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ORIGINAL CONTRIBUTION

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High- and low-molecular-weight lignosulfonates and Kraft lignins as oil/water-emulsion stabilizers studied by means of electrical conductivity

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Abstract Electrical conductivity measurements were used to study the creaming rates in oil/water emulsions stabilized with five lignosulfonates and one Kraft lignin. The creaming process resulted in a narrow dispersion band separating the water-rich and the oil-rich phases. An electrode was designed to follow this zone in the emulsion as a function of time. This makes it possible to calculate the amount of water separated from the emulsion directly from the creaming profiles. The stability concerning creaming was also evaluated with data obtained from visual inspection. Equivalent creaming profiles indicate that the electrode design used is suitable for stability measurements in the systems examined. Droplet interaction in diluted emulsions was studied with video-enhanced microscopy.

Key words Lignosulfonates – Oil/water emulsions – Creaming rates – Conductivity measurements

Introduction

Lignosulfonates and Kraft lignins

Lignosulfonates (LS) and Kraft lignins are isolated from spent liquors used in the sulfite pulping and kraft pulping process, respectively [1]. Purified LS have found widespread practical applications because of their dispersing, stabilizing, binding and complexing properties [2–4].

LS are crosslinked polydisperse polyelectrolytes in which the molecules are compact spheres in aqueous solutions [5]. The molecule contains sulfonate groups as well as carboxylic, phenolic and methoxyl groups, and the basic repeating building unit in the molecule is a phenylpropane derivate [6]. The structure may be nonuniform with regard both to number and distribution of anionic groups, and also in the structure of the hydrocarbon backbone. Due to ionic groups in the interior of the molecule, LS show typical polyelectrolyte expansion, where the LS molecule swells or shrinks as the concentration of the counterions varies from low to high, respectively [7, 8]. The charged sulfonate groups near the surface of the molecule matrix make LS readily soluble in water [9]. Like LS, Kraft lignins are crosslinked polydisperse polyelectrolytes and sulfonated Kraft lignins find similar uses as LS.

LS and Kraft lignins as emulsion stabilizers

Several investigations and applications have shown that LS are exceptional oil-in-water emulsion stabilizers [10]. Although LS do not form micelles, the molecule has both hydrophilic and lipophilic moieties; however, these two parts are not separated in a way that promotes high surface activity.

The nonsolubility of LS in aliphatic and aromatic hydrocarbons, and the lack of pronounced surface- and interfacial-tension lowering properties, indicates that LS adsorb at the oil-water interface rather than in the interface [11–13]. A solution pressure has to be developed by the LS to force it into the interface. This means that a relatively high amount of LS must be added to give stable emulsions. The semirigid LS film gives rise to mechanical, steric and electrostatic stabilization. The solubility of LS is reduced in electrolyte-contaminated solutions, and this will force more LS to the oil-water interface. A reduction in emulsion stability due to a reduction in the zeta potential on the oil droplets will be compensated by an increase in the condensed layer adsorption. This leads to stable emulsions even in saturated salt solutions.

LS are of a highly polydisperse nature. There are indications that the low-molecular-weight fractions associate in solution and that high-molecular-weight fractions have a higher degree of molecular branching than the lower-molecular-weight fractions [14, 15]. Several investigations have shown that LS can function as dispersants or flocculants depending on their molecular weight [3, 16, 17]. Low-molecular-weight LS act as stabilizers, while higher-molecular-weight LS are of sufficient molecular length to enable them to be adsorbed onto the surface of adjacent particles. This bridging will promote flocculation and destabilize the dispersion. Other authors have reported better dispersant properties for high-molecular-weight LS in concentrated kaolin suspensions [18]. The influence of molecular weight on dispersant properties indicates that this molecular property will also affect the stabilities of water-continuous emulsions. Adsorption of LS on negatively charged polystyrene latex surfaces indicates that the adsorption process is not only governed by electrostatic interactions, but also by a sort of hydrophobic interaction. It has been proposed that the hydrophobic phenyl propane ring may be of significance in this respect [17].

