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SORET COEFFICIENT AND THERMAL DIFFUSION CONSTANT OF AQUEOUS SOLUTIONS OF SUGARS

RICHARD S. JOHNSON AND WILLIAM NIEDERMEIER
Division of Clinical Immunology and Rheumatology, Department of Medicine, The Medical College, University of Alabama in Birmingham, Birmingham, Alabama 35233 (U. S. A.)

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ABSTRACT

The Soret coefficient was determined on aqueous solutions of glyceraldehyde, dextrose, sucrose, raffinose and stachyose. At 37°C the value of this coefficient ranged from 1.1×10^{-3} to 2.8×10^{-3}, with units of deg^{-1}. The Soret coefficient was found to be a hyperbolic function of the molecular weight of the sugar. The thermal diffusion constant can be expressed as $1.5 \pm 0.1 \times 10^{-8}$ $cm^2.deg^{-1}.sec^{-1}$. There appears to be no theoretical treatment of solutions that adequately accounts for these observations.

INTRODUCTION

Although sugars are well characterized from the standpoint of chemical and physical properties, and much is known about their biological synthesis and utilization, there is still a great deal to be learned concerning the thermochemical aspects of their solutions. Examples of such thermochemical properties are the Soret coefficient and thermal diffusion constant. Therefore, a study of the Ludwig–Soret effect was undertaken on a series of sugar solutions. The objective was to obtain a correlation between molecular weight and the Soret coefficient as well as to evaluate the thermal diffusion constant. The literature values[1] of the Soret coefficient for a group of compounds (such as the hydroxides of lithium, sodium, and potassium) would lead one to suspect that the value of this coefficient might be proportional to the molecular weight of the solute.

If one follows the notation and sign convention adopted by De Groot[2] for a single-stage, vertical, thermal diffusion cell, the net flow in a binary liquid system is given by the relationship:

$$J_y = D\rho \frac{\partial n}{\partial y} - D'\rho\, nn' \frac{\partial T}{\partial y} \tag{1}$$

where J_y represents the flow of one component in the vertical (y) direction.

This flow, or current, is in units of mass flow per unit time per unit area, wherein the area is normal to the y direction. In this expression, ρ is the density, n and n' are the solute and solvent concentrations in weight fraction, T is the absolute

temperature, D is the ordinary diffusion constant, and D' is the thermal diffusion constant. At the steady state, $J_y = 0$. The Soret coefficient, σ, can be defined by the equation:

$$\sigma = D'/D \tag{2}$$

For fairly dilute binary systems, $nn' = n$. From this, it follows that

$$\sigma = -\frac{1}{n}\frac{dn}{dT} \tag{3}$$

For small, finite differences the approximate relationship is

$$\sigma \approx -\frac{1}{\bar{n}}\frac{\Delta n}{\Delta T} \tag{4}$$

where $\bar{n}$ is the average weight fraction of solute.

In this derivation of the Soret coefficient, for which the units are per degree, it is assumed that the cell is operating under convection-free conditions, and that the current is attributable solely to the temperature and concentration gradients.

EXPERIMENTAL

Apparatus

The Soret cell used in these studies is shown in Fig. 1. Cells of this type have been previously described in the literature. Riehl[3] was the first to use a Soret cell

