Extraction of a Polyelectrolyte Using a Supported Liquid Membrane. II. Extraction and Fractionation of Lignosulfonate

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Kontturi, A.-K., Kontturi, K., Niinikoski, P. and Sundholm, G., 1990. Extraction of a Polyelectrolyte Using a Supported Liquid Membrane. II. Extraction and Fractionation of Lignosulfonate. – Acta Chem. Scand. 44: 883–891.

It is shown that the extraction and separation of a polydisperse polyelectrolyte, lignosulfonate, can be performed using a supported liquid membrane with 1-decanol as solvent and trilaurylamine as carrier.

The design of a suitable membrane cell is presented and the influence of lignosulfonate and NaCl concentrations of the feed solution, the amine concentration, and the lignosulfonate, NaOH and HCl concentrations of the stripping solution on the flux of lignosulfonate through the membrane are presented. A simple model, which assumes that the rate-determining step of the process is the diffusion of the lignosulfonate–amine complex in the membrane phase, is used to correlate the experimental results.

A working system for the liquid membrane extraction of macromolecules has not hitherto been achieved. Such an extraction method would, however, have great practical use as a separation process, i.e. for the separation of proteins. A further benefit would be if it could also give fractionation according to molar mass.

In a previous paper[1] a suitable supported liquid membrane (SLM) formulation for the extraction of lignosulfonate was devised. In this study we have used this SLM to show that extraction of this polydisperse polyelectrolyte can be performed as a steady-state carrier-mediated process. It is further shown that this process can be handled with the aid of a simple mathematical model.

Experimental

Materials. The same lignosulfonate (LS) as described in Ref. 1 was used. Trilaurylamine (TLA) (Sigma, 85 %) and 1-decanol (Sigma, 98 %) were used as received. All other chemicals were *proanalysi* grade products.

Apparatus. The experimental set-up is shown in Fig. 1 and the membrane cell in Fig. 2. The preparation of the liquid membrane itself and the analyses have been described in Ref. 1. All experiments were performed at room temperature. The total measuring time for a run was 5 h. During this time 10 samples were collected with the fraction collector. A steady state was achieved in this cell in less than 3 h. The performance of the membrane cell was also followed by comparing the measured steady-state concentration of LS in the feed solution with the value calculated from the mass balance of the feed solution c_{calc}, given by eqn. (1), where c_i is the initial concentration of LS, $\dot{V}^f$ the flow rate

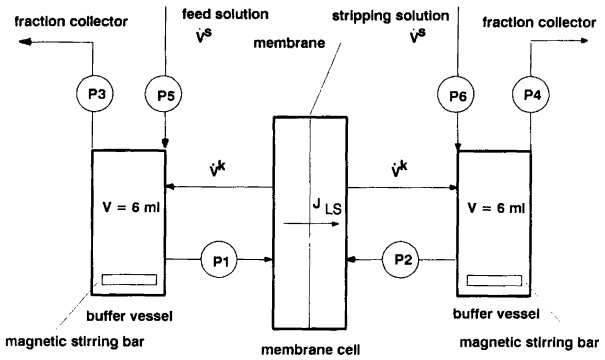

Fig. 1. The experimental set-up. The flow rate of circulation $\dot{V}$ = 150 ml h^{-1}. The flow rate of feed and stripping solution is 10 ml h^{-1}, J_{LS} is the flux of lignosulfonate, P1–P4 are Ismatec mini-micro 2/6 peristaltic pumps, and P5 and P6 are Desaga peristaltic pumps.

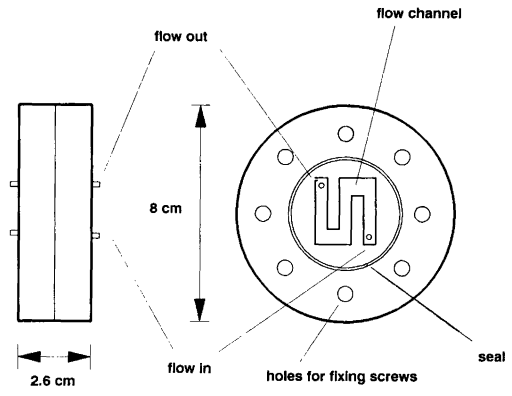

Fig. 2. The membrane cell (Teflon).

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$$c_{calc} = c_i - J_{LS}A/\dot{V}^f \quad (1)$$

of the feed solution and $J_{LS} = \dot{V}^s c_{LS}/A$ is the flux of LS (with A the active surface area of membrane, 3.4 cm^2, and $\dot{V}^s$ the flow rate of the stripping solution). The differences between c_{LS} and c_{calc} were found to be <2 %.

