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Ion-Mediated Water Flow*

I. Electroosmosis

Melvin Praissman, Irving F. Miller**, and Jesse M. Berkowitz

Division of Gastroenterology, Department of Medicine,
Nassau County Medical Center, East Meadow, New York 11554 and
Department of Physiology, The Mount Sinai Medical and Graduate Schools
of the City University of New York, New York, N.Y. 10029

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Summary. The electroosmotic flows of solution produced by the chloride salts of H, Na, K, tetramethylammonium (TMA) and tetraethylammonium (TEA) through three membranes of net negative charge and high water content (40 to 60%) have been obtained. The amount of solution transported, (EO_s), increased in the order: HCl, KCl, NaCl, TMACl and TEACl in a membrane of 43% hydration. In membranes 60% hydrated the order became HCl, KCl, NaCl, TEACl and TMACl. (EO_s) for a salt increased as membrane hydration became larger. The permselectivity of the three membranes for cations declined in the order: HCl, KCl = NaCl, TMACl and TEACl. Cation permselectivity also declined with increases in membrane hydration. The (EO_s) is a net solution flow and is the difference between the cation-induced water flow and the chloride-induced water flow in the opposite direction. In membranes of moderate to high H_2O content, co-ion transport is significant and the water-flow associated with co-ion movement must be determined if the contribution of the counter-ion $([EO]_{cation})$ to the (EO_s) is to be found. Cl-ion induced water flow was determined by assuming an identity of K and Cl ions. $[EO]_{cation}$ increased as the hydrated radii of the cations increased and for any particular cation $[EO]_{cation}$ was at least 100% greater in the 60% hydrated membrane than in the 43% hydrated membrane. The current-induced water flow was found to be composed of both an electroosmotic and an osmotic component. The latter represented between 10 and 40% of the total water flow.

Ion-mediated water flow, which is the result of frictional interactions between ions and water, may be of physiologic importance. One example of ion-mediated water flow is electroosmosis, which occurs when an electric current is applied across an ion-exchange membrane separating two electrolytic solutions. In permselective membranes, the counter-ion is responsible for completing the circuit. The ion as it moves through the membrane imparts

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** *Present address:* Department of Chemical Engineering, Polytechnic Institute of Brooklyn, Brooklyn, N.Y. 11201.

momentum to the surrounding solvent and the larger the frictional interaction between the ion and solvent, the greater will be the transfer of momentum. The flow of water that results from the passage of the counter-ion through the membrane is proportional to the current passed.

If unstirred boundary layers adjacent to the membrane are present, an osmotic flow of water may also occur during current passage and contribute to the water flow observed. The theoretical basis for the osmotic flow has recently been discussed [1, 12] and shown to result from differences in ion transport numbers between the membrane and bulk solutions. Because of the differences, concentration gradients can develop in the unstirred boundary layers adjacent to the membrane and cause an osmotic flow of water.

In this investigation, the solvent flows produced by the passage of hydrogen chloride, sodium chloride, potassium chloride, tetramethylammonium chloride (TMACl) and tetraethylammonium chloride (TEACl) through several different cation-selective membranes were determined at physiologic concentrations of solute (155 mEquiv/liter). Both ion-solvent interactions ("true" electroosmosis) and unstirred boundary-layer effects (osmosis) were found to contribute to the total current-induced water flow. It will be shown that as co-ion intrusion increased, significant corrections (amounting to 100% in some cases) had to be applied to the observed electroosmotic solution flows to obtain the electroosmotic flux of solvent associated only with the counter-ion.

Procedure

Physical Properties of the Membranes

Membranes composed of mixed group polyelectrolytes with an excess of polystyrene sulfonic acid groups (known as Biolon) and containing up to 60% water were obtained from Amicon Corporation (Lexington, Mass.) in square sheets approximately 30 cm on a side. All experiments were done on the same piece of membrane. Discs, 5.7 cm in diameter, were cut from each membrane after the ion and solution fluxes resulting from bi-ionic exchange had been determined [9]. The ion-exchange capacity of each membrane was determined on duplicate pieces following the method of Peterson and Gregor [8]. The ion-exchange capacity is given in Table 1 in terms of both its capacity and molarity. The duplicate determinations were within ±3%. The thickness and water content of each membrane in the hydrogen form was determined by standard procedures [8]. The average of two separate determinations for each membrane is shown in Table 1.

