

QUASI-ELASTIC LIGHT SCATTERING OF CETYLTRIMETHYL-
AMMONIUM BROMIDE IN AQUEOUS SALT SOLUTIONS

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Abstract. Quasi-elastic light scattering measurements have been performed on the CTAB-H₂O-NaCl system at 25° C. The diffusion coefficient (D) and the hydrodynamic radius (R_h) show three different types of behavior as a function of surfactant and salt concentration and indicate that the size and shape of CTAB micelles changes with ionic strength. At high NaCl concentration (2.0M) the system exhibits liquid crystalline growth.

Quasi-elastic light scattering (QELS), also called dynamic light scattering and photon correlation spectroscopy, is a relatively new experimental technique used for the determination of size and shape of proteins, polymers, micelles and other macromolecular aggregates¹⁻⁴. In this particular case, quasi-elastic light scattering has been used to determine diffusion coefficients (D) and obtain mean hydrodynamic radii (R_h) for micelles and information about the change in size and shape of CTAB micelles.

QELS studies have been performed on aqueous solutions of 0.005 to 0.050 M cetyltrimethylammonium bromide (CTAB) containing sodium chloride in the 0.01 to 2.00 M range. The experimental measurements were done at 25° C using as a light source an argon laser operating at 4880 Å with an output power of about 100 mW. The average scattered intensity of light and the time dependent correlation function of the scattered intensity were measured at an angle of 90°.

Intensity correlation data were derived using a multi-channel digital correlator. Diffusion coefficients were calculated by the method of cumulants from second and third order least square fits to the intensity correlation function.

Representative plots of the experimental values obtained for the mean diffusion coefficients at 25° C as a function of CTAB and NaCl concentrations are illustrated in Figure 1. The experimental values of D do not include any viscosity correction. Such correction or normalization, when applied, is only significant for concentrations of NaCl above 0.5 M and leads to a single point of convergence for all D lines at low surfactant concentration.

In general, for fixed concentrations of NaCl the diffusion coefficient exhibits three different types of behavior. At low added salt concentration (0.01 M to 0.05 M NaCl) D increases linearly as a function of surfactant concentration. At high salt content (1.50 to 2.00 M) D decreases and at intermediate concentrations of NaCl (0.10 to 1.00 M) D remains essentially constant. This type of variation of the diffusion coefficient is typical for aqueous systems containing aggregates of surfactants and added electrolytes and has been described in detail for sodium dodecyl sulfate (SDS) and CTAB and NaBr²⁻⁴.

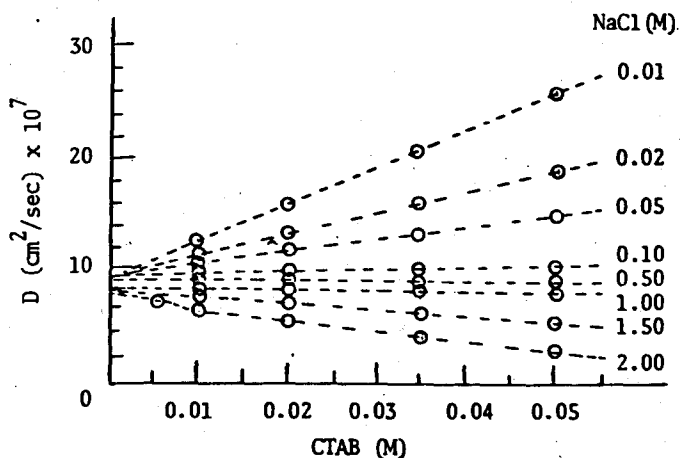


Figure 1. Experimental Diffusion Coefficients for the CTAB-H₂O-NaCl System at 25° C.

The qualitative features illustrated in Figure 1 for the system CTAB-H₂O-NaCl are consistent with the formation of spherical micelles for dilute surfactant solutions at low concentration of salt, a change to elliptical micelles for intermediate values and the formation of lamellar and liquid crystalline mesophases at high salt and surfactant concentration. Results obtained by surface tension and viscosity studies of CTAB-H₂O-NaCl indicate that the ternary system undergoes a phase transition at 25° C when the concentration of NaCl is about 0.50 M⁵.

The hydrodynamic radius (R_h) was obtained by direct application of the Stokes-Einstein relation (Eq.I)

$$R_h = kT/6\pi\eta D \quad (I)$$

where k is Boltzmann's constant, T the temperature (°K) and η the viscosity of the solvent. The limiting value of R_h at 25° C for CTAB micelles in the presence of NaCl was calculated using the value of D at the critical micellar concentration of CTAB ($9.2 \times 10^{-4} M$) is 27.8 Å.

It is obvious that the limiting value for R_h depends on the experimental value of D at the point of convergence of all diffusion lines and that the Stokes-Einstein equation applies to spherical aggregates.

This indicates that the size of CTAB micelles in the presence of NaCl is different from that of CTAB micelles in the CTAB-H₂O-NaBr and CTACl-H₂O-NaCl systems⁴ and suggests that the variation of micellar size cannot be interpreted satisfactorily only on the basis of ion exchange at the Stern layer but may also include an electrolyte effect on the bulk aqueous medium.

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