

Synergistic Effects of Lignin-Phenol-based Nonionic Surfactant with Anionic Surfactants in Aqueous Solution

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Surfactants made from modified lignin are attracting growing attention; therefore, a lignin-phenol nonionic surfactant named ML-AL has been prepared by modifying liquefied industrial alkali lignin (L-AL). Its basic physical and chemical properties have been shown to be favorable. In this work, anionic surfactants of sodium fatty acid soap (carbon numbers 12, 16, and 18) and sulfur-containing anionic surfactants (sodium dodecyl sulfate and sodium dodecyl benzene sulfonate) were chosen to mix with ML-AL in water-soluble media. The surface properties of each binary mixed solution system with anionic surfactant were investigated. At the same time, the mixed micelles formed by ML-AL and each anionic surfactant were studied. Non-ideal mixed micelles were obtained *via* ML-AL and the tested anionic surfactant. The interaction parameter (β_M) and excess free energy (ΔG_{excess}) were both negative. Meanwhile, the critical micelle concentration (CMC) values of mixed systems (formed by ML-AL and each anionic surfactant in aqueous solution) were lower than those of a single-component system (ML-AL or single anionic surfactant). There was an optimum dosage ratio of about 0.4 in terms of synergistic effects. This research could provide a foundation for practical applications of combinations with anionic surfactants in aqueous solution.

Keywords: Lignin-phenol; Nonionic surfactant; Synergy; Non-ideal mixed micelles

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INTRODUCTION

Lignin is the most abundant phenolic polymer in nature. It consists of a family of phenyl propane-type polymers as the basic structural units (Hatakeyama and Hatakeyama 2010; Chung and Washburn 2012). As a by-product of the chemical manufacturing processes for cellulose and pulp, its output quantity is huge. Industrial lignin is usually used as fuel in papermaking processes. Only a small amount, about 1 to 2%, is isolated and made into specialty products (Lora and Glasser 2002), of which lignin-based surfactants are a novel application.

Surfactants are chemicals that can reduce the surface energy of water with a small dosage. In the case of liquids, the surface energy of a phase in equilibrium with its vapor-saturated air is equal to the numerical value of surface tension (Chen and Dai 1985; Chen *et al.* 2001). Therefore, the energy performance of a surfactant aqueous solution can be shown intuitively through the detection of the surface tension. Surfactants have an amphiphilic structure that is composed of a hydrophilic group and a hydrophobic group. The hydrophilic end tends to approach the aqueous phase, while the hydrophobic end tends to escape from the water phase. Therefore, the surfactant molecule can form a

directional arrangement on the surface of the aqueous phase (the hydrophilic group located in the aqueous phase, the hydrophobic group located in the air phase); this is usually called 'surface adsorption' (Zhao and Zhu 2003). The forces of attraction between adjacent hydrophobic groups are much lower than those between the water molecules (Xiao and Zhao 2003). When the surfactant concentration increases, the excess surfactant molecules flock together and forms directionally arrayed aggregations that are called micelles (Zheng and Hu 1995). The surfactant concentration corresponding to the initial formation of micelles is known as the critical micelle concentration (CMC).

Regarding research on surfactants, there are two main lines of inquiry in the research and development field (Zheng and Hu 1995). The first is the investigation of the relationship between a surfactant's structure and its properties. The second is mixing surfactants with each other in order to obtain a new product with superior performance. The latter is an example of a synergistic effect.

A lignin-phenol-based nonionic surfactant named ML-AL was prepared in previous experiments, and its basic physical and chemical properties were surveyed (Mao and Wu 2013). The surfactant was used in the deinking of secondary fiber in the flotation process, both alone and in combination with other surfactants (Mao *et al.* 2012). The combined surfactants had better deinking ability than the single-component surfactants. Thus, there is a motivation to explore the interaction effects between different surfactant molecules.

