TRANSPORT ACROSS HOMOPOROUS AND HETEROPOROUS MEMBRANES IN NONIDEAL, NONDILUTE SOLUTIONS

I. Inequality of Reflection Coefficients for Volume Flow and Solute Flow

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ABSTRACT The Kirkwood formulation of the Stefan-Maxwell equations is used to develop the transport equations for a membrane bounded by nonideal, nondilute solutions. The reflection coefficients for volume flow and solute flow are not equal but are related by a simple expression that depends on the concentration of the bounding solutions. The ratio of the two coefficients is independent of heteroporous membrane structure and the thickness of adjacent boundary layers. Experimental measurements of these reflection coefficients for sucrose transport across Cuprophan verify this relationship; this indicates that the Onsager reciprocal relation, which is assumed by the theory, holds for nonideal, nondilute solutions. The two reflection coefficients may be made operationally identical by a simple redefinition of the osmotic driving force.

INTRODUCTION

Most studies of nonelectrolyte transport through biological membranes are interpreted in terms of the Kedem-Katchalsky equations (1) derived from irreversible thermodynamics; if only a single solute is present,

$$J_v = -L_p(\Delta P - \sigma_v RT\Delta c_s) \tag{1 a}$$

$$J_s = J_v(1 - \sigma_s)\bar{c}_s - \omega_P RT\Delta c_s, \tag{1 b}$$

where J_v is volume flux, J_s is solute flux, L_p is the hydraulic conductivity of the membrane, ω_P is the phenomenological permeability of the membrane for the solute, $\bar{c}_s$ is a mean solute concentration and RT has its usual meaning.[1] In the derivation of Eq. 1 *a* and *b*, the bounding solutions are regarded as ideal and dilute ($c_s\overline{V}_s \ll 1$, where $\overline{V}_s$ is the partial molar volume of the

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[1] Note that the signs of the transmembrane pressure difference ΔP and concentration difference Δc_s are opposite to the usual presentation. This is done for consistency with the differential form that follows. Flux is positive in the direction of increasing x, and $\Delta P = \int_0^\alpha (dP/dx)dx = P(\alpha) - P(0)$, where $x = 0$ and $x = \alpha$ correspond to the two faces of the membrane. A similar equation can be written for Δc_s.

solute), and the Onsager reciprocal relation (ORR) is assumed; under these conditions, the reflection coefficients for volume and solute flow, σ_v and σ_s, respectively, are equal.

The validity of the ORR in membrane transport has been verified for rather dilute solutions (2). However, experiments reported here, using more concentrated solutions, yield values of σ_s which do not equal σ_v. Before attributing this difference to a failure of the ORR at higher concentrations, the expected influences of solution nonideality and nondiluteness on the relationship between the two coefficients must be determined.

In this paper, the transport equations for a membrane bounded by nonideal, nondilute solutions are developed. It is shown that σ_s and σ_v are not equal in such solutions, even when the ORR holds. A simple relationship between σ_s and σ_v is derived, that depends on the diluteness and ideality of the bounding solutions and is independent of the degree of heteroporosity of the membrane and the thickness of adjacent boundary layers. Experimental measurements of σ_s and σ_v for sucrose transport across Cuprophan are presented, that verify the predicted relationship and indicate that the ORR remains valid for membrane transport in concentrated solutions.

THEORY

The theoretical development summarized below is based on the Kirkwood formulation of the Stefan-Maxwell equations (3). The local fluxes of solvent and solute are expressed in terms of generalized diffusivities and the exact chemical potential gradients of the two components. The equations are linearized and integrated across the membrane to yield flux equations similar in form to Eq. 1 *a* and *b* and involving three interaction coefficients. The definitions of σ_s and σ_v are used to express the reflection coefficients in terms of the interaction coefficients, at which point the relation between σ_s and σ_v becomes apparent.

