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Separation of Counterions during Pressure-Driven Transport of Electrolyte Mixtures across Charged Porous Membranes

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ABSTRACT

It has been previously predicted theoretically that a substantial separation of counterions will occur during the pressure-driven transport of electrolyte mixtures across charged porous membranes. This presumption has been supported experimentally using negatively charged sulfonated polysulfone and ternary electrolyte solutions with a simple coion like Cl^-. In dilute solutions the selectivity has approached values between 8 and 10 and sometimes even greater. The experimental findings of the relationship of selectivity to feed ionic strength and feed composition agree fairly well with the theory. Moreover, the theoretical prediction is also supported by the correlation of selectivity with mobilities of counterions and transmembrane volume flow. The less mobile counterions of symmetrical mixtures like KCl/LiCl have a rejection inferior to the more mobile ones when porous charged membranes are used. The reverse effect was observed when more dense membranes of the same polymer and degree of substitution were employed. However, some deviations from normality were noticed when the $KCl/MgCl_2$ mixture was used such as changes in the sign of the selectivity logarithm and the nonmonotonic dependences of the selectivity on the feed ionic strength and transmembrane volume flow. This leads to the assumption that the mobility of the Mg^{2+} ion in the membrane phase is lower than that of the K^+ ion, which is just opposite of their bulks. This relative decrease in the Mg^{2+} ion's mobility has been interpreted in terms of stronger electrostatic interactions with membrane fixed charges. Moreover, the lack of anomalies when the LiCl/$MgCl_2$ solution is used leads to the assumption that the mobility of the Mg^{2+} ion in the membrane phase is between that of Li^+ and K^+ ions.

INTRODUCTION

The phenomenon of significant separation of counterions differing in their mobilities and/or charges during pressure-driven transport of electrolyte mixtures across charged porous membranes was predicted in References 1 and 2. Similar aspects based upon computations can be found in References 3. Based on some data from the literature, the principal conclusions of the theory can be confirmed qualitatively (2). Thus, for instance, a much better rejection is observed for multiple-charged counterions than for single-charged ions even if only a low amount of the former is added to a solution (4–8). The same regularity was reported by Bevan as was cited in a private communication (9). By using a NaCl/$MgCl_2$ solution, it was found that Mg^{2+} ion rejection increased from 70% to almost 100% when its mole fraction decreased. Moreover, a negative rejection of NaCl was found with larger $MgCl_2$ mole fractions. An increase of sodium sulfate rejection during reverse osmosis using anion-exchange membranes when sodium chloride was added to the feed solution was found experimentally (10).

The pressure-driven transport of KCl/LiCl mixtures through a porous membrane made from a fluorocarbon polymer was studied by Igawa et al. (11). Despite the fact that these membranes have negative fixed charges, the authors put forward an explanation based upon the dependency of rejection on the kind of electrolytes and the ratio of cation and anion mobilities within the membrane. This idea differs from the theory presented in Reference 2. However, experimental findings concerning the separation of the electrolyte solution are in qualitative agreement with this theory. While the rejection of pure KCl and LiCl differs only slightly, the rejection becomes quite different with a mixture of these electrolytes, which can be explained as a typical consequence of "decompensation." Due to this, the selectivity reaches values of about 10. Increasing the molar fraction of LiCl leads to a drastic improvement of KCl rejection; by adding a small amount of LiCl to the feed, KCl rejection becomes negative.

The experiments cited in Reference 2 were performed for purposes other than to check the validity of the theory. This means that several substantial correlations were not examined. The purpose of this paper is to experimentally investigate the relationships of the selectivity to the properties of the feed solutions and the operational conditions, and to determine whether they match the theoretical predictions.