Materials and methods

Materials

The sodium LS (UP364, UP365, UP366, UP407, UP411) and the Kraft lignin (Diwatex UP329) were purified, fractionated and analyzed by Borregaard Lignotech. The LS samples are present as five different molecular-weight fractions. The properties are summarized in Tables 1 and 2. The properties of the Kraft lignin fraction are summarized in Table 3. Hexadecylpyridinum chloride (CPC) of analytical grade was supplied by Fluka. Exxsol D80 was supplied by Esso Norge AS, and is a light petroleum distillate with carbon fractions in the range C_9–C_{16}. Sodium chloride was of analytical grade and was supplied by Merck. All emulsions were made from distilled water further purified by a Serapur PRO 90CN deionizing and adsorbing unit.

Composition and preparation of the emulsions

The oil/water ratio was held constant for all the emulsions (48 g oil, 72 g water). The water phase contained 10 mM NaCl to improve the sensitivity and accuracy of the conductivity measurements. Three different LS and Kraft lignin concentrations (0.5, 1.0 and 2.0% on the basis of the internal phase weight) were used. In addition, emulsions stabilized with complexes LS (1.0%) and CPC (0.14 and 3.45%) were studied. The emulsion was mixed with an S 25N–25F dispersing tool connected to a Ultra-Turrax T25 dispersion unit (IKA Labortechnik, Janke & Kunkel). The mixing speed was 8000 rpm, and the mixing time was 3 min for the LS- and Kraft-lignin-stabilized emulsions, and 2 min for the LS + CPC-stabilized emulsions.

Table 1 Properties of the sodium lignosulfonate (*LS*) fractions

Sample description	UP364	UP365	UP366	UP497	UP411
pH (10% solution)	9.4	9.6	8.8		
Solids, %	92	96.5	97.2		
Calcium, %	0.11	0.02	0.06		
Sodium, %	5.94	6.03	7.17		
Total S, %	6.2	6.1	7.1	4.7	6.4
Inorg. S, %	0.01	0.07	0.28	0.2	0.1
Org. S, %	6.1	6	6.8	4.5	6.3
Methoxyl, %	11.9	12.1	9.2	12.7	10.8
Carboxyl, %	4.5	5.4	5.9		
Phenolic OH, %	2.4	2.4	2.4		
Red. sugars, %	0.6	0.4	4.3		
Mol. weight (HPLC)					
M_w	62 700	76 400	9 300		
M_n	13 900	16 300	5 100		

Table 2 Molecular weight of desulfonated and highly sulfonated sodium LS

Molecular weight (g/mol)	UP407 (%)	UP411 (%)
> 59000	14.9	2.8
< 59000	85.1	97.2
< 38000	72.2	89.2
< 16000	47.9	70.9
< 6600	26.2	48.8
< 2755	12.2	26.0
< 1740	8.3	16.6

Table 3 Properties of the Kraft lignin fraction

Sample description	Diwatex UP329	Molecular weight (g/mol)	(%)
pH (10% solution)	10.6	> 12500	30.8
Solids, %	97.9	< 12500	69.2
Total S, %	5.5	< 10000	58.7
Inorg. S, %	0.6	< 7000	45.5
Org. S, %	4.8	< 5000	33.1
Methoxyl, %	10.2	< 3000	19.2
Carboxyl, %	8.1	< 2000	10.3
Phenolic OH, %	1.9	< 1000	1.5

Conductivity measurements and electrode design

Immediately after production, 90 ml emulsion was filled in a cylindrical glass container (d = 25 mm, h = 185 mm) containing the electrode. The electrode was connected to a Hewlett Packard 42638 LCR meter operating at a frequency of 1 kHz, and the conductivity was measured every 60 s under constant temperature conditions (25.0 ± 0.1 °C). The electrode was coated with gold to eliminate polarization effects and to prevent corrosion of the electrode material.

