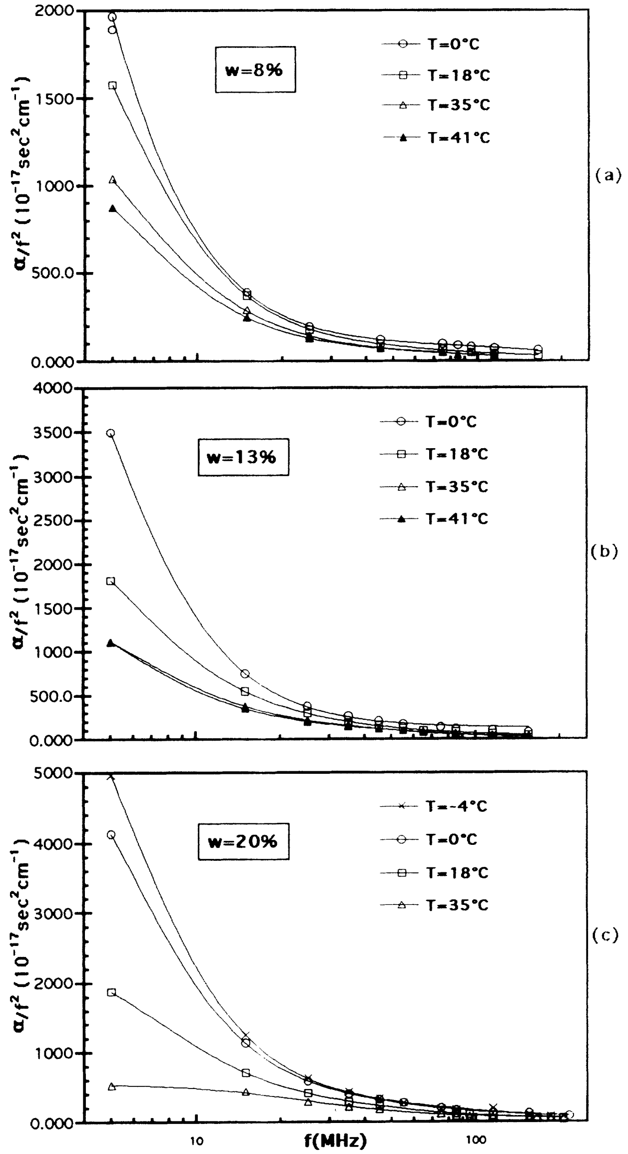

FIG. 6. Ultrasonic spectra in the three investigated micellar samples (a)–(c) for some temperatures. Continuous lines through the experimental points are best fitting curves with two relaxation times equations, as explained in the text. Parameters of these equations are reported in Table I.

TABLE I. Best fitting parameters to the two-relaxation equation for ultrasonic spectra. Index 1 denotes the slow process and 2 the fast one. [f (MHz); A, B, (10^{-17} sec^2 cm^{-1})].

T (°C)	B	A_1	f_1	A_2	f_2	$10^3\mu_1$	$10^3\mu_2$
(sample B2, $w=13$ wt %, critical)							
0.0	62.3	8123.6	4.159	116	66.1	24.821	5.633
18.0	41.6	2783.7	5.892	157.5	39.0	12.322	4.616
35.0	17.54	1550.0	6.350	142.1	47.0	7.473	5.071
41.0	24.40	1708.2	5.747	118.4	53.2	7.459	4.786
(sample B3, $w=20$ wt %)							
−4.0	41.00	8713.8	5.450	200.7	104.7	34.840	15.420
0.0	67.5	6747.7	5.808	197.6	74.3	28.900	10.831
18.0	44.70	2351.0	7.437	222.0	53.2	13.092	8.844
35.0	40.00	489.7	25.000	30.0	60.0	9.189	1.351
(sample B4, $w=8$ wt %)							
0.0	36.2	5575.0	3.500	60.7	167.1	14.270	7.413
18.4	14.62	2953.4	5.123	50.7	144.2	11.351	5.480
35.0	31.47	1657.0	6.000	33.0	54.0	7.576	1.358
41.6	26.6	1377.0	6.017	33.9	63.4	6.335	1.641

We can then restrict our attention to discrete (two) relaxation processes operating in our micellar solutions. A similar conclusion was also found in butoxyethanol solutions [4,8–13].