EXPERIMENTAL

Membranes

The membranes used in these investigations were made from sulfonated polysulfone. The original polymer was polysulfone type P-1700 purchased from Amoco, Göttingen. It was sulfonated using the SO_3/triethylphosphate (SO_3/TEP) complex which was first applied in solution (12) and then in a solid (13). The degree of substitution (DS) can be adjusted by varying the reaction time. This reaction method is more appropriate than chlorosulfonation since the polymeric backbone is less damaged (14). The sulfonated polysulfone was used in the form of the lithium salt. 25% of the polymer were dissolved in NMP; no additives were used. The solution was cast on a glass plate using a die of 0.3 mm width. The residence time of the as-cast films at ambient air was 10 and 15 minutes. The films were then immersed in a precipitation bath of isopropanol and water in different ratios. The temperature was 298 K. Posttreatment with deionized water for 3 hours followed a washing with 1 N HCl. The membranes were stored in a solution of 60% glycerol, 39.4% deionized water, and 0.6% propionic acid prior to use. The preparation conditions as well as the pure water volume flows are listed in Table 1.

Measurements

The reverse osmosis experiments were carried out in a closed loop reverse osmosis unit equipped with a 5-L feed tank, a membrane piston pump adjustable from 3 up to 43 bar, 6 cells in series, and a manometer of high accuracy. Devices for metering pressure and flow were also installed. The effective membrane area was 12.6 cm^2. The unit was thermostated at 293 K. Before being tested, each membrane was conditioned at

TABLE 1
Membrane Parameters

Membrane No.	Polymer	DS	Evaporation time (minutes)	Precipitation bath % by volume: Water	Precipitation bath % by volume: Isopropanol	Volume flow ($L\cdot m^{-2}\cdot d^{-1}$)
1	SPSU	0.35	10	50	50	3900
2	SPSU	0.70	10	40	60	4400
3	SPSU	1.35	10	15	85	8200
4	SPSU	0.35	15	20	80	680
5	SPSU	0.70	15	10	90	550
6	SPSU	1.35	15	5	95	600

the pressure at which it was to be used for 24 hours using desalted and filtered (0.2 μm) water.

Analysis

A 0.058 M NaCl solution was used for characterizing the membranes. The performance of the membranes is measured as volume flow J_v and rejection R. J_v is measured gravimetrically, and $R = 1 - (c_p/c_b)$, where c_p is the permeate concentration and c_b is the bulk concentration. These values were measured by conductivity and will also be found in Table 1. The other ions were determined using ion-selective electrodes. The selectivity is defined as

$$\eta = (c_{2p}/c_{1p})/(c_{2b}/c_{1b})$$

where c_{2p} and c_{1p} are the concentrations of the corresponding electrolytes in the permeate and c_{2b} and c_{1b} those in the bulk phase.

RESULTS AND DISCUSSION

The physicochemical basis for transmembrane electrolyte transport through charged membranes, which also governs the separation process, is as follows. Provided the feed contains only one type of counterion, the electric field that arises when a pressure difference is applied acquires such strength that the electromigration flow of counterions compensates for the convective flow almost completely. In the presence of counterions with different mobilities, however, this compensation becomes impossible for various species. The electric field has a mean value, and due to this an "overcompensation" for the more mobile counterions exists as well as an "undercompensation" for the less mobile ones. Since in the case of membranes with rather high electrochemical activity for binary feed solutions such a compensation is almost complete, the corresponding "decompensation" may have striking consequences. Seemingly, the separation increases with diminishing feed ionic strength. Furthermore, transmembrane diffusion obviously tends to equalize the effect of separation. Thus, with increasing transmembrane pressure, an increase in separation can be expected as long as the concentration polarization remains negligible.

The foregoing picture is only for simple symmetrical electrolyte solutions containing evenly charged counterions. When unsymmetrical electrolyte mixtures are used, the interaction between convective transport and electric migration is accompanied by a kind of Donnan dialysis (15). In this case the separation of the counterions is controlled by the charges of the counterions and not by the mobilities (for more details see Refs. 1 and 2). This brings about a peculiar behavior for those types of electrolyte mixtures where higher-charged counterions have a lower mobility (16) than lower-charged ones. In this case, the two separation factors operate in opposite directions. We illustrate this below with the $KCl/MgCl_2$ mixture.

