

## Some Physicochemical Properties of TTAB–Butanol Micellar Aqueous Solutions

J. L. Del Castillo,<sup>\*,†</sup> M. J. Suárez-Filloo,<sup>†</sup> A. Castedo,<sup>†</sup> T. Svitova,<sup>‡</sup> and J. R. Rodríguez<sup>†</sup>

*Departamento de Física de la Materia Condensada, Facultad de Física, Universidad de Santiago. E-15706 Santiago de Compostela, Spain, and Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky Prospect 31, 117915 Moscow, Russian Federation*

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Conductivity ( $\sigma$ ) measurements are performed on micellar systems consisting of tetradecyltrimethylammonium bromide (TTAB) in the presence of *n*-butanol (BuOH). It is found that  $\sigma$  vs BuOH molarity dependence at fixed TTAB concentration shows an unusual sinusoidal behavior. Other parameters of the systems are studied and an approximation to the conductivity of the system is made. The unusual dependence of conductivity on alcohol concentration at fixed surfactant concentration is discussed and some evidence of the competition of the viscosity of water–alcohol solution and the degree of ionization on conductivity of the systems are presented, rather than a phase transition as it was proposed earlier.

### Introduction

Surfactant systems are characterized by a very wide variety of morphologies of aggregates formed by self-assembly of molecules in aqueous solution. In other words, the surfactants exhibit a very wide richness of different phase structures. The study of these phases is a matter of common scientific and technological interest from both theoretical and experimental points of view. Intermediate chain alcohols are commonly added to surfactant solutions in order to improve their characteristics. One reason for this is that alcohols oppose the strong hydrophilicity of these surfactants. It has been shown<sup>1</sup> that alcohol may be distributed between aqueous and micellar phases and may accumulate both in the palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. Alcohols also exhibit the typical characteristics of surfactants,<sup>2</sup> thus earning the appellation of cosurfactants.

The influence of alcohols on surfactant aqueous solution properties has been extensively studied in recent years.<sup>3,4</sup> Nevertheless, there remain some aspects which warrant further investigation and particularly some specific regions of the phase diagrams.<sup>5</sup>

Zana and co-workers have reported extensive studies on the effect of linear alcohols on the critical micellization concentration (cmc), micelle molecular weight, ionization degree ( $\beta$ ), and solubility and diffusion coefficients of the micelles in solutions of alkyltrimethylammonium bromides, with particular emphasis on the pentanol–tetradecyltrimethylammonium bromide (TTAB) system.<sup>6,7,8</sup> They have shown that the incorporation of alcohol into the micelles produces noticeable changes in micellar shape and in its transport properties. On the one hand, it causes micelle swelling, and on the other hand, the decrease of micelle's surface charge density increases the degree of ionization.

Nevertheless, only a few publications address the possible effects of the difference in viscosity between water and alcohol. The conductivity of a system decreases with viscosity and, as the viscosity of the alcohol is higher than that of the water, the conductivity of the system seems to be affected by alcohol concentration. However, the cmc also decreases directly in relation to alcohol concentration.<sup>3,4,6</sup> That is why the addition

of alcohol to the ionic surfactant solution may induce the possible concurrence of several factors with opposing influences on the system.

In this work we investigate the influence of alcohol on properties of cationic surfactant solutions such as conductivity, viscosity, and surface tension over a wide range of surfactant and alcohol concentrations. A simple theoretical model, with a qualitative description of conductivity on alcohol and surfactant concentration dependence, is proposed. The different possible mechanisms of the observed unusual conductivity dependence are discussed.

### Experimental Section

Tetradecyltrimethylammonium bromide cationic surfactant was obtained from Aldrich-Chemie (stated purity >99%), middle chain alcohol and 1-butanol from Merck (stated purity >99.5%), and water was bidistilled.

Conductivities were measured using a Kyoto Electronics conductimeter (type CM117) with a nominal constant of the conductivity cell equal to 1.0. The precise cell constant was determined using KCl solutions. The solvent, water–surfactant or water–alcohol depending upon the run, was continuously added by an automatic computerized diluter Metrohm (type Dosimat 665).

