

Selective Transport of Inorganic Ions along CA Membranes

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Synopsis

Transport of inorganic ions along asymmetric cellulose acetate (CA) membrane from aqueous binary systems with a common ion: KCl–NaCl, Na₂SO₄–CuSO₄, K₂CrO₄–KNO₃, KCl–CaCl₂, and NaCl–LiCl was studied. The transport proceeds via the support matrix of the membrane and can be measured by the growth of whiskers on its exposed surface and the change of composition of the solution. Differences in the growth rates resulted from differences in transport rates of the various ions. The selectivity of the membrane is attributed to the interaction support matrix–water–ion.

INTRODUCTION

The selectivity of CA membranes towards inorganic ions in solution has been of fundamental interest in desalination and ultrafiltration of water by reverse osmosis (RO) (see, e.g., Refs. 1 and 2). The membranes are asymmetric: a very thin (< 0.5 μm), dense skin on top of a thick (≈ 100 μm) porous matrix which supports the skin (see, e.g., Ref. 3). The pressure driven transport process occurs across the membrane, with the selectivity attributed to the dense skin properties while the porous layer is considered to be a mechanical support only.³⁻⁵

In this work, the relative selectivity of the CA membrane towards inorganic ions in a transport process along the membrane was studied. The membrane, partly submerged in an aqueous solution, loses water by evaporation from that part of its surface which is exposed to the atmosphere. Because of the affinity of the membrane to water, the lost water is replaced by water flowing along the membrane as solution, without the application of pressure. The direction of flow is perpendicular to that applied in RO. The continuous evaporation of water causes the eventual saturation of the solution in the exposed part of the membrane, leading to whisker growth.⁶ The rate of growth is proportional to the rate of transport of the solute. Systems of two salt components with a common ion enabled the determination of the relative transport of the counter ions. The binary systems investigated were: KCl–NaCl, Na₂SO₄–CuSO₄, KNO₃–K₂CrO₄, KCl–CaCl₂, NaCl–LiCl, and NaCl–CaCl₂. The salt components of each system do not form solid solutions nor react chemically with each other.

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EXPERIMENTAL

The experimental details concerning the casting of the tubular CA membrane and the growth procedure of whiskers have been described previously.⁶ A schematic representation of the experimental setup is given in Figure 1. All membranes used were freshly prepared and unannealed. The stock solutions were prepared from analytical grade dried salts, in deionized water. The growth solutions (15 mL) were prepared by mixing the appropriate solutions of the components before introducing the membrane. For each series of measurements, single component runs were used as control. Experiments were carried out at room temperature (23–28°C), with the evaporation of pure water, measured under the same conditions, serving as temperature and humidity controls. Growth rates are given as weight of whiskers (mol) per hour of growth.⁶

The composition of the solutions was determined by atomic absorption spectrometry ($\pm 2\%$) and that of the whiskers by X-ray diffraction and electron probe microanalysis.

RESULTS

KCl–NaCl and Na₂SO₄–CuSO₄ Systems

The total concentration of NaCl–KCl was varied between 0.5–5.0 m with the concentration ratio K^+/Na^+ being 4.00, 1.00, and 0.25. The composition of the solutions, the weight of the whiskers and their X-ray analyses were determined at various times up to 55 h. The concentration ratio K^+/Na^+ in the solution was found to increase linearly with time, independent of the initial concentration. The ratio K^+/Na^+ for $t = 0$ and $t = 52$ h is given in Table I. The relative enrichment in K^+ with time is dependent on the initial concentration ratio of the components. X-ray analyses show enrichment of the whiskers in NaCl with growth time, complementary to the behavior in the solution.

The growth rate of the whiskers⁶ as a function of the initial total concentration in the solution is shown in Figure 2. For comparison, single

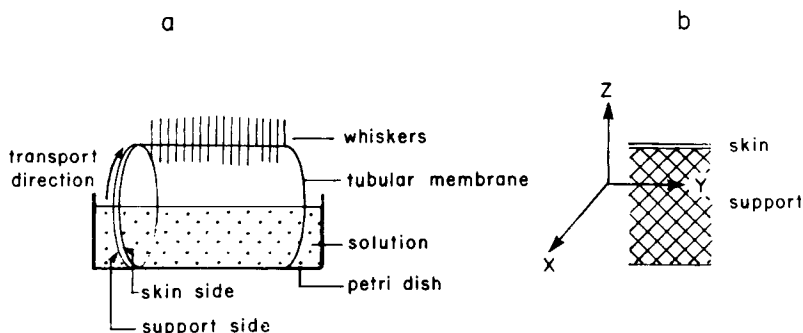


Fig. 1. (a) Schematic set up of a transport process along the membrane (arrow), resulting in whisker growth; (b) X, Y-directions of transport along the membrane, Z-direction of transport applied in reverse osmosis.

