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Transport properties of alkyltrimethylammonium bromide surfactants in aqueous solutions

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Abstract Differential mutual diffusion coefficients of *n*-alkyltrimethylammonium bromides [$CH_3(CH_2)_{n-1}N(CH_3)_3Br$, C_nTAB] (n = 10, 12, 14, 16) have been measured in aqueous solutions at 298.15 K using a conductimetric cell and an automatic apparatus to follow diffusion. The cell is based on an open-ended capillary, and the technique follows the diffusion process by measuring the resistance of a solution inside the capillaries at various times. The electrical conductances of those solutions have also been measured to calculate the critical micellar concentration (cmc). Thermodynamic analysis of the data suggests that the free ion concentration decreases at concentrations above the cmc, in agreement with theoretical predictions. The obtained values of the micellization parameters were used to model the mutual diffusion coefficients of C_nTAB aqueous solutions.

Keywords Diffusion · C_nTAB · Aqueous solutions · Transport properties

Introduction

Studies in the area of transport properties of surfactants in aqueous solutions will provide fundamental new information with applications to processes in areas as diverse as detergents, paint, separation, paper coatings, food, pharmacy, and corrosion [1, 2, 3, 4, 5].

Also, environmental concern has prompted a need for systems based on water as solvent, in particular aqueous systems of biologically compatible surfactants and polymers as well as substances derived from renewable resources. The importance of the surfactants is also revealed by their solubility. Many organic compounds (e.g., oil) are almost insoluble in pure water. In the presence of surfactant micelles these compounds can be solubilized and transported into aqueous solutions.

Many techniques are used to study diffusion of surfactant solutions. However, methods such as NMR, polarographic, and capillary-tube techniques can only be used to measure intradiffusion coefficients [6, 7, 8]. It is very common to find misunderstandings in the scientific literature concerning the meaning of the parameter frequently just denoted by D and merely called the diffusion coefficient. In fact, it is necessary to distinguish between self-diffusion, D^0 (intradiffusion, tracer diffusion, single-ion diffusion, ionic diffusion), and mutual diffusion (interdiffusion, concentration diffusion, salt diffusion) [6, 7, 8, 9].

Derivation of relationships between intradiffusion and interdiffusion coefficients in surfactant systems have been attempted [9], but because of their limited success, interdiffusion coefficients are still much need. Also, mutual diffusion coefficients provide important information about the kinetics of surfactants in aqueous solutions. Mutual diffusion coefficients of ionic surfactants are scarce in the literature [10, 11]. The open-ended capillary cell [12] has been used to successfully measure differential mutual diffusion coefficients of electrolyte solutions in a large concentration range and therefore has been used here [13, 14].

In this paper, the effect of chain length of *n*-alkyltrimethylammonium bromides [$CH_3(CH_2)_{n-1}N(CH_3)_3Br$, C_nTAB] (n = 10, 12, 14, 16) on mutual diffusion coefficients, at 298.15 K, is analyzed in a concentration range containing the critical micellar concentration (cmc). Different micellar parameters (e.g., dependence of cmc on chain length as seen by both diffusion and conductance measurements, percentage of micelles, diffusion coefficient of micelle at infinitesimal concentration, radius of the micelles, and Nernst diffusion coefficient) will be discussed by comparing these results with those obtained by conductance measurements by using a Shedlovsky-type conductance cell. A discussion of the diffusion coefficients as a function of surfactant and concentration on the basis of a semi-empirical equation for dilute solutions of associated symmetrical electrolytes will be attempted. Such discussion will allow the analysis of the effect of the thermodynamic factor (activity coefficient) on the diffusion coefficients.

Experimental

Reagents

Dodecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide were obtained from Aldrich (pro analysi, > 99% reagent grade). Tetradecyltrimethylammonium (pro analysi, > 99%) was obtained from Sigma. Decyltrimethylammonium bromide (> 98%) was obtained from Fluka. All solutes were used without further purification. Aqueous solutions were prepared by using doubly distilled (diffusion measurements) and triply distilled (conductance measurements) water. All solutions were freshly prepared just before each experiment.

