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Studies on the solubilization of aqueous methylene blue in surfactant using MEUF

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ABSTRACT

The solubilization of methylene blue (MB) in sodium dodecyl sulfate (SDS) using hollow fiber membrane was studied. In MEUF, the effects of important factors (MB and SDS concentrations, temperature and electrolyte concentration) on the permeate and retentate concentrations of MB and SDS, equilibrium distribution constant (K_d) and micelle loading (L_m) were investigated. It was found that MB molecules could be solubilized fully within micelles of SDS. The increase of feed SDS concentration promoted retentate MB concentration. Temperature could change the SDS micellization effect. The addition of NaCl could improve the retentate MB and SDS concentrations and reduce significantly the permeate SDS concentration.

1. Introduction

The effluents containing methylene blue (MB) may lead to serious problems, which has a harmful influence on human health and environment. Many methods have been applied to remove dyes from wastewater in the current literatures, such as chemical oxidation, adsorption, precipitation, biodegradation, flotation, ion exchange, nanofiltration and reverse osmosis. However, there are inherent deficiencies in these technologies, such as high cost, low efficiency and inconvenient operation [1,2]. Accordingly, micellar-enhanced ultrafiltration (MEUF) is recognized in the disposal of trace amounts and low concentration of organic matters and/or heavy metal ions. This technology has a series of advantages of high efficiency, low energy consumption, small space demand, no phase change, low operative pressure and high permeate flux [3–5]. Furthermore, it is feasible to be inserted into the entire treatment process. For example, reactive dyes were removed from an aqueous solution by coagulation and MEUF combined processes [6]; electrolysis and MEUF processes were combined for heavy metal removal [7].

In MEUF process, the surfactant containing hydrophobic and hydrophilic groups is added into the solution containing organic matters or heavy metal ions. The surfactant aggregates to form large amphiphilic micelles that bind the solutes. The micelle is made up of the inner core (constituted by hydrophobic groups), palisade layer (constituted by CH_2 groups) and outer layer (constituted by hydrophilic groups). The organic matters get embedded in the micelles via "like dissolves like" principle while heavy metal ions are adsorbed on the opposite-charged micelles via electrostatic interaction [8,9]. The micelles along with the solutes are rejected into the retentate stream by ultrafiltration membrane. Due to different solubilization principles, organic and inorganic contaminants could be retained simultaneously by MEUF [10,11]. The solubilization system of organic matters or heavy metal ions with surfactant is a dynamic balance system, namely, the location of solutes in micelles changes with time. It spends only 10^6–10^{10} s on solutes within micelles [12]. If solubilization effect is seen as the distribution of solutes between micelles and water, the equilibrium distribution constant (K_d) and micelle loading (L_m) could be estimated [3,13,14].

Large ionic dyes, such as MB and eriochrome blue black, can be solubilized into the hydrophobic and hydrophilic medias in micelles, or dissociate to ions which are adsorbed on the surfactant micelles [15,16]. Therefore, opposite-charged surfactant should be utilized to retain these organics in order to obtain the high rejection in MEUF, which was proved by the literatures [17,18]. The type of surfactant is the dominant factor affecting the solubilization capability. In this study, anionic surfactant sodium dodecyl sulfate (SDS) was chosen to solubilize cationic MB molecules.

MEUF method aims to discharge the permeate solutions containing water, small amounts of solutes and free surfactants into streams and recycle the organic matters, heavy metal ions

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Table 1
Properties of MB.

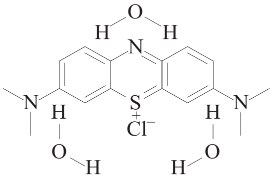
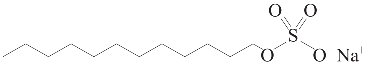
Formula	Molecular structure	Molecular weight	Type
$C_{16}H_{18}ClN_3S{\cdot}3H_2O$		373.90 g/mol	Cationic dye

Table 2
Properties of SDS.

