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PHASE STUDIES IN CETYLTRIMETHYLAMMONIUM BROMIDE SOLUTIONS

ABSTRACT

The results of viscosity, electrical resistance, light scattering, and density measurements involving mixtures of cetyltrimethylammonium bromide, potassium bromide, and water are reported. They refute one published suggestion that such mixtures consist of rather stable emulsions and another that they contain detergent crystallites. The results of the current work support the conclusion reached in an earlier study that rod-like surfactant micelles are formed upon the addition of sufficient KBr to cetyltrimethylammonium bromide solutions.

Key words: cetyltrimethylammonium bromide, micelles, viscosity, light scattering, density, electrical conductivity.

INTRODUCTION

Surfactants (surface active agents) are fascinating substances with many uses, e.g., as detergents, lubricants, fungicides, bactericides, corrosion inhibitors, and catalysts. A major factor responsible for their intriguing solution behavior is the clustering of surfactant ions (molecules in the case of nonionic surfactants) to form colloidal aggregates called micelles. McBain (1913) first suggested their existence as a way of reconciling low osmotic activity and relatively high conductivity in soap solutions. Since that time investigators have devoted considerable effort to the determination of micelle sizes and shapes. In one such study, Debye and Anacker (1951) examined the light scattering properties of cetyltrimethylammonium bromide (CTAB), KBr and H₂O mixtures. They found that some of the solutions appeared turbid to the eye and scattered light with appreciable dissymmetry, i.e., the intensity of light scattered at angle Θ (less than 90° and measured from the forward direction) was significantly

greater than the intensity of the light scattered at 180° - Θ . From their light scattering data, they calculated CTAB micelles in 0.233 M KBr to have a molecular weight of about 1.9×10^6 and a rod-like shape. P. A. Winsor (1955) suggested that the "visibly turbid solutions" of CTAB investigated by Debye and Anacker (1951) were rather stable emulsions and not single phase systems. About the same time Kushner and Hubbard (1955) broached the possibility that Debye and Anacker (1951) "were determining the particle weight of crystallites of detergent rather than micelles" since "their measurements were made so close to the salting out region of their detergent." The present paper is a belated response to these suppositions.

Some facts are easier to ascertain than others. The person who claims to be a nonvegetarian need only consume one hamburger at the "golden arches" to make his point. On the other hand, the person who maintains that he is a strict vegetarian has a tougher job proving this to skeptics who know that private conduct often is inconsistent with public declaration and behavior. Determining whether a mixture is an emulsion (droplets of one liquid dispersed in a

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second) or a true solution is a task whose potential for difficulty covers a broad range. If the mixture possesses suspended droplets that can be seen readily in a microscope or if it produces two liquid layers after a reasonable time lapse, the question is easily resolved. If, however, droplets are not observed and/or layers not formed, one is left to wonder whether a microscope with higher magnification or the exercise of a patience might not settle the question on the side of an emulsion. With our visibly turbid mixtures of CTAB/KBr/H₂O, we ran out of readily accessible microscopes (no droplets were seen with instruments having magnifications as high as 450X) and did not have the patience to wait longer to see if someone could witness bilayer formation (i.e., we failed to trigger coacervation by centrifugation).

Determining whether our turbid mixtures contain crystallites (minute surfactant crystals) is a problem with difficulties similar to those just discussed with regard to emulsions. If crystallites were to grow large enough to be visible to the eye, the question would be resolved. The failure of macroscopic crystals to develop in a reasonable time, however, would not rule out the existence of their colloidal counterparts.

If any mixture which starts out as a single phase becomes a two phase system as the result of a change in conditions (concentration, temperature, pressure), the appearance of the new phase will usually be accompanied by marked changes in the system's bulk properties. Thus, if we were to start out at an elevated temperature with an aqueous solution of an oil whose concentration was only slightly less than that of a saturated solution and then cool it with stirring in the presence of an emulsifying agent, we would find in most cases that the bulk properties of the system would change noticeably when the water became saturated with

the oil and an emulsion formed. If the solute were a solid instead of an oil and we dropped to temperatures such that crystallites formed when saturation was achieved, we could likewise expect sharp changes in mixture bulk properties. These changes would generally take place regardless of the chemical natures of the solvent-solute pair involved. The slope of any plot of a physical property versus an independent variable (concentration, temperature, pressure) would invariably change discontinuously at the point at which the new phase (droplets of the emulsion or crystallite) appeared.

