

# Thermodynamics of micelle formation of the ephedrine-based chiral cationic surfactant DMEB in water, and the intercalation of DMEB in montmorillonite

Annamária B. Páhi<sup>a</sup>, Dénes Varga<sup>a</sup>,  
Zoltán Király<sup>a,\*</sup>, Ágnes Mastalir<sup>b</sup>

<sup>a</sup> Department of Colloid Chemistry, University of Szeged, Aradi Vt. 1, H-6720 Szeged, Hungary

<sup>b</sup> Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary

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## Abstract

The solubility and the micelle formation of the chiral cationic surfactant (1*R*,2*S*)-(–)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB) in aqueous solution were investigated by conductometry and titration microcalorimetry in the temperature range of 278–328 K. The Krafft temperature of DMEB is  $T_K = 280$  K and the solubility of the surfactant at this point is 4.5 mM. The cmc versus  $T$  curve passes through a shallow minimum close to room temperature. The micelle formation changes from endothermic to exothermic at this characteristic temperature. The apparent degree of dissociation of the micelles  $\alpha_{app}$  increases slightly as the temperature is raised. The isosteric enthalpies of micelle formation,  $\Delta H_{st\ mic}$ , are close to the calorimetrically measured enthalpies,  $\Delta H_{mic}$ , provided that the real degree of dissociation,  $\alpha_{st} = 1$ , is used in the calculations.  $\Delta H_{mic}$  and the temperature dependence of  $\Delta H_{mic}$  of DMEB are markedly similar to those of sodium dodecylsulfate and dodecyltrimethylammonium bromide. The micelle formation of DMEB is favored by both enthalpy and entropy at and above room temperature. The enthalpy–entropy compensation results in a slight decrease in the Gibbs free energy on increase of the temperature. Sodium montmorillonite (M) was rendered organophilic by DMEB via ion-exchange to produce the clay/organocomplex DME-M. The swelling properties of the organoclay were investigated by XRD measurements in a variety of organic solvents. The basal spacing of DME-M varied from 1.8 to 3.5 nm, depending on the nature of the solvent. DME-M is a heterogenized ephedrine derivative, which may be regarded as a potential catalyst for enantioselective organic syntheses.

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**Keywords:** Chiral surfactant; Conductometry; Microcalorimetry; Micelle; Montmorillonite

## 1. Introduction

Amphiphilic molecules possessing chemical or biochemical functionalities in their structures are called functional surfactants [1]. These compounds exhibit interesting surface-active properties, which cannot be achieved by their traditional counterparts. The synthesis and characterization of chiral surfactants have been intensively pursued because of their fundamental scientific and technological importance. The applications of chiral surfactants include the recognition of racemic compounds in

the presence of chiral aggregates in solution [2,3], chromatographic and electrophoretic chiral separations of enantiomers [4–8], surfactant-templated syntheses of ordered chiral mesoporous sol–gel materials [9,10], and asymmetric catalysis for the synthesis of enantiomerically pure compounds [11–13].

Natural ephedrine (1*R*,2*S*)-(–)- $\alpha$ -(1-methylaminoethyl)benzyl alcohol, is a model molecule of  $\beta$ -aminoalcohols with two chiral centers in the molecule. (1*R*,2*S*)-(–)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB) consists of a hydrophobic dodecyl chain covalently bound to a positively charged ephedrine group with a quaternary ammonium nitrogen. The single-tailed cationic surfactant DMEB is a homolog of dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS), the prototypes of cationic and anionic surfactants, respectively (Fig. 1). DMEB has been applied as a chiral selector in capillary electrophoresis in order to separate a

\* Corresponding author. Tel.: +36 62 544211; fax: +36 62 544042.

E-mail addresses: [panna@chem.u-szeged.hu](mailto:panna@chem.u-szeged.hu) (A.B. Páhi), [vargad@chem.u-szeged.hu](mailto:vargad@chem.u-szeged.hu) (D. Varga), [zkiraly@chem.u-szeged.hu](mailto:zkiraly@chem.u-szeged.hu) (Z. Király), [mastalir@chem.u-szeged.hu](mailto:mastalir@chem.u-szeged.hu) (Á. Mastalir).

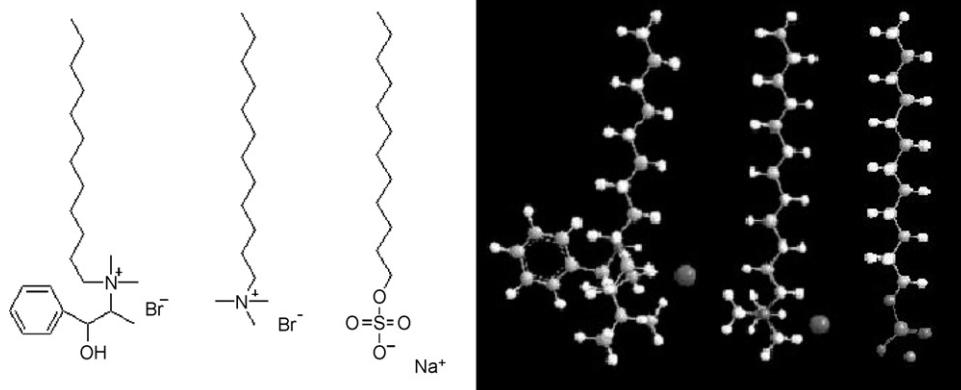


Fig. 1. The structure of (1*R*,2*S*)-(-)-*N*-dodecyl-*N*-methylephedrinium bromide (DMEB) as compared with the structures of dodecyltrimethylammonium bromide (DTAB) and sodium dodecylsulfate (SDS), prototypes of cationic and anionic surfactants, respectively.