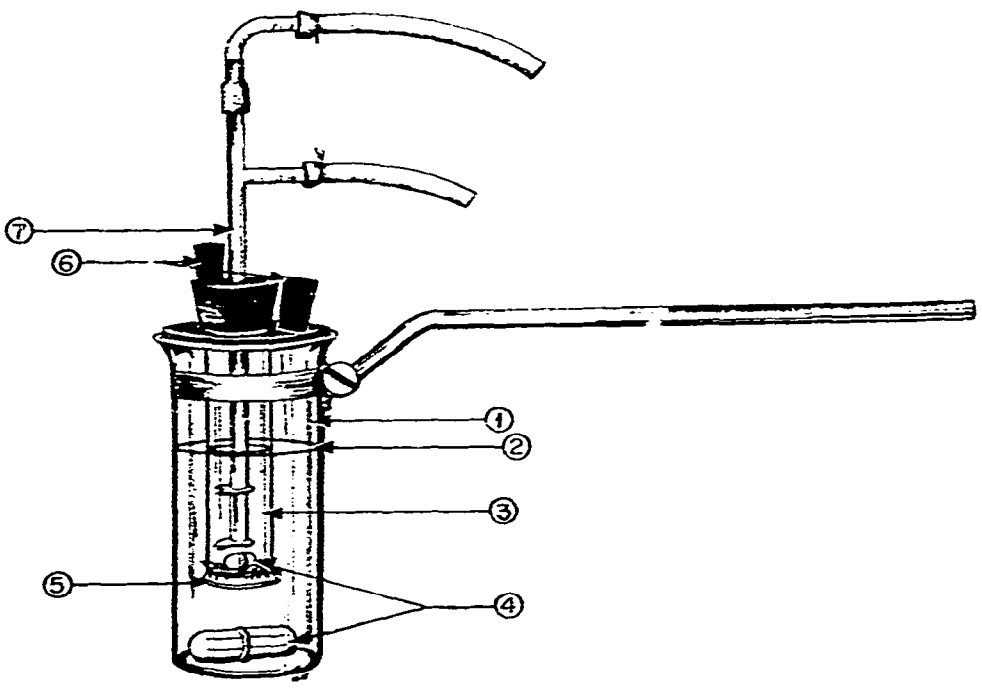

Fig. 1. General view of the cell; (1) outer compartment, (2) liquid level, (3) inner compartment, (4) stirring bars, (5) permeable membrane, (6) sample ports, (7) heat exchanger.

with agitated solutions and to have the hot and cold portions separated by a permeable membrane. The apparatus used by Morin *et al.*[4] required nearly three liters of solution. Because only 110 ml of solution was required in the present case, it can be considered as a small scale cell.

The external portion of the cell was a 180 ml electrolytic beaker, which was about 11 cm high and 6 cm in diameter at the top. The inner compartment was cut from a 2.5 cm diameter test tube. The heat exchanger used to cool the inner compartment was of the form of a cold finger condenser and was fabricated from copper. Rubber stoppers were used as closures. The single layer of cellophane used as the membrane was tied with cotton sewing thread around the flared end of the inner compartment. This cellophane was cut from commercially available dialyzer tubing, which was made of regenerated cellulose by the viscose process. It was 20 μ thick and had an average pore diameter of 48 Å. The solutions were agitated by means of rotating, magnetic, Teflon coated stirring bars. These bars were turned by means of a permanent magnet that was rotated underneath the cell.

The entire cell was immersed in a constant temperature water bath maintained at 55.0°C. The inner compartment was cooled by pumping an ethylene glycol–water solution maintained at 0.0°C through the heat exchanger. This resulted in the temperature of the bulk of the solutions in the hot and cold compartments being 48.1°C and 25.9°C, respectively. By this means the temperature difference between the two compartments of the cell was 22.2°C, and the average temperature was 37.0°C. The ports in the top of the cell, used for temperature measurement and sampling purposes, are clearly visible in Fig. 1. Temperature measurements of the bulk of the solutions were made with an Anscheutz thermometer. Thus, temperature measurements were obtained to 0.1°C.

The difference in concentration of the solute in the two compartments of the cell was determined as means of their difference in refractive index. A visual type Brice–Phoenix differential refractometer was used for this measurement. This instrument is commercially available* and its optics have been described in the literature[5]. Differences of index of refraction can be determined to the sixth decimal place.

Chemicals

The mono-, di-, and tri-saccharide sugars were dextrose, sucrose and raffinose, respectively. All of these were of CP grade. The tetrasaccharide chosen was stachyose, because it represents the best characterized sugar of all the tetrasaccharides and it is readily available in a purified form. Although glyceraldehyde is not a true sugar, it represents the first member of the aldose series. The DL form was used in this study. All of the water used for solution preparation was distilled from a borosilicate glass still.

*Phoenix Precision Instrument Co., Philadelphia, Pa., U. S. A.

Procedure

Prior to use, the cell was washed with a 70% ethanol–water mixture in an effort to reduce the growth of micro-organisms. Before installing the membrane on the inner compartment of the cell, the cellophane was soaked for several hours in a portion of the solution under consideration. This was done in order to swell the membrane and to rid it of any readily removable sulfur compounds. Both compartments of the cell were then filled and the temperature differences attained. After several hours the liquid level in the two compartments was adjusted to the same height and the cell was carefully stoppered. The length of each run was 72 h. Preliminary work with this cell, operating under these conditions, showed that the steady state was reached after about 60 h.

At the end of a run the bulk concentration of the solutions were determined with the differential refractometer. For sucrose, the computation of concentration based on difference of index of refraction was done by use of the literature values[6]. For the other substances refractive index–concentration curves were obtained from laboratory data. These curves were almost linear. For example, with dextrose at 30°C and with light of 546 nm wavelength the relationship can be represented as

$$z = 1.4523 \times 10^{-3}\, m + 5.11 \times 10^{-6}\, m^2 \tag{5}$$

where z is the difference in index of refraction of the solution with respect to water and m is the weight percent composition. This equation was fit to the data in the range of 0 to 20% by weight of dextrose.