Flux Equations from the Kirkwood Formulation

The Kirkwood formulation for the flux of the *i*th species (s, solute; w, solvent) relative to a stationary membrane gives (reference 3, p. 255)

$$\frac{d\mu_i}{dx} = RT\frac{d \ln a_i}{dx} + \overline{V}_i\frac{dP}{dx} = RT\sum_{j-s,w}\frac{J_j}{cD_{ij}}, \qquad (i = s,w), \tag{2}$$

where μ_i and a_i are the chemical potential and the activity of the *i*th species, $c = c_w + c_s$ is the total molar concentration, and the $\{D_{ij}\}$ are the multicomponent diffusivities of the pair (i,j). The ORR, which is assumed to be valid, implies that $D_{ij} = D_{ji}$. The activity gradients of the solute and solvent are related by the Gibbs-Duhem equation (4): $\Sigma_i\, c_i d \ln a_i = 0$; rearranging,

$$d \ln a_w = -\frac{c_s}{c_w} d \ln a_s. \tag{3}$$

The activity of the solute is related to its concentration by $a_s = \gamma_s c_s$, where γ_s is the activity coefficient of the solute; therefore

$$d \ln a_s = \frac{1}{c_s}\left(1 + \frac{d \ln \gamma_s}{d \ln c_s}\right) dc_s. \tag{4}$$

Substituting Eqs. 3 and 4 into Eq. 2,

$$\frac{RT}{c_s}\left(1+\frac{\mathrm{d}\ln\gamma_s}{\mathrm{d}\ln c_s}\right)\frac{\mathrm{d}c_s}{\mathrm{d}x}+\overline{V}_s\frac{\mathrm{d}P}{\mathrm{d}x}=\frac{RTJ_s}{cD_{ss}}+\frac{RTJ_w}{cD_{sw}}$$

$$-\frac{RT}{c_w}\left(1+\frac{\mathrm{d}\ln\gamma_s}{\mathrm{d}\ln c_s}\right)\frac{\mathrm{d}c_s}{\mathrm{d}x}+\overline{V}_w\frac{\mathrm{d}P}{\mathrm{d}x}=\frac{RTJ_s}{cD_{ws}}+\frac{RTJ_w}{cD_{ww}}.$$

The equations above must be integrated across the membrane of thickness α to become comparable to Eq. 1 *a* and *b*. The integration of the right-hand sides is accomplished formally (3), defining

$$r_{ij}=RT\int_0^\alpha\frac{\mathrm{d}x}{cD_{ij}};$$

since $D_{sw}=D_{ws}$, then $r_{sw}=r_{ws}$. The integrals of the left-hand sides are approximated by assuming that the concentrations of the solutions bounding the membrane are close enough that each multiplier of $\mathrm{d}c_s/\mathrm{d}x$ can be separately averaged. Then,

$$\frac{1+\Gamma}{\bar{c}_s}RT\Delta c_s+\overline{V}_s\Delta P=r_{ss}J_s+r_{sw}J_w$$

and

$$-\frac{1+\Gamma}{\bar{c}_w}RT\Delta c_s+\overline{V}_w\Delta P=r_{sw}J_s+r_{ww}J_w,$$

where $\bar{c}_i=[c_i(0)+c_i(\alpha)]/2$ for $|\Delta c_i|/c_i\ll 1$ and $\Gamma\equiv\overline{\mathrm{d}\ln\gamma_s/\mathrm{d}\ln c_s}$; Γ is a measure of the influence of nonideality on the transport process. Solving for J_s and J_w, and using $J_v=J_w\overline{V}_w+J_s\overline{V}_s$ and $\overline{V}_s\bar{c}_s+\overline{V}_w\bar{c}_w=1$,

$$J_s=\frac{1}{\mathcal{D}}\left[(\overline{V}_s r_{ww}-\overline{V}_w r_{sw})\Delta P+\frac{r_{ww}(1-\overline{V}_s\bar{c}_s)+\overline{V}_w\bar{c}_s r_{sw}}{\bar{c}_s(1-\overline{V}_s\bar{c}_s)}(1+\Gamma)RT\Delta c_s\right] \tag{5 a}$$

$$J_v=\frac{1}{\mathcal{D}}\Bigg[(\overline{V}_w^2 r_{ss}-2\overline{V}_w\overline{V}_s r_{sw}+\overline{V}_s^2 r_{ww})\Delta P$$
$$-\frac{\overline{V}_w^2\bar{c}_s r_{ss}+\overline{V}_w r_{sw}(1-2\overline{V}_s\bar{c}_s)-\overline{V}_s r_{ww}(1-\overline{V}_s\bar{c}_s)}{\bar{c}_s(1-\overline{V}_s\bar{c}_s)}(1+\Gamma)RT\Delta c_s\Bigg], \tag{5 b}$$

where $\mathcal{D}=r_{ss}r_{ww}-r_{sw}^2$. The solute and volume fluxes depend on three interaction coefficients, r_{ww}, r_{sw}, and r_{ss}.

