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Electrotransport of weak-acid anions through anion-exchange membranes

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Abstract

Concentration dependencies of the membrane electric conductivity under alternating current and fluxes of anions through anion-exchange membranes (AEMs) under direct current were measured in 0.002–1.0 M sodium salt solutions of carbonic and phosphoric acids. Several commercial AEMs were studied: AFN, AMX, ACS and ACM produced by Tokuyama Soda (Japan), Anion 204SZRA by Ionics (USA), ADP by Morgan (France) and MA-40, MA-41 by Schekino (Russia). Transport properties of these membranes are interpreted as functions of the internal solution pH. The mechanism of (hydro)carbonates transfer through AEMs is discussed.

Keywords: Anion-exchange membranes; Weak-acid anions; Ion transport; Conductivity

1. Introduction

Anions of weak acids are one of the main components of natural waters [(hydro) carbonates]; they are formed in the course of microbiological synthesis (amino acids) during the destruction of fertilisers, etc. Membrane methods and, in particular, electrodialysis with ion-exchange membranes are widely used for the

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purification and conditioning of weak-acid solutions. This determines the interest of the actual study the aim of which is the investigation of peculiarities of weak-acid anion transfer in membrane systems.

2. Experimental

The main characteristics of the membranes studied are collected in Table 1. The electric conductivity of the membranes was measured

Table 1
Main characteristics of the AEMs studied

Membrane	Ionogenic groups	E.C. meq/g Cl⁻ form of dry membrane	W.C. gH₂/gCl⁻ form of dry membrane	Thickness, μm	Electric conductivity (κ, mS/cm) in 0.05 eq/dm³ solutions			
					NaCl	NaHCO₃	Na₂CO₃	NaOH
MA-40	=NH, ≡N	2.0–2.2	0.40 ± 5	460 ± 10	2.67	0.15	0.17	0.75
AFN	-N(CH₃)₃⁺	2.0–3.5	0.40–0.55	175 ± 15	8.3	11.8	12.4	17.8
AMX	-N(CH₃)₃⁺	1.4–1.7	0.25–0.30	170 ± 10	4.3	2.8	3.5	8.9
ACS[a]	-N(CH₃)₃⁺	1.4–2.0	0.20–0.30	175 ± 15	2.5	0.56	0.52	3.0
ACM[a]	-N(CH₃)₃⁺	1.4–1.7	0.13–0.18	120 ± 10	1.0	0.22	0.24	0.027
ADP	-N(CH₃)₃⁺	1.15	0.08–0.15	160 ± 10	5.16	2.95	2.68	—
Anion 204SZRA	-N(CH₃)₃⁺	2.4 meq/g dry resin	0.46 of wet resin only	560 ± 10	7.82	4.73	4.34	—
MA-41	-N(CH₃)₃⁺	1.58	0.32	570 ± 20	7.13	4.95	6.01	18.5

[a]Membranes with a modified surface.

under alternating current with a clip-cell [1]. The fluxes of anions through AEMs were measured under direct current using desalination channels DC formed by the AEM studied and a cation exchange membrane (MK-40) with the "concentration clamp" method [2,3]. The cell used permitted solution circulation; the membrane active area was 9 cm² [3]. The electrical resistance and pH of the inlet and outlet solutions of DC were registered simultaneously. The obtained results were compared with similar data for strong-acid anions Cl⁻, F⁻, NO_3^- and SO_4^{2-}.

3. Results

Concentration (*C*) dependencies of the specific electrical membrane conductivities (κ) are shown in Fig. 1. One can see that the membranes with the same ion-exchange groups exhibit close transport properties (Table 1). Thus, the strongly basic membranes bearing quaternary ammonium groups display close values of conductivity in sodium hydrocarbonate, carbonate or chloride solutions (Fig. 1a). The conductivity of the weakly basic membrane MA-40 bearing

secondary and tertiary ammonium groups is noticeably lower in carbonate or hydrocarbonate solutions than in chloride solutions (Fig. 1b). The concentration dependencies of the electrical conductivity were found to be well approximated by straight lines in logκ–log*C* coordinates, in the case of both weak and strong electrolyte solutions. In the case of strong electrolytes, the slope of the lines varied from 0.07 to 0.35 [4].

