Estimation of Critical Micellar Concentration Through Ultrasonic Velocity Measurements

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SYNOPSIS

A technique based on ultrasound propagation velocity measurements has been developed to investigate surfactant's behavior in aqueous solutions. Applications to the estimation of the critical micellar concentration of two emulsifiers, sodium dodecyl sulfate and dodecylbenzene sulfonic acid sodium salt, and a mixture of them are discussed. A simple model was developed to interpret the experimental ultrasound propagation velocity measurements. The model provides a theoretical foundation to the experimental results as well as a valuable tool for smoothing out the disturbances affecting the experimental data. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In very dilute solutions emulsifiers dissolve and exist as monomers, but as the surfactant concentration exceeds the so-called critical micellar concentration (cmc), small aggregates, or micelles, are formed.[1,2] The hydrophobic part of the emulsifier molecules constitutes the core of the micelle, while the ionic head groups lay at the interface with the surrounding solvent. Many of the practical applications of emulsifiers are related to the presence of micelles. In particular, the hydrophobic environment in the core of the micelles enhances the solubility of organic compounds in water solutions. This property is widely used in the detergent field[3] as well as in the emulsion polymerization processes.[4]

Typically, the cmc is experimentally evaluated from the inflection point exhibited by the plot of various appropriate physical properties of the solution as a function of the emulsifier concentration. Surface tension, conductivity, light scattering intensity, and osmotic pressure have been used to evaluate the cmc.[1,5] It is worth noting that the change in these physical properties at the cmc occurs in a more or less narrow concentration range rather than at a precise point. Accordingly, the estimated

cmc values may change slightly with the adopted experimental technique.[6]

In this work we discuss a technique based on the on-line monitoring of ultrasound propagation velocity (usv) as a function of emulsifier concentration, that can be used to measure cmc. This principle was first used by Mehrotra and Jain[7] to measure the cmc of chromium soaps in a mixture of benzene and dimethyl formamide using off-line usv measurements with 1-MHz pulse frequency. The potential of the technique is discussed by considering cmc measurements of a single and a pair of emulsifiers at various values of temperature and ionic strength.

EXPERIMENTAL

The usv measurements were obtained using a sensor manufactured by Nusonics[8] and described in detail elsewhere.[9,10] This is based on the pulse traveling technique that measures the time needed by an ultrasonic pulse to travel between two piezoelectric transducers positioned at a fixed distance. The sensor provides on-line (approximately one value per second) and *in situ* measurements, because it can be directly inserted in the emulsion without using an external sampling circuit.

The experimental runs were performed starting from an initial mixture of water and emulsifier above the cmc and then continuously adding pure water

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to reduce the emulsifier concentration. The mean residence time, defined as the ratio between the vessel volume and the volumetric inlet flow rate of water, was kept constant and equal to at least 30 min to guarantee that equilibrium conditions were reached inside the vessel. Since the overall change in usv during the experiments is rather small (about 2 m/s), it is necessary to obtain accurate and stable measurements. For this, water was boiled before usage to avoid the formation of gas bubbles that may disturb the usv measurements.[9] The adopted usv sensor provides about one measurement per second, however only six of them per minute were recorded, so that during the entire duration of a single experiment ($\sim$ 100 min), about 600 data were collected. The experimental values shown in the figures reported in this article are raw data, not filtered.

It was found that the slope of the usv values as a function of the emulsifier concentration exhibits a discontinuity that can be attributed to the formation of emulsifier micelles, and then used to estimate the cmc. The accuracy in the determination of the emulsifier concentration value where this discontinuity occurs is increased by the continuous nature of the on-line data, but it becomes more uncertain when off-line techniques are used.[7] For a deeper understanding of the experimental results, a simple mathematical model was developed to evaluate the uvs in emulsions. The model also provides a useful tool for smoothing out the inevitable disturbances in the usv measured values that are apparent at the scale where the experiments reported in this work are considered.