Formula	Molecular structure	Molecular weight	Type	CMC
$C_{12}H_{25}NaO_4S$		288.38 g/mol	Anionic surfactant	8.0 mM

and surfactants enriched in the retentate. These make the MEUF technology more economical. For instance, the chelation and acidification methods were used to recover SDS from a MEUF retentate containing Cd^{2+} or Zn^{2+} by ultrafiltration [19]; the surfactant hexadecyl pyridinium chloride (CPC) from retentate and permeate solutions was recovered by a two-step chemical treatment process [8].

In the present work, the effects of feed MB and SDS concentrations, temperature and NaCl concentration on permeate and retentate concentrations of MB and SDS were studied. In addition, the equilibrium distribution constant (K_d) and micelle loading (L_m) values, of MB between SDS micelles and water were also estimated. As is well known, the addition of surfactant causes the secondary pollution. Nonionic surfactant is often utilized to reduce the permeate surfactant concentration. It was found in this work that the NaCl which is economical and nontoxic could improve retentate MB and SDS concentrations and decrease significantly the permeate SDS concentration.

2. Materials and methods

2.1. Specimen preparation

MB offered from Shanghai SSS reagent Co., Ltd., China, was selected as a kind of dye. SDS offered from Tianjin Kermel Chemical Reagent Co., Ltd., China, was selected as a kind of surfactant. The properties of MB and SDS are listed in Tables 1 and 2 respectively. NaCl and HCl were purchased by Sinopharm Chemical Reagent Co., Ltd., China. NaOH with a purity of 96% was offered from Tianjin No. 3 Chemical Reagent Factory. In addition, the distilled water was used in all experiments.

2.2. Ultrafiltration

Ultrafiltration was performed in an experimental setup (ZM50-1) with the hollow fiber membrane (ZU503-22), procured from Yidong Membrane Engineering Equipment, Ltd., Dalian, China. The membrane was made of polysulfone. The pore size of the membrane was 10,000 Da and the effective membrane area was 0.8 m^2. The feed tank was initially filled with 2 L solution. The retentate stream was recycled to the feed tank. When the feed solution was left over 0.5 L, permeate and retentate solutions were collected to be determined. After each run, the membrane had to be washed with distilled water to ensure that the permeability remain almost constant.

2.3. Measurement and analysis

UV spectroscopy analysis on MB and SDS was performed with Shimadzu UV-2550 (P/N206-55501-93) spectrophotometer from Japan. The SDS concentration was analyzed by the methylene blue spectrophotometric method (ISO-7875-1-1996) [20]. The concentration of MB was analyzed at the wavelength of 663 nm. Blank samples of distilled water were used for MB measurement in permeate and blank samples of 1 CMC SDS for that in retentate.

2.4. Calculations

Ultrafiltration of micellar solutions could be considered as a research method helpful in estimating the equilibrium distribution constant (K_d) and micelle loading (L_m) [13,21,22].

According to the law of mass action, one definition of K_d is defined as:

$$K_d = \frac{D_m}{S_m - D_w} \tag{1}$$

The L_m is defined as:

$$L_m = \frac{D_m - D_w}{S_m - S_w} \tag{2}$$

where S_m and D_m are the concentrations of surfactant and dye pollutant in retentate, S_w and D_w are the concentrations of surfactant and dye pollutant in permeate.

3. Results and discussion

3.1. Variation of MB concentration

The feed MB concentration varied from 2 to 24 mg/L, the SDS concentration was fixed at 8.0 mM (one CMC). The experiments were conducted at 0.03 MPa and 25 °C. As shown in Fig. 1, as the initial MB concentration increased, the permeate MB concentration increased from 0.019 to 0.140 mg/L, and retentate MB concentration ascended from 6.44 to 36.45 mg/L linearly. It was obvious that with the increase of the amount of MB molecules in feed solution, MB molecules distributed between the water and micelles increased accordingly [23]. However, the SDS concentrations in permeate and retentate kept about 3.0 mM and 13.0 mM respec-