Figure 1 shows the logarithm of selectivity as a function of the feed's ionic strength. As can be seen from the graphs for the symmetrical KCl/LiCl mixture as well as for the nonsymmetrical $MgCl_2/LiCl$ mixture, the separation increases monotonically with diminishing feed ionic strength. Theoretical analysis of the symmetrical mixtures predicts a saturation of ln η with diminishing I (in contrast to the $MgCl_2/LiCl$ mixture). A theoretical explanation for the absence of that saturation has not yet been found. The selectivity of the $KCl/MgCl_2$ mixture has a maximum, and even ln η changes its sign at very low I. This is apparently caused by the fact that due to electrostatic interactions with negative fixed charges, the mobility of double-charged Mg^{2+} ions in the membrane phase is diminished to a larger extent than that of K^+. Therefore, despite the fact that the bulk mobility of Mg^{2+} ions is higher than that of K^+, in the membrane the

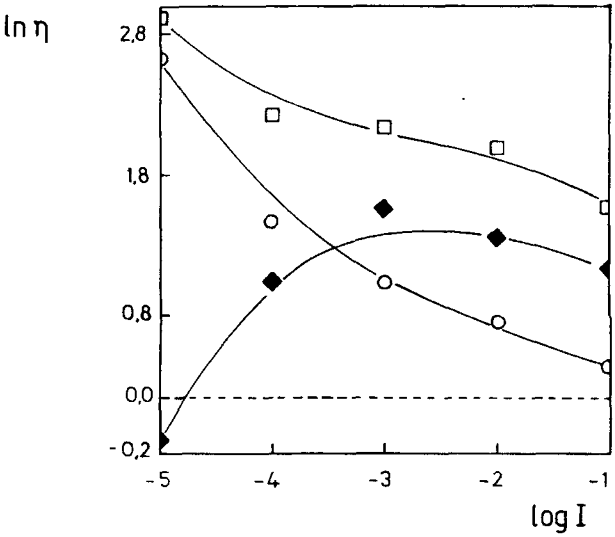

FIG. 1 Selectivity η as a function of feed ionic strength I. Membrane No. 3 (DS 1.35). Solutions (1/1 in ionic strength): (□) $MgCl_2/LiCl$; (○) KCl/LiCl; (◆) $KCl/MgCl_2$. ΔP = 2.3 MPa, 25°C.

opposite case holds. Moreover, because no anomalies were observed for the $MgCl_2/LiCl$ mixture, it can be assumed that the mobility of Li^+ ions in the membrane phase is lower than that of Mg^{2+}. Thus, the mobility of Mg^{2+} ions in the membrane phase is seemingly positioned between those of K^+ and Li^+.

There are also some more subtle correlations which are not immediately seen from the physical picture of the phenomenon but which follow from the theoretical analysis performed in References 1 and 2. In particular, it has been shown that for symmetrical mixtures containing few mobile counterions, linear plots should be observed in the selectivity–volume flow relationship. This means an exponential increase in selectivity with transmembrane volume flow, as shown in Fig. 2. Once again, this special behavior can be seen for nonsymmetrical mixtures. There is either a more rapid increase in ln η at small J_v or the plots pass a minimum which additionally gives rise to a change in sign of the value of selectivity. This minimum depends on the ratio of the mobilities of the counterions. All these principal types of behavior have been observed experimentally, as

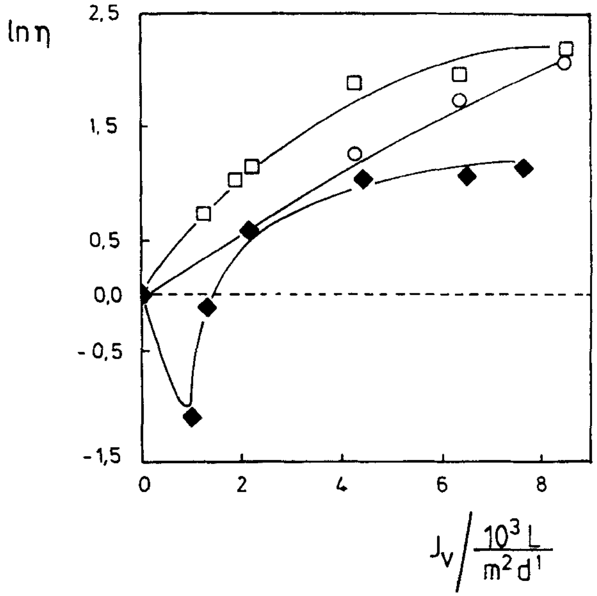

FIG. 2 Selectivity η as a function of transmembrane volume flow J_v. Membrane No. 2 (DS 0.70). Solutions (composition 1/1 in relative normality, $I = 10^{-4}$ mol/L): (□) $MgCl_2/LiCl$; (○) $KCl/LiCl$; (◆) $KCl/MgCl_2$. 25°C.