Surface tension measurements were performed using the Du–Noüy ring technique; a Krüss (type K-12) tensiometer was used for this measurements. Continuous dilution was also applied in a similar way to the conductivity measurements.

Viscosity was measured in a vertical capillary flow viscometer Schott Geräte (control unit AVS440) operating with twin light barrier sensing. No continuous dilution was applicable for this kind of measurements, and individual samples were prepared.

All of the experiments were performed under constant temperature, using thermostat baths with the temperature kept constant within  $\pm 0.1$  K.

### Results

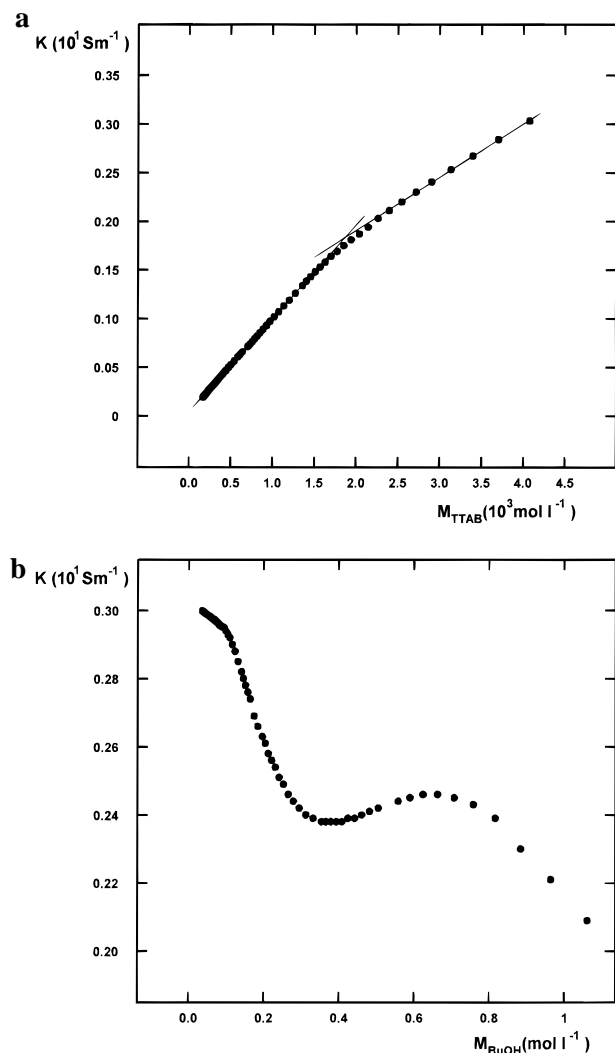
Two series of conductivity measurements were carried out. In the first, the measurements were performed at several constant concentrations of alcohol and varying surfactant molarity, and conversely, in the second series, conductivities were measured at different fixed surfactant molarities with variable alcohol concentration.

\* Author to whom correspondence should be addressed.

<sup>†</sup> Departamento de Física de la Materia Condensada.

<sup>‡</sup> Institute of Physical Chemistry.

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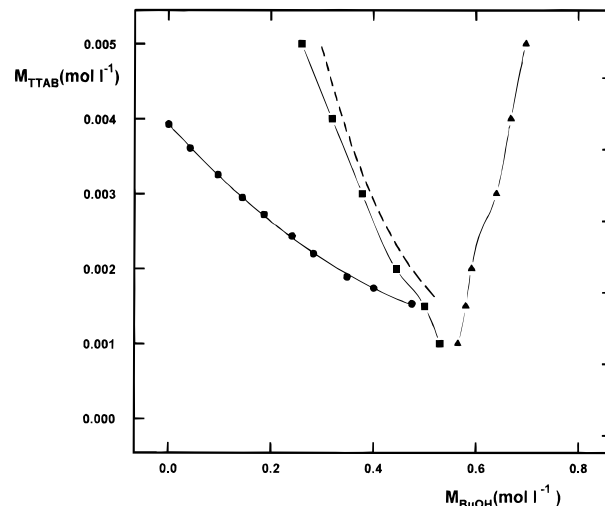


