Thermodynamics Properties of Micellization of Organosilicone Modified Gluconamide-Type Surfactant

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Thermodynamic properties of micellization of N-3-propylmethyltrisiloxane-N-glucosylamine in water over a temperature range of 298 to 313 K been studied with surface tension method. On the basis of these results, the thermodynamic parameters *i.e.*, Gibbs energy (ΔG°_m), enthalpy (ΔS°_m) and entropy (ΔH°_m) of micellization have been evaluated.

Key Words: Thermodynamics Properties, Micellization, Organosilicone, Gluconamide, Surfactant.

INTRODUCTION

With an increasing environmental concern, sugar-based surfactant with hydrophilic sugar groups has attracted the attention of researchers worldwide, because sugar-based surfactants have good excellent biodegradability, good dermatological compatibility and the absence of toxic effects[1].

Generally silicone surfactant with hydrophobic siloxane group can produce lower surface tension than hydrocarbon surfactant. Because the flexible siloxane backbone can adopt orientations while it lies flat on the surface of the water, favouring exposing the low surface energy methyl groups substations to the air[2,3].

These unique properties prompted a lot of researchers to integrate sugar and siloxane's advantage. In spite of a few papers and patents have reported siloxane modified sugar based surfactants[4-10], relatively little is known about the thermodynamics properties of micellization of this interesting class of compounds. In this work, we reported the thermodynamics properties of micellization of N-3-propylmethyltrisiloxane-N-glucosylamine [abbreviated as Si(3)N-GA] in water over a temperature range of 298 to 313 K

EXPERIMENTAL

3-Aminopropylmethyldiethoxysilane, hexamethyldisiloxane were purchased from Beijing Chemical Reagents Company and were used without further purification. Double distilled water was used for the analysis and for the measurements of primary properties.

Infrared spectroscopy was performed with a Fourier Transform Infrared Spectrometer (Hitachi 270-30). The surfactants were smeared directly onto a KBr plate. Proton nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectroscopy was recorded in CDCl$_3$ with aVarian INOVA-400 MHz spectrometer. Since TMS cannot easily be used as internal standard because of the overlapping with other methyl signals, we used the residual protons of the solvent at 7.26 ppm as the reference.

Measurement of surface tension: Equilibrium surface tension values of the surfactants in aqueous solution were obtained by the Wilhelmy plate method using a model K12 Krüss tensiometer (Hamburg, Germany). Prior to measurement, the surface tension of the distilled, deionized water was measured. These values were in the range of 72.3 ± 0.3 mN/m. Surfactant solutions were then prepared with this water and the samples were left for 15 min prior to surface tension measurement.

Synthesis of 3-aminopropyltrisiloxane: The mixture of 3-aminopropylmethyldiethoxysilane (28.79 g, 0.15 mol), hexamethyldisiloxane (121.89 g, 0.75 mol) and tetramethyl ammonium hydroxide (0.735 g, 0.008 mol) was heated for 2 h at 90 °C under nitrogen atmosphere, with stirring. The resulting quaternary ammonium hydroxide was then deactivated by heating for 0.5 h at 130 °C and the excess hexamethyldisiloxane was simultaneously distilled from the mixture. The liquid product was purified by fractional distillation. Colourless liquid, 22.2 g (yield: 52.9 %), boiling point (b.p.) 85 °C/1.5 mmHg. IR (KBr, ν_{max}, cm^{-1}): 3300 (O-H), 1260 (Si-Me$_3$), 1100 (Si-O-Si), 840 (Si-Me$_3$), 760 (Si-Me$_3$). ^{1}H NMR(CDCl$_3$, ppm) δ: 0.004 (s, 3H, SiCH$_3$), 0.08 (s, 18H, Si(CH$_3$)$_3$ × 2), 0.44 (t,

2H, J = 8.4Hz, SiCH$_2$), 1.40-1.44 (m, 2H, CH$_2$CH$_2$NH$_2$), 1.5 (s, 2H, NH$_2$), 2.64 (t, 2H, J=7.2Hz, CH$_2$N). Elemental analysis (%) calcd for C$_{10}$H$_{29}$NO$_2$Si$_3$: C, 49.26; H, 10.45; N, 5.01. Found: C, 49.40; H, 10.28; N, 5.09.

