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Study on the surface activity and aggregation behavior of a polyether surfactant for acidification

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Abstract: Four kinds of biological phenolamine resin block ethers (BPPC) surfactants with different molecular weights were synthesized from biological phenol, formaldehyde and polyvinyl polyamines. The structure of BPPC was characterized by Ft-ir and H NMR. The surface properties of BPPC polyether surfactant and the change curve of surface tension with concentration in aqueous solution at different temperature were studied by surface tension method. The results showed that the critical micelle concentration (cmc) of BPPC and the γ_{cmc} increased with the increase of EO content. With the increase of molecular weight, number of branched chains and length of branched chains, cmc and γ_{cmc} decreased. The thermodynamic calculation results show that BPPC shows enthalpy/entropy compensation during micellization in aqueous solution. The compensation temperature T was all (300 ± 2) K, and with the increase of molecular weight, number of branched chains and length of branched chains, the stability of BPPC formed in aqueous solution was enhanced.

1.Introduction

Amphiphilic block polyethers with both hydrophilic and hydrophilic groups have been produced on a large scale and widely used in oil fields^[1]. At present, the raw materials have high price and environmental hazards, which greatly limit their application. Biological phenol, extracted from natural cashew nut shell oil, is a kind of natural alkylphenol, which has a wide range of sources and is an important raw material for the synthesis of green surfactants. It has been studied in the fields of modified paint, coating, varnish and phenolic resin^[2,3].

In aqueous solution, the enthalpy change and entropy change show a linear relationship among various processes such as oxidation-reduction, hydration and protein dissociation of some solutes, which is called enthalpy/entropy compensation^[4-8]. Experiments have proved that the micellization process of surfactants also shows this enthalpy/entropy compensation phenomenon^[9,10]. By studying the enthalpy/entropy compensation of micellization of surfactants, some important information about micellization process and micellization structure can be obtained^[11,12]. In this paper, four biological phenolamine resin amphiphilic block polyether surfactants were synthesized from biological phenols from biomass resources^[13]. The surface properties and the temperature effect and enthalpy/entropy compensation of their aggregation behavior in aqueous solution were studied by surface tension method, and the main driving factors of BPPC aggregation process were summarized^[14]. It is of guiding significance to further study the relationship between structure and properties of phenolamine resin block polyether surfactants and to explain the practical application mechanism of micelle catalysis, solubilization, oil displacement and demulsification^[15].



2.Surface property test of biological phenolamine resin block polyether (BPPC)

The drop volume method was used to accurately determine the surface tension of four kinds of BPPC polyether surfactants, and the critical micelle concentration (cmc) of each surfactant and the surface tension (γ) at the critical micelle concentration were obtained, and the surface performance parameters were calculated according to Gibbs formula:

$$\Gamma_{\text{cmc}} = \frac{-c}{nRT} \left(\frac{d\gamma}{dc} \right) \quad (1)$$

$$A_{\text{min}} = \frac{1}{N_A \Gamma_{\text{CMC}}} \quad (2)$$

cmc is characterization of surfactants on the surface activity and micelle ability is an important parameter, the smaller the cmc, surface active agent of surface activity and micelle ability is higher. By four kinds of the surface tension of the product along with the change of the concentration curve of cmc, Γ_{cmc} and A_{min} thus calculated, listed in table 1.

Tab. 1. The surface activity parameter of BPPC

The Sample	cmc/(mg/L)	γ_{cmc} (mN/m)	$\Gamma_{\text{cmc}}/(\times 10^{-6} \text{mol/m}^2)$	$A_{\text{min}}/\text{nm}^2$
BPPC1	72.2	39.5	0.3610	3.3265
BPPC2	60.5	35.6	0.3535	3.4087
BPPC3	34.7	34.1	0.3490	3.4320
BPPC4	25.9	30.2	0.3285	3.6612

As can be seen from table 2, with the increase of EO content, the ability of BPPC polyether surfactant to reduce surface tension decreases. As the molecular weight, number of branched chains and length of branched chains of series BPPC polyether surfactants increased, their cmc decreased. The reason may be that with the increase of molecular weight, number of branched chains and length of branched chains, the micellar radius and surface area of BPPC surfactant increase, the number of molecules required to form micelles decreases, and the minimum area occupied by each molecule increases.

