Extraction of a Polyelectrolyte Using a Supported Liquid Membrane. I. Choice of a Suitable Carrier–Solvent System

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Experiments aimed at choosing the correct solvent–carrier–support system for a supported liquid membrane, which is to be used for the extraction of a polyelectrolyte, lignosulfonate, are presented. It is shown that a good combination is decanol–trilaurylamine–polytetrafluoroethylene (Millipore).

Liquid membrane extraction has so far had its main application in the field of metal extraction.[1] However, the treatment of mixtures of macromolecules, especially charged ones, is a fascinating new field of research. The importance of many polyelectrolytes is evident from both scientific and industrial points of view.

In this study we have chosen to look at the applicability of liquid membrane extraction to the separation and fractionation of a charged macromolecule, lignosulfonate, which is a polydisperse polyelectrolyte formed during the sulfite cooking process. Lignosulfonate has several industrial applications.[2,3] Recently we have developed methods for the determination of diffusion coefficients and effective charge numbers for polyelectrolytes, and these quantities have been experimentally determined for lignosulfonate as a function of pH, ionic strength, temperature, valency of the counterion, dielectric constant and at the same time also as a function of the molar mass of this polyelectrolyte.[4–9] Lignosulfonate is a spherical macromolecule which resembles globular proteins. It has, for instance, two kinds of ionizing groups (SO_3 and OH^-). It is not an ampholyte, but when the temperature is increased above about 40 °C, or alternatively if one uses concentrated $MgCl_2$ solutions, its effective charge becomes zero,[7,8] just as is the case for proteins at their isoelectric point.

The liquid–liquid extraction of lignosulfonate has been studied.[10] The extraction is based on an ion-exchange reaction between an aliphatic amine dissolved in an oil phase and lignosulfonic acid. In this extraction some fractionation of the lignosulfonate according to molar mass is also achieved.[10]

The disadvantages of this liquid–liquid extraction are organic solvent losses coupled to the need for large amounts of solvent, and difficulties in separating the two phases. Therefore no large-scale application of this method is in operation. These disadvantages can be avoided by the use of a supported liquid membrane containing the amine–organic solvent system.[11] Liquid membrane extraction is a carrier-mediated process in which three different modes of transport have been used. These are facilitated diffusion, counter-transport and co-transport, of which the latter two have been applied to liquid phase separations.[1]

The main problem in devising a working supporting liquid membrane extraction system is to find the right carrier–solvent–support combination to produce a membrane of sufficient stability for the intended application. In this first part of our work to devise a liquid membrane extraction process for a macromolecule like lignosulfonate, we report how to construct a liquid membrane of sufficient stability for this purpose.

Stability considerations for a supported liquid membrane (SLM)

The most important factor preventing the widespread use of SLMs is their instability. Often the lifetime of the membrane is only hours or days, whereas industrial applications would require months.[1,12] The stability of the membrane is limited by several factors:[13–15] (i) The solubility of organic solvent or carrier into the surrounding aqueous phases. (ii) The flow of aqueous solution along the membrane causes lateral shear forces, which may remove the organic phase from the membrane. (iii) The penetration of water into the pores of the membrane. This is caused either by pressure differences and/or infavourable interfacial tensions. (iv) A water flux may develope through the membrane. This is caused by differences in osmotic pressure due to differences in electrolyte concentration between the two aqueous phases.

According to our experience, if water is transported through the SLM all other components of the aqueous phase will also pass through it, and selectivity is lost. In general, aliphatic solvents are retained in the pores of the hydrophobic support better than aromatic ones. Instability is commonly caused by the penetration of water into the

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pores of the membrane rather than by the dissolution of solvent into the aqueous phase.[13,16] Interfacial tension is an extremely important factor affecting the stability of an SLM. Many carriers are surface-active and decrease the surface tension between the organic solvent and the water phase. Strongly surface-active agents are known to destroy an SLM within hours.[11]

Danesi *et al.*[13] give some criteria for selecting the components of an SLM. The support should be hydrophobic and its pore size as small as possible, the solvent and the carrier should be insoluble in water, and the solvent–water interfacial tension should be as large as possible. Also, the concentration differences between the two aqueous phases should be minimized. These are general rules. In practice it is necessary to determine experimentally the optimal solvent–support–carrier combination for an SLM, bearing in mind the intended extraction process.

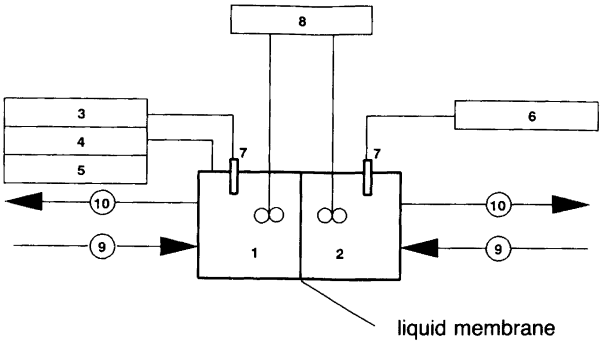

Fig. 1. The experimental set-up: (1) feed solution, (2) stripping solution, (3) pH meter (Radiometer pHM82), (4) autoburette (Radiometer ABU80), (5) titrator, (6) pH meter (Radiometer pHM26), (7) glass electrode (Ingold U455), (8) stirrer motor (Heidolph), (9) peristaltic pump (Ismatec ip–12), (10) peristaltic pump (Desaga).