RESULTS AND DISCUSSION

The results of the determination of the Soret coefficient, sigma, on solutions of five different concentrations of sucrose are shown in Fig. 2. It is seen that there is a random scatter of the points around the average value of $\sigma = 2.25 \times 10^{-3}$. The value

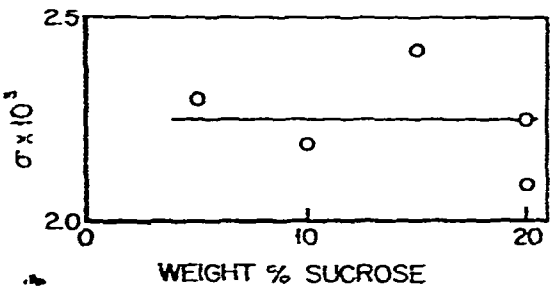

Fig. 2. The Soret coefficient of aqueous sucrose solutions at 37°C.

of sigma was independent of concentration. These results are typical of those obtained with the other four sugars used in this study. Although sucrose is highly soluble in water, 20% represents a practical upper limit of concentration because of the assumptions made in Eqn. (4). The same concentration range of 5 to 20% was used for

dextrose. The upper limits of concentration for the other sugars ranged from 2.5 to 10% because of limited solubility. The values obtained for sigma, along with the standard deviations, are summarized in Table I under the heading "Obs.". These standard deviations are consistent with the errors incurred in determining concentration and temperature differences. Stachyose was done in duplicate. The other values are the average of five determinations.

TABLE I

SORET COEFFICIENTS AND DIFFUSION CONSTANTS OF AQUEOUS SUGAR SOLUTIONS AT 37 °C

Sugar	$\sigma \times 10^3$		$D \times 10^6$	$D' \times 10^8$
	Obs.	*Calc.*		
Glyceraldehyde	1.1±0.1	1.08	12.3	1.4
Dextrose	1.6±0.1	1.74	8.5	1.4
Sucrose	2.2±0.1	2.32	6.7	1.5
Raffinose	2.7±0.2	2.62	5.8	1.6
Stachyose	2.8±0.3	2.77	5.1	1.4

The sigma value for sucrose of 2.2×10^{-3} falls between Tanner's[7] average value of 1.8×10^{-3} and the value from the work of Wereide[8] of 2.8×10^{-3}. These values from the literature were obtained at the same average temperature and over the same concentration range as the present case. These workers also found no correlation between sigma and concentration. In the literature, there appear to be no Soret coefficient values for the other sugars.

Through judicious curve fitting a hyperbolic equation was found which describes sigma as a function of the molecular weight of the sugar. A graph of the data plotted in this manner is shown in Fig. 3. The curve is that described by the equation

$$1/y = 58.3/x + 0.274 \qquad (6)$$

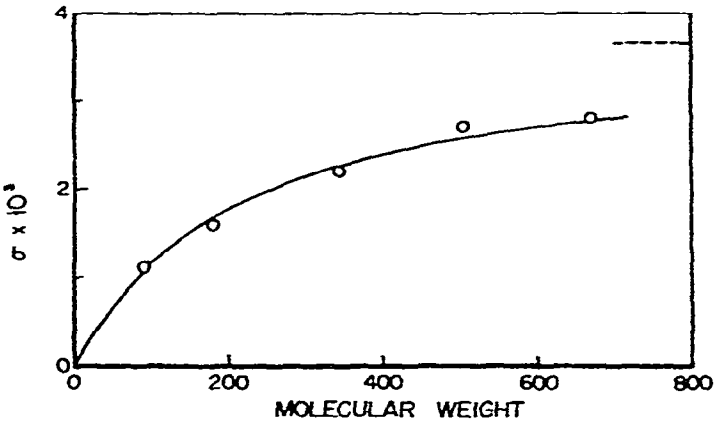

Fig. 3. The Soret coefficients of a series of sugars, plotted as a function of the molecular weight of the anhydrous sugars.

where $= \sigma \times 10^3$ and x is the molecular weight of the anhydrous sugar. The constants were obtained by the method of least squares. Eqn. (6) is the linear form of the hyperbolic relationship.

$$y = \frac{a^2bx}{abx+1} \tag{7}$$

which can be derived through several changes of variable from the equilateral hyperbola, $y' = 1/x'$. In Eqn. (6) the coefficient of $1/x$ is the reciprocal of a^2b, and the constant term is simply $1/a$.