Diffusion measurements

The open-ended capillary cell used was constructed in this laboratory and is essentially the same as that previously reported [12]. The cell has two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by approximately 14 mm.

The upper (top) and lower (bottom) tubes, initially filled with solutions of concentrations 0.75 *c* and 1.25 *c*, respectively, were surrounded with a solution of concentration *c*. This ambient solution was contained in a 200×140×60-mm glass tank, which was immersed in a bath thermostated at 298.15 K. The tank was divided internally by Perspex sheets, while a glass stirrer created a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions were such that the concentration at each of the open ends was equal to the ambient solution value *c*, that is, the physical length of the capillary tube coincided with the diffusion path, such that the boundary conditions described in ref. [12] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl-effect [12] is reduced to negligible proportions. In contrast to a manual apparatus, in which diffusion is followed by measuring the ratio of resistances of the top and bottom tubes, $w = R_t/R_b$, by an alternating current transformer bridge, in our automatic apparatus w was measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A Bradley Electronics Model 232 power source supplied 30 V (stable to ± 0.1 mV) to a potential divider that applied a 250-mV signal to the platinum electrodes in the top and bottom capillaries. By rapidly (< 1 s) measuring the voltages V' and V'' from the top and bottom electrodes relative to the central electrode at ground potential, w was then calculated from the DVM readings.

To measure the differential diffusion coefficient D at a given concentration c, 2 L each of a "top" solution of concentration 0.75 *c* and a "bottom" solution 1.25 *c* were prepared. The "bulk" solution of concentration *c* was produced by mixing accurately measured volumes of 1 L of "top" solution with 1 L of "bottom" solution. The glass tank and the two capillaries were filled with solution *c*, immersed in the thermostat, and allowed to come to thermal equilibrium. The quantity $TR_{\mathrm{inf}} = 10^4/(1+w)$ was then measured very accurately (where $w = R_t/R_b$ is the electrical resistance ratio for solutions of concentration c of the top (t) and bottom (b) diffusion capillaries at infinite time). $TR = 10^4/(1+w)$ is the equivalent at any time t.

The capillaries were then filled with "top" and "bottom" solutions, which were allowed to diffuse into the "bulk" solution. Resistance ratio readings were taken at various times, beginning 1,000 min after the start of an experiment. The diffusion coefficient was evaluated by using a linear least-squares procedure to fit the data, followed by an iterative process which uses 20 terms of the expansion series of the solution of Fick's second law for the present boundary conditions. The theory developed for this cell has been described previously [12].

Conductance measurements

Solution electrical resistances were measured with a Wayne–Kerr model 4265 Automatic LCR meter over the frequency range 0.5–2.5 kHz and extrapolated to infinite frequency. A Shedlovsky-type conductance cell was used [15]. Cell constants (approximately 0.8465 cm^{-1}) were determined to ± 0.02% from measurements with KCl (reagent grade, recrystallized, and dried) using the procedure and data reported by Barthel et al. [16]. Measurements were made at 25.00 ± 0.01°C in a Grant thermostat bath. The micellization parameters were obtained by using at least 15 points in each region (i.e., pre-micelle and post-micelle).

Results and discussion

Table 1 shows the experimental diffusion coefficients of the even chain length *n*-alkyltrimethylammonium bromide surfactants (n = 10, 12, 14, and 16) in aqueous solutions. These results are the average of three experiments performed on consecutive days. The experimental procedure shows good reproducibility, as shown by the small standard deviations (S_{Dav}). The accuracy of the systems (uncertainty 1–2%) has been demonstrated by measurements on other solutions of different electrolytes (e.g., see refs. [17, 18, 19]).

