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Superseparation: Soret Effect Reversed

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COMMUNICATION

Superseparation: Soret Effect Reversed

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Abstract

The Soret effect is attributable primarily to the fact that osmotic pressure is the same across a solution when heating one side and cooling the other. When Whatman #40 filter paper was interspersed throughout an aqueous solution to minimize disturbance of the Soret effect caused by convection, the Soret effect was reversed. The concentration increased exponentially from nearly pure water at the cooled surface to many times the initial concentration at the heated surface. If the solution and filter paper were degassed, then the Soret effect was normal. We conclude that microbubbles of air (about 9% by volume) were entrained in the solution by the filter paper so that water vaporized on the warmer side of each bubble and condensed on the cooler side, thereby concentrating the solution near its heated surface and diluting it near its cooled surface.

About 100 years ago Soret demonstrated that a partial separation of solute and solvent occurs in a solution when one side is heated and the opposite side is cooled. If the heated upper surface of a 1-*M* solution is at 50°C while the cooled lower surface is maintained at 0°C, the solution near the cooled surface will become slightly more concentrated than the solution near the heated surface (*1*). At these temperatures the ratio of concentrations at the heated and cooled surfaces ought to be about 273/(273 + 50) or 0.85, for which the Soret coefficient would be $\sigma = (1/c)(\Delta c/\Delta T) = -3.1 \times 10^{-3}\,{}^\circ\mathrm{K}^{-1}$. This small separation of solute and solvent is achieved only after many hours or a few days when the solution between heated and cooled surfaces is a few centimeters in depth. The steady-state linear concentration gradient is attributed primarily to the diffusion of the solute molecules toward the cooled surface and the solvent molecules toward the heated surface until the osmotic pressure, which is proportional to the absolute temperature, is the same throughout the solution. Several lesser influences effect the Soret coefficient. These include (a) the effect of temperature on the diffusion coefficients of solute in solvent and solvent in solute, (b) the effect of temperature on the dissociation constant of solutes which ionize in the solvent, (c) the relative density of solute and solvent, and (d) convection within the solution which diminishes the Soret effect (*2*). In a study intended to minimize the influence of convection within the solution, several inert matrix materials were introduced into.the solution. Most of these materials appeared to diminish the convection and enhance the Soret effect. However, when several layers of filter paper (Whatman #40) were introduced into a 1-*M* solution of sucrose, a reversal of the Soret effect was discovered. The solution near the heated surface became highly concentrated whereas the solution near the cooled surface became very dilute.

The design of the Soret cell used for the results reported here is shown in Fig. 1. Water was circulated to and from the upper chamber and heated by a Lauda K-2/R temperature bath. A similar bath circulated cold water to the lower chamber. The cell was routinely filled with the solution with or without a matrix and allowed to run 24 or more hours at selected temperatures before samples were removed. To remove a 10-μL sample from the upper (or lower) surface of the cell, the wire plug was removed from the upper *X* (or lower *Y*) PE 20 tubing and slight pressure was applied to a syringe which contained solution identical with that initially in the cell and joined to tubing *Z*. The sample was collected on a 6.5-mm diameter cellulose disk lying on a glass plate and was immediately protected from evaporation by a cover. To measure the osmolality of the sample solution, the saturated disk was introduced into the sample well of a Wescor Model 5100B vapor pressure osmometer. For an experimental run a sample was obtained from the heated surface of the Soret cell (after purging the PE 20 sampling tube 2 or 3 times) and measured in the osmometer. Next a sample was obtained from the cooled surface and measured. Then a sample of the original solution in the cell was measured and finally a standard solution was measured. This sequence was repeated 7 times, and the average and standard deviation for each of the four solutions was obtained. A repeat run was made on subsequent days to verify steady-state results for a given combination of solution and matrix material.

Average osmolalities are given in Table 1 of samples withdrawn from the heated and cooled surfaces of several solutions in the Soret cell. Solutions without a matrix in the cell gave a less negative Soret coefficient than when a matrix was included. That is, all solutions tested, which included a matrix of glass beads or of polyurethane air filter with the solution, gave

