



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

The Effect of Temperature on Thermodynamic Parameters of Micellization of Some Surfactants

¹Gholamreza Dehghan Noudeh, ²Mohammadreza Housaindokht and ³Bibi Sedigeh Fazly Bazzaz

¹Department of Pharmaceutics, School of Pharmacy, Kerman University of Medical Sciences, Kerman, Iran

²Department of Chemistry, School of Sciences, Ferdowsi University, Mashhad, Iran

³Department of Medicinal Chemistry, School of Pharmacy,
Mashhad University of Medical Sciences, Mashhad, Iran

Abstract: The micellization of anionics surfactants (SDS, sodium dodecyl sulphate and SU, surfactin) and cationic surfactants (BC, benzalkonium chloride, TTAB, tetradecyltrimethylammonium bromide and HTAB, hexadecyltrimethylammonium bromide) were investigated at various temperatures using a du Nouy ring tensiometer. The cmc decreased to a certain minimum and then increased with the temperature, displaying a U-shaped behavior. This behavior was analyzed using a power-law equation. The thermodynamic parameters of micellization, ΔG_m , ΔH_m and ΔS_m were obtained at different temperatures.

Key words: Critical micelle concentration (cmc) Power-law exponent, micellization, thermodynamic parameters, surfactant, surfactin

INTRODUCTION

Cationic surfactants are known to exhibit excellent antistatic effects and softness. Hydrocarbons higher than C16 are normally employed in cosmetics and toiletries (Kang *et al.*, 2001). As for anionics, Sodium Dodecyl Sulfate (SDS) is the best known and is widely used in industry and it has been extensively studied in relation for its micellization, properties and phase behavior (Kekicheff *et al.*, 1989; Kekicheff, 1989). Biosurfactant production from microorganisms has been studied extensively for more than a decade (Fiechter, 1992). Biosurfactants are amphiphilic in nature and reduce the surface tension of medium in which they are produced. These surface-active compounds have found many applications in industry, agriculture, mining and oil recovery, with functional properties as wetting, foaming and emulsifiers in pharmaceutical and cosmetic products. *Bacillus subtilis* produces a lipopeptide, called surfactin, with exceptional surface activity (Peypoux *et al.*, 1999; Heerklotz and Seeling, 2001). The compound has been characterized as a cyclic lipopeptide containing a carboxylic acid (3-hydroxy-13-methyl tetradecanoic acid) and seven amino acid residues. Structural characteristics show the presence of a heptapeptide with an LLDLLDL chiral sequence linked, via a lactone bond, to α -hydroxy fatty acid (Peypoux *et al.*, 1999). It has advantages over chemical surfactants in biodegradability and effectiveness

at extreme temperature or pH (Randhir, 1997). If the economic problems could be solved, this compound would certainly find new applications in agriculture and environment by the petroleum industries (Peypoux *et al.*, 1999). Last decade, it has shown diverse new activities including emulsification, foaming (Razafindralambo *et al.*, 1998).

The capacity to aggregate in solutions is one of the characteristics of surfactants. When aggregations are formed, various physical properties of the surfactant solutions change abruptly within a narrow concentration range. Micelles are one type of aggregation and the narrow concentration range is called the Critical Micelle Concentration (cmc), above which micelles exist in the solutions. Micellization is affected by various factors including surfactant species (hydrophobic volume, chain length, head group area), temperature, pressure, ionic strength, pH, etc. For ionics and amphoteric, micellization is affected by temperature as the hydrophobic and head group interactions change relative to temperature. Accordingly, cmc versus temperature studies have already been performed to obtain information on these interactions (Miller *et al.*, 1990). For non-ionic surfactants, the cmc decreases with increasing temperature due to an increase in hydrophobicity caused by the destruction of hydrogen bonds between water molecules and hydrophilic groups. Therefore, the log cmc of non-ionic surfactants vs. the reciprocal of temperature plot is nearly linear (Kang *et al.*, 2001). However, for ionic

surfactants, cmc decreases to a minimum value and then increases, displaying a U-shaped behavior (Stead and Taylor, 1969). The minimum is characterized by the minimum cmc, C_{cmc}^* and the temperature, T^* , at C_{cmc}^* . Furthermore, it would appear that the effect of temperature on cmc can be represented by the power law $|C_{cmc} - C_{cmc}^*| = A |T - T^*|^n$ (Kang *et al.*, 2001). At present, it would seem that the exponent n is characteristic to the surfactant system. This article reports on the effect of temperature, i.e., C_{cmc}^* , T^* and n , on the cmc of anionic surfactants such as SDS (sodium dodecyl sulphate), surfactin (a lipopeptide biosurfactant) and cationic surfactants such as BC (benzalkonium chloride), TTAB (tetradecyltrimethylammonium bromide) and HTAB (hexadecyltrimethylammonium bromide), in their aqueous region at 15, 25, 30 and 35°C were reported using surface tension measurements.