Relation Between the Reflection Coefficients σ_s and σ_v

The experimental values of σ_s and σ_v are obtained using the following equations, which proceed from Eq. 1 *a* and *b*:

$$\sigma_s=1-\frac{J_s}{\bar{c}_s J_v}\bigg|_{\Delta c_s=0} \tag{6 a}$$

$$\sigma_v=\frac{\Delta P}{RT\Delta c_s}\bigg|_{J_v=0}. \tag{6 b}$$

Using Eq. 5 *a* and *b*, each reflection coefficient can be written in terms of the interaction coefficients:

$$\sigma_s = \frac{\bar{c}_s(\overline{V}_w^2 r_{ss} - 2\overline{V}_w\overline{V}_s r_{sw} + \overline{V}_s^2 r_{ww}) - \overline{V}_s r_{ww} + \overline{V}_w r_{sw}}{\bar{c}_s(\overline{V}_w^2 r_{ss} - 2\overline{V}_w\overline{V}_s r_{sw} + \overline{V}_s^2 r_{ww})} \tag{7 a}$$

$$\sigma_v = \frac{(1+\Gamma)[\overline{V}_w^2\bar{c}_s r_{ss} + \overline{V}_w r_{sw}(1 - 2\overline{V}_s\bar{c}_s) - \overline{V}_s r_{ww}(1 - \overline{V}_s\bar{c}_s)]}{\bar{c}_s(1 - \overline{V}_s\bar{c}_s)(\overline{V}_w^2 r_{ss} - 2\overline{V}_w\overline{V}_s r_{sw} + \overline{V}_s^2 r_{ww})}. \tag{7 b}$$

By inspection,

$$\sigma_s = \sigma_v\left(\frac{1 - \bar{\nu}_s}{1 + \Gamma}\right), \tag{8}$$

where $\bar{\nu}_s \equiv \overline{V}_s\bar{c}_s$ is a measure of the nondiluteness of the solutions bounding the membrane.

In the experiment section that follows, simultaneously measured values of σ_v and σ_s are used to test Eq. 8. The experimental coefficients are found from Eq. 6 *a* and *b*, using values of Δc_s that refer to the concentrations in the bulk solutions on either side of the membrane. These concentrations differ from those immediately adjacent to the membrane because of the presence of boundary layers. It is shown in Appendix A that Eq. 8 is expected to hold for the experimental reflection coefficients in the presence of boundary layers, indeed, even if the membrane is heteroporous.

EXPERIMENT

A novel membrane transport apparatus (5) was used to measure simultaneously ω_P, L_p, σ_v, and σ_s. For the solute-membrane system sucrose-Cuprophan 150PM, σ_v was found to be greater than σ_s over the entire concentration range studied (300–900 mM).

Methods

The phenomenological transport coefficients for each membrane sample were determined in a single experiment with the membrane transport chamber described previously (5). The apparatus enables the concurrent measurement of the concentration difference across the membrane (by laser interferometry) and the volume flow through it (by calibrated capillary tubes). The pressure head across the membrane was held constant, and the transmembrane concentration difference decreased exponentially with time from its initial value. Plots of volume flow and rate of change of concentration difference ($\delta\Delta c_s/\delta t$) as a function of Δc_s were straight lines whose slopes and intercepts were used to determine ω_P, L_p, σ_v, and σ_s. For the experiments reported here, a constant hydrostatic pressure difference of ~140 cm H_2O was opposed by an initial concentration difference of 40 mM sucrose; the initial volume flow was against the hydrostatic pressure head. As Δc_s decreased during the experiment, the volume flow eventually changed direction. A typical experiment lasted 6 h.

In all experiments, the temperature of the chamber was maintained at 37°C by the circulation around the chamber of water from a temperature-controlled bath. The solutions on each side of the membrane were stirred by magnetically coupled spinner blades driven at 300 rpm. All experiments were performed on samples from a single batch of Cuprophan 150PM.