is shown in Fig. 2. Moreover, graphs obtained for the $KCl/MgCl_2$ mixture over time substantiate the relatively reduced mobility of the Mg^{2+} ions in the membrane phase.

A further correlation predicted theoretically is an increase in separation with an increase with the portion of less mobile counterions in the feed mixture. This is assumed for any symmetrical mixture as well as for nonsymmetrical ones provided that the higher-charged counterions have a higher mobility than their lower-charged counterparts. Such a mutual dependence has also been observed experimentally (Fig. 3). Moreover, at the relatively high feed ionic strength of 10^{-1} mol/L, even the $KCl/MgCl_2$ mixture fits this relationship (see Fig. 3a). The trend for this mixture is inverted at a low feed ionic strength of 10^{-4} mol/L (see Fig. 3b). Separation decreases with an increasing amount of $MgCl_2$ in the feed. This reversal in the behavior of $MgCl_2$ is in agreement with theoretical predictions, and it is brought about because the Donnan dialysis mechanism of separation monotonically increases with diminishing ionic strength. However, the intensity of the mechanism based upon the interplay between convection and electric migration tends to saturation. At higher ionic strength the latter mechanism prevails, which results in increasing separation with an increasing portion of Mg^{2+}, which is the less mobile counterion. At lower feed ionic strengths there is a complex superposition of the two separation mechanisms. Thus, in principle, various dependences can be expected, monotonic as well as those with extrema. By using differently charged porous membranes, these various dependences were found experimentally (17). For those kinds of membranes which predominately reject according to a Donnan mechanism, the separation should always increase with the share of the less mobile counterions, which is Li^+ in the case of $KCl/LiCl$ mixtures. Such an increase is a quite general regularity and has been observed for a number of charged porous membranes in this study (see Fig. 4 and (5) for more examples). Alternatively, using sufficiently dense membrane where steric hindrance begins to play a significant role, the situation may be quite changed as Fig. 5 illustrates. Here the Li^+ ions are always rejected better than the K^+ ions and the separation increases with augmenting share of LiCl in the feed.

Thus, the sign of $\ln \eta$ and its dependence on the feed composition of symmetrical mixtures are rather specific for weakly charged membranes, so the aforementioned investigations can be used for characterization of the membrane types employed in these experiments. Mixtures like $MgCl_2/LiCl$ are less suitable for that purpose because the extent to which the mobility of double-charged ions is decreased within the membrane certainly depends on the chemical and physical behavior of the latter. Therefore, one can never be sure that the mobility of double-charged ions is

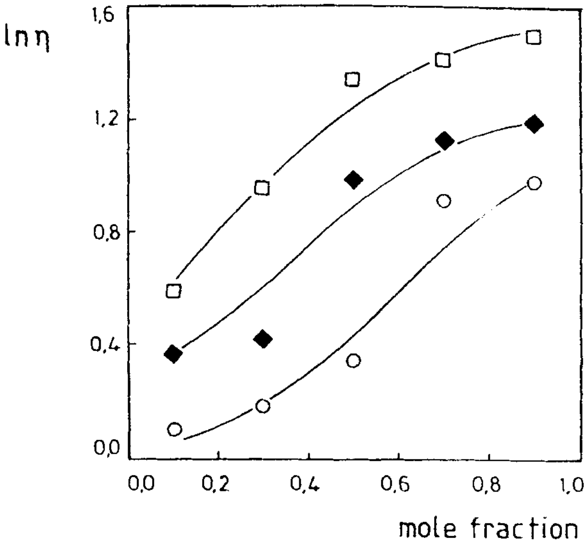

FIG. 3a Selectivity η as a function of feed composition (relative normality of the second electrolyte). Membrane No. 2 (DS 0.70). Solutions ($I = 10^{-1}$ mol/L): (□) $MgCl_2/LiCl$; (○) $KCl/LiCl$; (◆) $KCl/MgCl_2$. 25°C, ΔP = 2.3 MPa.