Methods. The membrane cell was operated in two transport modes: co-transport and counter-transport. The principle of the former mode has been described in Ref. 1. On the basis of the results obtained, the basic cell configuration chosen for co-transport was as shown in (2). In co-transport

0.01 M HCl + 1 g l^{-1} LS | 0.1 M TLA/decanol | 0.01 M NaOH

feed solution membrane stripping solution (2)

$$TLA(o) + HCl(aq) \rightleftharpoons TLAH^+Cl^- \quad (3)$$

$$x\text{TLAH}^+\text{Cl}^-(o) + \text{LSM}_n(aq) \rightleftharpoons (\text{TLAH})_x\text{LSM}_{n-x}(o) + x\text{MCl}(aq) \quad (4)$$

the reactions at the feed side are reactions (3) and (4), where o refers to the organic and aq to the aqueous phase. At the stripping side the reaction is reaction(s) (5), where m is either H^+ or Na^+.

$$(\text{TLAH})_x\text{LSM}_{n-x}(o) + x\text{NaOH}(aq) \rightleftharpoons x\text{TLA}(o) + \text{Na}_x\text{M}_{n-x}\text{LS}_{n-x} + x\text{H}_2\text{O} \quad (5)$$

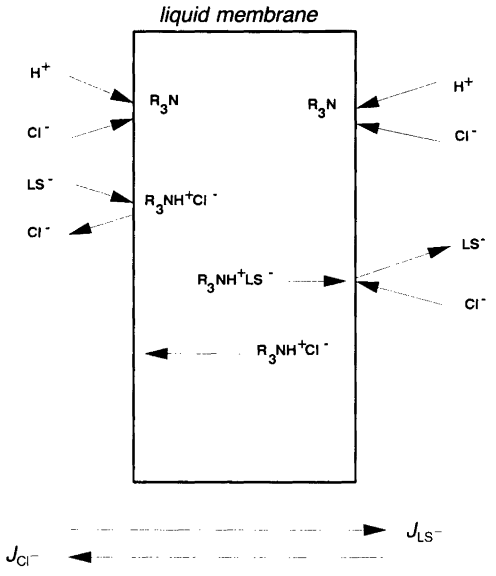

Fig. 3. The principle of counter-transport liquid membrane extraction of lignosulfonate (LS). *J* denotes the flux of LS or the Cl^- ion.

In this transport mode LS and H^+ are transported in the same direction across the membrane, but if the stripping solution is made acidic using HCl counter-transport of LS and Cl^- ions will occur. This transport mode, the principle of which is shown in Fig. 3, is of interest because NaCl is a much cheaper stripping reagent than NaOH. To study counter-transport the basic cell configuration was as shown in (6).

0.01 M HCl + 1 g l^{-1} LS | 0.1 M TLA/decanol |

0.01 M HCl + 0.5 M NaCl (6)

In the counter-transport mode the reactions at the feed side are as for co-transport, reactions (3) and (4), but at the stripping side the reaction is reaction (7).

$$(\text{TLAH})_x\text{LSM}_{n-x}(o) + x\text{MCl}(aq) \rightleftharpoons x\text{TLAH}^+\text{Cl}^-(o) + \text{LSM}_n(aq) \quad (7)$$

Results

The influence of the following experimental parameters on the flux of lignosulfonate using co- and counter-transport were studied: lignosulfonate, HCl and NaCl concentrations of the feed solution, amine concentration of the membrane phase, and lignosulfonate, HCl and NaOH concentrations of the stripping solution. The value of one parameter at a time was varied, keeping the others at the values given in formulae (2) and (6).

The LS concentration of the feed solution was varied between 10^{-1} and 40 g l^{-1}. The influence of this variable for the case of co-transport is shown in Fig. 4. In general the repeatability ot these measurements was better than 5 %, but at higher LS concentrations, >5 g l^{-1}, the repeatability of the measurement decreased to about 15 %. In the case of counter-transport the LS concentration has the same gen-

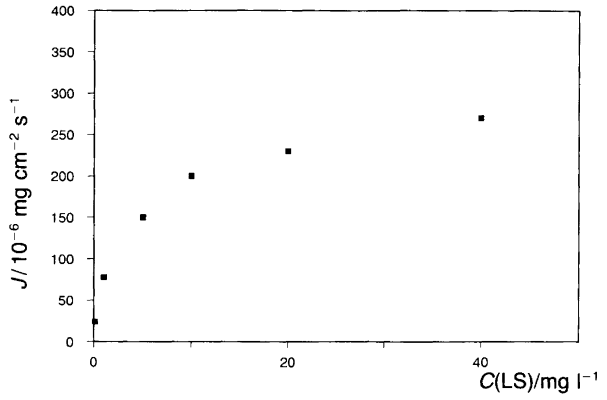

Fig. 4. The flux of lignosulfonate as a function of its concentration in the feed solution at the beginning of the experiment (co-transport): feed, 0.01 M HCl; membrane, 0.1 M TLA; strip, 0.01 M NaOH.

eral effect on the flux, J_{LS}, as in the case of co-transport. This result is as expected, because reaction (4) on the feed side is the same for both forms of transport. It should be noticed at this point that experiments with no TLA present were also run. These gave "background" J_{LS} values of <5 mg cm^{-2} s^{-1}, which clearly show that significant transport of lignosulfonate only occurs in the presence of the carrier.