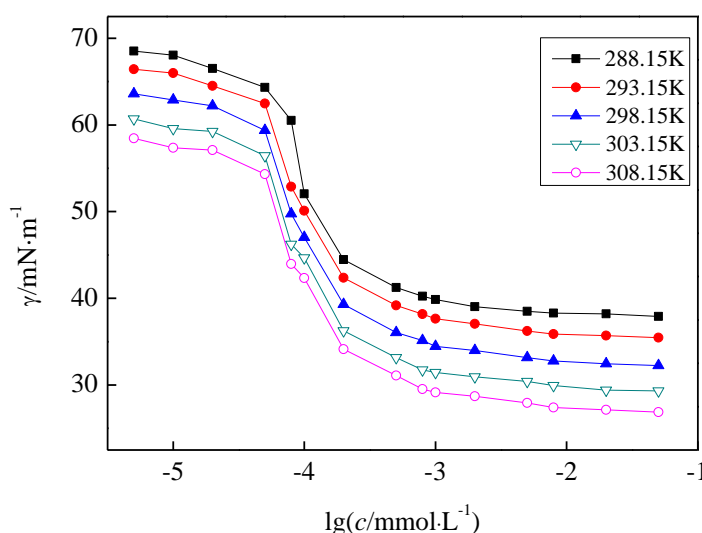


Fig.1 Surface tension (γ)-lgc plots of CPEC in aqueous solution at different temperatures

Figure 1 is the γ -lgc curve of BPPC1 aqueous solution at different temperatures (the γ -lgc curve of BPPC2, BPPC3 and BPPC4 aqueous solutions is similar to this curve). From this figure, the critical micelle concentration cmc of BPPC1 at different temperatures can be determined, as shown in table 2.

Tab. 2. The Critical micelle concentration (cmc) of BPPC in aqueous solution

T/K	$10^6 \text{cmc}/\text{mol}\cdot\text{L}^{-1}$			
	BPPC1	BPPC2	BPPC3	BPPC4
288.15	3.84	2.87	1.41	0.95
293.15	3.74	2.71	1.34	0.90
298.15	3.44	2.33	1.24	0.82
303.15	3.24	2.15	1.16	0.76
308.15	3.14	2.09	1.11	0.72

It can be seen from table 2 that, for any BPPC polyether surfactant within the temperature range under investigation, the cmc of its aqueous solution decreases with the increase of temperature, which is consistent with the law of low molecular non-ionic surfactant.[§]The influence of temperature on the critical micelle concentration is complex, and for non-ionic surfactants, it is mainly hydration. The increase of temperature weakens the cooperation of the hydrophilic group in BPPC polyether surfactant molecules and enhances the "dehydrating" effect of the hydrophilic group, which is conducive to the formation of the church group and causes its cmc to decrease with the increase of temperature. Studies have shown that when the concentration is higher than cmc, polyether molecules exist in an aggregation state in aqueous solution. At a specific temperature, the sequence of cmc values of series BPPC polyether surfactants in aqueous solution was as follows: With the increase of EO content, micellization ability decreased.

3. The thermodynamic function of BPPC in aqueous solution

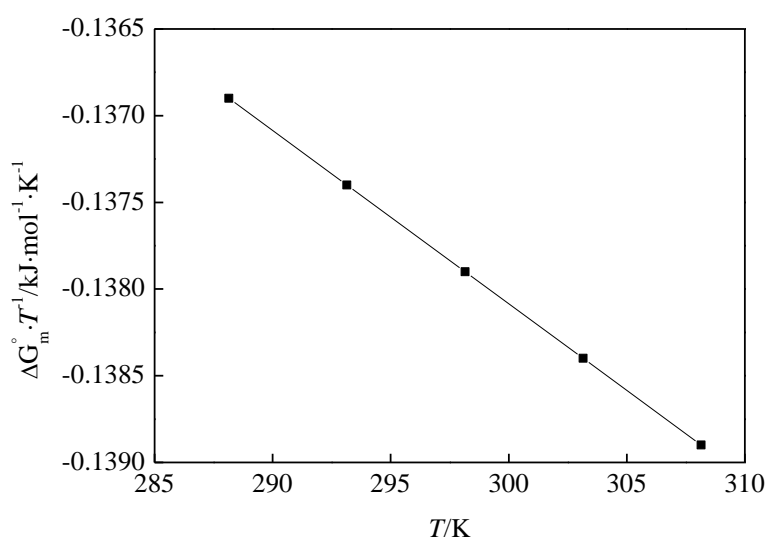
According to the mass action model of the micellization process, the change of Gibbs function of the non-ionic surfactant in the micellization process in aqueous solution can be written as^[16]:

