An Investigation of Anomalous Osmosis and Thermoosmosis

Measurements of water flux, solute flux, and electrochemical potential were made simultaneously in a membrane transport system designed for the studies in anomalous osmosis and thermoosmosis using a series of cations with a common anion. The cation exchange membrane employed was dimensionally stable. The anomalous osmosis appeared to be composed of two components, the normal osmosis and a facilitated osmosis; whereas the thermoosmosis was composed solely of a facilitated component. The anomalous water flux did not correlate with the solute flux or the electrochemical potential. Anomalous osmosis depended strongly upon the cation species.

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SCOPE

Anomalous osmosis and thermoosmosis can be important in dialysis and other membrane unit operations (Hansen and Anderson, 1967) as well as in biological transport (Praissman et al., 1973). Previous experimenters have measured the solvent flux, the solute flux, and the electrochemical potential; however, these measurements have not all been done in the same experiment, nor has the effect of membrane swelling been analyzed. In the experiments presented herein, these three measurements were made simultaneously, employing a membrane whose swelling characteristics are not dependent upon salt concentration. In addition, one study (Hansen and Anderson, 1967) contained a measurement of the anomalous osmosis in an anion exchange membrane for a series of acids, that is, a series of salts with differing anions and a common cation. In the present study, a series of salts with a common anion and differing cations were studied for anomalous osmosis in a cation exchange membrane.

The transport of water and solute, as well as the electrochemical potential difference across a polystyrene-divinyl benzene-sulfonic acid cation exchange membrane, were measured under conditions where anomalous osmosis (isothermal, concentration gradient in solute across the membrane) and thermoosmosis (uniform concentration, temperature gradient across the membrane) can occur. The solute species NaCl, KCl, glucose, $(CH_3)_4NCl$, $(C_2H_5)_4NCl$, and $(C_3H_7)_4NCl$ were used in the anomalous osmosis studies at concentrations ranging from 10^{-4} to 2 mol/l; the solute concentration ratio across the membrane was ten, and the system was maintained at 25 ± .1°C. In the thermoosmosis studies, the solute species NaCl and $(CH_3)_4$ NCl were used at uniform concentrations of 0.05, 0.1, or 0.25 mol/l, and the temperature gradients established across the membrane ranged from 5 to 7 ± .1°C (that is, approximately 20° to 25°C and 20° to 27°C, respectively).

The solute species chosen provide a means to characterize the behavior of the osmotic flux for systems with different cations and a common anion (Cl^-). The solutes NaCl and KCl are thought to interact more strongly with water than the quaternary ammonium chloride salts (for example, Frank and Wen, 1952). In addition, the solute glucose was included so that the effect of a nonelectrolyte on osmotic transport could be ascertained.

CONCLUSIONS AND SIGNIFICANCE

Experimentally, the cation exchange membrane exhibited anomalous osmosis with ionic solutes but purely normal osmosis with the uncharged solute glucose, as was expected. For the particular membrane, which maintained its dimensionality independent of solute concentration, the anomalous osmotic effect appeared to be a facilitated transport of solvent in the direction of normal osmosis. This facilitated component was greatly dependent upon the cation of the solute as can be seen from Figure 7. The potassium cation generated the largest anomalous osmosis component followed by sodium, then the three quaternary amines produced decreasing anomalous osmosis with increasing order of molecular weight, and finally, the glucose produced no anomalous osmosis. Thus, it appears that the cation itself and/or the interaction of the cation with the ion exchange membrane are key factors in anomalous osmosis.

The solvent (water) flux was compared with the solute flux; the former being much larger than the latter. The solute flux was linearly dependent upon the concentration gradient for all concentration levels in contrast with the solvent flux, which exhibited the anomalous osmosis. The electrochemical potential across the membrane was changing throughout the experiment, whereas the anomalous osmosis attained a steady state. These facts suggest that the anomalous osmosis is unrelated to the solute flux or to the electrochemical potential across the membrane.

The thermoosmosis experiments which were more difficult to perform indicated that the total osmotic phenomena was similar to the facilitated component of the anomalous osmosis. With equal concentrations on both sides of the membrane, the temperature difference generated fluxes of solvent and solute and an electrochemical potential difference across the membrane. The solvent flux seemed to be

unrelated to either the solute flux or the electrochemical potential. The solute flux was much nearer in magnitude to the solvent flux than for anomalous osmosis. Both the solvent and solute fluxes proceeded in a direction opposed to the thermal gradient. The nature of the cation had a significant effect upon the observed thermoosmosis; the quaternary amines produced greater thermoosmosis than the sodium cation. From this study it appeared that the thermoosmosis was caused by the same general phenomena as anomalous osmosis.

Thermoosmosis and anomalous osmosis have been known for many years. In fact, anomalous osmosis was reported by Dutrochet in 1835, while just after the beginning of this century, Lippman (1907) and Aubert (1912) reported the phenomenon of thermoosmosis. Freundlich (1922) surmised that thermoosmosis and anomalous osmosis possess a fundamental similarity. Graham discussed studies of anomalous osmosis in the Bakerian lectures in 1854. Many researchers have reported findings in anomalous osmosis. In contrast, few have investigated thermoosmosis, probably because these measurements are difficult.

Osmosis in aqueous systems is defined as the passage of solvent through a permeable barrier from a more dilute solution to a more concentrated solution. The rate of flow is generally taken as roughly proportional to the concentration gradient (or activity gradient) in solute. This proportional relationship is commonly referred to as normal osmosis. The common activity coefficient corrections are insufficient to produce the proportional relationship of flow to concentration difference under conditions of anomalous osmosis. In these instances, the graph of the flux of water through membranes as a function of concentration difference may increase or decrease, pass through maxima or minima, and even proceed in a direction from the more concentrated solution to the more dilute solution. In general, if the solvent flux from dilute to concentrated solution exceeds that of normal osmosis, the phenomenon has been referred to as anomalous positive osmosis (Carr and Sollner, 1962; Tasaka et al., 1969; Fujita and Kobatake, 1968). If the solvent flux proceeds from the more concentrated to the more dilute solution, the term *anomalous negative osmosis* has been used (Carr and Sollner, 1962).

Anomalous osmosis involves isothermal conditions and a difference in solute concentration across a membrane. In addition, the membrane must be charged, that is, an ionic species is attached to the membrane matrix, and the solute species must be an electrolyte. The only imposed driving force necessary for the occurrence of anomalous osmosis is a solute concentration (equivalently activity) gradient. Under these conditions, anomalous phenomena only applies to the solvent. The solute always transfers with the solute concentration gradient. Deviations from a proportionality between the solute flux and the solute concentration gradient are generally attributed to the concentration dependence of the effective diffusion coefficient through the barrier (Lakshminarayanaiah, 1969).

Thermoosmosis, classified as *positive* and *negative* osmosis by Carr and Sollner (1962) for clarity, implies the flux of a solvent through a charged membrane under the influence of a temperature gradient across the membrane. No electrolyte concentration gradient exists. The electrolyte solute can proceed in either direction with respect to the thermal gradient (Carr and Sollner, 1962).

