



Micelles and structural variation of the solution synergistically changing the viscosity of sodium aluminate solutions

Baoyin Chen, Guihua Liu^{*}, Tiangui Qi, Zhenjiang Fu^{*}, Leiting Shen, Yiling Wang, Zhihong Peng, Qiusheng Zhou

School of Metallurgy and Environment, Central South University, Changsha 410083, Hunan, P.R. China

ARTICLE INFO

Keywords:

Sodium aluminate solution
Viscosity
Organic compound
Viscous flow activation energy
Surface tension

ABSTRACT

Complicated organic behavior in the sodium aluminate solution limits the economical alumina production and improvement in alumina quality by Bayer process. Sodium gluconate (SG) or sodium stearate (SS) in sodium aluminate solution containing sodium oxalate (SO) changed the interfacial occurrence of anionic organics. The single anionic organic compounds or mixed organics initially decreased and then raised the viscosity of the sodium aluminate solution, and further increasing total organic carbon (TOC) remarkably increased the viscosity of the industrial sodium aluminate solution. Correspondingly, increasing concentration of anionic organic compound raised initially and then reduced diffusion coefficient. The minimum viscosity of the solution nearly occurred at the critical micelle concentration (CMC) of the anionic organic compound. Anionic organics also increased the viscous flow activation energy of sodium aluminate solutions. The disordered structure of sodium aluminate solution reduced the viscosity and increased the diffusion coefficient at low concentrations of organics less than CMC. Further increasing the concentration of organic compound more than CMC, micelles then contributed to the ordered structure of the sodium aluminate solution, increasing viscosity and reducing the diffusion coefficient of the sodium aluminate solution. Therefore, a large amount of micelles and the different solution structures synergistically changed the viscosity and diffusion coefficient of the sodium aluminate solution.

1. Introduction

169.55 million tons of alumina were produced in 2022 [1]. More than 95 % of alumina has been produced by Bayer process [2]. Owing to the circulation of Bayer liquor, 40 g·L⁻¹ total organic carbon (TOC) may be received in sodium aluminate solutions (Bayer liquor) [3]. Organic carboxylates and hydroxylates in the Bayer liquor predominantly exist in anionic organics, generally acting as anionic surfactants [4,5]. These organics generally give rise to soda loss, reduce product quality, produce dangerous and harmful gases [6], reduce seed precipitation rate, deteriorate the separation properties of red mud, and generate rich foams. However, some organics in Bayer liquor play positive roles in alumina production. Many scholars reported that the low concentration of 15-crown-5-ether (8×10^{-4} mol·L⁻¹) [7], ethers (<500 mg·L⁻¹) [8], Na₄EDTA, and EDTA (<10 mmol·L⁻¹) [9] all improved precipitation rate and benefited to particle agglomeration [10]. Owing to the surface activity of anionic organic compounds in the sodium aluminate solution

[8,11,12], these anionic organic compounds may change the interfacial properties at gas–solid–liquid and the structure of sodium aluminate solutions. Some organic compounds may change the structure of sodium aluminate solutions due to complexing aluminate anions against precipitation, such as tartrate, gluconate, and citrate [13]. Therefore, as an important parameter determining the structure of sodium aluminate solutions, the viscosity of sodium aluminate solutions gets minor attention. Investigation on the viscosity of sodium aluminate solutions may benefit the removal of organic compounds, production efficiency, and alumina quality.

Many researchers have reported the effect of organic compounds on viscosity in common aqueous solutions or organic solvents. The viscosity of the diluted organic solutions depended on the ionic strength and length of the organic alkyl chain. Seddon *et al.* [14] observed that the viscosity of 3-alkyl-3-methylimidazolium solutions increased with the increase in the length of the organic alkyl chain. Many organic compounds have been found to reduce the viscosity of heavy oils, which

^{*} Corresponding authors at: No.932, Lushannan Road, Changsha City, Hunan Province, 410083 P.R. China.

E-mail addresses: liugh303@csu.edu.cn (G. Liu), 213501019@csu.edu.cn (Z. Fu).

<https://doi.org/10.1016/j.molliq.2024.124557>

Received 7 December 2023; Received in revised form 19 March 2024; Accepted 21 March 2024

Available online 24 March 2024

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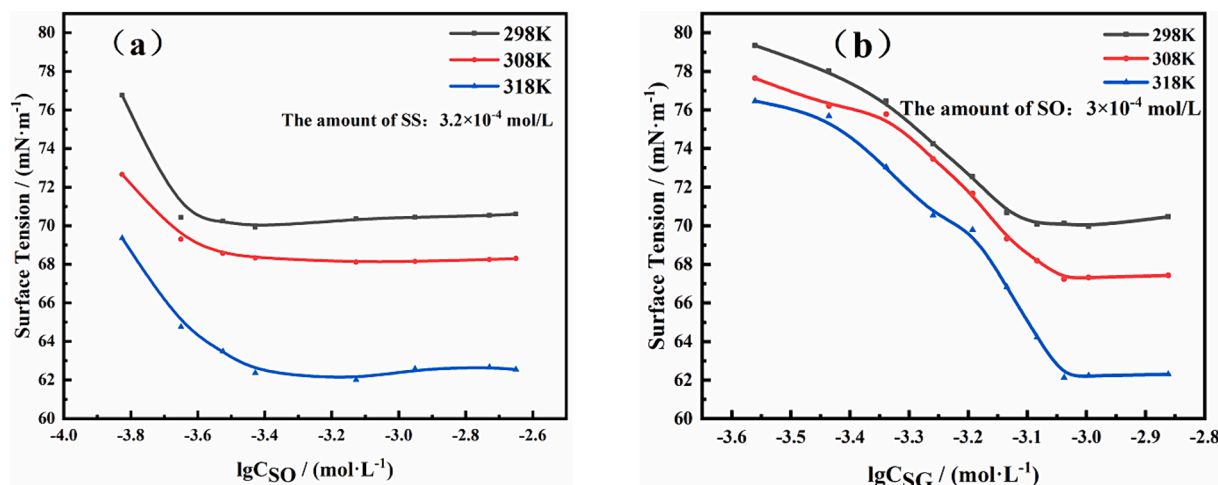


Fig. 1. Effect of organic mixtures on surface tension of sodium aluminate solutions at different temperatures (a-SO/SS, b-SG/SO) ($C_{Na2OK} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{Al2O3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

benefited both the recovery and transportation of heavy oils[15,16]. At the same time, many changes in the viscosity of some electrolyte solutions have been widely reported. Fuoss and Strauss [17] found that the viscosity of polyelectrolyte solutions increased as the solution was diluted. When the solutions were diluted, the intra-chain electrostatic and repulsion of the polyelectrolyte solutions were enhanced, thus reducing the viscosity of the solutions [18]. In contrast, owing to the complex interaction among ions, some aqueous electrolyte solutions exhibit anomalies in viscosity[19,20], increasing concentration first decreased and subsequently increased the viscosity of KCl, RbCl, and CsCl [21].

Meanwhile, Some papers have reported the variation in the viscosity of sodium aluminate solutions. Ikkatai *et al.* [22] and Cheng *et al.* [23] investigated the influence of temperature, caustic soda (Na_2O_k) concentration, and alumina concentration on the viscosity of sodium aluminate solutions, and then provided a mathematical model of the viscosity of sodium aluminate solutions. Li *et al.* [24] found that sodium ions raised the viscosity of Bayer liquor compared to potassium ions in the aluminate solution. Yu *et al.* [11] concluded that the viscosity of sodium aluminate solutions increased with increasing concentration of sodium oxalate (SO) and sodium acetate (SA), but did not give further explanation about the effect of organic compounds on the viscosity. Furthermore, the mechanism remains unclear.