According to the microheterogeneous model developed for membranes equilibrated in strong electrolyte solutions [5], the increase in κ with *C* is explained by an increase in the conductivity of the electroneutral solution contained within fissures, caverns and large pores of the membrane, the slope of the logκ–log*C* lines being equal to the volume fraction of this electroneutral solution. In most cases of weak-acid electrolytes, this slope was different than that for the same membrane equilibrated in strong electrolyte [4]. For instance for the AMX membrane in strong-acid salt solutions, the slope was 0.17 (for Cl⁻, F⁻, NO_3^- and SO_4^{2-}); it was close for HCO_3^- (0.19) and CO_3^- (0.21), and lower for HPO_4^{2-} (0.14), PO_4^{3-} (0.06) and $H_2PO_4^-$ (−0.23) solutions.
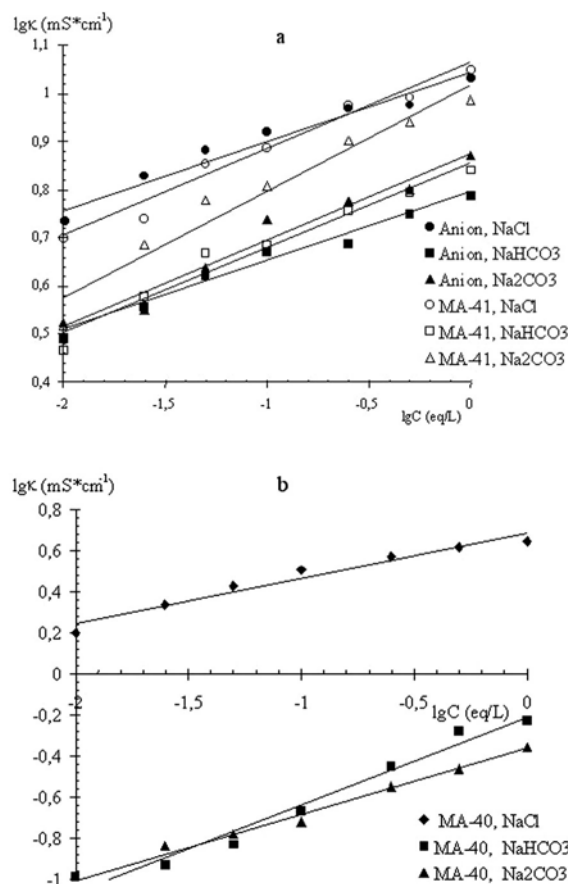
Fig. 1. Concentration dependence of electric conductivity of AEMs: Anion 204SZRA and MA-41 (a) and MA-40 (b) equilibrated with NaCl, NaHCO$_3$ and Na$_2$CO$_3$ solutions.

Fig. 2. H$_2$CO$_3$ concentration in the outlet solution of empty DC (curve 1) and DC with anion-exchange resin AV-17 (curve 2) vs. current density normalized on the limiting current density. The inlet NaHCO$_3$ solution concentration is 0.002 M, h = 0.1 cm, L = 3 cm, V = 1.6 cm/s.
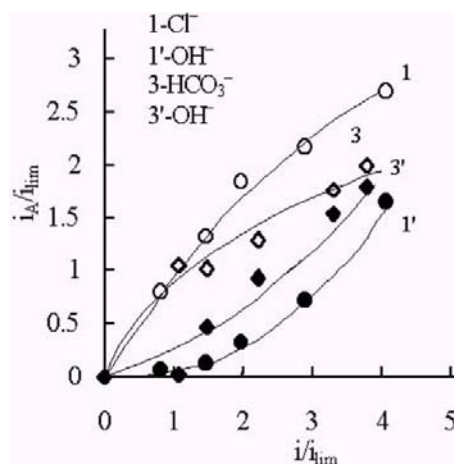
Fig. 3. Dependence of partial currents of anions through MA-40 membrane of empty DC upon total current normalized on the limiting one. The feed solution is 0.002 M NaCl (curves 1, 1′) or NaHCO$_3$ (curves 3, 3′); L = 3 cm, h = 0.1 cm, V = 1.6 cm/s. In the case of NaCl the effective transport numbers T_{NaCl} are determined from the volumes of concentrated NaCl and NaOH solutions added into the outlet solution stream to restore inlet solution values. In the case of NaHCO$_3$, T_{HCO3} is found from difference of inlet and outlet concentration and pH of the solution; T_{OH} is calculated as $T_{OH} = 1 - T_{HCO3}$; the partial current is found from Eq. $i_A = i\,T_A$ (A is Cl$^-$, HCO$_3^-$, OH$^-$ anions).