When reactions (3) and (4) are at equilibrium the presence of large amounts of chloride should inhibit the formation of the LS–amine complex. The result of varying the HCl concentration is very much the same for both modes of transport, and is shown for the case of co-transport in Fig. 5. The flux J_{LS} reaches a maximum at 10^{-3} M HCl and then decreases. Evidently some acidity is needed for the reaction between TLA and HCl to occur. 0.1 M HCl is sufficient to reduce J_{LS} to a value close to the background measured without any amine present. If reaction (4) is at equilibrium, increasing the chloride concentration should drive this reaction to the left and J_{LS} should decrease. Steady-state J_{LS} values were obtained even if the HCl concentration in the steady state at initial values $<10^{-2}$ mol l^{-1} was clearly lower than at the beginning of the experiment. The conclusion is that the H^+ concentration has no influence on J_{LS} as long as it is large enough to transfer all TLA to $TLAH^+Cl^-$.

In order to study further at constant pH the influence of

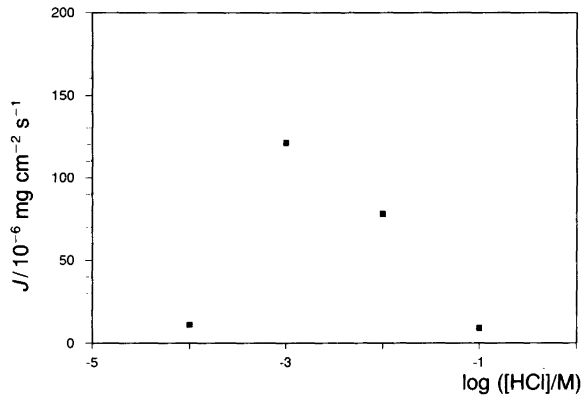

Fig. 5. The flux of lignosulfonate as a function of the logarithm of HCl concentration in the feed solution (co-transport): feed, 1 g l^{-1} LS; membrane, 0.1 M TLA; strip, 0.01 M NaOH.

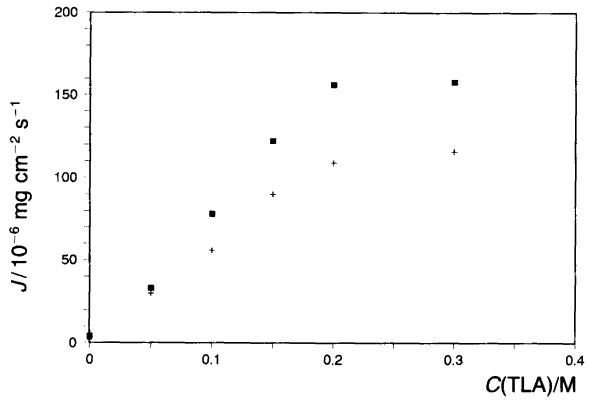

Fig. 7. The flux of lignosulfonate as a function of TLA concentration in decanol: (+) counter-transport, (■) co-transport; other concentrations are given in formula (6) for counter-transport; for co-transport the feed is: 0.1 M LS + 1 g l^{-1} LS, and the strip is 0.01 M NaOH.

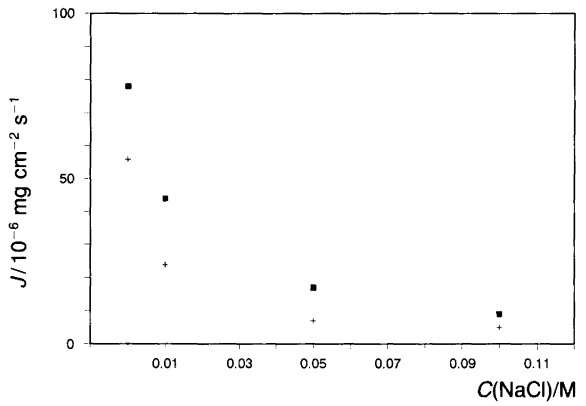

Fig. 6. The flux of lignosulfonate as a function of NaCl concentration in the feed solution: (+) counter-transport, (■) co-transport; other concentrations are given in formula (6) for counter-transport; for co-transport the feed is 0.01 M HCl + 1 g l^{-1} LS, the membrane is 0.1 M TLA, and the strip is 0.01 M NaOH.

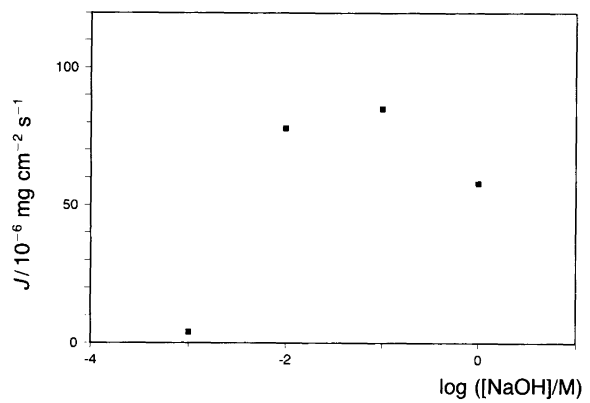

Fig. 8. The flux of lignosulfonate as a function of the logarithm of NaOH concentration in the stripping solution; feed, 0.01 M HCl + 1 g l^{-1} LS; membrane 0.1 M TLA.

the chloride concentration in the feed on the flux J_{LS}, we also varied this parameter by addition of NaCl. The experimental result for both forms of transport is shown in Fig. 6. The behaviour of J_{LS} is in accordance with the prediction made from reaction (4).