Herein, the surface tension of the synthetic sodium aluminate solution containing organic compounds was determined, and the critical micelle concentration (CMC) of four organic compounds and organic mixtures was then given. Meanwhile, the viscosity of sodium aluminate solutions containing organic compounds was further studied. Based on the formation of micelles and viscous flow activation energy, the mechanism of the organic compounds changing the viscosity and structure of the sodium aluminate solution was finally discussed. These results provide an insight into the structural changes of the sodium aluminate solution and interfacial properties, and further benefit the economical removal of organic compounds, the increases of precipitation efficiency, and the improvement of alumina quality.

2. Experimental

2.1. Materials

Solution: The synthetic sodium aluminate solution ($C_{Na2OK} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, the molar ratio of caustic soda Na_2O_k to alumina Al_2O_3 in solution $\alpha_k = 1.45$) was prepared by dissolving sodium hydroxide and aluminum hydroxide into the distilled water. Firstly, sodium oxalate

(SO, $\text{Na}_2\text{C}_2\text{O}_4$), sodium gluconate (SG, $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COONa}$), sodium stearate (SS, $\text{C}_{17}\text{H}_{35}\text{COONa}$), and sodium oleate (SOL, $\text{C}_{17}\text{H}_{33}\text{COONa}$) were used to prepare aqueous solutions. Afterward, the above organic solutions were added to the synthetic sodium aluminate solution, and the sodium aluminate solution containing the organic compound was then received. Meanwhile, Bayer liquor with $31.2 \text{ g}\cdot\text{L}^{-1}$ TOC from an alumina refinery (Longkou Donghai Alumina Co., Ltd.) was mixed with the above synthetic sodium aluminate solution, and the Bayer liquor with different TOC was finally present.

The surfactants and other reagents were of analytical grade. The sodium hydroxide and aluminum hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd and the surfactants were purchased from Shanghai Macklin Biochemical Technology Co., Ltd.

2.2. Methods and procedures

2.2.1. Surface tension and CMC

50 mL sodium aluminate solution containing organic compounds was held for 1 h and then the surface tension was measured by a fully automatic tensiometer (Krüss-K100, Germany) and Wilhelmy plate at different temperatures under water bath[25]. The CMC of sodium aluminate solution containing organic compounds were determined from the breakpoints of the tangent line both below and above the CMC [26]. The tangent lines were completed by simultaneously fitting Eq. (1):

$$\gamma = a \log C + b \quad (1)$$

where a and b are fitting parameters. γ is the surface tension. C is the organic concentration. The intersection point of the two straight lines was then determined as the CMC.

2.2.2. Determination of TOC

The industrial sodium aluminate solution ($C_{Na2OK} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$) was used to determine TOC with a TOC analyzer (Shimadzu, TOC-LCPH, Japan).

2.2.3. Measurement of solution viscosity

NXS-11B rotational viscometer (Chengdu Instruments Co., China) was used to determine the viscosity of the sodium aluminate solution under a water bath.

The shear stress τ in experiments was determined according to Eq. (2):

$$\tau = Z \times \alpha \quad (2)$$

Table 1
Interfacial parameters of organic compound in sodium aluminate solutions.

Organic compounds	Interfacial parameters	Temperature / K		
		298	308	318
SO	CMC/mol·L ⁻¹	1.17×10^{-3}	1.78×10^{-3}	2.29×10^{-3}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	3.63×10^{-6}	2.67×10^{-6}	2.75×10^{-6}
	A_{min}/m^2	4.57×10^{-19}	6.21×10^{-19}	6.03×10^{-19}
	$\delta/\text{\AA}$	2.07	1.53	1.57
SG	CMC/mol·L ⁻¹	7.41×10^{-4}	8.32×10^{-4}	1.12×10^{-4}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	5.34×10^{-6}	4.28×10^{-6}	4.34×10^{-6}
	A_{min}/m^2	3.10×10^{-19}	3.87×10^{-19}	3.82×10^{-19}
	$\delta/\text{\AA}$	6.61	5.30	5.37
SS	CMC/mol·L ⁻¹	2.40×10^{-4}	3.80×10^{-4}	6.17×10^{-4}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	7.05×10^{-6}	3.83×10^{-6}	3.31×10^{-6}
	A_{min}/m^2	2.36×10^{-19}	4.33×10^{-19}	5.02×10^{-19}
	$\delta/\text{\AA}$	19.58	10.65	9.19
SOL	CMC/mol·L ⁻¹	3.02×10^{-4}	3.39×10^{-4}	4.68×10^{-4}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	6.50×10^{-6}	4.98×10^{-6}	4.35×10^{-6}
	A_{min}/m^2	2.55×10^{-19}	3.34×10^{-19}	3.82×10^{-19}
	$\delta/\text{\AA}$	21.96	16.81	11.47
SO/SS	CMC/mol·L ⁻¹	2.29×10^{-4}	2.57×10^{-4}	3.31×10^{-4}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	6.30×10^{-6}	2.44×10^{-6}	3.05×10^{-6}
	A_{min}/m^2	2.64×10^{-19}	6.79×10^{-19}	5.45×10^{-19}
	$\delta/\text{\AA}$	3.61	1.35	1.64
SG/SO	CMC/mol·L ⁻¹	8.51×10^{-4}	1.07×10^{-3}	1.17×10^{-3}
	$\Gamma_{max}/\text{mol}\cdot\text{m}^{-2}$	5.24×10^{-6}	3.90×10^{-6}	3.52×10^{-6}
	A_{min}/m^2	3.17×10^{-19}	4.26×10^{-19}	4.71×10^{-19}
	$\delta/\text{\AA}$	6.49	4.83	4.36

where Z is a constant. $Z = 0.2767 \text{ Pa}\cdot\text{gram}^{-1}$; α is the value of the viscometer.

2.2.4. Interfacial parameters

According to the Gibbs equation, the maximum surface excess (Γ_{max}) was rewritten in the following Eq. (3):

$$\Gamma_{max} = -\frac{1}{2.303RT} \lim_{c \rightarrow c_{cmc}} \left(\frac{\partial \gamma}{\partial \log c} \right)_T \quad (3)$$

where R is $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. T is the temperature of the sodium aluminate solution.

The minimum cross-sectional headgroup area (A_{min}) and the saturated adsorption layer thickness (δ) were calculated according to the following Eqs. (4) and (5):

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \quad (4)$$

$$\delta = \frac{\Gamma_{max} M}{\rho} \quad (5)$$

where N_A is Avogadro's constant, M and ρ are the molar mass and density of the surfactant.

2.2.5. Viscous flow activation energy

The viscous flow activation energy was determined according to the Arrhenius Eq. (6):

$$\eta(T) = A e^{\frac{E_\eta}{RT}} \quad (6)$$

where the $\eta(T)$ is the viscosity of the sodium aluminate solution containing organic compound at different temperatures, A is a constant, E_η is the viscous flow activation energy, and R is $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

2.2.6. Diffusion coefficient

The diffusion coefficient was calculated according to the Stokes-Einstein Eq. (7) [27]:

$$D = \frac{kT}{6\pi\eta r^*} \quad (7)$$

where K is Boltzmann's constant, T is the temperature, η is the viscosity of the sodium aluminate solution, and r^* is the hydration radius of the sodium aluminate. The diameter of.

$\text{NaAl}(\text{OH})_4$ was estimated by cation radius plus the anionic radius, $r^* (\text{Na}^+) + r^* (\text{Al}(\text{OH})_4^-) = 1.91 + (1.4 + 0.285) = 3.595 \text{ \AA}$ [28].

3. Results and discussion

3.1. Effect of organics and temperature on the surface tension of sodium aluminate solutions

SO, SG, SS, and SOL all notably reduced the surface tension of sodium aluminate solutions, as shown in Fig. S1. The results were all consistent with that reported by P. Wu [5], mainly due to high ionic strength in the sodium aluminate solution. Meanwhile, elevating temperature decreased the surface tension of sodium aluminate solutions. In addition, the surface tension of the saturated interface (γ_m) ordered by $\text{SO} > \text{SG} > \text{SOL} \approx \text{SS}$, mainly relating to the long hydrophobic alkyl chains.

