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Precise Measurement of Ultrasonic Absorption in Micellar Solutions in the Frequency Range from 0.2 to 10 MHz

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A cylindrical resonator for the measurement of ultrasonic absorption has been designed. It was found that a newly designed resonator can determine the absolute value of the ultrasonic absorption coefficient of water at frequencies above 0.7 MHz. For aqueous solutions it has a sufficient resolution power down to 0.2 MHz by means of a reference measurement. Precise measurements of ultrasonic absorption were carried out for aqueous solutions of dodecyltrimethylammonium bromide using a newly designed resonator and two other previously reported resonators. The ultrasonic relaxation spectra show a single relaxation process within the investigated frequency range. The relaxation process can be ascribed to a "fast" relaxation related to the exchange of a surfactant between micelles and bulk solution. The kinetic parameters for the exchange process were estimated on the basis of Teubner's theory.

Precise measurements of the ultrasonic absorption below 10 MHz are very important for a variety of ultrasonic relaxation studies, such as the kinetics of micellar solutions,[1–5] the dynamics of segmental motions of polymer chains in a solution[6,7] and the dynamics of simple molecules.[8,9] For a kinetic study of micellar solutions, a precise measurement within this frequency range is inevitably required since it is well known that most micellar solutions show an ultrasonic relaxation phenomena within the frequency range 0.1 to 10 MHz.

For frequencies below 1 MHz, however, few measurements have been carried out and only an ultrasonic study has been reported for the typical micellar solutions of sodium dodecyl sulfate by Yasunaga et al.[4] using an ultrasonic reverberation method. Although the reverberation method has been an available technique for measuring ultrasonic absorption within this frequency range, it usually requires a great volume of a sample (several to ten liters).[10] Also, its accuracy is sometimes insufficient. Therefore, applications of this technique have been limited to the micellar solutions with high ultrasonic absorption coefficients.

On the other hand, a cylindrical resonator method which was originally developed by Eggers,[11] has proved to be a powerful technique for measuring the ultrasonic absorption coefficient of liquids and solutions at frequencies below 10 MHz. However, it is still difficult to make precise measurements using this method on samples with low ultrasonic absorption coefficients, such as water and dilute aqueous solutions at frequencies below 2.5 MHz. The main reason for the difficulty is that the mechanical loss of the cylindrical resonator sharply increases with a decreasing frequency. In order to reduce the mechanical loss, a few improvements have been made; for example, Eggers et al.[12,13] developed a pressure concave resonator and Choi et al.[14,15] proposed a plano-concave resonator and an optical detector using Raman-Nath light diffraction.

Recently, we have succeeded in reducing the mechanical loss of a cylindrical resonator without using a pressure concave resonator and without using an optical detector. Our improvement was simply in using a pair of X-cut quartz transducers with large diameters. It was found that a newly designed resonator can determine the absolute value of the ultrasonic absorption coefficient of water at frequencies above 0.7 MHz. For aqueous solutions it has a sufficient resolution down to 0.2 MHz, by means of a reference measurement.

In this paper we present a detailed description of the resonator and results regarding precise measurements of the ultrasonic absorption on aqueous solutions of a cationic surfactant, dodecyltrimethylammonium bromide, at frequencies from 0.2 to 10 MHz. The experimental results are discussed on the basis of a theory developed by Teubner.[16]

Experimental

Principle of the Resonator Method. Prior to a description of the resonator cell, the principle of the resonator method will be briefly presented. With this method, a resonator cell consists of a liquid column sealed by two X-cut quartz transducers. A frequency-variable oscillator drives the input transducer and produces a series of standing waves in the liquid column at resonance frequencies; then, sharp resonance peaks are detected by an output detector. At the n-th resonance frequency, f_n, the quality factor, Q, of the cell is given by

$$Q^{-1} = \Delta f_n / f_n, \tag{1}$$

where Δf_n is the half-power bandwidth (hereafter abbrevi-

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ated as HPB) of the n-th resonance peak. For an ideal cylindrical resonator containing a liquid sample, the Q factor is given by

$$Q^{-1} = \alpha\lambda/\pi, \tag{2}$$

where α is the ultrasonic absorption coefficient of the sample and λ the ultrasound wavelength. In practice, Eq. 2 does not hold since there are several inherent factors called "mechanical" loss in the design of the cell. Therefore, Eq. 2 should be modified as follows:

$$Q^{-1} = \Delta f_n/f_n = \frac{\alpha\lambda}{\pi} + Q^{-1}{}_{mechanical}, \tag{3}$$

where $Q^{-1}{}_{mechanical}$ represents the mechanical loss of the cell. For a determination of the ultrasonic absorption coefficient of a sample, $Q^{-1}{}_{mechanical}$ should be eliminated by a reference measurement in the same cell at the same frequencies using a suitable liquid. Then, the excess absorption per wavelength $(\alpha\lambda)_{excess}$ in the liquid is obtained from Eq. 4.