The electrode was made up of two 210 mm iron rods of 1 mm diameter. The lower 30 mm of the electrode was divided into insulated and noninsulated areas in the following way: 0–7 mm, 10–17 mm, 20–27 mm, and from 30 mm and up to the connection points were insulated areas, while the areas in-between were noninsulated. Teflon was used as insulating material. Figure 1 demonstrates how the electrode was place in the measuring cell.

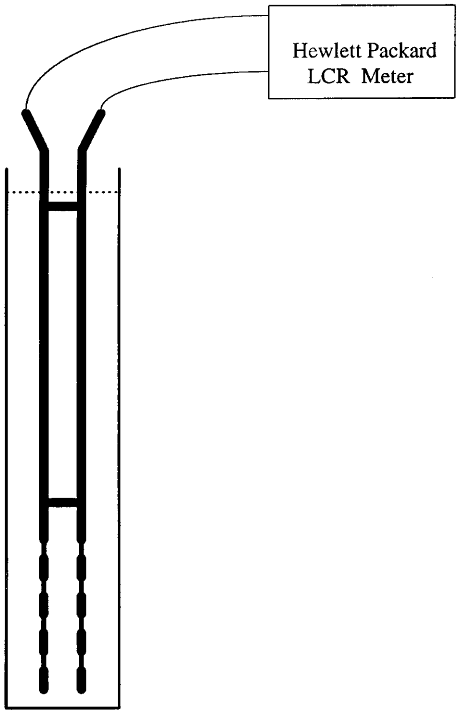


Fig. 1 Schematic diagram of the electrode where the insulated and noninsulated areas are shown