The influence of the concentration of TLA in the decanol phase was then studied. According to reactions (3) and (4), increasing the value of this parameter should increase the flux of LS; the experimental result, presented in Fig. 7, confirms this. Beyond a concentration of amine of about 0.2 mol l^{-1} in the organic phase J_{LS} ceases to increase.

The compositions of the stripping solutions are different for the two forms of transport. In co-transport we have two parameters to study: the NaOH and the lignosulfonate concentrations. The result of changing the NaOH concentration is shown in Fig. 8. It should be added that for the highest concentration, 1.0 mol l^{-1}, the steady state was difficult to achieve; the flux of lignosulfonate tended to increase continuously with time.

According to reaction (5), an increase of the LS concentration should decrease J_{LS}. However, increasing this parameter from 0 to 1050 mg l^{-1} had no effect, and this in fact is to be expected, since the back-extraction of LS is impossible, as no amine–hydrochloride complex can be formed in the alkaline stripping solution. The result, however, confirms that LS can be extracted by this method against its concentration gradient.

In the case of counter-transport, we looked in particular at the influence of the Cl^- concentration in the strippping solution on J_{LS}. The result is shown in Fig. 9.

As indicated in the introduction, for a polyelectrolyte such as LS it is also of great interest to see how the fractionation according to molar mass occurs. A clear influence on this fractionation is exerted only by two composition parameters: the concentration of LS in the feed solution and the concentration of amine in the organic phase. The result is presented in Table 1 for the case of co-transport. For the case of counter-transport a very similar result was obtained, namely that the fraction of low molar mass, <5000 g mol^{-1}, increases with increasing LS concentration but decreases with increasing amine concentration (for C_{LS} = 1.0 g l^{-1}). The general conclusion is that the molar mass distribution is determined by the composition of the feed solution or the organic phase, or both together. The composition of the stripping solution has almost no influence.

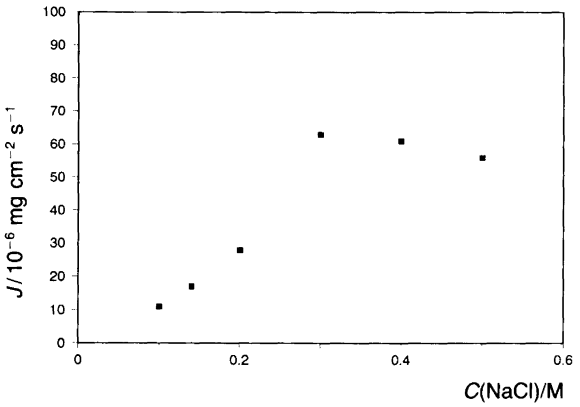

Fig. 9. The flux of lignosulfonate as a function of NaCl concentration in the stripping solution (counter-transport).

Table 1. The effect of (a) feed lignosulfonate (LS) concentration (with 0.1 M amine) and (b) amine concentration in the liquid membrane (with 1 g l^{-1} LS) on the molar mass distribution of lignosulfonate as a percentage of total sample.

Concentration	Molar mass/g mol^{-1}				
	>40 000	>20 000	>10 000	>5000	<5000
(a) LS/g l^{-1}					
0.1	10	22	38	59	41
1	4	8	19	40	60
5	0	1	5	22	78
10	2	3	6	17	83
20	1	1	2	10	90
40	0	1	2	8	92
(b) amine/M					
0.05	0	1	3	15	85
0.10	4	8	19	40	60
0.15	5	13	30	54	46
0.20	8	18	37	60	40

Discussion

Transport of LS through the liquid membrane consists of five stages: the diffusion of LS in the aqueous diffusion layer just adjacent to the membrane, the diffusion of the LS complex across the liquid membrane, and the heterogeneous reaction at the interfaces of both feed and stripping sides. Both the diffusion and the rate of the reaction forming $TLAH^+Cl^-$ are fast compared to those of LS.

The effect of diffusion layers on the whole transport process is minor. This is evident if one considers the hydrodynamics of channel flow. Rousar *et al.*[2] have derived eqn.

$$Sh = 1.85\ \Phi\ (ReSc)^{1/3}(d_h/L)^{1/3} \qquad (8)$$

(8) for channel flow, where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number, Φ = 0.9388, d_h is the hydraulic diameter and L is the length of the flow channel. In addition, the entrance length, L_h, for fully developed flow can be estimated by eqn. (9).[3]

$$L_h/d_h = 1.12\times10^{-2}\ Re \qquad (9)$$

In our experimental situation the flow was laminar, Re = 14, L_h = 0.026 cm (L = 6.1 cm), and the average thickness of the diffusion layer about 0.006 cm. Using this value in

Fick's law the difference between bulk and surface concentrations is estimated to be less than 300 mg l^{-1}, and therefore we assume in the subsequent caalculations that the surface and bulk concentrations are equal.