REAGENTS

All aqueous electrolyte systems investigated in this work involved the chloride ion, thereby permitting measurement of the electrochemical potential between Ag-AgCl electrodes. The solute concentration ratio across the membrane was maintained at ten for all systems studied in the anomalous osmosis experimentals. The systems and concentration ranges (mol/l) investigated in the anomalous osmosis studies were, respectively: (1) NaCl (Mallinckrodt), 0.0001 to 2; (2) KCl (Fisher), 0.01 to 2; (3) α-D-glucose (Fisher), 0.025 to 2; (4) $(CH_3)_4NCl$ (Eastman), 0.0016 to 2; (5) $(C_2H_5)_4NCl$ (Eastman), 0.01 to 0.7; and (6) $(C_3H_7)_4NCl$ (Eastman), 0.01 to 0.2. Similarly, the systems and concentrations (mol/l) used in the thermoosmosis experiments were: (1) NaCl, 0.05, 0.1, and 0.25; and (2) $(CH_3)_4NCl$, 0.1 and 0.25. The remaining reagent, the capillary tube cleaning solution, was prepared by mixing equal volumes of sulfuric and chromic acids.

MEMBRANE

All experimental results presented herein were for the same piece of cation-exchange membrane (MC 3470, copolymer of styrene and divinyl benzene with sulfonic acid groups, Ionac, Inc., Birmingham, N. J.); thus, membrane variations were eliminated. From manufacturer's data, the membranes are 96% selective to Na^+ when exposed to a concentration gradient of 0.5 mol/l NaCl (0.5 mol/l to 1.0 mol/l); with an imposed pressure differential of 2 atm (30 lb./sq.in.), approximately 10^{-5} mol/cm^2-min of water are transported through the membrane. The ion exchange capacity of the membrane is 0.85 meq/dry gram of membrane. These membranes are quite tenacious and exhibited no serious dimensional changes for the solute concentrations investigated in this work. Measurement of dimensional changes which occur during membrane soaking indicated a wet volume/dry volume ratio of 1.25. This membrane volume expansion was independent of concentration and stabilized quickly (that is, within an hour). Therefore, the experimental results were not subject to membrane pore size variations.

APPARATUS

An air bath (fabricated of PLEXIGLAS®) provided a temperature-controlled environmental housing for the anomalous osmosis membrane transport experiments and a support for three motors; one being the power source for a chain-drive cell stirrer assembly, and the other two serving as prime-movers for air circulation blowers in the air bath space. Other items, such as the differential voltmeter, conductivity meter, and timer, were placed for convenient usage during the course of an experiment.

It was anticipated that temperature control inside the air bath would be critical for maintenance of isothermal cell conditions during anomalous osmosis experiments, and hence, a considerable design effort involving a mathematical model for the thermal dynamics of the chamber was undertaken. Minimization of offset and maximum control stability resulted. The design features included auxiliary heating, proportionally-controlled heating, and auxiliary cooling.

The experimental requirements for the thermoosmosis studies differed since a uniform temperature-controlled environment was not required. Instead, as illustrated in the piping diagram

(Figure 1), a temperature-controlled water bath (32° or 37°C ± 0.5°C) supplied warm fluid to the jacket of one copper end chamber. Cold tap water (15° ± 1°C) flowed into the other copper end chamber. Thermistors located in the cells next to the membrane indicated cell temperatures of 20° for 15°C water and 25° for 32°C water, and 27° for 37°C water.

Figure 2 illustrates the cell assembly, which consists of a membrane clamped and sealed with o-rings between a set of 50 mm I.D. symmetric glass cells, 8.2 cm in length. The other ends of the glass cells were clamped and sealed with copper end chambers through which the stirring shafts and detection devices entered horizontally. Top and bottom connections of 8-mm standard glass tubing served as exit and entry ports. The effective free volume of each assembled cell chamber was 167 cc. Based upon previous work (Carr and Sollner, 1962; Tasaka et al., 1969), cell dimensions were established to make expected electrolyte concentration changes insignificant and to permit proper positioning of the sensing devices. Each cell was identical when viewed facing the membrane.

One four-blade turbine, positioned slightly off-center and approximately 3.2 mm from the membrane surface, agitated each cell with a clockwise motion when viewed from the copper ends. During the anomalous osmosis experiments, a speed of 55 rev./min. was used. Changes in stirring speed did not significantly alter the salt and water fluxes observed, and hence, membrane diffusion was the rate limiting factor in this system. In initial experiments, the stirrers caused oscillations in the measurement capillaries, indicating the sensitivity of the capillary measurement to minor pressure fluctuations. This problem was corrected by altering the location of the exit ports from the glass cells.

Temperature in the cells was detected by Isocurve Miniprobe thermistors (Fenwal), nominally rated at 2000 ohms. Conductance measurements were made by use of a modified type CDC 304 conductivity electrode (Radiometer, Copenhagen). The electrodes were modified to form a water-tight seal (o-ring) when inserted in the copper end chambers. The output meter (Radiometer CDM3) provided readings of conductance with a reliability of ± 1%. Electrochemical potential were measured by Ag-AgCl electrodes, fabricated by a technique discussed by Greyson (1962), and sealed in the copper

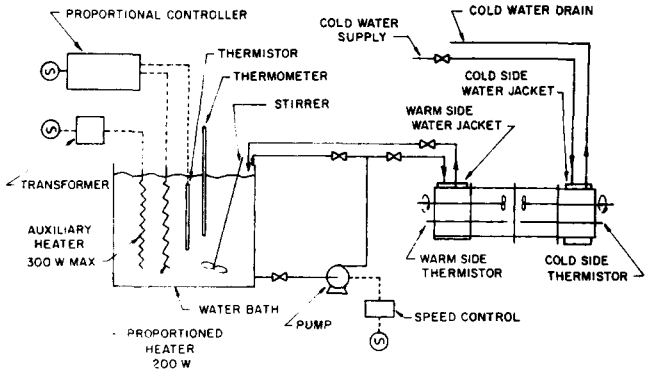

Fig. 1. Flow schematic, thermal control system, thermoosmosis.

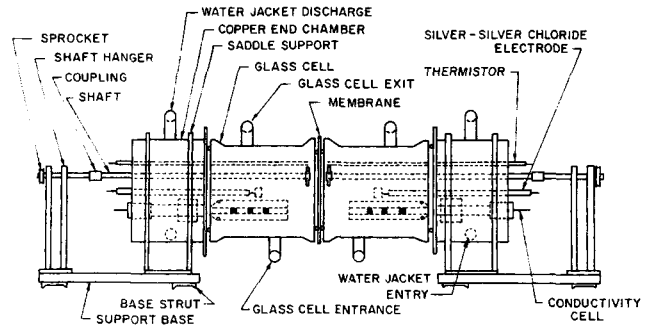

Fig. 2. Cell assembly schematic.

