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Application of Polybutadiene-Based Polymeric Surfactants in Liquid Membrane Separation

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ABSTRACT

New polybutadiene-based surfactants (LYF) were synthesized by sulfonation of liquid polybutadiene with acetal sulfate at an elevated temperature, and their properties in a liquid surfactant membrane (LSM) separation process were examined by comparison with the two polyisobutylene-based surfactants ECA4360 and EM301. It was found that LYF surfactants had satisfactory overall properties as regards stability, swelling, and demulsification of the W/O emulsion in the cases of both acidic and caustic internal aqueous phases.

Key Words. Polybutadiene-based surfactant; Sulfonated liquid polybutadiene; Liquid membrane

INTRODUCTION

The separation technique using a liquid surfactant membrane (LSM) has been noted as a novel method for separating and concentrating metal ions and some organic compounds. Recently, a growing interest has been focused on the development of new surfactants suitable for LSM separa-

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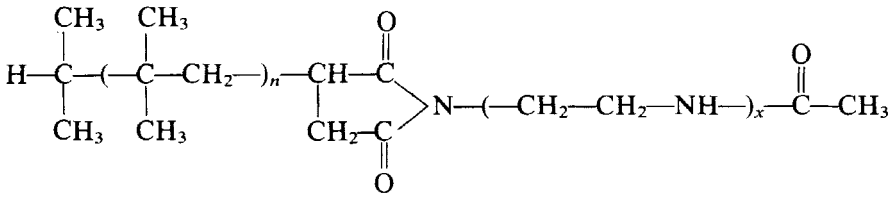
tion processes. It has been found that surfactants having two long alkyl chains in the hydrophobic site, such as glutamic acid dialkyl esters, are more suitable for the LSM process than are typical commercial LSM surfactants such as Span 80 and polyamine (1–3). Furthermore, it is well worth noticing that polymeric surfactants have become more and more important for strengthening the liquid membrane and increasing the stability of the resulting emulsion. So far, the best polymeric surfactants for LSM are mainly polyisobutylene-based ones (4–6). In this work, new polybutadiene-based LYF polymeric surfactants were synthesized, and their properties in LSM processes were examined.

EXPERIMENTAL

Materials

The starting liquid polybutadiene sample was kindly provided by Jin Zhou Petroleum Co. Its molecular weight was 1600 according to the manufacturer, and the 1,2 content was 38.8 mol% according to the results of an ^{1}H-NMR analysis obtained in our laboratory. Two surfactants, ECA4360 and EM301, were used for comparison. EM301 was claimed to be a sulfonated polyisobutylene (6), while ECA4360 has the following chemical structure (4):



where n = 10–60 and x = 3–10.

The kerosene used had a boiling point range of 180–250°C. Other chemicals were all reagent grade.

Preparation, Extraction, and Demulsification of a W/O Emulsion

W/O emulsions with different surfactants were prepared under the same conditions: The volume ratio of an organic kerosene phase to an internal aqueous phase = 1:1; surfactant concentration in the organic phase: 4 (wt)%; stirring: 2000 rpm/20 min. Potassium chloride (about 2000 ppm) was added to the internal aqueous phase as a tracer. Extraction was carried out as follows: An aqueous solution of 1 wt% HCl was used as an

external aqueous phase, the volume ratio of the W/O emulsion to the external phase = 1:5, and the stirring rate was 300 rpm. Demulsification of W/O emulsions was performed by using high pulsed voltage. The principle of this method was described previously (7). In our experiments, batch demulsification was carried out in a glass container with a Pt grounded electrode sealed in the bottom and a movable high voltage electrode put into the top part of an emulsion to be demulsified. A pulsed voltage was applied on the high voltage electrode by a pulsed voltage generator made in our department. The average voltage for demulsification was 2.5 kV, the pulse duration was 0.2 ms, and the frequency was 300 Hz. The demulsification times were 5 minutes (no carrier) and 10 minutes (with carrier). All procedures mentioned above were carried out at room temperature (about 17°C).

Measurements

Infrared spectra were recorded on an Alpha Centauri IR spectrometer (Mattson Company, USA). Interfacial tensions were measured on a JZHY-180 interfacial tensiometer. The concentrations of K^+ in aqueous solutions were determined by a P-E 3030 atomic absorption spectrometer. The water contents of the W/O emulsion after extraction and the oil phase after demulsification were measured by using a water separator, such as the Dean–Stark trap. The apparatus was similar to that used in esterification reactions (8), and the emulsions or oil phases were first mixed with a certain amount of gasoline.