Synthesis of N-3-propylmethyltrisiloxane-N-glucosylamine: 3-aminopropyltrisiloxane (1.8 g, 0.0064 mol), was dissolved in 50 mL of dry methanol. D-(+)-gluconic acid δ-lactone (1.147 g, 0.0064 mol) was added and the mixture was heated to reflux temperature for 6 h. After cooling to room temperature and evaporation of the solvent the solid residue was gently crushed, washed several times with hexane at 30 °C and dried under reduced pressure to a constant mass. The yield was white powder, 2.369 g.

IR (KBr, cm^{-1}): 3300 ν(O-H), 1646 [ν(C=O) in amide], 1547 [δ(N-H) in amide], 1467cm^{-1} [ν(C-H) in -CH$_2$-], 1260 ν(Si-Me$_3$), 1146-1035 cm^{-1} [ν(C-O), δ(O-H) and ν(Si-O-Si)], 840 ν(Si-Me$_3$), 760 ν(Si-Me$_3$). ^{1}H NMR (CDCl$_3$, ppm) δ:0.03 (s, 3H, SiCH$_3$), 0.10 (s, 18H, Si(CH$_3$)$_3$·2), 0.45 (t, 2H, J = 8.4 Hz, SiCH$_2$), 1.54 (s, 2H, SiCH$_2$CH$_2$CH$_2$), 3.26 and 3.13 (d, 2H, CH$_2$N), 4.30 (s, 1H, H2), 4.13 (s, 1H, H3), 3.74 (m, 4H, H4 + H5 + H6 + H6'). Elemental analysis (%) calcd for C$_{16}$H$_{39}$NO$_8$Si$_3$: C, 41.98; H, 8.59; N, 3.06. Found: C, 42.10; H, 8.40; N, 3.19.

RESULTS AND DISCUSSION

The glucosamide-based trisiloxane surfactant was prepared by the two step process described in **Scheme-I**.

Amine intermediate was synthesized by the base-catalyzed reaction of a silane monomer 3-aminopropylmethyl diethoxysilane and hexamethyldisiloxane. The complete substitution OCH$_3$ by Me$_3$SiO was checked by ^{1}H NMR spectroscopy, following the disappearance of OCH$_3$ absorption peak at 3.48 ppm as well as the appearance of Si-Me$_3$ characteristic absorption at 0.10 ppm. Similarly in IR spectrum, the appearance of Si-CH$_3$ deformation absorption at 1260 cm^{-1} and Si-Me$_3$ characteristic absorption at 840 and 760 cm^{-1} (Fig. 1), respectively also support the formation of the 3-amino-propylmethyltrisiloxane.

D-(+)-Gluconic acid δ-lactone was ring-opened by nucleophilic attack of the primary amine. The amidation of the
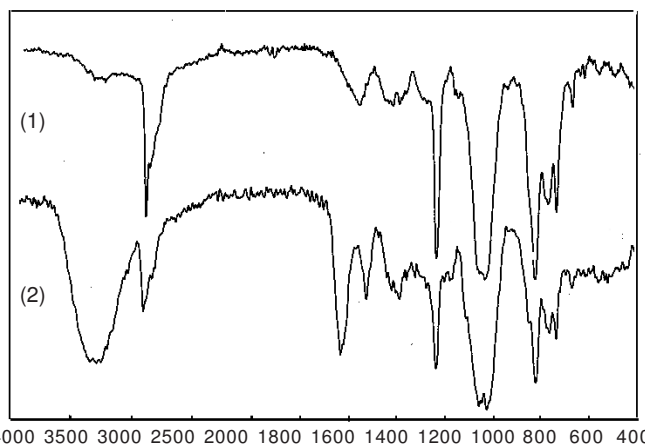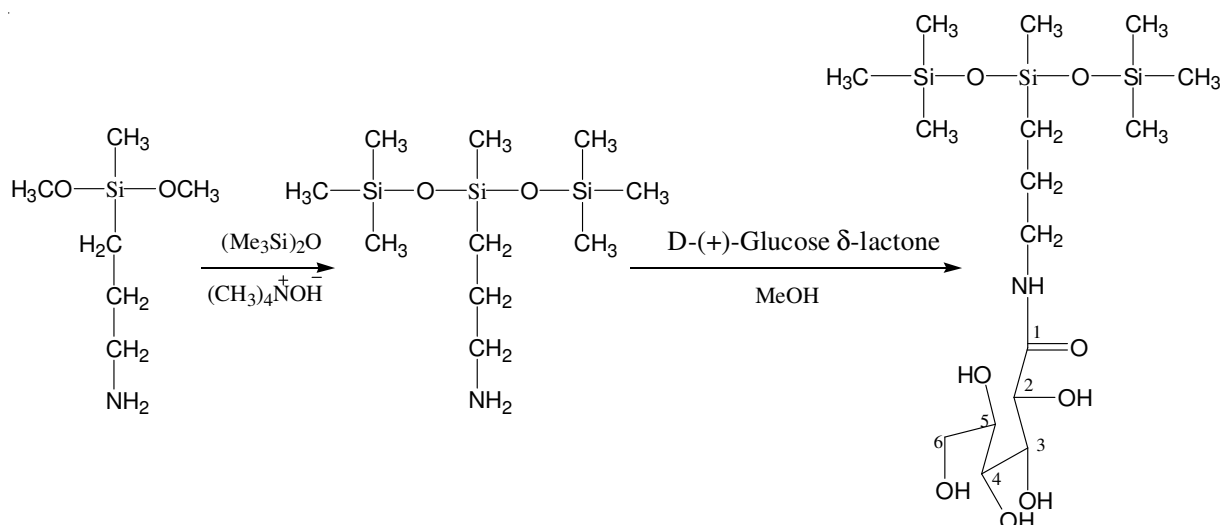

