

Surface-Active Agents Based on Propoxylated Lignosulfonate

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Synopsis

A commercial lignosulfonate was modified by the addition of propylene oxide. The products obtained had a degree of propoxylation ranging from 19% to 49%. The modified lignosulfonates retained high solubility in water and high salinity tolerance, while their interfacial activity increased dramatically in comparison with the original lignosulfonate. Aqueous solutions of propoxylated lignosulfonates exhibited very low interfacial tensions (down to 10^{-1} – 10^{-2} mN/m) against both a pure hydrocarbon (isooctane) and a crude oil (Lloydminster crude).

INTRODUCTION

Lignosulfonates are a broad class of wood-based chemicals made from the spent liquor generated in the sulfite pulping process. Thermal degradation and sulfonation reactions that take place during the cooking of wood convert high molecular weight native lignin into a water-soluble polydisperse anionic polyelectrolyte with a molecular weight varying from 1000 to 20,000. The functional groups of lignosulfonate include primary and secondary hydroxyl, phenolic hydroxyl, methoxyl and ether groups, carbonyl, carboxyl, as well as sulfonate groups. This high content of different types of polar groups and the complex polymer structure make lignosulfonates completely insoluble in oil, whereas they are miscible in all proportions with water.

Although long recognized for their surface-active properties, lignosulfonates do not possess a well-defined hydrophobic-hydrophilic molecular architecture and do not form micelles. Their effectiveness as emulsion stabilizers, for example, is the result of lignosulfonate adsorption at the oil/water interface forming a highly charged interfacial layer.

The use of lignosulfonates in enhanced oil recovery (EOR) dates back to 1931, when de Groote and Monson¹ patented a process involving the use of sulfite spent liquors in water-flooding operations. In the late seventies, Kalfoglou² obtained a patent for the use of lignosulfonates as sacrificial adsorbents. Experiments conducted in our laboratory have shown that lignosulfonates either alone,³ or in admixture with petroleum sulfonates,^{4,5} were able to considerably improve oil recovery from model sand packs. The latter system appeared of particular interest because of the very low values of oil/water

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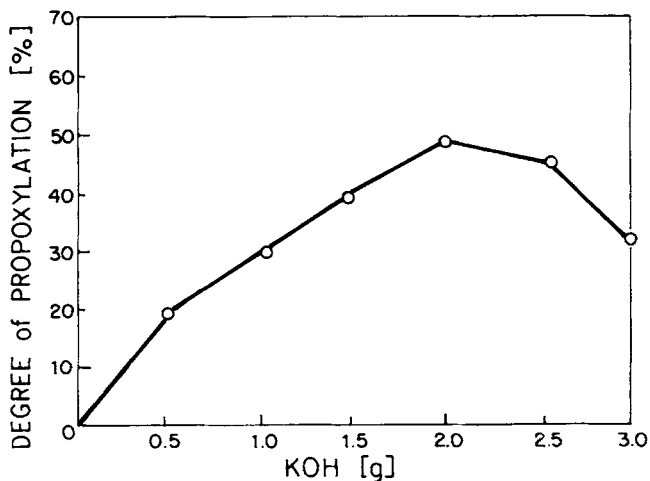


Fig. 1. Degree of propoxylation as a function of the amount of catalyst charged.

interfacial tensions (IFT) attained. This is necessary in order to mobilize residual oil strongly held in the porous reservoir rock by capillary forces.

It was also observed, however, that solutions containing petroleum sulfonates exhibited poor salinity tolerance, especially vis-à-vis divalent and polyvalent