Water was deionized and boiled, and the emulsifiers were used without any further purification. Sodium lauryl sulphate (SLS), potassium chloride (KCl), and sodium chloride (NaCl) were provided by Carlo Erba Analyticals. Dodecylbenzene sulfonic acid sodium salt (DBS) was provided by Aldrich.

MATHEMATICAL MODEL

In the homogeneous aqueous solution of a generic electrolyte at high dilution conditions, the ultrasound velocity can be expressed in the form[11]

$$c = c_w + \alpha E + \beta E^{3/2} \tag{1}$$

where c and c_w are the ultrasound velocities in the aqueous solution and in pure water, respectively, E is the electrolyte concentration, and α and β are adjustable constants. This relation can be used in the case of the aqueous solution of an emulsifier at con-

centrations below the cmc. In particular, because the cmc of most emulsifiers is typically below 10^{-2} mol/L, the term $\beta E^{3/2}$ can be neglected[11] and eq. (1) reduces to

$$c = c_w + \alpha E. \tag{2}$$

On the other hand, for emulsifier concentration values larger than the cmc, the system becomes heterogeneous due to the formation of micelles. In a heterogeneous system the usv is influenced not only by the overall composition but also by the characteristics of the dispersed particles. The two main parameters to be considered to evaluate the sound propagation velocity are the ratios λ/d_m between the sonic wavelength, λ and the particle size, d_m; and η_m/η_w between the viscosity inside the particle, η_m and that in the continuous medium, η_w. Because the instrument adopted in this work uses a 1.5-MHz pulse frequency, f, the corresponding wavelength, is equal to $\lambda = c/f \cong 10^{-3}$ m, where we have used an approximate value for the ultrasound velocity equal to $c = 1500$ m/s, which corresponds to pure water at 25°C.[12] By considering a typical size of the micelles $d_m = 10^{-8}$ m,[1] we obtain for the first ratio $\lambda/d_m \sim 10^5 \gg 1$. It is worth noting about viscosity values that polarized fluorescence measurements of probe molecules dissolved in micelles show that the micellar core microviscosity is considerably larger than water viscosity.[1,3,13] In particular, the microviscosity of a micelle of SLS lies in the range 15–40 cP,[1,13] while the water viscosity is around 1 cP. Accordingly the second parameter usually takes values much larger than one, i.e., $\eta_m/\eta_w > 10$.

From the arguments above it appears that we have very fine particles with high internal viscosity, and the sound propagation velocity can be best described using the scattering theory. Following the scheme proposed by Ahuja,[14] the sound propagation velocity in the mixture of water and micelles is given by

$$c^2 = c_w^2 \frac{1 - \phi L \cos \varepsilon}{[1 - \phi(1 - \beta_m/\beta_w)]} \cdot \frac{}{\times [1 + \phi L(\tau \cos \varepsilon + s \sin \varepsilon)]} \tag{3}$$

In the above equation the subscripts w and m indicate the water phase and the micelles, respectively; ϕ is the volume fraction of micelles in the aqueous solution; β is the compressibility; and the remaining variables are defined as follows:

Table I   Recipes and Operating Conditions of Experimental Runs

Experimental Run	1	2	3	4	5	6
Soap	DBS	SLS	DBS + SLS 50% + 50%	SLS	SLS	SLS
$E°$ (mol/L)	0.0306	0.0432	0.0381	0.0337	0.0218	0.0256
Salt	—	—	—	—	KCl	NaCl
$S°$ (mol/L)	—	—	—	—	0.012	0.103
T (°C)	50	50	50	40	50	50
cmp$_{exp}$ 10^3 (mol/L)	5.5	9.0	7.4	8.8	7.0	1.7
cmc$_{lit}$ 10^3 (mol/L)	5.8	9.6	—	8.8	—	0.3
Reference	Paxton[17]	Atwood and Florence[1]	—	Atwood and Florence[1]	—	Schick[19]
β_m 10^{11} (cm s^2/g)	3.40	4.65	4.40	4.45	4.65	4.65

