# A Different Interpretation of Einstein's Viscosity Equation Provides Accurate Representations of the Behavior of Hydrophilic Solutes to High Concentrations

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ABSTRACT: Viscosities of aqueous solutions of many highly soluble hydrophilic solutes with hydroxyl and amino groups are examined with a focus on improving the concentration range over which Einstein's relationship between solution viscosity and solute volume, V, is applicable accurately. V is the hydrodynamic effective volume of the solute, including any water strongly bound to it and acting as a single entity with it. The widespread practice is to relate the relative viscosity of solute to solvent, η/η_0, to V/V_{tot}, where V_{tot} is the total volume of the solution. For solutions that are not infinitely dilute, it is shown that the volume ratio must be expressed as V/V_0, where $V_0 = V_{tot} - V$. V_0 is the volume of water not bound to the

solute, the "free" water solvent. At infinite dilution, $V/V_0 = V/V_{tot}$. For the solutions examined, the proportionality constant between the relative viscosity and volume ratio is shown to be 2.9, rather than the 2.5 commonly used. To understand the phenomena relating to viscosity, the hydrodynamic effective volume of water is important. It is estimated to be between 54 and 85 cm^3. With the above interpretations of Einstein's equation, which are consistent with his stated reasoning, the relation between the viscosity and volume ratio remains accurate to much higher concentrations than those attainable with any of the other relations examined that express the volume ratio as V/V_{tot}.
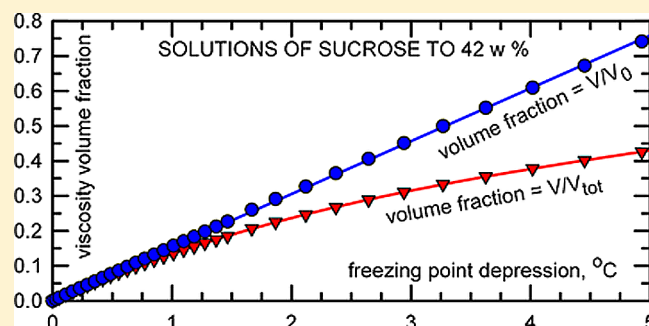
INTRODUCTION

Einstein's doctoral dissertation at the University of Zurich[1] and the resulting 1906 publication[2] presented a relationship, based on hydrodynamic principles, between the volume fraction of the solute and the viscosity of the solution at infinite dilution relative to that of pure solvent, eq 1.

$$(\eta/\eta_0 - 1) = (V/V_{tot}) \qquad (1)$$

The viscosity of the solution is denoted by η and that of the pure solvent by η_0. V was defined as the hydrodynamic effective volume of dissolved solute and V_{tot} as the total volume of the solution. This relationship was derived for solutes only at infinite dilution and for solute particles that are perfectly spherical, rigid, undissociated (i.e, not ionic), and that have molar volumes significantly greater than the molar volume of the solvent. Using a then available measurement of 1 wt % sucrose solution in water, Einstein found that dissolved sucrose had a hydrodynamic effective molar volume greater than the volume expected from the molar volume of the solid.

Subsequent to Einstein's publication, Bancelin in 1911 tested eq 1 with dilute monodisperse suspensions of gambose, a tree resin with particles 15 Å in radius (8511 cm^3 per mole of particles), and found that $(\eta/\eta_0 - 1) = 2.9(V/V_{tot})$ best represented the measurements,[3] Å = 10^{-8} cm. Bancelin communicated this to Einstein, who published a correction in 1911 after finding a mistake in one of the equations of his 1906 publication.[4] The corrected relation is eq 2.

$$(\eta/\eta_0 - 1) = 2.5(V/V_{tot}) \qquad (2)$$

Equation 2 has become the basis of the relationship used in the past century to describe and understand viscosity phenomena. Real solutes are not necessarily perfectly spherical, and real solutions are not infinitely dilute. Also, it is now understood that the proportionality constant of 2.5 in eq 2 increases as the shape of the solute deviates from perfectly spherical. With ellipsoids, the value of the proportionality constant has been calculated to increase to as high as about 3.4, depending on the axial ratio of the ellipsoid.[5] For more irregular shapes, the values are generally unknown.[6] Einstein commented as follows on the fact that the effective volume of sucrose, in a hydrodynamic sense, is significantly greater than that of the solid:[1] "It seems to me that from the point of view of the molecular theory, this result can hardly be interpreted otherwise than by assuming that the sugar molecule in the solution impedes the mobility of the water in its immediate vicinity." He also made the approximation that "a dissolved

molecule of sugar (i.e., the molecule together with water held by it) behaves in the hydrodynamic sense as a sphere." In the phrase "together with the water held by it", he thus defined, early on, the hydration number as the number of water molecules adhering to the solute with sufficient binding energy so as to become part of the solute and behave as a single entity with it. During the years between 1970 and 1974, Einstein's publications on viscosity[2,4] were the most cited of his works, quoted four times as often as his 1916 article on general relativity and eight times as often as his 1905 paper on radiation and light quanta for which he received the Nobel Prize.[7] Einstein's primary interest does not appear to have been viscosity but rather molecular size, as may be concluded from the title of his thesis[1] and of the subsequent publication,[2] "A New Determination of Molecular Dimensions". The work focused on how to calculate Avogadro's number and the size of molecules. The subsequent interest in viscosity should not come as a surprise. The unknown genius who discovered the wheel certainly found out soon thereafter that the wheel turned a lot easier with spittle or grease on the axle, lubrication! Wheels and moving parts do not work well without it.

There have been many attempts to modify eq 2 so as to make it applicable to realistic concentrations, generally by adding an empirical power series in V/V_{tot}. Ford has reviewed such attempts and also reported that Einstein's derivation really led to a more complete relationship, eq 3,[8] although this form does not appear explicitly in Einstein's papers.[2,4]

$$\frac{\eta}{\eta_0} = \frac{[1 + 0.5(V/V_{tot})]}{[1 - (V/V_{tot})]^2} \tag{3}$$

Thomas expanded eq 2 by a power series up to six terms in V/V_{tot} on the basis of viscosity measurements of large particle suspensions using polystyrene, latex, glass, and so forth of radii greater than 45 Å.[9a] The first two terms, eq 4, have been used for approximating solution viscosities.

$$(\eta/\eta_0 - 1) = 2.5(V/V_{tot}) + 10.05(V/V_{tot})^2 \tag{4}$$

Batchelor and Green provided a theoretical treatment for dilute suspensions (V/V_{tot} up to ~0.1) of perfectly spherical particles and reported $(\eta/\eta_0 - 1) = 2.5(V/V_{tot}) + c_i(V/V_{tot})^2$, with c_i = 7.6 for rigid spheres and 5.2 for elastic ones.[9b] Vand used c_i = 7.35 for glass spheres.[9c] A term of $(V/V_{tot})^2$ was used as early as 1936.[9d] Suspensions of colloidal particles (e.g., clay, starch, gum arabic, etc.)[9d] and of high molecular weight polymers do not always obey such relationships because of changes in the aggregation of colloids and in entanglements of polymer chains with changes in concentration and temperature.[9e] As a result, prior knowledge of the actual molar volumes of the suspended particles in water becomes uncertain.