CTAB/KBr/H₂O mixtures which are transparent at elevated temperatures become "visibly turbid" on cooling. Transparent mixtures at room temperature (small KBr concentrations) can be made visibly turbid through the addition of KBr. We decided to monitor several physical properties of CTAB/KBr/H₂O mixtures as their transparency was altered by changes in temperature and concentrations of CTAB and KBr. A marked change in a physical property accompanying a drop in temperature or an increase in KBr or CTAB concentration would indicate the appearance of a new phase, i.e., a second liquid (droplets in an emulsion) or a solid (crystallites). The absence of a marked change would serve as support for the maintenance of a single phase system despite the increase in turbidity.

EXPERIMENTAL

CTAB was prepared from cetyl bromide and trimethylamine according to the method of Scott and Tartar (1943). Analysis indicated 21.6% Br (theoretical 21.9%). Some of the light scattering measurements were made with an instrument similar to that used in an earlier investigation (Debye and Anacker 1951) and some were made with a Brice-Phoenix photometer. Light with a wavelength of 4358 Å was employed in all scattering

measurements. Density studies were conducted with the instrumentation described earlier (Cartan and Anacker 1960). Two Ostwald viscometers (modified by the incorporation of coiled capillary tubing between the bulbs to increase flow time) were constructed and employed for viscosity measurements. Resistance measurements were obtained with a medicine dropper cell and a model RC 16B conductivity bridge from Industrial Instruments Inc.

RESULTS AND DISCUSSION

In some viscosity measurements involving mixtures of KCl, KOH, H_2O , and the soap sodium oleate, Bungenberg de Jong and van Alphen (1947) found that as the weight of KCl for a fixed weight of surfactant in a constant mixture volume increased, the relative viscosity initially rose, achieved a maximum, and then fell. Winsor (1955) rationalized this behavior in terms of emulsions involving surfactant micelles. The results of an experiment in which we measured flow time (approximately proportional to viscosity) through a viscometer of 0.02585 M CTAB as a function of KBr concentration (solutions dilute with respect to KBr were water clear whereas those at higher salt concentrations were visibly turbid) are plotted in Figure 1. The absence of a maximum in the plot implies that Winsor's (1955) emulsion explanation of the results obtained by Bungenberg de Jong and van Alphen (1947) is inapplicable to our system.

An example of the effect upon viscosity of phase separation produced by an increase in solute concentration is provided by Hermans (1962). He examined solutions of poly- γ -benzyl-L-glutamate in *m*-cresol and found a discontinuity in the slope of the viscosity versus concentration curve at a concentration c^* . According to Hermans, the system is an isotropic solution below c^* and a mixture of an

isotropic and an anisotropic phase above it. The results of our measurements of flow time of solutions of CTAB in 0.1806 M KBr as a function of CTAB concentration are plotted in Figure 2. No slope discontinuity is present and there is no need to invoke the formation of a mixture of phases.

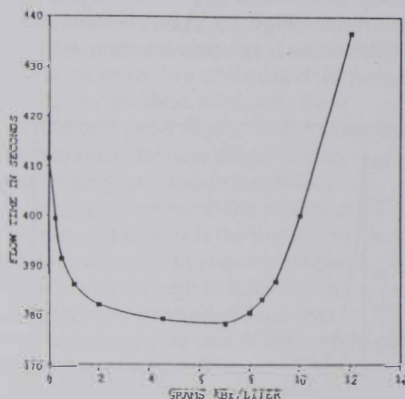


Figure 1. Viscometer flow times as a function of KBr concentration. All solutions are 0.0258 molar in CTAB. Temperature = $32.8^{\circ}C$.

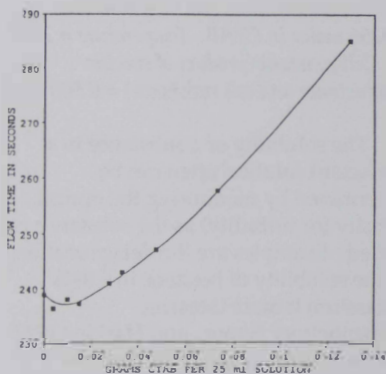


Figure 2. Viscometer flow times as a function of weight of CTAB added to 25 ml of 0.181 molar KBr. Temperature = $34.5^{\circ}C$.