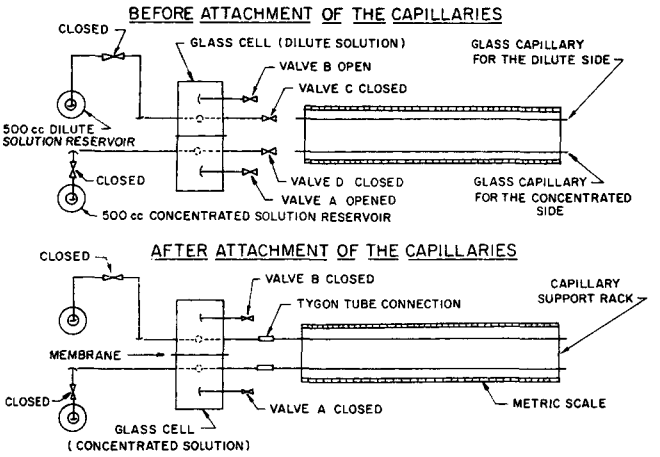

Fig. 3. Glass piping system.

end chambers with o-rings. A pair of electrodes, prepared simultaneously, exhibited voltage deviations from each other of 0.1 mv or less. Differential voltages across the membrane were read on a high impedance meter to ± .5 mv, quite adequate for this research.

Figure 3 depicts the piping system constructed of standard 8-mm O.D. glass tubing. The cells were filled and drained via a valve manifold, a waste reservoir, and a vacuum source (not shown). During the temperature stabilization of an experiment, the capillaries were not attached and valves A and B (top ports) were open. After the system had stabilized, valves A and B were closed, and the measurement capillaries (6 mm O.D.) were attached without air bubbles to the bottom ports with Tygon tubing after valves C and D were removed. The capillaries (1 mm bore and 121 cm long) were half filled with the solution corresponding to the cell to which the capillary tube was attached. As the osmotic water flow progressed, the solution in one capillary would proceed toward the cell and the meniscus in the other tube would move away from the cell. Since the transport area of the membrane is 28.3 cm^2 (based on the mean o-ring seal diameter), while the effective capillary cross-sectional area is 0.00785 cm^2, the capillaries magnify the fluid velocity through the membrane by a factor of about 3600, an indication of the sensitivity possible with this measurement.

EXPERIMENTAL PROCEDURES

After steady temperature conditions had been achieved, water flow, conductance, and electrochemical potential difference measurements were accepted as steady state values only when the menisci in the capillaries were moving linearly and both at the same rate. Considerable difficulty achieving this condition was encountered because of the dissolution, evolvement, or size change of small gas bubbles in the solution. In some cases, trial experiments were run for more than a day without equal capillary water fluxes being achieved. In every case, this difficulty (as well as leaks) was detected by the water flow rates in the two capillaries differing significantly. The problem with the gas bubbles was reduced by degassing fresh solutions overnight, by gentle warming of the solutions to a temperature slightly above the temperature of the experiment just prior to use, and by allowing time for the gas solubility to further stabilize prior to taking experimental data (this time varied with solute concentration).

It was observed that the time for equalization of the two capillary fluxes varied with solute concentration since more dilute solutions required more time to achieve nearly equivalent rates of fluid motion. For example, the times to reach steady capillary flow for the concentration differences 0.2 to 2 m/l and 0.0001 to 0.001 m/l were 2 hr. and 15 hr., respectively. This resulted for two facts: (1) the flux of water was higher for the higher concentrations permitting a higher noise level from gas bubble problems, and (2) the gas is less soluble at higher concentrations. When the menisci movements were

nearly the same, the capillaries were monitored for a sufficient period (3 hr.) to ensure steady state.

The degassed and pre-warmed solutions were added to the 500-ml vacuum flasks (Figure 3). Using vacuum and control valves, fluid slowly filled each membrane cell, without air bubbles. After the fill operation, valves A and B (Figure 3) were opened to prevent pressure buildup as the system was warmed. The stirrers were turned on, and temperature, conductance, and differential electrical potential readings were periodically measured during the warming cycle. During thermal equilibration (1 to 2 hr.), the capillaries were thoroughly cleaned with the sulfuric-chromic acid solution and flushed with deionized water to prevent formation of air bubbles in the capillary during an experiment. The capillaries were then attached to the cells.

Frequently, fluid positions in the capillaries were adjusted using gentle syringe suction at the open ends, and using addition of fluid by manipulation of valves A and B (Figure 3). Rates of meniscus movement in the capillaries varied from about 4 cm in 100 s (0.2 m/l to 2 m/l KCl) to about 2 cm in 10,000 s (0.0001 m/l to 0.001 m NaCl) in anomalous osmosis experiments. The latter rate, which is similar to that found in thermoosmosis, corresponds roughly to 1 drop of water transferred in 3 hr. (assuming 0.02 cc of water is contained in a drop).

Evaporation out of the open ends of the capillaries was determined to be virtually nonexistent. In addition, although the 25°C temperature in the cells was maintained in studies of anomalous osmosis, temperature deviations 2° below 25°C did not significantly alter the final, stable water flux values, although these fluctuations did effect stability. Finally, the horizontal capillaries did not differ in elevation by more than a fraction of a mm, which was negligible.

COMPARATIVE FEATURES OF THE APPARATUS AND METHOD

The air bath-temperature control system is well suited to studies of anomalous osmosis as visual observation of the membrane cell assembly is enhanced, and system leaks are readily identified. In contrast, other workers (for example, Fujita and Kobatake, 1968; Toyoshima et al., 1967; Tasaka, et al., 1969) immersed a membrane-cell assembly in a temperature-controlled water bath. The temperature gradient for thermoosmosis was directly measurable, in contradistinction to Carr and Solner (1962). In the present work, the osmosis, electrical conductance, electrochemical potential, and temperature were all simultaneously measured. In contrast, other works did not measure all of these properties simultaneously; for example, see Mackay and Meares (1959); Hansen and Anderson (1967); Praissman et al. (1973); Weinstein and Caplan (1968); Tombalakian (1966); Rastogi (1964); and Voellmy and Läuger (1966). Weinstein and Caplan stressed the importance of use

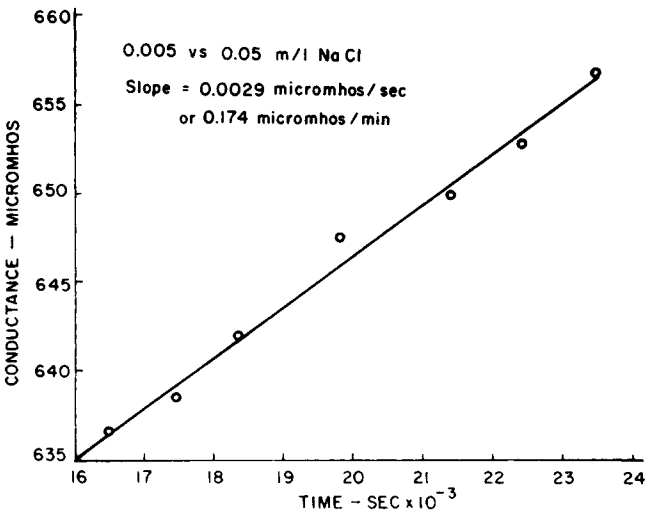

Fig. 4. A sample of conductance-time data, anomalous osmosis.