The term "hydration number" is being used widely in different contexts, with different experimental approaches, and is a rather inadequately defined quantity. Diffraction techniques, such as X-ray, neutron, extended X-ray absorption fine structure (EXAFS), and molecular dynamics simulations, often use the term hydration number for the number of water molecules that are immediately adjacent to the solute particle or within a particular distance. Sometimes, the terms coordination or solvation numbers are also used in this context. As used in the present work, the term hydration number, denoted by H_T, refers to the average number of water molecules binding to solute sufficiently strongly as to become part of the solute and behave as a single entity with it. The

minimum binding energy required was found to be very near 13.3 kcal mol^{-1} (55.6 kJ mol^{-1}).[10] Water thus bound to the solute does not change the number of solute particles but decreases the amount of unbound "free" water that is available as solvent or for hydrating any additional solute. H_T is used here to distinguish it from other unrelated hydration numbers that measure different quantities. The subscript T relates to the aforementioned thermodynamic minimum binding energy. H_T is a dynamic quantity indicating the average of the distribution of solute·$(H_2O)_n$ entities. Curved colligative property plots are straightened out when account is taken of the amount of water lost as solvent by being strongly bound to solute and acting as one particle with it. Only the amount of free water available as solvent is used in calculating molalities (m = moles in 1000 g of H_2O) for concentrated solutions of electrolytes and non-electrolytes in freezing point depressions,[11] boiling point elevations, osmotic pressures, and vapor pressure lowering.[10] With vapor pressure measurements, the activity coefficient of the free water remains at unity even at very concentrated solutions.[12]

This type of definition of hydration number, H_T, is not unique; it was used, for example, by Stokes and Robinson,[13] by Scatchard,[14] by Berkeley and Hartley over 100 years ago,[15] and by Einstein,[1,2,4] among many others. H_T values correlate with experimental sequential binding energies of gas-phase ion–water clusters, with theoretical calculations of sequential binding energies of water to solute, with the ordering of solutes in the Hofmeister series, with limiting conductivities of ions, with the charge density of ions, with results from dielectric relaxation measurements, with dynamic hydration numbers of biologically important ions, and so forth.[10−12] Hydration (or coordination) numbers from diffraction measurements do not show such relations because they do not measure quantities directly related to such phenomena. Diffraction determines the number of water molecules immediately surrounding the immersed object and their interesting arrangements in space, rather than their binding energy. The larger the immersed object, the more water molecules that can fit immediately around it. For example, bromide ions have hydration numbers of 6 or greater by diffraction measurements. Conversely, bromide ions have $H_T = 0$,[10,11,13] and this can cause confusion as to which is the correct number. $H_T = 0$ does not mean that there is no water around the particle. Anything immersed in water will have water around it. Water stabilizes Br$^-$ by solvation, not by hydration (H_T) as defined here, and all experimental sequential binding energies of water to Br$^-$ are lower than 13.3 kcal mol^{-1}. For Br$^-$ + H_2O → Br$^-$·H_2O, the binding energy is −12.6 kcal mol^{-1}; for Br$^-$·H_2O + H_2O → Br$^-$·$(H_2O)_2$, it is −12.3; for Br$^-$·$(H_2O)_2$ + H_2O → Br$^-$·$(H_2O)_3$, it is −11.5, and so forth, with the sequential binding energies decreasing monotonically.[16] Clearly, Br$^-$ is stabilized by solvation but is not "hydrated" in the sense defined here. Water molecules also solvate other water molecules and water clusters in the same fashion. Residence times of water molecules around solutes with $H_T = 0$ are nearly the same as the those of water molecules around other waters.[10−12] A clear distinction is made between strongly bound water of hydration and water solvating or surrounding the solute but not binding strongly enough to become part of the solute and become a single entity with it, as postulated by Einstein.[1]

■ RESULTS

In this work, concentrated aqueous solutions of hydrophilic compounds containing hydroxyl and amino groups are examined. These types of solutes are chosen because of their high water solubility, which produces the large changes in viscosity needed for testing the performance of various equations. The focus is on improving the accuracy and concentration range over which quantitative relations between the viscosity and volume ratio of solute to solvent remain accurate, the effect on the viscosity of the number of water molecules tightly bound to the solute (the hydration number H_T), and the form of the volume ratio used in eqs 2−4.

Viscosity data of hydrophilic solutes demonstrate that the proportionality constant of eq 2 is 2.9, as also found by Barcelin over 100 years ago.[3] This is demonstrated below.

Freezing point depression measurements of raffinose (a trisaccharide) solutions[17] have H_T = 11.9.[11] Viscosity and density measurements are also available at 0 °C.[18] H_T values usually, but not always, decrease to various extents with increasing temperature;[10,19,20] they have never been reported to increase. The H_T value of raffinose from freezing point depression measurements and that of solutions at 0 °C would be the essentially the same. Even though viscosity is not a colligative property, the hydration number, H_T, of solutes is the same, whether one intends to measure solution viscosities or any of their colligative properties under the same conditions.

Equation 2 can be written as $(\eta/\eta_0 - 1) \times V_{tot}/V = k$, where k is the proportionality constant (2.5 in eq 2). The molar volume of hydrated raffinose is obtained by dividing the molar mass of the anhydrous pure compound by its density (504.42/1.592 = 316.85 cm^3) and adding the volume of each of 11.9 water molecules, 18.0175 cm^3 at 0 °C (18.0175 × 11.9 = 214.41 cm^3). The sum is the hydrodynamic effective molar volume of dissolved solute, 531.26 cm^3 mol^{-1}, and the total effective volume of the solute at each molality is V = 531.26 × m cm^3. The molar volume of a bound water molecule is taken as remaining unchanged, and evidence in support of this is provided in the Discussion section. Figure 1 shows a plot of $(\eta/\eta_0 - 1) \times V_{tot}/V$ versus molality. The zero intercept is the proportionality constant k at infinite dilution.