Results and discussion

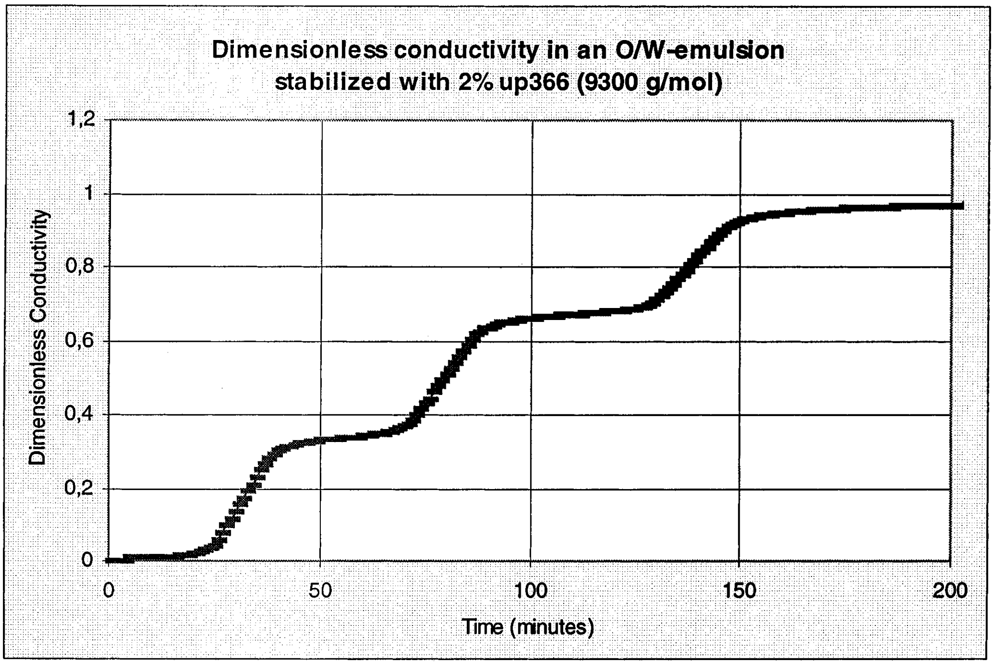
Conductivity measurements

The creaming process in the emulsions studied resulted in a distinct boundary between the water-rich and the oil-rich phases. A freshly prepared emulsion had a white colour. After a few minutes a dark brown zone containing LS and water could be seen in the lower part of the cell. Samples from the water-rich phases were studied using video-enhanced microscopy (VEM) [18], and it was shown that the water phases contained only traces of oil. The electrode was designed to utilize the narrow extension of the zone separating the water-rich and the oil-rich phases, and the dividing of the electrode into alternating insulated and noninsulated parts made it possible to follow this zone as it propagated in the measuring cell as a function of time. Figure 2 demonstrates how the conductivity in a 40/60 (w/w) oil/water emulsion stabilized with 2.0% UP366 increased as the creaming process progressed. The trend in the measured conductivity in this sample is representative for all the emulsions studied. The data are given as the normalized conductivity, G:

$$G_{\mathrm{nt}} = \frac{(g_{\mathrm{nt}} - g_{\mathrm{initial}})}{(g_{\mathrm{end}} - g_{\mathrm{initial}})} ,$$

in which G_{nt} is the normalized conductivity at a given time t, g_{nt} is the measured conductivity at the same time t, g_{initial} is the measured conductivity at time $t = 0$ and g_{end} is the last value measured. When the measurements start at time $t = 0$, it is reasonable to

Fig. 2 Dimensionless conductivity in an oil/water emulsion (40/60 w/w) stabilized with 2.0% lignosulfonate (UP366) as a function of time



assume that each of these levels has an equal contribution to the total conductivity in the system. This initial situation is rapidly changed due to the creaming process. The first plateau in Fig. 2 reveals the frontier moving along the first insulated area on the electrode. Only small changes in the sample conductivity are measured in this area. When the frontier reaches the first noninsulated area a dramatic increase in the conductivity is observed. The total conductivity in the sample will at this time be dominated by the changes that occur in this area. The conductivity profile flattens out when the frontier reaches the next insulated area and so on.

The derivatives of the conductivity plot in Fig. 2 show how fast the conductivity changes as a function of time. Figure 3 shows that there is fast growth and fast reduction when the water-rich phase reaches the noninsulated and the insulated area, respectively. At each peak there is a horizontal plateau where the derivative shows only small alteration. The plateau represents the linear increase in the conductivity that can be seen in Fig. 2, and the midpoint of each plateau represents the phase boundary located in the middle of each noninsulated level.

Generally, the conductivity is directly proportional to Φ_{water} [19]. VEM revealed that Φ_{water} in the water-rich phases was very close to 100%. This makes it possible to calculate the amount of water separated from the emulsions directly from the conductivity profiles when the fixed positions of the noninsulated areas (7–10, 17–20 and 27–30 mm) are known.

Lignosulfonates and Kraft lignin as emulsion stabilizers

The amount of water separated from different LS and Kraft lignin samples was calculated at three time positions. The results are listed in Table 4 and are given as percentages of the total water-cut of the emulsions. Although all the LS and the Kraft lignin studied are efficient oil/water-emulsion stabilizers, the fast creaming rates observed reflect a relatively high mean droplet size due to the moderate homogenization energy used.

Table 4 Separation of water from oil/water emulsions stabilized with different amounts of LS and Kraft lignin

Sodium LS and Kraft lignin samples	10% Separated water (min)	20% Separated water (min)	30% Separated water (min)
UP364 0.5%	35	75	125
” 1.0%	35	80	140
” 2.0%	50	120	190
UP365 0.5%	30	70	115
” 1.0%	40	95	155
” 2.0%	50	115	180
UP366 1.0%	40	95	150
” 2.0%	35	85	145
UP407 0.5%	30	65	100
” 1.0%	35	75	125
” 2.0%	50	115	195
UP411 0.5%	25	60	100
” 1.0%	30	70	125
” 2.0%	45	105	185
Diwatex UP329 1.0%	40	90	150
” 2.0%	70	150	240

