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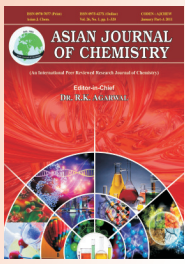

Separation and Characterization of Petroleum Sulfonate Components

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The objective of this research was to establish a systematic method to isolate and characterize petroleum sulfonate components. Petroleum sulfonate was separated into unsulfonated oil and oil-soluble components, an intermediate component and a hydrophilic component according to their polarities using column chromatography. Petroleum ether, 2-butanone, 95 % isobutanol and water were used as the eluent. The separation was monitored by infrared spectroscopy. The petroleum sulfonate components were characterized by elemental analysis and electrospray ionization-mass spectrometry. The experimental results showed that the petroleum sulfonate was composed of surfactant components with different polarities. The S and N contents increased with the increasing polarity of petroleum sulfonate components, whereas the average relative molecular mass decreased. The intermediate component, obtained by mixing with a water-soluble component at a 3:1 ratio, had the lowest interfacial tension.

Keywords: Petroleum sulfonate component, Column chromatography, Infrared spectroscopy, Electrospray ionization mass spectrometry.

INTRODUCTION

Petroleum sulfonates are mixtures obtained by treating high-boiling-point petroleum fractions with oleum, sulfur trioxide, or sulfuric acid followed by neutralization[1,2]. The quality and composition of similar petroleum sulfonates may have different complexities because of diverse raw material oils and sulfonation processes.

Petroleum sulfonates are widely used as surfactants to lower the interfacial tension between oil and water in the tertiary oil recovery process. The composition and molecular structure of petroleum sulfonates are vital factors for reducing the interfacial tension of a given oil[3,4]. Analytical characterization methods have various problems because of impurities, the effects of salts and the interference caused by unreacted oil in the sulfonate. Providing a reproducible and accurate technique for studying the structure of petroleum sulfonate components used in different fields would be highly desirable. Characterizing such complex mixtures directly is extremely difficult. Several chromatographic methods have been developed to characterize alkylbenzene sulfonates. The distribution of their alkyl chains was first determined by gas chromatography[5]. These complex mixtures are now determined by high-performance liquid chromatography to avoid the conversion of these alkylbenzene sulfonates into volatile compounds[6,7]. Column chromatography clearly separates petroleum sulfonate components with different polarities, which aids further research and the complex formulation of petroleum sulfonates[8].

The equivalent weight of petroleum sulfonate affects its relative solubility in oil and water and its hydrophilic and hydrophobic nature. Determining the average equivalent weight of petroleum sulfonate is desirable when selecting an appropriate petroleum sulfonate for recovery techniques. United States patent no. 4255270[9] proposed a method to determine the average equivalent weight in which at least one highly pure hydrocarbon should be identified. Marquez *et al.*[10] determined the equivalent weight using size exclusion chromatography, which requires a prebuilt standard curve. Molecular weight distribution was studied by chromatography using charcoal[11] or, more effectively, silica gel[8].

In the present study, different petroleum sulfonate components were isolated using column chromatography and monitored using infrared spectroscopy. Each component was then characterized by elemental analysis and electrospray ionization-mass spectrometry (ESI-MS). The interfacial tension of the petroleum sulfonate components and component compounds were also investigated.

EXPERIMENTAL

Silica gel for column chromatography was provided by the Qingdao Waves Silica Gel Desiccant Plant, with a particle size from 0.15 to 0.23 mm, w(Cl) ≤ 0.02 %, w(Fe) ≤ 0.02 %,

pH = 6-7, w(Pb) ≤ 0.001 %, w(As) ≤ 0.0003 % and heated mass fraction reduction ≤ 3 %. Petroleum sulfonate with an effective mass fraction of 36.74 % was provided by Shengli Oilfield Zhongsheng Environmental Protection Co., Ltd. Petroleum ether with a boiling range of 60 to 90 ºC, 2-butanone and isobutanol were all analytically pure. Deionized water was used as the experimental water.

Purification of desalted petroleum sulfonate: The petroleum sulfonate industrial product contained volatile, unsulfonated oil, inorganic salt and other impurities. The petroleum sulfonate was purified by extraction according to Jiang *et al.*[12]. The experimental process consisted of the following. A certain quality of petroleum sulfonate industrial product was placed in an oven and dried at 110 ºC to a constant weight. The dried material was then dissolved with hot ethanol. Inorganic salt is insoluble in ethanol. The insolubles were filtered and washed in a sand-core funnel to white alternately with hot ethanol and petroleum ether. The desalted sample was obtained by removing the solvent from the filtrate.