**Figure 1.** (a) Specific conductivity vs TTAB molarity at butanol concentration 0.35 M. Inflection point marks the beginning of surfactant aggregation in the micelles. (b) Specific conductivity vs butanol molarity at TTAB concentration 0.003 M. Note the existence of three singular points: cmc, minimum, and maximum, respectively.

Figure 1a shows a typical experimental result obtained in the first series. Two linear regions of  $\sigma$  vs TTAB concentration dependence, at low and high surfactant concentration, are observed. This is a well-known situation, representative of micellization processes, and the intersection point of these straight lines has been used to obtain the cmc. Experimental cmc values (solid points) are plotted in Figure 2, for concentrations of butanol up to 0.5 M. It is seen that cmc is a monotonically decreasing function of alcohol molarity which can be well fitted with a second-order polynomial regression.

Assuming that the molar conductivity of micellized surfactant ions not compensated by bound counterions is equal to that of the free surfactant ions,<sup>9</sup> the degree of ionization  $\beta$  can be approximated as the ratio between the slopes of  $\sigma$  vs TTAB concentration dependence above and below cmc. This degree is defined as  $p/n$ , where  $p$  is the charge number in  $e^-$  units and  $n$  the aggregation number. This series of conductivity measurements therefore allows us to find the dependence of cmc and the degree of ionization on alcohol concentration. The degree of ionization is also well described by a second-order polynomial, but in this case it increases with alcohol molarity. The results are summarized in Table 1.

We have found that at concentrations of alcohol higher than 0.5 M, cmc determination by this procedure was very difficult,



**Figure 2.** cmc (●), minimum (■), and maximum (▲) loci of conductivity curves vs butanol molarity. Dashed line is the theoretical prediction for minimum locations.

**TABLE 1: Degree of Ionization  $\beta$  at Different Butanol Concentrations**

[BuOH]/M	$\beta$
0.00	0.25
0.05	0.27
0.11	0.31
0.15	0.35
0.20	0.41
0.25	0.46
0.30	0.51
0.35	0.56
0.39	0.64
0.40	0.65
0.48	0.74

because the degree of ionization is close to unity and the two conductivity straight lines below and above the cmc have almost the same slope.

In Figure 1b an example of the experimental data obtained in the second series at constant TTAB concentration is displayed. This figure shows that the changes of alcohol molarity lead to a more complicated dependence on conductivity than that in the first series. For low alcohol concentrations, an abrupt change in the slope of the curve is observed. In fact, the point in Figure 1b where the slope changes corresponds to the same cmc value as that in series 1a, the alcohol concentration now being the control parameter. For concentrations of alcohol higher than 0.2 M, the curve has an uncommon sinusoidal shape. In Figure 2 we represent the locations of the cmc's (circles), minimums (squares), and maximums (triangles) of conductivity dependence on BuOH molarity, linked by smoothing lines. It is seen from Figure 2 that both the cmc and the location of the minimum decrease when the alcohol concentration increases, while location of the maximum has opposite behavior.

In a similar system, Li and Rosenblatt<sup>10</sup> have found a kink in the shape of the curve for conductivity dependence on temperature at several alcohol concentrations. The authors have explained this kink as the result of a nematic–isotropic phase transition. The conductivity vs alcohol concentration dependence obtained from their results shows a shape which is very similar to that found in our case.