$E°$: initial emulsifier concentration. $S°$: salt concentration. T: vessel temperature. cmc$_{exp}$: cmc evaluated through linear interpolation of the experimental data. cmc$_{lit}$: literature value of cmc measured with other techniques. β_m: micelle compressibility. Stirrer speed: 200 rpm.

$$L = \frac{\rho_m/\rho_w - 1}{[(\rho_m/\rho_w + \tau)^2 + s^2]^{1/2}} ; \tag{4}$$

$$\varepsilon = \tan^{-1} \frac{s}{\rho_m/\rho_w + \tau}$$

$$\tau = \frac{1}{2} + \frac{\delta}{4R_m}$$

$$\times \frac{(2\eta_w + 3\eta_m)^2}{(\eta_w + \eta_m + R_m\eta_w/3\delta)^2 + (R_m\eta_w/3\delta)^2} ;$$

$$\delta = \sqrt{2\eta_w/\rho_w\omega} \tag{5}$$

$$s = \frac{3\delta^2}{4R_m^2}(2\eta_w + 3\eta_m)$$

$$\times \frac{(1 + R_m/\delta)(\eta_w + \eta_m + R_m\eta_w/3\delta) + R_m^2\eta_w/3\delta^2}{(\eta_w + \eta_m + R_m\eta_w/3\delta)^2 + (R_m\eta_w/3\delta)^2} \tag{6}$$

where ρ is density, R_m is the average micelle radius, and ω is the angular frequency of the sound wave. The equations above can be substantially simplified by considering that $\eta_m \gg \eta_w$ and, because $\omega = 2\pi\ f$ rad/s, also $\delta = 4\ 10^{-7}\ m \gg R_m$. Thus eqs. (5) and (6) reduce to

$$\tau = \frac{1}{2}\left(1 + \frac{9\delta}{2R_m}\right) \quad \text{and} \quad s = \frac{9\delta^2}{4R_m^2}\left(1 + \frac{R_m}{\delta}\right) \tag{7}$$

when substituted in eq. (4) leads to $\varepsilon = \pi/2$ and $L = (\rho_m/\rho_w - 1)/s$. With these approximations the expression of the sound propagation velocity (3) yields

$$c^2 = c_w^2$$

$$\times \frac{1}{[1 - \phi(1 - \beta_m/\beta_w)][1 - \phi(1 - \rho_m/\rho_w)]}. \tag{8}$$

It is worth noting that in this expression the viscosity and the size of the micelles are not involved. For this particular system we have in fact recovered the expression originally derived by Wood[15] for dispersions of very fine solid particles in a liquid, for which we have indeed $\eta_m \gg \eta_w$ and $\lambda \gg d_m$.

Note that the volume fraction of micelles in the aqueous solution ϕ is given by

$$\phi = \frac{(E - \text{cmc})MW_m}{\rho_m + (E - \text{cmc})MW_m} \tag{9}$$

where MW_m is the molecular weight of the emulsifier.

RESULTS AND DISCUSSION

Table I summarizes the recipes and the operating conditions of all the experimental runs performed. In all cases a change in the slope of the usv values as a function of the emulsifier concentration was observed. The value of emulsifier concentration where the change in slope occurs was evaluated

through a linear interpolation of the experimental data and used to estimate the cmc values reported in Table I. As a comparison, literature cmc values estimated through other techniques are shown in the same table, together with the corresponding references. In the following we discuss in detail the single experimental runs by showing in each figure the measured usv values together with the results of the mathematical model described above. In particular, the values below the cmc are computed through eq. (2), and those above the cmc through eq. (8). The literature values of the cmc were used in the model calculation. However, similar results would have been obtained using the cmc values estimated through the linear interpolation of the experimental data described above. In all computations the value of α has been kept constant and equal to $1.65 \; 10^7 \; cm^4/mol$ s, while the values of β_m, which were fitted for each experimental run, are summarized in Table I. The density values for SLS and DBS have been evaluated through the group contribution method reported in Van Krevelen[16] leading in both cases to $\rho_m \cong 1.2 \; g/cm^3$.