$$(\alpha\lambda)_{excess} = \pi[(\Delta f_s - \Delta f_r)/f_n] \tag{4}$$

In Eq. 4, Δf_s and Δf_r represent the corresponding HPB values of the n-th resonance peak in the sample and the reference liquid, respectively.

Design of Resonator. The absolute value of the ultrasonic absorption coefficient can be determined using a resonator having a negligible mechanical loss compared with $\alpha\lambda/\pi$ of the liquid sample. Then, an accurate measurement can be easily performed. Therefore, a reduction of the mechanical loss is an essential point for the design of a resonator.

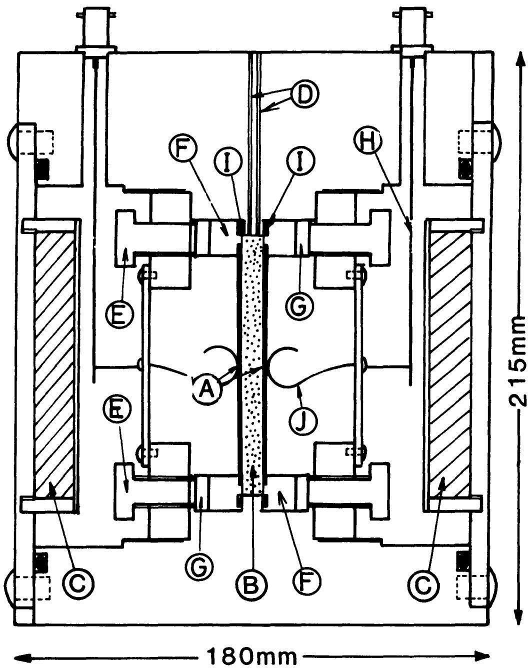

Fig. 1. Sectional view of the ultrasonic resonator, (A): X-cut quartz transducers, (B): cavity (sample room), (C): desiccant, (D): filling hole, (E): screw for parallelism adjustment, (F): supporter for transducer, (G): spacer, (H): lead, (I): O-ring, (J): electrode.

Figure 1 shows the resonator cell designed for this study. The dimensions of the cell are ca. 180 mm in width, 240 mm in length, and 215 mm in height, respectively. The acoustical path length is ca. 7 mm, and the liquid column has a total volume of ca. 50 ml, together with the dead space. The following improvements were carried out to reduce the mechanical loss as much as possible.

For the cell: (1) In order to separate the resonance frequency of the cavity from that of the total cell system, a sufficiently heavy cell (ca. 60 kg) was made of stainless steel (SUS 27). (2) Parallelism between transducers also contributes to the mechanical loss at the lower frequency region; thus, it was coarsely adjusted by measuring the distance between two transducers (with a precision of ±1/100 mm) using a dial indicator and was finally tuned by inspecting the pulse echo pattern on a synchroscope in a way similar to the usual pulse method. (3) Each transducer was supported only at its back surface with a holder to minimize the mechanical load on its surface. This makes the transducer vibrate better in thickness mode. (4) Two thin filling holes (1 mm in diam.) were drilled to minimize the disturbance of the resonance condition. (5) Desiccant (silica gel) was sealed within a cage attached to the wall of the cell since the mechanical loss of the resonator greatly depends on the humidity in the chamber behind the transducer.

For transducers: (1) In the frequency range below 2 MHz, the diffraction of sound makes a major contribution to the mechanical loss. The diffraction was suppressed by using a pair of quartz transducers with large diameters(90 mm). (2) A high quality factor of the transducers is also required in order to reduce the mechanical loss. For this purpose, the fundamental frequencies of the two transducers were matched within 0.05% (2.001 and 2.002 MHz, respectively) and their surfaces were polished to within optical grade. These transducers were purchased from Valpay-Fisher Co. Inc., U.S.A.