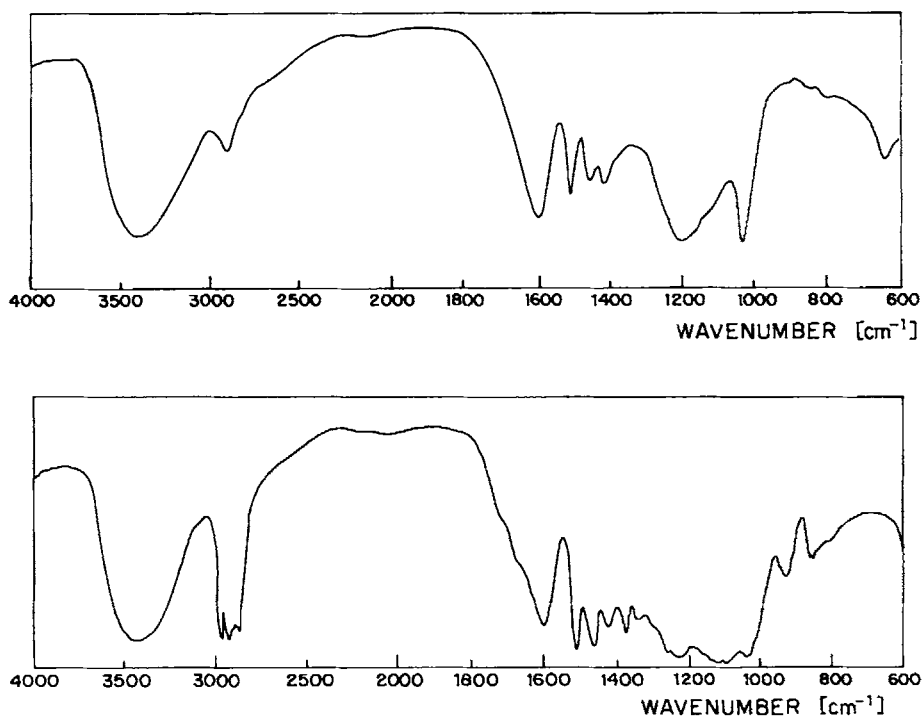


Fig. 2. (a) IR spectra of unmodified Marasperse N-22 lignosulfonate; (b) IR spectra of Marasperse N-22 lignosulfonate modified by addition of 46% of propylene oxide.

TABLE I
Aliphatic to Aromatic Proton Ratios as Determined by NMR

Sample	Aromatic protons	Aliphatic protons (3-4 ppm)	Aliphatic protons (0.8-1.2 ppm)
(I)	1	2.40	0.20
(II)	1	5.25	3.12
(III)	1	4.33	2.22

cations. Solutions of lignosulfonates, on the contrary, show excellent salinity tolerance, but, alone, are not very effective in reducing the IFT. Consequently, to improve their performance in EOR and similar applications, lignosulfonates must be modified to provide them with greater affinity to oil while maintaining good compatibility with water and salinity tolerance. The present work deals with the modification of a commercial lignosulfonate, Marasperse N-22, by copolymerization with propylene oxide.

EXPERIMENTAL

Materials

Marasperse N-22, a commercial lignosulfonate manufactured by American Can Co., Greenwich, CT, was used as the raw material. Lloydminster crude oil

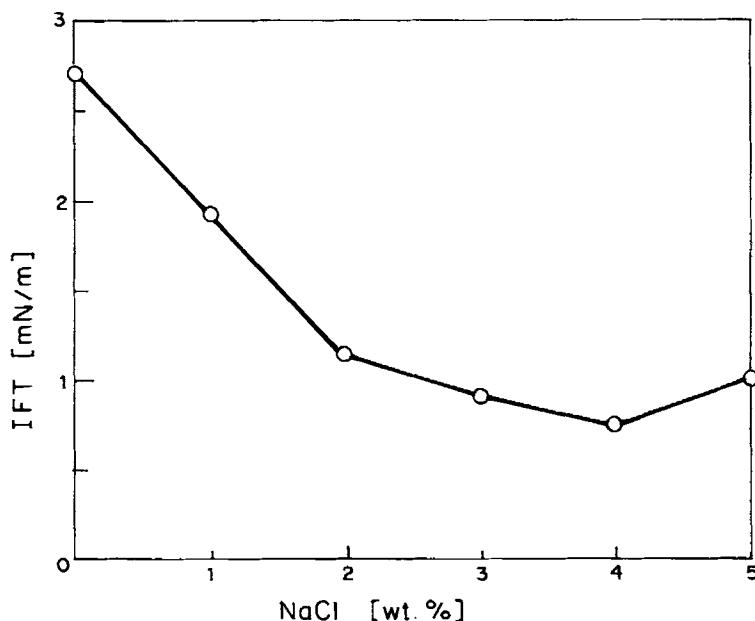


Fig. 3. Effect of NaCl concentration on the interfacial tension of 1% aqueous solution of modified Marasperse N-22 lignosulfonate (degree of propoxylation = 32%) against isooctane as the organic phase.

was obtained from Esso Resources Canada Ltd. Propylene oxide, hexane, isooctane, sodium chloride, and potassium hydroxide were reagent-grade products supplied by Fisher Scientific. Distilled water was used in all preparations.

Propoxylation Reaction

The procedure was similar to that recently described by Wu and Glasser.⁶ The reactions were carried out in a 1000 mL stainless-steel reactor equipped with an electric heater, pressure gauge, safety valve, and a thermocouple.