RESULTS AND DISCUSSION

Synthesis of LYF Surfactants

The LYF polymeric surfactants were synthesized by sulfonation of the above-mentioned liquid polybutadiene sample with acetal sulfate, which was prepared by slowly adding concentrated sulfuric acid into an equal weight of acetic anhydride at room temperature. It was found that the sulfonation reaction of polybutadiene with acetal sulfate was very slow at room temperature and could easily be conducted at an elevated temperature. A typical synthesis procedure was as follows: A solution of 50 g polybutadiene in 50 g kerosene was introduced into a three-necked flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. After heating to 130°C, the sulfonating agent was added dropwise while the temperature was kept at 130°C. The reaction was continued for another 30 minutes at the same temperature. The reaction mixture was used in LSM processes without further treatment. For characterization of the

sulfonated products, a portion of the reaction mixture was precipitated and then extracted with ethanol for 4 times to remove the solvent and the unreacted sulfonating agent, and the purified sulfonated polybutadiene was then dried in vacuum at about 100°C for 2 days.

The IR spectra of the polybutadiene sample before and after sulfonation are presented in Fig. 1. The bands at 1040 and 1172–1241 cm^{-1}, character-

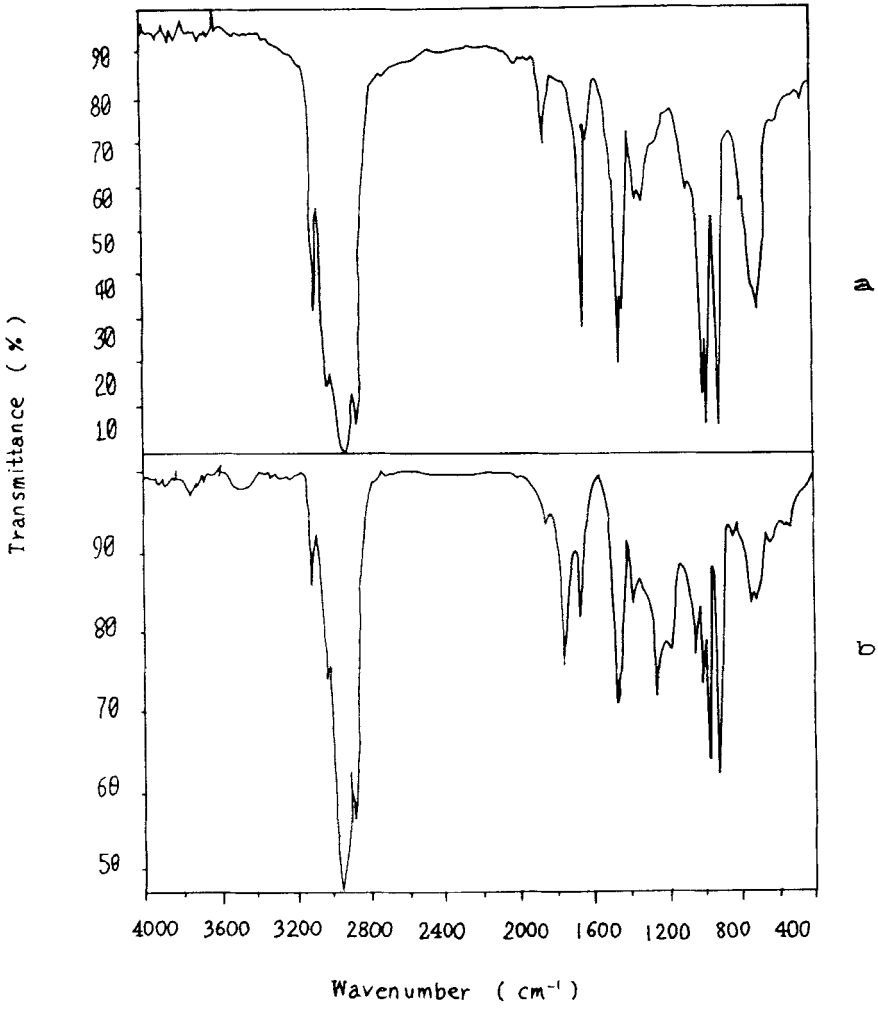


FIG. 1 IR spectra of polybutadiene (a) and sulfonated polybutadiene LYF-G4 (b).

istic for SO_2 vibration, appeared after sulfonation, whereas the intensity at 1620 cm^{-1}, a characteristic peak of C=C double bonds, decreased accordingly, indicating that the sulfonation was affected by the reaction of the sulfonating agent with the double bonds of the polybutadiene. However, the reason for the new band at 1737 cm^{-1} is not yet clear. One of the advantages of LYF surfactants is the ease of controlling their degree of sulfonation and, hence, their hydrophile–lipophile balance by changing the amount of sulfonating agent used and the reaction conditions. According to the results of S analysis, the degrees of sulfonation of LYF-G2 and LYF-G4 were 2.7 and 5.4 mol%, respectively.