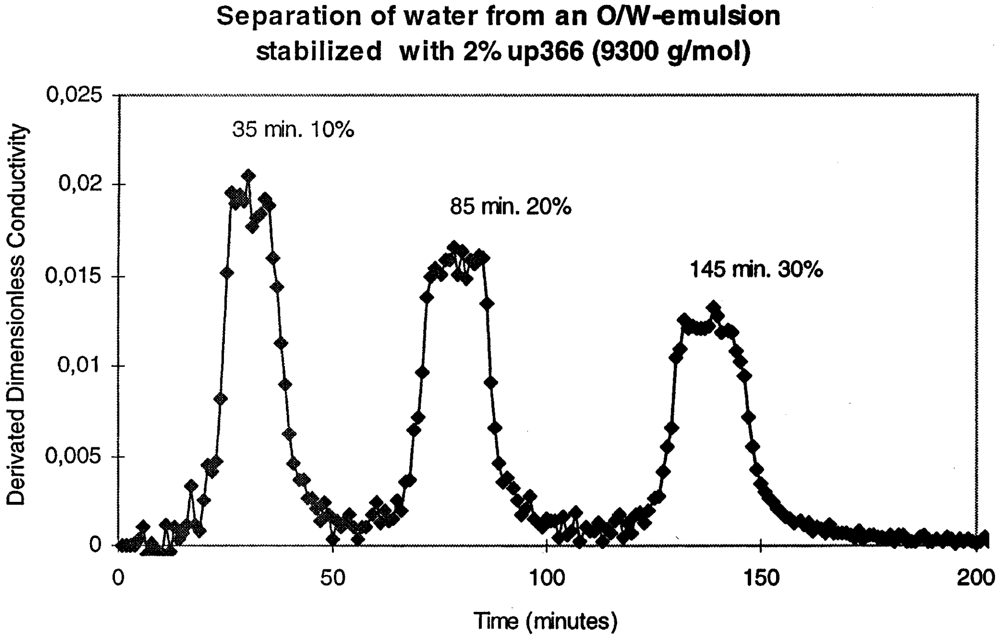


Fig. 3 The derivatives of the conductance plot shown in Fig. 2

The high-molecular-weight (UP364, UP365) and the desulfonated and the highly sulfonated LS (UP407, UP411 respectively) give rise to approximately identical emulsion stabilities. The stability is significantly improved when increasing the LS concentration which indicates an increased adsorption on the droplet surface when the LS concentration is high. For the low-molecular-weight LS (UP366) the picture is somewhat different. The creaming process is slightly more rapid, and the lack in stability gained by increasing the amount of LS indicates effective adsorption on the droplet surface at low LS concentrations. The increased emulsion stability observed using high-molecular-weight LS could be due to multilayer adsorption giving both steric and electrokinetic stabilization [2, 3]. Also, for the Kraft lignin studied (Diwatex UP329) the creaming rate declines when increasing the polymer concentration and the 2% sample has the slowest creaming rate of all the emulsions studied. It has been shown that the adsorption of LS on polystyrene latex particles increases when the degree of sulfonation is low [17]. The emulsion stability obtained, and the low degree of sulfonation of the Kraft lignin fraction indicate effective adsorption onto the oil droplets. The structural differences that are known to exist between LS and Kraft lignins could also be important in this respect [20].