IV. DISCUSSION

A. Sound velocity

It is well known that addition of small amounts of hydrogen bonded solutes to water increases the sound velocity of solutions well above the values in pure components. This behavior is well evidenced, for example, by the presence of maxima in the sound velocity versus concentration plots (at fixed temperatures) observed in monohydric alcohols [14,15] and alkoxyethanols [3,4]. On the other hand, in aqueous solutions of ionic surfactants, the sound velocity increases almost linearly with the surfactant concentration up to the CMC and thereafter it again increases or decreases about linearly (see Refs. [16,17], and references therein) with a discontinuity at CMC. Depending on the surfactant species, the slopes can be different and the break point at CMC more or less sharp. This behavior is considered to be an indication of micelle formation above the intersection of the two straight lines.

Looking at plots in Fig. 2 we can see that our C_6E_3 nonionic solutions display a similar behavior. Even if the experimental points are not sufficient for a detailed analysis (especially for concentrations below the CMC), a changing slope on passing from lower to higher concentrations is evident for all the investigated temperatures.

Changes in the slope are quite sharp for $T \geq 18\,^{\circ}\mathrm{C}$ and become smoother at lower temperatures where, to our knowledge, literature offers no clear indications about the CMC line for $T < 25\,^{\circ}\mathrm{C}$ or on its existence. Another behavior observed from Fig. 2 is the gradual change of the slope of the sound velocity above CMC from positive to negative values as the temperature increases.

We will show that the changes of the above-mentioned slopes are probably related to the change with temperature of the sign of $\beta_s - \beta_w$, the difference between the apparent adiabatic compressibility of surfactant in micellar solutions (β_s) and the adiabatic compressibility of water (β_w). For this purpose we can write the volume of solutions below CMC as

$$V = n_w V_w + n_s \phi_{v,1} \ , \tag{3}$$

where n_w and n_s are the moles of water and surfactant while V_w and $\phi_{v,1}$ are the molar volume of water and the apparent molar volume of surfactant, respectively. $\phi_{v,1}$, besides the volume of the surfactant molecule, also takes into account the volume for solvation effects around its monomeric form below CMC. The adiabatic compressibility of solutions is then

$$\beta = -V^{-1}(\partial V/\partial p)_S = f_w \beta_w + f_s \beta_{s,1} \ , \tag{4}$$

where the volume fractions f_w and f_s are defined as $f_w = n_w V_w / V$ and $f_s = n_s \phi_{v,1} / V$ and

$$\begin{aligned} \beta_w &= -V_w^{-1}(\partial V_w/\partial p)_S \ , \\ \beta_{s,1} &= -\phi_{v,1}^{-1}(\partial \phi_{v,1}/\partial p)_S = \phi_{K,1}/\phi_{v,1} \end{aligned} \tag{5}$$

are the compressibility of water and the apparent compressibility of surfactant, respectively, and $\phi_{K,1}$ is the usual apparent molar compressibility of surfactant. On passing from Eq. (3) to (4), we neglected contributions from pressure-dependent relaxation processes related to $(\partial n/\partial p)_S$. This approximation is consistent with the small relaxational compressibility found in the analysis of sound velocity dispersion. Equation (4) can be put in the forms

$$\beta = \beta_w + (\beta_{s,1} - \beta_w)\phi_{v,1} C = \beta_w + (\beta_{s,1} - \beta_w)\phi_{v,1}\rho w / M_s \quad (C < C_{\mathrm{CMC}}) \ , \tag{6}$$

where $C = n_s / V$ (mol/cm^3) is the concentration, ρ the density of solutions, w the weight fraction of C_6E_3, and $M_s = 234.34$ its molecular weight. At $C = C_{\mathrm{CMC}}$ we get β_{CMC}. By supposing $\beta_{s,1}$ and $\phi_{v,1}$ independent of concentration we then find that, at fixed temperature, β varies linearly with C. Neglecting density variations, the same trend holds for $\beta(w)$.

Relations similar to Eqs. (3)–(6) hold for $C > C_{\mathrm{CMC}}$ where $\phi_{v,1}$ and $\beta_{s,1}$ for monomers must be substituted by the corresponding $\phi_{v,m}$ and $\beta_{s,m}$ for surfactant molecules in micellar conditions. It is then simple to get

$$\beta = \beta_{\mathrm{CMC}} + (\beta_{s,m} - \beta_w)\phi_{v,m}(C - C_{\mathrm{CMC}}) \quad (C > C_{\mathrm{CMC}}) \tag{6'}$$

showing the linear change of β with C above CMC.

The concentration dependence of the sound velocity is more complicated since it is given by $c = (\rho\beta)^{-1/2}$. However, neglecting the $\rho(C)$ dependence with respect to $\beta(C)$ and developing c in powers of C one finds that $c(C)$ must have a roughly linear variation with a slope depending on $(\beta_w - \beta_{s,1})$ for $C < C_{\mathrm{CMC}}$ and on $(\beta_w - \beta_{s,m})$ above CMC.