Measurements of pH of the depleted outlet streams show that this value is decreased, in comparison with the feed solution, in the case of hydrocarbonate solutions whatever the value of the applied current. The difference increases with the current. The concentration of H$_2$CO$_3$ molecules in the outlet solution calculated from the pH and conductivity values grows with the current as shown in Fig. 2. The desalted solution becomes more acidic and the H$_2$CO$_3$ concentration increases when AV-17 anion-exchange beads are inserted into the desalination compartment (DC) (Fig. 2). For example, at a voltage
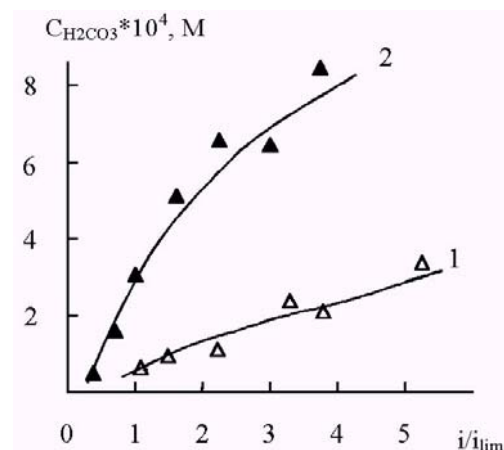
$\Delta\varphi = 4.0$ V applied to a cell pair formed by a MA-40 and a MK-40 membranes with a path length $L = 3$ cm, an intermembrane distance $h = 0.1$ cm, an average linear flow velocity $V = 1.6$ cm/s and using a 0.002 M sodium hydro-carbonate or chloride feed solution, the pH values of the desalted outlet solution are: 4.4 (NaCl, empty DC); 9.4 (NaCl, DC with a monolayer of AV-17 ion-exchange resin); 7.2 (NaHCO$_3$, empty DC); 6.8 (NaHCO$_3$, DC with AV-17 monolayer). The feed solution pH was 6.2 (NaCl) or 8.3 (NaHCO$_3$).

The measurements of partial currents with the "concentration clamp" method (Fig. 3) show that the OH$^-$ current density through the MA-40 membrane is higher when the feed solution contains weak-acid anions. In the case of MA-41 membrane the results obtained were similar.

4. Discussion

4.1. Intrinsic pH and membrane ionic composition variation with solution dilution

Earlier experiments [4] showed that pH of the internal solution (intrinsic pH) in AEMs equili-brated with diluted strong (NaCl) or weak-acid (NaH$_2$PO$_4$) salt solutions was higher than the pH of the external one. The intrinsic pH grows with a diluting external solution. It is explained by the fact that with dilution the ionic fraction of OH$^-$ ions and the concentration ratio C_{OH}/C_{Cl} in the solution increase, while the H$^+$ ion concentration in the membrane decreases due to the Donnan exclusion.

It is well known that an increase in pH of a solution containing a mixture of mono- and multi-charged weak-acid anions displaces the equilibrium towards the formation of the multi-charged anions. Therefore, an increase in intrinsic pH value provokes an enrichment of the membrane capacity available for ion exchange with multi-charged weak-acid anions. Hence, in dilute solutions one can expect to find a mem-brane enriched with multi-charged anions.

This assumption is confirmed by ion-exchange isotherms determined for the MA-41 membrane in 0.005 N NaHCO$_3$+Na$_2$CO$_3$ solu-tions with pH varying from 8.42 to 10.8. These isotherms, presented in coordinates "carbonate equivalent fraction in the membrane–carbonate equivalent fraction in the solution", have a convex upwards shape and are characterized by an effective ion-exchange constant equal to 9 [6].

4.2. Conductivity variation with dilution

The ionic composition variation in the mem-brane with diluting external solution may be so noticeable that it leads to an electrical conduct-ivity variation of the membrane not taken into account by the microheterogeneous model [5]. Thus, the negative value of the slope of the logκ –log$C$ lines in the case of the strongly basic membranes AFN, AMX, ACS and ACM in NaH$_2$PO$_4$ solutions [4] may be accounted for by the fact that the conductivity of these membranes is higher in Na$_2$HPO$_4$ than in NaH$_2$PO$_4$ solution of the same concentration. When the NaH$_2$PO$_4$ solution concentration decreases, the intrinsic pH increases, and has the same effect on the conductivity as in the case where a NaH$_2$PO$_4$ solution is replaced with a Na$_2$HPO$_4$ one.

When the pH of the external solution is high, the concentration of non-associated OH$^-$ ions in the membrane with strongly basic quaternary ammonium groups may be sufficiently large to assure a considerable contribution of these ions to the current conductance, especially if taking into account high mobility of these ions (Table 1, [7]). This phenomenon can be one of the causes of relatively high conductivity of mem-branes in solutions containing multi-charged anions (Fig. 1a, Table 1). Low values of the MA-40 membrane conductivity in solutions with elevated pH (Fig. 1b, Table 1) are caused by high association of the weakly basic secondary and tertiary ammonium groups with OH$^-$ ions in the membrane. Effectively, the concentration of free

OH⁻ ions in the membrane $\bar{C}_{OH}$ is related to the ionization degree of the ionogenic groups by a well-known equation:

$$\alpha \bar{c}_{OH}/(1-\alpha) = K_i$$

where K_i is the ionization constant of the ionogenic groups. When changing a mono-charged weak-acid anion for a multi-charged one, or diluting external solution, the relative concentration of OH⁻ ions in the solution increases; hence, the intrinsic pH and $\bar{C}_{OH}$ values grow. As a consequence, in these cases α should decrease as well as the membrane conductivity.