VEM was used to study diluted samples from the oil-rich phases. Pictures of oil/water emulsions stabilized with low- and high-molecular-weight LS respectively, are shown in Figs. 4 and 5. The pictures reveal a distinct difference in the oil droplet interaction in the two samples. The high-molecular-weight LS gives rise to a strongly flocculated system indicating that the molecule is of sufficient length to be adsorbed onto more than one droplet, thereby promoting flocculation [3, 15, 16]. The low-molecular-weight LS on the other hand, gives rise to discreet droplets with no sign of flocculation. This is also the case for the Kraft lignin indicating that these molecules are of insufficient length to be adsorbed onto more than one droplet. For high-molecular-weight LS a stretched configuration has been reported at low concentrations and a coiled configuration at higher concentrations due to supression of the dissociation of the ionic groups [15]. The creaming rates measured indicate a reduction in the bridging ability of the LS molecules in the more concentrated emulsions.

Accuracy of the conductivity measurements

The validity or accuracy of the conductivity-measurement method was verified by comparing results based on conductivity data with results based on visual observations. The creaming process was studied in emulsions stabilized with LS and LS/CPC complexes. The oil/water ratio and the sample preparation procedure are the same as described earlier. The homogenization time was 2 min and the high-molecular-weight LS (UP364) was used as the polyelectrolyte. The amounts of emulsifiers used are listed in Table 5, and are given as percentages of the internal phase weight.

Figure 6 shows how the dimensionless conductivity evolves as a function of time in the emulsions studied. In Fig. 7 the creaming profile for equivalent emulsions is given on the basis of visual observations. For each system the percentage of water separated from the

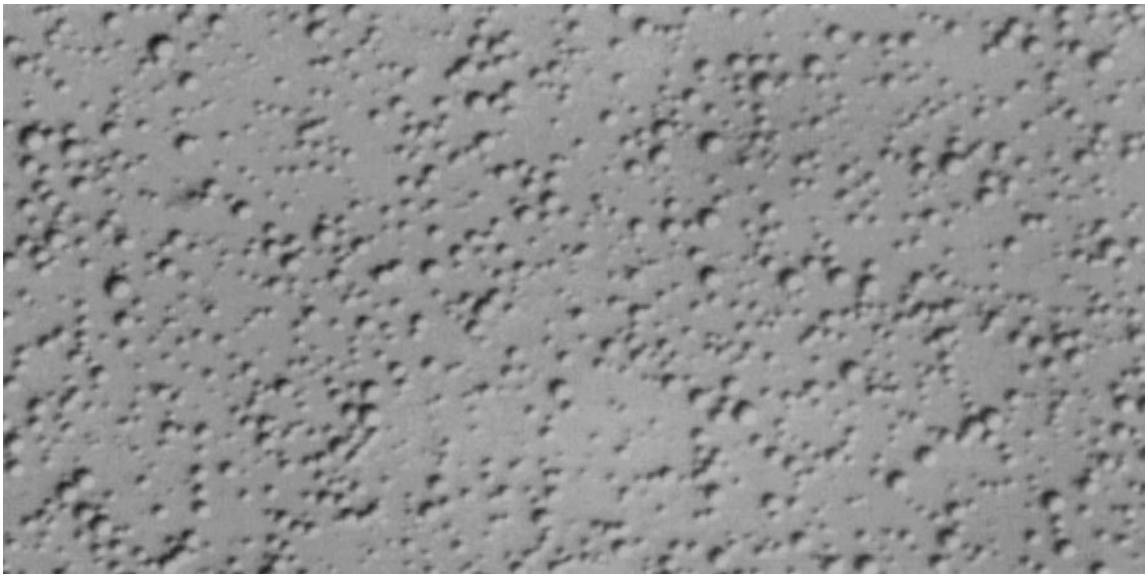


Fig. 4 Oil droplets stabilized with low-molecular-weight lignosulfonate (UP366). 1 cm on the image corresponds to a distance of 15.5 μm