Measurement System and Temperature Control. Our apparatus for the resonator method consists simply of two frequency synthesizers (Rockland Model 5100, 0—2 MHz, John-Fluke Model 6039 A, above 2 MHz), a resonator cell and two detectors (Yokogawa Hewlett Packard Model 3400 RMS voltmeters). A detailed description of the apparatus has been published elsewhere.[17] Any temperature drift in a sample makes it difficult to obtain an accurate HPB reading since the resonance frequency is very sensitive to drift due to temperature fluctuations. The temperature of a water bath was controlled with an accuracy of $\pm 10^{-3}$ °C by means of a digital temperature-control system. The temperature drift in the sample could also be minimized using the sufficiently large heat capacity of the cell (due to its large size and weight).

Materials. Dodecyltrimethylammonium bromide (hereafter abbreviated as DTAB) and the other chemicals used in this study were purchased from Nakarai Chemicals Co. Ltd. and used without further purification. A chemical analysis of the DTAB was carried out at Prof. Tsuge's laboratory at our university and the purity of the sample was confirmed to be: C_{12}=99.9%, C_{10}=0.0%, and C_{14}=0.1%.

Ultrasonic Absorption and Sound Velocity Measurements. Three cylindrical resonators were used to measure the ultrasonic absorption in the frequency range

0.2—10 MHz: the resonator designed here (0.2—2 MHz); the other two reported previously,[17)] one with 50 mm diameter crystals with a fundamental frequency of 2 MHz (0.8—3.2 MHz), and the other with a 30 mm diameter, 5 MHz crystals for the frequency range above 2.2 MHz. The ultrasonic absorption coefficients of aqueous solutions of DTAB were determined by the reference measurement on the basis of Eq. 4 using distilled, degased water as a reference liquid. The sound velocity was measured mostly with the cylindrical resonators and occasionally with an ultrasonic interferometer working at a fixed frequency 4.000 MHz.

Results and Discussion

Characteristic Properties of Resonator. Figure 2 shows the HPB values for water measured at 25 °C (using the designed resonator). For a comparison, the results using the other two resonators are also plotted. The HPB values of a resonator without a mechanical loss can be calculated using a modified form of Eq. 2:

$$\Delta f_n = \frac{\alpha}{f_n^2}\cdot\frac{u}{\pi}\cdot f_n^2, \tag{5}$$

where u is the sound velocity in the sample. Equation 5 shows that Δf_n should vary linearly with the square of the resonance frequency, f_n^2, in non-relaxing liquids. The solid line in the figure represents the HPB values of water calculated from Eq. 5. In that calculation, the ultrasonic absorption and sound velocity values for water at 25 °C were taken as $\alpha/f^2=22.6\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$ and $u=1.497\times10^5\,\mathrm{cm\,s^{-1}}$, respectively. The deviation of the HPB data from a straight line represents the mechanical loss of the resonator at that frequency. If the obtained HPB values fall directly on a straight line, an absolute measurement of the ultrasonic absorption is possible using this resonator. It is readily seen from Fig. 2 that an absolute measurement for water is possible at frequencies above 0.7 MHz using a combination of these three resonators.

Figure 3 shows the resolution power of the designed resonator for measuring the ultrasonic absorption coefficient. Three lines represent the HPB values of water calculated from Eq. 5 at 15, 20, and 25 °C, respectively. The resonator can detect small differences (ca. $2.6\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$) in α/f^2 of water at these temperatures. In the case of benzene having a higher ultrasonic absorption coefficient ($860\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$ at 20 °C), the low-frequency limit of an absolute measurement goes down to ca. 0.5 MHz.