Fig. 1. FT-IR spectra of (1) 3-aminopropyltrisiloxane, (2) N-3-propylmethyltrisiloxane-N-glucosylamine

primary amine proceeded in the presence of the methanol at reflux temperature. The structure of amide was confirmed by proton nuclear magnetic spectroscopy. The protons of the carbon adjacent to the free amine (CH$_2$-NH$_2$) are seen at 2.64 ppm, while the same protons after amide formation through coupling with the lactone (CH$_2$-NHCO) shift to 3.26 and 3.13 ppm. This shift is observed in the spectrum (Fig. 2), verifying the absence of free amino groups and indicating pure glucosylamine surfactants up to the detection limit of the analysis. In amide the hydrogen of C1 and C2 are adjacent to the carbonyl function and shows a low-field shift, 4.30 ppm and 4.13 ppm respectively. The signals of the hydrogen atoms in C3-C6 were assigned according to the literature. All other hydrogen atoms have observed in their normal positions. In IR spectrum strong absorption at 1646 and 1547 cm^{-1} indicate the formation of amide bonds.

Thermodynamic properties of micellization Si(3)N-GA: The equilibrium surface tensions of dilute aqueous solutions of N-3-propylmethyltrisiloxane-N-glucosylamine were measured (Fig. 3). The surface tension of Si(3)N-GA aqueous solution decreased with increasing the surfactant concentration until the CMC above the CMC, the surface tension became steady. As shown in Fig. 3, Si(3)N-GA is highly

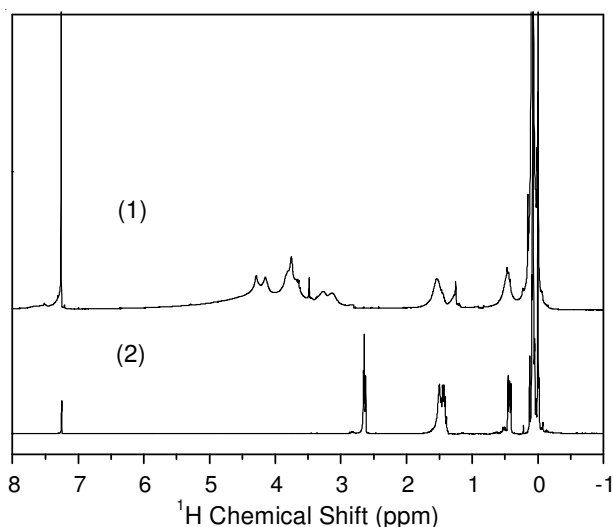**Scheme-I:** Synthesis of N-3-propylmethyltrisiloxane-N-glucosylamine