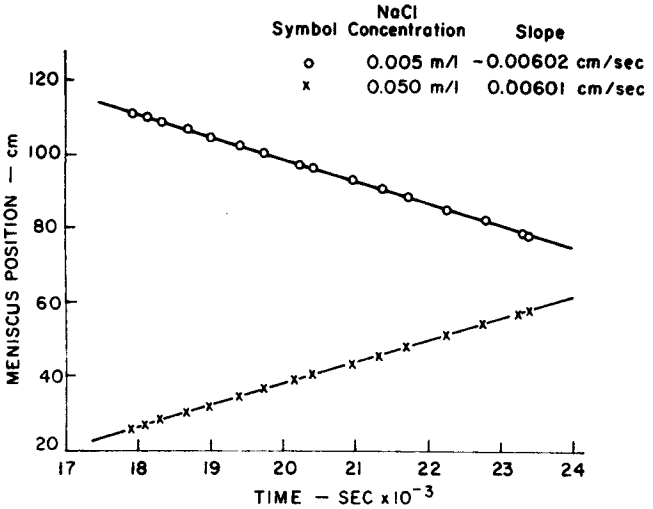

Fig. 5. Movement of the fluid in the capillaries versus time.

of separate horizontal capillaries as was done herein. As discussed previously, solution degassing was necessary for successful experimentation; this was found by other workers (for example, Carr and Sollner). Mackay and Meares also experienced difficulty in attaining steady flows at low current levels in studies of electroosmosis in ion exchange membranes.

Most experiments employ sufficient stirring so that the membrane and not the solution boundary layer is the dominant resistance to transport; however, it is important that this assumption be checked and that other effects, such as pressure fluctuations, be evaluated. Finally, to avoid membrane-to-membrane variations in study of fundamental behavior, it is suggested that, as in this work, the same piece of membrane be used in all experimentation. In addition, as in this work, it is also apparent that a membrane with swelling characteristics independent of solute concentration or known as a function of solute concentration be used so that studies of anomalous osmosis and thermoosmosis will not be obscured.

RESULTS—ANOMALOUS OSMOSIS

The anomalous osmosis experiments were performed using the apparatus and procedures discussed previously. The quantities measured were the flow rate of the solution into and out of the cell chambers, the electrical conductivity in each cell chamber, and the potential difference between the two cell chambers. From these experimentally determined values, the water flux, the solute flux, and the potential difference across the membrane were obtained.

Solute Flux and Water Flux—Anomalous Osmosis

Electrical conductance measurements provide a means for estimation of solute flux across the membrane. A sample plot of experimental results for the cell containing the lower solute concentration is presented as Figure 4. Similarly, measurements of the meniscus motion in the capillaries as a function of time provide a means to estimate the water flux. Figure 5 represents a sample plot for meniscus motion in the capillaries versus time. As shown, for this particular concentration pair 0.005 and 0.05 m/l NaCl), linearity was achieved after approximately 5 hr. The line on the graph with the negative slope (0.005 m/l) represents meniscus motion in toward one cell while the other line (0.05 m/l) indicates motion away from the other cell. The solute flux and the water flux both can contribute to the volume change in the cell as a function of time, and therefore evaluation of the fluxes from measurements of conductance and fluid motion in the capillaries must be performed in the following manner.

It is assumed that the electrolyte concentration (c)

sensed by the conductivity cell is confined only to the stirred cell chamber (Volume = V_f). Therefore, in terms of electrolyte transport, the cell volume does not change. Fluid enters the cell from the capillary (at a volumetric flow rate equal to the meniscus velocity times the capillary cross sections area, U_cA_c) containing a solution of the initial cell concentration C_0. Fluid also exits through the membrane (cross sectional area = A) as pure water, filtering out the electrolyte. Finally, solute enters the cell (flux = J_s) through the membrane due to the solute concentration gradient. Therefore, a mass balance for the rate of movement of solute in and out of the cell chamber can be written as

$$V_f \frac{dc}{dt} = A J_s + A_c U_c C_0 \tag{1}$$

The change in conductance with respect to time can be expressed as a total differential, that is,

$$\frac{dk}{dt} = \left(\frac{\partial k}{\partial c}\right)_T \frac{dc}{dt} + \left(\frac{\partial k}{\partial T}\right)_c \frac{dT}{dt} \tag{2}$$

Under conditions of anomalous osmosis, the temperature T is constant (in this work, equal to 25°C) and, accordingly, $dT/dt = 0$. Therefore, Equation (2) reduces to

$$\frac{dk}{dt} = \left(\frac{\partial k}{\partial c}\right)_{25°} \frac{dc}{dt} \tag{3}$$

Substitution for dc/dt in Equation (2) and solution for the solute flux J_s yields

$$J_s = \left[\frac{dk}{dt} \Big/ \left(\frac{dk}{\partial c}\right)_{25°}\right] \frac{V_f}{A} - \frac{A_c U_c C_0}{A} \tag{4}$$

The equation relating the solute flux and the water flux through the membrane can be developed by consideration of the volume of either cell V_{fc} including the fluid contained in the attached capillary. At any instant in time, the following equation is valid:

$$V_{fc} = \overline{V}_s n_s + \overline{V}_w n_w \tag{5}$$

Since the partial molar volumes are effectively constant, Equation (5) can be differentiated with respect to time t to yield

$$\frac{dV_{fc}}{dt} = V_s \frac{dn_s}{dt} + V_w \frac{dn_w}{dt} \tag{6}$$

The change in cell volume with respect to time (dV_{fc}/dt) is equal to the meniscus velocity U_c times the capillary cross section area (A_c). Therefore, Equation (6) becomes

$$U_c A_c = V_s \frac{dn_s}{dt} + V_w \frac{dn_w}{dt} \tag{7}$$

Since the volume under consideration V_{fc} includes that in the cell plus that in the capillary, the change in the number of moles of water is due to the flux of water through the membrane, and the change in the number of moles of solute is due to the flux of solute through the membrane. Therefore,

$$\frac{dn_w}{dt} = A J_w \tag{8}$$

and

$$\frac{dn_s}{dt} = A J_s \tag{9}$$

Substitution of Equations (8) and (9) in Equation (7) yields

$$U_c A_c = \overline{V}_s A J_s + \overline{V}_w A J_w \tag{10}$$

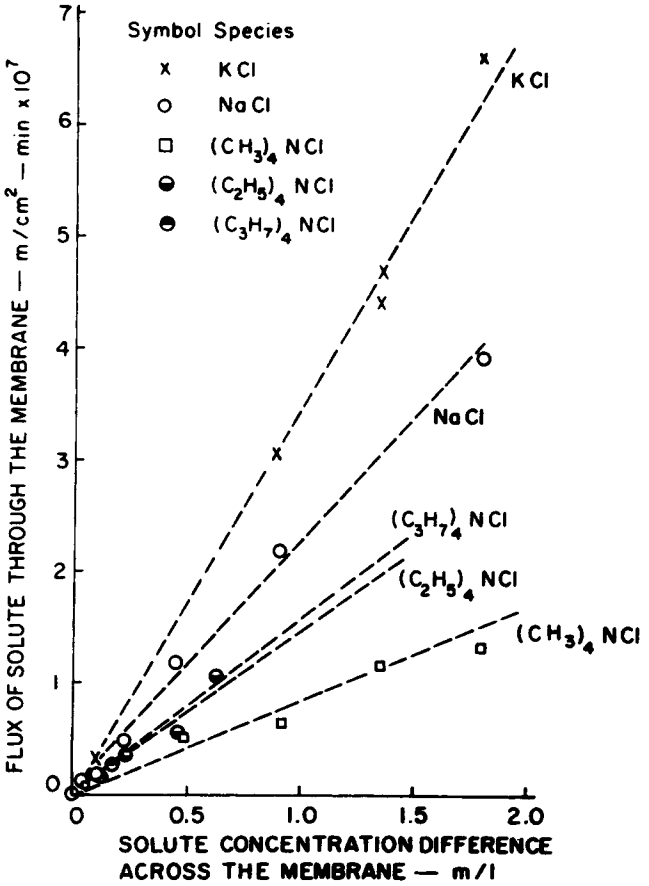

Fig. 6. Solute flux versus solute concentration difference.