Fatty acid soaps are effective at trapping the ink particles stripped from the secondary fibers. Alkyl sulfates and alkyl benzene sulfonate are conducive to the formation and stabilization of foam. Therefore, fatty acid soaps and sulfur-containing surfactants are widely used in the deinking process. These are all anionic surfactants. In the present work, sodium fatty acid soap (carbon numbers 12, 16, and 18), sodium dodecyl sulfate (SDS), and sodium dodecyl benzene sulfonate (SDBS) were chosen to mix with the nonionic surfactant ML-AL. The objective of this work was to study the surface properties of the binary mixed solution in the whole aqueous system, as well as the interaction effects between the two components in the mixed micelles. Surface tension and critical micelle concentration (CMC) can be regarded as the most important surface properties of such a system. Special attention was given to the interaction parameter β_M and the excess Gibbs energy ΔG_{excess} .

EXPERIMENTAL

Materials

Alkali lignin (AL) was prepared from black liquor *via* the acid precipitation method using sulfuric acid. Heavy black liquor was provided by Guigang Your Sugar. The AL was purified with a dioxane/water solution.

First, L-AL was obtained by liquefaction, which was carried out according to the process described in the literature (Sui and Wu 2011; Jin *et al.* 2011). Then, 5 g of L-AL was treated with 15 mL of epoxy chloropropane for 2 h at a temperature of 90 °C and grafted with 40 mL of laurinol for 1.5 h at 135 °C. These steps of the modifying reaction were done in an aqueous alkaline medium. The resulting lignin-phenol-based nonionic surfactant was denoted ML-AL. Diagrams of the structures of ML-AL and the tested anionic surfactants can be seen in Fig. 1.

All other chemicals used in the experiments were of analytical grade. All solutions were made and diluted as required with double-distilled water prior to use.

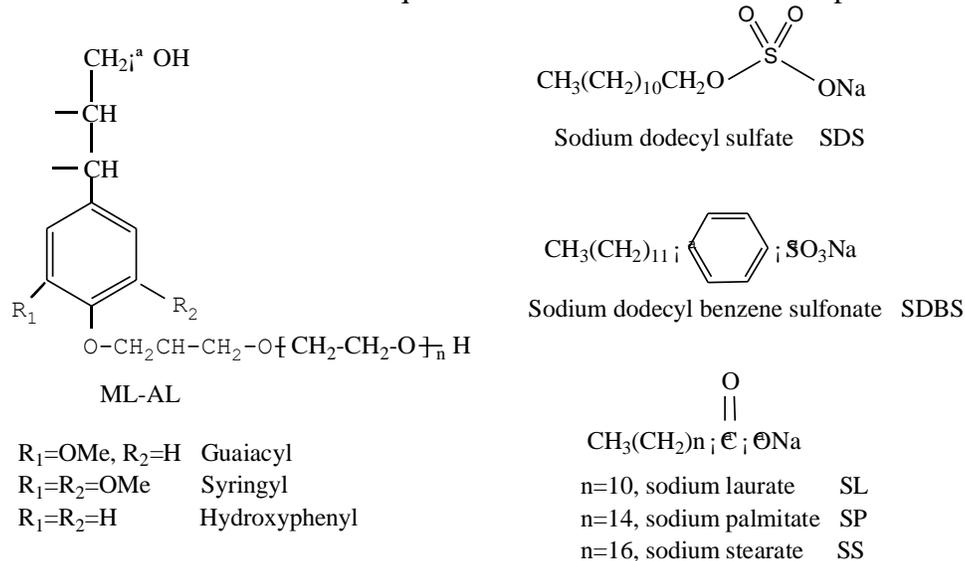


Fig. 1. Structures of ML-AL and tested anionic surfactants

Methods

Surface tension measurements

Surface tension measurements were performed using a DCAT21 instrument (Dataphysics, Germany) based on the Wilhelmy plate technique. In this method, a thin plate, ordinarily made of platinum and iridium, is used. The Wilhelmy equation is

$$\gamma = F/P \cos \theta, \quad (1)$$

where P is the wetted perimeter of the plate, F is the force measured by the balance on the top, and θ is the contact angle (Stamm 2008). The plate was burned in the flame of a Bunsen burner before each experiment. After cleaning the plate with the burning method, the liquid wets the plate completely. That is, the contact angle is reduced to near-zero values. Then, the Wilhelmy equation simplifies to:

