Density, Kinematic Viscosity, Speed of Sound, and Surface Tension of Tetradecyl and Octadecyl Trimethyl Ammonium Bromide Aqueous Solutions

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Density, kinematic viscosity, surface tension, and speed of sound of tetradecyl and octadecyl trimethyl ammonium bromide aqueous solutions have been determined. The influence of each surfactant concentration upon these physical properties has also been studied at 298 K. The experimental values of these physical properties have been employed to determine the critical micellar concentration for each surfactant, as well as to analyze the effect of chain length upon this characteristic parameter.

1. Introduction

Aqueous and nonaqueous surfactant solutions that possess a dual character (hydrophilic and hydrophobic) are employed in different industrial applications.¹ These applications (i.e., pharmaceutical, cosmetic, or cleaning products) use the special characteristics generated by the presence of these kind of substances on physical properties, such as the diminution of surface tension.²

One of the important characteristics relevant to these colloidal systems that has generated a great number of applications and research studies is the aggregation phenomenon that is produced under certain experimental conditions. The aggregation phenomenon can produce different kinds of aggregates, most importantly, micelles³ and microemulsions.⁴

2. Experimental Section

Materials. The surfactants employed in the present paper (tetradecyl trimethyl ammonium bromide, TDTABr, CAS number 1119-97-7; octadecyl trimethyl ammonium bromide, ODTABr, CAS number 1120-02-1) were supplied by Fluka with a purity \geq 98 %.

Bidistilled water was used to prepare the water and amine mixtures. All the aqueous solutions were prepared by mass using an analytical balance (Kern 770) with a precision of 10^{-4} g. The uncertainty of the samples preparation in mole fraction was \pm 0.0002.

Density and Speed of Sound. The density of water and aqueous solutions of different solutes was measured with an Anton Paar DSA 5000 vibrating tube densimeter and sound analyzer, with an accuracy of $\pm 10^{-6}$ g·cm⁻³ in relation to density and ± 0.01 m·s⁻¹ for the speed of sound. The uncertainty in the density and speed of sound measurements was $\pm 5 \cdot 10^{-6}$ g·cm⁻³ and ± 0.08 m·s⁻¹, respectively. In general, each value came from an average of three measurements.

Viscosity. The kinematic viscosity (ν) was determined from the transit time of the liquid meniscus through a capillary viscosimeter supplied by Schott (Cap No. 0c, 0.46 \pm 0.01 mm internal diameter, $K = 0.003201 \text{ mm}^2 \cdot \text{s}^{-1}$), measured with an uncertainty of $\pm 0.00008 \text{ mm}^2 \cdot \text{s}^{-1}$ using eq 1.

$$\nu = K \cdot (t - \theta) \tag{1}$$

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Table 1.	Density /	o, Speed	of Sound	u, Kinen	atic Vis	scosity v	, and
Surface 1	Fension σ	for Wat	er (1) +	TDTABr	(2) at 29	98 K	

$C_2 \cdot 10^{-2}$	ρ	ν	и	σ
$mol \cdot L^{-1}$	g•cm ⁻³	$\overline{\text{mm}^{2} \cdot \text{s}^{-1}}$	$m \cdot s^{-1}$	$mN \cdot m^{-1}$
0	0.997053	0.8957	1496.8	72.5
0.1	0.997062	0.8962	1496.9	60.4
0.2	0.997064	0.8968	1497.2	51.7
0.3	0.997087	0.8991	1497.3	44.0
0.5	0.997106	0.9015	1497.4	40.6
1.0	0.997153	0.9078	1497.5	38.0
1.5	0.997204	0.9144	1497.6	37.8
2.0	0.997268	0.9215	1497.7	37.6
2.5	0.997307	0.9290	1497.8	37.4
3.0	0.997349	0.9368	1497.8	37.1
3.5	0.997402	0.9450	1497.9	37.0
4.0	0.997458	0.9537	1497.9	36.9
4.5	0.997500	0.9627	1498.0	36.8
5.0	0.997545	0.9722	1498.1	36.7
5.5	0.997604	0.9820	1498.1	36.7

where *t* is the efflux time; *K* is the characteristic constant of the capillary viscosimeter; and θ is a correction value to prevent the final effects. An electronic stopwatch with an accuracy of \pm 0.01 s was used to measure efflux times. The capillary viscometer was immersed in a bath (Selecta Frigiterm) controlled to \pm 0.1 °C. In the measurements, a Schott-Geräte AVS 350 Ubbelohde viscometer was used. Each measurement was repeated at least five times. The dynamic viscosity (η) was obtained from the product of the kinematic viscosity (ν) and the corresponding density (ρ) of the mixture, in terms of eq 2 for each mixture composition.