Table 1 Diffusion coefficients (*D*) of *n*-alkyltrimethylammonium bromides [$CH_3(CH_2)_{n-1}N(CH_3)_3Br$, C_nTAB] (n = 10, 12, 14, 16) in aqueous solutions at 298.15 K at different concentrations (*c*)

c (mol dm^{-3})	D^a (10^{-9} m^2 s−1)	S_D (10^{-9} m^2 s−1)
(n = 10)		
0.001	1.010	0.002
0.003	1.000	0.002
0.005	1.006	0.005
0.010	0.972	0.008
0.050	0.890	0.001
0.100	0.348	0.001
(n = 12)		
0.001	0.944	0.011
0.005	0.939	0.010
0.007	0.927	0.008
0.015	0.820	0.014
0.017	0.725	0.001
0.030	0.303	0.001
0.050	0.378	0.002
(n = 14)		
0.001	0.910	0.003
0.003	0.700	0.002
0.004	0.675	0.020
0.005	0.566	0.012
0.008	0.362	0.010
0.010	0.322	0.012
0.020	0.402	0.010
0.050	0.695	0.020
(n = 16)		
0.0005	0.995	0.001
0.0007	0.900	0.001
0.0008	0.820	0.001
0.0010	0.734	0.027
0.0020	0.294	0.002
0.0050	0.510	0.001

[a] *D* is the mean diffusion coefficient of three experiments

[b] S_D is the standard deviation of that mean

The experimental diffusion coefficients shown in Table 1 can be fitted by using a polynomial equation

$$D = a_0 + a_1 c^{1/2} + a_2 c + a_3 c^{3/2} \qquad (1)$$

where the coefficients a_0, a_1, $a_{2,}$ and a_3 are adjustable parameters.

The fits to the experimental data points were obtained by using the mean square deviation method; the goodness of the fit can be assessed by the correlation coefficient (R^2) using a 95% confidence interval. Table 2 shows the coefficients a_0–a_3 of Eq. (1). These may be used to calculate values of diffusion coefficients at specified concentrations within the range of the experimental data.

Table 3 shows the micellization parameters [critical micellar concentration (cmc), degree of counterion dissociation of micelles (β), molar conductivity at infinitesimal concentration of the surfactant solution below cmc (Λ_0), and limiting equivalent conductivity for C_nTAB micelles ($\lambda^+{}_0$)] for the different C_nTAB solutions. The obtained parameters are compared with those reported in the literature which were calculated using different techniques and methods [20, 21, 22, 23, 24, 25]. The cmc is obtained from the empirical data of specific conductivity (κ) as a function of surfactant concentration by using the following equation: cmc = $b_M/(m_1-m_M)$, where m_1, m_M, and b_M are the fitting parameters of $\kappa = f(c)$ to a straight-line equation to post- and pre-micelle regions, respectively. For each surfactant, the following values for those coefficients were found: ($C_{10}TAB$) b_M = 4,612.7 ± 2.9 μS cm^{-1}, m_M = 30,225.9 ± 10.1 μS cm^{-1} M^{-1}, m_1 = 100,519.2 ± 158.5 μS cm^{-1} M^{-1}; ($C_{12}TAB$) b_M = 1,093.7 ± 4.3 μS cm^{-1}, m_M = 26,894.7 ± 209.8 μS cm^{-1} M^{-1}, m_1 = 98,181.8 ± 106.3 μS cm^{-1} M^{-1}; ($C_{14}TAB$) b_M = 280.16 ± 0.77 μS cm^{-1}, m_M = 26,185.6 ± 106.2 μS cm^{-1} M^{-1}, m_1 = 97,245.5 ± 352.9 μS cm^{-1} M^{-1}; ($C_{16}TAB$): b_M = 69.34 ± 0.37 μS cm^{-1}, m_M = 22,519.4 ± 17.8 μS cm^{-1} M^{-1}, m_1 = 94,426.8 ± 137.15 μS cm^{-1} M^{-1}. The values of cmc we obtained for the different surfac-

Table 2 Fitting coefficients (a_0–a_3) of a polynomial equation [$D/(\mathrm{m}^2\ \mathrm{s}^{-1}) = a_0 + a_1(c/\mathrm{mol\ dm}^{-3})^{1/2} + a_2(c/\mathrm{mol\ dm}^{-3}) + a_3(c/\mathrm{mol\ dm}^{-3})^{3/2}$] to the mutual differential diffusion coefficients of alkyltrimethylammonium bromide surfactants (C_nTAB) in aqueous solutions at 298.15 K

