

Nitrate removal using supported liquid membranes: transport mechanism

A.M. Neplenbroek, D. Bargeman and C.A. Smolders

University of Twente, Department of Chemical Technology, P.O. Box 217, Enschede (Netherlands)

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Abstract

A new method is developed for the removal of nitrate ions from water. Nitrate ions can be removed from water almost completely, with a mobile carrier, by counter-transport of chloride ions through a supported liquid membrane. The transport characteristics of this process, in which the water phases are flowing parallel to flat membranes, are described. The results show that depending on the experimental conditions the flux is determined by the diffusion of the carrier through the membrane or by the diffusion of the nitrate ions through a laminar water layer at the feed side. The selectivity of the membrane, which depends on the type of the organic solvent, determines the influence of the chloride concentration in the stripping phase on the membrane flux. Furthermore the effect of carrier concentration is investigated.

Keywords: coupled, facilitated transport; facilitated transport; liquid membranes; supported liquid membranes; liquid membrane stability

Introduction

Supported liquid membranes (SLMs) have been introduced as a promising new separation technique for the selective removal of ions from an aqueous solution. Especially for low concentrations of ions in water (below some hundreds of ppm [1]) it is useful to employ SLMs because high enrichment factors can be obtained. The quantity of nitrate ions in ground water is in that range, and is becoming a problem for preparing drinking water.

Almost every research work on SLMs is done on systems in which metal ions are being re-

covered, obviously for economical reasons. Besides hundreds of cation separation systems published in literature only a few examples are known for the separation of anions. Liacono et al. [2] used a counter-transport of chloride ions to remove CrO_4^{2-} anions from a water phase. Another example of a counter-transport process, between chloride- and hydroxide ions, is given by Molnar et al. [3]. In this latter article the transport mechanism was not entirely clear and some complexities in the chemistry of facilitated diffusion were observed. Anions can also be removed by a co-transport mechanism. In this way systems were developed for the concentration of picrate ions [4,5], nitrate ions [6] and chloride ions [7]. In these cases transport depends on the concentration of the co-ions (usually protons) in the feed solution.

Correspondence to: D. Bargeman, University of Twente, Department of Chemical Technology, P.O. Box 217, Enschede, The Netherlands.

In this paper the development of an SLM-process for the removal of nitrate ions with a counter-transport of chloride ions will be described. To approach the circumstances of a practical separation process, a membrane cell has been used in which the water phases are not stirred but flow parallel to the flat membrane. The influence of process parameters, like water flow velocities, composition of the SLM phase and of the water phases, on the transport is studied. These data are not only of interest for insight in this new method, necessary to optimize it, but are also important in relation to the stability of the SLMs. Other experiments showed that these parameters, the hydrodynamics and the composition of the system, have a large influence on the life times of the membranes [8,9].

Nitrate removal from water

The contamination of groundwater with nitrates is becoming a serious problem in the preparation of drinking water both in Europe and in the United States. It has been said that "nitrate is the first world-wide environmental pollutant resulting from man's ingenious technology" [10]. In the Netherlands the EC-norm of 50 ppm nitrate in ground water sources is more and more being exceeded. Especially on sandground concentrations of nitrate of 100 ppm in wells are no exceptions and in a few cases concentrations up to 500 ppm are observed.

Especially in the last few years new processes for the removal of nitrate from water have been developed or adjusted. A selection of these methods mentioned in literature is:

- Fixed-bed anion-exchange [11];
- Electrodialysis (ED) [12];
- Reverse osmosis (RO) [13];
- Bacteriological treatments [14,15];
- Solvent extraction (SX) [16].

Recently the development of SLM's is also proposed as a separation method. The use of

SLMs can be advantageous as compared to the five methods mentioned above. These advantages, especially for the removal of nitrate ions from water, and the choice of a suitable carrier are described in Ref. [17]. Two possible methods, by which ions can be removed via a coupled transport mechanism, are:

- Co-transport; Kreevoy et al. developed a method in which nitrate ions are removed from a water phase together with protons by a complexation with a very strong alkaline lipophilic carrier in a supported liquid membrane [6]. In this process the transport is regulated by the pH and the nitrate concentrations in the water phases. Due to the removal of protons from the feed the pH in the feed increases and the driving force for nitrate complexation is diminished.
- Counter-transport: by applying a counter-transport mechanism the problem of the dependence of the transport on the pH can be overcome. Therefore a process was developed in this work, making use of a continuous anion-exchange between nitrate and chloride ions through an SLM. In Fig. 1 a schematic representation of this process is given.

Advantages of such a process as compared to the use of a co-transport of protons is that the driving force for the "up-hill" concentration is provided by the high chloride concentration in the stripping phase and it therefore is independent of other than nitrate ions in the feed.