variety of drug enantiomers [6,14,15]; as a surfactant template for the fabrication of enantioselective sol–gel thin films [16]; as a chiral phase transfer catalyst for asymmetric induction in the Michael reaction [17]; and as a micellar microenvironment for the synthesis of optically active  $\alpha$ -amino acids [18]. Further, ephedrine derivatives have proved to be efficient catalysts in the enantioselective addition of diethylzinc to arylalkylaldehydes, under both homogenous [19,20] and heterogenous [21,22] reaction conditions. These examples imply the potential use of DMEB as a chiral catalyst in organic syntheses.

The micellar behavior of DMEB in aqueous solution has recently been investigated by means of surface tension measurements, conductometry, potentiometry and UV spectroscopy [23], and by surface tensiometry, fluorescence probe, light scattering and microscopic techniques [24]. The results of these studies are from certain important aspects contradictory. For instance, Oremusová and Greksáková reported that the hydrodynamic radius of DMEB aggregates at 303 K was 3.3 nm, which is consistent with the formation of spherical micelles [23]. In contrast, Roy et al. observed the formation of polydisperse giant vesicles at this temperature, with radii ranging from 165 nm to 1.1  $\mu\text{m}$  [24].

We report here on the thermodynamics of the micelle formation of DMEB in aqueous solution, studied by conductometric titration and thermometric titration in the temperature range 278–328 K. In addition, the surfactant was immobilized in a cation-exchanger host material, montmorillonite (M), to give a clay/organocomplex dodecylmethylephedrinium montmorillonite (DME-M). The swelling properties (interlamellar expansion) of this ephedrine-based intercalation material were investigated by X-ray diffraction measurements in a variety of organic solvents.

## 2. Experimental

### 2.1. Materials

DMEB (purity: 99%) was purchased from Sigma–Aldrich and used as received. Water was percolated through ion-exchanger columns, followed by distillation, to give a specific conductance ( $\kappa$ ) of 0.5–2.1  $\mu\text{S cm}^{-1}$  in the temperature range

studied. High-purity sodium montmorillonite EMX-826 was provided by Süd-Chemie AG (Germany). The nominal cation-exchange capacity of the clay was  $CEC = 0.75$  mequiv  $\text{g}^{-1}$ .

### 2.2. Methods

#### 2.2.1. Solution conductivity

Specific conductance measurements were performed in the temperature range 278–328 K with a PC-interfaced OK-114 conductometer (Radelkis, Hungary) equipped with an OK-0907P platinum electrode with sheet plates (cell constant  $\kappa_{\text{cell}} = 1.02 \text{ cm}^{-1}$ ). The measuring vessel was fitted with a magnetic stirrer and thermostated at  $T \pm 0.05$  K. In a typical experiment, 25 mL of distilled water, or a dilute surfactant solution ( $c < \text{cmc}$ ) was titrated with 25 mL of a concentrated surfactant solution ( $c > \text{cmc}$ ) at 1-min intervals in aliquots of 0.5 mL by using a PC-controlled Titroline-96 volumetric titrator (Schott AG, Germany). The concentration of the titrant was less than 10 mM in order to eliminate incipient precipitation of the surfactant in the stock solution.

#### 2.2.2. Titration microcalorimetry

Thermometric titration experiments were performed in the temperature range 288.15–328.15 ( $\pm 2 \times 10^{-4}$ ) K with a Thermal Activity Monitor LKB-2277 isothermal heat-flow microcalorimeter (ThermoMetric, Sweden) [25]. A twin detector, supplied with a sample cell and a reference cell, was used. The sample cell was equipped with a stirring facility (60 rpm) and a Lund microtitrator. In a typical experiment, the calorimeter vessel was loaded with 2 mL of a dilute DMEB solution ( $c < \text{cmc}$ ), and 500  $\mu\text{L}$  concentrated DMEB solution ( $c > \text{cmc}$ ) was injected into the vessel at 120-min intervals in aliquots of 20  $\mu\text{L}$ . As for the conductometry, the concentration of the titrant was less than 10 mM in order to avoid the occurrence of precipitation in the titration syringe held outside the calorimeter at room temperature. The experiment was computer-controlled via DigiTam 4.1 software.

#### 2.2.3. X-ray diffraction measurements

EMX-826 montmorillonite was rendered organophilic with DMEB via ion-exchange at 313 K [26]. The hydrophilic clay

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