Owing to the interaction of various organic compounds, the effect of two organic mixtures on the surface tension of sodium aluminate solution is shown in Fig. 1. Compared to Fig. S1, increasing organic concentration and temperature both reduced surface tension, adding SS or SG further reduced surface tension of the sodium aluminate solution containing SO to $70.35 \text{ mN}\cdot\text{m}^{-1}$ and $70.08 \text{ mN}\cdot\text{m}^{-1}$, respectively. This is mainly attributed to the hydroxyl groups in SG and the long alkyl chain in SS.

3.2. Interfacial properties of organic compounds in the sodium aluminate solution

To determine the interfacial parameters of organic compounds in the sodium aluminate solution, CMC, maximum surface excess (Γ_{max}), minimum cross-sectional headgroup area (A_{min}), as well as the saturated adsorption layer thickness (δ) were calculated according to data in Fig. 1 and Fig. S1. Results are then shown in Table 1.

From Table 1, the CMC and A_{min} of the single organic compound in the sodium aluminate solutions at 298 K followed the order: $\text{SO} > \text{SG} > \text{SOL} > \text{SS}$, because the high molecular weight and organic compounds with hydroxyl group both easily assemble on the surface of the sodium aluminate solution. Meanwhile, the δ ordered by $\text{SOL} > \text{SS} > \text{SG} > \text{SO}$. These results suggest that organic compounds with long alkyl chains exhibit a tilted state with great A_{min} and less δ at the gas-liquid interface

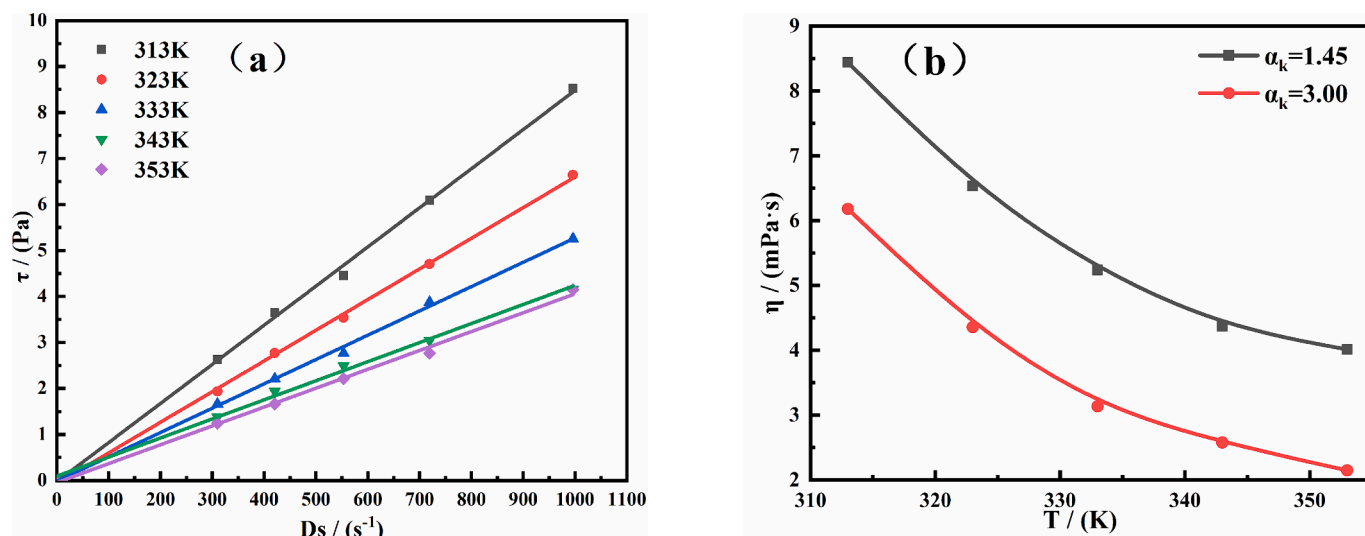


Fig. 2. Rheological curves of sodium aluminate solutions at different temperatures (a) and effect of temperature and molar ratio on the viscosity of the sodium aluminate solution (b) ($C_{Na2O} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{Al2O3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

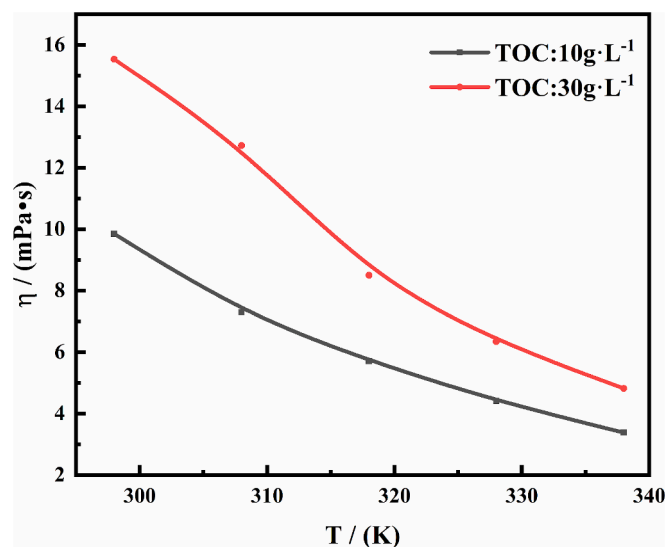


Fig. 3. Effect of TOC on the viscosity of the industrial sodium aluminate solution at different temperatures ($C_{Na2O} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{Al2O3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

different from “upright” at the interface for the low molecular weight organics. In addition, SG with the hydroxyl group and SO with a double bond slightly change the occurrence at the interface of the sodium aluminate solution [29]. In addition, compared to SS in water, CMC was becoming much less owing to the counterion in the solution with high ionic strength, as proven by Corrin-Harkins equation [5,30,31].

Furthermore, adding SS into the sodium aluminate solution containing SO reduced CMC. However, adding SO into the sodium aluminate solution containing SG increased CMC. This result suggests that mixed organic compounds will change the interfacial properties of sodium aluminate solutions. In terms of molecular structure, SS and SG are classified as straight-chain alkyl carboxylates, each possessing a single carboxyl group. SS and SG exhibit longer carbon chains and greater hydrophobicity compared to SO [32]. SO with two carboxyl groups, characterized by great CMC, can strongly interact with water molecules in the sodium aluminate solution to form a large number of hydrogen bonds. This interaction then changes water structures near the anionic surfactant micelles and weakens the hydrophobic effect, leading to the

rise of CMC. Consequently, SS and SG promoted micelle formation in the sodium aluminate solution relative to SO, leading to the concentration of SO reaching the minimum viscosity being higher than the CMC of the mixed SO/SS or SG/SO.

In addition, elevating temperature slightly increased CMC and A_{min} , but reduced Γ_{max} and δ due to occurrence changing from upright to tilted and loose at the interface [33].

3.3. Viscosity of the sodium aluminate solution without organic compound

The solution viscosity is from the internal friction of the sodium aluminate solution, and the internal friction is determined by the microstructure of the sodium aluminate solution. As shown in Fig. 2(a), the shear stress τ and shear rate Ds at different temperatures all followed the linear relationship with a zero intercept, proving Newtonian fluid of the sodium aluminate solution.

As different molecular ratios (α_k) and temperatures occur at different operations in the Bayer process, the effect of temperature and molecular ratio on the viscosity of the sodium aluminate solution without organic compound can be seen in Fig. 2(b).

Elevating temperature remarkably reduced the viscosity of the sodium aluminate solution in Fig. 2(b), mainly due to $Al_2O(OH)_6^{2-}$ and polymeric aluminate ions changing into $Al(OH)_4^-$ ions [34–36], and the increase in intermolecular distance. Meanwhile, a low molecular ratio remarkably increased the viscosity of the solution because reducing molar ratio with a high concentration of alumina favors the formation of polymerized aluminate ions and ion pairs in the solution [37–39].