Stability of LSM Systems

The break-up ratio of an emulsion (D) is generally used to evaluate the stability of an LSM. It is defined by Eq. (1):

$$D = \frac{V_{e,w}C_{e,KCl}}{V_{i,w}C_{i,KCl}} \times 100\% \quad (1)$$

where $V_{e,w}$ and $V_{i,w}$, and $C_{e,KCl}$ and $C_{f,KCl}$ are the volumes and the KCl concentrations of the external and internal aqueous phases, respectively.

Table 1 shows the effect of surfactants on the stability of W/O emulsions at different experimental conditions. It can be seen that the LYF surfac-

TABLE 1
Breakup Ratios of W/O Emulsions Prepared with Different Surfactants[a]

Internal aqueous phase	Surfactant	Mixing time (minutes)				
		10	20	30	40	50
5 wt% HCl solution	ECA4360	0.50	1.13	1.19	1.55	1.95
	EM301	0.44	0.73	0.95	1.12	1.30
	LYF-G2	0.21	0.37	0.59	0.66	0.72
	LYF-G4	0.21	0.24	0.35	0.73	0.95
5 wt% NaOH solution	ECA4360	0.21	0.49	0.68	0.99	1.10
	EM301	2.80	4.76	5.64	6.35	7.13
	LYF-G2	0.28	0.46	0.52	0.75	0.95
	LYF-G4	0.18	0.22	0.31	0.41	0.52
5 wt% NaOH solution[b]	ECA4360	1.01	1.98	2.89	4.12	4.98
	EM301	2.01	3.14	4.19	5.16	5.93
	LYF-G2	0.92	1.47	1.82	2.29	2.81
	LYF-G4	1.42	2.37	3.47	4.42	5.76

[a] 1 wt% HCl solution was used as the external aq. phase.
[b] The oil phase contained 2 wt% TBP.

TABLE 2
Swelling Ratio Y of W/O Emulsions during Extraction[a]

Surfactant	Internal aqueous phase		
	5 wt% HCl solution	5 wt% NaOH solution	5 wt% NaOH solution[b]
ECA4360	4.0	4.0	20.0
EM301	2.2	—[c]	12.6
LYF-G2	2.0	0	0
LYF-G4	1.2	2.0	14.0

[a] The external aqueous phase: 1 wt% HCl solution; extraction time 50 minutes.
[b] The oil phase contained 2 wt% TBP.
[c] The emulsion stability was too poor to obtain the Y value.

tants form stable W/O emulsions, no matter whether the internal aqueous phase is a strong acid or a strong base. When a carrier, tributyl phosphate (TBP), was added to the kerosene phase, the LYF surfactant with the lower sulfonic acid content showed the best stability.

Swelling and Demulsification

Due to permeation of water from an external aqueous phase to an internal aqueous phase, the volume of the internal aqueous solution will increase during the extraction procedure. The swelling ratio Y of a W/O emulsion is defined by the following expression:

$$Y = \frac{V'_{i,w} - V_{i,w}}{V_{i,w}} \times 100\% \quad (2)$$

TABLE 3
Water Content (wt%) of the Oil Phase after Demulsification

Surfactant	Internal aqueous phase		
	5 wt% HCl solution[a]	5 wt% NaOH solution[a]	5 wt% NaOH solution[b]
ECA4360	0.69	1.67	4.98
EM301	3.33	4.10	4.60[c]
LYF-G2	0.40	2.10	0.60
LYF-G4	0.46	2.83	3.08

[a] Demulsification time was 5 minutes.
[b] The oil phase contained 2 wt% TBP, and the demulsification time was 10 minutes.
[c] Only two-thirds of the emulsion was demulsified, and the water remaining in the emulsion was not included.

where $V_{i,w}$ is the initial volume of the internal aqueous phase in a W/O emulsion, and $V'_{i,w}$ is the volume after extraction. The data listed in Table 2 indicate that W/O emulsions prepared with LYF surfactants exhibited low degrees of swelling. Generally speaking, the swelling ratio of a W/O emulsion becomes larger when TBP is added. As can be seen in Table 2, the swelling ratio of LYF containing W/O emulsions can be controlled by changing the degree of sulfonation.

Demulsification was found to be more difficult when the carrier TBP was added, especially for the EM301 system. W/O emulsions prepared with LYF surfactants were easy to demulsify, and the oil phases had lower water contents, as can be seen in Table 3.

Based on the above-stated results, it is concluded that LYF surfactants have satisfactory overall properties of an LSM as regards stability, swelling, and demulsification in the cases of both acidic and caustic internal aqueous phases.

SYMBOLS

D	break-up ratio (%)
$V_{e,w}$	volume of the external aqueous phase (mL)
$V_{i,w}$	volume of the internal aqueous phase (mL)
$V'_{i,w}$	volume of the internal aqueous phase after extraction (mL)
$C_{e,KCl}$	KCl concentration in the external aqueous phase (ppm)
$C_{i,KCl}$	KCl concentration in the internal aqueous phase (ppm)
Y	swelling ratio of a W/O emulsion (%)

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