Raffinose or its hydrated form is not perfectly spherical. It is clear from Figure 1 that the proportionality constant is nearer to 2.9 than it is to 2.5 at infinite dilution. The linearity of the plot also indicates that H_T remains constant in the narrow concentration range of available measurements.

The same approach can be used with viscosities of sucrose solutions available at 20 °C.[21] Known H_T values from colligative properties are as follows.[10,11] Two different sets of measurements of freezing point depressions yield H_T = 6.0 and 5.0.[10] Osmotic pressure measurements yield H_T = 4.9 at 0 °C, 4.4 at 30 °C, and 3.8 at 57.7 °C.[10] Vapor pressure measurements yield H_T = 4.9 at 0 °C and 4.3 at 30 °C.[12] Boiling point elevations yield H_T = 4.0.[10] Therefore, H_T at 20 °C must be 4.3 ± 0.1. The hydrodynamic effective molar volume of dissolved sucrose is the sum of the molar volume of the pure solid, (342.292 g mol^{-1})/(1.58 g cm^{-3}) = 216.64 cm^3 mol^{-1}, and the molar volume of 4.3 waters of hydration, 4.3 × 18.047 cm^3 = 77.60 cm^3 at 20 °C; the sum is 294.24 cm^3. The effective volume of hydrated sucrose at each molality is V = 294.24 × m cm^3. A plot of $(\eta/\eta_0 - 1)/(V/V_{tot})$ versus molality extrapolated to m = 0.0 yields the proportionality constant k at infinite dilution. Sucrose and its hydrates also are not perfectly
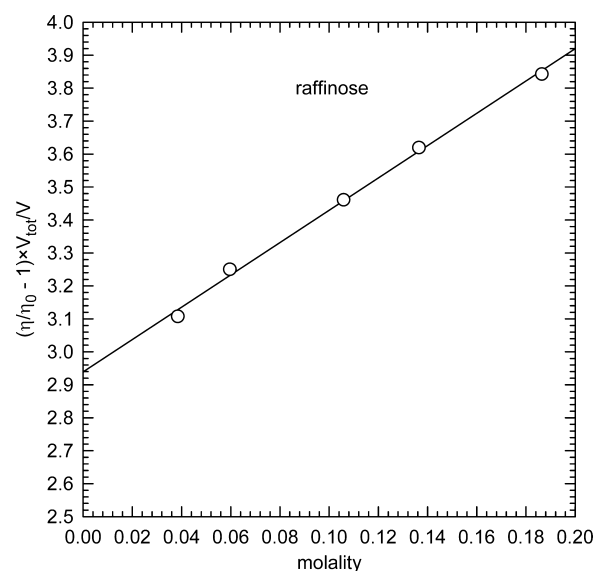

Figure 1. Plot of $(\eta/\eta_0 - 1) \times (V_{tot}/V)$ for raffinose solutions at 0 °C versus m.

spherical. The plot is shown in Figure 2 for fairly dilute solutions. Again, the proportionality constant is near 2.9 at infinite dilution.
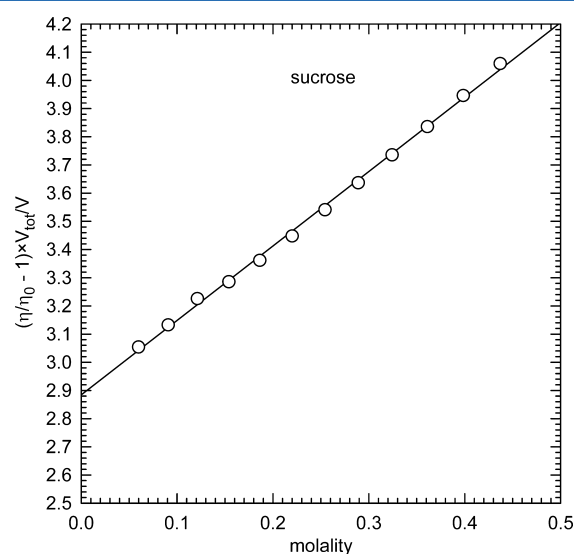

Figure 2. Plot of $(\eta/\eta_0 - 1) \times (V_{tot}/V)$ for sucrose solutions at 20 °C versus m. The line is a linear regression.

Einstein did not calculate the hydration number of sucrose, but it is obtainable from his published results. With then available data of a 1 wt % solution of sucrose at 18 °C and eq 2, he noted that the ratio of the hydrodynamic effective volume of 1 g of dissolved sucrose to the corresponding volume of the solid was 1.61. With the then available molar volume of 208 cm^3 for solid sucrose and with eq 2, one obtains the hydrodynamic effective molar volume of dissolved sucrose as 208 × 1.61 = 335 cm^3. The excess effective molar volume then is 335 − 208 = 125 cm^3, which yields H_T = 7.0 when divided by 18, the molar volume of one water molecule. The value of 7.0 at 18 °C is too high for sucrose when compared to the H_T values from colligative properties. The high value is due to Einstein's approximation that hydrated sucrose is spherical (2.5 instead of

2.9 in eq 2) and to his using the somewhat inaccurate then available values for viscosity and for the density of solid sucrose. These factors also led to Einstein reporting a value of 6.56×10^{23} for Avogadro's number,[4] a quantity not firmly established at the time. This value is greater than the current, more accurate one.

Whether $(\eta/\eta_0 - 1) = 2.9(V/V_{tot})$ at infinite dilution is valid for other solutes can be tested by estimating their hydrodynamic effective molar volume at infinite dilution, V, by plotting $V = (\eta/\eta_0 - 1) \times V_{tot}/k$ versus molality with k values of 2.5 and of 2.9 and extrapolating to $m = 0$. Experimental values of $(\eta/\eta_0 - 1)$, V_{tot}, and of the molality are available for several highly soluble compounds, for which H_T values also are available from colligative properties.