Membrane Permselectivity

The permselectivities of the membranes for the chloride salts of H, Na, K, TMA and TEA were determined by concentration potential measurements. The emf of the cell:

$$\text{SCE} \quad |C_{\text{II}}| \quad \text{membrane} \quad |C_{\text{I}}| \quad \text{SCE}$$

Table 1. Properties of the Biolon membranes (hydrogen form)

Membrane	Thickness (μ)	Capacity (mEquiv/g)[a]	Molarity (mEquiv/cm^3)[b]	Water content (% by weight)
I	210 ± 10	0.83 ± 0.01	0.45 ± 0.005	43 ± 1.1
II	300 ± 10	1.07 ± 0.005	0.43 ± 0.009	60 ± 1.5
III	170 ± 10	1.33 ± 0.035	0.64 ± 0.003	58 ± 1.4

[a] Dry hydrogen form.

[b] Volume of the hydrated membrane.

was measured using a two-compartment cell constructed of polymethylmethacrylate. SCE refers to a saturated calomel electrode (Beckman, Model G Futura with ceramic junction). Nitrogen was bubbled across each face of the membrane to provide stirring at the membrane-solution interfaces. Any asymmetry potential difference that existed between the two SCE was determined for each ion by filling both sides of the cell with the solution of higher concentration (C_{II}) and recording the potential (Leeds and Northrup, Model K-4) at frequent intervals until it became constant (about 10 min). The asymmetry potential differences were never greater than 0.4 mV usually falling between 0.1 to 0.2 mV.

In the concentration potential measurements, the solution of higher concentration was added first to one side of the cell and then the solution of lower concentration was added. The first potential measurement was obtained within 1.5 min and additional values were obtained at approximately 2-min intervals. Each determination lasted about 10 min. The value at zero-time was determined by extrapolation and the asymmetry potential added to this value.

The concentration potentials for all five ions were determined on the same piece of membrane and the ions were tested in the following order: H, K, Na, TMA and TEA. The concentration of ions was 0.180 M in one compartment (C_{II}) and 0.130 M in the other (C_I), and the C_{II} to C_I ratio was 1.38. After the concentration potentials had been obtained for the five ions, the membrane was restored to its hydrogen form and the measurements then repeated a second time with the same piece of membrane.

Current-Induced Solution Flow Measurements

The cell used to measure current-induced solution flow is depicted in Fig. 1. It was machined from a piece of solid polymethylmethacrylate rod, 8.9 cm in diameter and consists of two identical halves. Each half consists of a chamber, 2.5 cm in diameter and 10.2 cm in length (total volume about 50 cc), that had been bored out from the rod. A cylindrical Ag-AgCl electrode (diameter approximately equal to that of the exposed membrane, 2.5 cm) fashioned from silver screen was attached to a thin silver wire also coated with AgCl. This was inserted into the chamber and the wire pushed through a water-tight rubber stopper (Fig. 1). A Heath regulated L.V. Power Supply in series with a Weston Milliammeter and a Heath Decade Resistance Box (EUW-3) made up the external circuit.

A membrane was secured between the half-cells with an "*O*" ring gasket and the half-cells held firmly together with parallel clamps. Each side of the cell was filled with the same solution through inlet ports at the base and care was taken to exclude bubbles. At the top of each half-cell a Swagelok (Crawford Fitting Co., Solon, Ohio) connection

