PHASE BEHAVIOR AND PHYSICOCHEMICAL PROPERTIES OF WATER/CETYLTRIMETHYLAMMONIUM BROMIDE/N-
PROPAHOL/ALLYLBENZEN MICELLAR SYSTEMS

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Water/n-propanol/cetyltrimethylammonium bromide/allylbenzene micellar systems were formulated. The ratio (w/w) of n-propanol/cetyltrimethylammonium bromide equals 2/1. The extent of the micellar region as function of temperature was determined. The micellar systems were characterized by the volumetric parameters, density, excess volume, ultrasonic velocity and isentropic compressibility. The micellar densities increase with the increase in the water volume fraction. Excess volumes increase with the water volume fraction and temperature. Ultrasonic velocities increase with water volume fraction up to 0.8 then decrease. Ultrasonic velocities increase with temperature for water volume fractions below 0.8 and increase for water volume fractions above 0.8. Isentropic compressibilities decrease with the water volume fraction up to 0.8 then increase. Isentropic compressibilities increase with temperature for water volume fractions below 0.8 and decrease for water volume fractions above 0.8. Structural transitions from water-in-oil to bicontinuous to oil-in-water occur along the micellar phase. The particle hydrodynamic diameter of the oil-in-water micellar systems decrease with temperature. In the diluted region nanoemulsions systems were observed.

Experimental

Materials

Allylbenzene (ALB), n-propanol (n-ProOH), and cetyltrimethylammonium bromide (CTAB), were purchased from Sigma-Aldrich Chemical Company. All of the components were used as supplied without further purification. Triply distilled water was used for all experiments.

Methods

Sample preparation for pseudoternary phase diagram at constant temperature

The behavior of a four-component system is described in pseudoternary phase diagrams in which the weight ratio of surfactant/co-surfactant is fixed. The determination of the phase diagram was performed in a thermostated bath (T ± 0.1 K). Ten weighted samples composed of mixtures of (surfactant + co-surfactant) and oil were prepared in culture tubes sealed with viton-lined screw caps at predetermined weight ratios of surfactant/co-surfactant/oil. The mixtures were titrated with water along dilution lines drawn to the aqueous phase apex from the opposite side of the triangle. In all of the samples tested, evaporative losses were negligible. Nearly all samples were equilibrated during a time interval of up to 24 h. The different phases were determined visually and by optical (crossed polarizers) methods. Appearance of turbidity was considered as an indication for phase separation. The phase behavior of such samples was determined only after sharp interfaces had become visible.
The completion of this process was accelerated by centrifuging the samples. Every sample that remained transparent and homogeneous after vigorous vortexing was considered as a one phase region in the phase diagram.\textsuperscript{11,12} The solubilization capacity was determined for the one phase region of the relevant pseudoternary phase diagrams. Li et al.\textsuperscript{13} proposed the total one phase area in the phase diagram as a solubilization parameter. We call this area $A_T$. The relative error in determining the $A_T$ was estimated to be $\pm 2\%$ for all systems studied.

**Ultrasonic velocity and density**

The ultrasonic velocity and density of the various one phase transparent samples were measured using a density and sound velocity analyzer (DSA 500M- Anton Paar, Austria) with a sound velocity resolution of 0.5 ms\(^{-1}\) and density resolution of $(5\times10^{-6})$ g cm\(^{-3}\). A 3 ml degassed sample is introduced using Hamilton glass syringe into a U-shaped borosilicate glass tube that is being excited electronically to vibrate at its characteristic frequency. The characteristic frequency (high frequency (above 100 kHz) acoustic waves) changes depending on the density of the sample. Through precise determination of the characteristic frequency and a mathematical conversion, the density of the sample can be calculated. The measuring cell is closed by an ultrasonic transmitter on the one side and by a receiver on the other side. The transmitter sends sound waves of a known frequency through the sample. The velocity of sound was calculated by determining of the period of received sound waves and by considering the distance between transmitter and receiver. Due to the high dependency of the density and velocity of sound values on the temperature, the measuring cells have to be thermostated precisely with two integrated Pt 100 platinum thermometers together with Peltier elements provide an precise thermostating of the sample that equals $\pm 0.01^\circ$C. Viscosity-related errors were automatically corrected over the full viscosity range by measuring the damping effect of the viscous sample followed by a mathematical correction of the density value. The instrument automatically detects gas bubbles in the density measuring cell by an advanced analysis of its oscillation pattern and generates a warning message. Each sample was degassed before placing it in the analyzer. Measurements were made at 298, 310, 318 K.

**Dynamic light scattering**

Zetasizer Nano S (ZEN 1600) by Malvern Instruments Ltd. (Worcestershire, United Kingdom) for the measurements of the size of diluted micellar particles. The equipment includes a 4mW, 633 nm He-Ne laser. Size measurement range between 0.6 nm to 6 $\mu$m, size measurement angle equals 173$^\circ$. 1.5 ml micellar sample was introduced in a disposable polystyrene cuvettes and measured at temperatures range between 303 and 323 K by steps of 5 K. The particle hydrodynamic diameter was calculated from the translational diffusion coefficient ($D$) using the Stokes-Einstein relationship:

$$d_H = \frac{k_BT}{6\pi\eta D}$$  \hspace{1cm} (1)

where $d_H$ is the hydrodynamic diameter, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature and $\eta$ is the solvent viscosity.

The results are averages of 3 experiments.