Column chromatography: Silica gel for column chromatography (0.9 mm diameter, 970 mm length) was preactivated at 120 ºC for 6 h. The eluents for column chromatography were the following: (i) Combination 1 was successively eluted with 80 mL petroleum ether, 80 mL toluene, 80 mL ether, 80 mL 2-butanone, 80 mL of an isobutanol solution with an isobutanol mass fraction of 95 % and 100 mL deionized water. The components were tagged as a, b, c, d, e and f, respectively. (ii) Combination 2 was successively eluted with 80 mL petroleum ether, 80 mL 2-butanone, 80 mL of an isobutanol solution with an isobutanol mass fraction of 95 % and 100 mL deionized water. The components were tagged as A (unsulfonated oil), B (oil-soluble petroleum sulfonate), C (intermediate petroleum sulfonate) and D (water-soluble petroleum sulfonate), respectively.

The characteristic functional groups of unsulfonated oil and each petroleum sulfonate component were analyzed using a NEXUS FT-IR infrared spectrometer (Nicolet, Madison, Wisconsin, USA).

Elemental analysis of petroleum sulfonate components: The contents of C, H, N and S were analyzed by combustion chromatography using an Element Analyzer (VARIO ELIII, Hanau, Germany).

Electrospray ionization-mass spectrometry: The relative molecular mass distribution of the petroleum sulfonate components were determined using a high-resolution Bruker maxis UHR-TOF mass spectrometer (Bruker Daltonics Inc., Billerica, USA). The determination conditions were the following: ESI source, 180 ºC temperature, 105 Pa nebulizer pressure, negative ion mode detection, 50-1500 *m/z* scanning range and 6 L/min drying gas flow rate. The sample molecules did not crack when analyzed by ESI-MS. The peaks on the spectrum were molecular ion peaks or quasi-molecular ion peaks; therefore, the relative molecular mass distribution could be obtained. The average relative molecular mass was calculated according to eqn. 1.

$$\overline{M} = \sum_{i=a}^{n} M_i \frac{A_i}{\sum_{i=a}^{n} A_i} + 18 \quad (1)$$

$\overline{M}$ is the average relative molecular mass of petroleum sulfonate. M_i is the mass-to-charge ratio. A_i is the abundance.

Interfacial tension analysis: The dynamic interfacial tension of the oil-water system was determined by the spinning drop technique using a TX-500C interfacial tension meter (BOWING INDUSTRY CO. Stafford, Texas, USA) at 50 ºC and 6,000 rpm/min[13]. Simulated mineralized water (5829 mg/L salinity) was used and the crude oil was obtained from the 15th station of Gudao (Shengli Oilfield, China). The concentration of the aqueous solutions that contained petroleum sulfonate components was 0.3 %.

RESULTS AND DISCUSSION

The petroleum sulfonate industrial product contained the following: 31.13 % volatile components, 23.38 % unsulfonated oil, 7.74 % inorganic salts and 36.74 % surface-active substances. The recovery rate was 98.99 %; therefore, petroleum sulfonate could be considered to be purified for the quantitative analysis. The desalted samples that contained unsulfonated oil and surfactant were used as the raw material for the subsequent column chromatography experiments.

Column chromatography separation and infrared spectrum analysis: The column chromatography results with eluent combination 1 at 25 ºC are shown in Table-1. The table shows that petroleum sulfonate was a complex surfactant composed of components with different polarities. The eluent ribbon was clear and the elution dose was sufficient, therefore, the petroleum sulfonate components could be clearly separated. The structural information of the desalted components was analyzed by infrared spectroscopy. Fig. 1 shows the infrared spectra.

TABLE-1
COLUMN CHROMATOGRAPHY RESULTS
WITH ELUENT COMBINATION 1

Component	W (%)	Recovery rate (%)
a	35.16	98.70
b	10.43	
c	3.21	
d	2.78	
e	26.34	
f	20.78	