The reactor was charged with 20 g of lignosulfonate, 100 mL of propylene oxide, and a desired quantity of potassium hydroxide (0–3 g). All reagents were charged under nitrogen. When the reaction was finished (about 300 min), the reactor was cooled down to room temperature and the reaction products were collected.

Product Isolation

The mixture after reaction contains propoxylated lignosulfonate, propylene oxide homopolymer, unreacted propylene oxide, and the KOH catalyst. First, propylene oxide monomer and homopolymer were removed by extracting the mixture with three portions (100 mL each) of hexane. The products were subsequently dissolved in a small amount of water. The solution was neutralized with HCl and then mixed with 1000 mL of 20% NaCl to precipitate the propoxylated lignosulfonate. This final product was isolated by filtration and dried at 60°C in a vacuum oven.

Product Analysis

NMR spectra were recorded by means of a Varian XL 300 spectrometer in D₂O as a solvent (99.75 atom. % D, Baker grade). Infrared spectra were recorded on a Perkin-Elmer Model 267 instrument using the KBr pellet technique.

Sample equilibration for IFT measurements has been described previously.⁷ Isooctane and Lloydminster crude oil were employed as the oil phases. All IFT measurements were conducted at 25 ± 0.5°C using a University of Texas Model 300 Spinning Drop Tensiometer.

RESULTS AND DISCUSSION

Reaction Products and Their Characterization

Wu and Glasser⁶ found that the degree of propoxylation (i.e., the weight of propylene oxide polymer added divided by the weight of the lignin substrate, as %) of kraft lignin was strongly dependent on the amount of KOH catalyst present. A series of reactions with varying amount of KOH was carried out to ascertain the optimum catalyst concentration for the propoxylation of lignosulfonate. The results shown in Figure 1 indicate that the optimum amount of catalyst was 2 g, i.e., 10% by weight on the lignosulfonate charged.

Infrared spectra of propoxylated lignosulfonate and unmodified lignosulfonate are compared in Figures 2(a) and (b). A spectrum of the unmodified Marasperse N-22 had a broad OH-adsorption band with a maximum at 3400 cm^{-1} . After modification with propylene oxide, the width and intensity of this band decreased and the maximum shifted to 3440 cm^{-1} . The spectra also revealed an increase in the intensity of the C-H adsorption bonds at 2900 cm^{-1} ; on the other hand, the modification reduced the intensity of the adsorption band of aromatic rings at 1600 cm^{-1} .

The increase in the aliphatic to aromatic proton ratio is also evidenced by the NMR spectra. Table I provides a comparison of aliphatic and aromatic proton content in the unmodified lignosulfonate (I) in the unextracted reaction products (II) and in the final extracted product having a 48% degree of propoxylation (III). It is evident that the aliphatic proton content is considerably increased after the reaction, although a part is subsequently removed by the extraction procedure.

The solubility of the propoxylated lignosulfonate in water is very high. The solution remains clear even at concentrations up to 50%. Salt tolerance of the product is also high. Concentrations of NaCl below 10% have little effect on its solubility. When the concentration of NaCl exceeds about 10%, partial precipitation occurs. The amount of precipitate depends on the concentration of both the modified lignosulfonate and NaCl.

Interfacial Tension

The interfacial tension values of aqueous solutions of propoxylated lignosulfonates were measured against isooctane as the organic phase at three different salinities. The results are summarized in Table IIa, b, c, d, e, and f. The most important trend observed is the marked increase in interfacial activity with increasing degree of propoxylation. Unmodified Marasperse N-22 lignosulfonate has been shown to give high IFT against isooctane, which varied only little with concentration (from about 35 mN/m at 1% to 20 mN/m at 10% lignosulfonate) and was little influenced by salinity. By comparison, the propoxylated lignosulfonates exhibit IFTs that are much more strongly dependent on concentration. The IFTs observed with the samples having a high degree of propoxylation are seen to drop to very low values (10^{-1} mN/m or even less), i.e., approaching the level of activity that is desirable in enhanced oil recovery operations. As shown in Table III, even lower IFTs were obtained against Lloydminster crude oil.