RESULTS

Transport measurements were made at four mean sucrose concentrations. The values of ω_P, L_p, and σ_v were similar to those reported in a previous study in which σ_s was not determined

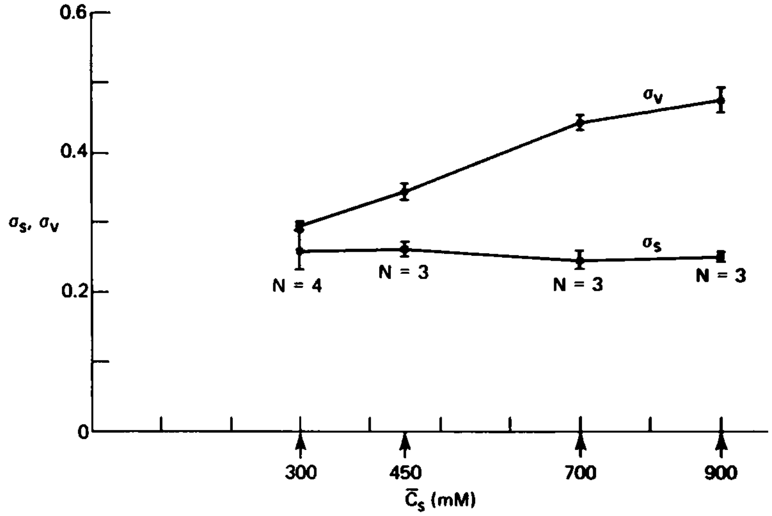

FIGURE 1 Concentration dependence of volume flow (σ_v) and solute flow (σ_s) reflection coefficients for sucrose transport across Cuprophan; ± 1 SEM error bars are shown.

(6). As shown in Fig. 1, σ_s is essentially independent of $\bar{c}_s$, whereas σ_v decreases as $\bar{c}_s$ decreases, and at low $\bar{c}_s$ approaches σ_s.

DISCUSSION

As noted above, the equality of σ_s and σ_v is predicted by the irreversible thermodynamic description of membrane transport in ideal dilute solutions, subject to the assumption that the ORR is valid. Other descriptions of transport in ideal dilute solutions yield the same result. Levitt (7) used a kinetic treatment to describe solute and solvent transport through an array of pores in which the molecules of the two species could not pass one another and found that $\sigma_s = \sigma_v$ when the fraction of pores containing solute was vanishingly small. A continuum hydrodynamic model by the same author (8) yielded the same result, in contrast to an earlier hydrodynamic analysis by Anderson and Malone (9).

In this paper, it is shown that σ_s and σ_v are not equal when the membrane is bounded by nonideal, nondilute solutions. The relationship between σ_s and σ_v is given by a simple expression (Eq. 8) dependent on $\Gamma = d \ln \gamma_s / d \ln c_s$, which is a measure of the nonideality of the bounding solutions, and $\bar{\nu}_s = \bar{V}_s \bar{c}_s$, which is a measure of their nondiluteness. As shown in Appendix A, this relationship between σ_s and σ_v is independent of certain membrane structure and the presence of boundary layers. Thus, even if the ORR holds, σ_s is expected to be a concentration-dependent fraction of σ_v, approaching σ_v as the solutions become more dilute ($\bar{\nu}_s \rightarrow 0$) and more ideal ($\Gamma \rightarrow 0$).

Our measurements of sucrose transport across Cuprophan indicate that σ_s and σ_v are not equal (Fig. 1). The experimental values of σ_s/σ_v are plotted against $\bar{c}_s$ in Fig. 2. The measured ratios correlate well with those predicted by Eq. 8 and thus provide experimental evidence for the validity of the theory on which it is based, suggesting in turn that the ORR holds for

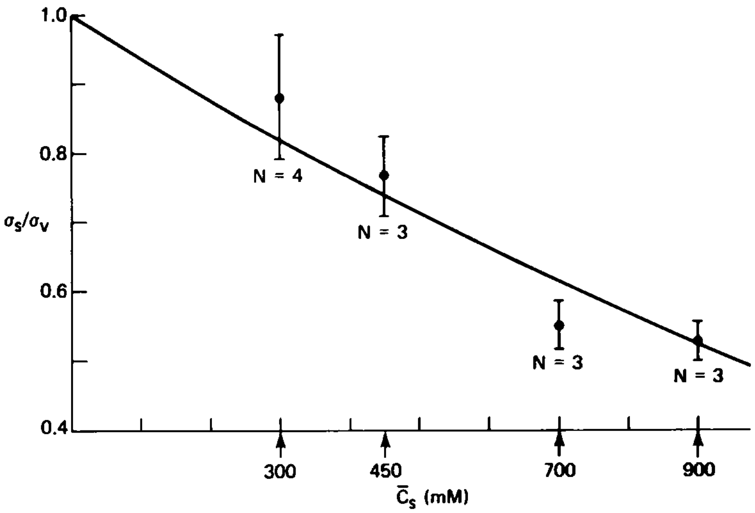

FIGURE 2 Concentration dependence of σ_s/σ_v for sucrose transport across Cuprophan. (●) Experiment; ±1 SEM error bars are shown. (———) Eq. 8.