MATERIALS AND METHODS

Materials: The cationic surfactants such as BC (Sigma), TTAB (Merck), HTAB (Fluka) and anionic surfactants such as SDS (Merck) and surfactin (a lipopeptide biosurfactant produced by *B. subtilis* ATCC 6633), Water was doubly distilled. The materials were the highest purity.

Methods: A DuNouy tensiometer (modle-703, Sigma) was used to determine the surface tension. Different aqueous concentrations of surfactants were prepared. Surface tension was measured with a platinum ring. The surface tension-concentration plots were used to determine Critical Micelle Concentration (cmc). The surfactant solution was mixed thoroughly using a magnetically driven stirrer. The temperature was maintained within $\pm 0.1^\circ\text{C}$.

RESULTS

Critical micelle concentrations (cmc) and minimum cmc The surface tension of surfactants solution with different concentrations in water at 15, 25, 30 and 35°C were determined. For calculating cmc, tangents are drawn on the two portions of the plots. The cmc_s of the cationic (BC, TTAB, HTAB) and anionic (SDS, Surfactin) surfactants determined at various temperature. The cmc decreased to a certain minimum point and then increased when temperature increased (Fig. 1). By fitting a polynomial function of temperature to cmc data and finding the minimum of this function, it is usually possible to determine the minimum cmc (C_{cmc}^*). The curves in

Table 1: T^* values for all the surfactants at different temperatures

Surface active agent	$T^*(^\circ\text{C})$
SDS	21.48
SU	21.75
BC	24.81
TTAB	24.00
HTAB	24.56

Table 2: n values for all the systems

Surface active agent	n
SDS	1.70
SU	1.98
BC	1.10
TTAB	1.04
HTAB	1.36

Fig. 1 are polynomial functions fitted to the surfactants and the minimum cmc values determined from these polynomials. The temperature, T^* , at which C_{cmc}^* occurred was determined.

Temperature dependence of cmc and power-law exponent:

The temperature dependence of the cmc can be described by a power law between the reduced cmc and temperature, C_r and T_r , where the reduced variables are defined as $C_{red} = C_{cmc}/C_{cmc}^*$ and $T_r = T/T^*$. T_r and C_r can be related to each other through the following equation (Kang *et al.*, 2001):

$$|(C_{cmc} - C_{cmc}^*)/C_{cmc}^*| = A|T - T^*/T^*|^n \text{ or } |C_r - 1| = A|T_r - 1|^n$$

Where A is the constant and n is the exponent, which appear to be characteristic to the surfactant system. The curves in Fig. 2 are 6th-order polynomial functions fitted to those of surfactants cmc_s (correlation coefficients, $R^2 = 1$). The T^* for these of surfactants were determined from Fig. 1 (Table 1). It was for anionic surfactants (SDS, Surfactin) around 21°C and for cationic surfactants (BC, TTAB, HTAB) around 24°C. Table 2 shows the n values of the fittings Eq. this equation: $\ln|C_r - 1| = n \ln|T_r - 1| + \ln A$ to the cmc data. These quantities are like to the other reports in the literature (Kang *et al.*, 2001).

Thermodynamics of micelle formation: Various thermodynamic quantities like the free energy ΔG_m , the enthalpy ΔH_m , the entropy ΔS_m and the heat capacity $\Delta C_{p,m}$ micellization were obtained by using the following relationships and temperature dependence of cmc fitted equations:

$$\Delta G_m = RT \ln C_{cmc} \Delta H_m = -RT^2 \ln C_{cmc} / dT \Delta S_m = (\Delta H_m - \Delta G_m) / T$$

The relationship between thermodynamic parameters and temperatures were observed for all systems and this is shown in Fig. 2.