Generally speaking, due to strong hydrophobic interactions, the apparent adiabatic compressibility $\beta_{s,1}$ of surfactant monomers is very low and sometimes negative [17–19] so that the slope of $c(C)$ below the CMC is positive as shown in Fig. 2. On the other hand, $\beta_{s,m}$ is usually slightly lower than the compressibility (β_s) of pure surfactant [17–19] and it shows a temperature coefficient which is positive (opposite to β_w). In addition, the values of $\beta_{s,m}$ can be comparable to β_w. As a consequence, the slope of the sound velocity above CMC can result either positive or negative and temperature dependent. For example, at 25 °C it is $\beta_w = 4.475 \times 10^{-5}$ bar^{-1} and we measured β_s (pure C_6E_3)$= 5.3 \times 10^{-5}$ bar^{-1}. As temperature increases, β_w decreases and $\beta_{s,m}$ should increase so that we expect a temperature crossing point where the slope of $c(C)$ changes from positive to negative values as shown in Fig. 2.

B. Sound attenuation

The main result of our analysis of the absorption data was the two relaxation times equation followed by the experimental spectra in the more concentrated solutions B4, B2, and B3. The strengths (μ_1, μ_2) and the relaxation frequencies (f_1, f_2) reported in Table I are displayed in Figs. 7 and 8 as functions of temperature and concentration.

In order to discuss these quantities one must first identify the peculiar relaxation processes to which they are related. As is well known, this association constitutes one of the major tasks in the study of sound propagation in liquid systems. The most reliable approach to this problem is to consider other sources of information concerning the physical-chemical properties of the underlying system and to proceed to the identification by eliminating some possible relaxation processes on the basis of reliability or other physical arguments. For example, in our micellar solutions we can exclude contributions to sound attenuation from concentration fluctuations directly related to diffusional processes or from structural effects since the ultrasonic spectra do not follow the RS, CC, or CD continuum distribution equations typical of such processes. The observation of discrete (two) times relaxational behavior, the nature of micellization phenomena buildup in our samples, and the order of magnitude of the characteristic relaxation times, induce us to associate the two processes to the perturbation, caused by the passage of ultrasonic waves, of some exchange equilibria related to the micellization processes.

On the other hand, aqueous solutions of ionic surfactants also display two relaxation processes and there is a general agreement that they should be associated with the perturbation of exchange equilibria between micelles and the surrounding bulk medium. It is then reasonable to attribute the two processes in our nonionic micellar solu-

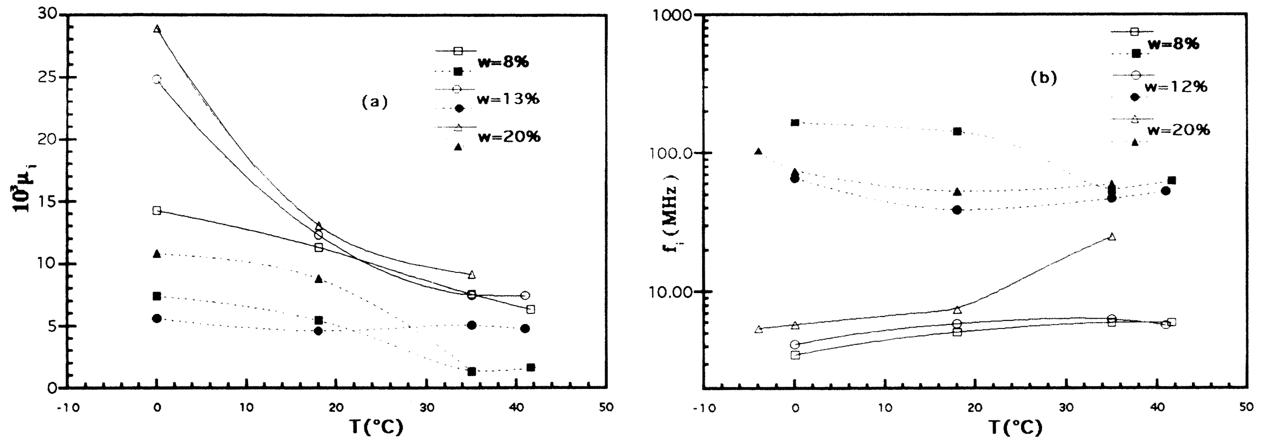

FIG. 7. The temperature dependence of the strengths μ_i [maximum absorption coefficient per wavelength (a)] and of relaxation frequencies f_i (b) of the slow (open symbols, continuous smoothed lines) and fast (full symbols, dashed smoothed lines) relaxation processes in the investigated micellar solutions.