Experimental

Chemicals. The solvents chosen for testing were dichloroethane (Merck, p.a.), methylisobutylketone (Fluka, p.a.), cyclohexane (Merck, p.a.), 1-pentanol (Merck, p.a.), 1-octanol (Merck, 97 %) and 1-decanol (Sigma, 98 %). Clearly, for our purpose the carrier should be an aliphatic amine. Those studied were trioctylamine (Aldrich, 97 %), dodecylamine (Merck, 95 %), dimethyloctylamine (Aldrich, 95 %) and trilaurylamine (Sigma, 85 %). The use of purer trilaurylamine did not alter our results significantly. These amines were used as received.

The lignosulfonate (LS) was purchased from Rauma-Repola Ltd. Its analysis and molar mass distribution is given in Ref. 9.

The supports used were polytetrafluoroethylene (PTFE, Millipore, Fluoropore type, pore size 0.2 μm, thickness 175 μm, porosity 70 %), polyvinylidene difluoride (PVDF, Millipore, Durapore type, pore size 0.22 μm, thickness 100–150 μm, porosity 75 %) and polypropylene (PP, Celanese Plastics, Celgard type, pore size 0.04 μm, thickness 25 μm, porosity 45 %).

Apparatus. The experimental set-up is shown in Fig. 1. The membrane area was 2 cm^2 and the volumes of the feed and stripping compartments were 85 ml each. These volumes and the flow rates were such that steady state in the cell was reached in about 10 h. The runs usually lasted for about 30 h. The rotation rate of the stirrer was 500 r.p.m.

Measurements. The supporting membrane was immersed in the organic solution (amine dissolved in the solvent) for 30 min. The cell was assembled and the feed and stripping compartments were filled. The levels of the water phases were kept equal in order to prevent pressure differences.

The membrane cell had the general compositions shown in cell (I). All experiments were carried out at room temperature (23 ± 1 °C). The pH of the feed solution was kept

$$0.01\ \text{M HCl} + 1\ \text{g l}^{-1}\ \text{LS} \mid \text{amine} + \text{solvent} \mid 1.25\ \text{M NaOH} \qquad \text{(I)}$$

aqueous feed solution	liquid membrane	aqueous stripping solution

constant by adding hydrochloric acid to the solution using a Radiometer pH-stat. Samples were collected after every 45 min. The reproducibility of the measurements was ca. 5 %.

Analyses. The concentration of lignosulfonate was determined by UV spectrophotometry at the wavelength 282 nm. The pH of the water phases was monitored with a glass electrode. The flow rates (ca. 14 ml h^{-1}) were measured by weighing.

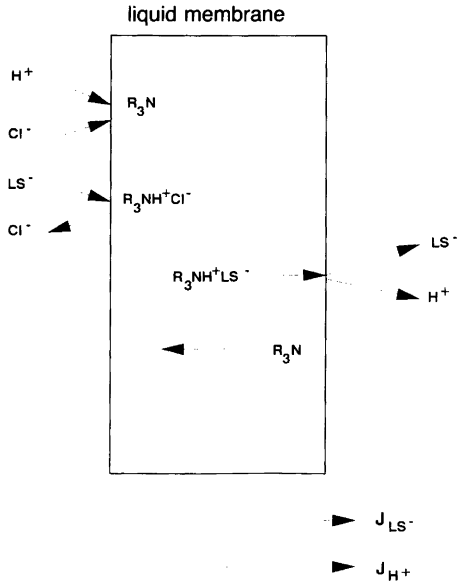

Fig. 2. A schematic diagram of the SLM extraction. *J* denotes the flux of the lignosulfonate (LS) or hydrogen ion.

Principle of the extraction method. A schematic diagram of the SLM extraction process is presented in Fig. 2. The transport mode of lignosulfonate is so-called co-transport, because the extractant and the hydrogen ions pass through the membrane in the same direction from the feed side to the stripping side.[1] The reactions at the feed side are (1) and (2), in which o denotes the organic phase and aq the

$$R_3N(o) + HCl(aq) \rightleftharpoons R_3NH^+Cl^-(o) \quad (1)$$

$$xR_3NH^+Cl^-(o) + LSM_n(aq) \rightleftharpoons (R_3NH)_xLSM_{n-x}(o) + xMCl(o) \quad (2)$$

aqueous phase. M is the counterion associated with lignosulfonate (H^+ and Na^+). The reactions at the stripping side are (3) and (4).

$$R_3NH^+Cl^-(o) + NaOH(aq) \rightleftharpoons R_3N(o) + H_2O + NaCl(aq) \quad (3)$$

$$(R_3NH)_xLSM_{n-x}(o) + xNaOH \rightleftharpoons xR_3N(o) + xH_2O + Na_xM_{n-x}LS \quad (4)$$

From reactions (1) and (3) it is seen that chloride ion competes with lignosulfonate ion. Thus its transport should be minimized.

