

# The Extraction and Fractionation of Lignosulfonates with Long Chain Aliphatic Amines

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The separation and fractionation of lignosulfonates was studied using the following aliphatic amine-organic solvent systems: dodecyl amine, dioctyl amine and trioctyl amine dissolved in 1-butanol, 1-pentanol, methyl isobutyl ketone, 1,2-dichloroethane or cyclohexane.

The degrees of extraction were close to 100%. By carrying out the extraction in several steps it was possible to achieve fractionation of the lignosulfonates according to molar mass. This fractionation can be influenced by altering the amine-solvent system.

The lignosulfonates of spent sulfite liquors form a potentially valuable source of chemicals for use as emulsifying and dispersing agents or as starting material for synthesizing other chemicals. However, in order to be able to use these lignosulfonates they should be obtained in a pure state and in suitable fractions according to molar mass.

Extraction with liquid ion exchangers such as aliphatic amines dissolved in a water-immiscible organic solvent could be suitable for this purpose.<sup>1,2</sup>

In most of the studies reported the organic solvent has been an alcohol such as butanol,<sup>3,4</sup> butanol-benzene,<sup>5</sup> or higher alcohols.<sup>6</sup> Melms & Mühlberg<sup>7</sup> have studied the effect of different solvents and amines on the extraction of lignosulfonates from beach spent sulfite liquors. They found that the more polar the solvent the higher was the degree of extraction. Values of 80...90% were reported. They also found that primary amines were more efficient than secondary and the tertiary amines were the least suitable. Finally Hämälä *et al.*<sup>8</sup> have patented an extraction method using methyl isobutyl ketone as the solvent. The degree of extraction reported was 99%.

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In the work done so far very little attention has been given to how the nature of the amine, the solvent and the amine-solvent combination affects the degree of extraction and the fractionation of lignosulfonates according to molar mass. In this report we concentrate on the influence of these factors using, as a model substance, purified lignosulfonate. We were able to show that fractionation is indeed both very solvent-dependent and dependent on the structure of the amine. It is thus possible to control the fractionation by choosing a suitable amine-organic solvent combination.

## Experimental

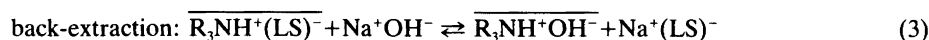
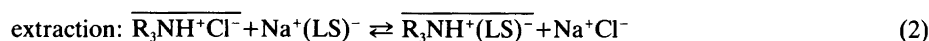
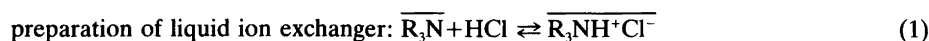
*Reagents.* The following amines, all obtained from Merck-Schuchardt, were used: dodecyl amine (DOD), dioctyl amine (DIO), trioctyl amine (TOA). The solvents used were: 1-butanol (BUT) from BDH, 1-pentanol (PEN) from Merck-Schuchardt, methyl isobutyl ketone (MIK) from Fluka, 1,2-dichloroethane (DCE) and cyclohexane (CYH) both from Merck. All these reagents were analytical grade. Other solvents such as chloroform, trichloroethylene, toluene and carbon tetrachloride were also tried

Table 1. Composition of the sodium lignosulfonate.

component	weight-%
lignosulfonates	97.200
carbohydrates	1.077
formic acid	0.002
acetic acid	0.016
sodium	2.282

but phase separation was found to be too difficult in all cases.

The sodium lignosulfonate, which was used as



The corresponding procedures were:

1. Preparation of the liquid ion exchanger (amine hydrochloride): Equal volumes of a solution of 0.05 M amine in an organic solvent and 1 M HCl were shaken for 5 min. The organic phase was washed twice with distilled water to remove excess HCl.

2. Extraction: Equal volumes of liquid ion exchanger and lignosulfonate solution were mixed in a beaker for 5 min at room temperature using a magnetic stirrer. The phases were separated by centrifugation for 30 min at 6000 rpm.