$$\gamma = F/P \quad (2)$$

Because the flotation deinking experiments with the secondary fiber were performed at 50 °C, surface tension detection was also carried out at 50 °C. The molar ratio of ML-AL was 0.8, 0.6, 0.4, and 0.2. The starting solution was prepared with 1000 ml volume and a total molar concentration of 12.5 mmol/L. Other solutions were obtained by dilution. The volume of each solution taken out for surface tension experiment was 100 mL.

Measurement of contact angle

The measurement of the contact angle was also performed using the Wilhelmy method. A4 print paper sheet was cut into strips with a width of about 10 mm and fixed into the sample holder. To measure the contact angle, the DCAT21 initially detects the

surface by moving up the sample vessel with the liquid until the balance detects a weight difference (because the probe gets lighter when it dips into the liquid). The position of the liquid surface is memorized when the probe meets the surface. The liquid surface moves up farther to the defined immersion depth (immersion depth: 5 mm). Then, the liquid surface moves down to the stored initial position. The advancing contact angle was obtained by the move-up procedure, and the receding contact angle was obtained by the move-down procedure.

Determination of the critical micelle concentration (CMC)

The detection of the CMC was performed using a series of surface tension measurements on the same sample with decreasing concentrations. The surface tensions of the investigated surfactant and mixtures with anionic surfactants were determined under different molar concentrations. By plotting the surface tension (γ) versus the molar concentration of the surfactants $[C]$, the CMC values were determined from the knee point in the slope of the resulting plot. The CMCs of the ML-AL and the anionic surfactants applied in this work are listed in Table 1.

Table 1. CMC of ML-AL and Anionic Surfactants

Samples	CMC* (mmol/L)	Samples	CMC* (mmol/L)
SDS	8.10	SL	35.48
SDBS	1.60	SP	2.24
		SS	0.56
* Parameters obtained from the literature (Zheng and Hu 1995; Zhao and Zhu 2003)			

RESULTS AND DISCUSSION

Surface Properties of the Binary Mixed Solution in the Whole System

Surface tension and the critical micelle concentration

The surface tension values of ML-AL with different anionic surfactants are shown in Fig. 2 at a temperature of 50 °C. The corresponding CMC values are listed in Table 2. The CMC value is the concentration of a surfactant solution at which the molecules of the surfactant start to build micelles. That means that the CMC is a phase transition point. The slopes of several physical properties change as a function of the concentration; in particular, the surface tension shows an inflexion point at the CMC (Asadov *et al.* 2012; Cheng *et al.* 2012).

The surface tension of both ML-AL and mixed surfactants (ML-AL and each anionic surfactant) aqueous solutions decreased drastically with increases in the solute molar concentration. However, a turning point appeared along the curve, implying the formation of micelles. The corresponding concentration was determined to be the CMC. The smaller the value was, the more easily the surfactant formed micelles.

The carbon numbers of SL, SP, and SS are, respectively, 12, 16, and 18. Compared with SDS, the structure of SDBS is equal to a benzene ring inserted in the middle of the SDS molecule, which can be seen in Fig. 1. This can be taken as an increment of the 2.5 carbon number (Zhao and Zhu 2003). Table 1 shows that the length of the carbon chain or hydrophobic property increased; the surfactant reduced the surface

energy more efficiently, leading to a decrease in the CMC value. Table 2 shows that a similar conclusion was established for the mixed aqueous solution surfactant system. The lower CMC value was obtained when ML-AL was mixed with a longer carbon chain surfactant. However, the CMC of ML-AL and SS mixed micelles was a little higher than that for SL and SP. The somewhat lower solubility of SS may explain this phenomenon.