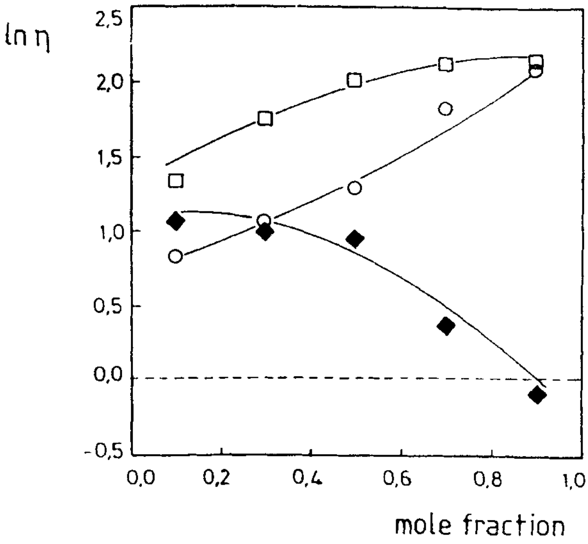

FIG. 3b Selectivity η as a function of feed composition (relative normality of the second electrolyte). Membrane No. 2 (DS 0.70). Solutions ($I = 10^{-4}$ mol/L): (□) $MgCl_2/LiCl$; (○) $KCl/LiCl$; (◆) $KCl/MgCl_2$. 25°C, ΔP = 2.3 MPa.

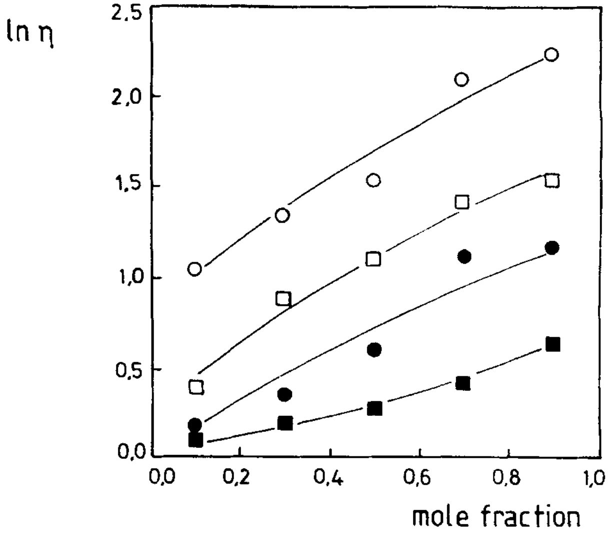

FIG. 4 Selectivity η as a function of feed composition (relative normality of the second electrolyte). Membranes: (□) No. 1 (DS 0.35); (○) No. 3 (DS 1.35). Solution KCl/LiCl: open symbols, $I = 10^{-4}$ mol/L; filled symbols, $I = 10^{-1}$ mol/L. 25°C, ΔP = 2.3 MPa.

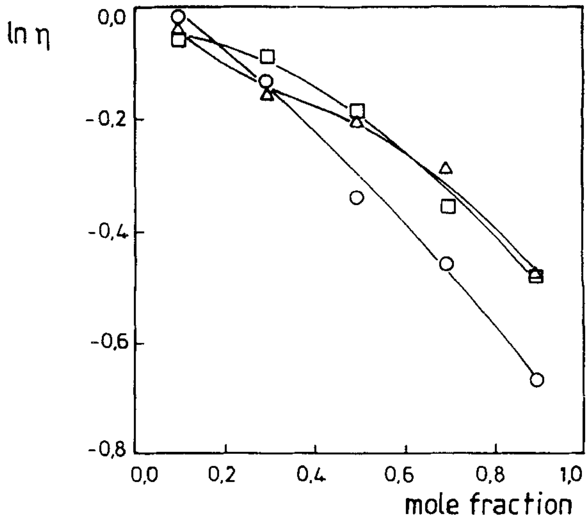

FIG. 5 Selectivity η as a function of feed composition (relative normality of the second electrolyte). Membranes: (□) No. 4 (DS 0.35); (○) No. 5 (DS 0.70); (△) No. 6 (DS 1.35). Solution: KCl/LiCl; $I = 10^{-3}$ mol/L. 25°C, ΔP = 2.3 MPa.

not decreased to such an extent that it is lower than that of single-charged ones, regardless of their value.