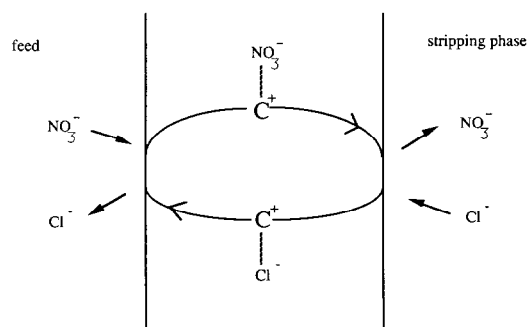


Fig. 1. Counter-transport mechanism; continuous anion-exchange between nitrate and chloride ions.

Transport model

A number of separate steps can be distinguished when a (specific) ionic species is transported from the feed to the stripping phase. These steps consist of:

- Diffusion of the ion from the bulk of the feed to the membrane surface;
- Complexation at the surface with a carrier molecule;
- Diffusion of the carrier-bound ion through the LM-phase;
- Decomplexation at the surface with the stripping phase;
- Diffusion of the permeate ion to the bulk of the stripping phase.

In Fig. 2 an ideal concentration profile, with linear concentration gradients, for the permeating ion (in our case NO_3^-), is given. In this figure $[\text{NO}_3^-]_F$ and $[\text{NO}_3^-]_S$ are the bulk concentrations of nitrate ions in the feed and stripping phase respectively; the index “i” denotes the concentrations in the water phases at the membrane interface. An over-bar indicates the concentration of ions bound to the carrier in the membrane. Because of the low dielectrical constant of the organic phase the concentrations of free ions are negligibly small. In case of a counter-transport mechanism a similar profile can be given for the second ion.

The thicknesses of the laminar boundary

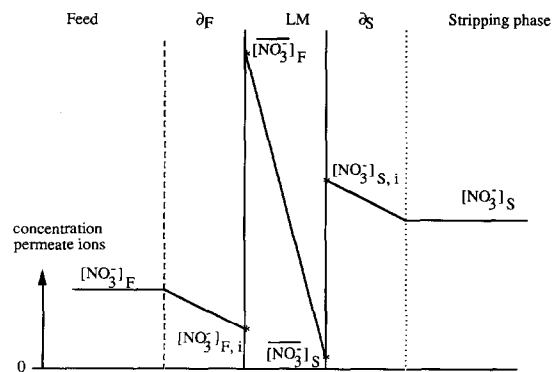
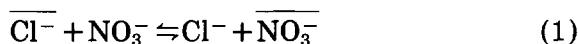


Fig. 2. Schematic concentration profile for transport of permeating ions through a SLM.

layers are given by ∂_F and ∂_S . These values are a function of the flow conditions of the water phases parallel to the membrane. In literature one generally assumes that the chemical reactions taking place at the interfaces are very fast as compared to the diffusion steps.

The concentration of ions at each boundary, in the membrane and in the water phases, is determined by the following equilibrium reaction:



For this anion-exchange system and extraction constant K_{ex} (valid at each of the two boundaries) can be defined as:

$$K_{\text{ex}} = \frac{[\text{Cl}^-] \overline{[\text{NO}_3^-]}}{[\overline{\text{Cl}^-}] [\text{NO}_3^-]} = \frac{k_{\text{NO}_3^-}}{k_{\text{Cl}^-}} \quad (2)$$

in which $k_{\text{NO}_3^-}$ and k_{Cl^-} are the distribution coefficients for nitrate and chloride ions between the membrane and water phases.

Several review papers on liquid membranes appeared in the literature during the last decades. The theoretical progress and various numerical methods for solving the transport models were reviewed by Schultz et al. [18,19]. The complex transport model is getting considerably more simple when transport is limited by diffusion through only one phase (either the membrane phase or one of the boundary layers). At stationary transport through the membrane the different diffusive fluxes are equal to each other and equal to the overall flux J . In the experiments described in this paper we are dealing with instantaneous chemical reactions and a miniscule quantity of free ions in the organic phase. For that reason we want to realize that overall-transport is limited by diffusion of the carrier molecules through the membrane phase. During the permeation experiments to be described the influence of different parameters on the overall flux will be determined.

Experimental

Materials

The carrier. Symmetrical quaternary ammonium salts (with a length of the alkyl chain varying from 8 to 12 C-atoms) were used as carriers. All carriers were delivered in bromide form, by Fluka, and used without further purification.

The solvent. *Ortho*-nitrophenyloctylether (*o*-NPOE; Fluka) and decanol ("gold marke"; Aldrich) have been used as membrane solvents. Both solvents were used without further purification.