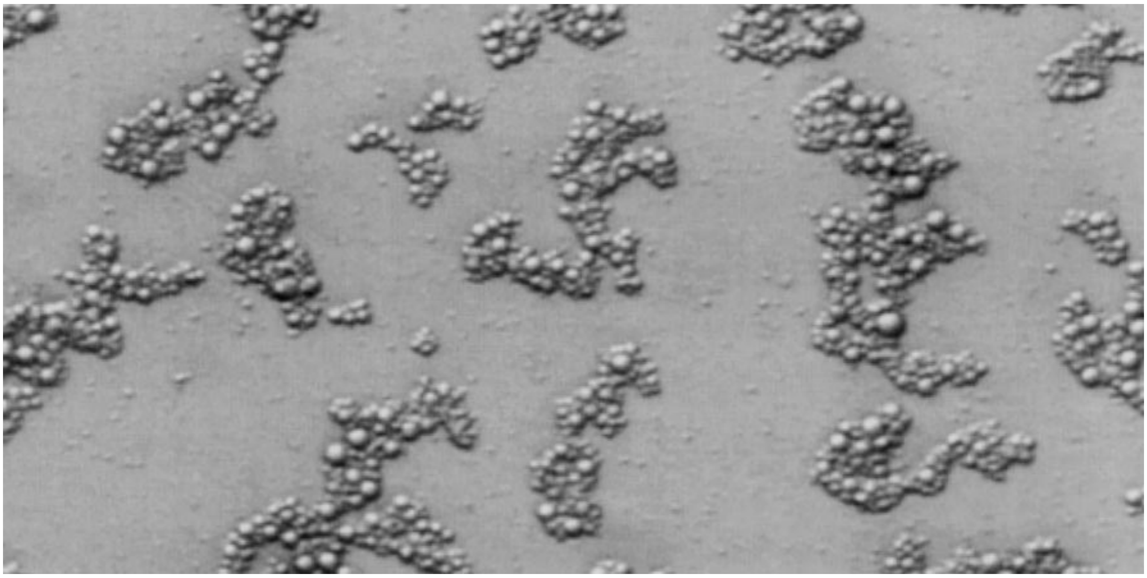


Fig. 5 Oil droplets stabilized with high-molecular-weight lignosulfonate (UP365). 1 cm on the image corresponds to a distance of 15.5 μm

Fig. 6 Dimensionless conductivity in oil/water emulsions (40/60 w/w) stabilized with lignosulfonate (UP364) and lignosulfonate/hexadecyl pyridinium chloride (*CPC*)-complexes as a function of time