3.4. Viscosity of the industrial sodium aluminate solution with high TOC

In addition to SO with low molecular weight, industrial sodium aluminate solutions generally contain high molecular weight organic compounds and medium molecular weight organic compounds with long alkyl chains and other functional groups [5,40]. Effects of TOC and temperature on the viscosity of sodium aluminate solutions are dotted in Fig. 3.

Similar to the viscosity variation in Fig. 2(b), elevating temperature remarkably reduced the viscosity in the industrial sodium aluminate solution. Different from the viscosity of the sodium aluminate solution ($<8.5 \text{ mPa}\cdot\text{s}$ at 298.15 K) without organic compound in Fig. 2(b), the high viscosity of the industrial sodium aluminate solution ($>9.85 \text{ mPa}\cdot\text{s}$ at 298.15 K) was observed in Fig. 3. Increasing TOC remarkably raised

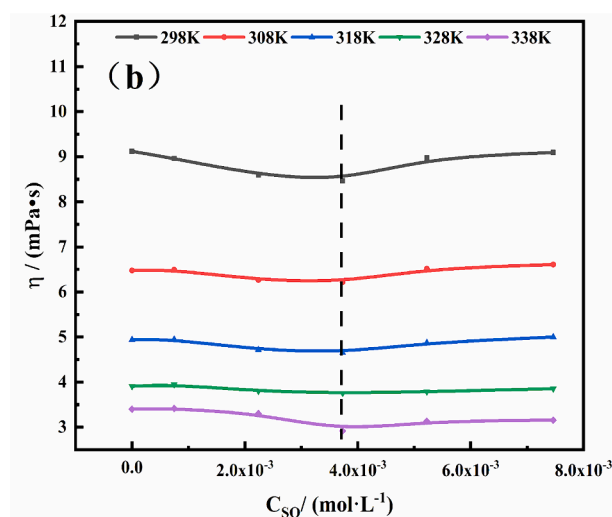
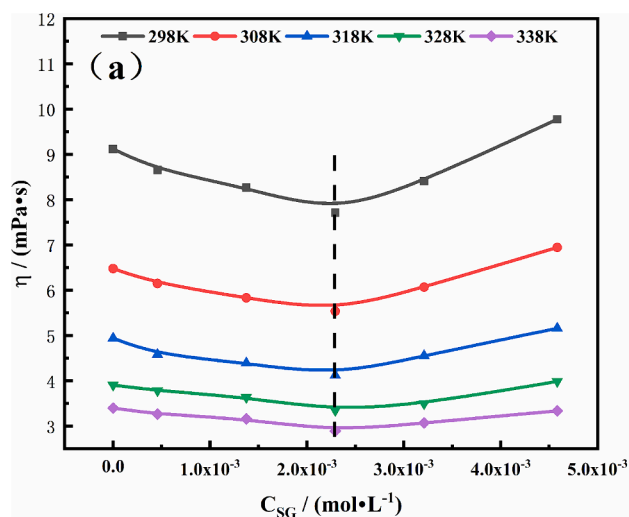


Fig. 4. Effect of organic concentration and temperature on viscosity of the sodium aluminate solution (a-SG, b-SO) ($C_{Na2O2K} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{Al2O3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

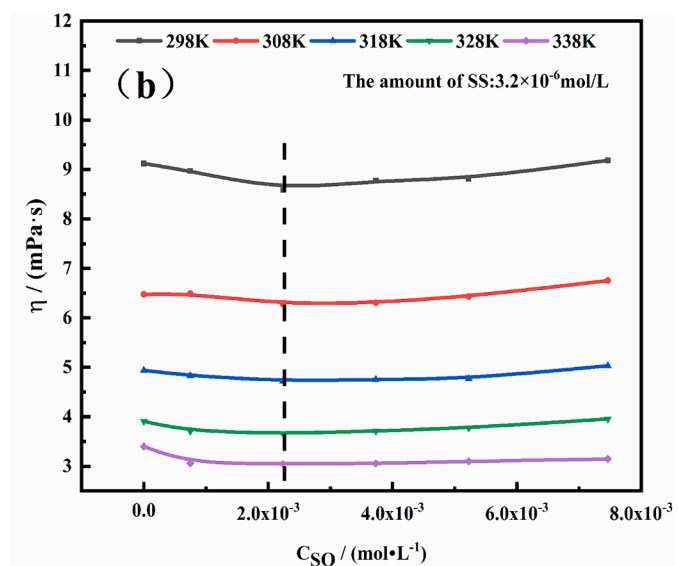
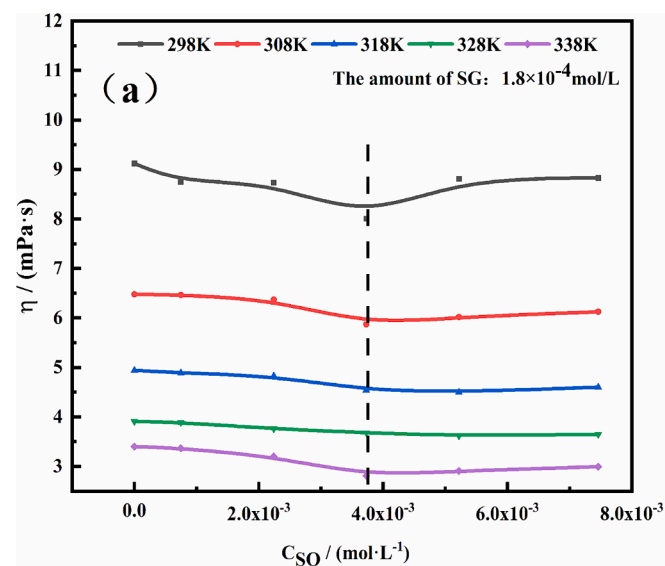


Fig.5. Effect of mixed organic concentration and temperature on viscosity of the sodium aluminate solution (a-SO/SG, b-SO/SS) ($C_{Na2O2K} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{Al2O3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

viscosity of the sodium aluminate solution. For example, the viscosities of the sodium aluminate solution with TOC of $10 \text{ g}\cdot\text{L}^{-1}$ and $30 \text{ g}\cdot\text{L}^{-1}$ were $9.85 \text{ mPa}\cdot\text{s}$, and $15.53 \text{ mPa}\cdot\text{s}$ at 298.15 K , respectively. Meanwhile, the viscosity of the sodium aluminate solution with TOC of $10 \text{ g}\cdot\text{L}^{-1}$ and $30 \text{ g}\cdot\text{L}^{-1}$ was $3.38 \text{ mPa}\cdot\text{s}$ and $4.82 \text{ mPa}\cdot\text{s}$ at 338 K , respectively. This fact proves that organic compounds in the industrial sodium aluminate solution remarkably increase the internal friction of the solution possibly due to changes in the structure of the sodium aluminate solution, and that elevating temperature lessens the organic effect on viscosity. Therefore, the exploration of the effect of organic compounds on the viscosity of the sodium aluminate solution is interesting and worthwhile.

3.5. Effect of the organic compound on the viscosity of the sodium aluminate solution

To provide insight into the organic compound effect on the structure of the sodium aluminate solution, the synthetic sodium aluminate solution with a low concentration of organic compound was adopted. SO

and SG with short alkyl chain and SS with long alkyl chain were then added. The effect of the single organic compound on the viscosity of the sodium aluminate solution was first studied, and the effect of the mixture of organic compounds was then investigated.

3.5.1. Effect of the single organic compound on the viscosity of the sodium aluminate solution

Fig. 4 displays the effect of the single organic compound on the viscosity of the sodium aluminate solution. Relative to the sodium aluminate solution without organics, SG and SO in the solution changed the viscosity of the solution.