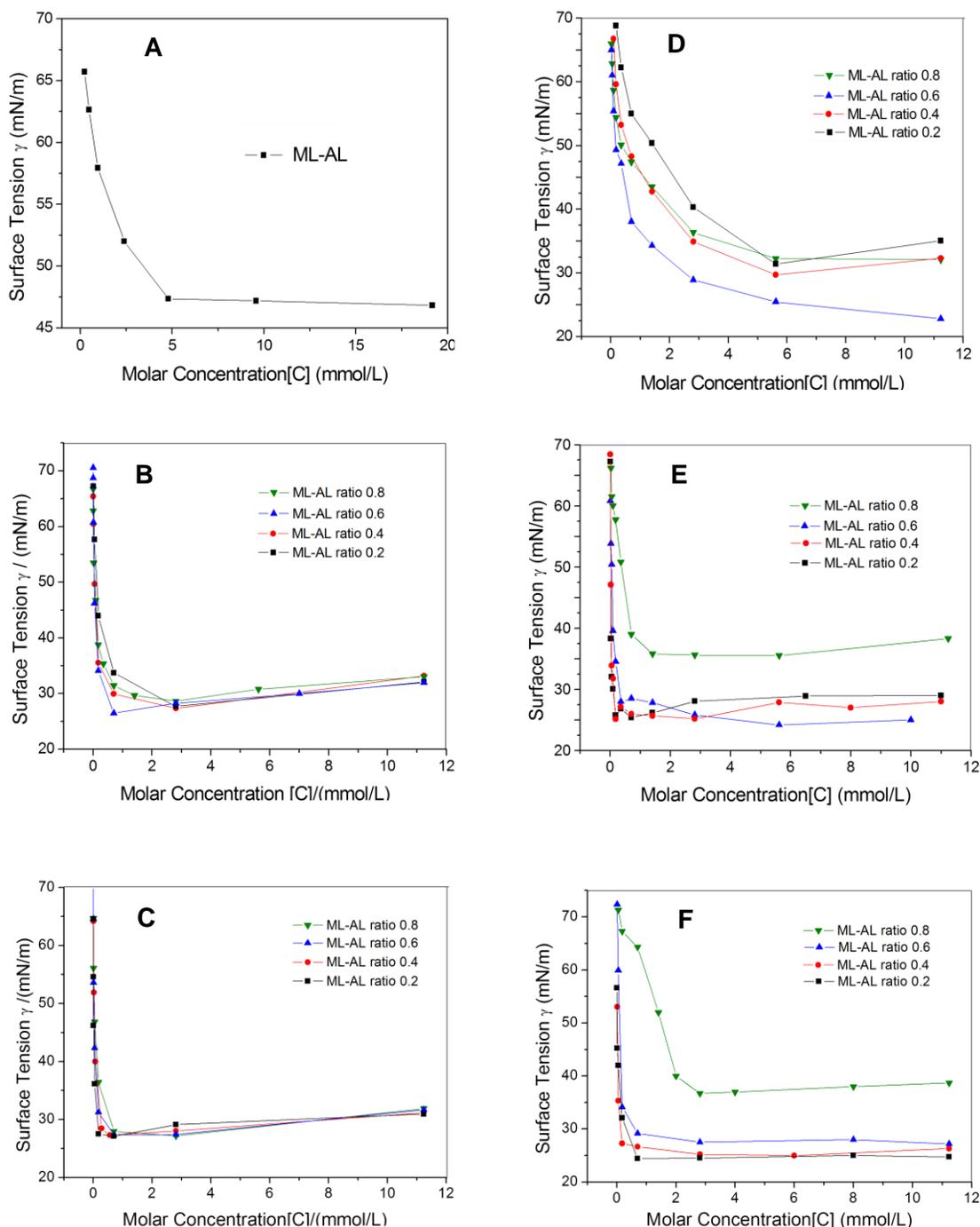


Fig. 2. The surface tension of mixed surfactant aqueous solution through ML-AL and the anionic surfactants: a) ML-AL, b) SDS, c) SDBS, d) SL, e) SP, f) SS

Table 2. CMC Values of Mixed Surfactants Aqueous Solution through ML-AL and the Anionic Surfactants