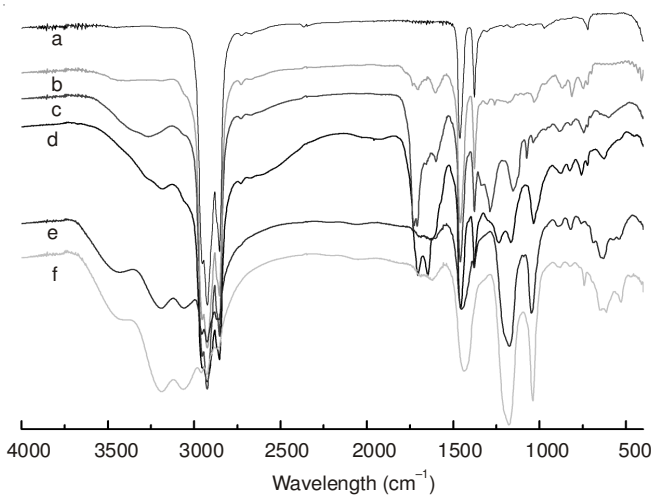

Fig. 1. Infrared spectra of components a, b, c, d, e, and f

Fig. 1 shows that the peaks at 2923 and 2850 cm^{-1} were asymmetric stretching vibrations of $-CH_3$ and $-CH_2-$. The peaks near 1460 and 1378 cm^{-1} were an asymmetric deformation vibration and symmetric deformation vibration of $-CH_3$, respectively. The peaks at 1593 and 1656 cm^{-1} were stretching vibration for the C=C bond. The band at 1728 cm^{-1} was a stretching vibration for the C=O bond. The symmetric stretching vibration and asymmetric stretching vibration of the S=O bond of sulfonate caused peaks at 1175 and 1045 cm^{-1}. The wide and weak absorption band at 975-761 cm^{-1} was caused by the stretching vibration of the S-O band of sulfonate. Petroleum ammonium sulfonate was the ammonium salt of organic acids. In addition to the anionic bands, a strong and wide peak was also caused by the N-H stretching vibration of the cation. The center of the peak was near 3200 cm^{-1}.

These results indicate that the main constituent of component a was saturated alkane. Component a did not contain benzene rings or sulfonic acid groups. Components b, c and d had similar spectra. They all contained benzene rings, sulfonic acid groups and C=O bonds. Apparently, components e and f had fewer substances that contained C=O bonds than components c and d. However, components e and f had more sulfonate than components b, c and d. This likely indicates that components c and d had more petroleum carboxylate with a weaker polarity because carboxylate ions exhibit symmetric stretching vibration and asymmetric stretching vibration. Asymmetric stretching vibration was found at 1610-1560 cm^{-1}, whereas symmetric stretching vibration was found at 1440-1360 cm^{-1}. Generally two or three broad absorption peaks were observed. However, components e and f were mainly petroleum sulfonate. Moreover, the content of sulfonic acid groups and NH_4^+ in component f was significantly higher than in component e.

The infrared spectra showed that components e and f had less $-CH_3$ and $-CH_2-$ than components b, c and d. Virtually no asymmetric stretching vibration peaks of $-CH_3$ and $-CH_2-$ were found in the component f spectrum. A weaker absorption band emerged in the component e spectrum. This indicates that component f was mainly composed of an unsaturated aromatic hydrocarbon structure with no alkane substituents, whereas minor alkane substituents existed in component e.

Fig. 1 and Table-1 show that the structures of components b, c and d were similar and the mass fractions of components c and d were small when petroleum sulfonate was separated by eluent combination 1. Therefore, toluene and ether were omitted. The b, c and d fractions were directly eluted by 2-butanone with a slightly larger polarity. The column chromatography experiments were performed using eluent Combination 2 at 25 ºC. Table-2 shows the results.

TABLE-2
COLUMN CHROMATOGRAPHY RESULTS WITH ELUENT COMBINATION 2

Component	w (%)	Recovery rate (%)
A	34.75	98.07
B	15.86	
C	26.79	
D	20.87	

Table-2 shows that the mass fraction of component B was 15.86 % and the mass fraction sum of components b, c and d was 16.42 %. These two values are similar; therefore, the petroleum sulfonate components were separated by eluent combination 2.

Elemental composition of petroleum sulfonate components: The elemental compositions of petroleum sulfonate components A, B, C and D were analyzed using combustion chromatography. Table-3 shows the analytical results.

TABLE-3
ANALYTICAL RESULTS OF THE ELEMENTAL COMPOSITIONS OF PETROLEUM SULFONATE COMPONENTS

Sample	Elemental analysis (%)				Lipophilic group n(C)/n(H)
	C	H	S	N	
A	86.08	13.92	0	0	0.515
B	81.40	10.14	4.15	0.93	0.687
C	65.41	9.10	8.67	2.74	0.655
D	40.34	7.14	14.35	7.25	0.663

Sulfur content and nitrogen content increased significantly as the polarity of the petroleum sulfonate components increased. That is the sulfonic acid group content and NH_4^+ content gradually increased, which is consistent with the infrared spectroscopy results. Furthermore, with the increase in component polarity, the contents of C and H decreased, which is consistent with the relative intensities of the $-CH_3$ and $-CH_2-$ absorption bands in the infrared spectra. The substituted alkyl carbon number of the benzene ring was on the order of B > C > D.