Solution of Equation (10) for the water flux through the membrane results in

$$J_w = \frac{U_c A_c}{V_w A} - \frac{\overline{V}_s}{V_w} J_s \tag{11}$$

Equations (4) and (11) were used to compute values for the solute flux J_s and the water flux J_w. For all systems studied, $\overline{V}_w$ is nearly equivalent to V_w^0 (the molar volume of pure water), and the partial molar volume of the solutes was obtained from data in the literature (Millero, 1970). Sample calculations illustrated that the solute concentration changes were small, and hence the solute concentration entering the capillary was approximately constant as was assumed.

The $(\partial k/\partial c)_{25°}$ was evaluated at concentration C_0 by use of literature data for NaCl and KCl (Chapman, 1967) and by separate calibration experiments for the quaternary ammonium chloride salts. Use of C_0 for this calculation introduced only a few percent error as the solute concentration changed very little in the course of an experiment. The factor (dk/dt) is the slope of the experimental conductance-time plot. The conductivity cell used had a cell constant of 1.01 which was ignored as a correction to the data since the scatter in the k-t plot caused greater error than this value. The sample calculations also indicated that the osmotic flux is much larger than the solute flux (for example, for one case, $J_w/J_s = 680$).

Figures 6 and 7 present the plots of solute flux and osmotic flux as a function of the concentration difference for the anomalous osmosis studies. The solute flux always proceeded from the concentrated to the dilute solution, whereas the osmotic flux always proceeded from the dilute to the concentrated solution. As indicated by the dashed

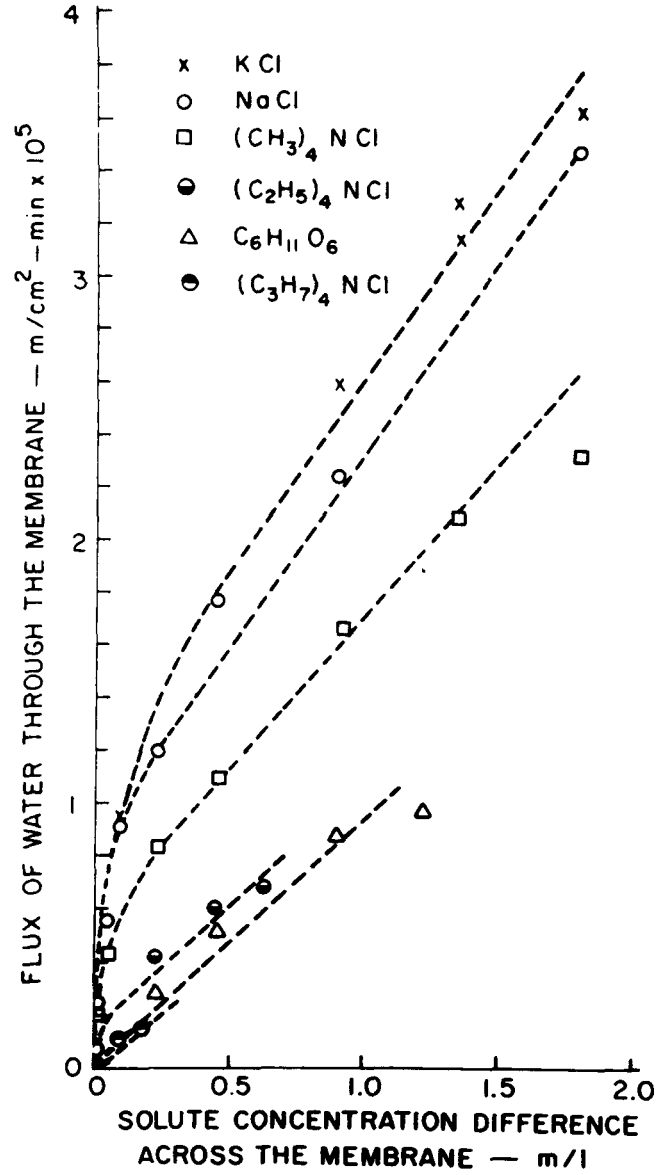

Fig. 7. Water flux versus solute concentration difference.

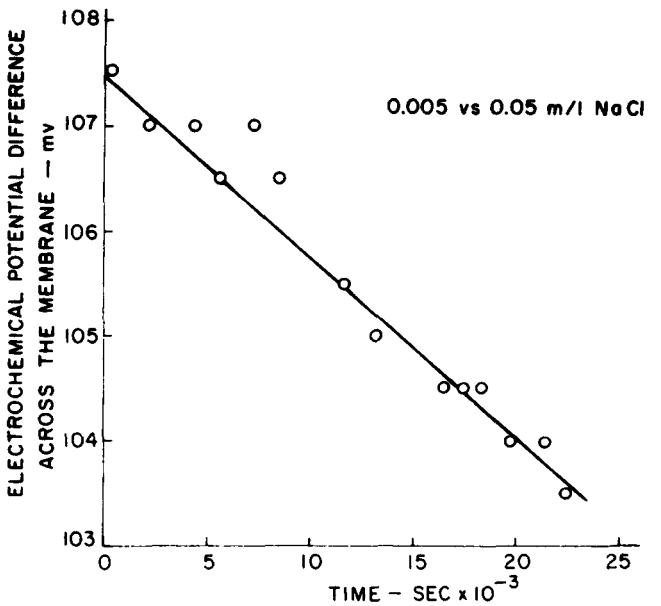

Fig. 8. Example of the variation of electrochemical potential difference with time.

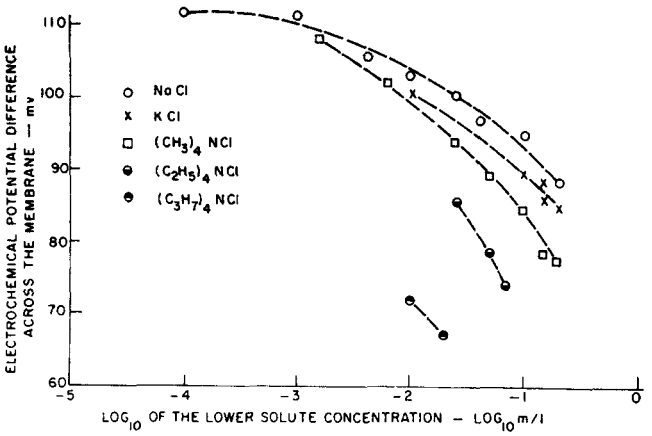

Fig. 9. Electrochemical potential difference versus $\log_{10}$ of the lower solute concentration.

lines in Figure 6, the solute flux appears to be linear with concentration difference for all systems studied while the osmotic flux (Figure 7) appears to be nonlinear at low concentrations and linear at high concentrations for most of the systems investigated. The only nonelectrolyte studied (dextrose) rises very gradually throughout the range of concentrations investigated. In all cases, the values of the osmotic flux greatly exceed the corresponding values of solute flux.