$$\eta = \nu \cdot \rho \tag{2}$$

Surface Tension. The surface tension was determined by employing a Krüss K-11 tensiometer using the Wilhelmy plate method. The plate employed was a commercial platinum plate supplied by Krüss. The platinum plate was cleaned and flame dried before each measurement. The surface tension of pure water was determined and compared with the literature to confirm that this method provides reliable results.⁵ The uncertainty of the measurement was ± 0.05 mN·m⁻¹. In general, each surface tension value reported came from an average of five measurements. The samples were thermostated in a closed stirring vessel before the surface tension measurements.



Figure 1. Physical properties of aqueous solutions of TDTABr: \bigcirc , kinematic viscosity; \bullet , speed of sound.

Table 2. Density ρ , Speed of Sound *u*, Kinematic Viscosity *v*, and Surface Tension σ for Water (1) + ODTABr (2) at 298 K

$C_2 \cdot 10^{-2}$	ρ	<u>ν</u>	и	σ
$mol \cdot L^{-1}$	g•cm ⁻³	$mm^{2} \cdot s^{-1}$	$m \cdot s^{-1}$	$mN \cdot m^{-1}$
0	0.997053	0.895710	1496.8	72.5
0.1	0.997053	0.895734	1497.2	62.3
0.2	0.997053	0.895760	1497.7	54.2
0.3	0.997053	0.895807	1498.0	48.7
0.4	0.997053	0.895835	1498.2	45.0
0.5	0.997053	0.895863	1498.0	42.8
0.6	0.997054	0.895913	1497.8	42.0
0.8	0.997054	0.895975	1497.2	41.4
1.0	0.997054	0.896020	1496.7	41.3
1.3	0.997054	0.896120	1496.0	41.0
1.6	0.997054	0.896226	1495.2	40.8
2.0	0.997055	0.896320	1494.2	40.4
2.5	0.997055	0.896477	1492.7	40.2
3.0	0.997056	0.896634	1491.6	39.6
4.0	0.997057	0.896935	1489.2	39.3

3. Results and Discussion

This work determines different physical properties (density, kinematic viscosity, surface tension, and speed of sound) to characterize aqueous solutions of different surfactants with a large chain length corresponding to the alkyl-trimethyl ammonium bromide family. Tables 1 and 2 summarize the experimental values obtained that correspond to the physical properties analyzed in the present work.

The addition of solutes employed in this work produces a common behavior in relation to the experimental values of density and viscosity (see Figure 1). An increase in the value of these physical properties has been observed when the surfactant concentration also increases. A similar behavior was also observed for the other system employed in this study. Another conclusion is related to the magnitude of the density and the kinematic viscosity value for each surfactant, where it was observed that an increase in the chain length produces an increase in both values (viscosity and density).

Different physical properties have been analyzed in the literature due to their ability to characterize the aggregation processes on the basis of the measured experimental values (i.e., electrical conductivity, surface tension). Density and kinematic viscosity do not change in behavior when the micellization (aggregation) point is reached. Therefore, these properties are not used to obtain information about the dynamics of the colloidal aggregates.

Figure 1 also shows another physical property (speed of sound) studied in the present work that is influenced by the micellization process. A behavior similar to that previously



Figure 2. Surface tension values of aqueous solutions of: ○, TDTABr; ●, ODTABr.

 Table 3. Critical Micelle Concentration Values for Different

 Surfactants

	$\operatorname{cmc}(\sigma)$	$\operatorname{cmc}(u)$
surfactant	$mol \cdot L^{-1}$	$mol \cdot L^{-1}$
HTABr OTABr DTABr TDTABr ODTABr	$\begin{array}{c} 0.99^{a}\pm 0.07\\ 0.26^{a}\pm 0.02\\ 6.0\cdot 10^{-2a}\pm 4\cdot 10^{-3}\\ 2.6\cdot 10^{-3}\pm 3\cdot 10^{-4}\\ 4.3\cdot 10^{-5}\pm 3\cdot 10^{-6} \end{array}$	$\begin{array}{c} 1.02^{a}\pm 0.05\\ 0.28^{a}\pm 1.4\cdot 10^{-2}\\ 6.5\cdot 10^{-2a}\pm 3\cdot 10^{-3}\\ 1.9\cdot 10^{-3}\pm 1\cdot 10^{-4}\\ 3.6\cdot 10^{-5}\pm 2\cdot 10^{-6} \end{array}$

^a Gómez-Díaz et al.⁷



Figure 3. Influence of chain length upon critical micelle concentration value.

observed by other authors and our research team was obtained.^{6,7} Figure 1 shows an example of the behavior observed for this kind of system, and the experimental data show two linear trends with different slopes. The intersection of these two lines allows the calculation of the critical micelle concentration.