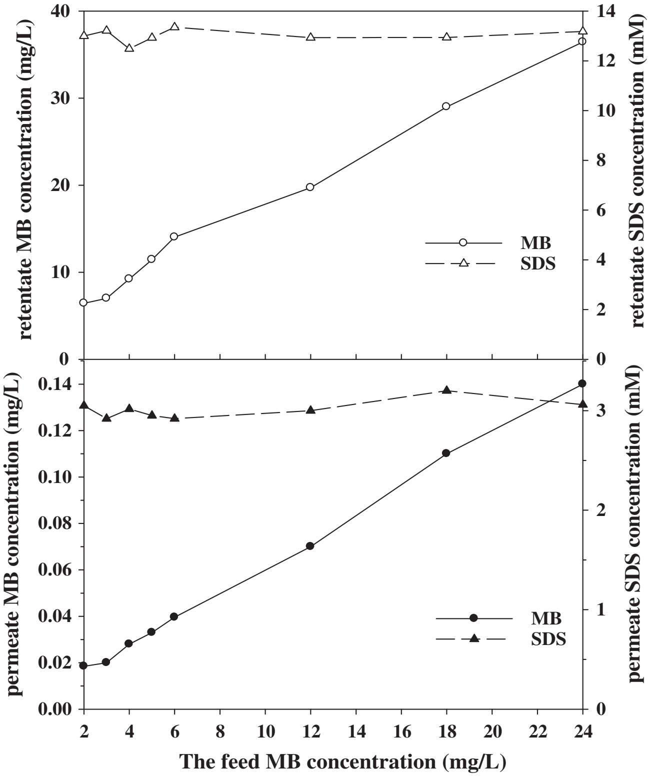


Fig. 1. Permeate and retentate concentrations of MB and SDS with the feed MB concentration.

tively. The results certified that the MB molecules in the wastewater could be solubilized fully within SDS micelles and that would not significantly transform the CMC of SDS.

It was observed from Fig. 2 that when the feed MB concentration varied from 2 to 6 mg/L, the distribution constant (K_d) remained about 26.60 mM^{-1}, since the ascending proportion of MB concentration in retentate accorded with that in permeate, then decreased to 19.76 mM^{-1}, because the solubilization capability of SDS was limited. Meanwhile, micelle loading (L_m) increased from 1.75×10^{-9} to 9.60×10^{-9} mM/mM, which indicated that micelles were still capable of binding more MB molecules [18].

3.2. Variation of SDS concentration

The feed surfactant concentration is one of the most important factors in MEUF. It may produce the bulk of the running cost and cause secondary pollution.

The feed MB concentration was fixed at 6 mg/L. The process was conducted at 0.03 MPa and 25 °C. The influence of the feed SDS concentration on MB and SDS concentrations in permeate and retentate could be shown in Fig. 3. As the feed SDS concentration increased from 1.4 to 72.0 mM, the retentate SDS concentration increased from 1.56 to 153.96 mM. The retentate MB concentration was 0.753 mM in the absence of SDS. Whereas, the permeate MB concentration was very low (0.04 mg/L), for most MB molecules were adsorbed on the ultrafiltration membrane. Meanwhile, with the initial SDS concentration increased from 0 to 8.0 mM, the retentate MB concentration increased quickly from 0.75 to 14.04 mg/L, and then increased gradually to 18.00 mg/L at 72.00 mM SDS, and there was a linear increasing trend of SDS concentration in retentate. Obviously, with the increment of SDS concentration, more micelles would be aggregated and more MB molecules solubilized in the micelles [8].

