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Density, Kinematic Viscosity, Speed of Sound, and Surface Tension of Hexyl, Octyl, and Decyl Trimethyl Ammonium Bromide Aqueous Solutions

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Density, kinematic viscosity, surface tension, and speed of sound of hexyl, octyl, and decyl trimethylammonium 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.

Introduction

The dualistic character of amphiphilic compounds, both having hydrophilic and hydrophobic parts, is the basis of their relationship to both external and internal interfaces in aqueous systems. The physicochemical properties of many of these molecules in solution have been studied and completely understood by means of a vast amount of experimental and theoretical work.[1,2]

Aqueous and nonaqueous surfactant solutions are employed in different industrial applications.[3] These applications use the special characteristics generated by the presence of these kind of substances on physical properties, such as the diminution of surface tension.[4]

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 aggregates with micelles[5] and microemulsions[6] being the most important systems. These kinds of systems have been employed in numerous research fields, such as reaction media[7] and synthesis of porous solids and nanoparticles.[8] The use of surfactant aqueous solutions, with and without some kind of aggregation, has an important implication: knowing the influence of the presence and aggregation of surfactants upon the value of physical properties could be shown as an important tool to explain and understand the behavior of these liquid phases in different operations.

Experimental Section

Materials. The surfactants employed in the present paper (hexyl trimethyl ammonium bromide, HTABr, CASRN 2650-53-5; octyl trimethyl ammonium bromide, OTABr, CASRN 2083-68-3; and decyl trimethyl ammonium bromide, DTABr, CASRN 2082-84-0) were supplied by Fluka with a purity ≥ 98 %.

Bi-distilled 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 ± 0.0002.

Density and Speed of Sound. The density of water and aqueous solutions of different solutes were measured with an Anton Paar DSA 5000 vibrating-tube densimeter and sound analyzer, with an accuracy of $\pm\ 10^{-6}\ \mathrm{g{\cdot}cm^{-3}}$ in relation to density and $\pm\ 0.01\ \mathrm{m{\cdot}s^{-1}}$ for the speed of sound. The uncertainty in the density and speed of sound measurements was $\pm\ 3{\cdot}10^{-5}\ \mathrm{g{\cdot}cm^{-3}}$ and $\pm\ 0.08\ \mathrm{m{\cdot}s^{-1}}$, 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 ± 0.01 mm i.d., $K = 0.003201\ \mathrm{mm^2{\cdot}s^{-1}}$), measured with an uncertainty of $\pm\ 0.00008\ \mathrm{mm^2{\cdot}s^{-1}}$ using eq 1:

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

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 ± 0.01 s was used to measure efflux times. The capillary viscometer was immersed in a bath (Selecta Frigiterm) controlled to ± 0.1 °C. A Schott-Geräte AVS 350 Ubbelohde viscometer was used in the measurements. 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:

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

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.[9] The uncertainty of the measurement was $\pm\ 0.05\ \mathrm{mN{\cdot}m^{-1}}$. 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.

Results and Discussion

This work determines different physical properties (density, kinematic viscosity, surface tension, and speed of sound) to

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

C_2 / mol·L^{-1}	ρ / g·cm^{-3}	u / m·s^{-1}	ν / mm^2·s^{-1}	σ / mN·m^{-1}
0.0	0.99700	1496.8	0.8957	72.5
0.1	1.00032	1510.6	0.9149	51.6
0.2	1.00385	1524.9	0.9406	44.3
0.3	1.00697	1537.3	0.9727	41.1
0.4	1.01042	1550.5	1.0113	38.3
0.45	1.01206	1557.7	1.0331	36.8
0.5	1.01374	1562.9	1.0564	35.8
0.6	1.01719	1575.3	1.1080	34.0
0.7	1.02102	1588.6	1.1660	32.5
0.8	1.02421	1599.1	1.2304	31.2
0.9	1.02768	1610.0	1.3014	30.5
1.0	1.03133	1620.6	1.3788	29.9
1.1	1.03412	1628.1	1.4626	29.5
1.3	1.04107	1644.8	1.6497	29.3
1.5	1.04762	1652.1	1.8626	29.1
1.7	1.05438	1660.0	2.101	29.1
2.0	1.06423	1670.3	2.508	28.9

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

C_2 / mol·L^{-1}	ρ / g·cm^{-3}	u / m·s^{-1}	ν / mm^2·s^{-1}	σ / mN·m^{-1}
0.00	0.99700	1496.8	0.8957	72.5
0.02	0.99762	1500.1	0.8990	69.4
0.04	0.99820	1503.1	0.9033	63.1
0.06	0.99873	1506.3	0.9083	59.5
0.08	0.99923	1510.0	0.9140	54.6
0.10	0.99968	1513.1	0.9200	51.1
0.12	1.00025	1516.4	0.9276	48.9
0.14	1.00079	1520.3	0.9355	46.5
0.16	1.00162	1522.7	0.9441	44.0
0.18	1.00190	1525.8	0.9534	41.7
0.20	1.00254	1529.6	0.9636	39.8
0.30	1.00500	1540.0	1.0245	36.4
0.40	1.00809	1546.5	1.1033	35.8
0.50	1.01050	1549.2	1.2001	35.5
0.60	1.01319	1552.2	1.3148	35.4
0.80	1.01807	1557.4	1.5981	35.2
1.00	1.02298	1562.7	1.9533	35.1