Nevertheless, we propose the hypothesis that the sinusoidal shape of the conductivity dependence on alcohol concentration (Figure 1b) is related to simultaneous competition between the degree of ionization  $\beta$ , the viscosity of the solvent  $\eta$ , and the cmc on the conductivity of our systems. It is evident that the

conductivity of the micellar solution has to increase with concentration of  $\text{Br}^-$  ions which, in turn, increases with an increasing  $\beta$ . On the other hand, the addition of the butanol increases the viscosity of the medium, which implies that conductivity should decrease. Therefore, in the presence of alcohol, conductivity increases due to the increase of  $\beta$  and the decrease of the cmc, and conductivity decreases due to the  $\eta$  rising.

### Theory

For a solution containing different types of electrically charged particles, the electrical conductivity is given by

$$\sigma = \sum_i n_i \mu_i q_i \quad (1)$$

where  $n_i$  is the number of charged particles of class  $i$  per volume unit,  $\mu_i$  is the mobility of an  $i$ th-type ion and  $q_i$  is the electrical charge of the  $i$ th-ion. When the Einstein relation  $\mu_i = D_i q_i / (k_B T)$  is taken into account (where  $D_i$  is the diffusion coefficient,  $k_B$  is the Boltzmann constant, and  $T$  is the absolute temperature), and the Stokes–Einstein relation  $D_i = k_B T / (6\pi\eta r_i)$  ( $r_i$  being the characteristic size of  $i$ th-particle), the mobility can be approximated by

$$\mu_i = \frac{q_i}{6\pi\eta r_i} \quad (2)$$

Regarding eq (2) and accounting for the fact that  $c_i = n_i / N_A$  (where  $N_A$  is the Avogadro number) we can write eq 1 as

$$\sigma = \frac{N_A}{6\pi\eta} \sum_i \frac{c_i q_i^2}{r_i} \quad (3)$$

which relates the conductivity with the viscosity and the electrical charges in solution.

**(a) Conductivity below cmc.** Below cmc, the solution contains the surfactant fully dissociated into monomer ions ( $\text{TTA}^+$ ) and counterions ( $\text{Br}^-$ ), with electrical charges  $+e^-$  and  $-e^-$ , respectively and the same concentration  $c$ , which is the total concentration of surfactant. After eq (3) is manipulated, the conductivity is given by

$$\sigma = \frac{N_A (e^-)^2 c}{6\pi\eta} \left( \frac{1}{r_{\text{TTA}^+}} + \frac{1}{r_{\text{Br}^-}} \right) \quad (4)$$

This relation corresponds to the left linear part of  $\sigma$  vs TTAB concentration dependence presented in Figure 1a.

**(b) Conductivity above cmc.** In the presence of micelles, the conductivity of the system can be calculated in a similar way, using eq 3

$$\sigma = \frac{N_A (e^-)^2}{6\pi\eta} \left[ \left( \frac{1}{r_{\text{TTA}^+}} + \frac{1}{r_{\text{Br}^-}} \right) \text{cmc} + \frac{\beta^2 n}{r_M} (c - \text{cmc}) + \frac{\beta}{r_{\text{Br}^-}} (c - \text{cmc}) \right] \quad (5)$$

Where  $r_M$  is the characteristic size of the micelles. The first term of this equation takes into account the conductivity of the monomer ions and  $\text{Br}^-$  ions just at cmc. The second term represents the conductivity of the partially ionized micelles. The third corresponds to the conductivity term by the counterions not linked to the micelles. The limiting value of monomer molar conductivity at  $C_{\text{TTA}^+} \rightarrow 0$  is  $21.5 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ , and

is about four times lower than that of the  $\text{Br}^-$  ion ( $78.1 \times 10^{-4} \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$ ). The calculation of the second term value in eq 5, using common values for  $\beta$ ,  $n$ , and  $r_M$  from the literature,<sup>4</sup> shows that its magnitude is about 10 times less than that of the third term in eq 5. Therefore, in a coarse initial approximation we can neglect the terms accounting for the conductivity of monomer ions and the micelles; thus, eq 5 is reduced to<sup>11</sup>

$$\sigma = \frac{N_A (e^-)^2}{6\pi\eta r_{\text{Br}^-}} [\text{cmc} + \beta(c - \text{cmc})] \quad (6)$$