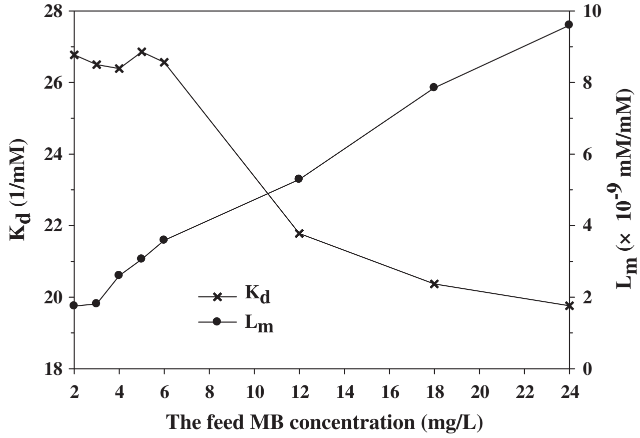


Fig. 2. The distribution constant and micelle loading with the feed MB concentration.

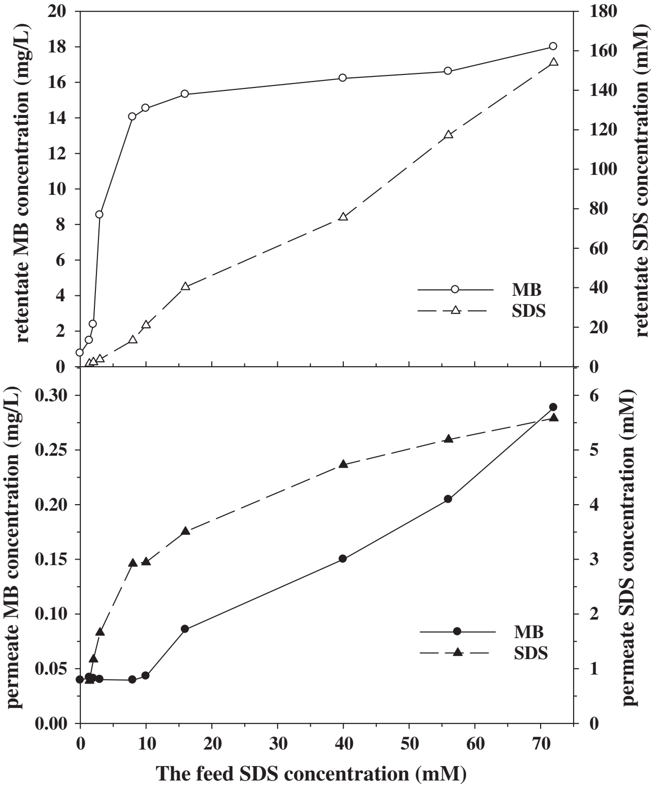


Fig. 3. Permeate and retentate concentrations of MB and SDS with the feed SDS concentration.

When the feed SDS concentration was lower than 8.0 mM, it was unexpected that the retentate MB and SDS concentrations increased, since it was often considered that surfactant monomers did not form micelles while surfactant concentration was below one CMC value. Due to the concentration polarisation effect, the gel layer was formed at the membrane/bulk solution interface. In the gel layer, the concentration of SDS might exceed the CMC value, then SDS micelles were formed [24,25]. In addition, even if the surfactant concentration was lower than 8.0 mM, the surfactant molecules could form small premicelles, which could result in the weak solubilization effect. However, when the surfactant concentration exceeded one CMC value, the solubilization effect was in progress obviously [12]. As mentioned above, the number

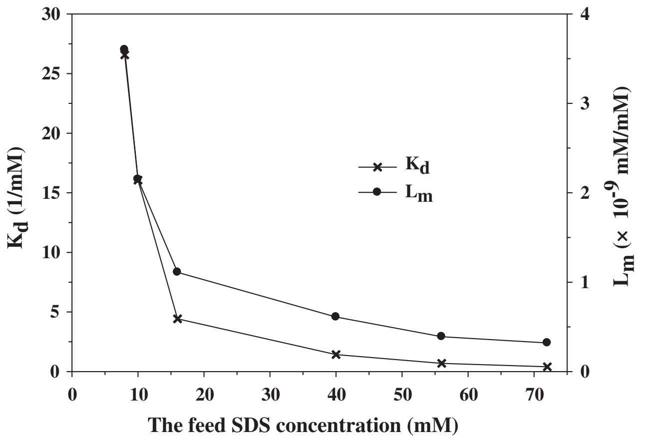


Fig. 4. The distribution constant and micelle loading with the feed SDS concentration.

of micelles ascended as the feed SDS concentration increased, which enhanced the MB solubilization in the micelles. When SDS concentration was higher than 8.0 mM, the increment of the retentate MB concentration was gentle, due to the feed solution getting saturated by the micelles [6].