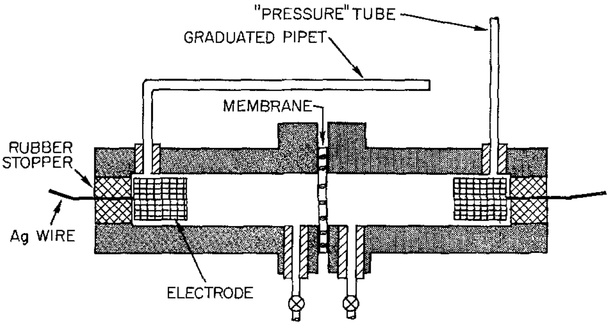

Fig. 1. Cell used to determine electroosmotic water transport. The cell constructed of polymethylmethacrylate consists of two identical halves and is described in the text. The membrane was secured with an "*O*" ring gasket. The electrode in the chamber with the bent pipette acts as the anode

permitted the attachment of either a "pressure" tube or a graduated pipette bent so that it would be horizontal. The chamber with the pressure tube was filled first and the level of solution in the tube adjusted to about 2 cm above the pipette (*see* Fig. 1). In this way a constant pressure in one direction was exerted on the membrane and prevented it from shifting. The difference in pressure between the two sides was not large enough, however, to cause a flow of solvent. Volume changes were followed in most experiments in a 0.20 ml graduated pipette. The Kimble pipette #37020 (Owens-Illinois) had a bore diameter of 1.4 mm and a rated tolerance of ±0.008 ml. The linearity of the pipette was established by determining the volume changes at constant current over a range of 15 to 16 subdivisions as a function of time. In filling the chamber containing the pipette, the solution was brought up into the pipette and stopped near the first subdivision. Current was applied and the volume of solution accompanying the current-induced ion transport into the chamber determined as a function of time.

Current-induced solution flows were usually measured at three current densities: 2.0, 4.0 and 6.0 mamp/cm^2. For each ion in a particular membrane, at least two separate determinations were made at the same current. After several runs, the positions of the pipette and pressure tube were reversed; the direction of current flow was reversed and this caused ion transport and its accompanying solvent flow to occur in the other direction. This served two purposes: it prevented the electrode on any one side from becoming depleted in chloride ion and secondly it permitted small leaks to be detected. In determining the current-induced solution flow in any membrane as a function of different cations the rate of solution flow was first determined for the H ion, then Na, K, TMA and lastly, TEA. The concentration of all solutions was 0.155 M.

Current-Induced Potential Differences

The polarization p.d. was measured in the cell used to determine current-induced solution flows (Fig. 1) following the procedure of Wedner and Diamond [12]. The same current densities and solutions listed in the previous section were used. Current was passed for 300 sec since it had been established in separate experiments that the maximum current-induced p.d. developed within 160 sec of the start of current passage. The potential difference that resulted was measured immediately after current passage ended. The decay to zero potential was followed for one half life and the p.d. at zero-time (end of current passage) estimated by extrapolation.

An estimate of the concentration changes responsible for the polarization p.d. was obtained by measuring the p.d. generated by solutions of different concentrations. The solutions were chosen to be symmetric about 0.155 M. The same procedures were followed as those used to determine membrane permselectivity.

Osmotic Water Flow

To determine the osmotic water permeability of each membrane, sucrose solutions of known osmolalities were placed in one compartment of the cell depicted in Fig. 1 (with electrodes removed) and water in the other. Water movement was followed in the graduated pipette. In separate experiments using ^{14}C-labeled sucrose, these membranes were found to be impermeable to sucrose.

Results

The transport numbers (fraction of current carried) of the various cations in the three membranes were calculated from concentration potential measurements by the Nernst equation:

$$\text{p.d.} = RT/nF(2t_{+} - 1)\ln(a_{\text{II}}/a_{\text{I}}) \qquad (1)$$

where p.d. is the measured potential difference, a_{II} and a_{I} the activities of the solutions separated by the membrane, and t_{+} the cation transport number. The activity was determined from the relationship $a = C\gamma$, where C is the concentration and γ the activity coefficient, in consistent units.