Winsor (1955) measured the electrical resistance of an aqueous solution of the soap undecane-3 sodium

sulfate as a function of the volume of cyclohexylammonium chloride added. His plots (see Fig. 2, Winsor 1955) exhibit sharp slope changes which he attributes to emulsion formation. We measured the resistance of 0.0256 M CTAB solutions of varying KBr concentration (concentrations based on the assumption that true solutions involved). A plot of the results, Figure 3, shows behavior which bears little resemblance to that found by Winsor.

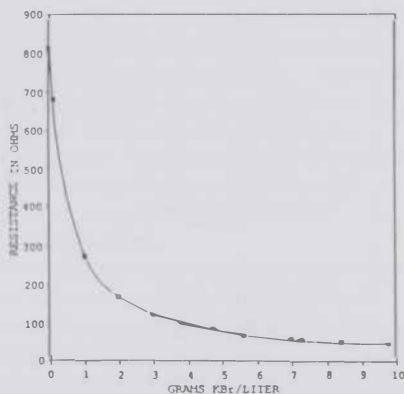


Figure 3. Electrical resistance as a function of KBr concentration. All solutions are 0.0256 molar in CTAB. Temperature = 29.8° C. Cell constant (product of specific conductance and cell resistance) = 0.500 cm¹.

The solubility of a substance in a surfactant solution often can be determined by monitoring the optical density (or turbidity) as the substance is added. Examples are the determination of the solubility of benzene in 6.8% potassium laurate (Stearns, Oppenheimer, Simon, and Harkins 1947) and in aqueous Tween 20 solutions (Matsumoto and Sherman 1969). The optical density (or turbidity) remains essentially constant with increasing amounts of added benzene until the point of saturation is reached. After emulsion droplets appear, there is a rapid increase in the optical density. The intersection of two virtually straight

lines of the plot of optical density versus weight of benzene added per unit mass of soap solution gives the solubility. We measured the 90° scattering of a 0.0256 molar solution of CTAB in excess of the solvent water as a function of added KBr. The results (recorder reading is essentially proportional to intensity of scattered light) are plotted in Figure 4. There is no sharp break in the plot that could signal emulsion formation. The marked increase in scattering at the higher KBr concentrations most likely reflects an increase in micelle size.

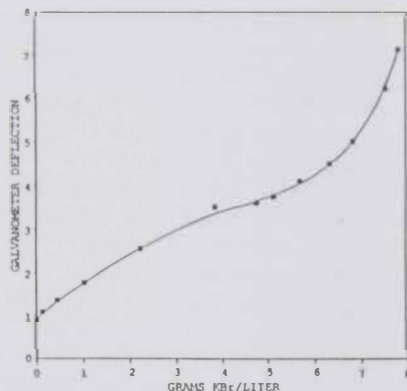


Figure 4. 90° light scattering (Rayleigh's ratio proportional to galvanometer reading) as a function of KBr concentration. All solutions are 0.0256 molar in CTAB. Scattering of water has been subtracted. Temperature = 32° C. $\lambda = 4358 \text{ \AA}$.

As hot and clear CTAB/KBr/H₂O mixtures are cooled, they gradually become visibly turbid. If an emulsion were to commence forming at some temperature during the cooling process, a plot of turbidity (or something proportional to it) versus temperature would be expected to show a sharp break, i.e., a slope discontinuity, at that temperature. After heating a solution 0.0156 molar in CTAB and 0.237 molar in KBr, we recorded the intensity of light scattered from it at 90° during its cooling in our light scattering photometer. Figure

5 summarizes the results. The absence of a break in the plot supports no emulsion formation. The increase in scattering with cooling most likely reflects growth in micelle size (Debye 1949).

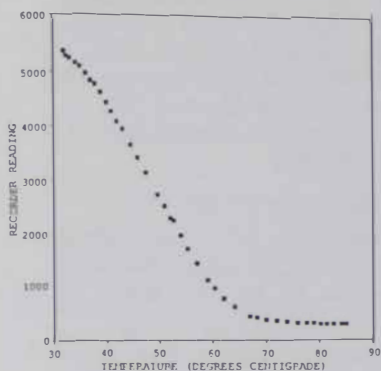


Figure 5. 90° light scattering (Rayleigh's ratio proportional to recorder reading) as a function of temperature. Solution 0.0156 molar in CTAB and 0.237 molar in KBr. $\lambda = 4358 \text{ \AA}$.