In order to obtain the minimum locations of the conductivity vs alcohol concentration curves, numerical solution of  $d\sigma/dc_{\text{BuOH}} = 0$  has to be found. The derivative  $d\sigma/dc_{\text{BuOH}}$  consists of three terms:

$$\frac{N_A (e^-)^2}{6\pi\eta r_{\text{Br}^-}} (1 - \beta) \frac{d\text{cmc}}{dc_{\text{BuOH}}} \quad (7a)$$

$$- \frac{N_A (e^-)^2}{6\pi\eta r_{\text{Br}^-}} [\text{cmc} + \beta(c - \text{cmc})] \frac{d\eta}{dc_{\text{BuOH}}} \quad (7b)$$

$$\frac{N_A (e^-)^2}{6\pi\eta r_{\text{Br}^-}} (c - \text{cmc}) \frac{d\beta}{dc_{\text{BuOH}}} \quad (7c)$$

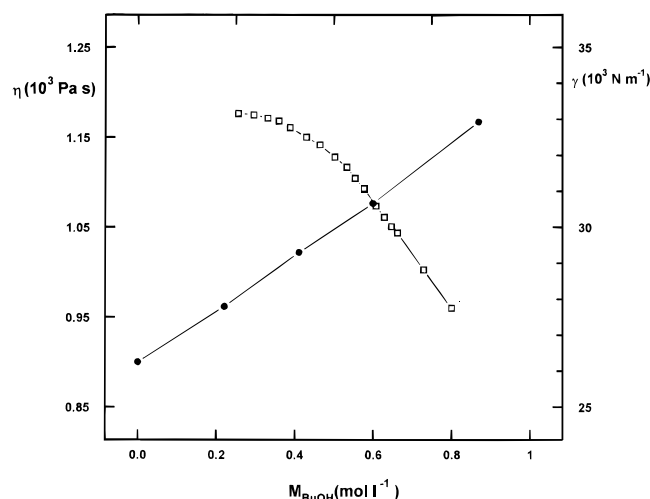
### Discussion

Although the viscosity values are known for the whole range of butanol in water solubility,<sup>12</sup> experimental data for cmc and  $\beta$  are only accessible for  $c_{\text{BuOH}} < 0.5 \text{ M}$ . Since the fitting we employ has no physical meaning, values extrapolated to butanol concentration above 0.5 M cannot be considered, and consequently only the minimum locations can be found from the analysis of derivative  $d\sigma/dc_{\text{BuOH}}$ .

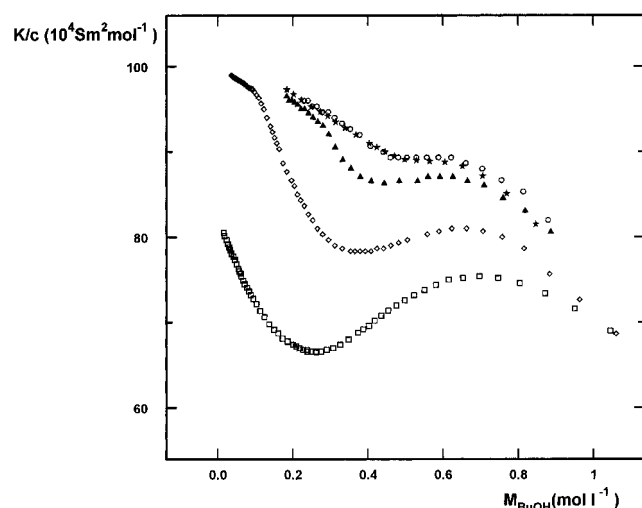
As the cmc decreases when alcohol concentration rises, the term 7a has a negative value. The term 7b is also negative because the viscosity increases with alcohol molarity. Further, the degree of ionization is a rising parameter with alcohol concentration; thus, the 7c term is numerically positive. The competition between these factors will be then the origin of the apparition of singularities in the curves of conductivity vs butanol concentration.