In Table 2, the effect of different cations in the same concentration range on membrane permselectivity is shown. The potential differences determined by concentration potential measurements (0.180 M *vs.* 0.130 M) were used in Eq. (1) to calculate the transport numbers. The agreement between duplicate

Table 2. Effect of different cations on membrane permselectivity

Cation[a]	Transport numbers[b]		
	Membrane I	Membrane II	Membrane III
H	1.0	1.0	1.0
K	0.92	0.85	0.85
Na	0.92	0.86	0.86
TMA	0.86	0.77	0.77
TEA	0.77	0.67	0.67

[a] Anion is chloride for all salts.

[b] Transport numbers calculated from Eq. (1). C_{II} 0.180 M; C_{I} 0.130 M. Concentration by chloride determination. Activity coefficients for TMACl and TEACl were obtained from Lindenbaum and Boyd [6].

Table 3. Comparison of rates of current-induced water flow, osmotic water flow and electroosmotic water flow

Cation	Membrane I			Membrane II			Membrane III		
	A[a]	B	C	A[a]	B	C	A[a]	B	C
H	1.01	0.00	1.01	2.73	0.00	2.72	3.36	0.00	3.36
K	4.94	0.59	4.35	8.97	1.74	7.23	9.25	1.74	7.51
Na	7.17	1.40	5.77	11.52	2.52	9.00	12.21	1.86	10.35
TMA	10.16	3.83	6.33	15.69	3.90	11.79	16.83	2.46	14.37
TEA	11.81	4.80	7.01	15.98	6.66	9.33	16.90	4.03	12.60

[a] Volume excluded by salt was subtracted from the total current-induced solution flow.

A. Total current-induced water flow rate in μliters/min.

B. Osmotic water flow rate in μliters/min.

C. Electroosmotic water flow rate in μliters/min. (C was obtained by subtracting B from A). All rates are at 6.0 mamps/cm^2.

runs for the chloride salts of H, K and Na was ±1.5% or less. For the TMA and TEA ions, the reproducibility declined to ±3.0%. The selectivity of these membranes for cations declined as the hydrated radius of the cations increased and as the hydration state of the membranes increased.

Except in a few cases, measurements of current-induced solution flows were made at three current densities (2.0, 4.0 and 6.0 mamps/cm^2) and the solution flow per equivalent of ions transported was found to be independent of current density. Table 3 lists the current-induced water flow rates found at 6.0 mamps/cm^2. The volume excluded by salt was subtracted from the total current-induced solution flow to obtain the value listed in column A. The current-induced water flow rates became larger as the size of the cation of the chloride salt increased. Large increases in water flow for a salt were also found as the water content of the membrane increased (Table 3).

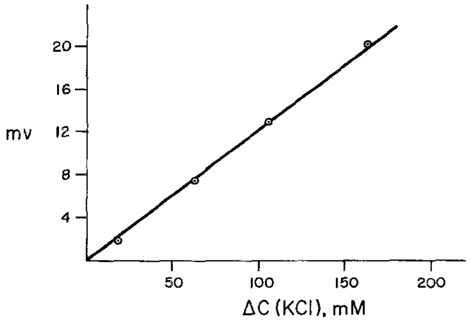

Fig. 2. Potential differences (mV) generated by KCl solutions of different concentrations in membrane I. The concentration difference between the two solutions is represented by ΔC and is symmetric about 155 mM

Following the procedure of Wedner and Diamond [12] the transient potential differences induced by current passage were determined at several current densities for each ion in the three membranes. Membrane I, which was 43% hydrated, showed the most pronounced changes in p.d. with increasing size of the cation. In solutions of KCl and at 6.0 mamps/cm^2 a p.d. of 8.8 mV was found immediately after current passage ceased; in solutions of TEA the p.d. was 70 mV. In the more hydrated membranes (II and III) smaller differences were found with the p.d. in solutions of TEA only double that found in solutions of K. In all three membranes, the p.d. found for solutions of HCl was less than 1 mV.

The concentration changes responsible for the polarization potential differences were determined by measuring the p.d. generated by solutions of different concentrations symmetric about 0.155 M. The solutions were chosen in this way because concentration enhancement on one side of the membrane was expected to equal depletion on the other side. Linear p.d. changes were found in most cases as illustrated for KCl in membrane I (Fig. 2). The largest effects were seen in membrane I where a concentration ratio of 1.5 for K was responsible for the observed current-induced p.d.; a ratio of 150 was found in the case of TEA. Much smaller differences were found in the more hydrated membranes. A concentration ratio of 1.3 accounted for the current-induced p.d. observed in solutions of KCl in membrane II and in solutions of TEA the ratio only increased to 3.6.