Electrolyte	a_0	a_1	a_2	a_3	R^2
$C_{10}TAB^a$	1.077×10^{-9}	-2.596×10^{-9}	2.453×10^{-8}	-7.440×10^{-8}	0.998
$C_{12}TAB^b$	9.472×10^{-10}	-7.551×10^{-10}	2.811×10^{-8}	-2.614×10^{-7}	0.996
$C_{14}TAB^c$	8.753×10^{-10}	8.527×10^{-9}	-2.817×10^{-7}	1.398×10^{-6}	0.991
$C_{16}TAB^d$	7.053×10^{-10}	6.073×10^{-8}	-2.708×10^{-6}	2.560×10^{-5}	0.999

[a] $0.001\ \mathrm{M} \le c \le 0.1\ \mathrm{M}$

[b] $0.001\ \mathrm{M} \le c \le 0.03\ \mathrm{M}$

[c] $0.001\ \mathrm{M} \le c \le 0.02\ \mathrm{M}$

[d] $0.0005\ \mathrm{M} \le c \le 0.005\ \mathrm{M}$

Table 3 Micellization parameters calculated using conductivity data of C_nTAB solutions at 298.15 K

	cmc (mM)	β	Λ_0 (S cm^2 mol^{-1})	$\lambda_0{}^+$ (S cm^2 mol^{-1})	N^c	r (Å)
$C_{10}TAB$	65.62 67.6[c] 64.6[b]	0.301	100.52	78.33	40	14.1
$C_{12}TAB$	15.34 15.2[a] 15.4[c] 14.2[b]	0.274 0.251[a]	98.18	84.36	55	16.63
$C_{14}TAB$	3.943 3.78[a] 3.79[c] 3.6[b]	0.269 0.227[a]	97.24	91.33	70	18.90
$C_{16}TAB$	0.9642 0.96[a] 0.955[c] 0.92[b]	0.238 0.243[a]	94.43	92.28	90	21.4

[a] See ref. [25]
[b] See ref. [21]
[c] See ref. [22]

tants are in good agreement with those reported earlier [20, 21, 22].

The values of the degree of counterion dissociation of micelles (β) were obtained from the ratio of the slopes of the lines above and below the cmc (m_M/m_1, see coefficients reported above). Good agreement is also observed between our measurements and literature data, when available, for molar conductivities [20]. If N and β are known, the charge ($N\beta$) and the radius (r) of the micelles can be calculated. Assuming the micelle as spherical, r is computed from the equation [26]

$$r = [3/(4\pi)(27.4 + 26.9n_C)N\ ]^{1/3} \tag{2}$$

where n_C is the number of carbon atoms per hydrocarbon chain of surfactant. The limiting ionic equivalent conductivity for C_nTAB micelles ($\lambda_0{}^+$), and the limiting equivalent conductivity of a surfactant solution (Λ_0) below the cmc can also be found in Table 3. Λ_0 was obtained from the slope of specific conductivity as a function of concentration in the pre-micelle region [26], and $\lambda_0{}^+$ was estimated by using the Stokes–Einstein equation

$$\lambda_0{}^+ \ = (N\beta e_0 F)/(6\pi\eta r) \tag{3}$$

where e_0 is the elementary charge (1.60209×10^{-19} C), F is the Faraday constant, and η is the viscosity of water (8.903551×10^{-4} kg m^{-1} s^{-1}) [27].