The viscosity of the sodium aluminate solution initially decreased and then increased with the increase of organic compound concentration by adding SO or SG into the sodium aluminate solution. For example, the viscosity of the sodium aluminate solution decreased to the minimum of $7.71 \text{ mPa}\cdot\text{s}$ and $8.47 \text{ mPa}\cdot\text{s}$ at $2.29 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ SG and $3.73 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ SO (at 298 K), respectively. Interestingly, the above concentrations were nearly equal to CMC of SO ($1.17 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) and SG ($7.41 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) in Table 1. The circumstance suggests that pre-

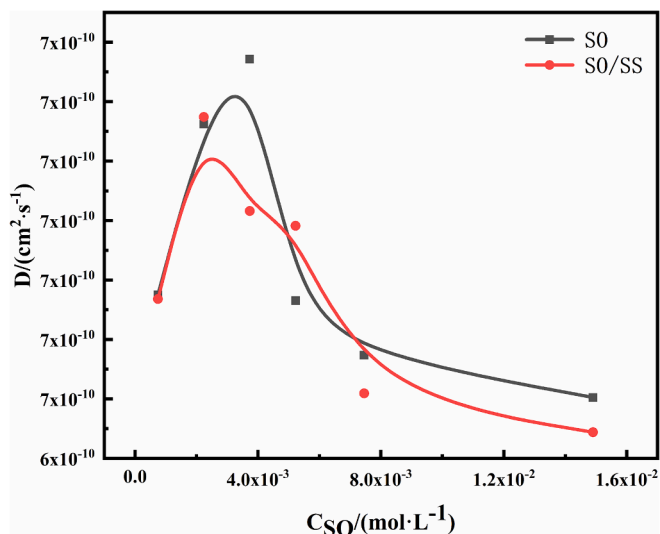


Fig. 6. Effect of SO concentration on the diffusion coefficient in the sodium aluminate solutions ($C_{\text{Na}_2\text{O}_K} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{\text{Al}_2\text{O}_3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

micelles and micelles had a remarkable effect on the viscosity of the sodium aluminate solution. Generally, the anionic polar carboxyl group in SO or SG, acting as structure-breaking at low concentrations, results in the disordered structure of the solution [41] accordingly decreasing the solution viscosity. When organic concentration is more than CMC, pre-micelles or micelles with large spherical polar heads in turn act as structure-making, benefiting the ordered structure of solution and raising viscosity. Furthermore, an increase in organic concentration promotes the ordered structure of the solution, giving rise to a further increase in viscosity in Fig. 3. The large micelle in the sodium aluminate solution also raises the intermolecular friction.

In addition to the increase in molecular distance, elevating temperature also increased the solubility of the organic compound in solution, the increase of CMC and fewer micelles then reduced molecular friction. Thus, high temperature reduced viscosity. This fact also explains that the minimum viscosity of the solution was not easily found at high temperatures (at 338 K).

3.5.2. Effect of organic mixtures on the viscosity of the sodium aluminate solutions

Similarly, the effect of the organic mixture on the viscosity of sodium aluminate solution is shown in Fig. 5.

Elevating temperature reduced the viscosity. Increasing the

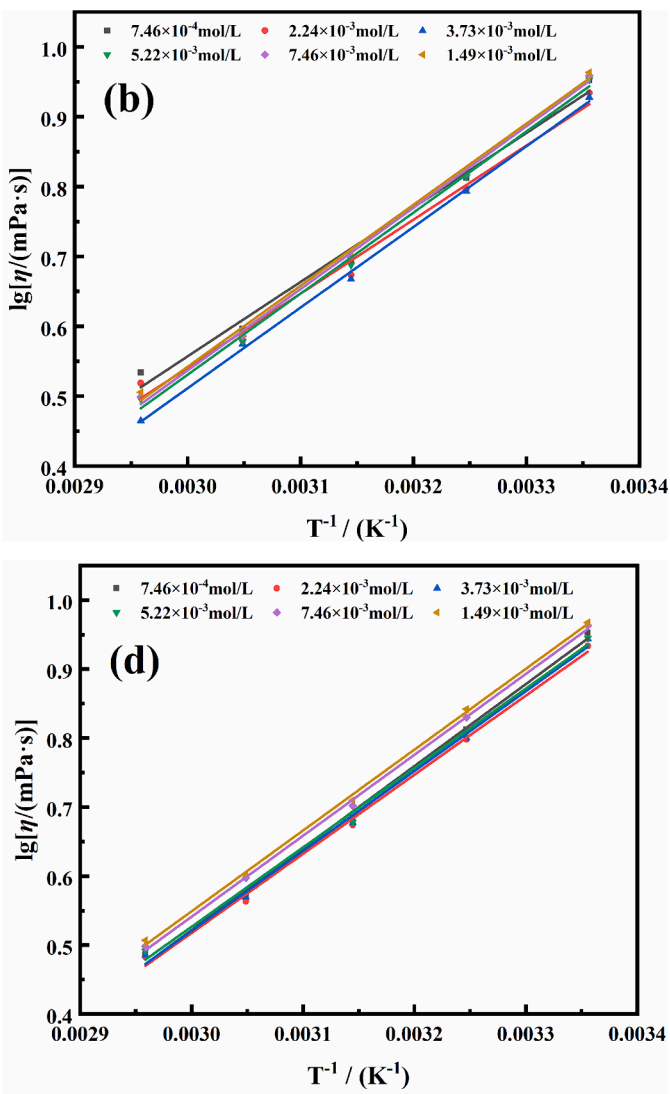
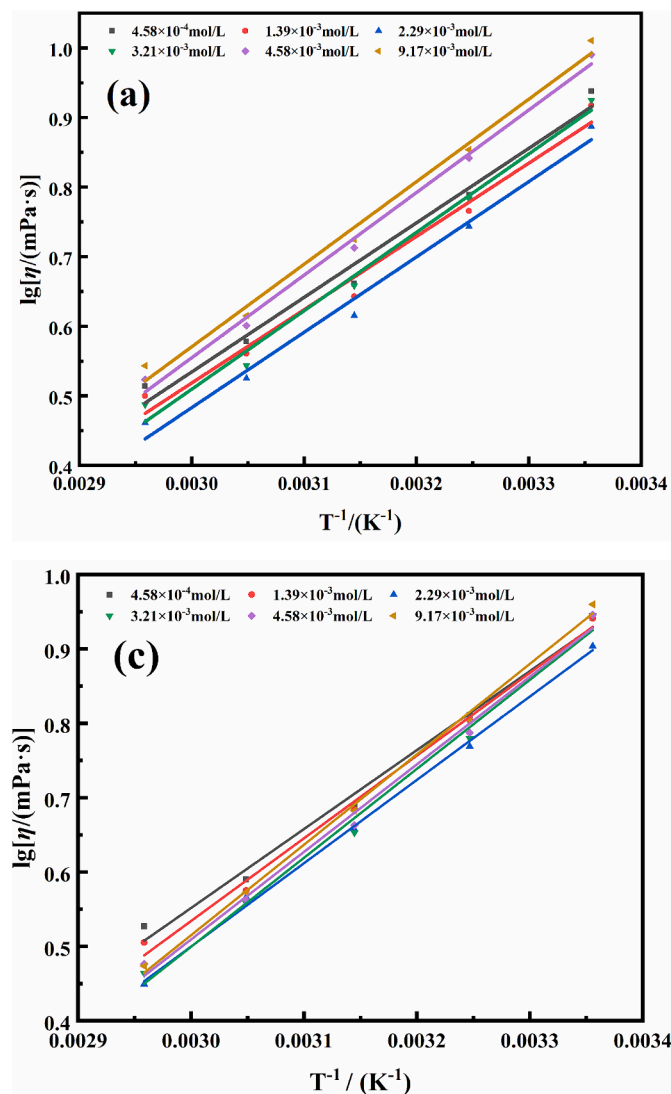


Fig. 7. Relationship between logarithmic viscosity $\lg\eta$ and temperature T^{-1} in the sodium aluminate solution after adding different organic compound (a-SG, b-SO, c-SO/SG, d-SO/SS) ($C_{\text{Na}_2\text{O}_K} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{\text{Al}_2\text{O}_3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