Relative molecular mass and distribution of petroleum sulfonate: Electrospray ionization-MS is able to analyze the solution sample directly. No sample heating or vaporization process was required, which is different from conventional ionization technology, such as electron impact (EI) and chemical ionization (CI), therefore it is particularly suitable for strong polar, hard volatile, or thermally unstable compounds. Electrospray ionization is a soft ionization technique. The sample molecules do not crack and ions with multiple electric charges can be produced using this technique. Therefore, large-molecular-mass ions can be determined by the conventional *m/z* range of the mass spectrometer. Compounds with a relative molecular mass between 10 and 100,000 can be determined rapidly, sensitively and accurately. Figs. 2 to 4 show the ESI-MS spectra for each petroleum sulfonate component.

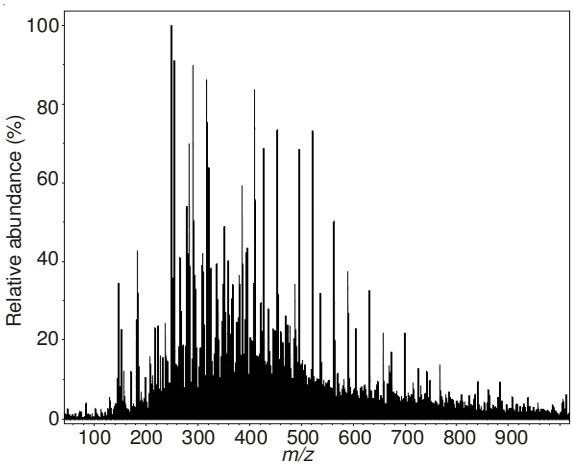

Fig. 2. Mass spectra of oil-soluble petroleum sulfonate

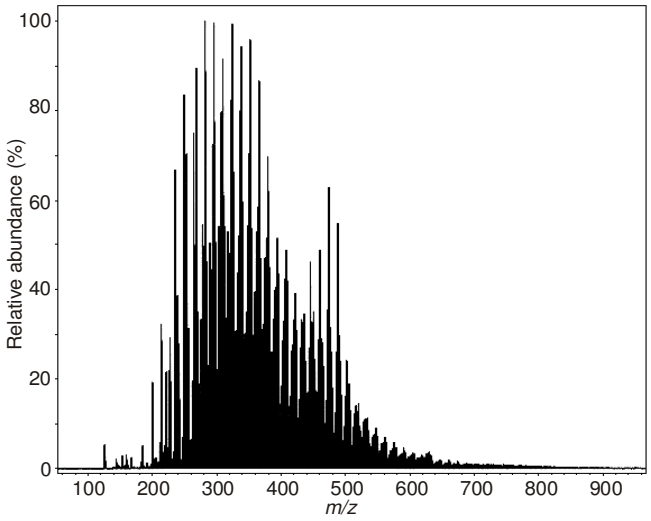

Fig. 3. Mass spectra of intermediate petroleum sulfonate

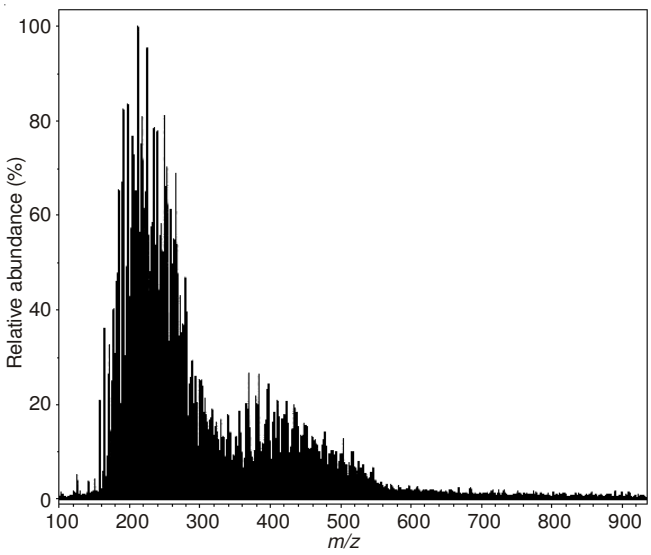

Fig. 4. Mass spectra of water-soluble petroleum sulfonate

The ESI-MS spectra present strong $[nMr\text{-}NH_4]^-$ quasi-molecular ion peak series. M_r was the relative molecular mass of petroleum sulfonate, including the mass of the ammonium ion. $[M_r\text{-}NH_4]^-$ reflected the peaks law of studied substances. M_r-98 indicates the relative molecular mass of lipophilic groups that corresponded to sulfonate. The relative mass distribution, carbon atom distribution and sulfonic acid group number of various components could be calculated by combining the mass spectrometry and elemental analysis results. Table-4 present these results. The average carbon number and sulfonic group number were calculated according to eqn. 2 through 4.