Results and discussion

Choice of solvent. The major problem in choosing the solvent was the penetration of water through the membrane. Most of the solvents used in conventional liquid–liquid extraction let water through the membrane. When water was passing through the membrane, the lignosulfonate concentration on the stripping side was increasing, and increasing the amine concentration in the membrane had no effect. In normal operation, variation of this concentration clearly affects the extraction process. Such experiments were irreproducible.

The solvents were first tested with a PTFE support. Dichlorethane and methylisobutylketone let water through the membrane. Cyclohexane did not, but it evaporated too easily.

Long-chain aliphatic alcohols were tried next because they are less volatile. These solvents impregnated the membrane well, but both 1-pentanol and 1-octanol let water through. 1-Decanol did not let water through, and it was therefore chosen as a solvent for further experiments.

Choice of support. PTFE was selected as support material because it is easily wetted by aliphatic alcohols and is chemically stable. The PP membrane was also easily wetted by 1-decanol, but the flux of lignosulfonate was very poor.

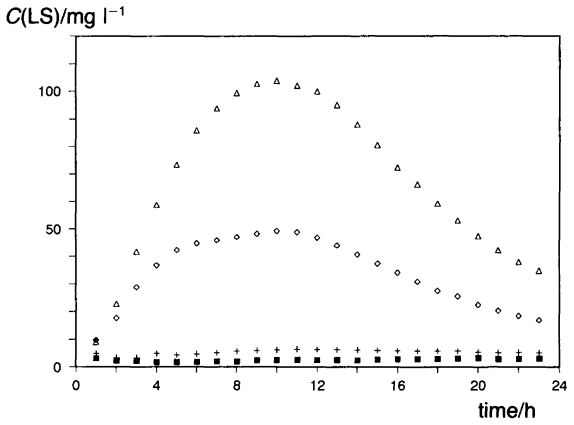

Fig. 3. The concentration of lignosulfonate in the stripping solution as a function of time for the system trioctylamine (TOA) in decanol: (■) no TOA, (+) 0.01 M TOA, (◇) 0.1 M TOA, (△) 0.2 M TOA.

We believe that the LS macromolecules cannot pass through the very small pores (0.04 μm) of this membrane.

The PVDF membrane was tested with cyclohexane and dichloroethane, which seemed to dissolve some of the polyethylene backing of the PTFE membrane. Dichloroethane did not easily impregnate PTFE. However, the tests with PVDF gave similar results as the tests with PTFE support, and thus made it clear that these solvents were not suitable for the intended purpose.

Choice of amine. The rate-determining step of the transport is most probably the diffusion of the amine–lignosulfonate complex in the liquid membrane. Thus the concentration of the lignosulfonate in the stripping solution should increase when increasing the amine concentration in the SLM. This is also experimentally born out, as seen from Fig. 3, where the concentration of lignosulfonate in the

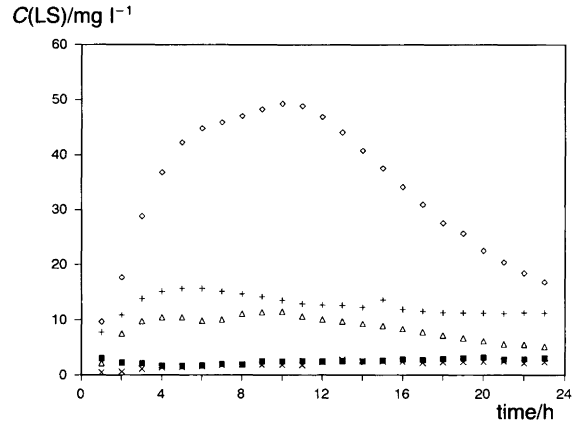

Fig. 4. The concentration of lignosulfonate in the stripping solution as a function of time for four different amines all at a concentration of 0.1 mol l^{-1} in decanol: (■) no amine, (+) trilaurylamine, (◇) trioctylamine, (△) dodecylamine, (×) dimethyloctylamine.

stripping solution is presented as a function of time for different trioctylamine concentrations.

In Fig. 4 is presented the concentration of lignosulfonate in the stripping solution as a function of time for the four different amines tested. It is seen that dimethyloctylamine does not extract lignosulfonate at all, and dodecylamine and trilaurylamine extract lignosulfonate only slightly compared to trioctylamine. With trioctylamine, however, no steady state was achieved, and in addition this carrier dissolved easily into the acidic feed solution, which became turbid during the run, so that this amine could not be chosen as a carrier. The choice of carrier was therefore trilaurylamine.

The system chosen for further experiments was thus trilaurylamine dissolved in 1-decanol with a porous Teflon support. This liquid membrane was stable for at least 48 h.

Finally, it should be pointed out that 1-decanol is not an ideal solvent when judged by the stability criteria described earlier because of its low interfacial tension against water. However, the solubility of our model macromolecule as an amine complex limits the choice of solvents,[10] and we feel that 1-decanol can successfully be used in laboratory experiments to study the transport mechanisms of lignosulfonate in the liquid membrane.

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