Limiting diffusion coefficients

Extrapolation of the fit of these equations to infinitesimal concentration gives the estimated diffusion coefficients obtained (i.e., $D^0 = a_0$ in Table 2) which account for the diffusion of both the surfactant cation and the anion under these conditions. From these, we can calculate the limiting intradiffusion coefficient of the surfactant cation $\left(D^0_{\text{cation}}\right)$ (Table 4) by using the Nernst equation (4) [15]

$$D^0_{\text{cation}} = \left[\frac{2}{D^0_{\text{exp}}} - \frac{1}{D^0_{\text{Br}^-}}\right]^{-1} \tag{4}$$

where D^0_{exp} is the limiting mutual diffusion coefficient of the electrolyte, and D^0_{cation} and $D^0_{\text{Br}^-} = 2{,}081\times10^{-9}$ m^2 s^{-1} [28] are the limiting self-diffusion coefficients of cation and anion, respectively.

As can be seen in Table 4, the agreement between the limiting D^0 values calculated from the differential mutual diffusion coefficients and those obtained by D'Errico [6] using pulse field gradient NMR techniques is reasonable. In addition, we can see that the limiting diffusion coefficient values for these surfactants decrease as the length of the hydrophobic chain increases. This effect leads to a decrease in the mobility of the surfactant, and, consequently, a decrease in the diffusion coefficient.

Determination and evaluation of critical micellar concentration

From the results shown in Table 1, we see that the diffusion coefficients of the *n*-alkyltrimethylammonium bromides (n = 10, 12, 14, and 16) in aqueous solutions decrease as the concentration is raised, and that above the critical micellar concentration (cmc) the drop in D is

Table 4 Limiting diffusion coefficients for the systems H_2O–C_nTAB

Surfactant	$D^0{}_{\text{exp}}$ (10^{-9} m^2 s^{-1})	$D^0{}_{\text{lit}}{}^a$ (10^{-9} m^2 s^{-1})	$D^0{}_{\text{cations}}$ (10^{-9} m^2 s^{-1})	$D^0{}_{\text{cations}}$ (10^{-9} m^2 s^{-1})[a]
$C_{10}TAB$	1.077	1.010	0.726	0.636
$C_{12}TAB$	0.947	0.917	0.613	0.588
$C_{14}TAB$	0.875	–	0.554	–
$C_{16}TAB$	0.705	–	0.424	–

[a] Data from ref. [6]

Table 5 Critical micellar concentration (cmc) obtained from diffusion and micelle diffusion coefficients (D_M) estimated from Eq. (9)

Surfactant	cmc_D[a] (mol dm^{-3})	R^2[b]	D_M (m^2 s^{-1})
C_{10}TAB	7.1×10^{-2}	0.95[c]	3.98×10^{-10}
C_{12}TAB	1.3×10^{-2}	0.80[d]	3.69×10^{-10}
C_{14}TAB	3.5×10^{-3}	–	–
C_{16}TAB	7.8×10^{-4}	–	–

[a] cmc estimated from diffusion measurements

[b] R^2 represents the correlation coefficient, using a confidence interval of 95% and Eq. (< equationcite > 9 < /equationcite >)

[c] $0.001 \le c \le 0.09$ M

[d] $0.001 \le c \le 0.05$ M

In all cases, Eq. (< equationcite > 1 < /equationcite >) and the values for constants shown in Table 2 were used to interpolate values of diffusion coefficients

enhanced as a result of the formation of the large micelle aggregates. Previous studies with ionic surfactants [29, 30] have shown slight increases in the diffusion coefficients at higher concentrations, possibly owing to micelle–micelle interactions and electrostatic effects. The cmc values calculated on the basis of the mutual diffusion coefficients as a function of $c^{0.5}$ were obtained from the intersection of the two straight lines which best fit the experimental data below and above the cmc. The results are summarized in Table 5. As the length of the hydrocarbon chain increases, the cmc decreases. Comparing these cmc values with those obtained by conductance experiments (Table 3), quite good agreement is found between the two techniques, with the differences observed for the longer chain surfactants. Although the reason for the latter is not clear, micelle aggregation does not occur at a single well-defined concentration, but over a limited concentration range, and it is possible that the two techniques are detecting different facets of this region. With the more hydrophobic longer-chain compounds different kinds of interaction with water molecules can result in a complex electrophoretic effect, and as a consequence the alteration of D in the cmc region becomes less distinct.