Fig. 2.   400 MHz ^{1}H NMR spectra in CDCl$_3$, (1) N-3-propylmethyl trisiloxane-N-glucosylamine, (2) 3-aminopropyltrisiloxane
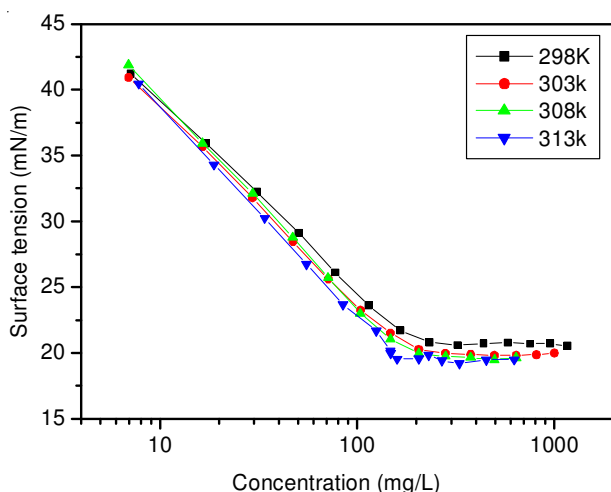

Fig. 3.   Plots of equilibrium surface tensions of aqueous solutions of the new trisiloxanes *versus* logarithm of molar concentration at different temperature

effective aqueous surfactant reducing the surface tension of water to approximate 21-22 mN/m. These values of γ_{CMC} are significantly lower than those reported for hydrocarbon surfactants[11] and are comparable to those reported for other low molecular weight silicone surfactants[12].

By applying the approximate form of the Gibbs adsorption isotherm equations (eqn. 1 and 2) to the steeply descending, linear portion of the surface tension *versus* log concentration plots (Fig. 2), the saturation adsorption values, Γ_{max}, at the air/water interface and the minimum area per surfactant molecule, A^m_s, at the air/water interface were obtained for each of the novel trisiloxane surfactants. The adsorption data and A^m_s are summarized in Table-1.

$$\Gamma_{max} = -\frac{1}{2.303RT}\left(\frac{\partial\gamma}{\partial\log c}\right)_T \quad (1)$$

$$A^s_m = \frac{10^{16}}{N_A\Gamma_{max}} \quad (2)$$

$$\Delta G^0_{mic} = RT\ln\left(\frac{CMC}{55.5}\right) \quad (3)$$

$$\Delta G^0_{ads} = RT\ln\left(\frac{C_\pi}{55.5}\right) - 6.022\pi A^s_m \quad (4)$$

where R = 8.3144 J/mol K, N$_A$ is Avogadro's number and A^m_s in Å^2 per molecule. $\pi(= \gamma_0 - \gamma)$ the surface pressure in the region of surface saturation and Cp the molar concentration of surfactant in the aqueous phase at a surface pressure π (in mN/m).

The enthalpies of micellization were calculated using eqn. 5:

$$\Delta H^0_m = RT^2\ln\left(\frac{\partial\ln CMC}{\partial T}\right) \quad (5)$$

Therefore, if the dependence of the CMC values on temperature is known, a plot of ln CMC *vs.* temperature can be constructed. The slope can then be found at each temperature.

These plots were found to be best fit with a second-order polynomial ($r^2 = 0.95$). The plot is presented in Fig. 4. The entropies of micellization were then calculated from eqn. 6

$$\Delta S^0_m = \frac{\Delta H^0_m - \Delta G^0_m}{T} \quad (6)$$

Thermodynamics of micellization were calculated for Si(3)N-GA in aqueous solution. The parameter values obtained are given in Table-2.
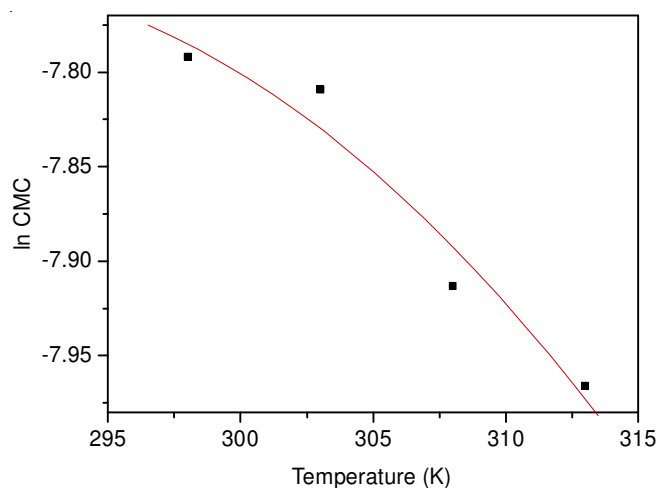