As the feed SDS concentration increased from 1.4 to 8.0 mM, the permeate SDS concentration ascended quickly from 0.78 to 2.92 mM, then ascended slowly to 5.58 mM for feed SDS concentration of 72.0 mM. Because when the feed surfactant concentration was higher than 8.0 mM, surfactant monomers formed micelles visibly. The permeate MB concentration kept about 0.04 mg/L for the feed SDS concentration from 0 to 8.0 mM, then increased to 0.29 mg/L at 72.0 mM SDS. The surfactant CMC was independent of the surfactant concentration. However, some micelles penetrated the membrane to the permeate solution, although some surfactant monomers were retained. Because of the membrane with a distribution of pore sizes, micelles that were larger than the nominal MWCO of membrane might filter the membrane into the permeate solution [26,27].

It could be concluded that 8.0 mM SDS was appropriate and economical to remove 6 mg/L MB, which was attributed to the weak damage to the UF membrane and relatively low secondary pollution of SDS.

As the addition of SDS concentration was higher than 8.0 mM, a large amount of micelles were aggregated. The distribution constant (K_d) and micelle loading (L_m) were estimated with the feed SDS concentration from 8.0 to 72.0 mM. Observed from Fig. 4, K_d and L_m decreased quickly from 26.56 mM^{-1} and 3.62×10^{-9} mM/mM for 8.0 mM SDS to 4.43 mM^{-1} and 1.11×10^{-9} mM/mM for 16.0 mM SDS, then decreased slowly to 0.41 mM^{-1} and 0.32×10^{-9} mM/mM for 72.0 mM SDS respectively. It was attributed to the increase of permeate MB concentration and the bigger increase extent of retentate concentration of SDS than that of MB.

3.3. Variation of temperature

SDS was added 8.0 mM to the aqueous solution that contained 6 mg/L MB. The pressure kept 0.03 MPa. It could be observed from Fig. 5 that the retentate SDS concentration increased slightly from 11.00 to 13.35 mM with temperature from 20 °C to 25 °C, then decreased to 9.50 mM at 45 °C, which was contrary to the variation of permeate SDS concentration. It decreased slightly from 3.65 to 2.92 mM, and then increased slightly to 4.00 mM. The variation of temperature could change the SDS micellization effect. When the temperature was lower than 25 °C, the CMC value of SDS would decrease slightly and the number of micelles would increase; when the temperature was higher than 25 °C, the trend was opposite. The permeate MB concentration kept about 0.04 mg/L from 20 °C to 45 °C. The retentate MB concentration increased from 9.50 to 15.71 mg/L with temperature from 20 °C to 35 °C. Due to molecular thermal motion, the increase of temperature could make the solubilizing space a little bigger in micelles, leading to the increase in the solubility of MB [12]. With temperature from 35 °C to 45 °C, the retentate MB concentration decreased to 13.0 mg/L. It was attributed to the decrease of the SDS micelles.