Figure 3 is a plot of $V = (\eta/\eta_0 - 1) \times V_{tot}/k$ versus molality for relatively dilute solutions of D-glucose at 20 °C.[21] With $k =$
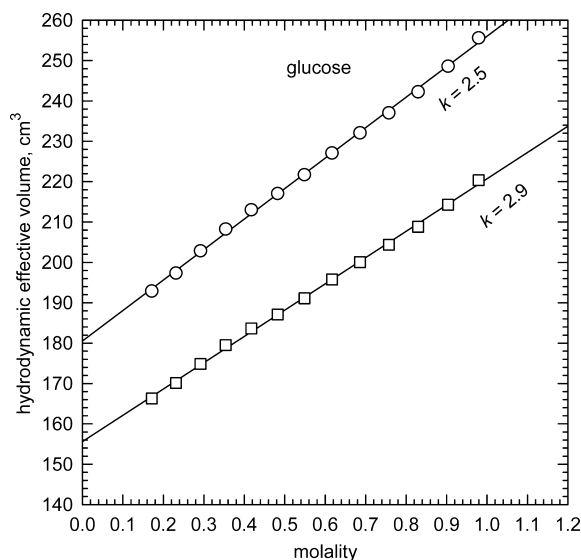
Figure 3. Glucose solutions at 20 °C. Plot of $V = (\eta/\eta_0 - 1) \times V_{tot}/k$ versus m.

2.5, the hydrodynamic effective molar volume of the solute extrapolated to $m = 0$ is estimated as 180.51 cm³. The effective molar volume thus obtained is based only on experimental data, without any assumptions regarding hydration numbers. The molar volume of pure glucose is 115.62 cm³. The excess volume of 65.17 cm³ divided by the molar volume of one water molecule at 20 °C yields $H_T = 3.6$. The H_T value from freezing point depressions is 2.5[11] and that from osmotic pressures at 0 °C is 2.6.[10] The H_T value at 20 °C cannot be greater than it is at the lower temperatures. With $k = 2.9$, extrapolation to $m = 0$ yields 155.62 cm³ mol⁻¹. The excess volume of 40.28 cm³ corresponds to $H_T = 2.2$, which is appropriately lower than the values from the freezing point depression and osmotic pressures at 0 °C and appropriately higher than $H_T = 1.7$ at 25 °C obtained from vapor pressure measurements up to as high as 7.5 m.[12]

Figure 4 plots the effective volume of the solute, V, versus the molality for solutions of tris(hydroxymethyl)aminomethane at 20 °C,[21] $V = (\eta/\eta_0 - 1) \times V_{tot}/k$. There is some scatter in the very dilute region, causing a small uncertainty in the extrapolated value. With $k = 2.5$, the effective molar volume of the solute extrapolated to infinite dilution is estimated to be 118.30 cm³. The molar volume of the pure compound is 89.54
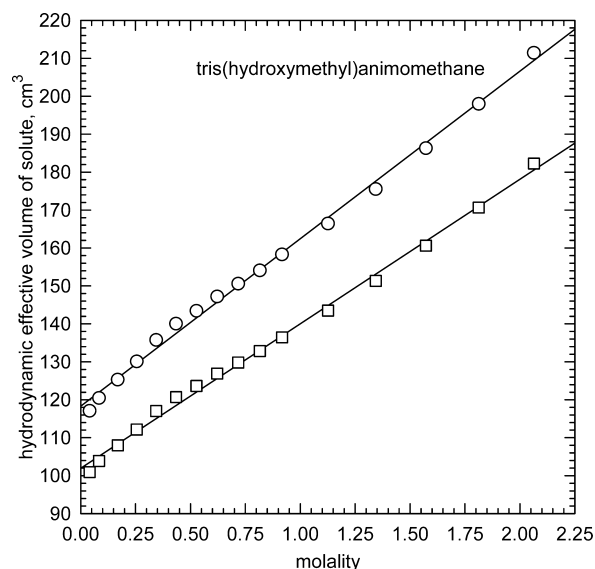
Figure 4. Solutions of tris(hydroxymethyl)aminomethane at 20 °C. Plot of $V = (\eta/\eta_0 - 1) \times V_{tot}/k$ versus m.

cm³. The excess volume of 28.76 cm³ yields $H_T = 1.59$. The H_T value from freezing point depressions is 0.70.[11] Again, the H_T value at the higher temperature cannot be greater than that at the lower temperature. With $k = 2.9$, the extrapolated effective molar volume at infinite dilution is 101.98 cm³. The excess volume of 12.44 cm³ corresponds to $H_T = 0.69$, which is marginally lower than that obtained from freezing point depressions.

The same patterns persist in plots similar to those of Figures 3 and 4 with, for example, solutions of (L)-(+)-tartaric acid (2,3-dihydroxybutanedioic acid), (D)-mannitol (2R,3R,4R,5R)-hexan-1,2,3,4,5,6-hexol), fructose, maltose, and lactose. The relevant plots with $k = 2.5$ and 2.9 for each are given in the Supporting Information, Figures S1−S4.

A question of symmetry is relevant to eq 2. Whereas relative viscosity is given by η/η_0, the relative volume of solute to solvent is expressed as V/V_{tot}, not as V/V_0, where V_0 is the volume of free water not bound to solute and available as solvent. At infinite dilution $V/V_0 = V/V_{tot}$. At concentrations other than infinite dilution, the volume of available free water solvent V_0 is the experimental V_{tot} minus the volume of hydrated solute, that is, including any waters of hydration that are strongly bound to it and are not available to act as solvent, $V_0 = V_{tot} - V$. Large particles dissolved or suspended in the water impede the flow of water solvent past them, but the water tightly held by the solute is not part of the solvent but of the solute. Because $V/V_{tot} = V/V_0$ at infinite dilution, the proportionality constant k by which the two volume ratios are multiplied should be the same whether one plots $(\eta/\eta_0 - 1)/(V/V_{tot})$ or $(\eta/\eta_0 - 1)/(V/V_0)$ versus molality and extrapolates to $m = 0$. That this is the case is shown in Figure 5 with dilute solutions of sucrose, where V is the total volume of hydrated sucrose, $m \times 294.28$ cm³.

