



Study of the effect of electrolyte and temperature on the critical micelle concentration of dodecyltrimethylammonium bromide in aqueous medium



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ABSTRACT

The effect of three organic electrolytes, viz. tetrapropylammonium bromide ($C_{12}H_{28}NBr$), tetrabutylammonium bromide ($C_{16}H_{36}NBr$), and tetrapentylammonium bromide ($C_{20}H_{44}NBr$) ($0.01 \text{ mol} \cdot \text{kg}^{-1}$) on the aggregation behaviour of a cationic surfactant, dodecyltrimethylammonium bromide (DTAB) (1.5 to 29.8) $\text{mmol} \cdot \text{kg}^{-1}$ in aqueous medium over a wide temperature range (288.15 to 318.15) K has been studied by conductivity measurements. From conductivity versus surfactant concentration plots, the critical micelle concentration (CMC) of DTAB has been determined, which shows that all the investigated electrolytes promote the aggregate formation of DTAB. The CMC values decrease to a certain minimum value around $T = 298.15$ K in all cases and then increase with further rise in temperature, displaying a typical U-shaped behaviour. Further, from the temperature dependence of CMC values, various thermodynamic parameters of micellization viz. standard free energy change (ΔG_m^0), standard enthalpy change (ΔH_m^0) and standard entropy change (ΔS_m^0) have been calculated. The values of ΔG_m^0 , ΔH_m^0 and ΔS_m^0 indicate that the electrolytes have arbitrated DTAB aggregation and micellization process is both enthalpy as well as entropy controlled. The results reveal the major role of hydrophobic interactions in the present (surfactant + electrolyte + water) ternary system. Fluorescence probe study has also been employed to affirm the CMC values obtained from conductivity measurements.

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1. Introduction

The organic electrolytes like sodium salts of organic acids or quaternary ammonium salts behave differently due to their weak surface activity and hydrophobicity. Among these, quaternary ammonium salts have been widely used and studied cationic salts [1–10]. Quaternary ammonium cations, also known as quats, are positively charged polyatomic ions of symmetrical R_4NBr structure, R being an alkyl group or an aryl group. Symmetrical tetraalkylammonium ions find numerous applications in phase-transfer catalysis [11–13], as disinfectants [14,15] and synthetic reagents [16,17]. Further, due to their antimicrobial activities, these cations have been used as anti-microbial agents in numerous disinfectants, antiseptics, perfumes and cosmetic agents [14,18]

An important area is the use of tetraalkylammonium cations as model compounds for the study of (solute + solute),

(solute + solvent) and (solvent + solvent) interactions for the hydrophobes [2–4,19,20]. Moreover, some of the short alkyl chained tetraalkylammonium salts have a possibility of penetration into the micellar interior of the surfactant due to hydrophobic interactions. As a result, they make the micelles shrink and qualitatively act as spacers between the surfactant head groups [21]. In spite of this, a detailed literature survey has revealed that, though, surfactants have been studied extensively in the presence of various additives like amino acids, sugars, inorganic electrolytes etc., to improve their properties [22–29], a lesser work has been reported with organic electrolytes like sodium salts of organic acids or tetraalkylammonium bromide salts [21,30,31].

Therefore, in the present work, we have studied the effect of three structurally different tetraalkylammonium bromide salts viz. $C_{12}H_{28}NBr$, $C_{16}H_{36}NBr$ and $C_{20}H_{44}NBr$ in order to understand the micellization behaviour of a cationic surfactant, DTAB, in aqueous medium, covering a wide range of temperatures (288.15 to 318.15) K. Structures of all the above mentioned quaternary ammonium salts have been illustrated in figure 1.

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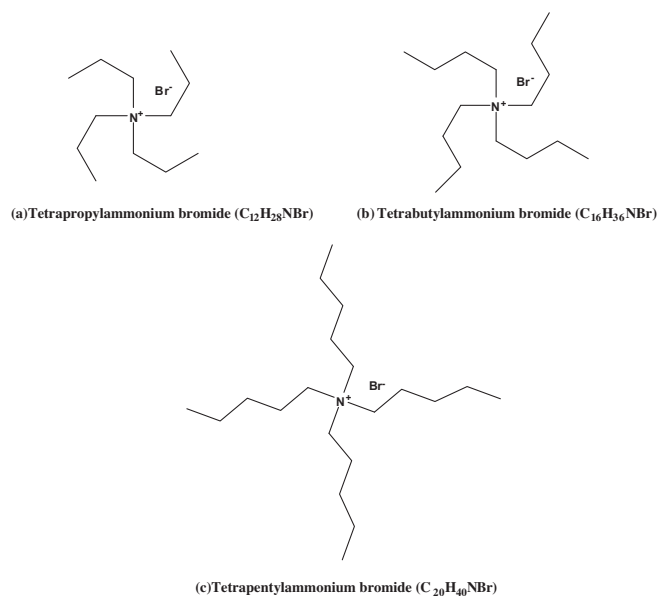


FIGURE 1. Molecular structures of quaternary ammonium salts along with the molecular formulas.

