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A conductance study to analyze the effect of organic solvents on micellization behavior of carbohydrate-surfactant system at variable temperatures

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ABSTRACT

In this paper, micelle formation of a well known anionic surfactant, sodium dodecyl sulfate (SDS) in aqueous solutions of four structurally different sugars viz. ribose, glucose, sucrose and raffinose at wide temperature range T = (293.15–318.15) K has been studied. From specific conductance data, the value of CMC and X_{CMC} have been calculated whose dependence on sugar concentration correlates well with the hydrophobic nature of sugar molecule. A non-linear trend in CMC values is attributed to the presence of both hydrophilic and hydrophobic dehydrations. From X_{CMC} values, thermodynamic parameters such as standard enthalpy ($\Delta H_m{}^\circ$), standard entropy ($\Delta S_m{}^\circ$), and standard free energy of micellization ($\Delta G_m{}^\circ$) have also been evaluated. The results of these thermodynamic parameters have been discussed in terms of the structural consequences of the intermolecular interactions. Enthalpy–entropy compensation gave linear dependence, thus suggesting that micellization of SDS is governed by the delicate balance of sugar–water interactions by changing the structural property of water in the presence of sugars. The effect of organic solvents such as dimethyl sulfoxide (DMSO), methanol (MeOH) and dioxane has also been discussed in detail.

1. Introduction

Carbohydrates have significant role to play in living systems due to their nutritional value as well as industrial utility. Being non-toxic in nature and benign to mammalian tissues, these are extensively used in cosmetic and pharmaceutical applications. Beside this, sugar based surfactant formulations have gained much importance in recent times because of their easy availability and renewable nature [1] owing to which most industrial developments in this field have been concentrated on carbohydrate feedstocks. Also, versatile nature of sugars e.g., difference in the number of carbon atoms, number of hydroxyl groups, their point of attachment, presence of aldehydic or ketonic group, open or ringed structure is responsible for different types of interactions existing between sugar-surfactant systems.

Surfactants, in the presence of carbohydrates have the ability to change the conformation of carbohydrates in aqueous solutions which can lead to changes in the appearance, stability or rheology of the solution [2–9]. The manifestation of such alterations in solution behavior is made possible on account of different interactions which are usually non-covalent such as electrovalent and hydrophobic or hydrogen bonding. [10]. However, the main driving force is the hydrophobic interactions involving surfactant chains [11]. Many researchers have made attempts to explore the behavior of these carbohydrates in aqueous and in presence of organic solvents by making use of volumetric, ultrasonic and viscometric properties [12–17]. However, relatively fewer works have been reported on the thermodynamic properties of saccharide–surfactant–water systems [18–20].

Therefore, in the present study, we attempt to analyze the effect of these four structurally different sugars (ribose, glucose, sucrose and raffinose) on the micellization behavior of sodium dodecyl sulfate (SDS), an anionic surfactant in terms of thermodynamic parameters in aqueous and in presence of organic solvents (DMSO, MeOH and dioxane). The chemical structures of sugars and surfactant (SDS) that have been attempted in this work have been shown in Fig. S1 (supplementary data).

2. Experimental

2.1. Materials and methods

Ordinary tap water of conductivity in the range $3–5 \times 10^{-6}$ S cm^{-1} at 298.15 K, after distillation from Millipore

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(Elix) distillation unit was further purified in the presence of alkaline $KMnO_4$. The water so obtained has the conductivity $1–2 \times 10^{-6}$ S cm^{-1} and pH in the range 6.7–6.9, both at 298.15 K. Pure water of such specification were used for all experimental purposes. Sodium dodecyl sulfate (SDS) was of biochemical grade was further purified as suggested in literature [21]. Ribose, raffinose, sucrose and glucose were used without any further purification. A high precision water thermostat (supplied by NSW – New Delhi) maintained temperature well within ±0.1 K over the entire range studied. Specific conductance has been measured with a digital conductivity meter CM-180, Elico Ltd. The instrument was calibrated at 298.15 K by measuring the limiting molar conductance, Λ_o (S cm^2 mol^{-1}) of Ph_4PBr, $NaBPh_4$, and Bu_4NBr in DMSO using the dip type conductivity cell. The temperature was maintained constant to ±0.1 °C by circulating water from thermostat through a double walled vessel containing solution. The circulation was done with the help of a high power digital water circulator supplied by Riviera Pvt. Ltd. (Mumbai). The sample was allowed to attain the temperature of the thermostat before taking the measurements. The cell constant was determined as 1.011 ± 0.001, and the Λ_o values of these electrolytes were found to be equal to 25.0, 38.3 and 36.4 respectively, which were in good agreement with those reported in literature [22,23]. The conductivity values of SDS were measured over a wide range of solvent concentrations (0.05, 0.10, 0.20) mol kg^{-1} in aqueous solutions of ribose, glucose, sucrose and raffinose at different temperatures from T = (293.15–318.15) K. The concentration of the solution was varied by adding aliquots of concentrated stock solution of SDS to the known volume of solution in the double walled conductivity cell by means of a 10–100 μL eppendorf micropipette. The accuracy of the conductance measurement was well within ±0.3%. The specification and mass fraction purity of the chemical used has been presented in Table 1.