3. Back extraction: The organic phase was back-extracted with 1 M NaOH using the same procedure as for extraction. The water phases from both extraction and back-extraction were washed twice with the solvent to remove excess amine, the water phase was then evaporated to dryness to remove the solvent. Thereafter water was added to make up the original volume of solution.

*Analytical methods.* The lignosulfonate concentration was determined spectroscopically by measuring the absorbance at 280 nm using a Beckman Acta M VI spectrometer. (The average absorption coefficient for the lignosulfonate was  $13.2 \text{ dm}^3 \text{ g}^{-1} \text{ cm}^{-1}$ ). The distribution of molar mass of the lignosulfonates were measured by gel

a model in the extraction experiments, was purified by ultrafiltration at Rauma-Repola Ltd, Rauma. Its composition is given in Table 1. The molar mass distribution as determined by gel chromatography was:

>40 000	>20 000	>100 000	>5000
23.5 %	40.9 %	59.0 %	72.5 %

*Extraction procedure.* The chemical reactions occurring during the amine extraction are (bars denote species in the organic phase; LS-lignosulfonate):

chromatography using a 50 cm long and 1.5 cm diameter column. The lignosulfonates were eluted from Sephadex G-75 with 0.25 M sodium chloride solution. The rate of elution was 30 ml/h. The chromatograms were recorded by measuring the transmittance of the effluent at 280 nm with a LKB flow-through UV-detector UVICORD 4700.

Calibration of the gel chromatograms was performed using the calibration method of Forss *et al.*<sup>9</sup> and Stenlund.<sup>10</sup> We estimate the reproducibility of our molar mass distributions to be  $\pm 3\%$ .

## Results and discussion

In the first part of the experiments the degree of extraction of the sodium lignosulfonate was determined using constant amine hydrochloride concentration varying the lignosulfonate concentration of the water phase. The results obtained with the three amines are given in Table 2 (Dodecylamine hydrochloride is almost insoluble in DCE and CYH). With some liquid ion exchangers a second organic phase, that is, a third phase, formed during the extraction. This phase was dark brown, sticky and difficult to separate from the two other phases. It was back-extracted together with the organic phase and dissolved easily in alkali.

Table 2. Dependence of the degree of extraction, E, and the distribution coefficient, D\*, on the lignosulfonate concentration,  $c_{LS}$ . The extractant is a) 0.05 M TOA · HCl, b) 0.05 M DIO · HCl and c) 0.05 M DOD · HCl in different solvents.

$c_{LS}/\text{gdm}^{-3}$	BUT		PEN		MIK		DCE		CYH	
	E/%	D	E/%	D	E/%	D	E/%	D	E/%	D
a) 5.0	96.0	24.0	94.0	15.7	58.0	1.38	70.0	2.33	98.0	49.0
10.0	82.0	4.56	66.0	1.94	55.0	1.22	58.0	1.38	81.0	4.26
20.0	47.5	0.90	39.0	0.64	38.5	0.63	41.5	0.71	50.0	1.00
30.0	32.7	0.49	27.0	0.37	30.3	0.43	34.7	0.53	34.0	0.34
40.0	26.3	0.36	20.0	0.25	26.0	0.35	28.0	0.39	25.0	0.33
50.0	20.4	0.26	15.8	0.19	21.0	0.27	22.4	0.29	20.4	0.27
b) 5.0	100.0	$\infty$	10.0	$\infty$	90.0	9.0	100.0	$\infty$	100.0	$\infty$
10.0	98.0	49.0	82.0	4.56	75.0	3.0	99.0	99.0	97.0	32.3
20.0	92.5	12.3	64.0	1.78	50.0	1.0	97.5	39.0	59.5	1.47
30.0	80.0	4.0	47.0	0.98	47.3	0.89	88.0	7.33	46.3	0.53
40.0	61.5	1.59	36.0	0.56	37.3	0.59	70.3	2.37	34.8	0.53
50.0	47.6	0.91	28.4	0.39	29.2	0.41	56.4	0.89	27.4	0.38
c) 5.0	100.0	$\infty$	100.0	$\infty$	98.0	49.0				
10.0	100.0	$\infty$	90.0	9.0	98.0	49.0				
20.0	99.0	99.0	72.9	2.70	79.0	3.76				
30.0	98.7	74.0	56.2	1.29	74.0	2.85				
40.0	81.8	4.48	43.1	0.76	62.3	1.65				
50.0	77.0	3.35	35.5	0.55	50.6	1.02				