If the observed HPB values deviate from those

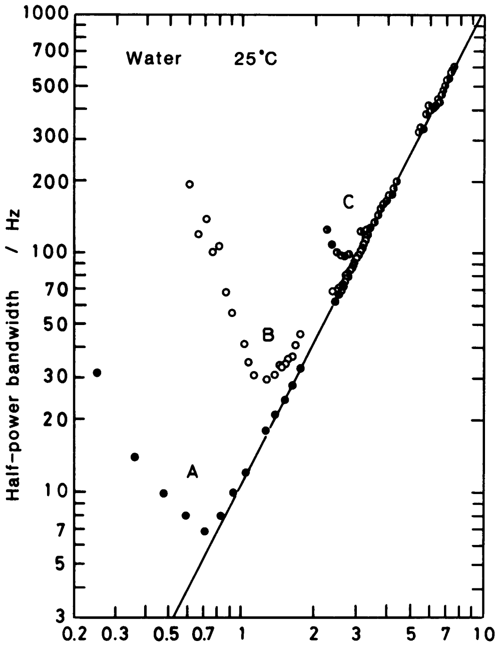

Fig. 2. The HPB values of resonance peaks for water at 25°C. A solid line represents the calculated HPB values of water from Eq. 5. For comparison, HPB values for the other two resonators used in this study are also plotted, (●): Resonator A (this work, 0.2—2 MHz), (○): resonator B (0.8–3.2 MHz), (◑): resonator C (2.2—8 MHz).

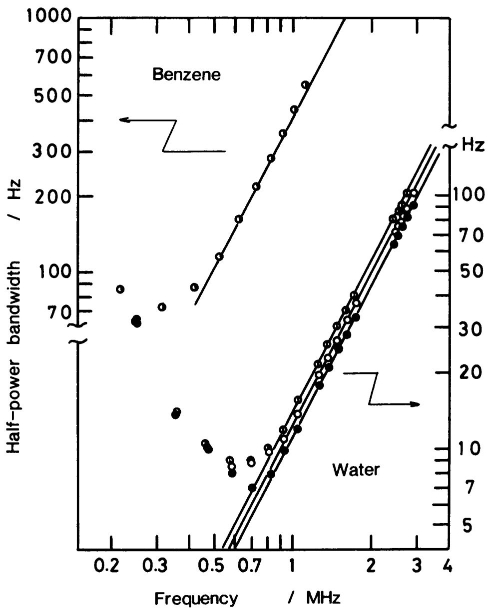

Fig. 3. The HPB values of resonance peaks observed in water at 15 (⦶), 20 (○), and 25 °C (●) and in benzene (◑) at 20 °C. Solid lines represent the HPB values calculated from Eq. 5. Following data (except α/f^2 of benzene) are taken from literature[31)] in the calculation, $\alpha/f^2=28.7\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$, $u=1.466\times10^5\,\mathrm{cm\,s^{-1}}$ (water at 15°C), $\alpha/f^2=25.2\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$, $u=1.483\times10^5\,\mathrm{cm\,s^{-1}}$ (water at 20°C), $\alpha/f^2=860\times10^{-17}\,\mathrm{s^2\,cm^{-1}}$, $u=1.324\times10^5\,\mathrm{cm\,s^{-1}}$ (benzene at 20°C).

calculated from Eq. 5, as is shown in Fig. 3 (for benzene at frequencies below 0.5 MHz and also for water below 0.7 MHz), the ultrasonic absorption coefficient can be determined by a reference measurement on the basis of the Eq. 4. Figure 4 shows the result of a reference measurement of the ultrasonic absorption of benzene at 20 °C. *o*-Xylene was used as a reference liquid because it has a similar acoustical impedance to that of benzene; also, no relaxation process in *o*-xylene was reported by Ohsawa[18] at the frequencies above 10 KHz. The ultrasonic absorption coefficient determined by the reference measurement is in good agreement with that determined by an absolute measurement using a pulse technique. This indicates that the designed resonator detects the reliable ultrasonic absorption coefficient at frequencies above 0.2 MHz.

Ultrasonic Absorption in Aqueous Solutions of DTAB. Figure 5 shows the result of ultrasonic absorption measurements for aqueous solutions of DTAB. The data are expressed as a plot of the absorption coefficient vs. the logarithmic frequency. An ultrasonic relaxation process can be observed within the frequency range investigated for all DTAB solutions. It is expressed well by the equation for a single relaxation

$$\frac{\alpha}{f^2} = \frac{A}{1+(f/f_r)^2} + B, \tag{6}$$

where f represents the measured frequency, f_r is the relaxation frequency, A the relaxation amplitude, and B the contribution to sound absorption from any other processes that may be occurring at higher frequencies beyond our frequency range. A linearlized least-square method was used to fit Eq. 6 to the ultrasonic absorption data and the relaxation parameters, A, B, and f_r, were determined. The solid lines in Fig. 5 represent the calculated ultrasonic relaxa-

