Ion-Exchange Membranes.   Application to the Treatment of Natural Rubber Skim Latex

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Synopsis

Ion-exchange membranes have been successfully used in the electrodialysis and electrodecantation of natural rubber skim latex for the recovery of ammonia as well as rubber.   Diffusivity of the membrane and current efficiency were studied.   An optimum condition is recommended for electrodecantation of skim latex.

Skim latex is a by-product of the natural rubber latex concentrate industry.   Field latex is ammoniated to ca. 0.3–0.5% (w/w) in order to reduce spoilage by bacteria and enzymes during subsequent processing operations, and when it is concentrated by centrifuging, some 70% of the aqueous medium is removed in the skim latex, the remainder being present in the concentrate.   The skim latex is normally treated for recovery of the small proportion of low grade rubber it contains, 2.5–10% dry rubber content.[1]   The ammonia present in the skim latex is normally neutralized by acid to permit coagulation of the rubber particles by reducing the pH value of the serum.   In many factories, however, skim latex is allowed to lose some of its ammonia by evaporation, the skim being stored in shallow open vessels for a few days.   The ammonia contained in the skim latex is thus usually lost; it might therefore be worthwhile to develop a process to recover ammonia as well as the rubber from the skim latex.

The investigation described in this paper explores the possibilities of using electrodialysis and electrodecantation to achieve these objectives.

ELECTRODIALYSIS

Electrodialysis is defined as the transfer of ions through an ion-exchange membrane under the influence of an externally applied electric field.

If the skim latex containing ammonia is subjected to an applied electrical potential, the negatively charged latex particles move towards the anode and the ammonium ions together with other cations present in the skim latex towards the cathode.   This is the basis of the method described below for effecting a separation of the two components.
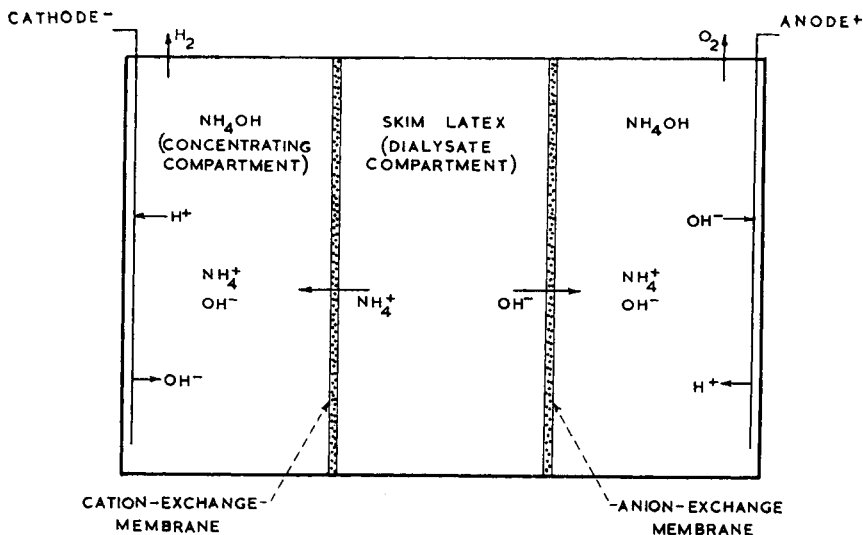
Fig. 1. Schematic representation of a three-compartment electrodialysis cell.

A three-compartment electrodialysis cell (Fig. 1) consists of a center compartment containing dialyzate which is separated from the electrode compartments by anion- and cation-exchange membranes.

When an external emf is applied between the electrodes, and the center compartment is filled with skim latex, the current starts flowing from right to left (Fig. 1) by the migration of NH_4^+ together with the traces of other cations (e.g., K^+, Mg^{++}) from the center (dialyzate) compartment into the cathode compartment and of OH^-, together with other anions (e.g., PO_4, CO_3) present in the skim, into the anode compartment. The ammonia content of skim latex is thus reduced, and the ammonia recovered at the cathode compartment. In an ideal system, 1 Faraday will cause the transport of 1 equiv. of cations from the center to the cathode compartment.

The negatively charged latex particles move towards the anode with consequent concentration at the anion-exchange membrane surface. The behavior of these accumulated latex particles is considered later.

Hydrogen and oxygen are liberated at the cathode and anode, respectively.