## cmc in Aqueous Solutions of One or More Emulsifiers

Figures 1(a,b) shows the usv values measured in experimental runs 1 and 2 in Table I, where two different emulsifiers, DBS and SLS, were used. The horizontal and vertical dotted lines represent the sound propagation velocity in water, c_w, and the literature cmc value, respectively. Note that the lit-

erature value for DBS cmc refers to a temperature of $25°C$.[17] It is seen that the change in slope of the experimental usv values occurs close to the literature cmc value. Moreover, the slope of the curve below the cmc is the same for the two emulsifiers (i.e., $\alpha = 1.65 \; 10^7 \; cm^4/mol$ s for both emulsifiers), while it is significantly different above the cmc. This is related to the internal structure of the micellar core. The core of DBS micelles seems to be stiffer than that of SLS micelles and consequently it has a lower compressibility value (see Table I).

The usv values measured in experimental run 3, where a 1 : 1 weight mixture of SLS to DBS was considered, are shown in Figure 2. The usv values vs. emulsifier concentration exhibit a broad change in slope in a region enclosed between the cmc of the two pure soaps. The cmc value used in the model is a weight average of the experimental cmc values of pure SLS and DBS (see Table I). It is worth noting that the slope of the curve above the cmc is similar to that of pure SLS shown in Figure 1(b). This supports the conjecture that there are no micelles of pure SLS and pure DBS, but rather micelles formed by both soaps that have a micellar core similar to that of pure SLS micelles.

Influence of Temperature on cmc

The cmc of SLS has been measured at two different temperature values: 50 and $40°C$ in experimental runs 2 and 4, respectively. The measured usv values are shown in Figures 1(b) and 3, together with the corresponding results of the mathematical model.
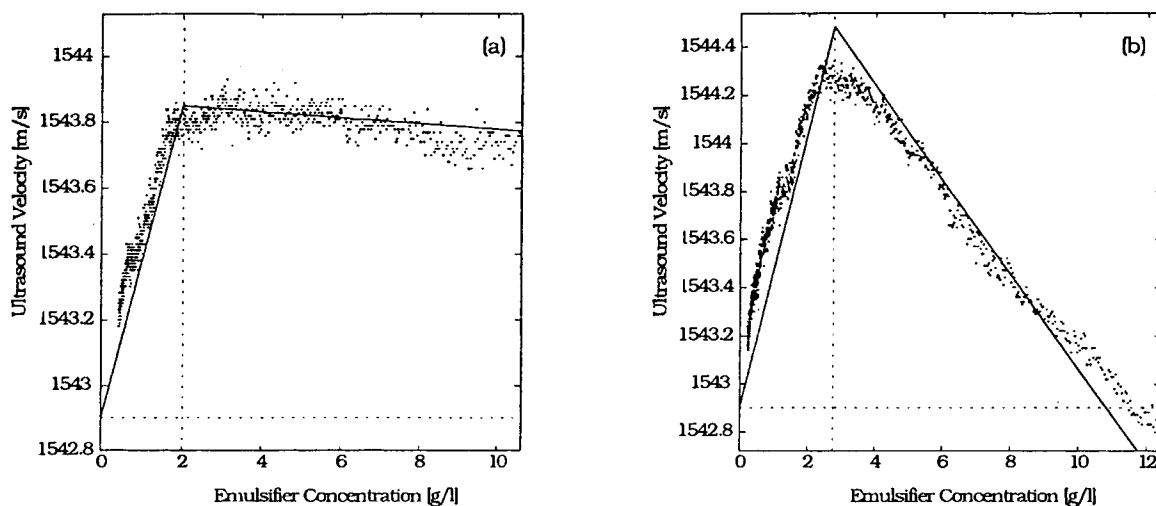
Figure 1 Ultrasound velocity vs. emulsifier concentration at $50°C$ for: (a) DBS and (b) SLS. Points: experimental results. Solid line: results of the model. Vertical dotted line: literature cmc data.[1,17] Horizontal dotted line: usv in pure water.[12]
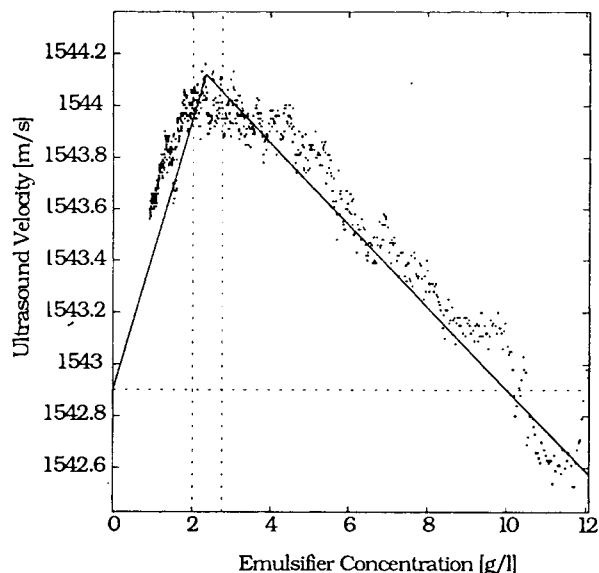
Figure 2 Ultrasound velocity vs. emulsifier concentration for a mixture of SLS and DBS (50/50 weight). Points: experimental results. Solid line: results of the model. Vertical dotted lines: literature cmc values for pure SLS[1] and pure DBS.[17] Horizontal dotted line: usv in pure water.[12]