Electrochemical Potential

A sample plot of the electrochemical potentials obtained versus time is presented as Figure 8. The potentials continued to decrease with time due to the slight decrease in the concentration ratio between the solutions on either side of the membrane as a result of solute and solvent transfer. The electrical potential was exhibiting this linear decrease after the water flux stabilized to a constant value. Representative voltages for each experiment are plotted in Figure 9 as a function of the logarithm of the lower solute concentration.

RESULTS—THERMOOSMOSIS

Again, similar measurements and computations were performed except that the computations indicated that for the thermoosmosis, the water flux and solute flux values were more nearly of the same order of magnitude. Therefore, the volume change in a cell compartment was more dependent on solute transfer through the membrane.

Solute Flux

The change in electrical conductance as a function of time in both cells was of interest since the direction of solute flux under conditions of thermoosmosis could not be a priori predicted. Measurements of small changes in conductance in a background solution of high conductivity were required. Thus, the resultant data included considerably more error than that shown in the anomalous osmosis studies. Conductance data obtained as a function of time from the thermoosmosis studies was subjected to a linear regression analysis. If the regression line was statistically significant, that is, the variance in the data could be explained by the use of the F test at the 95% confidence level, the data was accepted as representative of the experiment.

The solute fluxes were computed by use of Equation (4), ignoring the correction for the negligible flux of solute into or out of the cell due to fluid motion in the capillaries. Figure 10 presents a plot of the results ob-

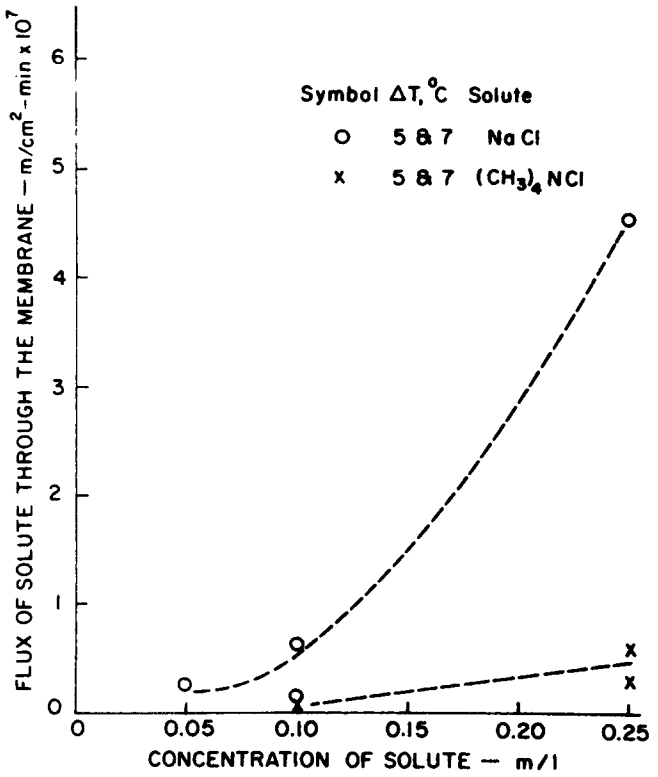

Fig. 10. Solute flux versus concentration of solute.

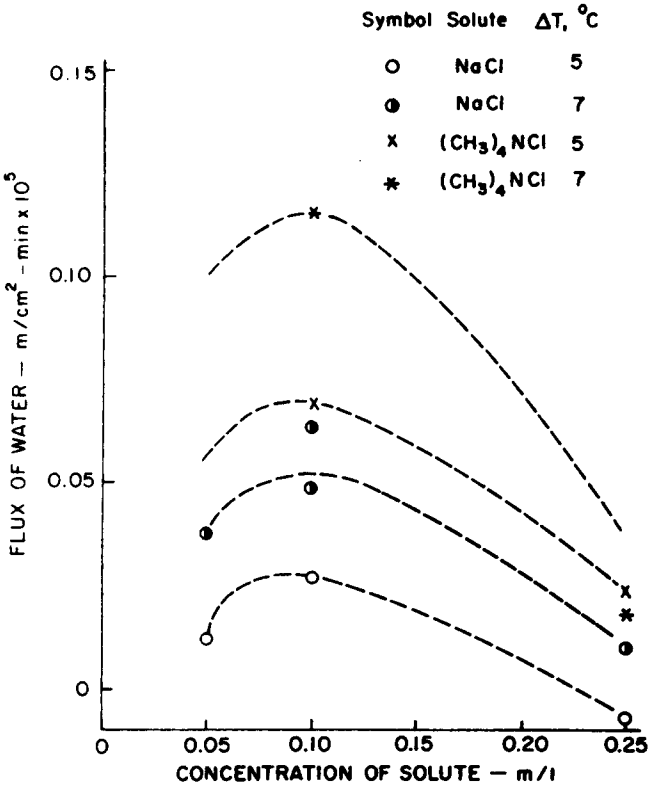

Fig. 11. Flux of water—thermoosmosis studies.

tained. The solute flux in the thermoosmosis experiments traversed the membrane from the colder solution to the warmer solution.

Water Flux

The computation of the water flux values for the thermoosmosis studies follows that used for the anomalous osmosis data except the influence of solute on cell volume is no longer small. Equation (11) was used in computation of the flux of water from the thermoosmosis data. The partial molar volumes of the solutes are effectively constant in these experiments and were obtained from data in the literature (Millero, 1970). The values used are 17.5 cc/m for NaCl and 107.4 cc/m for $(CH_3)_4NCl$.

Figure 11 presents a plot of the water flux values obtained as a function of system concentration. The computed values reflect the observations of the experiments, that is, osmosis was observed to occur from the colder solution to the warmer solution. Thus, osmosis and solute flux in the thermoosmosis experiments occurred in the same direction. This is in contrast to the anomalous osmosis experiments where osmosis and solute flux were opposite in direction. It is interesting to note that the maxima occur at a concentration of 0.1 m/l. It is also interesting to note that the computed values of water flux for $(CH_3)_4NCl$ exceed those for NaCl at the same solute concentration. In the anomalous osmosis experiments, the osmosis in NaCl systems was greater than the osmosis in $(CH_3)_4NCl$ systems at the same solute concentration difference across the membrane.

Electrochemical Potential

The differential electrochemical potential is a reflection of the temperature gradient across the membrane as the electrolyte concentrations were identical in both cell compartments. The voltage values are plotted in Figure 12 as a function of temperature difference. As shown, the differential voltages observed for NaCl tend to decrease with increased concentration for the limited concentration region studied. However, the voltages obtained for the higher concentration of $(CH_3)_4NCl$ (0.25 m/l) are apparently higher than the voltages obtained for the lower concentration of $(CH_3)_4NCl$ studied (0.1 m/l).

DISCUSSION OF EXPERIMENTAL AND LITERATURE RESULTS

There have been several theories proposed to explain and analyze anomalous osmosis and thermoosmosis; these theories include both qualitative and quantitative developments. None of the theories have satisfactorily explained the observed phenomena completely, and theoretical research still continues in this area. The results of this investigation will not be discussed theoretically in this paper because lengthy and debatable developments, discussions, and comparisons would be required.