nonideal, nondilute solutions. The values of Γ and $\bar{\nu}_s$ needed to test Eq. 8 were obtained as described in Appendix B.

Working from a formal irreversible thermodynamic description of membrane transport, Zelman (10) explored the effect of nonideality on the two reflection coefficients in a multiple solute system, and found $\sigma_s > \sigma_v$. Mikulecky (11), commenting on Zelman's work, took a similar approach, and obtained a similar result. These results differ qualitatively from the theory and experiment presented here. The main reason seems to lie in the definitions of chemical potential used by these authors, which satisfy the Gibbs-Duhem equation only if $\bar{V}_w c_w = 1$, which is the dilute solution approximation.

The maximum value of σ_v occurs when the membrane is impermeable to solute; in that case, $D_{ss}^{-1} \rightarrow -\infty$ (3), $r_{ss} \rightarrow -\infty$ by definition, and Eq. 7 *b* gives $\sigma_{v,\max} = \lim_{r_{ss} \to -\infty} \sigma_v = (1 + \Gamma)/(1 - \bar{\nu}_s)$. For an ideal dilute solution, $\sigma_{v,\max} = 1$. From Eq. 7 *a* or 8, $\sigma_{s,\max} = 1$, irrespective of concentration.

The equations for volume and solute flow developed by Kedem and Katchalsky (1) can be written in terms of a single reflection coefficient whose upper limit is unity by defining a modified osmotic driving force $\Delta\pi_s = (1 + \Gamma)RT\Delta c_s/(1 - \bar{\nu}_s)$. Then, at all concentrations,

$$J_v = -L_p(\Delta P - \tilde{\sigma}_v \, \Delta\pi_s) \qquad (9\,a)$$

and

$$J_s = J_v\,(1 - \sigma_s)\bar{c}_s - \tilde{\omega}_P \, \Delta\pi_s, \qquad (9\,b)$$

where $\tilde{\sigma}_v = (1 - \bar{\nu}_s)\sigma_v/(1 + \Gamma) = \sigma_s$ and $\tilde{\omega}_P$ is a modified phenomenological permeability, defined as $(-J_s/\Delta\pi_s)_{J_v=0}$. Eq. 9 *a* and *b* reduces to Eq. 1 *a* and *b* for ideal dilute solutions.

APPENDIX A

Reflection Coefficients of a Heteroporous Membrane with Boundary Layers

Consider a heteroporous membrane of thickness α bounded by boundary layers of thickness δ, with $x = 0$ at the left side of the membrane. Denote the transport properties of, and fluxes across, each parallel path by the subscript "i" and experimental transport properties based on the bulk concentration difference Δc_s by prime. Assume that the reflection coefficients of, and pressure drops across, the boundary layers are zero. Eq. 1 *a* and *b* holds for each path across the membrane, but with Δc_s replaced by $\Delta c_m = c_s(\alpha) - c_s(0)$.

Before evaluating σ_v' and σ_s', it is necessary to relate Δc_s to Δc_m. This is done by equating the solute fluxes across the boundary layers and the membrane. For the boundary layers, from Eq. 1 *b*,

$$J_s = J_v\bar{c}_s - \omega_b RT[c_s(0) - c_s(-\delta)] = J_v\bar{c}_s - \omega_b RT[c_s(\alpha + \delta) - c_s(\alpha)], \tag{A1}$$

where the subscript "b" denotes the boundary layer. From Eq. A1, the concentration difference across each boundary layer is the same; call it Δc_b. Since there is no discontinuity in concentration at the outer edge of the boundary layer,

$$\Delta c_s = \Delta c_m + 2\Delta c_b. \tag{A2}$$

The volume and solute fluxes across the membrane are

$$J_v = \Sigma J_{vi} = -\Delta P\Sigma L_{pi} + RT\Delta c_m \Sigma L_{pi}\sigma_{vi} \tag{A3 a}$$

$$\begin{aligned} J_s = \Sigma J_{si} &= \bar{c}_s\Sigma J_{vi}(1 - \sigma_{si}) - RT\Delta c_m \Sigma\omega_{Pi} \\ &= -\bar{c}_s\Delta P\Sigma L_{pi}(1 - \sigma_{si}) + RT\Delta c_m[\bar{c}_s\Sigma L_{pi}\sigma_{vi}(1 - \sigma_{si}) - \Sigma\omega_{Pi}]. \end{aligned} \tag{A3 b}$$