$$\Delta G_m^\circ = RT \cdot \ln \frac{\text{cmc}}{\omega} \quad (3)$$

$$\Delta H_m^\circ = -T^2 \frac{\partial(\Delta G_m^\circ/T)}{\partial T} \quad (4)$$

$$\Delta S_m^\circ = \frac{1}{T} (\Delta H_m^\circ - \Delta G_m^\circ) \quad (5)$$

Where, ω is the mass fraction of water. Because the order of magnitude of cmc of BPPC series polyether surfactants in aqueous solution reaches the level of 10^{-6} , it can be regarded as very small, so $\omega \approx 55.5 \text{mol/L}$. Based on this, the standard gibbs free energy change (ΔG_m°) of BPPC can be calculated. The slope at each temperature point ($\frac{\partial(\Delta G_m^\circ/T)}{\partial T}$) can be calculated from this curve, and the corresponding thermodynamic parameters such as the standard molar enthalpy change (ΔH_m°) and the standard molar entropy change (ΔS_m°) can be calculated by using formulas (2) and (3).

Figure 2 $\Delta G_m^\circ / T$ - T plot of BPPC1 in aqueous solution

Since the thermodynamic parameters of the four kinds of BPPC polyether surfactants in aqueous solution have similar regularity, the thermodynamic data of BPPC1 is taken as an example to discuss. The $\Delta G_m^\circ / T$ - T curve of BPPC1 is shown, and the thermodynamic data of BPPC1 is listed in table 3.

Table 3 Thermodynamic the parameters of the micellization of BPPC in aqueous solution

T/K	ΔG_m° KJ/mol ⁻¹	ΔH_m° KJ/mol ⁻¹	ΔS_m° KJ/mol · K ⁻¹	$-T \Delta S_m^\circ$ KJ/mol ⁻¹
288.15	39.45	8.30	0.1657	47.75
293.15	40.28	8.59	0.1666	48.85
298.15	41.11	8.89	0.1677	50.00
303.15	41.96	9.19	0.1688	51.17
308.15	43.11	9.50	0.1715	52.85

As can be seen from table 4, within the temperature range under investigation, all values of ΔG_m° are negative, indicating that the micellization process of BPPC polyether surfactant in aqueous solution is spontaneous, and the micelle solution system formed by it is a thermodynamic stable system. All values of ΔH_m° were positive, indicating that the micellization process was endothermic. All values of ΔS_m° were positive, indicating that the process of adding BPPC polyether surfactant molecules into micelles was easier.

4. Enthalpy/entropy compensation of BPPC micellization process

Lumry pointed out that micellization could be described as two processes: the surfactant molecular alkane chain "dehydrating" process, namely the destruction of the "iceberg structure" around the alkane chain, surfactant molecular alkane chain aggregation formation micelle process. Thus, the compensation between enthalpy change (ΔH_m°) and entropy change (ΔS_m°) in the micellization process of surfactants can be described as follows:

$$\Delta H_m^\circ = \Delta H_m^* + T_c \Delta S_m^\circ \quad (6)$$

Where, the slope is the compensation temperature, which is a parameter characterizing the "dehydrating" action in the micellization process, and it reflects the interaction between solute and

solvent. T_c Intercept is a parameter that characterizes the aggregation process of surfactant molecular alkane chain and reflects the interaction between solutes. When the surfactant monomer molecules dissolve in water, the water molecules will form structural water (i.e. iceberg structure) around the alkane chain with hydrogen bonds, leading to the decrease of entropy of water. The water system will try to repel the alkane chains of the surfactant molecules so as to break down these ice-like structures to increase the entropy of the system, which promotes the aggregation of these alkane chains to form micelles. As can be seen from table 4, within the temperature range under investigation, and are all negative, indicating that they play a major role in the contribution of, therefore, the formation of micelles of BPPC series polyether surfactants is mainly an entropy-driven process, which still obeys the entropy-driven mechanism, and the entropy driving force increases with the rise of temperature.