The support. Flat sheets Accurel[®], microporous polypropylene membranes, (obtained from Enka) have been used as supports. The thicknesses of the supports were measured with a Mitutoyo digital thickness meter and the porosities by determining the weight of the absorbed LM-phase with a known density. The average thickness of these membranes was 92.5 μm and the porosity 69%. The average pore size of the supports was 0.1 μm (Enka specification). This is the size of the open connections between much larger cellular voids in the membrane.

Membranes were prepared as follows: LM-solutions were prepared by dissolving the carrier in the solvent. By soaking the support in these solutions for at least 15 min the LM-phase is absorbed in the pores. Before using the membrane the attached liquid is removed from the surfaces with a tissue.

Extraction experiments

The distribution of nitrate and chloride ions over the LM-phase and the water phases were determined by extraction experiments. In contrast with the usual extraction methods described in literature the LM-phase was immobilized in the pores of a support before it was brought in contact with the water phase.

The carriers in the membrane liquid were

brought in nitrate form by immersing the SLMs overnight in 40 ml of 1 M NaNO₃-solution (the volume of the LM-phase in the support was 0.3 ml). After rinsing the membranes with distilled water they were immersed overnight in 30 ml aqueous solutions with different NaCl concentrations, varying from 0.00 M to 1.00 M. Introductory experiments showed that 1 night is long enough to reach equilibrium state. The nitrate and chloride concentrations in the water phase was analysed by high performance liquid chromatography (HPLC; anion column).

Permeability measurements

The experimental set up is illustrated in Fig. 3. The membrane cell and the buffer vessels are made of glass and connected with silicone rubber tubes. The microporous membrane with imbibed LM-phase is placed in the cell and then the system is filled with the aqueous phases. The total volume of each of the aqueous phases, including that of tubes, pumps, flow meters, buffer vessels and cell-halves, is 130 ml. The aqueous phases are flowing parallel to the membranes, in a tangential flow, with the help of centrifugal

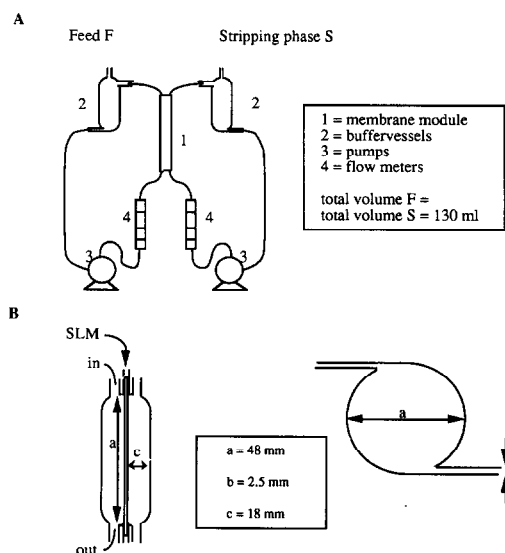


Fig. 3. (A) Experimental set up for the permeability measurements. (B) Dimensions of the membrane cell.

pumps (Ikawi MD-67) at room temperature. The water flow velocities are adjusted by flowmeters (Porter). With a volume of one cell-half of ca. 40 ml and a flow velocity of the aqueous phases of 5 ml/sec the average residence time in the cell half is 8 sec. The buffer vessels are necessary to remove air bubbles from the water phases. In experiments with different flow velocities of feed and stripping phases, small pressure differences over the membrane are avoided by adjusting the height of the buffer vessels.

The flow pattern of the aqueous phases parallel to the membrane surface is badly defined because of the shape of the membrane cell. This means that the mass transfer of components from the bulk of the water phases to the membrane interface can not be calculated. The flow pattern of water phases which are pumped parallel to the surface of non-supported flat membranes, will always be influenced by little movements of the membranes.

Periodically samples were taken from the feed and analysed by HPLC. It should be noted that in all experiments reported in this paper a one to one exchange of nitrate by chloride ions in the feed was obtained.

The stability of the SLMs (with *o*-NPOE as solvent) has also been checked by comparing the weight of the membrane before and after the permeation experiment. It was found that in all cases less than 2% of the LM-phases had been removed from the support during 7 hr under actual flow conditions of feed and stripping phases.

Results and discussion

Tetra-octylammonium (TeOA) compounds have been used as standard carriers. *o*-NPOE has been used as LM-solvent during the permeation measurements because, out of the solvents investigated, this solvent gave the most stable membranes [8]. In the extraction exper-

iments decanol has also been used to compare the influence of the type of solvent on the extraction behaviour.