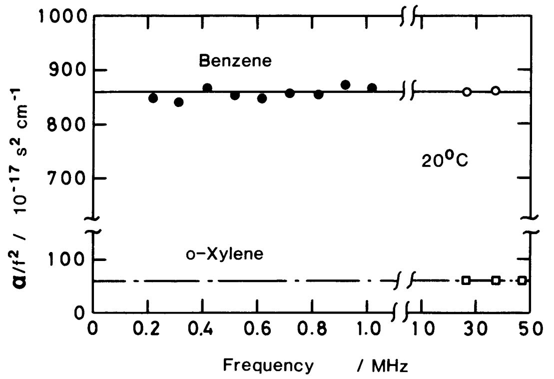

Fig. 4. Ultrasonic absorption coefficient of benzene determined by the reference measurement using the resonator (●) and that determined by pulse technique (○). Solid and chain lines show the average values of ultrasonic absorption coefficient determined by pulse technique for benzene (860×10^{-17} s^2 cm^{-1}) and *o*-xylene (61.2×10^{-17} s^2 cm^{-1}), respectively.

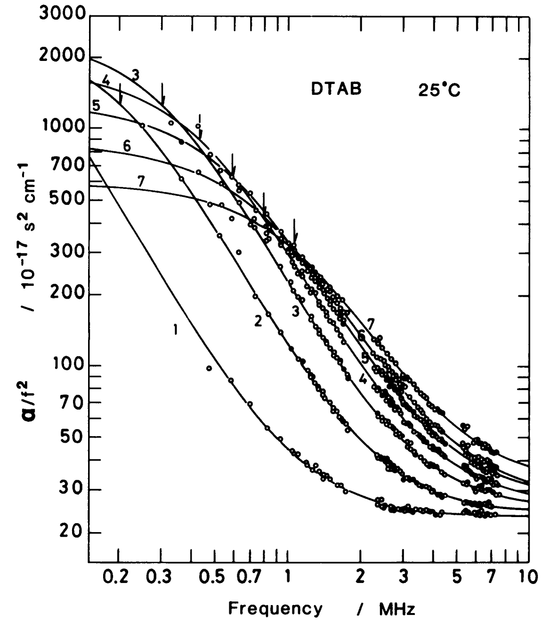

Fig. 5. Ultrasonic absorption as a function of frequency for aqueous solutions of DTAB at 25°C. The solid lines represent the calculated relaxation spectra from Eq. 6, and arrows show the location of relaxation frequencies. Numerical notations represent the concentration of solution, (1): 1.95×10^{-2} M, (2): 3.24×10^{-2} M, (3): 5.19×10^{-2} M, (4): 7.14×10^{-2} M, (5): 9.08×10^{-2} M, (6): 11.0×10^{-2} M, (7): 14.9×10^{-2} M.

Table 1. Ultrasonic Relaxation Parameters for Aqueous Solutions of DTAB at 25 °C

C	A	B	f_r	ρ	u	μ_{max}
10^{-2} M[b]	10^{-17} s^2 cm^{-1}	10^{-17} s^2 cm^{-1}	MHz	g cm^{-3}	10^5 cm s^{-1}	10^{-4}
1.95	3400	23.2	0.08_0	0.9974	1.500_3	2.04
3.24	2424	23.7	0.20_6	0.9975	1.501_1	3.75
5.19	2450	24.9	0.30_0	0.9978	1.501_4	5.52
7.14	1748	26.0	0.42_9	0.9978	1.501_5	5.63
9.08	1199	27.7	0.58_7	0.9983	1.501_7	5.28
11.0	800	27.4	0.79_0	0.9985[a]	1.502_1	4.75
14.9	551	32.3	1.0_6	0.9991[a]	1.502_6	4.39

a) Extrapolated values. b) M = mol dm^{-3}.