Whether the choice of V_0 over V_{tot} is a matter of symmetry and esthetics or of reality is addressed next. Conceptually, eq 4 with an additional term involving the square of the volume ratio of solutes is understandable in terms of interactions between solute molecules. At low concentration, this term will not be significant but will become so as the concentration increases. Collisions between solute particles, a second-order process,
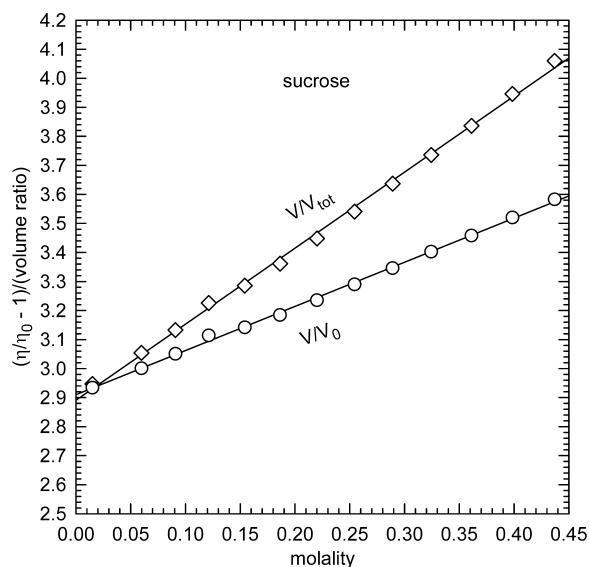
Figure 5. Sucrose solutions at 20 °C. Plots of $(\eta/\eta_0 - 1)/(V/V_{tot})$ and of $(\eta/\eta_0 - 1)/(V/V_0)$ versus m. The zero intercept is the value of k at infinite dilution. The zero intercepts are 2.891 with V/V_{tot} and 2.910 with V/V_0.

have been invoked by Vand[22] and others[9b,c] to rationalize deviations from simple first-order dependence on the volume ratio as the concentration increases. Whether or not volume ratios of V/V_0 are preferable to those of V/V_{tot} can be established by comparing their relative performance versus experimental data to high concentrations. Comparisons are made with the three relationships of eqs 5, 6, and 7, which include a second-order dependence on the volume ratios, and with eq 3, which also expresses the volume ratio as V/V_{tot}.

$$(\eta/\eta_0 - 1) = 2.9(V/V_0) + c_5(V/V_0)^2 \qquad (5)$$

$$(\eta/\eta_0 - 1) = 2.5(V/V_{tot}) + c_6(V/V_{tot})^2 \qquad (6)$$

$$(\eta/\eta_0 - 1) = 2.9(V/V_{tot}) + c_7(V/V_{tot})^2 \qquad (7)$$

Equation 4 fails even with very dilute solutions of the hydrophilic solutes of this work, most likely because the suspended large particles examined for establishing the relationship were spherical, or nearly so. Similar failures are found with the similar equations of Batchelor and Green, which pertain to perfectly spherical suspended particles and are only valid for low ratios of V/V_{tot}.[9b]

Obtaining the value of V requires knowledge of the hydration number H_T. This is obtained by finding the H_T value that yields the best agreement with experimental viscosities in the low range of $(\eta/\eta_0 - 1) = 0.0$ to ~0.75, where second-order effects are not pronounced and V/V_0 is not very different from V/V_{tot}. The effective molar volume of the solute is obtained as the molar volume of the pure substance plus $H_T \times 18.047$ at 20 °C, $H_T \times 18.2327$ at 50 °C, and so forth for other temperatures. At each concentration, V is the effective molar volume multiplied by m. H_T values obtained by each of eqs 5–7 for solutions of low viscosity, $(\eta/\eta_0 - 1) < 0.75$, are essentially the same. With H_T values so determined, the coefficient c_5 for eq 5 is determined by plots of $[(\eta/\eta_0 - 1) - 2.9(V/V_0)]/(V/V_0)^2$ versus $(\eta/\eta_0 - 1)$. Such plots show significant and random scatter at low concentrations but then become nearly horizontal, settling at values very near $c_5 = 5.6$ for a

considerable range of concentrations. The scatter is clearly due to the large percent of experimental uncertainty at very high dilution. Figure 6 shows examples for solutions at 20 °C of
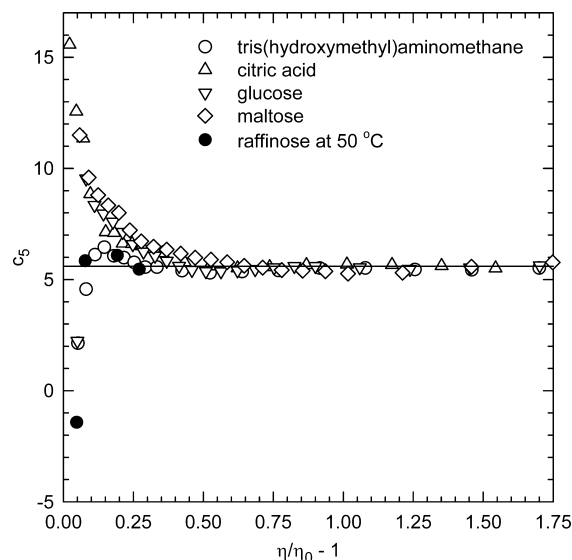

Figure 6. Plots of $[(\eta/\eta_0 - 1) - 2.9(V/V_0)]/(V/V_0)^2$ versus $(\eta/\eta_0 - 1)$ for obtaining c_5 of eq 5. Solutions of tris(hydroxymethyl)-aminomethane (○), citric acid (△), glucose (▽), maltose (◇), and raffinose (●). The horizontal line is drawn at 5.6.

citric acid, tris(hydroxymethyl)aminomethane, glucose (a monosaccharide), and maltose (a disaccharide). Raffinose (a trisaccharide) is shown at 50 °C, and the result of the highest available concentration also settles at 5.6 and does not show a significant effect of temperature on c_5. The same procedure is repeated for eqs 6 and 7. The resulting constants are $c_6 = 14.0$ and $c_7 = 12.5$, but these values are retained over a much narrower range of concentrations compared to those in eq 5.

Figure 7 shows the results of eqs 5–7 and of eq 3 for solutions of citric acid up to 30 wt %, $m = 2.23$, 428.7 g in 1000 g of water, for all reported measurements.[21] The hydration numbers for each of the four relationships are obtained from the best fit in the dilute range, $(\eta/\eta_0 - 1) < 0.75$, where second-order effects are minor. Up to about $(\eta/\eta_0 - 1) = 1$, eqs 5–7 yield agreement with experiment with a common $H_T = 1.33$. With eq 3, the hydration number that provides the best agreement with experiment in this range is 3.55. At $(\eta/\eta_0 - 1) > 1$, eq 5 with V/V_0 yields better agreement than any of the other relationships that use V/V_{tot}. Equations 6 and 7 yield similar results, evidently compensating for the lower value of 2.5 with a higher value of 14.0 compared to 2.9 and 12.5, respectively. Linear regression on the eq 5 circles (line not shown) yields slope = 1.004 and correlation coefficient = 0.9999. The line in Figure 7 is drawn with a slope of unity. Points on the line indicate excellent agreement between calculated and experimental viscosities.