Extraction

The advantages of the extraction method used here (in which the LM-phase is immobilized in the support) compared to extraction methods usually described in literature are:

- The contact area between the LM-phase and the water phase is high, because the liquid layer in the membrane is very thin;
- The separation of the water phase and the organic phase is very simple; no special techniques are needed (e.g. the use of centrifugation).

Figure 4 gives the relative amount of carrier (TeOA) complexed with nitrate ions as a function of the chloride ion concentration in the water phase, at equilibrium, for SLMs with *o*-NPOE and decanol as solvent. HPLC-analysis of the aqueous samples with a chloride concentration higher than 0.1 M was not possible. The absolute error in these results has been estimated at $\pm 5\%$.

By calculating the distribution coefficients $k_{\text{NO}_3^-}$ and k_{Cl^-} and using eqn. (2) the extraction constants can be calculated:

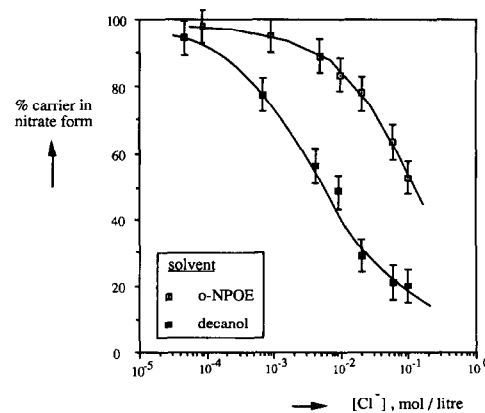


Fig. 4. Influence of chloride ion concentration and type of solvent on nitrate extraction. Volume LM-phase 0.3 ml; volume water phase 30 ml; carrier TeOA.

$$K_{\text{ex}}, (o\text{-NPOE}) = 154 \quad (3)$$

$$K_{\text{ex}}, (\text{decanol}) = 10 \quad (4)$$

These values are comparable with literature values for ion selective electrodes with similar compositions [20–22]. The same dependence of the selectivity on the nature of the membrane solvent (high selectivities for aromatic solvents) has been published for these systems. The causes for these phenomena, mainly given by the strength of the association between the anion and the exchanger, are discussed in Ref. [21]. The possibility to vary the selectivity of an SLM with the properties of the solvent can be very attractive for practical applications. To enable an effective desorption of the nitrate ions in the stripping phase to take place, the highest K_{ex} is not always desirable.

Permeation

The influence of various variables on the nitrate transport through the membrane will be discussed in comparison with the permeation under standard conditions.

Standard conditions

The standard conditions were chosen such that the transport of nitrate is determined only by the diffusion of the carrier through the membrane. These standard conditions are:

support	:Accurel [®] , thickness 92.5 μm
carrier	:TeOA
carrier concentration	:0.2 M
solvent	:o-NPOE
feed: $F_{t=0}$:0.004 M NaNO_3
stripping phase: $S_{t=0}$:4.0 M NaCl
water flow velocities F and S	:5.0 ml/sec

Figure 5 gives the nitrate concentration in the

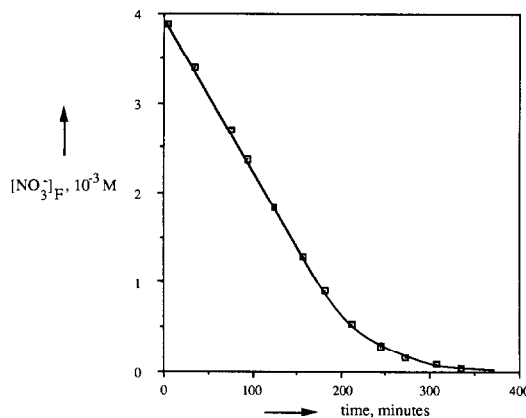


Fig. 5. Nitrate concentration in the feed as a function of time. Standard conditions as defined in the text.

feed as a function of time when the feed is treated under standard conditions.

The concentration of nitrate in the feed after 6 hr of permeation has decreased to less than 10^{-5} M and it is below the detection limit of the HPLC. So nitrate can be removed completely from the feed and transported to the stripping phase, in which the nitrate concentration is at least 400 times higher than the last measured value in the feed.

The first part of the curve (up to a time of three hours) can be described by a straight line (see Ref. [17]). From the slope of this line the nitrate flux J through the membrane can be calculated by:

$$J = -d[\text{NO}_3^-]_{\text{F}}/dt \times V/A \quad (5)$$

in which A is the membrane area in contact with the water phase (18.1 cm^2) and V is the volume of the feed (130 ml). Under these conditions J is: $19.7 \times 10^{-10} \text{ mol/cm}^2\text{-sec}$. The error in the flux determination is $\pm 10\%$.