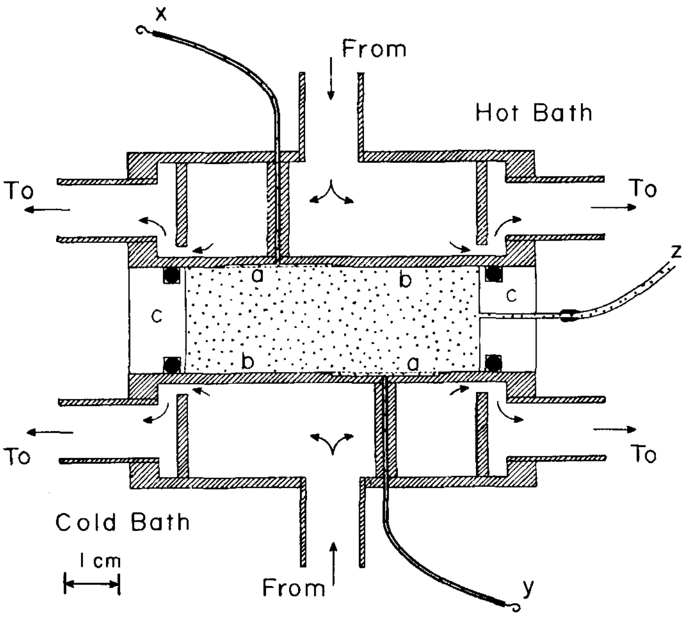

FIG. 1. Cross section of Soret cell employed. *a* denotes a Teflon-coated stainless steel screen (Millipore Cat. No. xx3002515); *b* denotes gold-plated surface of brass chamber through which hot or cold water was circulated; *c* denotes acrylic wall of cell with O-ring seals. To remove a sample from the hot surface the pin was removed from the end of the PE tubing at *X* and slight pressure was applied to a syringe (not shown) containing the solution and joined to the PE tubing at *Z*. Sample from the cold surface was similarly removed from the end of the PE 20 tubing at *Y*. Not shown in the figure is a plastic ring above the hot chamber and another below the cold chamber. The cell was sealed by clamping the upper and lower rings with six screws near the periphery of the rings. The acrylic wall *c* was sealed to the lower chamber with marine sealant. The entire system was surrounded by 2 cm of styrofoam insulation (not shown).

lower concentrations near the heated surface and higher concentrations near the cooled surface than with the solution alone. For a 1-*M* glycerol solution, $\pi_{60}/\pi_{10} = 0.85$, the same ratio as $T_{\text{lower}}/T_{\text{upper}} = 283/333$ when the solution was in a polyurethane matrix. Glucose and sucrose with glass beads gave similar ratios, $\pi_{60}/\pi_{10} = 0.89$ and 0.80, respectively. These results on nonelectrolytes tend to confirm Soret's expectation that the osmolality of a solution would be constant at all levels in a stable thermal gradient across the solution. Results on electrolytes deviate considerably from this expectation. For $CuSO_4$, $\pi_{60}/\pi_{10} = 0.43$. This suggests that $CuSO_4$ was more dissociated at 333°K than at 283°K, so that removing the solution from the heated surface reassociated some ions, and removing

TABLE 1

Soret Effect: Normal and Reversed

Solution (g solute/kg H_2O)	Matrix material	T_{upper} (°C)	T_{lower} (°C)	Elapsed time (hr)	π_{upper} (mosmolal SD)	π_{lower} (mosmolal SD)
342.3 Sucrose (1063 ± 8)[a]	None	65	15	48	974 ± 12	1114 ± 14
74.55 KCl (1718 ± 5)	None	65	15	48	1695 ± 20	1781 ± 3
342.3 Sucrose (1067 ± 4)	Glass beads	65	15	48	959 ± 13	1144 ± 10
281.6 $CuSO_4 \cdot 5H_2O$ (1265 ± 12)	Glass beads	65	15	26	590 ± 24	1388 ± 42
32.16 NaCl + 10 g gelatin (1002 ± 3)	Polyurethane air filter[b]	60	10	67	949 ± 9	1059 ± 13
92.1 Glycerol (982 ± 5)	Polyurethane air filter[b]	60	10	50	882 ± 4	1041 ± 4
24.06 NaCl (710 ± 2)	Whatman #40[c]	60	10	70	3126 ± 67	57 ± 8
342.3 Sucrose (1066 ± 9)	Whatman #40[c]	60	10	44	3018 ± 252	63 ± 12
Distilled H_2O (42 ± 3)[d]	Whatman #40[c]	60	10	24	46 ± 6	44 ± 3
Seawater	Whatman #40[c]	60	10	68	5450 ± 255	0
32.13 NaCl (1009 ± 4)	Whatman #40[e]	50	0	19	1026 ± 27	1004 ± 6

[a] Osmolality of solution as measured in osmometer ± standard deviation.

[b] "Breeze easy" manufactured by Midwest Air Filters, Inc. Chicago, Illinois 60622; solution and filter degassed 1 hr before loading into Soret cell.

[c] 75 filter paper disks (55 mm diameter) immersed in solution entrapped 5 to 10% gas by volume. The volume of gas, V_g, entrapped in the filter paper immersed in the solution was measured by injecting a volume of solution ΔV into the volume of the solution and matrix in the Soret cell, V, and measuring the increase in pressure from p to $p + \Delta p$. In these tests $V = 48$ cm^3, ΔV was about 0.4 cm^3, and Δp was usually around 100 cm H_2O. Thus, assuming that only the gas was compressed by Δp and its volume decreased by ΔV, $V_g = (1 + p/\Delta p)\Delta V$ and was about 9% of the cell volume. When the solution plus the 75 disks of filter paper were evacuated for 30 min, ΔV was <0.03 cm^3 and Δp was >135 cm H_2O so that V_g was $<0.4\%$ of the cell volume.

[d] The Wescor vapor pressure osmometer was routinely calibrated with 1000 mosmolal NaCl standard. It is not reliable below 100 mosmolal.