Molar Ratio of ML-AL in the System α_1	CMC ⁰ (mmol/L)				
	ML-AL + SDS	ML-AL + SDBS	ML-AL + SL	ML-AL + SP	ML-AL + SS
1.0	4.19	4.19	4.19	4.19	4.19
0.8	1.20	0.58	8.83	1.33	6.93
0.6	1.09	0.28	5.33	0.38	1.32
0.4	0.59	0.27	4.21	0.13	0.14
0.2	0.23	0.14	6.88	0.16	0.70
0.0	8.10	1.60	35.48	2.24	0.56

The CMC values of mixed micelles were even lower than for any kind of ML-AL and anionic surfactant in the system. The binary system of ML-AL and fatty acid sodium soaps data showed that there existed an optimum synergy ratio in the mixed system. Here, the dosage of ML-AL was about 0.4. The SDS and SDBS compound curve curvature decreased gradually, and the CMC also showed a minimum value. The minimum value appeared when the molar ratio of the ML-AL was between 0.2 and 0.4.

Determination of surface activity parameters

The Gibbs free energy of adsorption (ΔG), maximum surface excess (Γ_{max}), and the corresponding minimum surface area of the surfactant molecule (A_{min}) were obtained using the following equations (Zheng *et al.* 1995; Comas-Rojas *et al.* 2013). Calculated data are listed in Table 3.

$$\Delta G = RT \ln CMC \quad (3)$$

$$\Gamma_{max} = - \frac{1}{RT} \frac{d\gamma}{d \ln C} \quad (4)$$

$$A_{min} = \frac{1}{\Gamma \times N_A} \quad (5)$$

In Eqs. 3 through 5, C is the molar concentration of the surfactants (mol/L), R is the molar gas constant (8.314 J/(K·mol)), T is the thermodynamic temperature (K), and N_A is Avogadro's number (6.022×10^{23}).

The Gibbs free energy of adsorption (ΔG) reflects the tendency to form micelles. It is common knowledge that any closed system tends to minimize free energy as much as possible. That is because the lower free energy makes the system more stable. Negative values of ΔG indicate that the formation of micelles released energy and that the micelles formed spontaneously (Naskar *et al.* 2013).

Table 3 shows that a larger ΔG value corresponded to smaller CMCs, which similarly proved the easier formation of micelles. The optimum molar concentration of ML-AL mixed with SDS and SDBS was $\alpha_1=0.2\sim 0.4$, while the optimum ratio mixed with SL, SP, and SS was $\alpha_1=0.4$.

Table 3. Surface Activity Parameters of Mixed Micelles

Mixed Anionic Surfactants	α_1	ΔG KJ/mol	Γ_{max} $\mu\text{mol}/\text{m}^2$	A_{min} nm^2	Contact Angle	
					Advancing Angle	Receding Angle
SDS	0.8	-16.897	2.357	0.699	66.71	59.74
	0.6	-17.123	3.378	0.492	66.42	60.50
	0.4	-18.649	2.836	0.585	64.65	59.24
	0.2	-21.067	3.504	0.479	66.79	59.99
SDBS	0.8	-18.762	2.757	1.602	65.26	61.75
	0.6	-20.592	2.983	0.556	64.98	62.15
	0.4	-20.738	3.522	0.471	64.91	62.68
	0.2	-22.457	2.734	0.607	65.89	62.10
SL	0.8	-11.882	2.676	0.620	78.28	57.54
	0.6	-13.147	3.116	0.533	73.38	56.65
	0.4	-13.740	3.546	0.468	77.07	57.11
	0.2	-12.508	3.705	0.448	66.83	58.88
SP	0.8	-16.589	3.304	0.503	84.17	59.43
	0.6	-19.692	4.072	0.408	72.66	60.26
	0.4	-22.347	4.253	0.390	73.52	59.95
	0.2	-21.899	4.148	0.401	70.95	59.82
SS	0.8	-12.116	2.982	0.557	66.78	56.51
	0.6	-16.160	3.676	0.452	67.58	53.65
	0.4	-21.862	4.486	0.370	73.22	55.03
	0.2	-17.697	2.292	0.724	75.88	58.88

Γ_{max} represents the maximum adsorbed amount of the surfactant at the surface of the solution. Larger values corresponded to smaller surface area occupied by an individual surfactant molecule. For a specific surface area of the aqueous solution, larger Γ_{max} (or smaller A_{min}) means that more surfactant molecules were arranged on a unit area of the solution surface; in other words, there was a more intensive arrangement of the surfactant at the solution surface.