Effect of flow velocities of the aqueous solutions

In Fig. 6 the influence of the water flow velocities on the nitrate flux through the SLM is given while maintaining the other variables at their standard values. The flow velocities of F

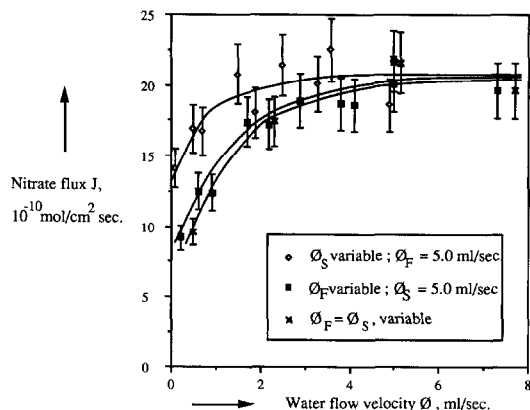


Fig. 6. Influence of the water flow velocity on nitrate permeation.

and S have been varied separately, while in addition experiments have been carried out in which the velocities of F and S were equal and were varied simultaneously.

Figure 6 shows that for all three curves the fluxes reach a plateau value with increasing water flow velocities. This means that at low water flow velocities the resistance against mass transfer through the laminary water layers (∂_F and ∂_S in Fig. 2) also has an influence on the overall flux. While increasing the water flow velocities, the thickness of the laminary layers will decrease and the concentration at the membrane boundaries will change: $[\text{NO}_3^-]_{F,i}$ will increase while $[\text{NO}_3^-]_{S,i}$ will decrease (see Fig. 2). Via the ion exchange equilibrium these boundary concentrations determine the composition of the complexes at the interfaces of the membrane phase and also the concentration gradient which acts as the driving force for transport. When reaching the plateau value a further change in these boundary concentrations obviously has no effect and the transport is limited by the diffusion of the carrier through the membrane. The experiments, described in the following paragraphs, will show that supply and removal of chloride ions does not play a significant role in this process under these conditions.

Figure 6 also shows that the reduction of the flux below the plateau value is reached at a higher flow rate when lowering the feed velocity than when lowering the velocity of the stripping phase. Furthermore, the curve obtained when varying only the flow velocity of the feed nearly coincides with the curve which is obtained when the flow velocities of both the feed and the stripping phase are varied simultaneously. From these facts it can be concluded that concentration polarisation effects are more important in the feed than in the stripping phase and that at equal velocities of the feed and the stripping phase the resistance against mass transfer in the feed boundary layer determines the overall concentration polarisation behaviour. This means that the limited supply of nitrate ions in the feed has a much larger influence on the amount of carrier in nitrate form in the membrane phase than a limited nitrate removal in the stripping phase does.

This can be understood when one takes into account the selectivity of the membrane and the difference in concentration of the permeants in the feed and the stripping phase as will be illustrated later. The same influence of varying the flow velocities on the flux was noticed by other workers in the field. For instance Babcock et al. [23] found for an SLM-system in which copper ions were removed that the flux decreases sharply when decreasing the flow velocity of the feed, while the flux was independent of the velocity at the stripping side.

For practical applications, e.g. making use of hollow fibers modules, this means that for an optimal operation of the process different flow velocities of the feed and the stripping phase can be used. For process design in which the extraction and stripping processes are performed in two different modules it is also possible to have different membrane surface areas at the feed and stripping side.

Taking into account the results given in Fig. 6 equal flow velocities of F and S of 5.0 ml/sec

were used during further experiments. The effects of concentration polarisation can then be neglected and the diffusion of the ions through the water phases is not the rate determining step in the transport process.

Effect of nitrate concentration in the feed

Figure 7 shows how the flux is influenced by the nitrate concentration in the feed. The black points are obtained by applying eqn. (5) to Fig. 5; that means that the slope of the curve for the nitrate concentration as a function of time is determined for an experiment in which one starts with 0.004 M NO_3^- . Apart from that the flux can also be measured by eliminating the influence of the presence of chloride ions in the feed. These values (open points in Fig. 7) are obtained by various experiments in which the chloride concentration was zero at the start of each measurement while the starting concentrations of nitrate in the feed was varied.

It appears from Fig. 7 that the same curve is obtained for both methods. This means that the presence of chloride ions in the feed, in this concentration region, has no influence on the overall flux.