The values of cmc obtained from either diffusion or conductivity measurements decrease strongly with the alkyl chain length, following the relationship (correlation coefficient = 0.996) $\log(\text{cmc}) = 2.0 - 0.32n_C$ where n_C is the number of carbons in the alkyl chain. This equation is in close agreement with another one previously cited in the literature for the same systems [$\log(\text{cmc}) = 1.7 - 0.30n$ [5]].

Effect of association on diffusion

At concentrations below the cmc, the C_nTAB surfactants are considered to be completely dissociated. As with non-associating electrolytes, in this pre-micelle composition range the diffusion coefficient may be estimated from the Onsager–Fuoss equation [15]. For concentrations above the cmc, an appreciable fraction of the solute transport can occur as a result of diffusion of the micelles. This type of ionic association will affect the diffusion coefficient in two ways: 1) by increasing of the mobility of the electrolyte; and 2) by reducing the activity of the solute as compared with a fully dissociated electrolyte; consequently the gradient of free energy with concentration will decrease [31]. Denoting the absolute mobilities of the ions by μ_1 and μ_2 (for cation and anion, respectively), that of the micelle by μ_M, and taking α as the percentage fraction of free monomer, we obtain the following semi-empirical equation for dilute solutions of these associated symmetrical electrolytes:

$$D_{\text{exp}} = 2K_B T\left[\alpha\frac{\mu_1\mu_2}{\mu_1+\mu_2} + (1-\alpha)\mu_{12}\right]\left(1 + c\frac{d\ln\gamma_\pm}{dc}\right) \tag{5}$$

Neglecting the electrophoretic effect in the mobility terms (the expression in square brackets) and assuming that the monomer concentration is approximately equal to that at the critical micellar concentration, the percentage of dissociated (free) monomer can be calculated from

$$\alpha = \frac{cmc}{c_T} \times 100\% \tag{6}$$

where c_T is the total concentration of the solution. Substituting Eq. (6) in Eq. (5), this can be rewritten as

$$D_{\text{exp}} = \alpha D^0 F_T + [2(1-\alpha)D_M]F_T \tag{7}$$

where F_T is a thermodynamic factor, $\left(1 + c\frac{d\ln\gamma_\pm}{dc}\right)$, and $(1-\alpha)$ represents the fraction of associated monomer. The percentage of micelles in solution at different concentrations can be estimated from the equation

$$\%\ \text{micelles} = \left(\frac{1-\alpha}{N}\right) \times 100\% \tag{8}$$

Equation (8) results from the combination of the mass balance equation $c_T = c_1 + Nc_M$ with Eq. (6); c_1, c_M, and N are the free monomer concentration, micelle concentration, and aggregation number, respectively [32]. D_M (Table 5) represents the diffusion coefficient of a micelle at the critical micellar concentration and is estimated from the interception of the plot of variation of diffusion coefficient with total concentration (c_T) predicted by Eq. (9) [29, 30, 31, 32]:

$$D_{exp} = D_M + \frac{D_1(nK)^{-1/n}}{n}\frac{1}{(c_T - c_{cmc})} \tag{9}$$

Table 6 Estimation of the fraction of free monomer (α) and thermodynamic factor (F_T) for $C_{10}TAB$ and $C_{12}TAB$

C_T[a] (mol dm^{-3})	α[b] (%)	% micelles	F_T[c]
$C_{10}TAB$			
0.000	100	0.00[d]	1.00[f]
0.080	89	0.35[d]	0.59[f]
0.085	84	0.52[d]	0.54[f]
0.090	79	0.68[d]	0.48[f]
$C_{12}TAB$			
0.000	100	0.00[e]	1.00[g]
0.015	87	0.23[e]	0.90[g]
0.016	81	0.33[e]	0.86[g]
0.017	76	0.42[e]	0.82[g]

[a] Data shown in Table 1 are used for interpolation of values of diffusion coefficients for some concentrations

[b] See Eq. (6)

[c] See Eq. (7)

[d] See Eq. (8) with $N = 31$ and ref. [6]