TABLE I
Molal Ratio of a/b in the Solution: Typical Results for KCl/NaCl , $\text{Na}_2\text{CO}_4/\text{CuSO}_4$,
and $\text{K}_2\text{CrO}_4/\text{KNO}_3$ Systems

a/b	C_0 (total) (m)	(a/b) , $t=0$	(a/b) , $t=52$ h	Relative enrichment (%)
K^+/Na^+	3.00	4.00	4.24	6
		1.00	1.09	9
		0.25	0.28	12
$\text{Cu}^{2+}/\text{Na}^+$	0.86	0.98	1.57	60
		0.48	0.81	70
		0.25	0.43	72
$\text{CrO}_4^{2-}/\text{NO}_3^-$	3.00	4.00	6.66	67
		1.00	1.54	54
		0.25	0.27	8

component growth rates of KCl and NaCl ⁶ are given. For the mixed system, a weighted molecular weight was used. The results indicate slower growth rates for the mixed systems compared to the single component ones. Similar results were obtained for the $\text{Na}_2\text{SO}_4-\text{CuSO}_4$ system. The growth rates of whiskers in the binary mixtures, for various $\text{Na}_2\text{SO}_4/\text{CuSO}_4$ concentration ratios, were found to be lower than those of the respective single components, for the same total concentrations. CuSO_4 was found to be relatively enriched in the growth solution while Na_2SO_4 was relatively enriched in the whiskers (Table I). Figure 3(a) shows the (white) whiskers on top of the membranes with blue CuSO_4 crystals in the bottom of the dish.

$\text{K}_2\text{CrO}_4\text{-KNO}_3$ System

The total concentration of $\text{K}_2\text{CrO}_4\text{-KNO}_3$ was varied between 0.5 and 3.0 m with the concentration ratio $\text{CrO}_4^{2-}/\text{NO}_3^-$ being 4.00, 1.00, and 0.25. The same analyses as reported above were carried out also for this system. The concentration ratio $\text{CrO}_4^{2-}/\text{NO}_3^-$ in the solution was found to increase linearly with time, independent of the initial concentration. Table I shows a typical example of the relative enrichment of CrO_4^{2-} in solution, depending on the initial concentration ratio. X-ray analyses showed comple-

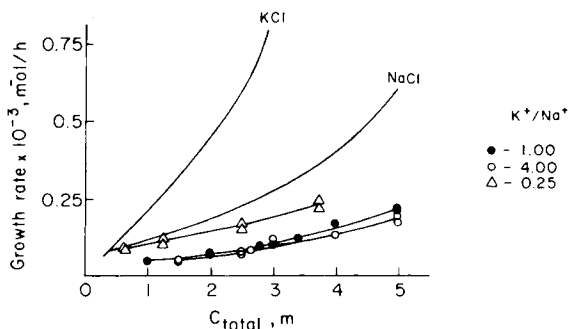


Fig. 2. Whisker growth in binary systems: (a) $\text{KNO}_3\text{-K}_2\text{CrO}_4$, $C_0(\text{total}) = 3.0$ m, $t_0 = 24$ h; (b) $\text{CuSO}_4\text{-Na}_2\text{SO}_4$, $C_0(\text{total}) = 1.7$ m, $t_0 = 50$ h.