The linear part of Fig. 5 results in the plateau value in Fig. 7, while the change in the decline of the $[\text{NO}_3^-]$ -time curve at nitrate concentra-

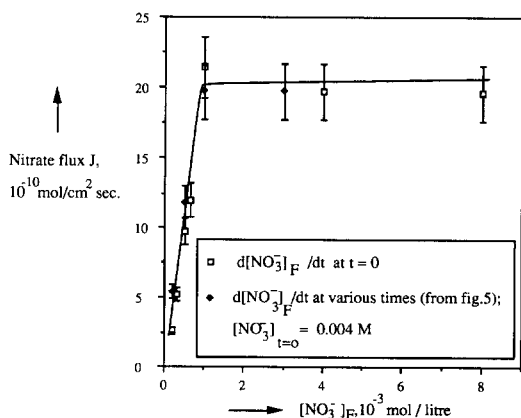


Fig. 7. Influence of nitrate concentration in the feed on nitrate permeation.

tions lower than 0.001 M gives a lower flux. The explanation for this decrease in flux is that at bulk concentrations of nitrate in the feed below 10^{-3} M the amount of carrier molecules in nitrate form at the feed interface diminishes and so the driving force for transport will reduce.

There are two possible causes for this reduction in driving force:

- (1) A reduced complexation of nitrate ions due to the ion exchange equilibrium;
- (2) A delayed nitrate supply due to concentration polarisation effects.

On account of the anion exchange equilibrium (eqns. 2 and 3), it can be calculated that above 0.001 M nitrate in the feed at least 98% of the carrier molecules in contact with the feed would be in the nitrate form; above the value of 0.0001 M nitrate still more than 80% would be in the nitrate form. Because of eqn. (6) a proportional decrease of the flux in this concentration region could be expected:

$$J = \Delta C D / d \quad (6)$$

in which ΔC is the concentration gradient of the carrier in nitrate or chloride form in the membrane, D is the diffusion coefficient of the carrier through the membrane and d is the effective pathlength of the carrier through the membrane. However the flux decline shown in Fig. 7 is much stronger. So concentration polarisation effects must be responsible for the reduction in driving force for transport. It is obvious that this behaviour (and so the critical nitrate concentration below which the resistance for mass transfer changes from diffusion through the membrane to diffusion through the boundary layer) depends on the flow velocities of the aqueous phases.

Because of these results a nitrate concentration of the feed of 0.004 M , at the start of the experiment, has been chosen as a standard condition. So almost all the carrier molecules at the membrane interface in contact with the feed are in the nitrate form so that the complexation

of carriers with nitrate ions is not the rate determining step in the transport process.

Effect of chloride concentration in the stripping phase

Figure 8 gives the flux as a function of the sodium chloride concentration in the stripping phase.

The nitrate flux increases with increasing NaCl concentration and reaches a plateau value for $[NaCl]_S > 2.0 M$. Qualitatively we can understand this behaviour if we realize that an increasing percentage of carrier in nitrate form is being transformed to the chloride form when increasing the chloride concentration in the stripping phase. For a more quantitative discussion we assume that the overall flux is determined by diffusion of the carrier through the membrane phase and that eqn. (6) is valid. If the diffusion velocities of the carriers in both nitrate and chloride form are equal to each other eqn. (6) can be converted to:

$$J = ([NO_3^-]_F - [NO_3^-]_S) \times \text{Constant} \quad (7)$$

A relative flux J' can be defined as:

$$J' = J/J_{\max} \quad (8)$$

in which J_{\max} is the maximal attainable flux for a certain membrane; this means that flux J_{\max}

is obtained when all the carrier molecules at the feed side are in the nitrate form and at the stripping side all are in the chloride form.

As stated in the previous paragraph the assumption can be made that at the feed side (under the prevailing conditions) all the carrier molecules are in the nitrate form; so

$$[NO_3^-]_F = 0.2 M$$

$[NO_3^-]_S$ can be calculated by applying eqn. (2) to the conditions at the interface between the membrane and the stripping phase, using the experimentally determined value for K_{ex} .

$$\frac{[NO_3^-]_S}{[Cl^-]_S} = \frac{[NO_3^-]_{S,i}}{[Cl^-]_{S,i}} \times 154 \quad (9)$$

As a result of the high chloride concentration in the bulk of the stripping phase it can be supposed that the influence of concentration polarisation effects for the chloride concentration at the membrane-interface is negligible, so: $[Cl^-]_{S,i} = [Cl^-]_S$. Assuming a value for $[NO_3^-]_{S,i}$ the relative flux can be calculated. Based on the previous paragraphs at the start of the experiment $[NO_3^-]_{S,i}$ is assumed to be 0.001 M (equal to the concentration polarisation of nitrate ions in the feed). The influence of $[Cl^-]_S$ on the theoretical relative flux has been given as a dashed curve in Fig. 8. To compare the trend between the two curves in this figure the maximal theoretical flux is fitted to the experimental plateau value of $22 \times 10^{-10} \text{ mol/cm}^2\text{-sec}$. The fact that the curves in both cases have the same trend towards $[Cl^-]_S$ confirms the validity of the theory and the assumptions.