Substituting Eqs. A2 and A3 *a* into Eq. A1,

$$J_s = \bar{c}_s(-\Delta P\Sigma L_{pi} + RT\Delta c_m\Sigma L_{pi}\sigma_{vi}) - \omega_b RT\left(\frac{\Delta c_s - \Delta c_m}{2}\right). \tag{A4}$$

Eqs. A3 *b* and A4 are solved for Δc_m as a function of Δc_s:

$$RT\Delta c_m = \frac{W_P RT\Delta c_s + \bar{c}_s\Delta P\Sigma L_{pi}\sigma_{si}}{W_P + \bar{c}_s\Sigma L_{pi}\sigma_{vi}\sigma_{si} + \Sigma\omega_{Pi}} \tag{A5}$$

where $W_P = \omega_b/2$.

The experimental reflection coefficient for volume flow, σ_v', is defined by Eq. 6 *b*. Setting the right-hand side of Eq. A3 *a* equal to zero, replacing Δc_m by the derived function of Δc_s, and rearranging,

$$\sigma_v' = \frac{W_P\Sigma L_{pi}\sigma_{vi}}{(\Sigma L_{pi})(W_P + \bar{c}_s\Sigma L_{pi}\sigma_{vi}\sigma_{si} + \Sigma\omega_{Pi}) - \bar{c}_s\Sigma L_{pi}\sigma_{si}\Sigma L_{pi}\sigma_{vi}}. \tag{A6}$$

The experimental σ_s' is found from Eq. 6 *a*. The expression for Δc_m when $\Delta c_s = 0$ is found from Eq. A5 and is substituted into Eqs. A3 *a* and A4 to give an expression for σ_s' that is identical to Eq. A6, except that the numerator is $W_P\Sigma L_{pi}\sigma_{si}$. Since the reflection coefficients of the individual pathways are related by $\sigma_{si} = \sigma_{vi}(1 - \bar{\nu}_s)/(1 + \Gamma)$, it follows that the same proportionality holds between σ_s' and σ_v'.

APPENDIX B

Numerical Values of $\bar{\nu}_s$ and Γ for Aqueous Sucrose Solutions

The values of $\bar{\nu}_s$ and Γ substituted into Eq. 8 were obtained from tabulated (12) densities (derived from specific gravity at 20°C) and freezing point depressions of aqueous sucrose solutions.

$\bar{\nu}_s$ The partial molar volume of the solute, $\overline{V}_s$, is defined as $\overline{V}_s = (\partial V_{soln}/\partial n_s)_{n_w}$ at constant temperature and pressure, where V_{soln} is the volume of solution and n_i is the number of moles of the ith species. The solution volume is given by $V_{soln} = (M_s n_s + M_w n_w)/\rho_{soln}$, where M is molecular weight and ρ is density; thus

$$\overline{V}_s = \frac{M_s}{\rho_{soln}} - \frac{M_s n_s + M_w n_w}{\rho_{soln}^2}\left(\frac{\partial \rho_{soln}}{\partial n_s}\right)_{n_w}. \tag{B1}$$

The density data in reference 12 are tabulated against a number of concentration measures, the most convenient of which is the weight percent of solute, A grams/100 grams solution. In a solution that is A weight percent solute, $n_s/n_w = (A/M_s)/[(100 - \mathrm{A})/M_w]$; rearranging,

$$A = \frac{100 M_s n_s}{M_s n_s + M_w n_w}. \tag{B2}$$

With the aid of Eq. B2, the derivative in Eq. B1 becomes

$$\left(\frac{\partial \rho_{soln}}{\partial n_s}\right)_{n_w} = \left(\frac{\mathrm{d}\rho_{soln}}{\mathrm{d}A}\right)\left(\frac{\partial A}{\partial n_s}\right)_{n_w} = \frac{100 M_s M_w n_w}{(M_s n_s + M_w n_w)^2}\frac{\mathrm{d}\rho_{soln}}{\mathrm{d}A},$$

and

$$\bar{\nu}_s = \overline{V}_s \bar{c}_s = \frac{M_s}{\rho_{soln}}\left(1 - \frac{100 - A}{\rho_{soln}}\frac{\mathrm{d}\rho_{soln}}{\mathrm{d}A}\right)\bar{c}_s. \tag{B3}$$