2. Experimental

2.1. Materials

The deionised distilled water with a conductivity of (2 to 3) $10^{-6} \text{ S} \cdot \text{cm}^{-1}$ and pH of 6.8 to 7.0 (at $T = 298.15 \text{ K}$) was obtained from a Millipore-Elix system and was used for all the experiments. Dodecyltrimethylammonium bromide (DTAB) of A.R. grade was obtained from S.D. Fine-Chem Ltd. (India) and was used after purification as mentioned in the literature [32]. Tetrapropylammonium bromide ($C_{12}H_{28}NBr$) from Fluka (Switzerland), tetrabutylammonium bromide ($C_{16}H_{36}NBr$) from SRL (India) and tetrapentylammonium bromide ($C_{20}H_{44}NBr$) from Acros Organics (Belgium), all were of A.R. grade and were dried in vacuum oven at $T = 333.15 \text{ K}$ for 24 h before use. Pyrene (A.R. grade) was obtained from MERCK (Germany) and was used as fluorescent probe without further purification. A summary of provenance and purity of the sample used have also been provided in table 1.

2.2. Methods

Conductivity measurements were carried out with digital Conductivity Meter Cyberscan CON-510. The principle by which instrument measure conductivity is simple *i.e.* two plates are placed in the sample, a potential is applied across the plates (normally a sine wave voltage), and the current is measured. Conductivity, the inverse of resistivity is determined from the voltage and current values according to Ohm's law. The concentration of the aqueous solution of DTAB (1.5 to 28.9) $\text{mmol} \cdot \text{kg}^{-1}$ was varied by adding small aliquots of concentrated stock solution of

surfactant to the known volume of pure water and aqueous tetraalkylammonium bromide salt solutions ($0.01 \text{ mol} \cdot \text{kg}^{-1}$) in the double walled vessel by means of a (10 to 100) μL Eppendorf micropipette. The temperature was maintained constant at $\pm 0.1 \text{ K}$ by circulating thermostated water through a double walled conductivity vessel containing the solution. The reproducibility of conductivity measurements was estimated to be $\pm 15 \mu\text{S} \cdot \text{cm}^{-1}$.

The fluorescence probe study of DTAB solutions was done with LS-55 Perkins Elmer Fluorescence Spectrophotometer. This Spectrophotometer is computer controlled and a pulsed Xenon discharge lamp is providing excitation with a pulse width at half peak height of $< 10 \mu\text{s}$ and pulse power 20 kW. The source is monochromated using a Monk-Gillieson type monochromator and can be scanned over the range of (200 to 800) nm. The fluorescence is passed through a similar monochromator, which can be scanned over the range of (200 to 900) nm. An arbitrary scale from (0 to 1000) is used by the instrument to detect the fluorescence signal. For analysis of samples a 10 mm path length quartz cuvette was filled with the appropriate solutions. The excitation wavelength was kept at 334 nm and the emission was recorded at (373 and 384) nm. The excitation and emission slits were kept at (8.0 and 2.5) nm, respectively. The experimental $2 \cdot 10^{-6} \text{ mol} \cdot \text{kg}^{-1}$ solution of pyrene used as a probe was prepared by a procedure reported in the literature [33].

3. Results and discussion

3.1. Effect of electrolyte on the CMC of DTAB

The conductivity, κ , values of DTAB in aqueous solutions with and without tetraalkylammonium salts ($0.01 \text{ mol} \cdot \text{kg}^{-1}$) at different temperatures (288.15 to 318.15) K are listed in table S1 of the supplementary material. In an effort to check the internal consistency of the conductivity measurements, we compared the conductivity data of DTAB in pure water with our previous measurements [34] as well as those reported in literature [35]. From figure 2, it can be observed that there is a reasonably good overlap (within the limit of experimental errors) of the present conductivity data with those reported in literature [34,35] initially up to $\sim 5.9 \text{ mmol} \cdot \text{kg}^{-1}$; above this concentration, however, the data were found deviating significantly when compared with those reported by Xing *et al.* [35]. Interestingly, however, the graph was found to be running parallel to each other in the post-micellar region with the CMC values extracted from these data in very close agreement with each other. There might be a couple of reasons to account for this anomalous observation that appears to be more apparent to bear directly on the lowest conductivity values in respect of the present study which can be as follows:

- (i) The purity of the solvent (water) and that of the surfactant (DTAB); the presence of the impurities, generally surface-active, reported to be present in the surfactant solutions [36] are expected to favour the micellization, which in turn is likely to reduce the formal charge due to the association of the surfactant ions resulting in the significant reduction in the conductivity.

TABLE 1
Specification and mass fraction purity of used chemicals.

Chemical name	Source	Purification method	Mass fraction purity ^a
Tetrapropylammonium bromide ($C_{12}H_{28}NBr$)	Fluka	None	0.98
Tetrabutylammonium bromide ($C_{16}H_{36}NBr$)	SRL	None	0.99
Tetrapentylammonium bromide ($C_{20}H_{44}NBr$)	Acros organics	None	0.99
Dodecyltrimethylammonium bromide (DTAB)	S.D.Fine	Recrystallization	0.98

^a Declared by the supplier.

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