\*  $E = (\bar{c}_{LS}/c_{LS}^0) \cdot 100\%$ ;  $D = \bar{c}_{LS}/c_{LS}$ ;  $\bar{c}_{LS}$  &  $c_{LS}$ -concentration of lignosulfonate in organic and aqueous phase;  $c_{LS}^0$ -original concentration in aqueous phase.

In the fractionation experiments the lignosulfonate was extracted from the water solution in three steps: 25, 50 and 75 % extraction. The distribution of molar mass of the extracted lignosulfonate was determined indirectly from the distribution of the lignosulfonates remaining in the water phase of the extraction. The results are given in Table 3, and can be compared with the distribution for the original lignosulfonates given in the experimental section.

From the data in Table 2 it can be seen that the degree of extraction and the distribution coefficient increases in the order tertiary < secondary < primary amine hydrochloride. This is due to the fact that unsubstituted amines are able to form intramolecular hydrogen bonds<sup>2</sup> and this increases their extraction capacity.

In order to obtain a good comparison between the physical properties of the solvents and degree of extraction with the three amines Table 4 was compiled. The data of this Table clearly show an expected result, that there is no correlation be-

tween the relative permittivity of the solvent and the degree of extraction. The E-values are the same for the least polar cyclohexane and the most polar butanol. This is contrary to the result of Melms & Mühlberg,<sup>7</sup> who claim that the degree of extraction decreases as the relative permittivity of the solvent diminishes. On the other hand other researchers, ie. Müller & Diamond<sup>11</sup> have also found the same type of result as above. It is evident that specific solvation processes affect the phase transfer of the amine-lignosulfonate complex as stated by Frolov *et al.*<sup>2</sup> It was also found that the formation of a third phase increases with decreasing substitution on the amine nitrogen and also with decreasing polarity of the solvent (Table 4).

The results of the fractionation experiments (Table 3) can be qualitatively classified into three categories depending on the composition of the liquid ion exchanger. This classification is given in Table 5.

The fraction is dependent on the organic sol-

Table 3. Distribution of molar mass of the unreacted lignosulfonate in the water phase of the extraction (in percentage of total sample).

Liquid ion exchanger	Molar mass				Liquid ion exchanger	Molar mass			
	>40 000	>20 000	>10 000	>5000		>40 000	>20 000	>10 000	>5000
DOD · HCl-BUT					DIO · HCl-MIK				
25 % extracted	19.2	35.1	54.8	71.2	25 % extracted	33.7	47.0	61.4	73.8
50 % "	11.4	25.7	48.6	68.6	50 % "	40.5	52.9	61.4	72.5
75 % "	0.7	6.9	16.0	31.2	75 % "	50.8	61.5	79.7	76.2
DIO · HCl-BUT					TOA · HCl-MIK				
25 % extracted	21.1	39.5	59.4	73.4	25 % extracted	32.9	51.1	69.6	81.4
50 % "	12.3	24.4	45.0	66.7	50 % "	45.2	61.5	73.6	81.1
75 % "	1.3	10.7	27.0	52.8	75 % "	93.4	98.6	100	100
TOA · HCl-BUT					DIO · HCl-DCE				
25 % extracted	22.0	39.7	62.2	77.0	25 % extracted	28.8	49.7	66.0	77.5
50 % "	15.6	31.7	51.9	69.5	50 % "	52.5	69.5	76.7	87.3
75 % "	5.0	10.9	26.1	45.0	75 % "	61.3	78.4	87.4	91.9
DOD · HCl-PEN					TOA · HCl-DCE				
25 % extracted	7.6	20.5	49.6	75.5	25 % extracted	25.9	46.8	68.4	82.1
50 % "	19.8	40.3	63.9	81.9	50 % "	53.3	78.5	91.9	97.8
75 % "	27.2	49.3	71.5	86.5	75 % "	98.8	98.7		100
DIO · HCl-PEN					DIO · HCl-CYH			100	
25 % extracted	7.0	25.1	50.1	79.9	25 % extracted	29.8	48.7	69.9	81.5
50 % "	11.3	24.8	42.3	58.8	50 % "	41.2	63.5	79.1	88.0
75 % "	25.9	42.3	61.2	74.6	75 % "	65.3	78.1	83.4	96.9
TOA · HCl-PEN					TOA · HCl-CYH				
25 % extracted	0.8	16.2	34.6	53.1	25 % extracted	32.4	51.4	70.5	82.9
50 % "	36.1	54.5	69.6	80.6	50 % "	39.2	61.8	78.4	86.9
75 % "	51.9	72.2	74.0	85.2	75 % "	76.1	81.8	92.2	97.4
DOD · HCl-MIK									
25 % extracted	17.5	33.5	53.9	72.3					
50 % "	12.8	27.6	46.1	64.2					
75 % "	0.2	18.9	53.9	81.9					