The wetting and permeability of surfactant play an important role in the pulping process of waste paper. The size of the contact angle reflect the wetting and permeability properties of the surfactant solution on the paper sheet (Zhang *et al.* 2012). The lower contact angles, both the advancing angle and the receding angle, suggest better wetting and permeability properties. From Table 3, the minimum values of contact angles were found when the dosage of ML-AL was near 0.4.

Interaction Between the Two Components in the Mixed Micelles

The mixture of nonionic and anionic surfactants in water was not an ideal solution; rather, it was of the non-ideal type. According to the literature (Poša and Ćirin 2012; Tiwari *et al.* 2013), the physico-chemical parameters of mixed micelles can be calculated using the following equations.

Molar ratio of ML-AL (x_1) in the real mixed micelles:

$$\frac{x_1^2 \ln(CMC^0 \alpha_1 / CMC_1 x_1)}{(1-x_1)^2 \ln[CMC^0 (1-\alpha_1) / CMC_2 (1-x_1)]} = 1 \quad (6)$$

Interaction parameter (β_M) of the two components in the micelle:

$$\beta_M = \frac{\ln(CMC^0 \alpha_1 / CMC_1 x_1)}{(1-x_1)^2} \quad (7)$$

Activity coefficient of the anionic surfactant (f_1) in the mixed micelles:

$$f_1 = \exp[\beta_M(1-x_1)^2] \quad (8)$$

Activity coefficient of ML-AL (f_2) in the mixed micelles:

$$f_2 = \exp[\beta_M x_1^2] \quad (9)$$

Excess free energy (ΔG_{excess}),

$$\Delta G_{\text{excess}} = RT[x_1 \ln f_1 + (1-x_1) \ln f_2] \quad (10)$$

where CMC^0 is the experimentally determined CMC value of the mixed micelles (listed in Table 2), α_i is the molar ratio, and CMC_i is the CMC of component i ($I = 1$ for ML-AL, $I = 2$ for the anionic surfactant, as listed in Table 1). The subscript M indicates that the data are interrelated with the micelles.

Table 4. Physico-Chemical Parameters of the Mixed Micelles

Mixed Anionic Surfactants	α_1	x_1	β_M	f_1	f_2	ΔG_{excess} kJ/mol
SDS	0.8	0.608	-2.357	0.577	0.445	-16.376
	0.6	0.545	-3.013	0.558	0.476	-16.470
	0.4	0.539	-3.572	0.547	0.464	-17.063
	0.2	0.531	-3.128	0.557	0.447	-17.293
SDBS	0.8	0.488	-2.625	0.229	0.782	-21.310
	0.6	0.474	-2.889	0.286	0.736	-19.031
	0.4	0.458	-2.833	0.356	0.667	-17.463
	0.2	0.341	-3.139	0.395	0.635	-15.534
SL	0.8	0.745	-2.556	0.714	0.242	-15.392
	0.6	0.652	-2.637	0.690	0.326	-15.885
	0.4	0.602	-2.746	0.647	0.370	-16.529
	0.2	0.558	-2.714	0.588	0.429	-16.817
SP	0.8	0.558	-3.045	0.454	0.584	-16.997
	0.6	0.508	-3.185	0.408	0.593	-17.822
	0.4	0.471	-3.339	0.427	0.570	-17.481
	0.2	0.443	-2.885	0.417	0.576	-17.384
SS	0.8	0.451	-2.223	0.379	0.630	-16.856
	0.6	0.358	-2.550	0.328	0.690	-15.538
	0.4	0.249	-4.356	0.288	0.717	-13.642
	0.2	0.128	-3.7619	0.262	0.752	-10.250

Equation 6 was transformed into the following form:

$$f(x) = x_1^2 \ln \left(\frac{CMC^0 \alpha_1}{CMC_1 x_1} \right) - (1-x_1)^2 \ln \left[\frac{CMC^0(1-\alpha_1)}{CMC_2(1-x_1)} \right] \quad (11)$$

Solution (x_1) was found in the interval of (0, 1) through the Newton iteration method.