Table 3. Density *ρ*, Speed of Sound *u*, Kinematic Viscosity *ν*, and Surface Tension *σ* for Water (1) + DTABr (2) at 298 K

C_2 / mol·L^{-1}	ρ / g·cm^{-3}	u / m·s^{-1}	ν / mm^2·s^{-1}	σ / mN·m^{-1}
0.000	0.99700	1496.8	0.8956	72.5
0.001	0.99711	1497.3	0.8975	65.4
0.005	0.99725	1497.8	0.8990	60.1
0.010	0.99737	1498.7	0.9048	57.6
0.020	0.99758	1500.8	0.9140	49.7
0.030	0.99785	1502.6	0.9224	43.4
0.040	0.99806	1504.3	0.9350	38.0
0.050	0.99833	1506.3	0.9449	36.9
0.060	0.99852	1508.0	0.9560	36.1
0.070	0.99879	1509.2	0.9642	35.5
0.080	0.99900	1509.7	0.9780	35.2
0.100	0.99937	1510.1	1.0016	35.2
0.120	0.99977	1510.6	1.0240	35.0
0.150	1.00040	1511.1	1.0624	35.2
0.200	1.00122	1511.7	1.1173	35.0
0.250	1.00209	1512.4	1.1812	35.1

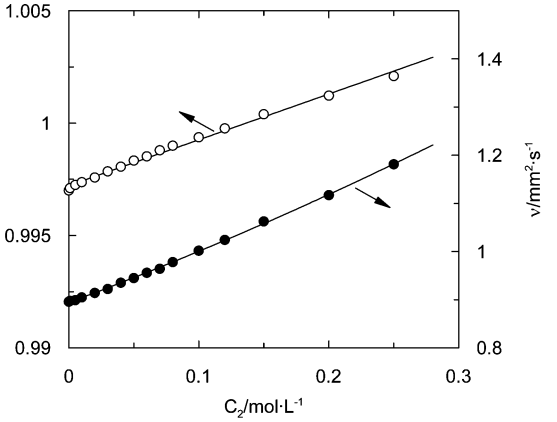

Figure 1. Density and kinematic viscosity of aqueous solutions of DTABr.

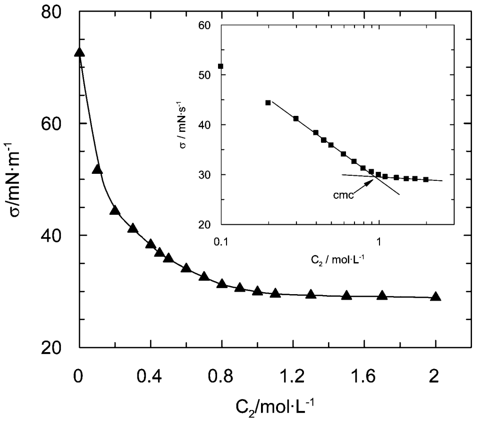

Figure 2. Surface tension values of aqueous solutions of HTABr.

characterize the aqueous solutions of different surfactants corresponding to the alkyl-trimethylammonium bromide family. Tables 1 to 3 summarize the experimental values obtained that correspond to the physical properties analyzed in the present study.

The addition of one solute, namely, surfactants, produces a common behavior in relation to the experimental values of density and viscosity. An increase in the value of these two physical properties has been observed when the surfactant concentration also increases. The same behavior has been observed for aqueous solutions made up of substances with similar characteristics.[10] Figure 1 shows the behavior found for these two properties in aqueous solutions of DTABr at 298 K. However, similar behavior was also observed for systems made up of the rest of the surfactants 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 different effects: an increase in the value of viscosity and a decrease of density.

These systems have been applied in a number of technologies due to the formation of micelles during the aggregation process under certain operational conditions. 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) process is reached. Therefore, these properties are not used to obtain information about the dynamics of the colloidal aggregates.