[e] Filter paper and solution degassed 1/2 hr by vacuum extraction; contained $<0.4\%$ gas by volume. See Footnote *c* above.

sample from the cooled surface and raising it to room temperature in order to measure its osmolality by vapor pressure depression dissociated some of its molecules. NaCl and KCl are nearly completely dissociated at these temperatures so they did not show this effect. However, even in the best matrix we employed, a combination of the air filter matrix and a 1% concentration of gelatin, the lowest ratio we achieved was 0.90 with 1 osmolal solution of NaCl.

When the matrix was Whatman #40 filter paper, π_{60}/π_{10} increased to extremely high values. Ratios greatly in excess of one were obtained for 1 osmolal solutions of NaCl, glycerol, sucrose, and seawater. In a 0.7-osmolal solution of NaCl, the ratio of concentrations near the hot and cold surfaces was over 200 when these surfaces were 333 and 283 °K, respectively. Inverting the temperature gradient also caused the concentrations to invert so that the high concentration was always associated with the high temperature regardless of whether it was removed from the upper or lower surface. The concentrations of samples removed from both surfaces maintained at 333 °K did not differ from the initial concentration. With distilled water in the cell with Whatman #40 paper, samples removed from surfaces at 333 and 283 °K did not differ from distilled water. Confining a 1-osmolal solution with Whatman #40 filter paper in closed vials and maintained 24 hr at 60 and 10 °C did not alter the osmolality of samples from either vial. When the filter paper and a 1000-mosmolal NaCl solution were degassed by evacuating the filter paper in the solution for one-half hour prior to entry into the cell, there was practically no separation and $\pi_{50}/\pi_0 = 0.965$.

A possible mechanism for the reversal of the Soret effect is that entrapped gas in the filter paper served as a channel for diffusion of solvent vapor. The vapor pressure of solvent increases exponentially with temperature. Thus, in an aqueous solution, vaporization into the entrapped gas would be greater toward the heated surface and thereby concentrate the solution nearer the heated surface. Water vapor would diffuse through the entrapped gas toward the cooled surface where the vapor pressure would be less, and it would condense and dilute the solution near the cooled surface. Since the diffusion coefficient for water vapor through air is approximately 10^4 times the diffusion coefficient for solute molecules through liquid water, water vapor near the heated surface will diffuse many times more readily toward the cooled surface than the rate solute can diffuse from high to low concentration. While the temperature increased linearly from cooled to heated surface, the vapor pressure of the solvent increased exponentially. When a steady state was achieved such that the solute concentrations throughout the solution were no longer changing, it can be assumed that the rate water vapor diffused toward the cooled surface at any distance from the cooled surface would be the same as the rate solute diffused toward the cooled surface at that same distance. The rate water vapor diffused and the rate solute diffused would be the same and greatest at the heated surface and the same and least at the cooled surface. At the heated surface the diffusion of water vapor was greatest because it is proportional to the vapor pressure gradient which was highest at the heated surface. The diffusion of solute was greatest at the heated surface because it is proportional to its concentration gradient which became greatest at the heated surface according to our hypothesis.

To test this hypothesis, we measured the steady-state concentration as a function of distance from the heated to the cooled surfaces. The space between the lower cooled surface and the heated upper surface was filled with 78 disks of Whatman #40 filter paper and flooded with 200 mosmol NaCl/kg H_2O. For 24 hr the heated and cooled surfaces were maintained at 50 and 0°C respectively. Then the bottom or disk #1, disks 19, 28, 38, 48, 68, and 78 or top disk were removed and each enclosed separately in a 10-mL syringe. Four 50-μL samples were squeezed from each disk and each sample's osmolality was measured in a Knauer freezing point depression osmometer. The average osmolality of solution from each disk was plotted as a function of the disk position from top to bottom. The regression line for the data was the exponential $\pi = 3.8e^{0.073n}$ for which the coefficient of determination was $r^2 = 0.98$ and where n was the disk number from 1 to 78. For four additional experiments, the r^2's for an exponential regression line were 0.95, 0.98, 0.95, and 0.97. When the same data for each of these 5 runs were fitted to a linear regression, the coefficients of determination were in all cases much less, i.e., r^2 was 0.69 ,0.69, 0.62, 0.77, and 0.76, respectively. Thus our expectation that the osmolality and concentration distribution increased exponentially from cold to hot surfaces was confirmed.

Continuous separation of seawater into potable water from the cooled surface was not possible in the cell illustrated in Fig. 1 because the entrapped air in the filter paper was slowly absorbed by the condensate and removed from the cell. Continuous production of potable water was achieved, however, from a film of seawater flowing down a heated surface and supported a fraction of a millimeter from a cooled surface on which the vapor condensed and drained into a collecting trough below.

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REFERENCES

1. M. Ch. Soret, *Arch. Sci. Phys. Nat.*, *12*, 615 (1884); C. C. Tanner, *Trans. Faraday Soc.*, *49*, 611 (1953); H. J. V. Tyrell, *Natl. Bur. Stand.* (*U.S.*), *Circ. 524*, 119 (1953).
2. M. G. Verlarde and R. S. Schechter, *Chem. Phys. Lett.*, *12*, 312 (1971); D. R. Caldwell, *J. Phys. Chem.*, *77*, 2004 (1973).

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