The results of the measurements described above gave strong evidence of rapid heterogeneous reactions at the interfaces compared with the diffusion of LS through the liquid membrane. This was confirmed by measurements in which the membrane thickness was doubled. This resulted in a decrease in the J_{LS} value by about 50 %. Because diffusion in the membrane is the rate-determining step we can assume further that the interfacial reactions (3)–(5) are at equilibrium.

Co-transport. Assuming that reaction (4) is at equilibrium, we can write eqn. (10) using the notation in Fig. 10, where

$$K = \frac{C_{2s,0}\, C^{x}_{Cl,0}}{C^{x}_{1s,o}\, C_{LS,0}} \tag{10}$$

K is the equilibrium constant of this reaction. Because of the low dielectric constant in the membrane all the components are strongly ion-paired, and therefore cross-diffusional effects can be neglected. As a result of this the diffusion is governed by a simple Fick's law for each component. It is also reasonable to assume that the surface concentrations of amine complexes at the stripping side are practically zero, $C_{2s,l} = 0$ and $C_{1s,l} = 0$, as well as that of free amine at the feed side, $C_{s,0} = 0$. These assumptions give eqns. (11)–(13). In the steady state we have eqn. (14).

$$J_{2s} = J_{LS} = D_{2s}\frac{C_{2s,0}}{l} \tag{11}$$

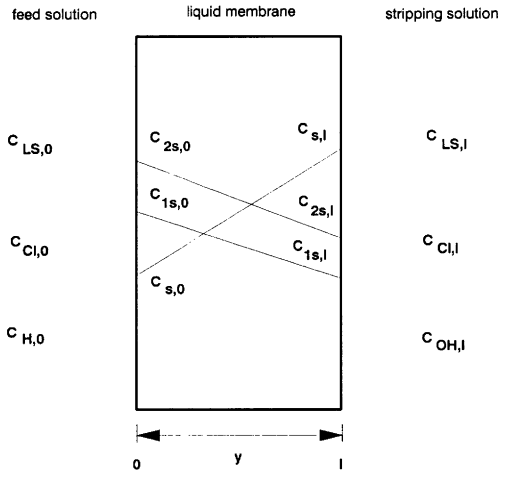

Fig. 10. A schematic drawing of the concentration gradients for co-transport of lignosulfonate (LS). 0 denotes species at the feed and l species at the stripping side, 2s denotes the amine–LS complex, 1s denotes the amine hydrochloride, s denotes the free amine. Cl, OH and LS denote the corresponding ions.

$$J_{1s} = D_{1s}\frac{C_{1s,0}}{l} \tag{12}$$

$$J_s = -D_s\frac{C_{s,l}}{l} \tag{13}$$

$$-J_s = J_{1s} + xJ_{LS} \tag{14}$$

Assuming that the total amount of amine remains constant in the membrane during the experiment we obtain eqn. (15).

$$C_{tot} = \frac{1}{l}\int_0^l (C_s + C_{1s} + xC_{2s})\,dy \tag{15}$$

These are the basic equations needed for the calculation of the flux of LS. The solution becomes simple if the stoichiometric coefficient x can be taken to be unity. From the physicochemical point of view it is reasonable to put $x = 1$, because values of x greater than unity are highly unlikely, since the heterogeneous reaction is assumed not to be rate-determining. Thus we assume $x = 1$ in the following derivations. Eqns. (10)–(15) give eqn. (16),

$$J_{LS} = \frac{C_{tot}}{1\left(\frac{1}{D_1} + \frac{1}{D_2}\frac{C_{Cl,0}}{KC_{LS,0}}\right)} \tag{16}$$

where $D_1 = 2D_sD_{2s}/(D_2 + D_{2s})$ and $D_2 = 2D_sD_{2s}/(D_s + D_{1s})$.

Eqn. (16) expressed a simple relationship between the flux J_{LS} and the concentrations C_{tot}, $C_{Cl,0}$ and $C_{LS,0}$. Using the previously given results we can now test this model of

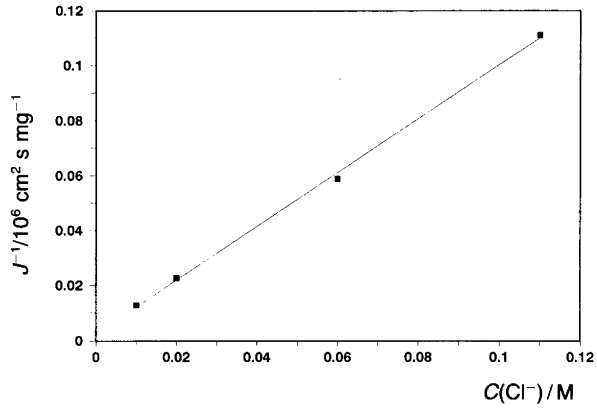

Fig. 11. The inverse value of the flux of lignosulfonate as a function of the total Cl^- concentration in the feed solution (co-transport); feed, 0.01 M HCl; membrane, 0.1 M TLA; strip, 0.01 M NaOH; the straight line is obtained by the least-squares method.