For any practical process one would make use of a multicompartment cell, which employs a multiplicity of membranes between two electrodes. This can be considered as a combination of many three-compartment cells without electrodes in their outer compartments. In a multicompartment cell, all the ions removed from a dialyzate compartment, i.e., the compartment in which the deionization occurs, are received in an adjacent compartment. The passage of 1 Faraday causes the transport of 1 equiv. of NH_4^+ from each dialyzate compartment to the concentrating compartment. Thus it is possible in this system to remove many times the amount of NH_4^+ transferred by 1 Faraday in a three-compartment cell.

General Considerations

In an electrodialysis cell, mass transfer takes place mainly owing to the following mechanisms through ion-exchange membranes: (*1*) molecular diffusion; (*2*) normal electrodialysis.

Molecular diffusion of ions through the membrane occurs owing to the concentration gradient across the membrane, irrespective of the applied potential. It is due to mainly the imperfect or low selectivity of the membrane. In a three-compartment electrodialysis cell, the mass transfer due to molecular diffusion may either impair or improve the electrodialysis, depending on the relative concentrations in the dialyzate and the concentrating compartments. It is bound to decrease the effective deionization when the concentration in the dialyzate compartment becomes weaker than that in the adjacent concentrating compartment. In order to find the effect of the molecular diffusion, it is required to know the diffusion coefficient or diffusivity of the ions in the membrane.

The mass transfer due to normal electrodialysis can be calculated as shown in eqs. (1) and (2) from the transport number of ions through the membranes together with the current flow measurements:

$$Q = t \, AiT/F \tag{1}$$

or

$$QF/AiT = E = t \tag{2}$$

where Q is the quantity of ions transferred (g.-equis.), t is the transport number of ions through the membrane, A is the membrane area (cm.^{2}), i is the current density (amp./cm.^{2}), T is time (sec.), 2nd F is the Faraday constant.

In other words, in the absence of any other mechanism of mass transfer such as molecular diffusion, across the membrane, the transport number of the ions through the membrane directly represents the current efficiency E, which is defined as the ratio of the actual transfer of ions through the membrane to the number of equivalents of electricity passed.

The transport number of ions through the membrane is also related to the selectivity of an ion-exchange membrane. Thus, a perfectly selective cation-exchange membrane would show a cation transport number equal to one and an anion transport number equal to zero, whereas a completely unselective membrane would show the same transport number as in a free aqueous solution.

In this investigation current efficiency measurements have been considered as representative for both the transport number and the selectivity of the membrane. The rate of transfer of ions through the membrane can be increased by increasing the current density, but this increases the concentration polarization at the membrane–solution interface. These concentration polarizations are important not only from the point of view of molecular diffusion but also for the transport number of the wanted

ions, through the permselective membranes. As the ions are progressively depleted at the membrane–solution interface, current is carried not only by the wanted ions, but also by the unwanted ions, i.e., H^+ or OH^- derived from water. Transport of these unwanted ions, even though carrying the current across the membrane, decreases the transport number of wanted ions through the membrane. Experimental determinations are, therefore, required to find the effect of current density on current efficiency.

Experimental

Experiments were carried out at ambient temperature. Membranes used were Permaplex C.10 and C.20 (cation-exchange) and Permaplex A.10 and A.20 (anion-exchange). These are heterogeneous ion-exchange membranes of nominal thickness 0.02 in.; size 5 in. $\times$ 5 in.

Molecular Diffusion. The experiments were conducted with ammonia solutions of various concentrations in two compartments separated by a cation-exchange membrane. The membrane was equilibrated with ca. $0.1N$ ammonium chloride solution in order to convert it into ammonium form.

The two compartments were filled with equal volume of different concentrations of ammonium hydroxide and the changes in their concentration with time were noted; the ammonia contents were estimated by titrating the samples against dilute sulfuric acid.

If the initial concentration of ammonium hydroxide in the first compartment is C_1^0 and that in the second compartment is C_2^0 and $C_1^0 > C_2^0$, and the final concentrations after time T are C_1 and C_2, respectively, it can be shown that, assuming the volume V of the liquid in both the compartments is the same and ammonia losses due to vaporization etc., are negligible,

$$- 1.15 \log [(C_1^0 + C_2^0 - 2C_2)/(C_1^0 - C_2^0)] = ADT/Vl \qquad (3)$$

where D is the diffusion constant (cm.²/sec.), A is the area of the membrane (cm.²), and l is the membrane thickness (cm.).