tions to similar equilibria, in particular to surfactant monomers-micelles and to free bulk water molecules—water molecules bound to head groups of micelles. This kind of assignment has already been suggested by various authors ([7,20,21], and references therein). We attribute the slow process (1) to the first equilibrium and the fast one (2) to the latter. On the other hand, this assignment is justified on the basis of the magnitude of the two "strengths" μ. Since μ in chemical reactions roughly depends on the volume change ΔV associated with the involved equilibrium and in our case it is $\mu_1 > \mu_2$ (see Table I and Figs. 7 and 8), we associate the slow process with the surfactant exchange equilibrium which is expected to have a larger volume change. Similar assignments have been made in several aqueous solutions of alcohols and ethers which display two relaxation processes.

According to Aniansson and Wall [22] and Teubner [23] in their treatment of micellar kinetics, the relaxation frequency and the "strength" of the slow process are given by

$$f_1=\frac{k}{2\pi}\left[\frac{1}{\sigma^2}+\frac{X}{\bar{n}}\right] \tag{7}$$

and

$$\mu_1=\frac{\pi}{\beta_\infty}\frac{(\Delta V)^2}{RT}C_{\mathrm{CMC}}\frac{(\sigma^2/\bar{n})X}{1+(\sigma^2/\bar{n})X}\,, \tag{8}$$

where k is the mean of the dissociation constants in the micellar region; σ^2 is the variance of the micelle size distribution; $\bar{n}$ is the mean aggregation number; $X=(C-C_{\mathrm{CMC}})/C_{\mathrm{CMC}}$ is a reduced concentration; $\beta_\infty \approx (\rho c_\infty^2)^{-1}$ is the adiabatic compressibility of solutions in the limit $\omega \rightarrow \infty$; and ΔV is the volume change associated to surfactant monomers in the bulk-micelle exchange. According to Eqs. (7) and (8) (i) f_1 should increase with the concentration C and increase little with temperature; (ii) μ_1 should increase more or less sharply

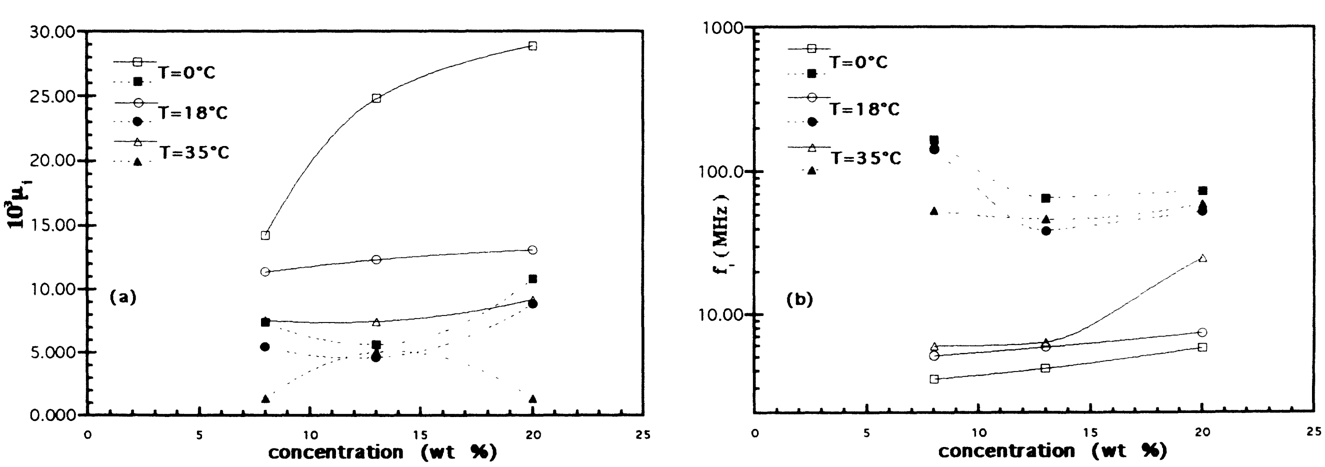

FIG. 8. The concentration dependence of the strengths μ_i (a) and relaxation frequencies f_i (b) of the slow and fast relaxation processes for some temperatures. Symbols and lines as in Fig. 7.

from 0 (at CMC) to reach an almost constant value at higher concentrations and, in addition, it should decrease a great deal as T increases. The trends of μ_1 and f_1 in Figs. 7 and 8 confirm these conclusions. However, the relaxation frequency in sample B3 (the highest concentration) at $T=35\,^{\circ}\mathrm{C}$ deviates from the predicted behavior. A possible explanation could be a change in the mean size of micelles, but this point deserves further detailed investigations.