Table 4. Degree of extraction, E, (calculated for an initial lignosulfonate concentration of 10 g/dm<sup>3</sup>) obtained with amines using different organic solvents with the physical properties indicated (relative permittivity, density and solubility in water). Formation of a third phase is indicated by a "+"-sign.

solvent	amine			TOA · HCl	DIO · HCl	DOD · HCl
	$\epsilon$	$\rho/\text{gcm}^{-3}$	sol. % (H <sub>2</sub> O)	E/%	E/%	E/%
BUT	17.8	0.809	6.8	82.0	98.0	100.0
PEN	13.9	0.814	2.7	66.0	82.0	90.0
MIK	13.1	0.978	1.9	55.0	75.0(+)	98.0(+)
DCE	9.9	1.24	0.9	58.0	99.0(+)	
CYH	2.0	0.779	0.05	81.0(+)	97.0(+)	

Table 5. Summary of the results of the fractionation experiments.

category 1 (high molar mass lignosulfonates extracted first)	category 2 (low molar mass lignosulfonates extracted first)	category 3 (no fractionation)
DOD · HCl-BUT DIO · HCl-BUT TOA · HCl-BUT	DIO · HCl-MIK TOA · HCl-MIK  DIO · HCl-DCE TOA · HCl-DCE  DIO · HCl-CYH TOA · HCl-CYH	DOD · HCl-PEN DIO · HCl-PEN TOA · HCl-PEN

vent except in the case of methyl isobutyl ketone. The order of fractionation changes with polarity of the solvent. With butanol, the most polar one, the high molar mass lignosulfonates are extracted first. With pentanol no fractionation occurs and with the least polar solvents dichloroethane and cyclohexane, the low molar mass lignosulfonates are extracted first. This result is valid in particular in the case of the secondary and tertiary amine salts. For the primary amine salt no such conclusion can be drawn due to the limitations set by its solubility in the solvents studied.

The results obtained clearly show that the extraction-fractionation process is complicated and depends on several factors such as solvation capacity and other physical properties of the organic solvent, intramolecular hydrogen bonding in the amine and amine-lignosulfonate complex, association and interfacial tension between the phases. Most probably the amine-lignosulfonate complex is formed in the aqueous phase and is then transported by diffusion into the organic phase. It is possible that the amine salt reacts with all lignosulfonate ions independent of their size but only some of the complex molecules

formed are transferred into the organic phase depending on whether thermodynamic or kinetic factors are controlling the process.

Finally it should be mentioned that experiments with spent sulfite liquors were done using the same liquid ion exchangers and the degree of extraction was found to be of the same order of magnitude as reported above.

It is evident that extraction experiments such as those reported here, while giving information about the best extraction procedure for practical spent sulfite liquors, do not answer the question of what the mechanism of the process is. We therefore intend to continue this research by treating the organic phase as a liquid membrane and using an external electric field to regulate the transport of amine-lignosulfonate complex, across the interface. This should give better mechanistic information and it may also be possible to achieve commercially interesting improvements in the extraction process.

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