Effect of Current Density on Current Efficiency. Experiments were conducted in a two-compartment electrodialysis cell with the use of a Permaplex cation-exchange membrane in order to determine the magnitude of the effect of current density on current efficiency for ammonia recovery. The compartments, which are separated by an equilibrated cation-exchange membrane, were filled with appropriate concentrations of NH_4OH of known volume. A d.c. voltage was applied by use of an iron cathode and lead anode and was adjusted to give a constant current flow throughout the experiment. The concentrations of NH_4OH on both the compartments were measured before and after each run. The equivalents of ammonia transferred were then calculated from the change in concentrations with due allowance for ammonia losses and concentration diffusion. The product of current and time gave the number of equivalents of electricity passed, which was in turn used for estimating current efficiency. The

actual area of the electrodes submerged into the electrolyte was used for finding the current density.

Electrodialysis of Skim Latex. Experiments on electrodialysis of skim latex were conducted in three- and five-compartment cells with the use of Permaplex cation- and anion-exchange membranes at moderate current densities, at which the effect of concentration polarization is negligible. Skim latex was placed in the center compartment and NH_4OH in cathode and anode compartments. The current efficiencies were calculated as before from the equivalents of ammonia recovered; the ammonia contents were estimated according to the B.S.I. method.[2]

Results

Molecular Diffusion. A plot of $-1.15 \log [(C_1^0 + C_2^0 - 2C_2)/(C_1^0 - C_2^0)]V$ against T gave a straight line through the origin (Fig. 2) of slope 1.226×10^{-3}. Substituting the values for A and l, the diffusivity D of ammonium hydroxide through Permaplex C.10 and C.20 membranes is found to be 3.868×10^{-7} cm.^{2}/sec.

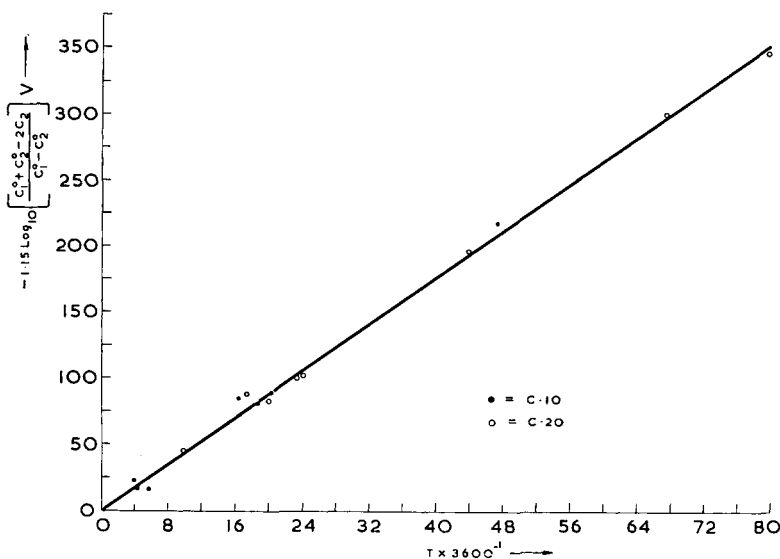Fig. 2. Plot of $-1.15 \log [(C_1^\circ + C_2^\circ - 2C_2)/(C_1^\circ - C_2^\circ)] V$ vs. T for ammonium hydroxide in Permaplex C.10 and C.20 membranes.

Effect of Current Density on Current Efficiency. The variation of current efficiency with current density is shown in Figure 3. A decrease of about 0.1 (or 10%) in current efficiency has been found with an increase of current density from 1 to 12 ma./cm.^{2}.