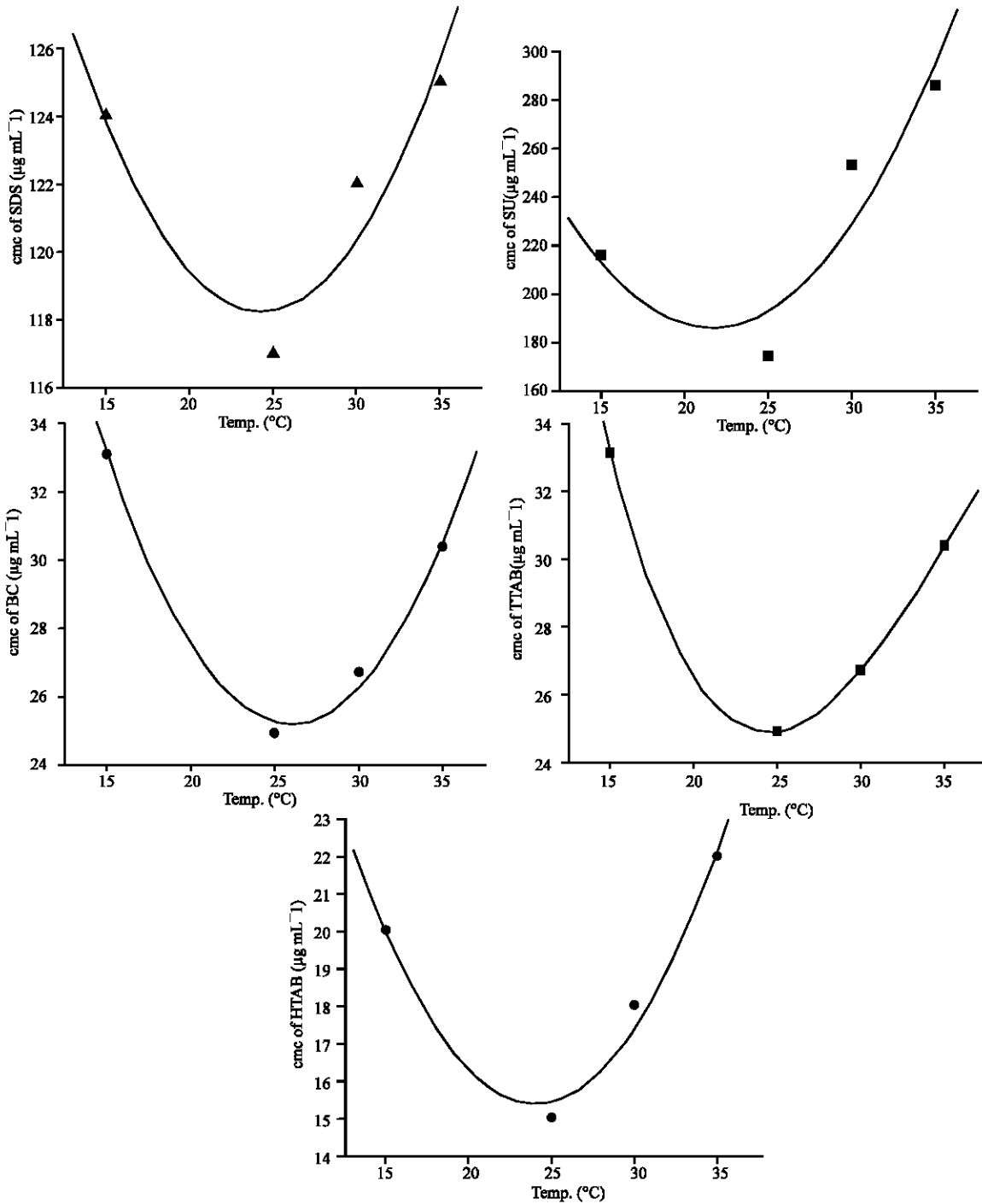


Fig. 1: cmc as a function of temperature for aqueous surfactants

Relationship between enthalpy and entropy of micellization:

A linear correlation between enthalpy and entropy of micellization was observed for all systems (correlation coefficient 0.999) and this is shown in Fig. 3.