Figures 7 and 8 show that the temperature and concentration dependences of the relaxation frequency (f_2) and strength (μ_2) of the fast process are more complex than those for the slow one. In particular they indicate that in the low temperature range f_2 depends on the concentration and decreases slightly as T increases. However, at the highest temperatures ($T>25\,^{\circ}\mathrm{C}$) they show a tendency to increase and become independent of concentration. The last finding is likely related to the close approach to the convolution line. As soon as μ_2 is concerned, the critical solution B2 seems to have a particular significance in that the strength is almost independent of temperature.

Comparing these results in C_6E_3 solutions with those observed in solutions with the lower homologous C_4E_1 [4,8,12], one finds that both systems show two relaxation processes where the orders of magnitude of the relaxation frequencies of both slow and fast processes are the same. However, in C_4E_1 solutions the concentration and temperature dependences of relaxation frequencies f_2 and strengths μ_2 are in general different [8,9] from those observed in the present study. The cause of it could be the possibility that the solute-solvent reaction site be the hydroxyl group of the C_4E_1 molecule and the oxygens of oxyethylene groups in the C_6E_3 molecules.

C. Critical behavior

The temperature dependence of the ultrasonic absorption and velocity in the critical sample B2 was accurately investigated at $f=5$, 15, and 45 MHz by approaching T_c from below. From about $\Delta T=T_c-T\cong 10\,^{\circ}\mathrm{C}$, we intensified the measurements taking several spectra and waited for a long time to allow a complete equilibrium in the sample. In order to do this, we put the ultrasonic cell into a Leeds-Northrup thermostating oil bath giving a $\pm 10^{-3}$ K constant temperature.

As shown in Fig. 4, on approaching T_c, α/f^2 displays a regular decreasing trend whatever the frequency is. Even if at $f=5$ MHz the attenuation shows a weak trend to reverse the slope, the experiments show unequivocally the absence of a marked increase of α/f^2 as $T\rightarrow T_c$. This increase is typical of binary critical mixtures of low molecular masses where the anomaly extends several degrees (10–20 °C) from T_c. We point out, in addition, that as $T\rightarrow T_c$ the sound velocity does not show peculiar behavior as a function of both temperature and frequency (see Figs. 1 and 3).

The lack of a divergentlike ultrasonic attenuation as a function of T in our critical $C_6E_3+H_2O$ sample is a confirmation of a previous observation by Borthakur and Zana [7] in the same system and at lower frequencies. However, a similar behavior has also been observed in other supramolecular binary critical mixtures such as $C_{12}E_6$ and microemulsions [24] as well as in n-C_4E_1 and iso-C_4E_1 aqueous solutions [3,4,8,10,13] which are thought to form micellar aggregates. A large number of experiments also shows the absence of temperature-dependent anomalous critical attenuation near a critical point of supramolecular binary mixtures at the ordinary frequency range of ultrasonic techniques.

On the other hand, there is experimental evidence that, on approaching T_c, the order parameter (concentration) fluctuations become very large even in supramolecular mixtures. For example, light scattering experiments by Corti, Minero, and De Giorgio [5] showed that the correlation length (ξ) of the order parameter of micellar $C_6E_3+H_2O$ solutions diverges with the usual power law $\xi=\xi_0\varepsilon^{-\nu}$, with $\xi_0=3.6$ Å and $\nu=0.63$. Similar results have been obtained in other micellar solutions of nonionic surfactants ($C_{12}E_6, \xi_0=16$ to 20 Å [5,25,26]; $C_{12}E_8$, $\xi_0=7.5$ Å [27]) as well as of 2-C_4E_1 and iso-C_4E_1 ($\xi_0=3.65$ to 4.45 Å [13]). Comparing these ξ_0 values with those found in small-molecule binary mixtures ($\xi_0=1$ to 3 Å [28]) one finds that the former are slightly larger. As a consequence the characteristic temperature-dependent relaxation rates ω_D ($=2D\xi^{-2}$) associated to energy fluctuations of wave number $q=\xi^{-1}$ and evaluated as

$$\omega_D=\omega_0\varepsilon^{z\nu}=[k_BT_c/(3\pi\eta_0\xi_0^3)]\varepsilon^{z\nu} \tag{9}$$

[$\varepsilon=(T_c-T)/T_c=\Delta T/T_c$; $z\sim 3.07$, dynamical critical exponent] are lower than in molecular binary mixtures. For example, we find $f_0=\omega_0/2\pi\sim 1$ GHz in $C_6E_3+H_2O$ ($\eta_0=1.9$ to 2.1 cP [5]); $f_0=0.4$ to 0.6 GHz in $C_4E_1+H_2O$ ($\eta_0=1.5$ to 2 cP [29]) to be compared with $f_0=19.6$ GHz in 3-methylpentane-nitroethane [30], $f_0=13$ GHz in cyclohexane-nitroethane [31], $f_0=5.6$ GHz in acid isobutyrric-water [32], $f_0=4$ GHz in aniline-cyclohexane [31], $f_0=1.9$ GHz in triethylamine-water [33].