4.3. Mechanism of carbonic acid anions transfer through an anion exchange membrane

An analysis of ion exchange, conductivity and partial current data permits proposing a mechanism for weak-acid anions transfer in DC (through an anion-exchange membrane). Consider the case of carbonic acid (Fig. 4). As it has been shown, in diluted solutions the intrinsic pH is higher in comparison with the external solution pH and the membrane is enriched with carbonate anions. Hence, a part of hydrocarbonate anions entering the membrane under the action of the external electric field at depleted interface dissociates with forming H⁺ ions and carbonate anions.

The H⁺ ions return into the depleted solution where they react with HCO_3^- ions that lead to an increase in concentration of H_2CO_3 in the outlet stream (Fig. 2). The carbonate anions migrate to the opposite membrane interface and pass into the enriched solution where they capture H⁺ ions from water molecules, increasing thereby the solution pH. Thus, pH of the depleted solution decreases and that of the enriched increases. The increase in pH of the enriched solution may be interpreted formally as transport of OH⁻ ions through the AEM (Fig. 3). These processes are intensified when the current becomes close or higher than the limiting current. In this case, the salt concentration at the depleted interface becomes as small as comparable with the H⁺ and OH⁻ ions concentration. In these conditions a significant part of the current is carried by the ions of water. The OH⁻ ions migrate into the membrane and H⁺ ions into the depleted solution. The fact that the water dissociation at currents close to the limiting one is higher when the membrane contacts with a weak-acid electrolyte may be explained by catalysis of this reaction by mono- and eventually two-charged weak-acid anions in the membrane. For example, a hydrocarbonate can react with a water molecule to give a carbonic acid molecule and an OH⁻ ion; the carbonic acid dissociates with forming a hydrocarbonate and a proton. The rate constant of these reactions is several orders higher than that of water dissociation or H⁺ and OH⁻ generation on quaternary ammonium ionogenic groups [8,9]. When anion-exchange beads are inserted into the DC, the active anion-exchange area increases while the cation-exchange one stays the same or decreases due to screening effect. For a same current value through the CEM and AEM of DC, the degree of concentration polarisation is higher at the cation-exchange surface with a smaller area. At the case of strong electrolyte solutions
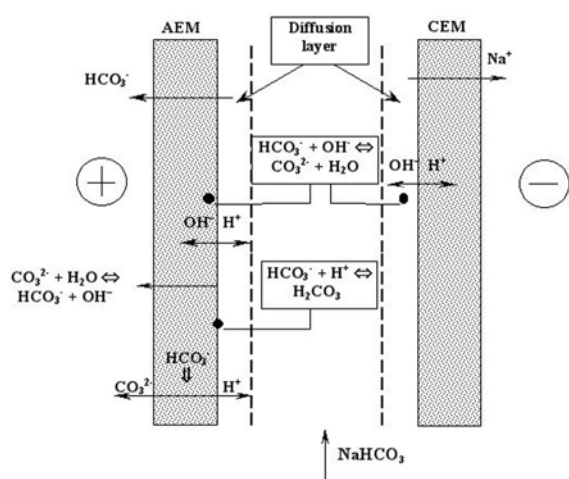

Fig. 4. Processes within empty desalination channel.

the rate of water splitting at the CEM in these conditions becomes higher than that at the AEM, and the depleted solution pH increases [10]. However, in the case of hydrocarbonate solutions the rate of water splitting at the AEM is higher due to the catalysis effect discussed above. That is why the depleted solution pH increases even in the presence of anion-exchange filler (Fig. 2.).

5. Conclusions

The membrane transport properties strongly depend on the intrinsic solution pH, which increases with the external solution pH and dilution of the external solution. When the intrinsic pH is high, the amount of the free OH^- ions in strongly basic membranes with quaternary ammonium groups may be great enough to give a noticeable contribution to the current transfer. This explains relatively high conductivity of such membranes in diluted solutions containing multi-charged weak-acid anions. In weakly basic membranes with tertiary and secondary ammonium groups, an increase in the intrinsic pH causes a decrease in the ionization degree of the iono-genic groups; hence, a decrease in conductivity. From this follows a low conductivity of these membranes in solutions with high pH containing multi-charged weak-acid anions.

Due to the fact that the internal membrane solution is enriched with multi-charged anions with an exclusion of H^+ ions, a part of hydro-carbonate ions dissociates when entering the membrane. This explains the decrease in the diluted solution pH and increase in the concen-trated, during current flow. Weak-acid anions can act a role of water splitting catalysators by participating in proton-transfer reactions. This mechanism of current transfer becomes essential when the current is close or higher that the limiting one.

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