Electrodialysis of Skim Latex. Skim latex, made at the Rubber Research Institute Experiment Station (Malaya) and preserved with high ammonia content (1.592% w/w) gave current efficiencies in the region of
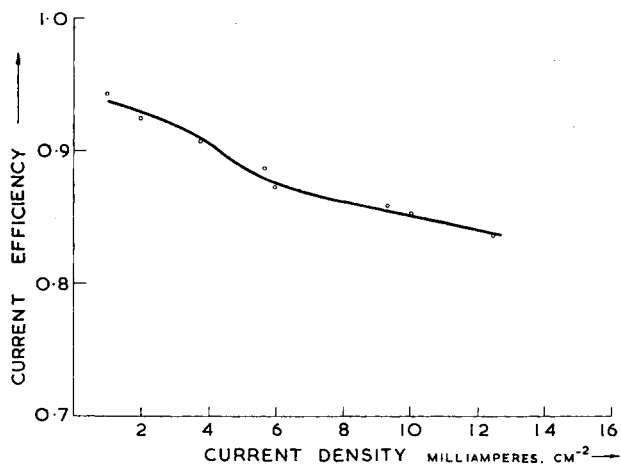
Fig. 3. Effect of current density on current efficiency.

0.83 ± 0.035 (or $83 \pm 3.5\%$) with moderate current densities (1.12–4.4 ma./cm.²).

Discussion

The diffusivity of ammonia is considerably higher than the value 8×10^{-8} for sodium chloride through Permaplex C.10, obtained by Kressman.[3] This higher value is possibly due to two factors. Firstly, the cation-exchange membranes are expected to be less selective in alkaline solutions than in neutral media. Secondly, in the case of ammonia there is likely to be an additional transport by diffusion of undissociated ammonia molecules through the pores of the membrane, due to the concentration gradient, irrespective of the ionic charge present in the membrane structure, whereas in the case of sodium chloride there will be no undissociated molecules present in the solution.

The current efficiency for skim latex is lower than that for ammonia solution. Skim latex contains other cations, such as K^+, Na^+, Mg^{++}, the concentration of potassium ion, which predominates, being about $0.04N$. These cations also transport current through the cation-selective membrane with consequent loss of efficiency of ammonium ion transport.

ELECTRODECANTATION

Electrodecantation of skim latex was considered as a method of concentrating the skim in the electrodialysis cell at the same time as removing ammonia from it. Electrodecantation can be defined as the stratification of a colloidal suspension into horizontal layers of different concentration as a result of the combined influence of the electrical potential and gravitational force. Even though no quantitative expressions have yet been put forward for the theory of electrodecantation, the principles involved based on the
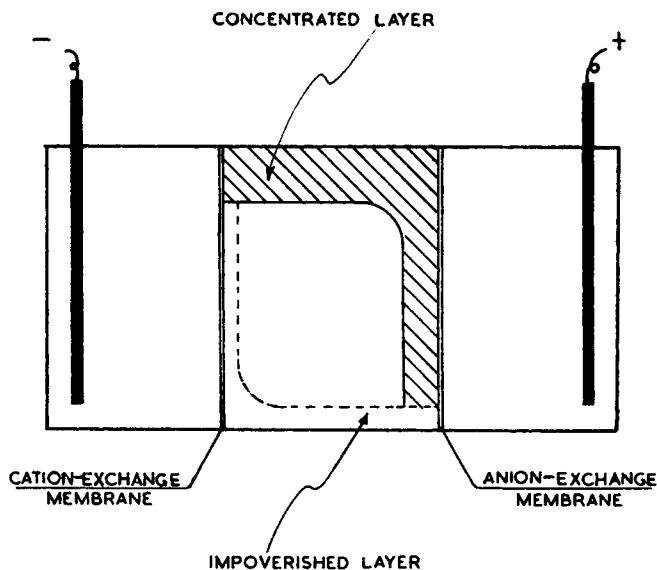
Fig. 4. Electrodecantation of skim latex.

pioneer work of Pauli and his co-workers in 1924[4] have been applied to the concentration of natural rubber latex.[5,6]

The rubber particles in the latex are less dense than the liquid in which they are suspended, but in the absence of any applied potential the Brownian movement of the rubber particles effectively counters any sedimentation due to gravitational forces on individual particles, so that no concentration gradients occur in the system. During electrodialysis of skim latex the rubber particles will move towards the anion-selective membrane, since they are negatively charged, and consequently their concentration near the membrane surface will rise. If the field strength (the voltage difference between the membrane divided by the distance between the membranes) is not so high that the particles are deposited on the membrane, then the bulk density of the suspension close to the membrane surface will be less than that of the rest of the latex in the cell and the accumulation near the membrane will then move upwards along the surface of the anion-selective membrane and form a relatively more concentrated layer on the surface. Similarly an impoverished layer/ formed at the cation-selective membrane will run downwards, collecting as a layer at the bottom. If this stratification is allowed to proceed, the two layers formed will gradually grow in thickness at the expense of the liquid between them (Fig. 4).