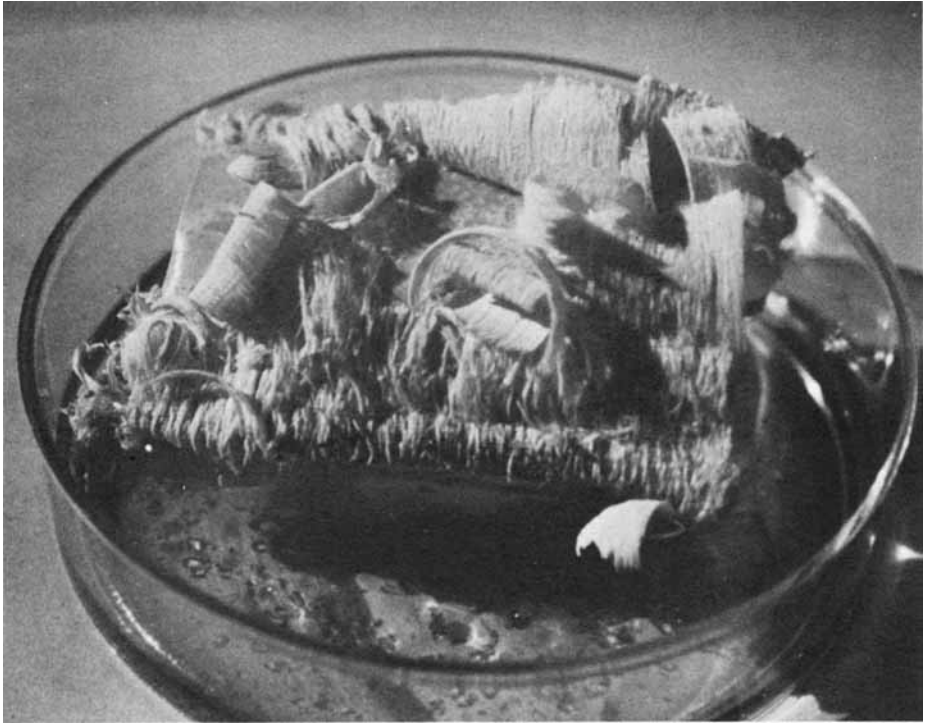


Fig. 3. Growth rate of whiskers of KCl, NaCl, and KCl-NaCl systems against initial concentration.

mentary results: The whiskers were found to be relatively enriched in KNO_3 . Figure 3(b) shows whiskers grown from K_2CrO_4 - KNO_3 solution. Note the separate colonies of (white) KNO_3 and (yellow) K_2CrO_4 whiskers.

Linear growth rates of the whiskers against initial total concentration were obtained for both the mixed systems and the single components. As in the former cases, the growth rates of the mixed systems were lower than those of the single components (Table II).

KCl-CaCl₂, NaCl-CaCl₂, and NaCl-LiCl Systems

CaCl_2 and LiCl are known to be deliquescent and do not crystallize from aqueous solutions, nor did their whiskers grow via CA membranes. Instead, small droplets (sweatlike) accumulated with time on the exposed surface of the membrane. The droplets were found to be saturated solutions having the following compositions: $\text{CaCl}_2:\text{H}_2\text{O} \approx 1:3$ and $\text{LiCl}:\text{H}_2\text{O} \approx 1:5$. The rate of accumulation was constant up to 55 h, for initial concentrations between 0.3–2.0 m CaCl_2 and 0.3–3.5 m LiCl . KCl whisker growth from KCl - CaCl_2 solutions was carried out for initial KCl and CaCl_2 concentrations between 0.27–2.40 m and 0.3–1.8 m, respectively. The whisker growth rate was observed visually to decrease with time, decrease in KCl concentration, and increase in CaCl_2 concentration. For higher CaCl_2 concentrations, sweatlike droplets similar to those found for pure CaCl_2 accumulated on the surface among the whiskers. For the lowest KCl and higher CaCl_2 concentrations, no whiskers grew at all. The weight of the wet membrane and whiskers increased linearly with time, the slope being denoted by R . The R values are summarized for various initial KCl concentrations in Figure 4(a). A minimum is observed in all cases, the curves becoming shallower with decreasing KCl concentration. Assuming linear relationship between the accumulation rate and the initial CaCl_2 concentration, KCl whisker growth can be separated from the CaCl_2 accumulation in the mixtures [Fig. 4(b)]. The concentration ratio $\text{K}^+/\text{Ca}^{2+}$ in the solution was found to increase with time, independent of the initial total concentration or concentration ratio. Table III shows typical results for one case. The relative enrichment for a given time was found to be dependent on the initial concentrations and concentration ratios.

XRD of the whiskers showed them to be pure KCl , free of CaCl_2 (< 2%). However, EPMA revealed scattered CaCl_2 inclusions in the KCl crystals, most of them concentrated at the "roots" of the whiskers. The total concentration of Ca^{2+} in this region was < 1%. Similar experiments were carried out with NaCl - LiCl and NaCl - CaCl_2 mixtures. The initial NaCl and LiCl concentrations were between 0.73–3.90 and 0.3–3.5 m, respectively; the

TABLE II
Growth Rates ($\times 10^{-3}$, mol/h) of Whiskers in the K_2CrO_4 - KNO_3 System