Figure 8 is a plot of solutions of (L)-tartaric acid up to 40 wt %, $m = 4.4418$, 666.67 g in 1000 g of water.[21] In the dilute domain $(\eta/\eta_0 - 1) < 0.75$, eqs 5–7 yield a common $H_T = 1.10$. Equation 3 requires a hydration number of 2.7 to match experiment in this domain. Again, up to about $(\eta/\eta_0 - 1) = 1$, all four relationships yield good agreement with experiment. Beyond this point, the use of V/V_0 yields better agreement than the other three relationships that use V/V_{tot}. Linear regression
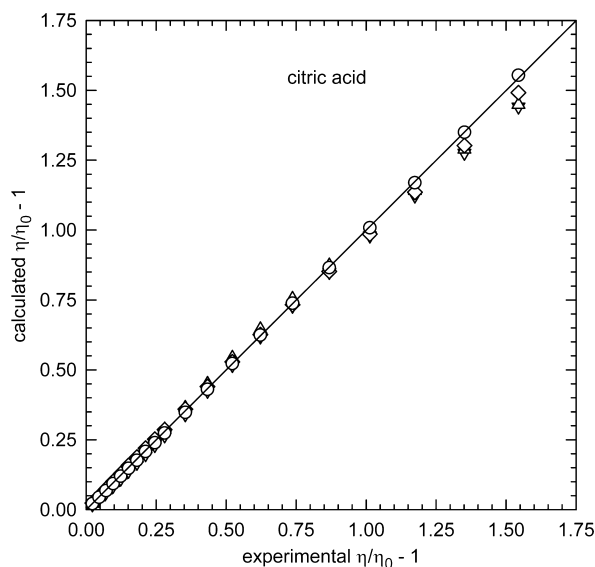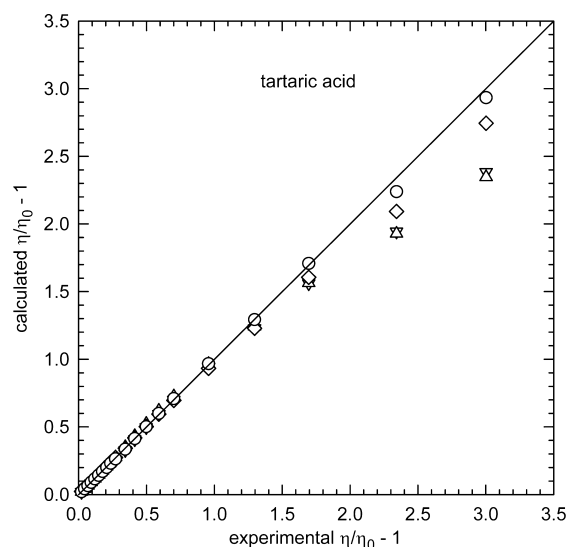
Figure 7. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for citric acid at 20 °C, up to 428.7 g in 1000 g of water and $V/V_0 = 0.3279$. (O) Calculated by eq 5, $(\eta/\eta_0 - 1) = 2.9(V/V_0) + 5.6(V/V_0)^2$. ($\nabla$) Calculated by eq 6, $2.5(V/V_{tot}) + 14.0(V/V_{tot})^2$. ($\triangle$) Calculated by eq 7, $2.9(V/V_{tot}) + 12.5(V/V_{tot})^2$. $H_T = 1.33$ for all three. ($\diamond$) Calculated by eq 3, $\{(1 + 0.5(V/V_{tot}))/(1 - (V/V_{tot})^2)\} - 1$. The line is drawn with a slope of unity.

Figure 8. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for tartaric acid at 20 °C, up to 470.7 g in 1000 g of water and $V/V_0 = 0.5093$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated by eq 3. $H_T = 1.10$ for eqs 5–7, and the hydration number is 2.7 for eq 3. The line is drawn with a slope of 1.000.

on the eq 5 circles (line not shown) yields slope = 1.002 and correlation coefficient = 0.9995. Experimental data are available up to 58 wt %, $m = 9.2$, 1381 g in 1000 g of water, but agreement with experiment deteriorates beyond 666.67 g of solute. Available measurements extend to 9.2 m, 1381 g of solute in 1000 g of water. At this point, the question arises as to which is the solvent and which is the solute.

Figure 9 is a plot of solutions of tris(hydroxymethyl)-aminomethane (2-amino-2-hydroxymethylpropane-1,3-diol) up to 32 wt %, $m = 3.885$, 470.6 g in 1000 g of water.[21] In the
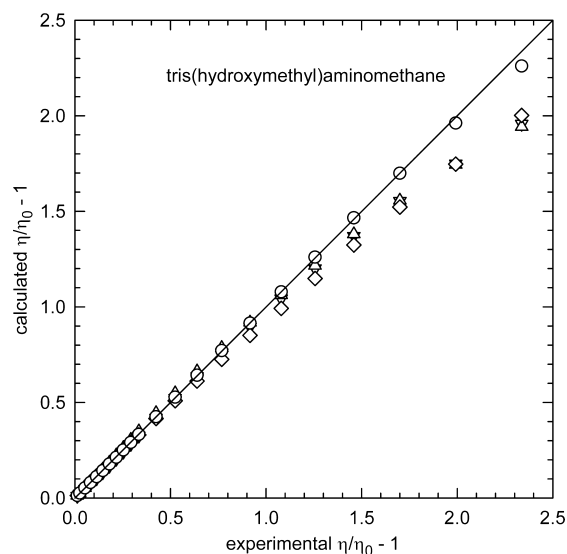

Figure 9. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for solutions of tris(hydroxymethyl)aminomethane at 20 °C, up to 470.6 g in 1000 g of water and $V/V_0 = 0.6187$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated eq 3. $H_T = 0.83$ for eqs 5–7, and the hydration number is 2.45 for eq 3. The line is drawn with a slope of 1.000.

dilute domain of $(\eta/\eta_0 - 1) < 0.75$, eqs 5–7 have a common H_T of 0.83; eq 3 requires a hydration number of 2.45 to match experiment. Up to $(\eta/\eta_0 - 1) = 1$, all four relationships yield good agreement with experiment. Beyond this point, eq 5 with V/V_0 yields better agreement than eqs 3, 6, and 7 with V/V_{tot}. Linear regression on the eq 5 circles (line not shown) yields slope = 0.9839 and correlation coefficient = 0.9998. Experimental data are available up to 40 wt %, $m = 5.50$, 666.3 g in 1000 g of water. Beyond 470.6 g of solute, agreement with experiment deteriorates.