In order to analyze our experimental data near the critical point and to investigate the origin of the apparent lack of acoustic anomalies, we must refer to the existing theories explaining the critical sound propagation. These theories include both the specific heat and bulk viscosity relaxational approaches and both mode-coupling and renormalization group concepts. As shown by Garland and Sanchez [30], theoretical predictions for critical sound attenuation from various approaches can be put in the same form of type

$$\alpha_\lambda(\omega,T)=A(T)G(\Omega)\,, \tag{10}$$

where α_λ is the ultrasonic absorption per wavelength, $A(T)$ is an amplitude, and $G(\Omega)$ is a scaling function of the reduced frequency $\Omega=\omega/\omega_D$. We will subsequently utilize only the Ferrell-Bhattacharjee form of Eq. (10) since comparisons with experiments in several molecular binary mixtures demonstrate a major reliability.

The FB treatment [34,35] of the sound propagation in binary critical mixtures is essentially based on the use of a complex frequency-dependent specific heat [$C_p(\omega,T)$] originated by a lagged response of the Fourier components of the concentration fluctuations to the adiabatic temperature oscillations driven by the propagating sound waves. This mechanism already used by Fixman [36] and Mistura [37] in their approaches to the critical sound attenuation, comes out far from the early Herzfeld-Rice [38] and Kneser [39] treatments of the sound propagation in polyatomic gases and molecular liquids. In the latter systems the lagging modes are the internal degrees of freedom (vibrational energy levels). In the FB model it is then considered a coupling between $\mathbf{C}_p$ and the complex compressibility [or the sound velocity $\mathbf{c}(\omega)$] of the system through a coupling constant $g=T_c\rho_c(\partial S/\partial p)_c$ and dynamic-scaling concepts are introduced to determine the frequency dependence of $\mathbf{C}_p$. As a final result, a temperature- and frequency-dependent complex sound velocity is obtained, the real part of which gives the critical sound dispersion $c(\omega)$ and the imaginary one the α_λ.

The FB expression for the amplitude $A(T)$ in Eq. (1) is given by [28,30]

$$A_F(T)=(\pi^2\tilde{a}cc_cg^2\Delta C_p)/(2z\nu T_cC_{p1/2}^2)b^{\tilde{a}/z\nu}\varepsilon^{-\tilde{a}} , \qquad (11)$$

where $\tilde{a}(=0.12)$ and ΔC_p are the critical exponent and the amplitude of the static specific heat singularity; $C_{p1/2}$ is approximately the specific heat at the characteristic reduced temperature $\varepsilon_{1/2}$ where α_λ falls to $\frac{1}{2}\alpha_{\lambda c}$ (at T_c) for a given frequency f; g is the adiabatic coupling constant; c and c_c are the sound velocity at T and T_c and $b=(\omega/\omega_0)\varepsilon_{1/2}^{-z\nu}$ is a dimensionless scale factor of order unity. In spite of a weak frequency dependence (through b and $C_{p1/2}$), $A(T)$ can be practically considered only a function of T [30].

The scaling function $G(\Omega)$ [see Eq. (10)] proposed by FB is given by

$$G_F(\Omega)=\Omega^{-\tilde{a}/z\nu}F(\Omega)=\Omega^{-\tilde{a}/z\nu}/[1+0.414(\Omega_{1/2}/\Omega)^{1/2}]^2 , \qquad (12)$$

where $\Omega_{1/2}$ is the reduced frequency at which $\alpha_\lambda(\omega,T)$ is one-half $\alpha_\lambda(\omega,T_c)$. From fittings to experiments it is found that $\Omega_{1/2}=2.1$.