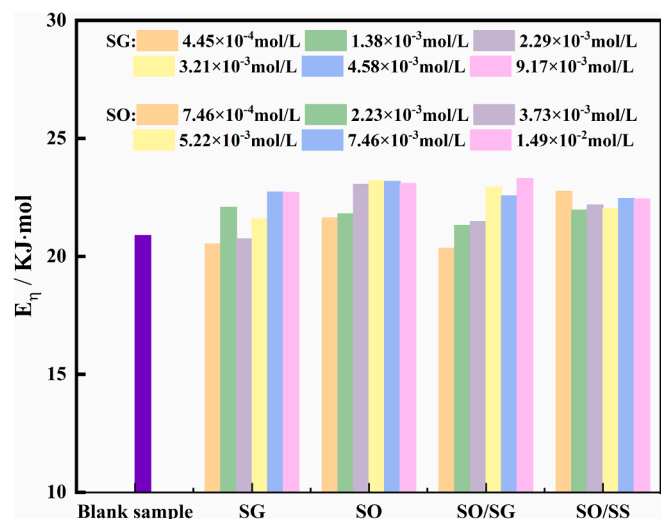


Fig. 8. Effect of the organic compound on viscous flow activation energy in the sodium aluminate solution ($C_{\text{Na}_2\text{O}_K} = 2.42 \text{ mol}\cdot\text{L}^{-1}$, $C_{\text{Al}_2\text{O}_3} = 1.67 \text{ mol}\cdot\text{L}^{-1}$, $\alpha_k = 1.45$).

concentration of the organic mixture in the sodium aluminate solution also generated a minimum viscosity at low temperatures. Compared to the results of the solution containing the single surfactant, adding $1.8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ SG into the solution containing SO resulted in the minimum viscosity of $8.01 \text{ mPa}\cdot\text{s}$, which was $0.46 \text{ mPa}\cdot\text{s}$ less than the viscosity of the solution containing single SO. Meanwhile, after $3.2 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ SS was added into the solution containing SO, the concentration of SO reaching the minimum viscosity was reduced from $3.73 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ to $2.24 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, which the minimum viscosity was $8.58 \text{ mPa}\cdot\text{s}$. This is due to that the long alkyl chain in SS results in a smaller CMC for the sodium aluminate solution with the SO/SS system than the single SO system, readily generating micelles. In addition, because SG and SS concentration were less than CMC, the minimum viscosity occurred at near CMC of SO, instead of CMC of the mixture in Table 1.

3.6. Effect of organic concentration on the diffusion coefficient of the sodium aluminate solution

To explore the effect of the organic compound on seeded precipitation rate in the sodium aluminate solution, diffusion coefficients in solution containing SO and organic mixture at 298 K are present in Fig. 6.

In contrast to the variation of viscosity, adding SO initially increased and then decreased the diffusion coefficient of the sodium aluminate solution. A similar variation was also observed in the sodium aluminate

solution by adding mixture of SO/SS. The maximum diffusion coefficient nearly occurred at CMC of the sodium aluminate solution with SO/SS. This is mainly due to structural changes in the sodium aluminate solution and water. The disordered structure of the sodium aluminate solution is generated at a low concentration (less than CMC) owing to SO or the mixture of SS and SO acting as structure-breaking. The charged micelles from the high concentration of organic compound (more than CMC), acting as structure-making, promote the formation of the ordered structural the sodium aluminate solution and water, notably reducing the diffusion coefficient. Meanwhile, a large amount of micelles in the solution also raised the viscosity, correspondingly further reducing the diffusion coefficient. In addition, the long alkyl chain in SS further reduced the diffusion coefficient, mainly owing to the enlarged micelles. Those findings are well in agreement with the facts that the low concentration of surfactant (organic additives) increased precipitation efficiency in the published papers, whereas high concentration of organic compounds notably reduced precipitation efficiency in practice. Furthermore, although some organic compounds were found to raise precipitation efficiency and benefit particle agglomeration in the synthetic sodium aluminate solution, organic additives were scarcely applied in alumina refineries, mainly owing to complex interaction among various organic compounds and high concentration of organic compounds ($\text{TOC} > 5 \text{ g}\cdot\text{L}^{-1}$) occurred in Bayer liquor. Consequently, the positive effect on precipitation disappeared [11].

3.7. Effect of organic concentration on the viscous flow activation energy of the sodium aluminate solutions

The viscous flow activation energy can provide a sensitive variation of viscosity at different temperatures. Based on data in Fig. 4 and Fig. 5, Fig. 7 presents the relationship between $\lg \eta$ and T^{-1} . The logarithmic viscosity of sodium aluminate solution containing anionic organic compound was linearly related to the reciprocal temperature with correlation coefficients more than 0.98. The correlation coefficients, as well as slope and intercept, are all displayed in Table S1.

Based on data in Fig. 7, Fig. 8 presents the variation of viscosity flow activation energy after adding the organic compound. Unlike the low viscous flow activation energy in the sodium aluminate solution without organic compound, adding organic compound slightly raised viscous flow activation energy. However, SS had minor effect on the viscous flow activation energy in solution containing SO, whereas $1.80 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ SG with hydroxyl group slightly generated a low viscous flow activation energy in solution containing SO. This finding implies that the viscosity of a solution containing anionic organics remarkably depends on temperature as proven in Fig. 4 and Fig. 5. Those circumstances are mainly attributed to the formation of micelles of SO. The charged micelles lead to the ordered structure of the sodium aluminate solution,

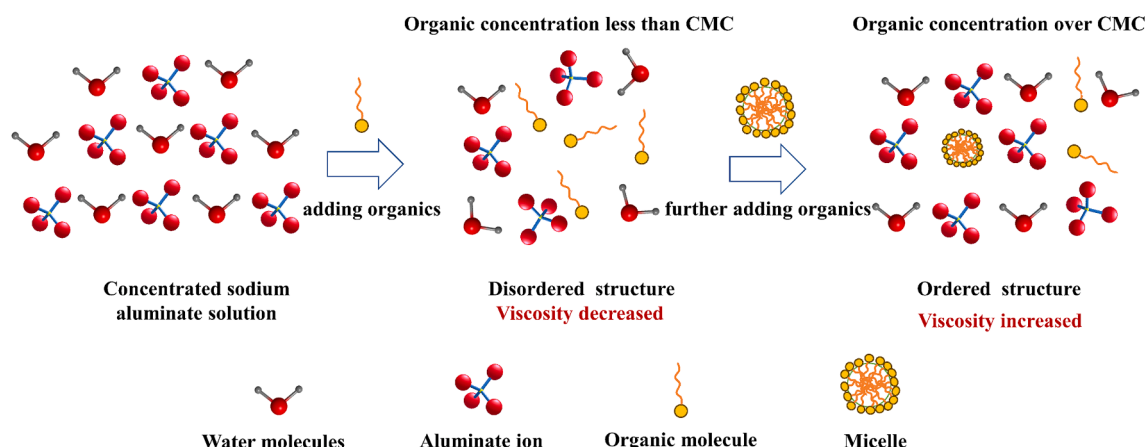


Fig. 9. Schematic diagram of organic effect on the structure of the sodium aluminate solution.

raising intermolecular friction and increasing viscosity. Accordingly, low diffusion coefficient and multilayer adsorption from micelles[42] on seeds both reduce precipitation efficiency and change the growth and agglomeration of gibbsite particles in alumina refineries.

In addition, SO with bicarboxy groups can further promote the ordered structure of the sodium aluminate solution due to its strong electrostatic field. This high viscous flow activation energy from high viscosity for SO in Bayer liquor generally generates fine particles with a high content of Na₂O in the coarse gibbsite during the seeded precipitation.