The vertical dotted lines represent the literature cmc values at the different temperatures.[1] It is seen that again the slope of the experimental ultrasound velocity data as a function of the emulsifier concentration exhibits a discontinuity in proximity of the cmc. It may be noted that in the homogeneous region (below the cmc), the usv increases linearly with the emulsifier concentration, following a line whose slope is practically independent of temperature. Accordingly, the value of the parameter α in eq. (2) was kept constant. On the other hand, above the cmc the curve is again linear, but the slope is now more strongly affected by temperature. A possible explanation of this behavior can be found in the dependence of the micellar size and structure on temperature.[18] In particular, at lower temperature values, the closer packing of the ionic head groups of the micelles may cause an increase in the internal stiffness and consequently a decrease in the compressibility (Table I).

### Influence of Electrolytes on cmc

It is known that the addition of a strong electrolyte, such as NaCl or KCl, significantly decreases the cmc of ionic emulsifiers.[1,19] The cmc of SLS in the presence of two different salts, KCl and NaCl, has been measured in experimental runs 5 and 6, respectively. The usv values obtained in the two experiments are

shown in Figure 4(a,b). It is seen that again the measured usv values are in good agreement with the model results and exhibit a slope discontinuity corresponding to the formation of micelles. In the case of NaCl [Fig. 4(b)] this is in good agreement with the cmc value reported in the literature[19] indicated by the vertical dotted line. In the case of run 5, a comparison with literature data can be done with the results reported in Schick[19] referring to a mixture with the same salt concentration as in run 5, but with a different kind of salt (NaCl rather than KCl). The cmc value obtained for this system[19] ($5.3e^{-3}$ mol/L) is reasonably close to the cmc value of $7.0e^{-3}$ mol/L estimated by linear interpolation of the data in Figure 4(a).

Finally, note that the slope of the curve above the cmc seems to be independent of the electrolyte type and concentration. The values of β_m used for the simulation of runs 2, 5, and 6 reported in Table I are in fact the same. This supports the conjecture that, at least in the cases examined here, a strong electrolyte modifies the aqueous environment but not the internal structure of the micelles.