The corresponding Soret coefficients computed from this equation, by using the known values of x, are shown in Table I under the heading "Calc.". It is seen that the computed values agree very well with the observations. The values of y when x has extreme values should be noted. When $x = 0$, $y = 0$. Intuitively, this appears to be correct, since sigma would be expected to be zero for a sugar with a molecular weight of zero. The limiting value of y when x becomes infinitely large leads to $\sigma = 3.65 \times 10^{-3}$, *viz.* the asymptote of the hyperbola.

The implication from this is that the value of sigma would have an upper limit. The broken line in Fig. 3 represents this asymptote. Unfortunately, this point is not amenable to experiment. The tetrasaccharide stachyose represents the upper practical limit of the oligosaccharides. Although linear oligosaccharides with a degree of polymerization of five through eight have been isolated, little is known about them and they are considered to be rare sugars[9]. Fairly low molecular weight water soluble polysaccharides, such as dextrans, are available. It is doubtful that the cellophane membrane would be permeable to these molecules. Moreover, dextrans are branched polymers with a molecular weight distribution. They would not be comparable to the sugars studied here.

From the definition of the Soret coefficient, Eqn. (2), it is obvious that the thermal diffusion constant, D', could be calculated if σ and D, the ordinary diffusion constant, are known. The ordinary diffusion constants of some of these sugars at 25°C are available from the literature. Fortunately, it is possible to calculate D at 37°C for all of these sugars.

Longsworth[10] found that the ordinary diffusion coefficient of sugars, amino acids, and peptides in aqueous solution at 25°C are given by the expression

$$D \times 10^6 = 24.182/(V^{1/3} - 1.280) \tag{8}$$

where D is the diffusion coefficient in square centimeters per second, and V is the apparent molecular volume of the solute in cubic centimeters per mole. This constitutes an empirial modification of the well-known Stokes–Einstein equation. Longsworth showed that this equation yields values of D within 2% of the values he observed with solutions containing 0.7 to 0.8 weight percent of the sugars dextrose, sucrose and raffinose. In turn, his observed values were within about 1% of the values tabulated in the literature[11,12] for the D of dextrose and sucrose at zero concentration. Therefore, Eqn. (8) probably gives ordinary diffusion constants at

zero concentration within a few percent of the correct value. By the use of Eqn. (8) one can calculate reasonable values for the D of glyceraldehyde and stachyose.

Although the apparent energy of activation, ΔE, for the processes of viscous flow and diffusion vary with solution concentration, the energy at zero concentration is 4.0 kcal/mol at room temperature for both processes for solutions of dextrose and sucrose[11,12]. Using this same energy increment for all the sugars in the present study, one can compute the value of D at 37°C, by use of the relationship

$$\ln \frac{D_2}{D_1} = \frac{\Delta E(T_2 - T_1)}{RT_1T_2} \tag{9}$$

This calculation is no doubt valid for the present study since the temperature difference was only 12°C. These quantities of D are shown in Table I. As one might expect, the value decreases as the molecular weight increases.

From the definition of the Soret coefficient, it is possible to calculate the corresponding value of D', which is the thermal diffusion constant in square centimeters per degree second. These values are tabulated in the extreme right column of Table I. It is interesting to note that for this group of sugars the thermal diffusion constant is simply expressed as $D' \times 10^8 = 1.5 \pm 0.1$.

In the case of gases, there has been good agreement between the thermal diffusion constants calculated from relationships based on kinetic theory and the actual observed values. This is not the case with liquids. Here, one is only able to make a qualitative description of thermal diffusion mechanisms. Because of the vast number of assumptions that one must make with liquids, attempts to predict the Soret coefficients have frequently been in error by orders of magnitude[13]. Thus, there appears to be no obvious explanation as to why the mathematical relationship between Soret coefficients and molecular weights for this series of sugars appears to be hyperbolic, or why the thermal diffusion constants change only slightly within the series.

CONCLUSIONS

Based on these results, it can be concluded that at 37°C the Soret coefficients of aqueous solutions of this series of sugars — glyceraldehyde through stachyose — are independent of the sugar concentration. There is only a small change in the numerical values of the Soret coefficients within the series, but the values can be described as a hyperbolic function of the molecular weights of the sugars. Moreover, the thermal diffusion constant can be expressed as $D' \times 10^8 = 1.5 \pm 0.1$. There is no theoretical treatment available to adequately describe these findings.

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