So an intermediate conclusion is that, contrary to the problems of concentration polarisation at the feed side, at the stripping side the ion exchange equilibrium is responsible for the reduction in the flux value when lowering the chloride concentration in the stripping phase.

The relative flux is a direct measure for the amount of carrier molecules which are in the

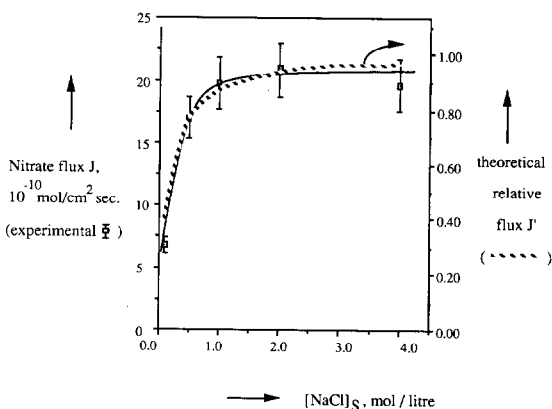


Fig. 8. Influence of chloride concentration in the stripping phase on nitrate permeation.

chloride form at the stripping side, because all the carrier molecules in contact with the feed solution are in the nitrate form, under the given conditions. From Fig. 8 it can be concluded that for 4 M NaCl, 96% of the carrier molecules in contact with the stripping phase is in the chloride form.

Because of these results a NaCl concentration in the stripping phase of 4.0 M has been chosen as the standard condition, so almost all the carrier molecules in the membrane in contact with the stripping phase are in the chloride form.

Effect of the carrier concentration

The dependence of the nitrate flux on the carrier concentration in the membrane phase and the relation between the carrier concentration and the dynamic viscosity has been measured. With these data the actual diffusion coefficient can be calculated from eqn. (6):

$$D = J \times d / \Delta C \quad (6)$$

In this formula the effective pathlength of the carrier through the membrane, d , can be obtained by multiplying the membrane thickness with the tortuosity factor, τ , of the support. This value is unknown and also influenced by the shape of the pores. Yet to be able to estimate this value the equation of Mackie and Meares is used [24]:

$$\tau = (1 + V_p) / (1 - V_p) \quad (10)$$

where V_p is the volume fraction of polymer in the support. The porosity of the membrane used in this work was 69%; a tortuosity factor of 1.90 is then calculated from eqn. (10).

To calculate the carrier concentration gradient in the LM-phase it is assumed that 100% of the carrier in contact with the feed is complexed with nitrate ions and at the stripping side 96% of the carrier is complexed with chloride ions. This value has to be multiplied by the porosity of the support to yield the concentra-

tion difference ΔC over the total SLM. This gives:

$$\Delta C = C \times 0.96 \times 0.69 \quad (11)$$

in which C is the concentration of carrier in the LM-phase.

For the diffusion of spherical particles through a liquid the Stokes–Einstein equation is valid [25]:

$$D = k \times T / 6\pi r \mu_0 \quad (12)$$

in which k stands for the Boltzmann constant, T is the absolute temperature, r is the radius of the diffusing species and μ_0 is the dynamic viscosity of the liquid. In Fig. 9 the actual diffusion coefficients calculated from eqns. (6), (10) and (11) and based on measured flux values are given as a function of the reciprocal viscosities. From this figure it can be concluded that in our system the Stokes–Einstein equation is valid for the diffusion of carrier molecules through the LM-phase, within experimental error.

Effect of type of carrier

The influence of the length of the alkyl chains of the carrier on the diffusion coefficient has

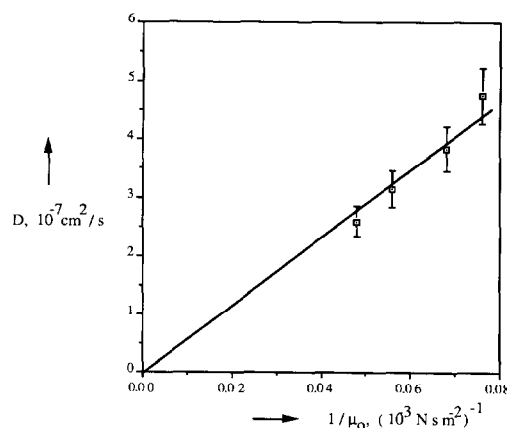


Fig. 9. The diffusion coefficient as a function of the reciprocal viscosity.

been determined (see Ref. [17]). From the results it appears that the diffusion coefficient decreases only slightly with increasing length of the alkyl chains of the quaternary ammonium salts (up to dodecyl chains). The experimental results are, within experimental error, in good agreement with an empirical model.