Figure 10 is a plot of solutions of (D)-mannitol. All available measurements are shown (to 15 wt %, $m = 0.969$, 177.44 g in 1000 g of H_2O).[21] In the domain $(\eta/\eta_0 - 1) < 0.40$, eqs 5–7 have a common $H_T = 2.15$; eq 3 requires a hydration number of 4.50. In this relatively narrow range of viscosity measurements, all four equations are fairly successful, with eq 5 best adhering to the ideal line. Linear regression on the eq 5 circles (line not shown) yields slope = 1.015 and correlation coefficient = 0.9999.

Figure 11 is a plot of solutions of the monosaccharide D-glucose at 20 °C up to 36 wt %, $m = 3.122$, 562.5 g in 1000 g of water.[21] In the domain $(\eta/\eta_0 - 1) < 0.75$, eqs 5–7 have a common $H_T = 1.89$; eq 3 requires a hydration number of 4.20. Up to about $(\eta/\eta_0 - 1) = 1$, all four equations match experiment well. Beyond this point, eq 5 with V/V_0 yields superior agreement than do eqs 3, 6, and 7 with V/V_{tot}. Linear regression on the eq 5 circles up to 32 wt % (line not shown) yields slope = 0.9898 and correlation coefficient = 0.9999. Beyond 562.5 g of solute, agreement with this set of experimental data deteriorates. Reported measurements are available up to 60 wt % or 1500.2 g in 1000 g of H_2O.

More recent viscosity measurements of D-glucose solutions than those plotted in Figure 11 have been reported by Fuchs and Kaatze at 25 °C as part of a dielectric relaxation study.[23] This set of measurements is described accurately by eq 5 without significant deviation up to a high concentration of $m = 4.561$, 821.7 g of solute in 1000 g of water (45.15 wt %), much
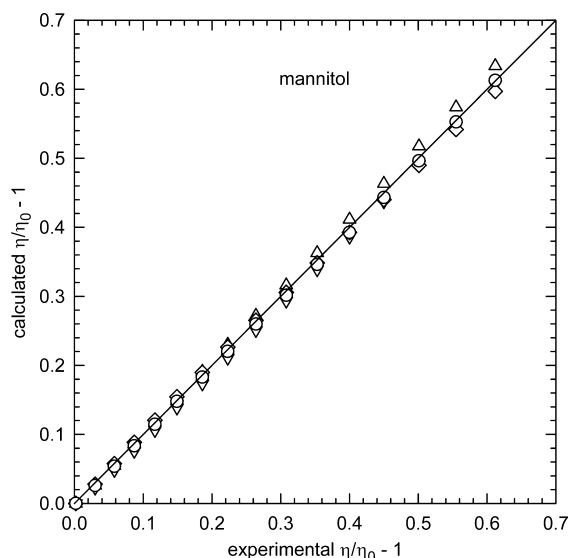
Figure 10. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for (D)-mannitol at 20 °C, up to 177.4 g in 1000 g of H$_2$O and V/V_0 = 0.1622. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. Diamonds by eq 3. H_T = 2.15 for eqs 5−7, and the hydration number is 4.50 for eq 3. The line is drawn with a slope of 1.000.
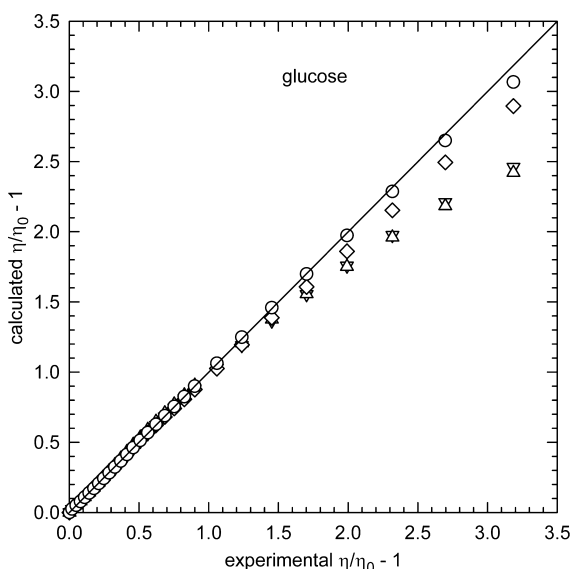

Figure 11. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for (D)-glucose at 20 °C, up to 562.5 g in 1000 g of water and V/V_0 = 0.5251. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. H_T = 1.89 for eqs 5−7; eq 3 requires a hydration number of 4.20. The line is drawn with a slope of unity.
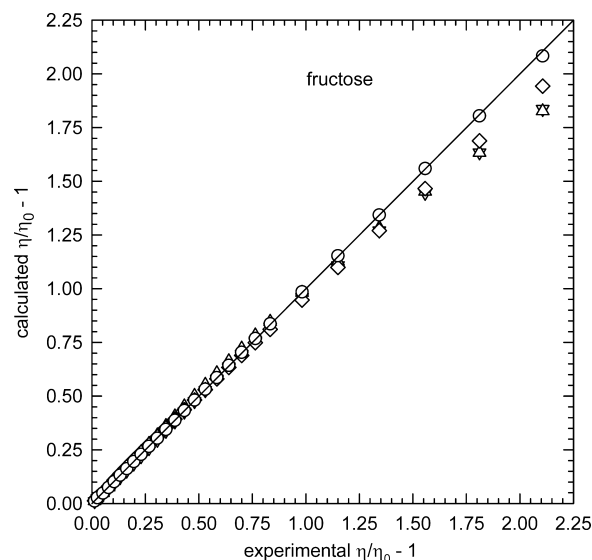

Figure 12. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for D-fructose at 20 °C, up to 515.3 g in 1000 g of water and V/V_0 = 0.4037. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. H_T = 1.65 for eqs 5−7; eq 3 requires a hydration number of 3.80. The line is drawn with a slope of unity.