Using sucrose solutions of known osmolalities, the osmotic water permeability (P_{osm}) was found to be 0.48 μliter H_2O/hr per mosm for membrane I and 1.11 μliters H_2O/hr per mosm in membranes II and III. An estimate of the osmotic component of the current-induced water flow can be made following Wedner and Diamond [12]. The concentration gradients in the unstirred boundary layers that are present during current passage were determined as already described. The osmotic water flows expected from these concentration differences were then calculated from P_{osm} with the assumption that the salt reflection coefficients were unity. The osmotic water flow rates are listed in Table 3, column B, and indicate that there is a greater accumulation and depletion of salt in the unstirred layers with the larger ions. The contribution of the osmotic water flow to the total current-induced water flow varies from 10% to about 40%.

Discussion

Recent work has helped to define the effect of unstirred boundary layers on current-induced water flow across permselective membranes. Barry and Hope [2] employing a segment of plant cell membrane and Wedner and Diamond [12] using the full thickness of mammalian gallbladder, found that current passage across these membranes caused changes in membrane p.d. which transiently remained after cessation of current flow. This polarization p.d. was shown to arise from differences in ion-transport numbers between the membrane and the adjacent solutions which caused local concentration changes at each membrane-solution interface. Besides causing a transient change in membrane p.d., these current-induced solution concentration changes in unstirred layers immediately adjacent to membranes were also shown to cause an osmotic flow of water.

These earlier studies [2, 12] have shown that current-induced solution flows cannot be attributed solely to electroosmosis unless there is perfect stirring to the membrane-solution interface. Barry and Hope [2], using sensitive experimental techniques, were able to separate the current-induced volume flows into an instantaneous electroosmotic component and one that represented the effect of unstirred layers. For the plant cells of *Chara australis*, about half of the current-induced volume flows were found to be contributed by the latter effect. Wedner and Diamond [12] evaluated the effects of transport number differences on current-induced solution flows in gallbladder by less direct methods. Depending on the salt and current density, 50 to 90% of the total current-induced solution flows were contributed by osmosis; i.e., electroosmotic contributions were 10 to 50% of the total.

In this investigation, the osmotic water component represented as much as 40% of the total current-induced water flow for the bulky tetraalkylammonium ions but was considerably less for the inorganic ions (H, Na

Table 4. Comparison of the differences in transport numbers between the membrane and bulk solutions

Cation	Transport number differences (Δtn)[a]		
	Membrane I	Membrane II	Membrane III
H	0.18	0.18	0.18
K	0.43	0.36	0.36
Na	0.52	0.46	0.46
TMA	0.49	0.40	0.40
TEA	0.47	0.37	0.37

[a] Δtn is the difference between the transport numbers in dilute solutions and in the membrane. The values in dilute Cl solutions are 0.82, 0.49, 0.40, 0.37 and 0.30 for H, K, Na, TMA and TEA, respectively. *See* Table 2 for the transport numbers in the membranes.