Numerous application properties of surfactants are based on two basic physical and chemical characteristics: micelle formation and surface adsorption (Ding *et al.* 2013; Ludzik *et al.* 2013). All of the tropisms of β_M in Table 4 were negative, so the solution systems containing ML-AL and the tested anionic surfactant belonged to the negative deviation system (Liu and Mi 2003). The negative deviation system is just the system with synergy effects. The value of $|\beta_M|$ was about 3. Hence, the interactions were characterized as a moderate intensity type. $\beta_M < 0$ indicates that, in the mixed micelles, the attractive interaction between the two different surfactant molecules was stronger than that of the identical molecules. Micellization could occur at lower concentrations.

In the micelles mixed by ML-AL and the tested anionic surfactant, the activity of the surfactant can be represented by ($f_i \cdot x_{iM}$) (the activity coefficient multiplied by the molar ratio of a surfactant in the mixed micelles). Taking cognizance of the fact that $f_i < 1$, the following conclusion was obtained: The activity of the surfactant was less than that of the actual molar ratio of a surfactant in the mixed micelles, which indicated that the micelle formation was achieved at a lower concentration. That is, the tendency for micelle formation increased.

The excess Gibbs free energy ΔG_{excess} reflects the stability of the micelles (Zhao and Zhu 2003; Masahiko and Scamehorn 1992). The effect of excess free energy basically mirrored that of the other parameters. It is already known that the surfactant molecules form a directional arrangement of micelles. The hydrophilic groups orient outwardly, and the hydrophobic groups orient inwardly. The ink detached from the waste paper is insoluble in water; however, it can approach the hydrophobic groups of the surfactant molecule. When the micelles are formed, the ink particles are placed in the middle of the micelles or among the surfactant molecules to form the micelles together. The more negative the ΔG_{excess} is, the more stable will be the mixed micelles. During the deinking process, the mixed micelles are more suitable for bringing ink particles out of the flotation system and preventing their re-accumulation on the secondary paper fibers.

Because the anionic surfactant was charged, the single surfactant molecule presented a relatively strong mutual repulsion force. Nonionic ML-AL entered the micelle among anionic surfactant molecules. The repulsion force was greatly reduced (Zhang *et al.* 2013). Such a system appears to be more conducive to micelle formation and surface adsorption. On the other hand, the hydrophilic group of the non-ionic surfactant molecules have polar structures. The dipole moment of the mixed system, involving positive and negative charge centers of molecules, became larger compared with the single-component solution. As a result, the interaction between the surfactant molecules was enhanced. These experimental phenomena manifested as a $\beta_M < 0$ and a reduction of CMC.

CONCLUSIONS

1. Non-ideal mixed micelles were formed by the nonionic surfactant ML-AL and anionic surfactants. For the binary mixture of an aqueous solution containing ML-AL and the tested anionic surfactants, the interaction parameter β_M was negative, which suggested that in the mixed micelles, there were attraction interactions between the two kinds of constituent molecules.

2. The longer hydroxyl chain, which had higher hydrophobicity, could provide better synergistic effects with the mixed surfactants system. Meanwhile, the surfactant had superior activity and adsorbed preferentially.
3. Optimum synergistic effects were achieved at a dosage ratio of approximately 0.4 in relation to the ML-AL and anionic surfactant binary system.
4. The values of ΔG_{excess} were negative, which indicated that the obtained non-ideal micelles were more durable than the micelles formed from single surfactants.

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