3.8. Mechanism of the organic compound on the viscosity of the sodium aluminate solution

Based on the results of surface tension and viscosity, the effect of the organic compound on the solution structure can be seen in Fig. 9. Owing to the anionic organic polar group acting as structure-breaking at low concentration, adding organic anions generated the disordered structure of the sodium aluminate solution or water, reducing viscosity and raising diffusion coefficient of the sodium aluminate. This then improves precipitation efficiency in practice. However, as the concentration of anionic organic compound increased more than CMC, the notably charged micelles with the strong electrostatic field from carboxyl or hydroxyl groups acted as structure-making, the ordered structure of solution was formed, increase in viscosity and reduction in diffusion coefficient then occurred. Furthermore, the micelles also raised the intermolecular friction, further increasing viscosity and reducing of diffusion coefficient. Low precipitation efficiency and slow precipitation rate with poor quality of gibbsite can be found. Elevating temperature raised CMC and changed solution structure, leading to reduction in viscosity and increase in diffusion coefficient of the sodium aluminate solution. Therefore, the different solution structures and a large amount of micelles synergistically changed the viscosity and diffusion coefficient of the sodium aluminate solution. Additionally, great TOC in the Bayer liquor will notably reduce precipitation efficiency and degrade alumina quality.

4. Conclusions

- (1) The CMC and A_{min} of single surfactants in sodium aluminate solutions at 298 K ordered by SO > SG > SOL > SS, opposing from Γ_{max} . Meanwhile, the δ followed the order at 298 K: SOL > SS > SG > SO. The SG with hydroxyl group or SS with long chain slightly changed interfacial parameters of CMC, Γ_{max} , A_{min} , and δ in solution containing SO.
- (2) Adding organic compound initially decreased and then raised the viscosity of the sodium aluminate solution, and elevating temperature reduced the viscosity of the sodium aluminate solution. Increasing total organic carbon (TOC) remarkably increased the viscosity of the industrial sodium aluminate solution. The minimum viscosity of the solution nearly occurred at CMC of the anionic organic compound. The logarithmic viscosity was linearly related to the reciprocal temperature. Adding anionic organic compound increased the viscous flow activation energy of sodium aluminate solutions compared to the sodium aluminate solution without organic compound.
- (3) Adding anionic organic compound less than CMC gave rise to the disordered structure of the sodium aluminate solution, reducing the viscosity and raising the diffusion coefficient of the solution. Increasing organic concentration over CMC raised the viscosity and decreased the diffusion coefficient of the solution. Moreover, adding SS with a long alkyl chain further reduced the diffusion coefficient of the solution. In addition to increased intermolecular friction of the sodium aluminate solution from micelles, the notably charged micelles acting as structure-making also led to the ordered structure of the sodium aluminate solution,

correspondingly increasing viscosity and reducing diffusion coefficient of the sodium aluminate solution.

CRediT authorship contribution statement

Baoyin Chen: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Guihua Liu:** Writing – review & editing, Methodology, Funding acquisition. **Tiangui Qi:** Writing – review & editing. **Zhenjiang Fu:** Writing – review & editing, Conceptualization. **Leiting Shen:** Writing – review & editing. **Yiling Wang:** Writing – review & editing, Investigation. **Zhihong Peng:** Writing – review & editing. **Qiusheng Zhou:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors gratefully acknowledge the financial support from the National Key Research and Development Plan Key Projects (2022YFC2904404) and the National Natural Science Foundation of China (51874366).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2024.124557>.

References

- [1] I.A. Institute, Alumina production statistics reports, 2022. <https://www.worldaluminium.org/statistics/aluminaproduction>.
- [2] G. Zhou, Y. Wang, T. Qi, Q. Zhou, G. Liu, Z. Peng, X. Li, Toward sustainable green alumina production: a critical review on process discharge reduction from gibbsitic bauxite and large-scale applications of red mud, Journal of Environmental Chemical Engineering 11 (2) (2023) 109433, <https://doi.org/10.1016/j.jece.2023.109433>.
- [3] G. Power, J.S.C. Loh, K. Niemelä, Organic compounds in the processing of lateritic bauxites to alumina addendum to Part 1: origins and chemistry of organics in the Bayer process, Hydrometallurgy 108 (1–2) (2011) 149–151, <https://doi.org/10.1016/j.hydromet.2011.03.011>.
- [4] G. Power, J.S.C. Loh, J.E. Wajon, F. Buseti, C. Joll, A review of the determination of organic compounds in Bayer process liquors, Analytica Chimica Acta 689 (1) (2011) 8–21, <https://doi.org/10.1016/j.jaca.2011.01.040>.
- [5] P. Wu, G.H. Liu, X.B. Li, Z.H. Peng, Q.S. Zhou, T.G. Qi, Effects of CMC and micelle formation on the removal of sodium benzoate or sodium Stearate in a sodium aluminate solution, Jom 72 (1) (2020) 263–269, <https://doi.org/10.1007/s11837-019-03853-6>.
- [6] Y. Zhang, R. Xu, H. Tang, L. Wang, W. Sun, A review on approaches for hazardous organics removal from Bayer liquors, Journal of Hazardous Materials 397 (2020) 122772, <https://doi.org/10.1016/j.jhazmat.2020.122772>.
- [7] J. Zeng, Z. Yin, Q. Chen, Intensification of precipitation of gibbsite from seeded caustic sodium aluminate liquor by seed activation and addition of crown ether, Hydrometallurgy 89 (1–2) (2007) 107–116, <https://doi.org/10.1016/j.hydromet.2007.07.001>.
- [8] X. Li, L. YAN, Q. ZHOU, Z. PENG, G. LIU, Effect of ethers additive B35 on seeded precipitation of sodium aluminate solution The Chinese Journal of Nonferrous Metals 21(02) (2011) 459–464. 10.19476/j.ysxb.1004.0609.2011.02.031.
- [9] B. LÜ, Q.Y. Chen, Z. YIN, H. HU, Effects of Na4EDTA and EDTA on seeded precipitation of sodium aluminate solution, Transactions of Nonferrous Metals Society of China 20(S1) (2010) 37–41. [https://doi.org/10.1016/S1003-6326\(10\)60008-8](https://doi.org/10.1016/S1003-6326(10)60008-8).
- [10] Y. Zhang, S. Zheng, H. Du, H. Xu, S. Wang, Y. Zhang, Improved precipitation of gibbsite from sodium aluminate solution by adding methanol, Hydrometallurgy 98 (1) (2009) 38–44, <https://doi.org/10.1016/j.hydromet.2009.03.014>.