On the other hand, Figure 2 shows the effect of both surfactant concentrations upon the value of the surface tension at 298 K. In this case, the presence of both surfactants produces a clear decrease in the surface tension value, but this decrease reaches a constant value at a certain surfactant concentration value. It has been shown that surface tension is a physical property influenced by the aggregation phenomenon, due to a change in the surface concentration of the surfactant.⁸ The aggregation process makes the surface surfactant concentration remain constant because the addition of new surfactant molecules is employed in the micelle formation; however, it does not have an influence on the surface tension remains at a constant value.

We plotted the experimental values of surface tension vs the surfactant concentration on a logarithmic scale. As a result, two linear trends can be observed (shown in Figure 2), and the intersection of the two lines allows the critical micelle concentration, cmc, to be determined.

The values corresponding to the critical micelle concentration obtained for each surfactant, employing different physical properties (surface tension and speed of sound), were quite similar. On the basis of the critical micelle concentration values determined (see Table 3 and Figure 3) for all the surfactants employed in this study and previous ones, we conclude that an increase in the alkyl chain length produces a clear decrease in the value of the concentration, which results in the aggregation of surfactant molecules in micelles.

4. Conclusions

The influence of surfactant nature, concentration, and the aggregation phenomenon upon physical properties has been analyzed in the present work. Different behaviors have been observed for the physical properties studied; i.e., for density, viscosity, and speed of sound, an increase in surfactant concentration produces an increase in these physical properties, whereas for surface tension, a clear decrease is observed. The aggregation phenomenon shows great influence upon the behavior of surface tension and speed of sound. Critical micelle concentration data are presented by different methods, and a larger chain length produces a decrease in the value of this parameter.

Literature Cited

- Herzog, B. S.; Marquardt, D.; Mueller, S. B.; Pedrussio, R. B.; Sucker, H. B. Influence of composition and phase relationship on cream consistency. *Pharm. Ind.* **1998**, *60*, 713–721.
- (2) Taboada, P.; Ruso, J. M.; Garcia, M.; Mosquera, V. Surface properties of some amphiphilic antidepressant drugs. *Colloids Surf.*, A 2001, 179, 125–128.
- (3) Fendler, J. H.; Fendler, E. J. Catalysis in micelar and macromolecular systems; New York: Academic Press, 1975.
- (4) Pileni, M. P. *Structure and reactivity in reverse micelles*; Amsterdam: Elsevier, 1989.
- (5) Álvarez, E.; Rendo, R.; Sanjurjo, B.; Sánchez-Vilas, M.; Navaza, J. M. Surface Tension of Binary Mixtures of Water + N-Methyldiethanolamine and Ternary Mixtures of this Amine and Water with Monoethanolamine, Diethanolamine, and 2-Amino-2-Methyl-1-Propanol from 25 to 50 °C. J. Chem. Eng. Data 1998, 43, 1027–1029.
- (6) Taboada, P.; Gutiérrez-Pichel, M.; Barbosa, S.; Mosquera, V. A Thermodynamic Study of Two Anionic Amphiphilic Penicillins in Aqueous Solution by Ultrasound Speed Measurements. *Colloids Surf.*, A 2003, 220, 29–34.
- (7) Gómez-Díaz, D.; Navaza, J. M.; Sanjurjo, B. Density, Kinematic Viscosity, Speed of Sound, and Surface Tension of Hexyl, Octyl, and Decyl Trimethyl Ammonium Bromide Aqueous Solutions. *J. Chem. Eng. Data* **2007**, *52*, 889–891.
- (8) Gutiérrez-Pichel, M.; Barbosa, S.; Taboada, P.; Mosquera, V. Surface properties of some amphiphilic antidepressant drugs in different aqueous media. *Colloid Polym. Sci.* 2003, 281, 575–579.

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