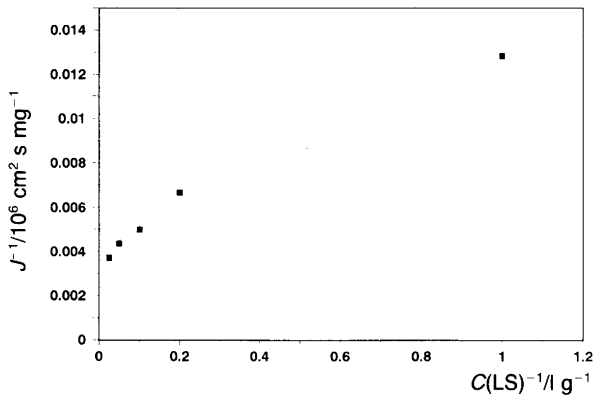

Fig. 12. The inverse value of the flux of lignosulfonate as a function of its inverse value in the feed solution (co-transport); feed, 0.01 M HCl; membrane, 0.1 M TLA; strip, 0.01 M NaOH; the straight line is obtained by the least-squares method.

the extraction process. It predicts that J_{LS} is linearly dependent on the total concentration of amine, and that $1/J_{LS}$ is directly proportional to $C_{Cl,0}$ and inversely proportional to $C_{LS,0}$.

From Fig. 7 one can see that J_{LS} is a linear function of C_{tot} up to the concentration 0.1 mol l^{-1}. The deviation from this linear behaviour at the concentration of 0.2 mol l^{-1} is probably due to aggregation of the amine. Fig. 11 shows further that $1/J_{LS}$ is a linear function of $C_{Cl,0}$ with good accuracy. In Fig. 12 we have presented $1/J_{LS}$ as a function of $1/C_{LS,0}$. As can be seen, the linear behaviour is not obvious. However, it must be remembered that at the higher LS concentrations a steady state was not attained.

If eqn. (16) is presented in the form of eqn. (17) one can

$$\frac{1}{J_{LS}} = \frac{1}{D_1 C_{tot}} + \frac{1}{D_2}\frac{1}{C_{tot} K C_{LS,0}} C_{Cl,0} \tag{17}$$

immediately see that the result presented in Fig. 11 can be used to obtain estimates for D_{2s} and K. The procedure is as follows: we notice that $D_s \gg D_{2s} \Rightarrow D_1 \approx 2D_{2s}$. Thus the estimate for D_{2s} is obtained from the intercept of the curve and y-axis. Realizing that $D_2 \approx D_{2s}$ ($D_s \approx D_{1s}$) we can obtain an estimate for K from the slope of the same curve. Before these calculations can be done the average molar mass of the lignosulfonate in the stripping solution must be known. The results for two different average molar masses are:

M_{av}/g mol^{-1} =	5000	20 000
$D_{2s}/10^{-9}$ cm^2 s^{-1} =	7	2
K =	3×10^7	9×10^7

As can be seen, the diffusion coefficient for the lignosulfonate complex is very small. When we compare this value to that given by Walden's rule a difference of an order of magnitude is noticed. This difference can be explained by the swelling of LS molecules in low dielectric media. A recent study[4] supports this conclusion.

An interesting result concerning the maximum flux of LS is obtained if one assumes the value of K to be infinitely high. Then eqn. (16) becomes eqn. (18). This relationship

$$J_{LS}^{max} = \frac{2D_{2s}C_{tot}}{l} \tag{18}$$

can be used to estimate fluxes in other solvent systems, provided that the heterogeneous reactions are fast enough. From this model one can furthermore draw the following qualitative conclusions about J_{LS}: the flux should increase if the diffusion coefficient of LS increases or the viscosity and the thickness of the membrane decrease.

Counter-transport. The results of the co-transport case showed that eqn. (4) is valid, and it must also be valid for the reaction at the feed side in the case of counter-transport, since exactly the same reactions are involved. However, the results clearly showed that the reverse reaction on the stripping side is not in equilibrium. Therefore the possibility of an interfacial reaction must be included in the model. Because the reaction rate at the stripping side depended on Cl^- ion concentration, the reaction sequence (19)–(22) is proposed, in which s refers to the interface. It

$$Cl^-(aq) \rightleftharpoons Cl^-(s) \tag{19}$$

$$(TLAH)_xLSM_{n-x}(o) \rightleftharpoons (TLAH)_xLSM_{n-x}(s) \tag{20}$$

$$(TLAH)_xLSM_{n-x}(s) + xCl^-(s) \rightarrow [(TLAHCl)_xLSM_{n-x}]^{x-}(s) \tag{21}$$

$$[(TLAHCl)_xLSM_{n-x}]^{x-}(s) \rightleftharpoons TLAH^+Cl^-(o) + [LSM_{n-x}]^{x-}(aq) \tag{22}$$

must be noticed that adsorbed Cl^- ions are on the aqueous side of the interface and adsorbed LS complexes on the organic side of the interface.