[e] See Eq. (8) with $N = 57$ and ref. [6]

[f] See Eq. (5) and Table 5, where $D_M = 3.98 \times 10^{-10}$ m^2 s^{-1}

[g] See Eq. (7) and Table 5, where $D_M = 3.69 \times 10^{-10}$ m^2 s^{-1}

An increase in the surfactant chain length is accompanied by a decrease in the micelle diffusion coefficient. Probably, the micelles with the higher aggregation number (e.g., $C_{12}TAB$ N (N = 57 [6]), will have a lower mobility and, consequently, a lower diffusion coefficient. For both surfactants, we may obtain different values for D_M when calculated for different concentration ranges. Thus, we may conclude that the applicability of Eq. (9) depends strongly on the concentration, probably due to intermicellar interactions, as discussed elsewhere [29, 30]. Comparison of micellar diffusion coefficients with literature data is difficult, because previous data on these systems [6] refer in general to self-diffusion coefficients of micelles, whereas in the present case the mutual diffusion coefficients are analyzed. Although a relationship has very recently been developed for comparison of such diffusion data for water-in-oil microemulsion aggregates [9], we are unaware of any similar relationship between self-diffusion and mutual diffusion coefficients for normal micelles.

Using the values for D_M (Table 5), the experimental diffusion coefficients, and the α values (Table 6) obtained from Eq. (6), we can use Eq. (7) to estimate the thermodynamic factors for these surfactants. These calculations are aimed at studying the effect of non-ideality in thermodynamic behavior, as given by F_T [Eq. (7)], on D. These estimates can be reasonable in the region just above the cmc. For example, for aqueous solutions of sodium alkanoate surfactants [31], good agreement (deviations up to 17%) was observed between our theoretical values and those obtained by experimental for solutions at concentrations 25–50% above the cmc. These depend on the hydrocarbon chain length, with the lower value corresponding to sodium decanoate, and the upper one to sodium heptanoate. For higher concentrations or for surfactants with higher aggregation numbers, larger deviations are observed, which is not surprising considering the uncertainty in the estimate of the fraction of free monomer (α), the limitations of the equation involved in determination of D_M, and the change with concentration of parameters such as viscosity, dielectric constant, and hydration—factors which are not taken into account in that model. This treatment also ignores the effect of intermicellar interaction on the diffusion behavior, in as much as we accept that effects of short-range interactions can also contribute for the deviations. As a consequence we only show in Table 6 estimates of the thermodynamic factors for decyltrimethylammonium and dodecyltrimethylammonium bromides within the same concentration range ($0 \leq c \leq 1.25$ cmc).

Table 6 shows that the non-ideality in thermodynamic behavior near the cmc, which is allowed for by the factor $F_T = \left(1 + c\frac{d\ln\gamma_\pm}{dc}\right)$, can be explained by the formation of micelles (0.35% and 0.23% for $C_{10}TAB$ and $C_{12}TAB$, respectively). In fact, the formation of these species reduces the number of free ions diffusing in the solutions, and, consequently, decreases the free energy gradient driving the diffusion process and, hence, the diffusion coefficient near the cmc. The decrease in fraction of free monomer at concentrations above the cmc is in agreement with theoretical predictions from more detailed thermodynamic analysis of micellization [33].

Conclusions

We have measured conductance and mutual differential diffusion coefficients of *n*-alkyltrimethylammonium bromides (C_nTAB, n = 10, 12, 14 and 16) in aqueous solutions, having in mind a contribution to a better understanding of the structure of these electrolyte solutions, their behavior in solution, and, last but not least, supplying the scientific and technological communities with data on these important parameters in solution transport processes. In fact, from these data, when we provide the critical micellar concentration (cmc) values, limiting diffusion coefficients (D^0), and some interacting parameters (α, the percentage fraction of free monomer, and F_T, the thermodynamic factor), we can obtain more information concerning the structure of these surfactants and its influence on these properties. For example, as the length of the hydrocarbon chain increases, we can see that cmc and D^0 decrease.

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