and K) (Table 3). The variations in the osmotic water flow may reflect the following factors: (1) Salt gradients in unstirred boundary layers result directly from differences in ion transport numbers between the membrane and bulk solutions. In dilute solutions, the transport numbers for H, Na, K, TMA and TEA are 0.82, 0.40, 0.49, 0.37 and 0.30, respectively. Δtn, which represents the difference between the transport numbers in the membrane and in bulk solution, is shown in Table 4 for the five cations. The 10 to 20% decline in Δtn in the more hydrated membranes (II and III) follows from a decline in membrane permselectivity in these membranes (Table 3). The decreased osmotic water flow contribution to the total current-induced water flow for the alkylammonium ions in membranes II and III (Table 3) may be a consequence then of this decline in Δtn. (2) Salt gradients in the unstirred boundary layers are dissipated by ion diffusion into or from the bathing solutions. The relative diffusion rates for K, Na, TMA and TEA are 1.0, 0.68, 0.61 and 0.44, respectively, while hydrogen, in solutions of HCl, has a diffusion rate 5 to 10 times faster than these ions. Salt gradients that might have developed during current passage through solutions of HCl would have dissipated more quickly than in solutions of the other ions because of hydrogen's much faster diffusion. This may help explain our findings that in HCl solutions no osmotic water flow could be detected during current passage (Table 3). In contrast, the largest osmotic water flows in all three membranes were observed in solutions of TEACl. TEA diffuses ten times slower than H and there is probably less dissipation of the salt gradient by diffusion in solutions of this cation. There are a number of other factors that control the formation and dissipation of the local salt gradients responsible for osmotic water flow. These are discussed in more detail in reports by others [1, 12].

If the total current-induced water flow is composed of an osmotic and an electroosmotic component, an estimate of the latter may be obtained by subtracting the osmotic component (column B, Table 3) from the total water flow (column A). The electroosmotic water flow is shown in column C, Table 3. To compare the electroosmotic water flows in terms of equivalents of current passed, an electroosmotic coefficient may be defined as:

$$(EO)_s = R(F/I) \tag{2}$$

where F is the Faraday, I the current in mamps and R the electroosmotic water flow rate given in column C, Table 3. The electroosmotic coefficients are listed in Table 5.

It is apparent from concentration potential measurements that when an electric current is passed through the cell depicted in Fig. 1, a significant

Table 5. Apparent and cation electroosmotic coefficients for the chloride salts of H, Na K, TMA and TEA[a]

Cation	Membrane I		Membrane II		Membrane III	
	(43% hydration)		(60% hydration)		(58% hydration)	
	$(EO)_s$[b]	EO_{cation}[c]	$(EO)_s$[b]	EO_{cation}[c]	$(EO)_s$[b]	EO_{cation}[c]
H	0.054	0.054	0.146	0.146	0.180	0.180
K	0.232	0.275	0.384	0.535	0.401	0.573
Na	0.308	0.358	0.481	0.646	0.553	0.736
TMA	0.338	0.423	0.630	0.978	0.768	1.170
TEA	0.375	0.580	0.499	1.000	0.673	1.290

[a] Hydrated ionic radius (Å): K 3.31; Na 3.58; TMA 3.67; TEA 4.00. [E. R. Nightingale, Jr., *J. Phys. Chem.* **63**:1381, (1959).]

[b] Apparent electroosmotic coefficient calculated from Eq. (2) in ml H_2O/mFarad of ions.

[c] Cation electroosmotic coefficient calculated from Eq. (4) in ml H_2O/mEquiv of cation.

amount of chloride leaves the measuring chamber as cations enter. This is especially significant in the case of TMA and TEA at 0.155 M (Table 2) in membranes II and III where the ratio of Cl to cation movement is in the order of 1:2 or 1:3. As the Cl ion flow is also accompanied by solvent, the observed electroosmotic flux is the result of the cation-induced water flux minus the anion or Cl-induced water flux in the opposite direction. These comments obviously apply to all the chloride salts used. Therefore, the electroosmotic coefficients, $(EO)_s$, reported in Table 5 are minimum estimates of the amount of solvent accompanying the passage of cations across these membranes.

As these membranes are cation selective, it is not possible to determine directly the solvent flow induced by Cl ion movement through them. In solution, the K and Cl ions are often considered physically identical except for their different charge states. Both ions have the same effect on water structure as reflected in identical Jones-Dole viscosity B- coefficients [5]. Furthermore, the K and Cl ions have almost identical limiting equivalent conductances in free solution and identical molecular weights – parameters that are measures of ion size and shape. For these reasons, the solvent flow induced by the passage of Cl ions can be assumed equal to the solvent flow induced by the passage of K ions.