At different TTAB concentrations, the equation formed by adding and annulling eqs 7 has been solved by the classical Newton method. The results obtained are displayed in Figure 2 (dotted line). Quantitative differences between the theoretically predicted and experimental values are observed, but qualitatively these curves are in good agreement. The former should be expected because of the simplification of the model. A better approximation could be obtained by considering both the contributions of micelles and tetradecyltrimethylammonium ions to the conductivity and the butanol distribution coefficient between water and micelles,<sup>13</sup> this would enable more precise solution viscosity values. In spite of the fact that  $\beta$  and cmc are unknown at high alcohol concentration, the existence of a maximum follows from eqs 7a–c.

In order to identify or to discard the possibility of a phase transition, we have measured the viscosity and surface tension as a function of alcohol molarity at constant surfactant concentration. Results are displayed in Figure 3, and as it is seen, no special singular point can be observed for the viscosity and surface tension dependence on alcohol concentration. It is well-known that viscosity is very sensitive to the shape of the



**Figure 3.** Viscosity (●) and surface tension (■) vs butanol molarity at TTAB concentration 0.003 M.



**Figure 4.** Molar conductivity vs butanol molarity at different TTAB concentrations: (□) 0.005 M, (◇) 0.003 M, (▲) 0.002 M, (○) 0.0015 M, (★) 0.001 M.

microscopic objects in a homogeneous suspension,<sup>14,15</sup> so no phase transition to different objects other than micelles is expected.

Moreover, some changes of the micelles spatial configuration may take place, as in the case of a nematic–isotropic phase transition. We have observed the textures of samples placed between crossed polarizers with different alcohol concentrations, and no differences have been found. Although the possibility of a new phase cannot be excluded, we think that the mechanism mainly responsible of the appearance of a minimum and a maximum in the conductivity curves is the competition among the cmc,  $\beta$ , and  $\eta$ .

The molar conductivity dependence on alcohol molarity at several surfactant concentrations is presented in Figure 4. In these cases, residual contribution, caused by water ionization, has been eliminated by subtraction of the water conductivity value measured in the same conditions. It is seen that at surfactant concentrations below cmc all the curves show fairly common behavior, tending toward  $0.01 \text{ S m}^2 \text{ mol}^{-1}$  at zero butanol concentration, which corresponds to the sum of the

monomer ions and counterions conductivities in accordance with the model. Also, it follows from eq 6 that, when  $\beta$  is close to 1, the molar conductivity of the systems is slightly dependent of the surfactant concentration. This result is also observed in Figure 4. At high alcohol concentration, about 1 M, all curves tend toward the same value, independently on surfactant concentration. The decrease of the molar conductivity at alcohol concentration above 1 M is only induced by the increase of the viscosity associated to the butanol. In the intermediate region the differences are due to the cmc/c ratio.

Finally, from these curves one can extract the values of molar conductivity at constant alcohol concentration. The plot vs surfactant concentration shows typical behaviour for micellar systems. The curve is composed of a horizontal straight line for values below the cmc and a concave decreasing function for higher surfactant concentration values.

## Conclusion

Systematic study of the influence of alcohol concentration on electrical conductivity of TTAB–BuOH mixtures is carried out over a wide range of alcohol and TTAB concentrations. It is found that at alcohol concentration above 0.2 M the electrical conductivity dependence on TTAB concentration shows an unusual sinusoidal behavior. The existence of a phase transition as a possible reason for the observed unusual conductivity dependence was checked by rheological and optical methods and also by tensiometry. It was found that neither changes in the optical texture of our system nor singular points on viscosity and surface tension dependence on alcohol concentration are observed. The mechanism responsible for this phenomena is proposed.

We conclude that the unusual sinusoidal behavior of conductivity on TTAB concentration is related to a delicate balance between increasing viscosity and degree of ionization against decreasing cmc with alcohol concentration. A theoretical model is proposed and it is found that theoretical predictions are in good qualitative agreement with experimental data.

## References and Notes

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