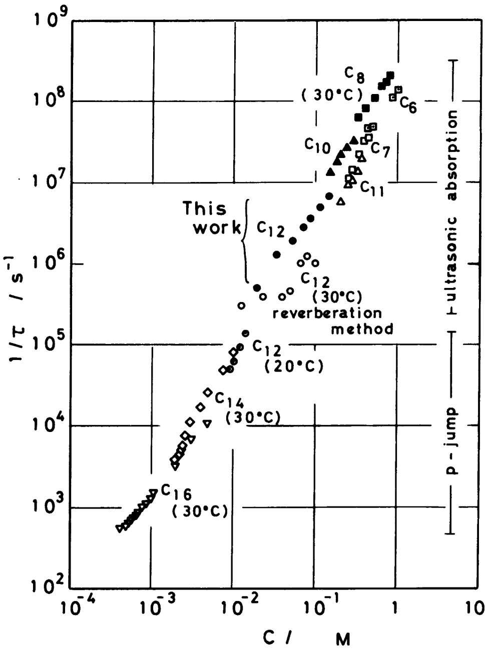

Fig. 6. Plot of reciprocal relaxation times vs. total concentration of surfactant. Filled symbols represent a series of alkyltrimethylammonium bromides: (●) this work C_{12}; (■) C_8[19]; (▲) C_{10}[2]. Open symbols represent a series of sodium alkyl sulfates: (⊡): C_6[2], (□): C_7[2], (△): C_{11}[2], (○): C_{12}[4], (⊙): C_{12}[18], (◇): C_{14}[1], (▽): C_{16}[1]. Data without notation about temperature are for measurements at 25 °C.

tion spectra from Eq. 6 and the arrows indicate the location of the relaxation frequency. Table 1 summarizes the determined values of the relaxation parameters for aqueous solutions of DTAB. As can be seen in Fig. 5 and Table 1, the designed resonator can detect an ultrasonic relaxation process having a small relaxation amplitude. The relaxation amplitude observed here is about two orders smaller in magnitude than those of aqueous solutions of sodium dodecyl sulfate investigated by using the reverberation method.[4]

The reciprocal relaxation times can be calculated from the relaxation frequency as $1/\tau=2\pi f_r$ and are plotted as a function of the total concentration of DTAB in Fig. 6. For a comparison, the results of P-jump[1,19] and ultrasonic relaxation[2,4,20] studies on aqueous solutions of a series of sodium alkyl sulfates and those of alkyltrimethylammonium bromides are also plotted. The present results are consistent with those reported in the literature. Our data sufficiently completes the range from 10^5 to $10^7\,s^{-1}$, which has been a vacant zone since there are few available methods for ultrasonic absorption and P-jump measurements. It can also be seen from Fig. 6 that the reciprocal relaxation time of solutions that are a series of alkyltrimethylammonium bromides is always located at the higher frequency side in comparison with those solutions of sodium alkyl sulfates.

Estimation of Kinetic Parameters for Micellar Formation. Judging from the investigated frequency range and other information from the literature,[1–3] the relaxation process observed here should be ascribed to a "fast" relaxation process, due to an exchange process of a surfactant between micelles and a bulk solution. The kinetic parameters for this process can be estimated by applying some of the important relations derived from a general model of the micellar formation proposed recently.

Teubner[16] has derived the following expression for the relaxation time of the ultrasonic relaxation due to a surfactant exchange process between micelles and a bulk solution, using the approximations introduced by Aniansson and Wall.[21]

$$\frac{1}{\tau}=2\pi f_r=\frac{k_{-1}}{\sigma^2}+\frac{k_{-1}}{\bar{m}}\left(\frac{C}{C_1}-1\right), \tag{7}$$

where C and C_1 represent the total and monomer concentrations of surfactant, respectively, and usually C_1 is assumed to be equal to the critical micelle concentration. Notations $\bar{m}$ and σ represent the mean aggregation number and the variance of the size distribution on proper micelles, respectively, and k_{-1} is the mean of the dissociative rate constant. He has further derived an expression for absorption maxima per wavelength, μ_{max}, as follows[22]:

$$\mu_{max}=\frac{\pi\rho u^2(\Delta V_s)^2C_1\frac{\sigma^2}{\bar{m}}\left(\frac{C}{C_1}-1\right)}{2RT\left\{1+\frac{\sigma^2}{\bar{m}}\left(\frac{C}{C_1}-1\right)\right\}}, \tag{8}$$

where μ_{max} is defined as $\mu_{max}=A f_r u/2$. Here ΔV_s[23] represents the change in the molar volume due to the exchange process, ρ is the density of the solution, R is the gas constant and T is the temperature.