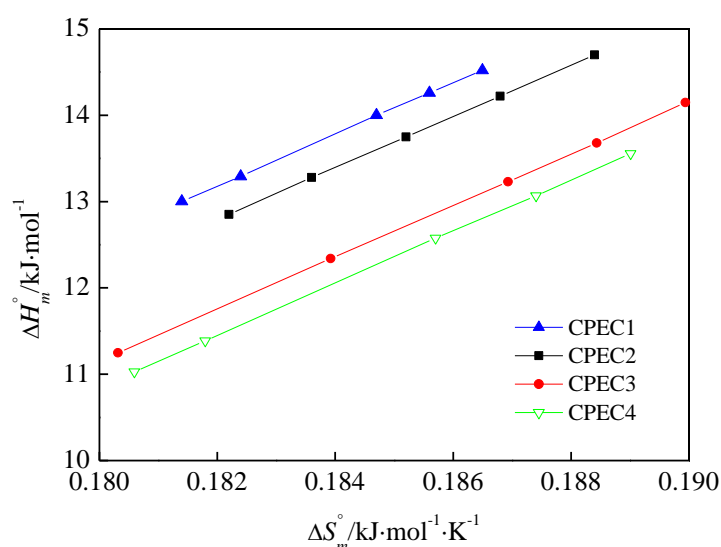


Figure 3 Enthalpy-entropy compensation plots of the micellization of 4 kinds of BPPC

Figure 3 shows the curve of ΔH_m° vs ΔS_m° of the four kinds of BPPC polyether surfactants in aqueous solution, and the curve presents a good linear relationship, satisfying formula (4), which indicates that the enthalpy and entropy compensation phenomenon exists in the micellization process of BPPC polyether surfactants in aqueous solution^[17].

Table 4 Fitting result for $\Delta H_m^\circ - \Delta S_m^\circ$ plots of a series of CPEC

	BPPC1	BPPC2	BPPC3	BPPC4
r	0.9999	0.9999	0.9998	0.9993
T/K_c	300.00	300.02	301.19	301.56
ΔH_m^* KJ/mol ⁻¹	41.42	41.82	42.83	43.15

As can be seen from table 5, the compensation temperature T_c of four polyether surfactants was around 300K, with no significant change, indicating that the "dehydrating" effect of these four BPPC polyether surfactants was similar. It decreases gradually, indicating that with the increase of molecular weight, number of branched chains and length of branched chains as well as the decrease of EO content, the structural stability of BPPC forming micelles in aqueous solution increases gradually. The formation of micelles in aqueous solution mainly depends on the hydrophilic group, while the hydrophilic group prevents the interaction between surfactant molecules. The formation of micelles depends on the balance of the two opposing forces. When the oil-loving groups of surfactant molecules are longer, the hydrophobic interaction between the molecules is enhanced, forming a relatively close aggregation structure, and the stability of the group is enhanced. When the content of

EO in surfactant molecules increases, the volume effect of hydrophilic groups arranged in the shell of micelles will make the intermolecular arrangement relatively loose, leading to the decrease of the stability of micelles. As can be seen from the data in table 5, Gibbs free energy decreases with the increase of molecular weight, number of branched chains and length of branched chains, as well as the decrease of EO content, which also proves that the stability of its micelle increases from the perspective of thermodynamics.

5. Conclusion

(1) The structure of the 4 synthesized BPPC polyether surfactants was characterized by ft-ir and H NMR, and the analysis results showed that the synthesized compounds were basically consistent with the theoretical structure.

(2) The drop volume method is adopted to determine the four BPPC under 298.15 K of cmc, γ_{cmc} , Γ_{cmc} and A_{min} surface performance parameters, the cmc decreased with the increase of EO content, molecular weight, branched chain number and length of branch chain.

(3) The micelization process of series BPPC polyether surfactants in aqueous solution is spontaneous, driven by entropy, and the entropy driving force increases with the rise of temperature.

(4) The enthalpy and entropy compensation phenomenon exists in the micelization of BPPC polyether surfactants in aqueous solution, and the compensation temperature T_c is all at (300 ± 2) K. With the increase of molecular weight, number of branched chains and length of branched chains, as well as the decrease of EO content, the structural stability of BPPC forming micelles in aqueous solution gradually increased.

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