3. Results and discussion

3.1. Micellization of SDS in sugar solutions

The conductivity data of SDS in (0.05, 0.10, 0.20) mol kg^{-1} aqueous solutions of ribose, glucose, sucrose and raffinose at T = (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K have been summarized in Table S1. The dependence of κ as a function of surfactant concentration has been shown in the representative plot (Fig. 1). The data have been further used to determine critical micelle concentration (CMC) from the plot of κ versus [SDS] by the usual conductivity procedure [24,25]. However, these CMC values in molar concentration unit were converted into mole fraction unit, X_{CMC} (Table 2). The effect of temperature on X_{CMC} value of SDS in the presence of sugars has been shown in Fig. 2 which reveals that the shape of the curves is markedly non-linear and each curve passes through a broad maximum at around T = (303.15–313.15) K. Similar non-linear temperature dependence of X_{CMC} values of ionic surfactants has been reported in literature [26,27]. However, it can be seen that X_{CMC} values show a regular decrease with increase in sugar concentration as well as with the size of the hydrophobic group of sugar molecule. This observation is similar to the effect of carbohydrates on the solution properties of surfactants observed by Moulik et al. [18], where it has been reported that CMC's of ionic and

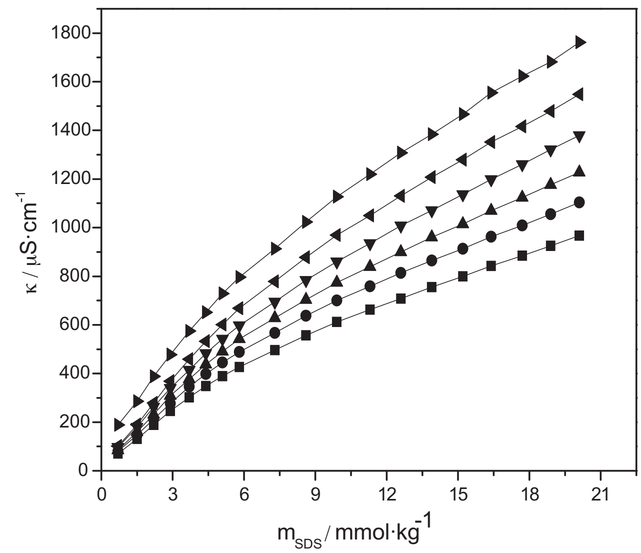

Fig. 1. Representative plot of κ versus molalities of SDS in 0.20 mol kg^{-1} aqueous solution of ribose at different temperatures: (*filled square*), T = 293.15 K; (*filled circle*), T = 298.15 K; (*filled up triangle*), T = 303.15 K; (*filled down triangle*), T = 308.15 K; (*filled left triangle*), T = 313.15 K; (*filled right triangle*), T = 318.15 K.

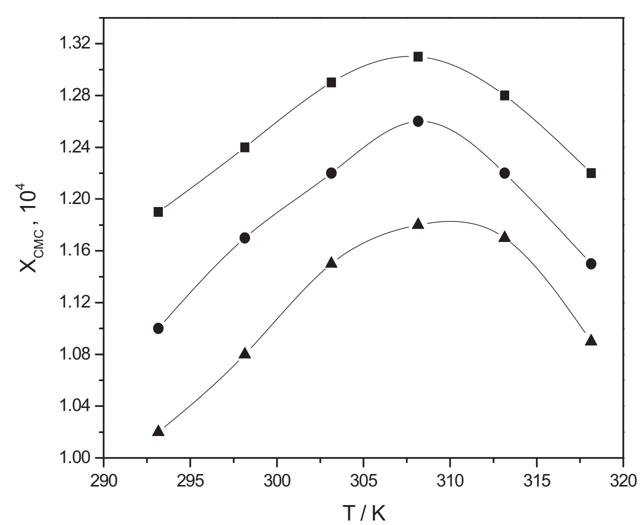

Fig. 2. Representative plot of X_{CMC} of SDS versus temperature at different molalities of ribose: (*filled square*), m_{Rib} = 0.05 mol kg^{-1}; (*filled circle*), m_{Rib} = 0.10 mol kg^{-1}; (*filled up triangle*), m_{Rib} = 0.20 mol kg^{-1}.

Table 1
Specification and mass fraction purity of chemical samples.

Chemical name	Source	Initial mole fraction purity	Purification method	Final mass fraction purity
Ribose	LobaChemie	0.97	None	0.97[a]
Raffinose	LobaChemie	0.97	None	0.97[a]
Sucrose	SD Fine	0.98	None	0.98[a]
Glucose	SD Fine	0.98	None	0.98[a]
Sodium dodecyl sulfate (SDS)	BDH	0.95	Recrystalized	0.98
DMSO	SD Fine	0.99	None	0.99[a]
Methanol	Ranbaxy	0.98	None	0.98[a]
Dioxane	SD Fine	0.99	None	0.99[a]

[a] Declared by supplier.