DISCUSSION

The cmc of cationic (BC, TTAB, HTAB) and anionic (SDS, surfactin) surfactants were found to be dependent on temperature and followed the expected U-shaped cmc-

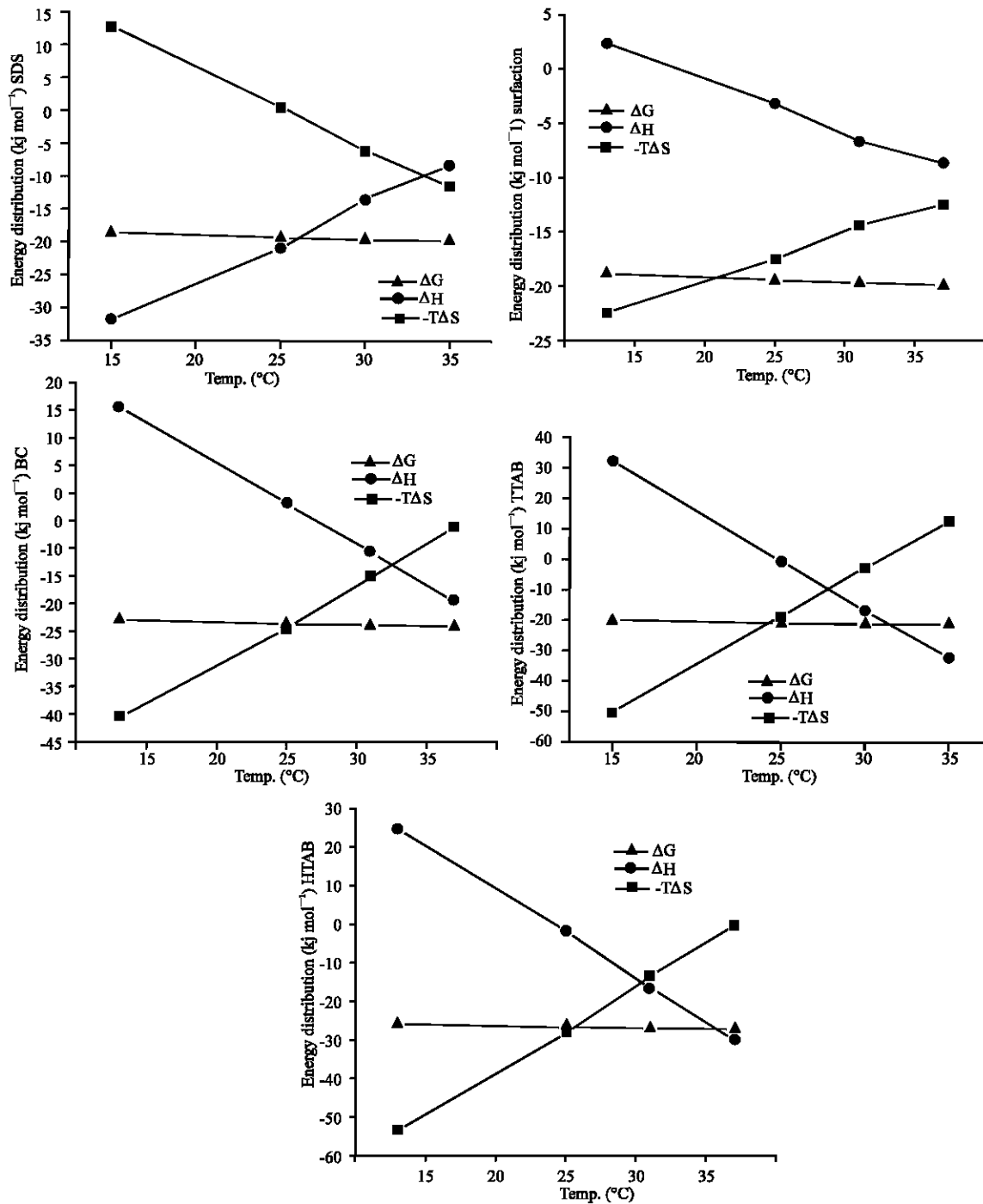


Fig. 2: Thermodynamic parameters of surfactants micellization at various temperatures

temperature curve. The temperature dependence of the cmc for these surfactants could be represented by a power law: $|C_r - 1| = A|T_r - 1|$ for these surfactants where $C_r = C_{cm}/C_{cm}^*$ and $T_r = T/T^*$ that were in good agreement with the literature. The free energy, ΔG_m , values are like with the reports in literature (Archer *et al.*, 1984; Evans and