$$\text{Upper limit: } C_{max} = (M\text{-}98)/13 \quad (2)$$

If all of the carbons are aromatic, then M is the average relative molecular mass of petroleum sulfonate.

$$\text{Lower limit: } C_{min} = (M\text{-}98)/14 \quad (3)$$

This equation is applicable if all of the carbons are aliphatic.

$$N_{(SO_3)} = (M\text{-}17) \times S\ \%/32.06 \quad (4)$$

$N_{(SO_3)}$ is the number of sulfonic acid groups.

TABLE-4
AVERAGE STRUCTURE PARAMETERS OF PETROLEUM SULFONATE COMPONENTS

Sample	W (%)	$\overline{M}$	Average carbon number	Sulfonic group number
B	24.97	419	22.93-24.69	0.52
C	42.18	361	18.79-20.23	0.93
D	32.86	279	12.93-13.92	1.17

Table-4 shows that the average relative molecular mass of the petroleum sulfonate components decreased as the sulfonic group numbers increased with increasing polarity. The sulfonic group number of the oil-soluble component was only 0.52, indicating that the oil-soluble component was not entirely petroleum sulfonate. According to the infrared spectroscopy results, the oil-soluble component contained some petroleum carboxylate. The intermediate component was mono-sulfonate. The water-soluble component contained a certain quantity of disulfonate. As the polarity increased, the average carbon number also showed a decreasing trend, which is consistent with the infrared spectroscopy and elemental analysis results.

Characteristics of oil-water interfacial tension: Oil-water interfacial tension is an important parameter for evaluating oil displacement performance of petroleum sulfonate. Fig. 5 shows the measured surface tension of the sulfonate components with Gudao crude oil in water at different times at 50 ºC.

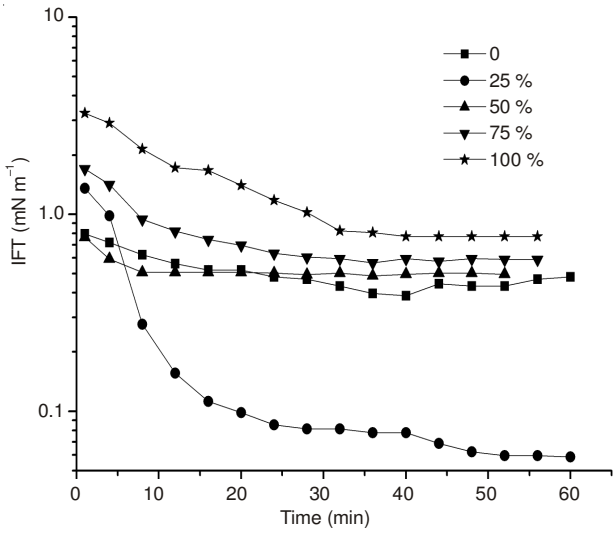

Fig. 5. Dynamic interfacial tension of petroleum sulfonate components

After the intermediate component and water-soluble component were mixed in proportion, their steady interfacial tensions were arranged in the following order: containing 25 % water-soluble component < intermediate component < containing 50 % water-soluble component < containing 75 % water-soluble component < water-soluble component.

The intermediate petroleum sulfonate had a larger average relative molecular mass, longer carbon chain and higher interfacial activity. This resulted in a significant decrease in oil-water interfacial tension but poor water solubility. The water-soluble component had lower average relative molecular mass and good water solubility but lower interfacial activity. Therefore, mixing intermediate petroleum sulfonate and water-

soluble petroleum sulfonate at certain proportions can improve the water solubility of intermediate petroleum sulfonate and reduce the interfacial tension of water-soluble petroleum sulfonate.

Conclusion

Column chromatography could clearly separate petroleum sulfonate components with different polarities, resulting in a high recovery rate. Infrared spectroscopy showed that the different components had different characteristic peaks. The contents of S and N in the elemental analysis exhibited the same trend as the content of S=O and NH_4^+ in the infrared spectra. The contents of the S and N elements increased as the polarity of petroleum sulfonate component increased, but the average relative molecular weight decreased. Oil-soluble petroleum sulfonate had a wider molecular weight distribution than the other components. Under the same conditions, the interfacial activity of intermediate petroleum sulfonate was better than water-soluble petroleum sulfonate and the best interfacial activity was obtained for sulfonate surfactants dosed with an intermediate-to-water soluble mass ratio of 3:1.

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