The conditions for stratification in the case of natural rubber latex were determined empirically by adjustment of the applied potential and dispersion concentration. Increase in field strength increased the deposition of rubber particles on the membrane surface. It was hoped that at

low field strengths when the particles are not held tightly against the membrane, no deposition would occur on the membrane surface. If this were not practicable it was expected that potentials of a magnitude which would normally cause some formation of deposit on the anion-selective membrane could be employed if the current was reversed periodically during the process.[7] In this way it was possible to free the rubber particles which stuck to the membrane and were still in a reversible state, and the rate of stratification increased without the attendant disadvantage of membrane deposition. The period of current reversal was adjusted empirically to suit the conditions.

Experimental

Experiments on electrodecantation of skim latex were directed to the following factors: (1) the influence of field strength and the effect of current reversal; (2) experiments on electrodecantation of skim latex with simultaneous electrodialysis under selected conditions.

Permaplex permselective membranes were used in all the experiments.

Field Strength and Current Reversal. In order to check the effect of field strength on the electrodecantation of skim latex, experiments were conducted in the three-compartment cell with different field strengths (0.08–0.58 v./cm.), and the appearance of the membrane was observed in each case; the different field strengths were obtained by varying the current density. The results obtained, however, indicated that even at low field strengths rubber is deposited on the membrane surface. Therefore attempts were made to avoid this deposition by using current reversal. In addition to frequent current reversal, prolonged reversal of current for a short time after a few hours of operation to remove the accumulated deposit on the membrane surface was also studied.

Experiments were carried out in three-compartment cells with three different membrane gaps. Several frequencies of current reversal were studied; for each frequency several field strengths were employed. The duration of current reversal was also studied. The current was reversed manually in the initial experiments by using a two-way (double pole) switch, later an automatic electronic device was used. In all the experiments in addition to observing the appearance of the membrane surface, samples were taken from the top and bottom of the skim compartment and their percentage total solids estimated to the B.S.I. method.[2]

As a result of these extensive trials, satisfactory conditions were selected for further work on the electrodecantation of skim latex.

Simultaneous Electrodecantation and Electrodialysis of Skim. Having found an optimum range of field strengths and current reversal intervals, experiments were then conducted on electrodecantation of skim latex with simultaneous electrodialysis in three- and five-compartment cells. Percentage total solids of top and bottom layers, current efficiency, etc. were found as before. The appearance of the membrane was also observed in each case.

Results

Field Strength and Current Reversal. Optimum conditions for obtaining stratification and a deposit free membrane surface during electrodecantation of skim latex are as follows: duration and frequency of current reversal, 10 sec. every 2 min. plus 5 min. prolonged current reversal at intervals of 6 hr.; field strength (acting between the membrane) on skim rubber particles X, not more than 0.4 v./cm.

Electrodecantation and Electrodialysis of Skim Latex. The current efficiency values obtained, membrane observations, etc. are given in Table I. The maximum concentration obtained for skim latex in the top layer was 14.2% total solids, which is 54.5% more than that of the initial concentration.

TABLE I

Electrodecantation of Skim Latex with Simultaneous Electrodialysis[a]

| | Skim latex (initial) | | | Skim latex (final) total solids, % | | Current density i, ma./ | Current effi- | |
Expt. no.	Total solids, %	NH₃, %	Field strength X, v./cm.	Top	Bottom	cm.²	ciency, E	Membrane observations
				Three-compartment cell				
1	9.20	1.552	0.156–0.234	14.20	4.25	1.86	0.832	No deposit
2	9.92	0.806	0.162–0.253	14.00	4.27	1.86	0.834	A layer of deposit (2 m.m. paste) on top of A. 20
3	10.17	0.457	0.164–0.242	14.80	4.37	1.86	0.816	Same as expt. 2
4	10.16	0.302	0.167–0.244	14.20	4.57	1.86	0.820	Same as expt. 2
5	10.38	0.270	0.169–0.252	14.00	4.21	1.86	0.802	Same as expt. 2
				Five-compartment cell				
1	9.20	1.485	0.159–0.222	14.00	3.65	1.86	0.835	No deposit
2	9.05	1.272	0.226–0.296	14.10	3.20	1.86	0.840	No deposit
3	9.20	1.485	0.158–0.222	13.92	3.33	1.86	0.819	No deposit

[a] Membranes: Permaplex A.20 and C.20; Duration and interval of current reversal: 10 sec./2 min. + 5 minutes prolonged current reversal at intervals of 6 hr.