Ninham, 1986). ΔH_m values were endothermic and decreased with temperature at $T < T^*$ and were exothermic and became larger in magnitude as the temperature increased at $T > T^*$. For these surfactants has been found that micellization is entropy-controlled at low temperatures and enthalpy-controlled at high

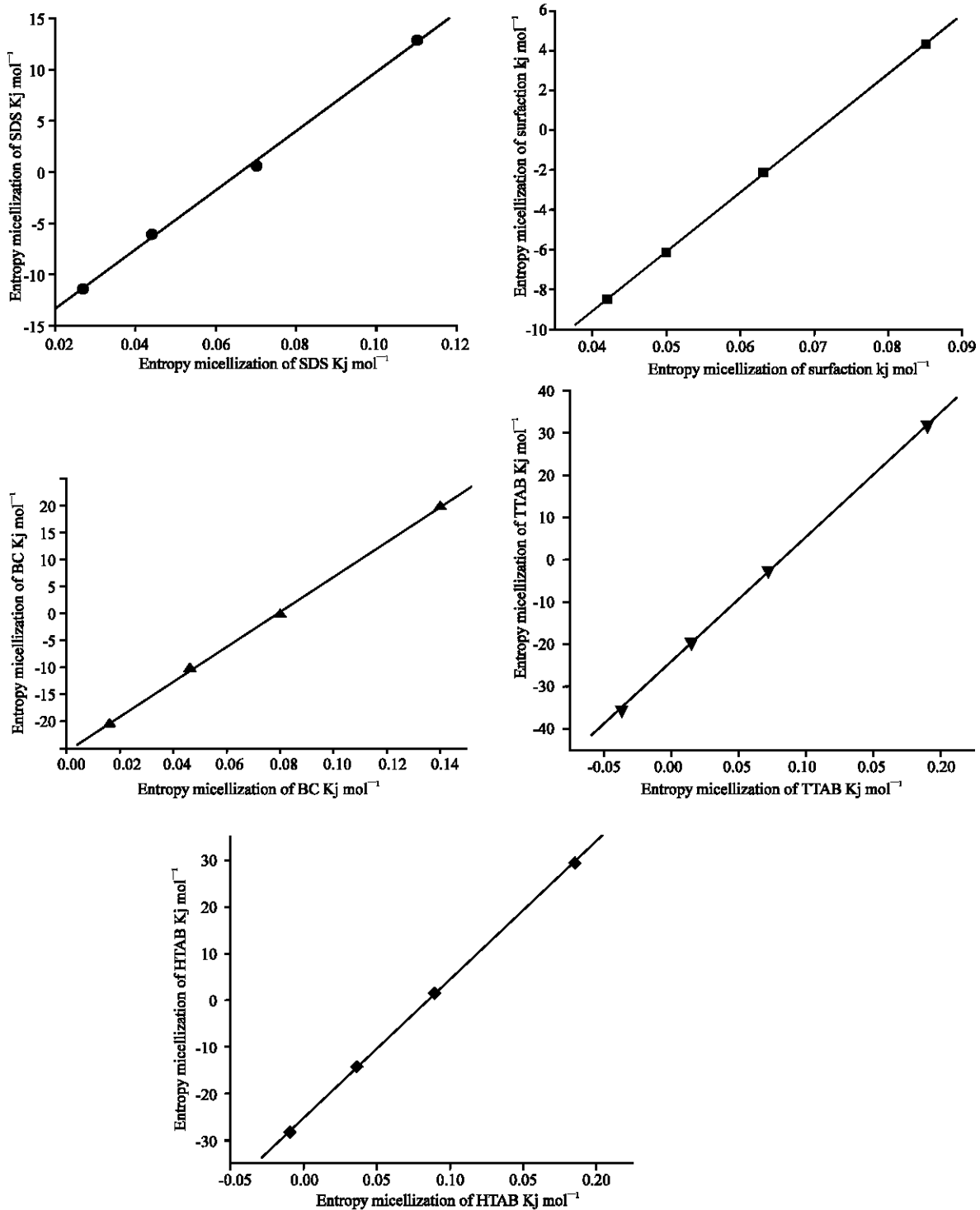


Fig. 3: Enthalpy-entropy compensation plot for all the systems

temperatures. ΔG_m is the sum of the enthalpic (ΔH_m) and entropic ($-T\Delta S_m$) contributions. As the temperature increased, the enthalpic contribution to the free energy increased, whereas the entropic contribution decreased