As Fig. 5 shows, the presence of ionogenic groups alone is not sufficient for the membrane performance to have a predominately Donnan rejection mechanism. Evidently the membrane structure is included in the separation process. A sufficiently porous matrix is the premise for hydration of the ionogenic groups. The membranes used for the experiments shown in Fig. 5 differ with respect to their degree of substitution; however, their water volume flows are comparable, which means they can be regarded as equal in their pore volumes.

Finally, the selectivity with respect to the mobilities of the counterions was investigated. It follows from the physical behavior of such ions, as well as from the analysis performed in References 1 and 2, that in the case of symmetrical mixtures the selectivity should increase with the difference in the mobilities. Figure 6 shows data obtained for KCl/N(CH_3)$_4$Cl and KCl/N(C_3H_7)$_4$Cl mixtures. The N(C_3H_7)$_4^+$ ion is obviously less mobile than N(CH_3)$_4^+$, and as could be expected, selectivity is higher for the latter mixture than for the former.

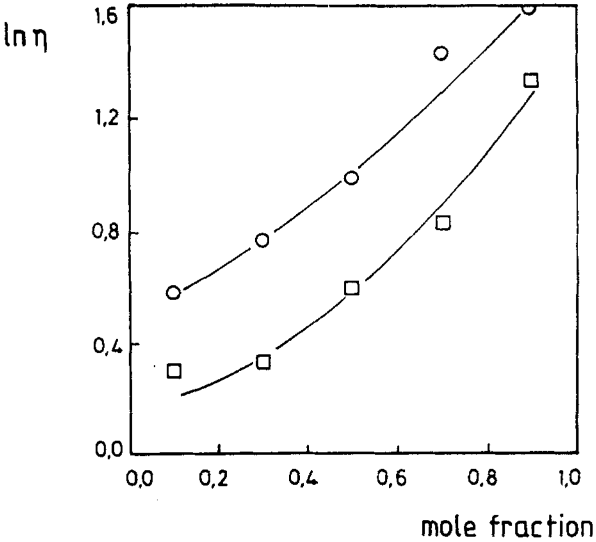

FIG. 6 Selectivity η as a function of feed composition (relative normality of the second electrolyte). Membrane No. 2 (DS 0.70). Solutions (I = 10^{-4} mol/L): (□) KCl/N(CH_3)$_4$Cl, (○) KCl/N(C_3H_7)$_4$Cl. 25°C, ΔP = 2.3 MPa.

CONCLUSION

It has been confirmed experimentally that rather high selectivity values from 8 to 10 and greater can be observed in the pressure-driven transmembrane transport of electrolyte mixtures containing ions of different mobilities and/or charges. The experimentally observed relationships between the selectivity of porous negatively charged sulfonated polysulfone membranes with respect to a number of symmetrical and nonsymmetrical binary mixtures with a common coion and feed ionic strength and composition as well as transmembrane volume flow are in agreement with the theoretical predictions. On the other hand, in the case of more dense membranes of the same polymer, the correlations are qualitatively different. Therefore, measurements similar to those used in this study may be employed for qualitative estimates of the membrane rejection mechanism.

The qualitatively different correlations observed for $KCl/MgCl_2$ and $MgCl_2/LiCl$ mixtures gave rise to the assumption that the mobility of Mg^{2+} ions in the membrane phase is reduced with respect to the bulk phase to a larger extent than that of K^+ and Li^+. This is apparently due to electrostatic interactions with fixed electric charges in the membrane. Hence, the mobility of Mg^{2+} ions in the membrane is positioned between those of K^+ and Li^+.

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