The electroosmotic coefficients for Cl were calculated for the three membranes from the following equation:

$$[EO]_{K=Cl} = (EO)_s/(t_c - t_a) \tag{3}$$

where $(EO)_s$ is the rate of water transport in ml/Faraday (Table 5) and t_c and t_a the transport numbers for the cation and anion, respectively.

The application of Eq. (3) may be clarified by the illustration that follows. In the case where the transport number for K is 0.90, for every 0.9 Equiv of K transported in one direction, 0.1 Equiv of Cl are transported in the other direction. Because of the assumed identity of the K and Cl ions, each ion induces the same amount of solvent flow and the observed solvent flow into the measuring chamber (Fig. 1) is as if 0.8 Equiv of K had passed; i.e., the difference between the K transport number and the Cl transport number.

The electroosmotic coefficients calculated from Eq. (3) represent that amount of solvent moved by the cation potassium. Because of the cited identity of the K ion and Cl ion the electroosmotic coefficient for K is assumed to be the electroosmotic coefficient for Cl. It may be further assumed that $[EO]_{\mathrm{Cl}}$ although determined for the salt KCl may be used for other chloride salts as long as the same membrane is being considered.

The measured electroosmotic flux for all the chloride salts is the difference between the cation-induced water flux and the chloride-induced water flux in the opposite direction which may be represented by:

$$(EO)_s(\text{observed}) = t_c[EO]_{\text{cation}} - t_a[EO]_{\text{anion}}. \tag{4}$$

To determine the electroosmotic coefficient for the cation-induced solvent flow, Eq. (4) is rearranged to:

$$[EO]_{\text{cation}} = \frac{(EO)_s(\text{observed}) + t_a[EO]_{\text{anion}}}{t_c}. \tag{4a}$$

The values $[EO]_{\text{cation}}$ then represent the solvent moved as a result of the passage of only cations through the membranes. In HCl the membranes completely exclude Cl and the $(EO)_s$ and $[EO]_{\text{cation}}$ are therefore identical (Table 5). With an increase in the size of the permeant molecules, however, the selectivity of the membranes for cations declines (Table 2). The transport number for the TEA ion was 0.67 for membranes II and III. This indicates that the apparent electroosmotic coefficient $(EO)_s$ is the result of 2 Equiv of TEA moving across the membrane into the measuring chamber while 1 Equiv of chloride moves across the membrane in the opposite direction. The electroosmotic coefficients calculated by Eq. (4a) for TEA in these two membranes are 100% greater than the apparent electroosmotic coefficients (Table 5).

The apparent electroosmotic coefficients give no insight into the amount of solvent moved by two cations of different size. The $(EO)_s$ for TMACl is larger than the values found for TEACl in membranes II and III, but the transport number for TEA is less than that for TMA in the two membranes (Table 2). When Eq. (4a) is applied, however, the $[EO]_{\mathrm{cation}}$ for TEA becomes larger than the $[EO]_{\mathrm{cation}}$ for TMA (Table 5).

The importance of membrane hydration to current-induced solvent flow is also clarified by considering the corrected electroosmotic coefficients. Significantly greater amounts of solvent (as much as 130%) are moved by the cations through the 60% hydrated membranes (II and III) than through membrane I which contains 43% water. In the apparent electroosmotic coefficients $(EO)_s$, however, the differences are about 50% (Table 5).

The effect of membrane hydration and ion size on apparent electroosmotic solvent flow reported in this paper agrees with previous reports by others [3, 4, 7, 10, 11]. We believe much of this earlier literature concerning current-induced solution flow must be treated with caution, however. In these earlier studies the important role played by transport number discontinuities in inducing an osmotic water flow during current passage was not considered. The volume flow observed was attributed solely to electroosmosis when it was to varying extents composed of both an electroosmotic and an osmotic component. In addition, there was no attempt made in these earlier communications [3, 4, 7, 10, 11] to define the net water flow in terms of the solvent moved by each ion. Consequently, the parameters that regulate ion-mediated water flow through permselective membranes, namely, membrane hydration and charge density and ion size, were only poorly defined. With the model developed here it should now be possible to interpret electroosmotic solvent flow in terms of these parameters.

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