For comparison purposes, it is convenient to transform α_λ in Eq. (10) into $\alpha/f^2(=\alpha_\lambda/cf)$ units. We have

$$\alpha/f^2(\omega,T)=A_{\mathrm{FB}}(T)F_{\mathrm{FB}}(\Omega) , \qquad (13)$$

where

$$\begin{aligned}A_{\mathrm{FB}}(T)&=(A_F/c)(2\pi/\omega_0)\varepsilon^{-z\nu}\\&=[(\pi^2\tilde{a}g^2c_c)/(2z\nu T_c)](\Delta C_p/C_{p1/2}^2)\\&\quad\times(2\pi/\omega_0)b^{\tilde{a}/z\nu}\varepsilon^{-(\tilde{a}+z\nu)}\end{aligned}$$

and

$$F_{\mathrm{FB}}(\Omega)=\Omega^{-1}G_F(\Omega)=\Omega^{-(1+\tilde{a}/z\nu)}F(\Omega) .$$

Equation (13) was considered in Sec. II as one of the fitting relaxational equations.

We used this equation for testing the experimental results in the critical sample B2 in the following conditions.

(a) As a function of frequency, at the critical point. At $T=T_c$ one gets from Eq. (13)

$$\alpha/f^2(T_c,\omega)=A_{\mathrm{crit}}f^{-(1+\tilde{a}/z\nu)} , \qquad (14)$$

where

$$\begin{aligned}A_{\mathrm{crit}}&=(A_F/c_c)\varepsilon^{\tilde{a}}f_0^{\tilde{a}/z\nu}\\&\approx(\pi^2\tilde{a}c_cg^2\Delta C_p)/(2z\nu T_cC_{p1/2}^2)b^{\tilde{a}/z\nu}f_0^{\tilde{a}/z\nu} . \qquad (15)\end{aligned}$$

(b) As a function of temperature, at fixed frequency. One finds from Eq. (13)

$$\alpha/f^2(T,\omega)=(c_c/c)\alpha/f^2(T_c,\omega)(1+C_{1/2}\Delta T)^{-2} , \qquad (16)$$

where $C_{1/2}=0.414/\Delta T_{1/2}$ and $\Delta T_{1/2}$ is the ΔT at which attenuation falls to one-half the value at T_c. Equation (16) shows that, as $T\rightarrow T_c,\alpha/f^2$ increases as $(1+C_{1/2}\Delta T)^{-2}$ approaching the critical value corresponding to the given f.

(c) As a function of frequency, at a given temperature. This dependence is given by Eq. (13).

As previously noticed, the observed temperature dependence of α/f^2 near T_c is in striking contrast with Eq. (16). Nevertheless, we also compared the predicted frequency dependences at T_c and $T\neq T_c$. According to Eq. (14) a plot of α/f^2 at T_c versus $f^{-1.06}$ should give a straight line with an intercept representing the ultrasonic absorption background and a slope giving A_{crit}. Values at T_c were taken extrapolating data for $T\rightarrow T_c$. In Fig. 9 we compare this plot (a) with a TR one (b): the good visual fitting to the experimental points in Fig. 9(a) is only apparent since the two relaxation times equation TR exhibits a better quality. A similar finding occurs in the fits at $T\neq T_c$: even if we find that on approaching T_c Eq. (13) exhibits an increasing apparent satisfactory fitting, the use of a TR equation is unequivocally better.

As a conclusion, we are then forced to assume that the large sound attenuation observed near T_c is mainly due to the micellar exchange processes analyzed in the preceding section, far from T_c. This situation looks quite similar to that found in some molecular binary critical mixtures (e.g., triethylamine-water [33], nitroethane-3-methylpentane [30], acid isobutyrric-water [32]) where a large background associated with chemical relaxation processes is superimposed on the critical effects. In the latter systems, however, the critical contributions can be more or less disentangled from the underlying background and, in any case, give rise to the characteristic increase of ultrasonic attenuation as $T\rightarrow T_c$.

The temperature and frequency dependences of the ultrasonic losses previously analyzed thus indicate that in supramolecular critical $C_6E_3+H_2O$ solutions the critical contributions in the investigated frequency range (5–160 MHz) are of negligible amplitude and are masked by the large background. This behavior is in contrast with that observed in molecular mixtures. Assuming that the FB treatment is also valid in supramolecular systems, we must search the origin of this difference in the critical amplitude A_{crit} given by Eq. (15). An inspection of this equation shows that, assuming an ordinary value for C_p, the small critical attenuations are reasonably originated by small g and/or ΔC_p values. The previously noticed smaller f_0 values in supramolecular mixtures (compared