The IFT values shown in Tables II and III show a strong dependence on the concentration of salt (NaCl). In Figure 3, the IFT of a 1% solution of the sample having a degree of propoxylation of 32% is plotted against salinity up to 5% NaCl. An initial sharp decrease is observed followed by leveling-off and a small increase at salt concentration above 4%. The optimum salinity, corresponding to the minimum interfacial tension, is approximately 4.0% NaCl. This is considerably higher than is the optimum salinity observed in the case of lignosulfonate/petroleum sulfonate synergistic mixtures (about 2.5% NaCl).⁷ This is very important in EOR applica-

TABLE II
 Interfacial Tension of Aqueous Solutions of Propoxylated Lignosulfonates Against Isooctane
 at Different Salinities as a Function of Degree of Propoxylation

Concentration of lignosulfonate-PO product (wt %)	Interfacial tension (mN/m), aqueous phase salinity (wt % NaCl)		
	0	1	3
(a) Degree of propoxylation = 19% (0.5 g KOH catalyst)			
0.1	12.40	11.60	9.58
0.25	10.60	10.50	7.64
0.5	8.42	8.01	6.69
1.0	6.37	5.83	4.43
2.0	4.22	4.10	3.18
3.0	1.93	1.43	2.71
5.0	1.51	1.37	1.76
10.0	1.42	1.30	1.65
(b) Degree of propoxylation = 30% (1.0 g KOH catalyst)			
0.1	8.37	6.26	4.62
0.25	6.43	5.48	3.23
0.5	5.48	4.20	2.84
1.0	3.21	1.80	1.57
2.0	2.97	1.60	1.32
3.0	1.50	1.43	0.95
5.0	0.98	1.07	0.86
10.0	0.84	0.92	0.66
(c) Degree of propoxylation = 32% (3.0 g KOH catalyst)			
0.1	7.18	3.67	2.94
0.25	4.34	3.08	2.32
0.5	3.32	2.45	1.74
1.0	2.71	1.91	0.94
2.0	2.01	1.32	0.81
3.0	1.22	0.83	0.53
5.0	0.94	0.61	0.49
10.0	0.45	0.42	0.37
(d) Degree of propoxylation = 40% (1.5 g KOH catalyst)			
0.1	5.61	3.68	3.41
0.25	4.22	2.42	2.07
0.5	3.83	1.78	1.72
1.0	1.58	1.40	0.98
2.0	1.22	1.12	0.70
3.0	0.92	0.79	0.56
5.0	0.74	0.73	0.51
10.0	0.56	0.75	0.48
(e) Degree of propoxylation = 46% (2.5 g KOH catalyst)			
0.1	3.84	2.93	2.82
0.25	2.61	2.05	2.21
0.5	1.68	0.87	1.43
1.0	0.93	0.43	0.70
2.0	0.47	0.28	0.38
3.0	0.42	0.17	0.21
5.0	0.25	0.080	0.26
10.0	0.22	0.072	0.18

TABLE II (Continued from the previous page.)

Concentration of lignosulfonate-PO product (wt %)	Interfacial tension (mN/m), aqueous phase salinity (wt % NaCl)		
	0	1	3
(f) Degree of propoxylation = 49% (2.0 g KOH catalyst)			
0.1	1.43	1.36	1.23
0.25	0.95	0.93	0.72
0.5	0.68	0.57	0.38
1.0	0.42	0.29	0.18
2.0	0.34	0.26	0.11
3.0	0.29	0.12	0.073
5.0	0.18	0.08	0.049
10.0	0.12	0.07	0.031

tions when the injected surfactant may come into contact with high-salinity brines.

CONCLUSIONS

- (1) A commercial lignosulfonate was reacted with propylene oxide to obtain products having a degree of propoxylation ranging from 19% to 49%.
- (2) The propoxylated products retained high solubility in water and high salinity tolerance while their interfacial activity increased dramatically in comparison with the original lignosulfonate.
- (3) Solutions of propoxylated lignosulfonate exhibited very low interfacial tensions both against a pure hydrocarbon (isooctane) and against a crude oil (Lloydminster crude).

TABLE III
Interfacial Tension of Propoxylated Lignosulfonate against Lloydminster Crude Oil*

Concentration of lignosulfonate-PO product (wt %)	Interfacial tension (mN/m), aqueous phase salinity (wt % NaCl)		
	0	1	3
0.1	7.41	3.89	1.32
0.25	3.26	2.06	0.75
0.5	1.31	1.07	0.38
1.0	0.82	0.53	0.23
2.0	0.58	0.32	0.11
3.0	0.31	0.18	0.12
5.0	0.23	0.11	0.089
10.0	0.12	0.083	0.064

* Degree of propoxylation: 32% (3.0 KOH catalyst).

- (4) In general, the properties of the propoxylated lignosulfonates are well suited for their potential use in enhanced oil recovery.

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