It is reasonable to assume that reaction (21) is the rate-determining step. Thus in the steady state we have eqn. (23), where Φ_{2s} is the surface coverage of the LS complex,

$$J_{LS} = k_f \Phi_{2s} \Theta_{Cl}^x \tag{23}$$

Θ_{Cl} that of the Cl^- ions and k_f the rate constant of reaction (21). Since the concentration of the LS complex is small in our experimental situation, Φ_{2s} can be written in the form of a linearized Langmuir isotherm, eqn. (24). The surface

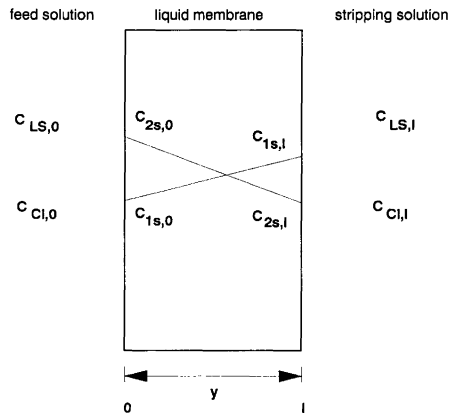

Fig. 13. A schematic drawing of the concentration gradients for counter-transport of lignosulfonate (LS). 0 and l denote the feed side and the stripping side. 2s denotes the amine–LS complex and 1s the aminehydrochloride.

$$\Phi_{2s} = b_{2s}C_{2s,l} \tag{24}$$

$$\Theta_{Cl} = \frac{b_{Cl}C_{Cl,l}}{1 + b_{Cl}C_{Cl,l}} \tag{25}$$

coverage for Cl^- ion, however, is given by eqn. (25), where b_{2s} and b_{Cl} are constants. The notations used for these concentrations are presented in Fig. 13. When steady state prevails we can write eqns. (26)–(29).

$$J_{LS} = J_{2s} = D_{2s}\frac{C_{2s,0} - C_{2s,l}}{l} \tag{26}$$

$$\frac{1}{x} = J_{1s} = -J_{LS} = \frac{1}{x}D_{1s}\frac{C_{1s,l} - C_{1s,o}}{l} \tag{27}$$

$$J_{LS} = \frac{k_f\, b_{2s}\, C_{2s,l}\, b_{Cl}^x\, C_{Cl,l}^x}{(1 + b_{Cl}C_{Cl,l})^x} \tag{28}$$

$$C_{tot} = \frac{1}{l}\int_0^l (C_{1s} + xC_{2s})\,dy \tag{29}$$

$$C_{tot} = xC_{2s,0} + C_{1s,0} - \frac{xJ_{LS}}{2}\left(\frac{1}{D_{1s}} - \frac{1}{D_{2s}}\right) l \tag{30}$$

Eqn. (29) gives eqn. (30) after integration. Because $C_{2s,0} \gg C_{1s,0}$ and both J_{LS} and l are small, which means that the third term in eqn. (30) is much smaller than $C_{1s,0}$, we obtain the result $C_{tot} \approx C_{1s,0}$.

Finally, with the aid of the above equations we obtain eqn. (31) for the flux of LS, where $A' = C_{tot}^x\, K\, (C_{1s,0}/C_{Cl,0}^x)$

$$\frac{1}{J_{LS}} = \frac{B}{A'} + \frac{1}{k_f A' b_{2s}}\left(\frac{1}{b_{Cl}C_{Cl,l}} + 1\right)^x \tag{31}$$

and $B = 1/D_{2s}$. Since in the co-transport case the value of $x = 1$ gave a good interpretation for the experimental data, the same assumption is made now. Thus we have eqn. (32),

$$\frac{1}{J_{LS}} = \left(\frac{1}{k_f\, A'\, b_{2s}} + \frac{B}{A'}\right) + \frac{1}{k_f\, A'\, b_{2s}\, B_{Cl}}\frac{1}{C_{Cl,l}} \tag{32}$$

which predicts that $1/J_{LS}$ depends linearly on $1/C_{Cl,l}$. From Fig. 14 one can see that this relationship is linear up to Cl^- ion concentrations of 0.3 mol l^{-1}. Obviously, at this concentration the amount of Cl^- ions at the interface reaches a maximum, and our model is no longer applicable. In Figs. 15 and 16 we present the dependences of J_{LS} on C_{tot} and $C_{Cl,0}$. These results are in accordance with the proposed model.

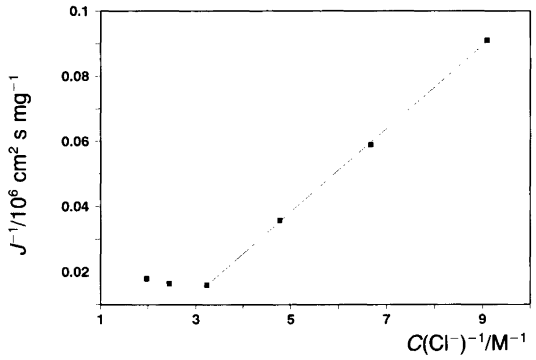

Fig. 14. The inverse value of the flux of lignosulfonate as a function of the inverse value of the total Cl^- concentration in the stripping solution (counter-transport); other concentrations are given in formula (6); the straight line is obtained by the least-squares method.