CONCLUSIONS

The use of usv measurements to investigate the formation of emulsifier micelles were discussed. Using an on-line sensor for measuring usv values, a simple
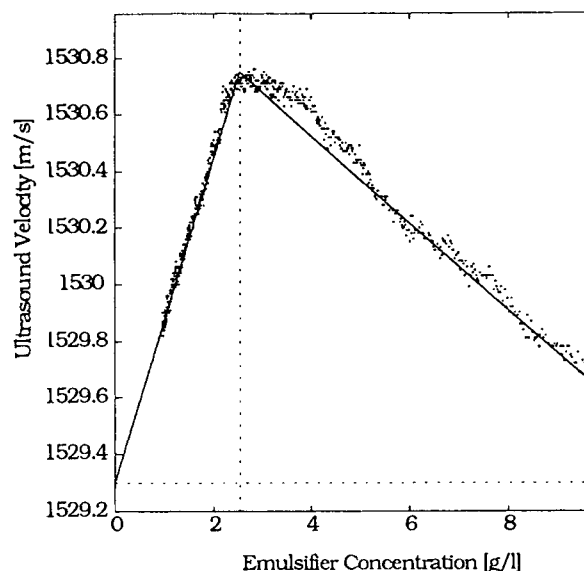
Figure 3 Ultrasound velocity vs. SLS concentration at 40°C. Points: experimental data. Solid line: results of the model. Vertical dotted line: literature cmc.[1] Horizontal dotted line: usv in pure water.[12]
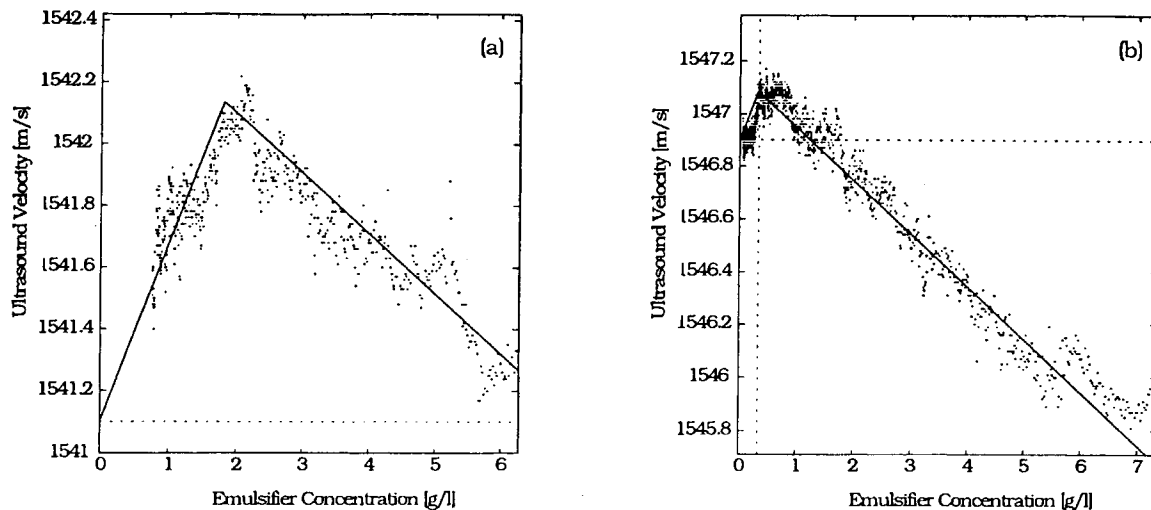
Figure 4   Effect of salts on the cmc of SLS. (a) KCl = 0.01 mol/L. (b) NaCl = 0.1 mol/L. Points: experimental data. Solid line: results of the model. Vertical dotted line: literature cmc.[19] Horizontal dotted line: usv in pure water.[12]

experimental apparatus was developed that allows the estimation of the emulsifier cmc. A mathematical model, which involves two adjustable parameters, was developed for simulating the experimental results. The model provides a useful tool for performing the cmc estimation as well as a theoretical support for the experimental findings. Moreover, the developed experimental technique in conjunction with the model provides qualitative information about the internal structure of the micellar core through the estimation of its compressibility.

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