An examination of Eq. 7 indicates that a graph of $1/\tau$ vs. (C/C_1-1) should give a linear correlation with the intercept and slope of the line providing values for k_{-1}/σ^2 and $k_{-1}/\bar{m}$, respectively (Fig. 7 shows that a linear correlation).

If values of the critical micelle concentration and the micelle aggregation number are available, kinetic parameters k_{-1} and σ^2 can be estimated from the values of k_{-1}/σ^2 and $k_{-1}/\bar{m}$. The value of the associative rate constant k_1 is further estimated on the basis of the assumption, $k_1=k_{-1}/C_1$. Table 2 lists the values of the estimated kinetic parameters. Here, the following data were used: $C_1=1.46\times10^{-2}$ M (from experiment[24]); aggregation number $\bar{m}=49$ (average value in the literature[25–28]).

ΔV_s is estimated from an analysis of the relaxation amplitude. Figure 7 also shows the results of a relaxation amplitude analysis. As is seen in the figure, there is a small disagreement[29] between

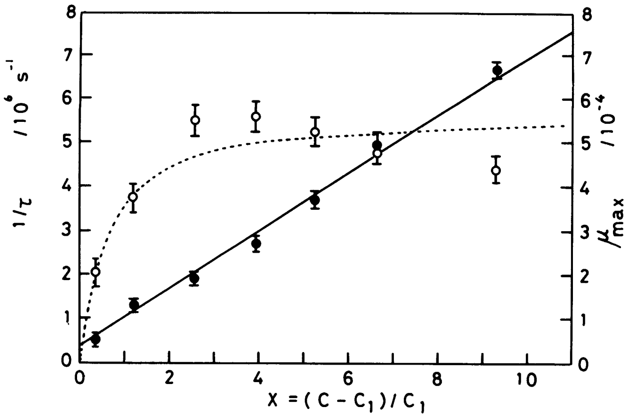

Fig. 7. Reciprocal relaxation times, $1/\tau$ (●), and absorption maxima per wavelength, μ_{max} (○), as a function of the ratio of micellar to monomer concentrations normalized with cmc, $X=(C-C_1)/C_1$. Solid and dotted lines represent values calculated from Eqs. 7 and 8, respectively.

Table 2. Kinetic Parameters for Aqueous Solutions of DTAB at 25 °C

k_1	k_{-1}	σ	$\sigma^2/\overline{m}$	ΔV_s
$M^{-1}\,s^{-1}$	s^{-1}	—	—	$cm^3\,mol^{-1}$
2.2×10^9	3.2×10^7	8.8	1.6	5.3

experiment and theory. The measured absorption maxima per wavelength, μ_{max}, at first, increases and reaches its maximum value, and then decreases with increasing concentration. On the other hand, a mathematical examination of Eq. 8 indicates that it should increase monotonically and never decrease with increasing concentration if $\sigma^2/\overline{m}$ and ΔV_s remain constant. A similar disagreement has been already reported by some investigators. Teubner[16] has pointed out that the disagreement may be due to a neglect of the activity coefficients and/or the monomer concentration decreasing with an increasing surfactant concentration above the critical micelle concentration. On the other hand, Gettins et al.[30] have pointed out that it may arise from a thermodynamical treatment in Teubner's theory. Though it is difficult, at this stage, to clarify the sources of the disagreement, the values of ΔV_s and kinetic parameters estimated here are quite reasonable if they are compared with those that have been reported in the literature.[1,16]

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22) It should be noted that the numerical factor of 2 is inserted in the denominator of Eq. 8 in order to make it compatible with the more practical definition of μ_{max} as previously defined in Ref. 32 and used in this study.

23) Note that ΔV in Teubner's theory represents the volume change of reaction per unit change of ordering parameter, ξ, at constant entropy and temperature (in our paper ΔV is expressed as ΔV_s). The ΔV is related to the volume change at constant pressure and temperature, $(\Delta V)_{P,T}$ as follows:

$$\Delta V = (\Delta V)_{P,T} - \frac{vT\theta^{\infty}}{C_p^{\infty}}\Delta S_P,$$

where ΔS_P represents the entropy change of reaction per unit change of ξ, and C_p, v, and θ are molar heat capacity at constant pressure, molar volume, and expansivity, respectively. Superscript ∞ represents the instantaneous or "frozen" properties measured at fixed ξ.

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