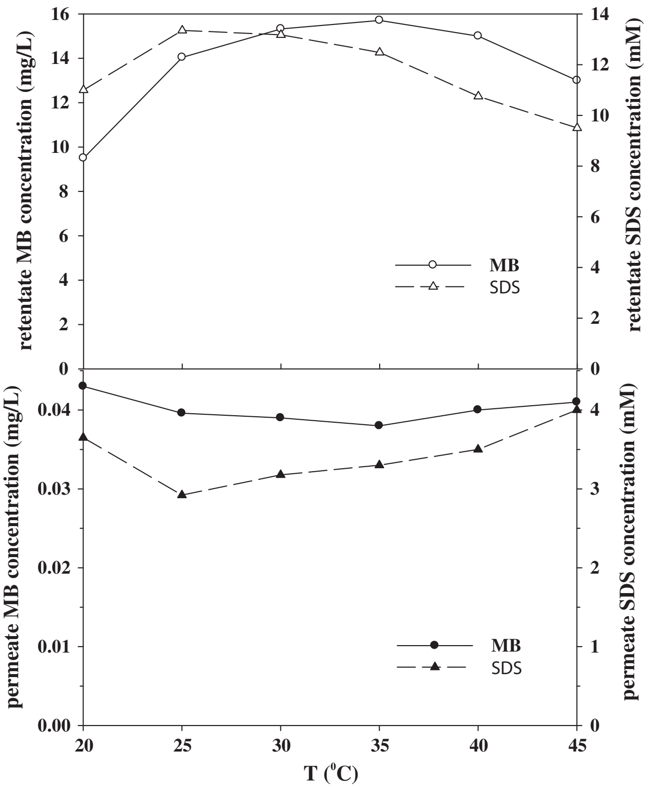


Fig. 5. Permeate and retentate concentrations of MB and SDS with the variation of temperature.

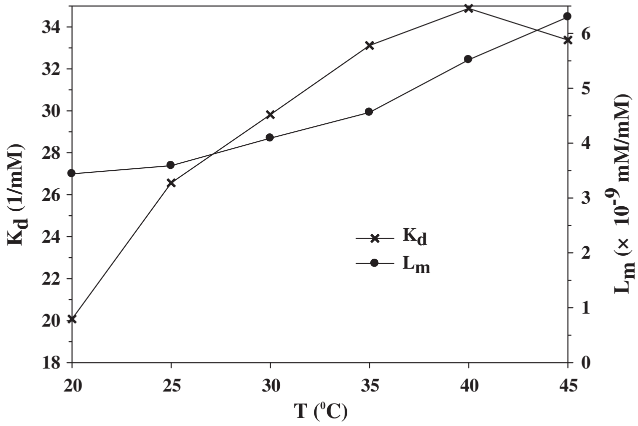


Fig. 6. The distribution constant and micelle loading with the variation of temperature.

It could be observed from Fig. 6 that the distribution constant (K_d) increased from 20.08 mM^{-1} at 20 °C to 34.88 mM^{-1} at 35 °C, then decreased slightly to 33.38 mM^{-1}. The micelle loading (L_m) increased from 3.44×10^{-9} mM/mM at 20 °C to 6.30×10^{-9} mM/

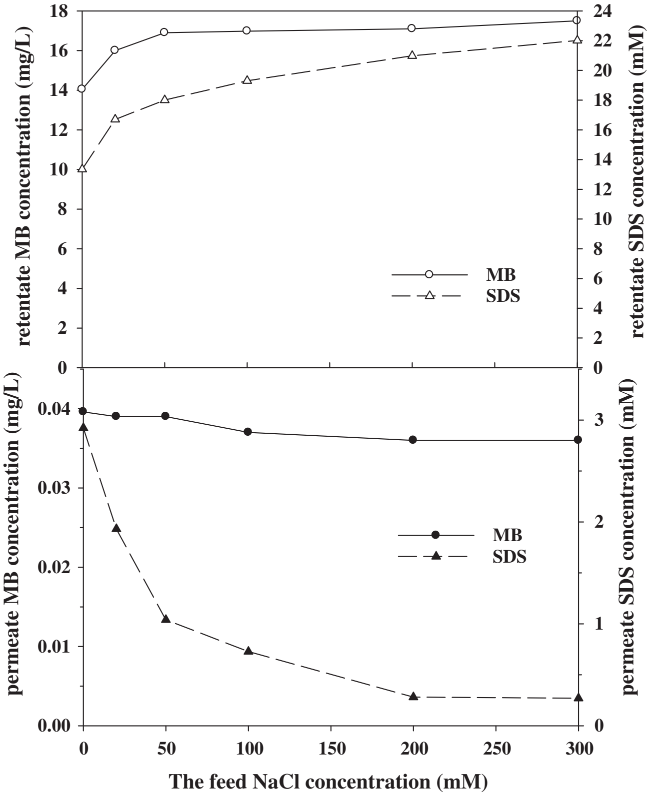


Fig. 7. Permeate and retentate concentrations of MB and SDS with the feed NaCl concentration.