Discussion

In considering the optimum current density obtained for the simultaneous electrodialysis and electrodecantation of skim latex, i.e., 1.86 ma./cm.², a concentration difference of more than about 2.5N across the membrane cannot be obtained due to high diffusivity of electrolyte through the Permaplex membrane; the diffusivity of ammonia through Permaplex membranes is high, as shown above. However, it is expected that a highly permselective and closely crosslinked membrane would help in decreasing the diffusivity of undissociated ammonia across the membrane.

The current efficiency values obtained are found to be in close agreement with those obtained earlier in the electrodialysis experiments showing that the current reversal has little effect on the electrodialysis.

During the simultaneous electrodialysis and electrodecantation of skim latex a layer of rubber deposit (pastelike) on the top part of anion-exchange membrane was observed when the ammonia content of skim latex was low. This could be explained as the tendency of the rubber particles to stick to the membrane in the place where they are present in a more concentrated form. This necessitates the continuous removal of concentrated skim from the top of the cell and renders a large-scale batch process impracticable.

Other factors, which have not been studied, such as the electrophoretic mobility of the rubber particles, viscosity and temperature of skim latex, etc., also influence the operation of electrodecantation processes. The electrophoretic mobility of the rubber particles, which is dependent on the density of electric charge on their surfaces, will be reduced during de-ammoniation, as the reduction in the pH of the serum is found to reduce the amount of negatively charged protein and resin adsorbed on rubber particles.[8] Therefore during the final stage of electrodialysis only very little stratification will take place. The conductivity of the skim latex also falls during electrodialysis, and the current density has to be decreased in order to maintain a constant field strength. To avoid the membrane deposit an increased flow rate would be required in the later stages, and the resulting turbulence might make electrodecantation impracticable in any case. Therefore in the final stages, electrodialysis only would be aimed at and higher current densities could then be employed.

As the viscosity of skim latex is much lower than the natural (ammoniated) rubber latex, its effect on electrodecantation is not expected to be as critical as it was found to be in the latter case.[9]

CONCLUSIONS

(1) The use of permselective membranes to remove and recover ammonia for natural rubber skim latex by electrodialysis is found to be feasible, and the current efficiency values obtained are in the region of $83 \pm 3.5\%$.

(2) The use of permselective membranes for the electrodecantation of skim latex with simultaneous electrodialysis to concentrate the skim latex while recovering ammonia from it, is also found to be feasible, provided steps are taken to avoid the deposit of rubber particles on the membrane surface.

The conditions recommended are as follows: field strength: not more than 0.4 v./cm.; current reversal: reversal of current for 10 sec. every 2 min. plus 5 min. prolonged current reversal at intervals of 6 hr. With these recommended conditions the maximum concentration obtained in the top layer of the skim compartment in these experiments was 1.5 times the initial value.

(*3*) The diffusivity of ammonia in Permaplex membranes is found to limit the maximum concentration difference attainable across the membranes.

(*4*) The experiments on both electrodialysis and electrodecantation of skim latex were confined to three- and five-compartment experimental cells.   More knowledge regarding the behavior of multicompartment cells with a plurality of membranes in a continuous process would be required before the practical possibilities of the process could be assessed.

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Résumé

Des membranes, échangeuses d'ions, sont utilisées avec succès dans l'électrodialyse et l'electrodécantation de la mousse de latex du caoutchouc naturel en vue de récupérer l'ammoniaque aussi bien que le caoutchouc.   Le pouvoir de diffusion de la membrane et l'efficacité du courant sont étudiés.   On recommande d'utiliser une condition optimale pour l'électrodécantation de la mousse de latex.

Zusammenfassung

Zur Elektrodialyse und Elektrodekantation von Naturkautschuk-Skimlatex wurden mit Erfolg Ionenaustauschermembrane verwendet, sowohl für die Rückgewinnung von Ammoniak als auch von Kautschuk.   Das Diffusionsverhalten der Membrane und die Stromausbeute wurden untersucht.   Für die Elektrodekantation von Skimlatex werden die optimalen Bedingungen angegeben.