Γ The derivation of the relationship between Γ and freezing point depression at constant pressure follows the classical approach (13), up to the point at which the solution is assumed to be dilute; the starting equation for the development which follows is thus

$$\frac{\Delta H_f}{RT^2}\mathrm{d}T = \left(\frac{\partial \ln a_w}{\partial x_s}\right)_T \mathrm{d}x_s,$$

where ΔH_f is the heat of fusion of the solvent at the freezing point of the solution (the effect of solute on the partial molal enthalpy of the solvent is neglected), and x_i is the mole fraction of the ith species. From the Gibbs-Duhem equation, $\mathrm{d}\ln a_w = -(x_s/x_w)\mathrm{d}\ln a_s$. Using Eq. 4, and rearranging,

$$1 + \Gamma = -\frac{c_s(1 - x_s)}{x_s}\cdot\frac{\Delta H_f}{RT^2}\cdot\frac{\mathrm{d}T}{\mathrm{d}c_s},$$

where $x_s + x_w = 1$ has been used and $\mathrm{d}T$ is the differential change in the freezing point of the solution. The mole fraction of solute in a solution which is A weight percent solute is found from the preceding section:

$$x_s = \frac{AM_w}{AM_w + (100 - A)M_s};$$

therefore,

$$1 + \Gamma = \frac{c_s M_s(100 - A)}{AM_w}\cdot\frac{\Delta H_f}{RT^2}\cdot\frac{\mathrm{d}\Delta}{\mathrm{d}c_s}, \tag{B4}$$

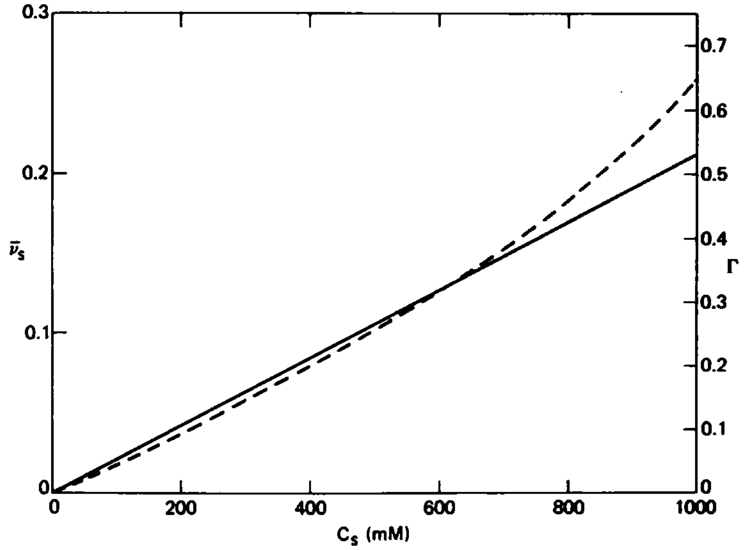

FIGURE 3 Concentration dependence of $\bar{\nu}_s$ (——) and Γ (----) in aqueous sucrose solutions. $\bar{\nu}_s$ is the volume fraction of solute; $\Gamma = d \ln \gamma_s / d \ln c_s$, where γ_s is the sucrose activity coefficient in a solution whose concentration is c_s.

where Δ is freezing point depression ($d\Delta = -dT$). Values of $(1 + \Gamma)$ computed from osmotic pressure data (14) were within 3% of those obtained from freezing point depression.

Eqs. B3 and B4 were used to find $\bar{\nu}_s$ and Γ as functions of c_s. Tabulated values (12) of ρ_{soln}, A, c_s, and Δ were fit to polynomials ρ_{soln} (A) and $\Delta(c_s)$, which were differentiated analytically to give the required derivatives. Corresponding values of A and c_s were obtained by interpolation. The resulting values of $\bar{\nu}_s$ and Γ are plotted against c_s in Fig. 3.

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