C_0 (total) (m)	K_2CrO_4	KNO_3	$4\text{CrO}_4^{2-}/1\text{NO}_3^-$	$1\text{CrO}_4^{2-}/1\text{NO}_3^-$	$1\text{CrO}_4^{2-}/4\text{NO}_3^-$
1	0.23	0.32	0.16	0.23	0.20
2	0.47	0.65	0.31	0.42	0.37

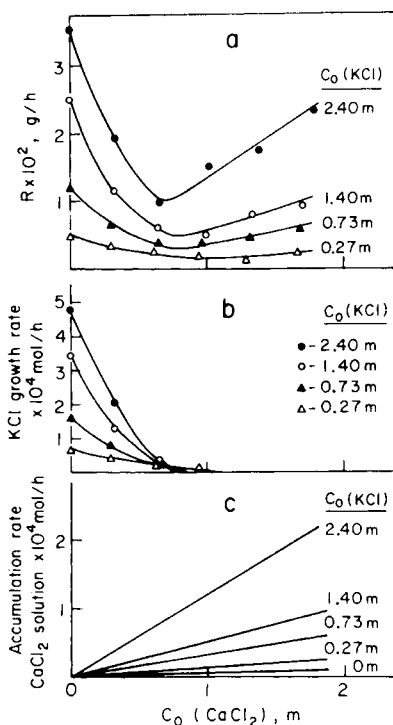


Fig. 4. KCl-CaCl₂ system: (a) The rate of increase in weight of the wet membrane and KCl whiskers, R , against CaCl₂ initial concentration; (b) KCl whisker growth rate and CaCl₂ accumulation rates as function of CaCl₂ initial concentration.

initial NaCl and CaCl₂ concentrations between 1.5–2.5 and 0.3–2.0 m, respectively. The behavior was found to be very similar to that obtained for the KCl-CaCl₂ system.

DISCUSSION

Most of the volume of the membrane is the porous matrix. Although both skin and support layers are in contact with the solution (Fig. 1), whiskers grow almost exclusively on the exposed surface of the support. This is in accordance with the salt-rejecting properties of the skin, as found by RO.¹⁻⁵ Therefore, it stands to reason that the solution is transported along

TABLE III
KCl Relative Enrichment in KCl-CaCl₂ Solution C_0 (total) = 2.7 m

t (h)	K^+ / Ca^{2+}	KCl relative enrichment (%)
0	3.19	—
5.5	3.84	20
11.4	3.95	24
23.6	4.14	30
34.2	4.29	34

the membrane via the porous support layer. That means that the differences in transport rates of the ions as found in this work are not due to the asymmetric structure of the membrane but rather to differences in interactions between the wet membrane and the hydrated ions. These interactions are specific to the ion and the system.

For the NaCl–KCl, Na₂SO₄–CuSO₄, and KNO₃–K₂CrO₄ systems, preferential transport of Na⁺ and NO₃⁻ was obtained. Considering the solubilities⁷ or mobilities⁸ of the single components, the opposite behavior is expected. Hence, the lower rate of transport is caused by a stronger interaction between the hydrated ion and the membrane: K⁺ > Na⁺, Cu²⁺ > Na⁺, and CrO₄²⁻ > NO₃⁻. The effective electrical field of these "slower" ions is higher than that of the second component in the binary mixture: The hydrated radius of K⁺ is smaller than that of Na⁺; the charge of CrO₄²⁻ or Cu²⁺ is double that of NO₃⁻ or Na⁺ ions. Although the pressure driven RO process is very different from the transport process investigated in the present work, complementary results were found⁹: preferential transport of Na⁺_{aq} and NO₃⁻_{aq}, both having a smaller effective electrical field compared to K⁺_{aq} and Cl⁻_{aq}. The effect of one ion on the ion permeability of the other one was also found in RO (see, e.g., Ref. 10).

The situation is different for the pairs NaCl–CaCl₂, NaCl–LiCl, and KCl–CaCl₂, in which there is only one growing component. The interaction between the membrane and the hydrated nongrowing component is so strong that the growing component is rejected. The salt transported initially is precipitated out as whiskers, and once the membrane is saturated with the nongrowing component, no transport of the growing component is possible. Complementary results were found in RO for the mixed NaCl–MgCl₂ system¹¹: solute separation of MgCl₂ is higher than that of NaCl (MgCl₂ chemistry is very similar to that of CaCl₂).

CONCLUSION

This study shows the selectivity of the support matrix of the CA membranes towards hydrated inorganic ions. A correlation between the effective electrical field of the hydrated ion and transport rate is pointed out.

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