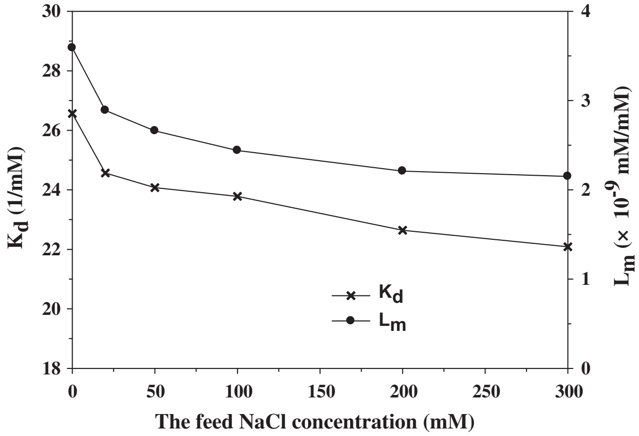


Fig. 8. The distribution constant and micelle loading with the feed NaCl concentration.

mM at 45 °C respectively. It was attributed to the change of MB and SDS concentrations which were distributed between micelles and water.

3.4. Variation of NaCl concentration

In this study, the NaCl concentration varied from 0 to 300 mM. The feed MB and SDS concentrations were fixed at 6 mg/L and 8 mM respectively. The experiments were carried out at 0.03 MPa and 25 °C. When NaCl was added to the solution, the Na$^+$ with opposite charge could result in a decrease of SDS CMC and an increase of the aggregation number and volume of the SDS micelles. Because Na$^+$ would insert into the polar head groups of anionic surfactant monomers, neutralize charges of micelles and finally weaken the electrostatic repulsion between the head groups, so surfactant aggregated micelles easily [19,28,29].

It was observed from Fig. 7 that the retentate MB and SDS concentrations increased from 14.04 mg/L and 13.35 mM^{-1} to 17.50 mg/L and 22.01 mM^{-1} respectively with the feed NaCl from 0 to 300 mM. This was explained by the fact that more SDS micelles were aggregated due to the decrease of SDS CMC, and thereby increasing MB molecules solubilized in the micelles. As a result, less SDS molecules were filtrated through the UF membrane and less MB molecules were adsorbed on the membrane surface. With the feed NaCl concentration from 0 to 300 mM, the permeate SDS concentration decreased about 90.75%. At the same time, the permeate MB concentration remained about 0.04 mg/L. So the NaCl could reduce immensely the secondary pollution and crucially did not influence the permeate MB concentration.

It could be observed from Fig. 8 that the distribution constant (K_d) and micelle loading (L_m) decreased with the feed NaCl concentration, from 26.57 mM^{-1} and 3.59×10^{-9} mM/mM for 0 mM NaCl to 22.09 mM^{-1} and 2.15×10^{-9} mM/mM for 300 mM NaCl respectively. The reason was that the increase extent of the retentate SDS concentration was higher than that of the retentate MB concentration.

4. Conclusions

As the feed MB concentration increased, permeate and retentate MB concentrations increased, because more MB molecules were distributed in water and micelles. The MB could be solubilized fully within micelles of SDS. The increase of feed SDS concentration involved the increment of retentate MB concentration due to more aggregated micelles. With the increase of temperature, the retentate MB concentration increased, and then decreased slightly. NaCl could promote the solubilization capability of SDS micelles for MB. The addition of NaCl could improve the retentate MB and SDS concentrations and reduce significantly the permeate SDS concentration. Moreover, the equilibrium distribution constant (K_d) and micelle loading (L_m) values were estimated.

Acknowledgements

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