Fig. 4. Variation of ln CMC with temperature

TABLE-1
AQUEOUS SURFACE ACTIVITY OF THE NEW TRISILOXANES AT DIFFERENT TEMPERATURE

Temperature	γ_{cac}(mN/m)	CAC (mol/L)	A^m_s (Å^2/molecule)	ΔG^0_{mic} (KJ/mol)	Γ_{max} (mol/m^2)
298	20.54	4.13×10^{-4}	65.1	-29.25	2.55×10^{-10}
303	19.70	4.06×10^{-4}	64.3	-29.78	2.59×10^{-10}
308	19.61	3.66×10^{-4}	61.5	-30.04	2.70×10^{-10}
313	19.54	3.47×10^{-4}	60.6	-30.18	2.74×10^{-10}

TABLE-2 THERMODYNAMIC PARAMETERS OF Si(3)N-GA				
Temperature(K)	ΔH_m^o (KJ/mol)	ΔS_m^o (J·K^{-1}/mol)	$-\Delta G_m^o$ (KJ/mol)	$T \cdot \Delta S_m^o$ (KJ/mol)
298	2.510	106.0	29.247	31.588
303	9.236	128.0	29.781	38.784
308	12.38	137.7	30.042	42.412
313	8.634	124.0	30.177	38.812

The data available indicate that the negative values of ΔG_m^o are mainly due to the large positive values of ΔS_m^o. ΔH_m^o is positive and is much smaller than the value of $T\Delta S_m^o$. Therefore, the micellization process is governed primarily by the entropy gain associated with it and the driving force for the process is the tendency of the hydrophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle.

This large entropy increase on micellization in aqueous medium has been explained in two ways: (1) structuring of the water molecules surrounding the siloxane chains in aqueous medium, resulting in an increase in the entropy of the system when the siloxane chains are removed from the aqueous medium to the interior of the micelle-hydrophobic bonding; (2) increased freedom of the hydrophobic chain in the nonpolar interior of the micelle compared to the aqueous environment

An increase in temperature seems to cause both ΔH_m^o and ΔS_m^o to become more positive, presumably because both the amount of water structured by the hydrophobic chain and the amount of water bound by the hydrophilic sugar group in the nonmicellar species increase with increase in temperature, resulting in a increase in ΔH_m^o and ΔS_m^o, respectively. Since these two parameters have opposite effects on ΔG_m^o, it may become more negative or less negative with temperature change, depending on the relative magnitude of the changes in ΔH_m^o and ΔS_m^o. From the above data, ΔG_m^o appears to become more negative with increase in temperature.

The values of ΔH_m^o in Table-2 indicate that the micellization processes in water are exothermic. The variation of ΔH_m^o with temperature is due to a change in the hydration of the head groups during micellization. The micellization of surfactants in water may be understood on the basis of water structure and hydrophobic interaction. Generally, the structure of liquid water is considered in terms of a 3-dimensional hydrogen bonded "flickering cluster" which retains much of the ordered structure of ice. The entropy change is positive in all cases. However it decreases with increasing temperature. The positive values of standard entropy of micelle formation ΔS_m^o are due to the melting of "flickering cluster" around hydrocarbon tails of the surfactant monomer and the increased randomness of the hydrocarbon chains in the micelle core. Amphiphilic monomers with a long hydrocarbon chain increase the orderliness of water by formation of a "Frank-Evan iceberg" around the hydrocarbon chain. This results in a decrease in the entropy of the system. The enthalpy entropy compensation plots for the Si(3)N-GA in all the solvent mixtures showed a good correlation between the thermodynamic parameters. The plots indicate that the change in ΔH_m^o is effectively balanced by a corresponding change in ΔS_m^o.

Free energy and enthalpy were negative whereas entropy was positive. The minimal effect of temperature on the thermodynamic parameters indicates that the process of micellization was spontaneous in nature.

Conclusion

By using Wilhelmy plate method, the surface tension of Si(3)N-GA at different temperatures (298-313 K). The results show that with the increase of temperature, the critical micelle concentration (CMC) of Si(3)N-GA slightly decreases, but the maximum surface excess concentration at the air/water interface increases. The micellization free energies (ΔG^o_{mic}) are in the range -29.247--30.177 kJ mol^{-1} in the studied ranges of temperature. The process of micellization of Si(3)N-GA in aqueous solution is mainly driven by the entropy.

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