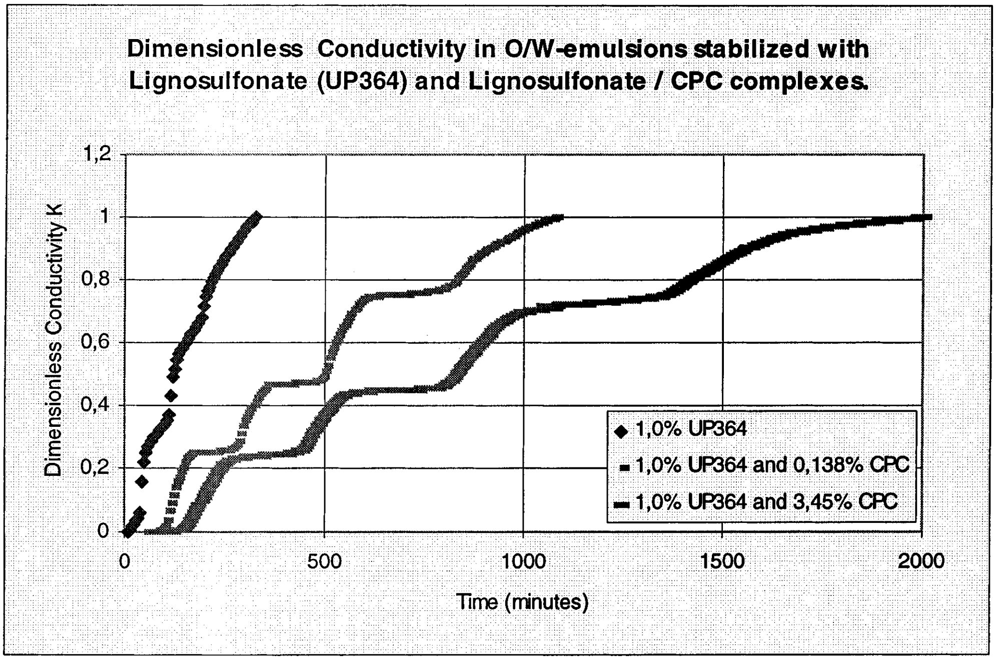


Table 5 Separation of water from oil/water emulsions stabilized with LS (UP364) and LS/hexadecylpyridinum chloride (*CPC*) complexes calculated from conductivity measurements and visual observations

Sample	Time (min)	Separated water (%) conductivity measurements	Separated water (%) visual observations
UP364 (%)	35	17	22
	110	34	34
	185	43	43
LS (1%) + CPC (0.14%)	50	9	12
	230	27	27
	445	38	42
LS (1%) + CPC (3.45%)	80	10	12
	360	25	27
	730	37	42

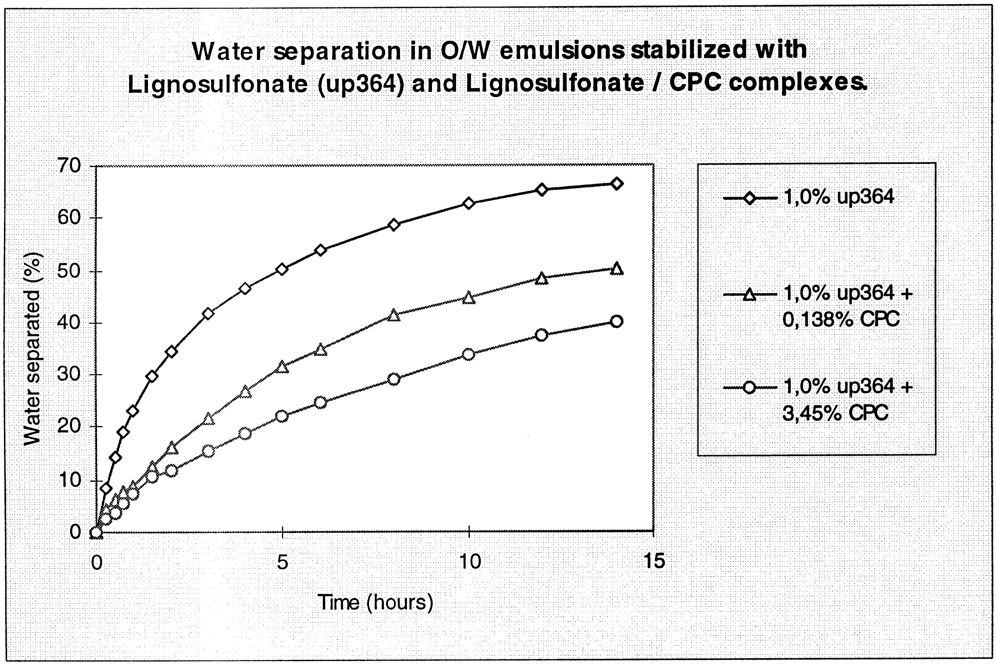


Fig. 7 Water separated from oil/water emulsions (40/60 w/w) stabilized with lignosulfonate (UP364) and lignosulfonate/CPC complexes as a function of time

emulsions was calculated at different stages in the creaming process. From the values listed in Table 5 it can be seen that there is good correlation between data found by the two methods. This is the case both when the creaming rate is fast, as in emulsions stabilized with LS, and in emulsions stabilized with LS/CPC complexes, where the creaming rate is slower. The deviation in the results is most likely to be due to uncertainty in the visual readings. To some extent there is also uncertainty connected with reproducing the emulsions.

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