(Fig. 2). Thus micellization was entropy-controlled at $T < T^*$ and enthalpy-controlled at $T > T^*$. An equal contribution took place at 306.52 K for SDS, at 309 K for Surfactin, at 304.20 K for BC, at 300.82 K for TTAB and at

302.30 K for HTAB. These results would seem to indicate that the exponent is a characteristic of a particular surfactant system. The micellization of these surfactants was entropy-dominant at low temperatures and enthalpy-dominant at high temperatures, which has also been observed in other surfactants. The temperature at which entropy and enthalpy contributed equally to the free energy of micellization was higher for anionic surfactants than for cationic surfactants. Relationship between enthalpy and entropy of micellization were linear correlation, the slope of the curves (Fig. 3) are 288, 297, 297, 290, 296 and 295 K, for SDS, Surfactin, BC, TTAB and HTAB, respectively, which are not far away from suggested value for water systems (Sulthana *et al.*, 1996).

ACKNOWLEDGMENTS

This study was supported by operating grants from the Vice President for Research of Mashhad University of Medical Sciences (MUMS).

REFERENCES

- Archer, D.G., H.J. Albert, D.E. White and R.H. Wood, 1984. Enthalpies of dilution and heat capacities of aqueous solutions of sodium n-dodecyl sulfonate and sodium 4-(1-methylundecyl) benzene sulfate from 347 to 451 °K. *J. Colloid Interf. Sci.*, 100: 68-81.
- Evans, D.F. and B.W. Ninham, 1986. Molecular forces in the self-organization of amphiphiles. *J. Phys. Chem.*, 90: 226-234.
- Fiechter, A., 1992. Biosurfactant: Moving towards industrial application. *Tibtech*, 10: 208-217.
- Heerklotz, H. and J. Seelig, 2001. Detergent-like action of the antibiotic peptide surfactin on lipid membranes. *Biophys. J.*, 81: 1547-1554.
- Kang, K.H., H.U. Kim and K.H. Lim, 2001. Effect of temperature on critical micelle concentration and thermodynamic potentials of micellization of anionic ammonium dodecyl sulfate and cationic octadecyl trimethyl ammonium chloride. *J. Colloids Surf. A: Physicochem. Eng. Aspects*, 189: 113-121.
- Kekicheff, P., 1989. Phase diagram of sodium dodecyl sulfate-water system: 2. Complementary isoplethal and isothermal phase studies. *J. Colloid Interf. Sci.*, pp: 131-152.
- Kekicheff, P., C. Grabielle-Madelmont and M. Ollivon, 1989. Phase diagram of sodium dodecyl sulfate-water system: 1. A calorimetric study. *J. Colloid Interf. Sci.*, 131: 112-121.
- Miller, D.D., L.J. Magid and D.F. Evans, 1990. Fluorescence quenching in double-chained surfactants. 2. Experimental results. *J. Phys. Chem.*, 94: 5921-5930.
- Peypoux, F., J.M. Bonmatin and J. Wallach, 1999. Recent trends in the biochemistry of surfactin. *Applied Microbiol. Biotechnol.*, 51: 553-563.
- Randhir, S.M., 1997. Utilization of molasses for biosurfactant production by two *Bacillus* strains at thermophilic conditions. *JAOCS.*, 74: 887-889.
- Razafindralambo, H. and Y. Popineau *et al.*, 1998. Foaming properties of lipopeptides produced by *Bacillus subtilis*: Effect of lipid and peptide structural attributes. *J. Agric. Food Chem.*, 46: 911-916.
- Stead, J.A. and H.J. Taylor, 1969. Some solution properties of certain surface-active N-alkylpyridinium halides: I. Effect of temperature on the critical micelle concentrations. *J. Colloid Interf. Sci.*, 30: 482-488.
- Sulthana, S.B., S.G.T. Bhat and A.K. Rakshit, 1996. Thermodynamics of micellization of a non-ionic surfactant Myrj 45: Effect of additives. *J. Colloids Surf. A: Physicochem. Eng. Aspects*, 111: 57-65.