- [11] H. Yu, B. Zhang, X. Pan, G. Tu, Effect of oxalate on seed precipitation of gibbsite from sodium aluminate solution, *Journal of Central South University* 27 (3) (2020) 772–779, <https://doi.org/10.1007/s11771-020-4330-1>.
- [12] P. Wu, G. Liu, X. Li, Z. Peng, Q. Zhou, T. Qi, Y. Wang, L. Shen, Removal of organics from Bayer liquors via foam flotation, *Journal of Cleaner Production* 336 (2022), <https://doi.org/10.1016/j.jclepro.2021.130353>.
- [13] H.L. Watts, D.W. Utley, Sodium gluconate as complexing agent in volumetric analysis of aluminum compounds, *Analytical Chemistry* 28 (11) (1956) 1731–1735, <https://doi.org/10.1021/ac60119a025>.
- [14] K.R. Seddon, A. Stark, M.-J. Torres, Viscosity and density of 1-Alkyl-3-methylimidazolium ionic liquids, *Clean Solvents* 819 (819) (2002) 34–49, <https://doi.org/10.1021/bk-2002-0819.ch004>.
- [15] J. Wang, R. Liu, B. Wang, Z. Cheng, C. Liu, Y. Tang, J. Zhu, Synthesis of polyether Carboxylate and the effect of different electrical properties on its viscosity reduction and emulsification of heavy oil, *Polymers* 15 (14) (2023) 3139, <https://doi.org/10.3390/polym15143139>.
- [16] F. Zhang, Q. Zhang, Z.H. Zhou, L.L. Sun, Y.W. Zhou, Study on the effect of different viscosity reducers on viscosity reduction and emulsification with Daqing crude oil, *Molecules* 28 (3) (2023), <https://doi.org/10.3390/molecules28031399>.
- [17] R.M. Fuoss, U.P. Strauss, Electrostatic interaction of polyelectrolytes and simple electrolytes, *Journal of Polymer Science* 3 (4) (1948) 602–603, <https://doi.org/10.1002/pol.1948.120030413>.
- [18] H. Yang, Q. Zheng, R. Cheng, New insight into “polyelectrolyte effect”, *Colloids and Surfaces a: Physicochemical and Engineering Aspects* 407 (2012) 1–8, <https://doi.org/10.1016/j.colsurfa.2012.05.031>.
- [19] K.A. Dill, T.M. Truskett, V. Vlasy, B. Hribar-Lee, Modeling water, the hydrophobic effect, and ion solvation, *Annual Review of Biophysics and Biomolecular Structure* 34 (1) (2005) 173–199, <https://doi.org/10.1146/annurev.biophys.34.040204.144517>.
- [20] J. Prelesnik, L. Maibaum, Effects of salts on the solvation of hydrophobic objects in water, *Journal of Physical Chemistry B* 125 (39) (2021) 11036–11043, <https://doi.org/10.1021/acs.jpcc.1c06833>.
- [21] S. Kumar, B. Bagchi, Anomalous concentration dependence of viscosity: hidden role of cross-correlations in aqueous electrolyte solutions, *The Journal of Physical Chemistry B* 127 (51) (2023) 11031–11044, <https://doi.org/10.1021/acs.jpcc.3c05117>.
- [22] T. Ikkatai, N. Okada, Viscosity, specific gravity, and equilibrium concentration of sodium aluminate solutions, in: D. Donaldson, B.E. Raahauge (Eds.), *Essential Readings in Light Metals: Volume 1 Alumina and Bauxite*, Springer International Publishing, Cham, 2016, pp. 162–169.
- [23] Q. Cheng, X. Li, Z. Peng, G. Liu, Q. Zhou, Viscosity of sodium aluminate solution, *J. CENT.SOUTH UNIV. (SCI ENCE AND TECHNOLOGY)* (02) (2005) 229–233.
- [24] J. Li, C.A. Prestidge, J. Addai-Mensah, Viscosity, density, and refractive index of aqueous sodium and potassium aluminate solutions, *Journal of Chemical and Engineering Data* 45 (4) (2000) 665–671, <https://doi.org/10.1021/jc000025d>.
- [25] N. Wu, J. Dai, F.J. Micale, Dynamic Surface tension measurement with a dynamic wilhelmy plate technique, *Journal of Colloid and Interface Science* 215 (2) (1999) 258–269, <https://doi.org/10.1006/jcis.1999.6270>.
- [26] E. Frottscher, J. Höring, G. Durand, C. Vargas, S. Keller, Model-free analysis of critical Micellar concentrations for detecting demixing in Surfactant mixtures, *Analytical Chemistry* 89 (6) (2017) 3245–3249, <https://doi.org/10.1021/acs.analchem.7b00339>.
- [27] R. Lamanna, M. Delmelle, S. Cannistraro, Solvent stokes-einstein violation in aqueous protein solutions, *Physical Review E* 49 (6) (1994) 5878–5880, <https://doi.org/10.1103/PhysRevE.49.5878>.
- [28] R. i., On the investigation of the physico-chemical properties and activating thermodynamic functions of the systems NaOH-H₂O and NaOH-H₂O-Al₂O₃, *Budapest:Bauxite-alumina-aluminium. Proceedings of Second International Symposium of the International Committee for Studies of Bauxites, Oxides and Hydroxides of Aluminum (ICSOPA)*, 1971.
- [29] K. Utriainen, Soap micelles in nonpolar media, 2018.
- [30] S.I. Karakashev, S.K. Smoukov, CMC prediction for ionic surfactants in pure water and aqueous salt solutions based solely on tabulated molecular parameters, *Journal of Colloid and Interface Science* 501 (2017) 142–149, <https://doi.org/10.1016/j.jcis.2017.04.046>.
- [31] J. Dey, N. Sultana, K. Ismail, Counter ion binding in solutions of sodium dodecylsulfate in water–ethylene glycol mixtures and the corrin-Harkins equation, *Journal of Molecular Liquids* 207 (2015) 107–111, <https://doi.org/10.1016/j.molliq.2015.03.030>.
- [32] B. Kumar, D. Tikariha, K.K. Ghosh, Effects of electrolytes on Micellar and Surface properties of some Monomeric Surfactants, *Journal of Dispersion Science and Technology* 33 (1–3) (2012) 265–271, <https://doi.org/10.1080/01932691.2011.561178>.
- [33] S. Ghosh, A. Ray, N. Pramanik, Self-assembly of surfactants: an overview on general aspects of amphiphiles, *Biophysical Chemistry* 265 (2020), <https://doi.org/10.1016/j.bpc.2020.106429>.
- [34] E.T. Nienhuis, M. Pouvreau, T.R. Graham, M.P. Prange, K. Page, J.S. Loring, A. G. Stack, A.E. Clark, G.K. Schenter, K.M. Rosso, C.I. Pearce, H.-W. Wang, Structure and reactivity of sodium aluminate complexes in alkaline solutions, *Journal of Molecular Liquids* 367 (2022) 120379, <https://doi.org/10.1016/j.molliq.2022.120379>.
- [35] G.Z. Mal'tsev, G.V. Malinin, V.P. Mashovets, V.A. Shcherbakov, Thermodynamic properties and H1 and Na23 NMR spectra of sodium hydroxide solutions, *Journal of Structural Chemistry* 6 (3) (1966) 353–358, <https://doi.org/10.1007/BF00779323>.
- [36] M. Abdallah, A.S. Fouda, D.A.M. El-Nagar, M.M. Ghoneim, Electrochemical and theoretical investigation for the protection of aluminum corrosion in hydrochloric acid using some azole derivatives, *Protection of Metals and Physical Chemistry of Surfaces* 54 (6) (2018) 1204–1212, <https://doi.org/10.1134/S2070205118060023>.
- [37] P. Sipos, The structure of al (III) in strongly alkaline aluminate solutions—A review, *Journal of Molecular Liquids* 146 (1–2) (2009) 1–14, <https://doi.org/10.1016/j.molliq.2009.01.015>.
- [38] G. Liu, Z. Li, T. Qi, Q. Zhou, Z. Peng, X. Li, Continuous changes in electrical conductivity of sodium aluminate solution in seeded precipitation, *Transactions of Nonferrous Metals Society of China* 25 (12) (2015) 4160–4166, [https://doi.org/10.1016/S1003-6326\(15\)64066-3](https://doi.org/10.1016/S1003-6326(15)64066-3).
- [39] Z. Li, G. Liu, X. Li, T. Qi, Z. Peng, Q. Zhou, Effects of cation on the morphology of boehmite precipitated from alkaline solutions by adding gibbsite as seed, *Crystal Growth & Design* 19 (3) (2019) 1778–1785, <https://doi.org/10.1021/acs.cgd.8b01756>.
- [40] P. Wu, T. Xue, G.H. Liu, X.B. Li, Z.H. Peng, Q.S. Zhou, T.G. Qi, Interfacial behavior and micellization of binary surfactant mixtures in the concentrated sodium aluminate solution, *Journal of Molecular Liquids* 334 (2021), <https://doi.org/10.1016/j.molliq.2021.116530>.
- [41] Y. Marcus, Effect of ions on the structure of water: structure making and breaking, *Chemical Reviews* 109 (3) (2009) 1346–1370, <https://doi.org/10.1021/cr8003828>.
- [42] P. Wu, G.H. Liu, X.B. Li, Z.H. Peng, Q.S. Zhou, T.G. Qi, Y.L. Wang, L.T. Shen, H. Fang, Y.L. Wang, Multilayer adsorption improving the organic removal by foam flotation from sodium aluminate solutions, *Colloids and Surfaces a- Physicochemical and Engineering Aspects* 654 (2022), <https://doi.org/10.1016/j.colsurfa.2022.130126>.