Virtually all property vs. surfactant concentration plots possess a narrow concentration range in which the slope changes rapidly but not discontinuously. If the segments of one of these plots taken immediately above and immediately below this range are extended, they will invariably intersect in the range. The concentration at which the intersection occurs is called the critical micelle concentration (CMC). It is generally thought that most of the surfactant added to a solution above the CMC forms micelles. Although micelles exist in solution below the CMC, most of the surfactant present in dilute solutions is monomeric, i.e., as surfactant ions or molecules. An analysis of the equilibrium existing between monomers and large and highly charged micelles (Anacker 1970) reveals that above the CMC the monomer concentration is close to that

of the CMC and increases very slowly with increasing total surfactant concentration. Because densities are sensitive to solution composition, they have been used to determine, among other properties, surfactant critical micelle concentrations (Cartan and Anacker 1960). We reasoned that if one can use density measurements to distinguish between the dominance of micelles and monomeric surfactant ions, as one must do in a critical micelle concentration determination, there should be a good chance of detecting the appearance of a new phase during emulsion or crystallite formation.

Figure 6 presents the results of an experiment in which the minimum current required to create a magnetic field strong enough to hold down a magnetically controlled float was measured as a function of the weight of KBr added to a 0.0257 molar CTAB solution in which the float was placed. Within experimental error, the plot is linear and provides no evidence for the formation of a new phase at any KBr concentration studied.

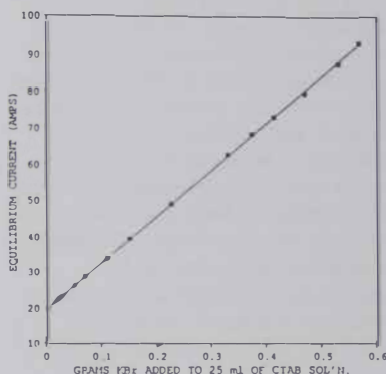


Figure 6. Equilibrium current versus grams KBr added to 25 milliliters of a 0.0257 molar CTAB solution. Difference in density between that of solution and magnetically controlled float is proportional to equilibrium current.

We considered preparing mixtures containing KBr and saturated with CTAB, thinking that equilibrium vapor pressure measurements might be helpful in resolving the emulsification question. A system consisting of an emulsion (with each of the two liquid phases containing H₂O, CTAB, and KBr), solid CTAB, and water vapor would have, according to the phase rule, one degree of freedom (degrees of freedom = number of components - number of phases + 2 = 3 - 4 + 2 = 1). Thus, if the single degree of freedom were to be used to select a temperature, phase compositions and water vapor pressure would be fixed. Differences in water/KBr weight ratios used to make up solutions could have no effect on water vapor pressure at a given temperature if the system contained an emulsion and crystalline CTAB. If only one liquid phase existed, water vapor pressure could vary. In preliminary work we found that we could prepare mixtures at 35° C which appeared to be unsaturated solutions with CTAB concentrations approximately 15 times greater than the most concentrated used in the work (Debye and Anacker 1951) that has been questioned (Winsor 1955; Kushner and Hubbard 1955). It became apparent that any system that might be prepared which was saturated with CTAB would be too far removed from those in question to provide meaningful comparisons. For this reason the phase rule study was abandoned. The effort did establish, however, that the measurements of Debye and Anacker (1951) were not made "close to the salting out region of their detergent."

CONCLUSIONS

No strong evidence exists to back suggestions that the "visibly turbid solutions" studied by Debye and Anacker (1951) were emulsions and that these investigators were possibly "determining the particle weight of

crystallites...rather than micelles." The formation of rod-shaped CTAB micelles remains the best basis for explaining the results of their study. The experimental and theoretical work of a number of other investigators (Backus and Scheraga 1951; Scheraga and Backus 1951; Halsey 1953; Trap and Hermans 1955; Götz and Heckmann 1958; Cohen and Vassiliades 1961; Herrmann 1964; Reiss-Husson and Luzzati 1964; Vassiliades 1970) provides support for their findings.

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