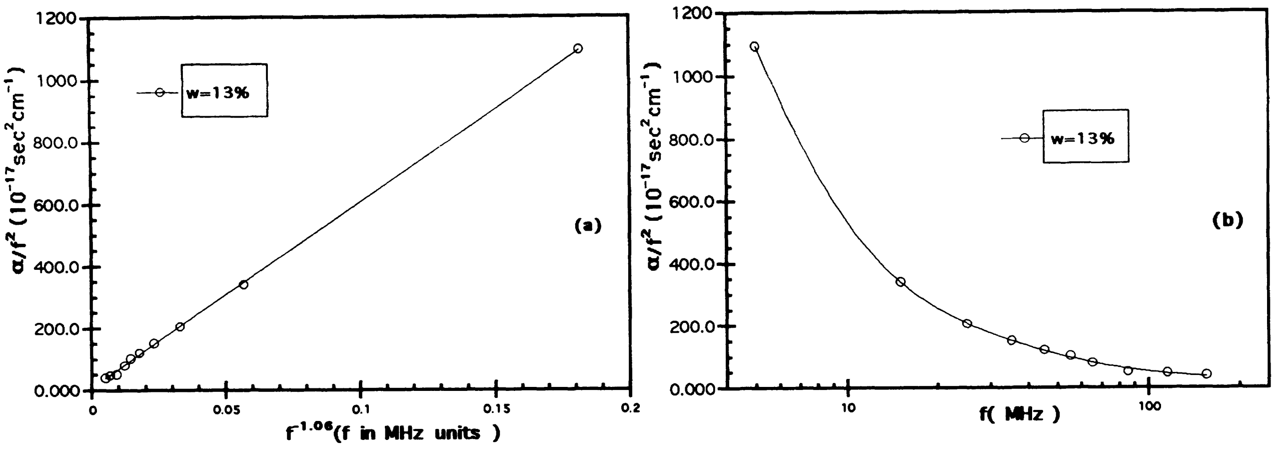

FIG. 9. The sound attenuation α/f^2 at $T=T_c$ in the critical sample B2 as a function of frequency. (a) is a Ferrell-Bhattacharjee plot α/f^2 vs $f^{-1.06}$ and (b) a usual $\log_{10}f$ plot. Continuous lines through the points are best fittings with the Ferrell-Bhattacharjee linearized form $(\alpha/f^2)_{T=T_c}=A_{\text{crit}}f^{-1.06}+B$ and with a two relaxation times equation, respectively. The correlation factor is $R=0.999\,83$ in (a) and $R=0.999\,91$ in (b).

with those in molecular mixtures) should, in fact, have a negligible role since $A_{\text{crit}}\approx f_0^{\alpha/z\nu}=f_0^{0.06}$. This term changes from 3 to 4 on going from $f_0=0.1$ to 20 GHz. Critical contributions to the ultrasonic attenuation should then be detectable in a frequency region well below the usual ranges.

The apparent absence of critical contributions near T_c at the ordinary frequencies of ultrasonic techniques also manifests in the temperature and frequency behaviors shown by the sound velocity. The Kramers-Kronig relations applied in the FB approach lead, in fact, to temperature- and frequency-dependent anomalies of the sound velocity near T_c. No such effects have been detected in our sample as shown in Figs. 1 and 3. This finding, however, agrees with the observation by FB [34] that sound velocity anomalies should be observed at frequencies much lower than the ordinary ones. A confirmation of such predictions comes from recent experiments by Harada and Tabuchi [40] showing sound velocity critical anomalies in oil–Aerosol OT (AOT)–decane microemulsions at $f=910$ Hz.

V. CONCLUSIONS

The analysis of the experimental results we performed in nonionic micellar $C_6E_3+H_2O$ solutions has shown that the supramolecular aggregates influence the sound propagation in three main aspects.

(a) The concentration and temperature behaviors of the low-frequency sound velocity depend on the difference between the compressibility of water and the apparent compressibility of the surfactant. In particular, solvation effects in the monomeric surfactant molecules below the CMC reduce the molar apparent compressibility of surfactant, thus originating an almost linear increase of the sound velocity. Above the CMC the apparent compressibility of micellar surfactant may become comparable with the compressibility of water so that, depending on the temperature, the sound velocity may increase or decrease with concentration.

(b) The ultrasonic absorption spectra in the micellar solutions are mainly due to two relaxation processes which have been associated to micellar exchange equilibria. The overall amplitude of these effects decreases with increasing temperature and is still large near the critical point.

(c) The sound propagation near the critical point is dominated by the large background due to micellar exchange equilibria. The absence of critical contributions at the ordinary frequencies of ultrasonic techniques (≥ 5 MHz) seems to be a characteristic feature of supramolecular binary mixtures and it was discussed in the framework of the Ferrell-Bhattacharjee treatment. The origin of this apparent lack of universality was attributed to the small values of the critical absorption amplitude which, in turn, is related to the negligible coupling between the adiabatic sound waves and the order parameter fluctuations and/or to the small values of the amplitude of the relaxing specific heat. The role of micellar aggregates in such findings remains an open problem.

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