Figure 2, on the other hand, shows the effect of one surfactant upon the value of the surface tension at 298 K. In this case, the presence of HTABr produces a 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. For this reason, surface tension has been used to determine the colloidal dynamics of numerous systems.[11] The aggregation process makes the surface surfactant concentration

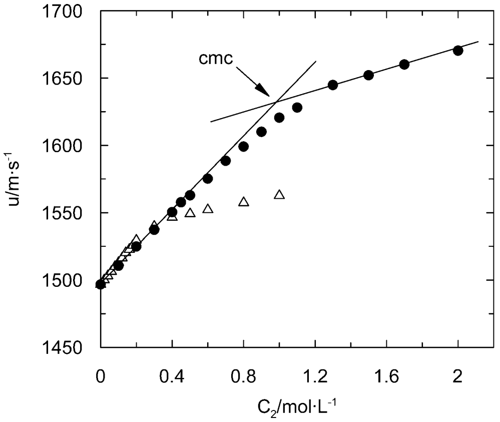

Figure 3. Speed of sound values for aqueous solutions of ●, HTABr; △, OTABr.

Table 4. Critical Micelle Concentration Values for HTABr, OTABr, and DTABr

surfactant	cmc (σ)/mol•L^{-1}	cmc (u)/mol•L^{-1}
HTABr	0.99	1.02
OTABr	0.261	0.275
DTABr	0.060	0.065

remain constant because the addition of new surfactant molecules is employed in the micelles formation but it has no influence on the surfactant concentration in the free liquid surface. So the surface tension remain with a constant value.

Using the experimental values of surface tension, different researchers have determined the surfactant concentration when the aggregation of molecules is produced. This determination procedure is carried out using, for example, a graph like the one shown in Figure 2 (i.e., plotting 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.

Similar behavior was observed for the other surfactants employed in this study. The cmc has also been determined for these surfactants. The calculated values for cmc values are shown in Table 4. The other physical property studied in the present work that is influenced by the micellization process is the speed of sound. A similar behavior was obtained to that previously observed by other authors.[12] Figure 3 shows an example of the behavior observed for this kind of systems. Similar to the influence of surfactant concentration on surface tension, two linear trends (with different slopes) are shown in Figure 3. The intersection of these two lines allows the calculation of the cmc. The values corresponding to the cmc obtained for each surfactant, employing different physical properties (surface tension and speed of sound), were quite similar. The value of the cmc, determined using the influence of the surfactant concentration upon the surface tension, was in some cases slightly lower than the corresponding values determined using the speed of sound. This characteristic is due to the influence of very small quantities of impurities upon the value of surface tension.

In Figure 3 it can be observed that the change in slope for the surfactant with a larger chain length (OTABr) is produced at low values of the surfactant concentration. On the basis of the cmc values calculated (see Table 4) for all the surfactants employed in this study, 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.

Conclusion

The presence of the surfactants employed in the present work upon the value of different physical properties has been studied. The influence of surfactant nature, concentration, and aggregation phenomenon upon these physical properties has been analyzed. Different behavior has 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 while for surface tension a 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

(1) Rosen, M. J. *Surfactants and Interfacial Phenomena*; Wiley: New York, 1978.

(2) Wenerström, H.; Lindman, B. Micelles. *Physical Chemistry of Surfactant Association*; University of Lund: Lund, 1978.

(3) 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.

(4) Taboada, P.; Ruso, J. M.; Garcia, M.; Mosquera; V. Surface properties of some amphiphilic antidepressant drugs. *Colloids Surf., A* **2001**, *179*, 125−128.

(5) Arias, M.; Garcia-Rio, L.; Mejuto, J. C.; Rodriguez-Dafonte, P.; Simal-Gandara, J. Influence of micelles on the basic degradation of carbofuran. *J. Agric. Food Chem.* **2005**, *53*, 7172−7178.

(6) Pileni, M. P. *Structure and Reactivity in Reverse Micelles*; Amsterdam: Elsevier, 1989.

(7) García-Río, L.; Hervés, P.; Mejuto, J. C.; Pérez-Juste, J.; Rodríguez-Dafonte, P. Pseudophase approach to reactivity in microemulsions: quantitative explanation of the kinetics of the nitroso group transfer reactions between *N*-methyl-*N*-nitroso-*p*-toluensulfonamide and secondary alkylamines in water/AOT/isooctane microemulsions. *Ind. Eng. Chem. Res.* **2003**, *42*, 5450−5456.

(8) Husein, M.; Rodil, E.; Vera, J. H. Formation of silver bromide precipitate of nanoparticles in a single microemulsion utilizing the surfactant counterion. *J. Colloid Interface Sci.* **2004**, *273*, 426−434.

(9) 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.

(10) Barbosa, S.; Taboada, P.; Mosquera, V. Viscosities of aqueous solutions of human serum albumin in the presence of two anionic penicillins at pH 7.4. *J. Chem. Eng. Data* **2004**, *49*, 483−485.

(11) Gutiérrez-Pichel, M.; Barbosa, S.; Taboada, P.; Mosquera, V. Surface properties of some amphiphilic antidepressant drugs in different aqueous media. *Prog. Colloid Polym. Sci.* **2003**, *281*, 575−579.

(12) 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.

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