Conclusions

A continuous anion exchange method has been developed for the removal and concentration of nitrate ions from water by counter-transport of chloride ions using a proper carrier molecule. This process is also applicable to transport of other anion combinations provided that the compositions of the aqueous phases are such that a reversible complexation of the ions can take place.

The transport mechanism could be described with a set of relations that are generally used for coupled transport of cations through liquid membranes.

The extraction results show that the selectivity of the liquid membrane depends on the type of solvent used.

The permeation measurements show that:

- The overall flux is limited by diffusion of the carrier molecules through the liquid membrane phase at standard conditions (carrier: 0.2 M TeOA; solvent: *o*-NPOE; feed concentration at $t=0$: 0.004 M NaNO₃; stripping phase at $t=0$: 4.0 M NaCl; flow velocities of feed and stripping phases: 5.0 ml/sec);

- Concentration polarisation effects on the feed side have a larger influence on the flux values than those in the stripping phase when the flow velocities of the aqueous phases are lowered. The supply of nitrate ions through the laminar boundary layer is also becoming rate determining for the overall flux when the nitrate concentration in the feed is decreased below a critical value of 10⁻³ M;

- Transport decreases when the chloride con-

centration in the stripping phase is lowered below 2 M. In contrast to the concentration polarisation effects at the feed side this is caused by a diminished nitrate desorption and so determined by the ion exchange equilibrium;

- The influence of the carrier concentration on the flux value can be explained using the diffusion law of Fick and the Stokes-Einstein equation. These relations are also valid for describing the diffusion transport of other carriers with longer alkylchains.

For practical applications the stability of the liquid membrane is of utmost importance. Since the variables investigated in the present article influence the stability of the membrane, further research concerning the optimization of the process has to be done. This will be described in following papers [8,9].

Acknowledgement

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List of symbols

A	membrane area (m ²)
C	carrier concentration in LM-phase (mol·m ⁻³)
ΔC	concentration gradient of the carrier in the SLM phase (mol·m ⁻³)
$\delta_F; \delta_S$	thicknesses of laminar boundary layers at feed or stripping phase interfaces respectively (m)
d	effective membrane thickness (m)
D	diffusion coefficient of carrier molecule in LM-phase (m ² ·sec ⁻¹)
J	overall flux of nitrate ions through SLM (mol·m ⁻² ·sec ⁻¹)
J'	theoretical relative flux (—)

J_{\max}	maximal attainable flux ($\text{mol}\cdot\text{m}^{-2}\cdot\text{sec}^{-1}$)
k	Boltzmann constant ($\text{J}\cdot\text{K}^{-1}$)
$k_{\text{NO}_3^-}, k_{\text{Cl}^-}$	distribution coefficients of ions between the membrane and the water phase (—)
K_{ex}	extraction constant (—)
μ_0	dynamic viscosity of LM-phase ($\text{N}\cdot\text{sec}\cdot\text{m}^{-2}$)
Φ	volumetric flow velocity of aqueous phases along the membrane ($\text{m}^3\cdot\text{sec}^{-1}$)
r	radius of diffusing carrier molecules in LM-phase (m)
τ	tortuosity factor (—)
t	time (sec)
T	absolute temperature (K)
$V_{\text{F}}; V_{\text{S}}$	volume of the feed or the stripping phase (m^3)
V_{p}	volume fraction of polymer in the support (—)
$\frac{[\text{NO}_3^-]_{\text{F}}}{[\text{NO}_3^-]_{\text{S}}}$	concentration of ions bound to the carrier in the membrane at the interfaces ($\text{mol}\cdot\text{m}^{-3}$)
$\frac{[\text{NO}_3^-]_{\text{F}}}{[\text{NO}_3^-]_{\text{S}}}$	bulk concentration of ions in the aqueous phases ($\text{mol}\cdot\text{m}^{-3}$)
$\frac{[\text{NO}_3^-]_{\text{F},i}}{[\text{NO}_3^-]_{\text{S},i}}$	concentration of ions in the aqueous phases at the membrane boundary ($\text{mol}\cdot\text{m}^{-3}$)
LM	liquid membrane
SLM	supported liquid membrane
ED	electrodialysis
RO	reverse osmosis
SX	solvent extraction
F	feed
S	stripping phase
TeOA	tetra-octylammonium
o-NPOE	ortho-nitrophenyloctylether

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