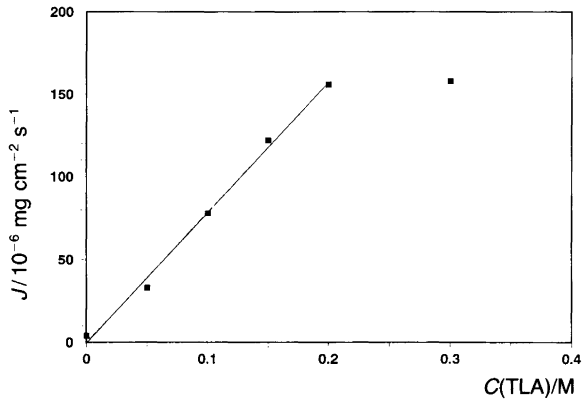

Fig. 15. The flux of lignosulfonate as a function of the concentration of amine in the liquid membrane (counter-transport); other concentrations are given in formula (6); the straight line is obtained by the least-squares method.

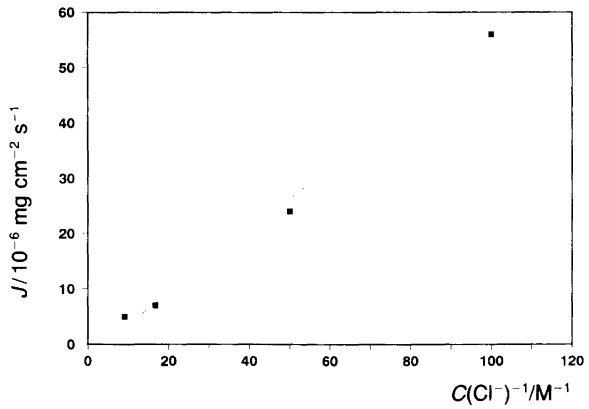

Fig. 16. The flux of lignosulfonate as a function of the inverse value of the total Cl^- concentration in the feed solution (counter-transport); other concentrations are given in formula (6); the straight line is obtained by the least-squares method.

The results obtained using high Cl^- concentrations in the stripping solution are puzzling: the fluxes decrease slightly instead of increasing. A possible explanation for this behaviour is the occurrence of salting-out phenomena. The decrease of J_{LS} when the concentration of Cl^- ion is greater than 0.3 mol l^{-1} can be explained using the influence of a salting-out effect as follows: The flux of LS can be written as eqn. (33), where J_{max} is J_{LS} when $C_{NaCl} = 0.3$ mol l^{-1}, and

$$J_{LS} = J_{max}(1 - k_s \Delta C_{NaCl}) \quad (33)$$

k_s is a salting-out coefficient. Using scaled particle theory k_s can be estimated as shown by Kontturi *et al.*[5] The data needed for the calculations were obtained from Refs. (5)–(10). The polarizability of LS is not known, but it was estimated to be large, $(100–500)\times10^{-21}$ cm^3, and the number of electrons was varied from 300 to 500 (the average molar mass was taken to be 5000 g mol^{-1}). With these values k_s varied from 0.3 to 2, and the range of variation for J_{LS} was from 59×10^{-6} to 38×10^{-6} mg s^{-1} cm^{-2}. The measured value 56×10^{-6} mg s^{-1} cm^{-2} (Fig. 14) is thus in the estimated range.

Conclusions

In this study we have shown that a supported liquid membrane can be used for the carrier-mediated extraction of a polyelectrolyte, lignosulfonate. The influence of the different composition parameters of both water phases and the oil phase on the flux of LS can be described using a simple model for the case of both co- and counter-transport. One interesting result is that the model predicts that only one amine molecule per LS molecule is needed to pull the LS into the oil phase.

The values of the flux of LS obtained experimentally in our system are far too low for practical purposes. However, the SLM itself can be improved, i.e. by making it thinner or by using a solvent of lower viscosity.

If the rate of mass transport is increased the kinetics of the heterogeneous reactions at the two interfaces may become rate-determining. We intend to study these reactions with the aid of a rotating diffusion cell.

Nomenclature

$C_{LS,0}$	concentration of lignosulfonate (LS) in the feed solution
$C_{LS,l}$	concentration of LS in the stripping solution
$C_{2s,0}$	concentration of LS–TLA complex at the feed side in the membrane
$C_{2s,l}$	concentration of LS–TLA complex at the stripping side in the membrane
$C_{Cl,0}$	concentration of chloride in the feed solution
$C_{Cl,l}$	concentration of chloride in the stripping solution
$C_{1s,0}$	concentration of TLAHCl at the feed side in the membrane
$C_{1s,l}$	concentration of TLAHCl at the stripping side in the membrane
$C_{s,0}$	concentration of free amine (TLA) at the feed side in membrane
$C_{s,l}$	concentration of TLA at the stripping side in the membrane
J_{2s}	flux of LS–TLA complex
J_{LS}	flux of LS
J_{1s}	flux of TLAHCl
J_s	flux of TLA
l	thickness of the liquid membrane
C_{tot}	total amine concentration
D_{2s}, D_{1s}, D_s	diffusion coefficients in the membrane
Φ_{2s}	surface coverage of LS–TLA complex at the stripping side
Θ_{Cl}	surface coverage of chloride ion at the stripping side

Acknowledgement. Financial support for this work from the Academy of Finland is gratefully acknowledged.

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Received February 21, 1990.