The literature documents several unusual observed patterns for the dependence of water flux on concentration in osmotic experiments with charged membranes (for example, Tasaka et al., 1969; Fujita and Kobatake, 1968). Other workers have noted that anomalous osmosis is usually composed of a normal component plus a facilitation component (Carr and Sollner, 1962). A characteristic of the normal osmotic component is that the flux of water is nearly proportional to the solute concentration difference across the membrane. In addition, the facilitated component should impart substantial curvature and nonlinear displacement of the water flux as a function of solute concentration.

In an empirical and heuristic manner, the normal and facilitated components can be found by examination of Figure 7. The curves for the electrolytes are characterized by a nearly linear region that commences at a concentration difference of approximately 0.25 m/l, and are also characterized by a steep ascending region below 0.25 m/l. The slopes of the lines for the electrolytes above 0.25 m/l are approximately the same. Thus, it appears that

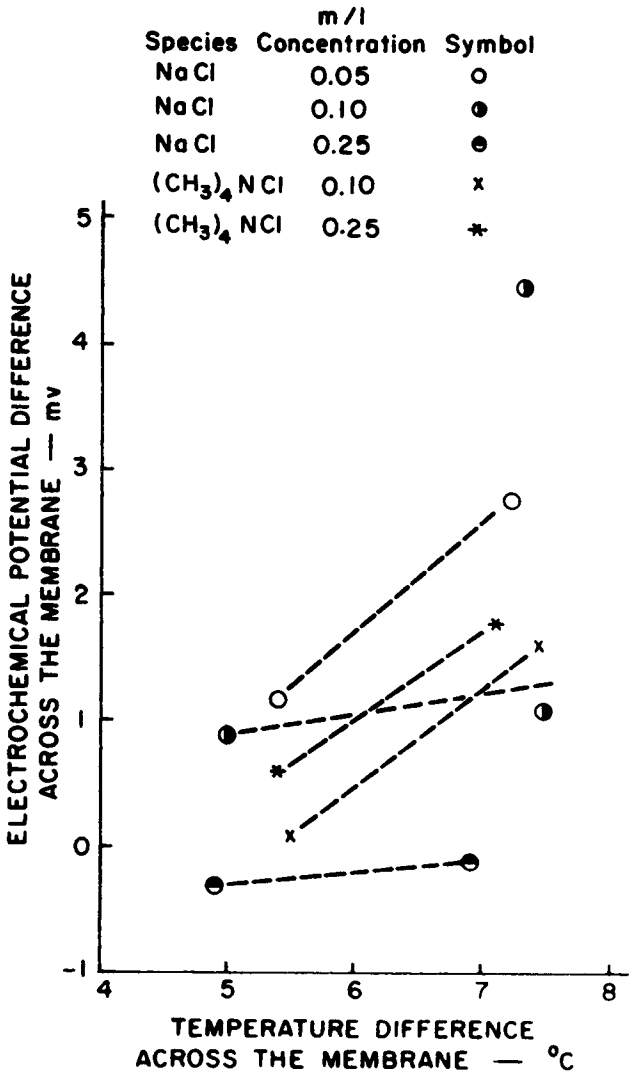

Fig. 12. Electrochemical potential differences—thermoosmosis.

there is a normal component generating the equal slopes at high concentration and a facilitated component which elevates the fluxes above the expected values. The presence of such a feature in the data indicates that the normal component for all solutes is affected by the particular membrane in the same manner. However, the different ascent rates cause the linear portion of the curves to appear at different levels in Figure 7. Since the facilitated component varies for the different cations, it may be viewed as the result of interaction between the cation and the cation exchange membrane.

It should be noted that the nonelectrolyte studied (glucose) exhibits a nearly linear trend and does not possess any steeply ascending regions. Therefore, the entire glucose plot represents only normal osmosis as expected since glucose is nonionic and not under the strong ionic influence of the fixed charge of the membrane. It is suggested that the facilitation is not related to a coupling with the overall solute flux since the solute flux is always linear with concentration and two to three magnitudes smaller than the facilitated osmotic flux (see Figures 6 and 7). Similarly, the electrochemical potential merely reflects the state of the concentrations in the two solutions and the change in these concentrations with time. The electrochemical potential changed continuously during the course of an experiment (Figure 8) due to transfer of solute, while the osmotic flux was observed to be constant. This indicates that coupling between the overall cell electrochemical potential difference and the osmotic flux is not a factor in this system.

The multitudes of peaks and valleys in the plots of osmotic flux versus concentration in the work of others did not appear in these studies of anomalous osmosis. However, other works used different membrane with more variable swelling characteristics, etc., so direct comparisons are difficult (Carr and Sollner, 1962; Fujita and Kobatake, 1968; Tasaka et al., 1969). However, almost all experimenters who investigated osmosis through cation exchange membrane found a facilitation in the values of the observed water flux which causes the osmosis to attain values higher than that possible from purely normal osmotic effects.

Various workers have observed anomalous negative osmosis. Weinstein and Caplan (1968) observed the phenomenon in study of the solvent flux through a membrane separating KCl solutions where the membrane (mosaic) contained both positive and negative fixed charges. Hansen and Anderson (1967) observed the effect in dialysis of acids through anion exchange membranes. The data of Hansen and Anderson shows deviations from a normal osmotic line for all acids studied with H_2SO_4 and H_3PO_4 definitely exhibiting net anomalous negative osmosis at low normalities, and then a net positive osmosis at higher normalities. The acids HNO_3 and HCl also indicate that negative osmosis is present in the system even though the net solvent flux was always in the positive direction. Fujita and Kobatake (1968) and Toyoshima et al. (1967) showed that for oxidized collodion membrane, anomalous negative osmosis occurred for the solute LiCl, but only anomalous positive osmosis occurred for KIO_3 and KCl. These authors demonstrated that the osmotic behavior of sucrose solutions did not indicate anomalous osmosis of any kind. Grim and Sollner (1960) showed both anomalous positive and anomalous negative osmosis using oxyhemoglobin collodion membrane in both the positive and negative charge state for single electrolytes. In the negative state, LiCl and $MgCl_2$ exhibited negative osmosis, while KCl and K_2SO_4 exhibited positive osmosis. In the positive state, KIO_3 and K_2SO_4 exhibited negative osmosis, while $MgCl_2$ and KCl exhibited positive osmosis. Grim and Sollner also studied systems where different electrolytes were separated by an ion exchange membrane, and the osmosis observed was both positive and negative. Studies of osmosis in a system where a membrane separates the solutions containing different electrolytes may have application in certain biological areas; for example, Praissman et al. (1973) in similar studies noted that anomalous osmosis may be the cause of the production of a hypotonicity in the gastric fluid relative to that in plasma. Praissman et al. (1973) felt that the osmotic flux in anomalous osmosis and electroosmosis resulted from a common mechanism. Tasaka et al. (1969) observed anomalous negative osmosis with both NaCl and LiCl solutions separating collodion-sulfonated polystyrene membrane. The direction of the water flux was dependent on the solute concentration ratio.

Dawson et al. (1969) noted that in studies of anomalous osmosis through Zeo-Karb 315 cation exchange membrane separating solutions of $SrBr_2$, the osmosis was positive for lower concentration differences, and then became negative as the magnitude of the concentrations and the concentration difference increased. Dawson et al. stated that the reversal in flow could not always be explained by thermodynamic treatments (for example, Kedem and Katchalsky, 1961) in a straightforward manner.