**Results and Discussion**

**Phase behavior**

Figure 1 presents the phase behavior of water/cetyltrimethylammonium bromide/n-propanol/allylbenzene systems at 298 K. The ratio (w/w) of n-propanol/surfactant equals 2/1. As shown in the Figure 1, the phase behavior of the cationic surfactant cetyltrimethylammonium bromide is similar to that of the anionic sodium dodecyl sulfate and is different from that observed with the nonionic surfactants sucrose monolaurate presented elsewhere.\textsuperscript{12,14,15} In the case of the cetyltrimethylammonium bromide, the transparent micellar region appears after the addition of about 10 wt. % of water. Similar findings on the behavior of cetyltrimethylammonium bromide in the presence of other aromatic oils were reported.\textsuperscript{12,14-17} The area of the one phase region varies very slightly with temperature.

**Volumetric properties**

The ultrasonic wave propagates through materials and as it transverses a sample, compressions and decompressions in the ultrasonic wave change the distance between molecules within the material, which, in turn, respond by intermolecular repulsions and attractions and probes the elastic properties of samples.\textsuperscript{18-20} Figure 2 represent the variation in the density as function of the water volume fraction for the water/n-propanol/ cetyl trimethylammonium...
Phase behaviour and properties of [C16H33NMe3]Br-n-PrOH-allylbenzene-H2O system

Figure 2. Variation of the density as function of water volume fraction along N80 for the micellar system presented in Figure 1.

Bromide /allylbenzene systems. The relation (2) can evaluate the excess volume of micelle formation, keeping in view the additivity of volumes of micellar, aqueous and oil phase,

\[ V^E = V_{mic} - \sum \phi_i V_i \] (2)

where

- \( V^E \) is the excess volume,
- \( V_{mic} \) is the measured micellar specific volume,
- \( \phi_i \) is the volume fraction of component \( i \) in the micellar system and
- \( V_i \) is the specific volume of component \( i \).

Figure 3. Variation of the excess volume as function of water volume fraction along N80 for the micellar system presented in Figure 1.

Figure 3 presents the variation in the excess volume as function of water volume fraction. In the case of the cationic surfactant cetyltrimethyl ammonium bromide the excess volume increases with the water volume fraction. The excess volume values are negative indicating that the system contracts upon addition of water. Similar behaviors of excess volume with ionic and nonionic surfactants were presented elsewhere.\(^{12,14,15}\) The values of excess volume were also determined as function of temperature and it was found that excess volume increases with temperature indicating expansion of the micellar systems with temperature. This behavior could be related to breakage of hydrogen bonds or to dissociation of ionic head groups.

Figure 4. Variation of the ultrasonic velocity as function of water volume fraction along N80 for the micellar system presented in Figure 1.

Figure 4 represents the variation of the ultrasonic velocity as function of the water volume fraction for the water/n-propanol/cetyltrimethyl ammonium bromide/allylbenzene systems. The ultrasonic velocity increases with the water volume fraction up to 0.8 thereafter decreases. The variation in the values of ultrasonic velocity as function of water volume fraction provides information on the state of water. At low water volume fraction the properties of water are very different from those of bulk water indicating the entrapment of water in the micellar core suggesting the presence of water-in-oil microstructure. The increase in the values of ultrasonic velocity upon addition of water indicates structural transitions along the water dilution line. For water volume fraction above 0.8 the ultrasonic velocity approaches that of pure water indicating that water is the continuous phase and oil-in-water microstructure is present. Since ultrasonic velocity is determined by the change of physical properties at the interface between the particle core and the continuous medium, the ultrasonic velocity variation shall also be correlated to the variation of the size of the particle core. In order to better understand these results, we analyzed the ultrasonic velocity in terms of isentropic compressibility \( k_s \), which represents a relative change of volume per unit of pressure applied at constant entropy. \( k_s \) is much more sensitive to structural changes than the velocity and can provide qualitative information about the physical nature of the aggregates. The isentropic compressibility \( k_s \) values have been evaluated with the help of the Laplace equation:\(^{21-23}\)

\[ K_S = \frac{1}{u^2 \rho} \] (3)

Figure 5 presents the variation of the isentropic compressibility \( k_s \) as function of the water volume fraction. The isentropic compressibility decreases with the water volume fraction below 0.8 and increases thereafter. The variation in the values of isentropic compressibility as function of increasing water volume fraction indicates structural transitions from water-in-oil to bicontinuous to oil-in-water microstructure. The values of the isentropic compressibility were determined as function of temperature (see Figure 6) and found to increase with temperature for water volume fractions below 0.8 while for water volume...
Diffusion properties

For diluted micellar systems consisting of closed aggregates the diffusion of the aggregated components is given solely by the aggregate diffusion. At water volume fraction of 0.90 and on the assumption that exchange processes are negligible for the surfactant, we can estimate the hydrodynamic diameter ($d_H$) of the micelles in the water-rich region at water volume fraction about 0.90 using equation 1. The variation in the values of the hydrodynamic diameter ($d_H$) at water volume fraction of 0.90 for the different systems used in this study as function of temperature are shown in Figure 8. As shown in Figure 8 the hydrodynamic diameter decreases with temperature from 299 nm at 303K to 256 nm at 318K. The value for the hydrodynamic diameter indicates that the micellar systems formed with cetyltrimethyl ammonium bromide are nanoemulsions.

Conclusion

Temperature insensitive micellar systems were formulated for performing reactions with hydrophobic reagents that will lead to a significant reduction in the vast amount of organic solvents used currently in organic syntheses, and consequently increase the safety and diminish the cost of chemical processes. Quantitative analysis of the studied properties enabled the characterization of structural transition along the micellar phase. Nanoemulsion system were revealed by the determination of the particle size diameters of the diluted systems. Since the particle size of the micellar system is an important parameter in determining the yield of isomerization reaction of allylbenzene, the results presented in this study recommend performing these reactions at water volume fractions above 0.85 or at surfactant contents slightly above the critical micelle concentration and at high temperatures.

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