The thermoosmosis data is apparently devoid of any

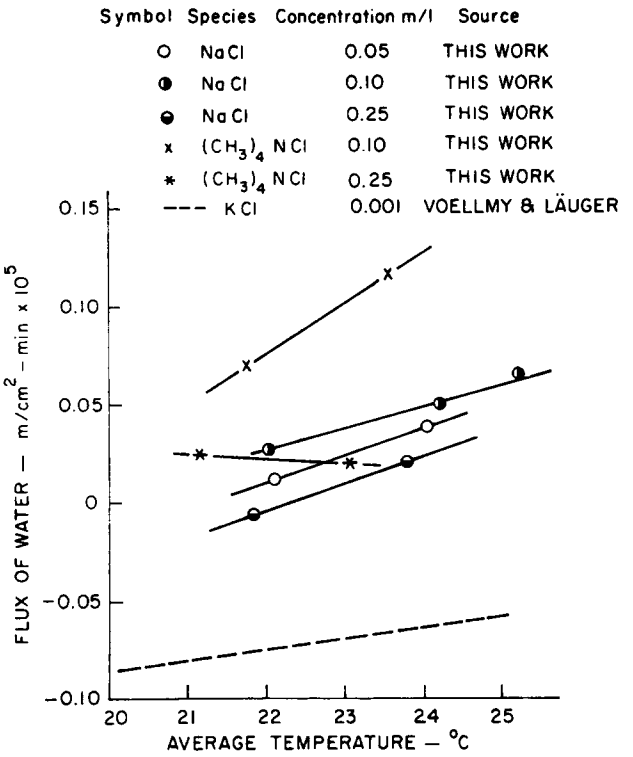

Fig. 13. Flux of water versus average temperature of the system.

normal component since thermoosmosis has not been observed unless a solute electrolyte and charged membrane are present. A continuation of the thought presented in the previous discussion leads to the suggestion that the thermoosmosis data (Figure 11) represents only a facilitated component. It appears that the thermoosmotic flux is not coupled to either the electrochemical potential difference or the solute flux because of the different patterns in the plots (see Figures 10, 11, and 12).

Unfortunately, studies of thermoosmosis are scarce in the literature so comparisons are difficult to make. However, Voellmy and Läuger (1966) did perform some studies with phenol sulfonic acid membranes with KCl as a solute. Since the membrane used in this work was somewhat similar (polystyrene-divinyl benzene-sulfonic acid), comparisons are useful. The data of their work can be compared with the data of this work by examination of Figure 13. In Figure 13, osmotic flux is plotted versus average temperature in order to follow the convention of Voellmy and Läuger. Below 38°C, Voellmy and Läuger observed an osmotic flux from the warm side to the cold side (shown negative here) for 0.001 m/l KCl. Above 38°C, the flux went from the cold side to the warm side of the membrane system. The data of this work is displaced above that for Voellmy and Läuger, perhaps as expected because of the different concentration levels. Examination of Figure 13 reveals that the crossover point where the direction of the flux may reverse is also concentration dependent. The downward slope of the 0.25 m/l $(CH_3)_4NCl$ data indicates that a rise in the value of the flux with average system temperature may not always be universal. The scant data presented here, along with the meager amount in the literature, certainly indicate that further experimental studies are warranted.

Carr and Sollner (1962) observed both negative and positive osmosis in studies of positively and negatively charged membranes. The characteristic peak observed by Sollner for K_2SO_4 and $MgSO_4$ solutions was also observed in this work for NaCl and $(CH_3)_4NCl$ (see Figure 11).

SUMMARY

Measurement of anomalous osmosis and thermoosmosis was conducted whereby the osmosis, changes in electrical conductance of the solutions, the electrochemical potential difference, and the temperatures were continually monitored. A preferred apparatus design and method of experimentation has been suggested. Comparative data based on use of chloride salts and a representative commercial cation exchange membrane indicate aspects of the phenomena noted by other workers.

Anomalous osmosis and thermoosmosis are likely caused by the same phenomenon (for example, see Carr and Sollner, 1962; Freundlich, 1922). Anomalous osmosis appears to be composed of two factors, a facilitated component and a normal component. Thermoosmosis seems to be caused by only the facilitated component. Theoretical explanations of the data from this work and from other workers are now being compiled.

ACKNOWLEDGMENT

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NOTATION

A = cross-sectional area of the membrane
A_c = cross-sectional area of the capillary
c = electrolyte concentration
C_0 = electrolyte concentration in the cell at time zero
J_s = molar flux of solute through the membrane
J_w = molar flux of water through the membrane
k = electrical conductance
n_s = moles of solute
n_w = moles of water
t = time
T = temperature
U_c = meniscus velocity
V_f = volume of the stirred cell chamber
V_{fc} = volume of the stirred cell plus connecting capillary
$\overline{V}_s$ = partial molar volume of solute
$\overline{V}_w$ = partial molar volume of water
V_w^0 = molar volume of water

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Onset of Fluidization and Slugging in Beds of Uniform Particles

A comprehensive investigation has been made of the boundaries of the regime of bubbling aggregative fluidization. Experiments were done with sand, glass beads, clover seed, and iron shot fluidized with helium, air, and freon-12 in columns 2.5, 5, 10, and 21 cm in diameter. Bed heights ranged from 1 to 60 column diameters, particle diameters from 0.07 to 1.1 mm, particle densities from 1300 to 7600 kg/m^3, and gas densities from 0.17 to 5.2 kg/m^3. Correlations are presented for the void fraction at the minimum bubbling point and for the superficial fluid velocity at the points of minimum fluidization, minimum bubbling, and minimum slugging.

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SCOPE

Fluidization of a bed of particles occurs when the particles are effectively suspended in a stream of fluid flowing through the bed, that is, their weight is balanced by the buoyancy and drag due to the fluid. Under certain conditions, normally in fluidization by gases, the regime called *aggregative fluidization* is observed which is characterized by the appearance of two phases: a dense phase in which the voidage is about the same as in the bed at the onset of fluidization, and a dilute phase in which the particle population is very sparse. At moderate fluid flow rates the dense phase is continuous and the dilute phase characteristically takes the form of a stream of rising bubbles. With increasing flow rate, however, a point may be reached where bubbles appear that extend across the bed; these bubbles are called *slugs*, and the condition is referred to as *slugging*. The practically useful regime of aggregative fluidization is bounded by the beginning of bubbling at low superficial fluid velocities and by the onset of slugging at high velocities. The bed-mixing action of the bubbles is responsible for most of the technical advantages of aggregative fluidization. The occurrence of slugging is accompanied by marked deterioration in both the quality of bed mixing and the quality of gas-particle contacting. The passage of slugs out of the bed, moreover, produces large pressure fluctuations and pounding which can be mechanically damaging to equipment.

It is thus practically important to be able to predict the limits of the regime of good aggregative fluidization. Attention is focused on: (1) the point of minimum bubbling, most precisely defined by aggregatively fluidizing a bed and then gradually reducing the fluid flow rate to the point where bubbles no longer appear, and (2) the point of minimum slugging, defined as the point at which

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