Linear regression on the eq 5 circles up to 34 wt % (line not shown), the penultimate point in Figure 12, yields slope = 0.9898 and correlation coefficient = 0.9999. Beyond 515.3 g of solute, agreement with experiment deteriorates. Experimental measurements are available up to 70 wt %, 12.95 m, or 2333.2 g in 1000 g of H$_2$O. Measurements older[24] than those of Figure 12 up to 26.96 wt % at 20 °C show hydration numbers within ±0.05 units of the above.

More recent viscosity measurements of D-fructose solutions than those plotted in Figure 12 have been reported by Fuchs and Kaatze at 25 °C.[23] These measurements are described accurately by eq 5 up to 816.1 g of solute in 1000 g of water (45.00 wt %), a range much higher than that of Figure 12. Agreement with experiment deteriorates beyond this point. The relevant plot is given in the Supporting Information, Figure S6.

Viscosity measurements of solutions of the monosaccharide D-galactose are available at 25 °C up to 18.24 wt %, m = 1.2383, 223.1 g in 1000 g of H$_2$O.[24] Solution densities were obtained from the data of Zhuo et al.[25] Figure 13 depicts the results of eqs 5−7 and 3. In the domain $(\eta/\eta_0 - 1) < 0.30$, eqs 5−7 match experiment with a common H_T = 1.96; eq 3 requires a hydration number of 3.95 and shows a small deviation at the highest point of this limited range of $(\eta/\eta_0 - 1)$. Linear regression on the eq 5 circles (line not shown) yields slope = 1.008 and correlation coefficient = 0.9998. Viscosity measurements are available[25] for relatively dilute solutions of galactose, D-xylose, and D-ribose, with H_T = 1.75, 0.85, and 0.27, respectively. The relevant plots are given in the Supporting Information, Figures S7−S9.

Figure 14 is a plot for solutions at 20 °C of the disaccharide sucrose up to 30 wt %, m = 1.2524, 428.7 g in 1000 g of water.[21] The H_T values for eqs 5−7 were obtained in the domain $(\eta/\eta_0 - 1) < 0.75$, where second-order effects would not be significant; a common value of 4.2 was obtained for all three. The hydration number for eq 3 was similarly obtained as 8.8. Up to $(\eta/\eta_0 - 1) = 1$, all four equations match the unity slope, but beyond this point, eq 5, using V/V_0, performs better
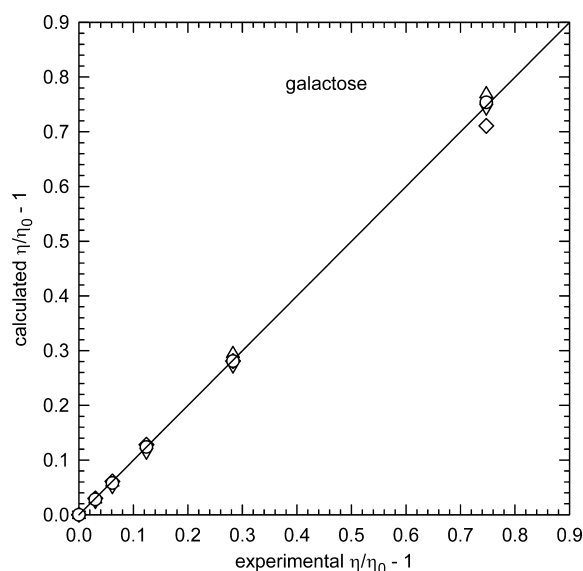
higher than the range described accurately in Figure 11. Agreement deteriorates beyond 821.7 g of solute. The relevant plot is given in the Supporting Information, Figure S5.

Figure 12 shows the plot for solutions of the monosaccharide D-fructose up to 34 wt %, m = 2.86, 515.3 g in 1000 g of water.[21] In the domain $(\eta/\eta_0 - 1) < 0.75$, eqs 5−7 have a common H_T = 1.65; eq 3 requires a hydration number of 3.80. Up to about $(\eta/\eta_0 - 1) = 1$, all four equations match experiment well. Beyond this point, eq 5 using V/V_0 yields superior agreement than do eqs 3, 6, and 7 that use V/V_{tot}.

Figure 13. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for D-galactose at 25 °C, to 223.1 g in 1000 g of H_2O and $V/V_0 = 0.1898$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated by eq 3. $H_T = 1.95$ for eqs 5–7, and the hydration number is 3.95 for eq 3. The line is drawn with a slope of unity.
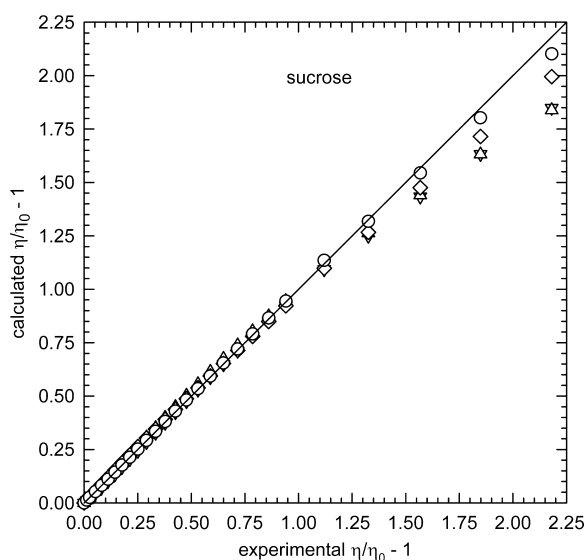

Figure 14. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for sucrose at 20 °C, up to 428.7 g in 1000 g of water and $V/V_0 = 0.4062$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated by eq 3. H_T of 4.2 for eqs 5–7, and the hydration number is 8.8 for eq 3. The line is drawn with a slope of unity.

than the other three approaches that use V/V_{tot}. Beyond 428.7 g of solute, agreement with experiment deteriorates. Viscosity measurements are available up to 84 wt %, corresponding to 5252.2 g of sucrose in 1000 g of water.

Results with solutions of the disaccharide maltose at 20 °C are shown in Figure 15, up to 26 wt %, $m = 1.0257$, 351.0 g in 1000 g of water.[21] In the early domain of $(\eta/\eta_0 - 1)$ up to 0.75, eqs 5–7 have a common $H_T = 5.1$; eq 3 has a hydration number of 10. Beyond $(\eta/\eta_0 - 1) \approx 1.0$ (~0.8 m), eq 5 performs better than the other three alternatives. Data are available to higher concentrations, but agreement deteriorates beyond 351.9 g of solute with this set of measurements. A
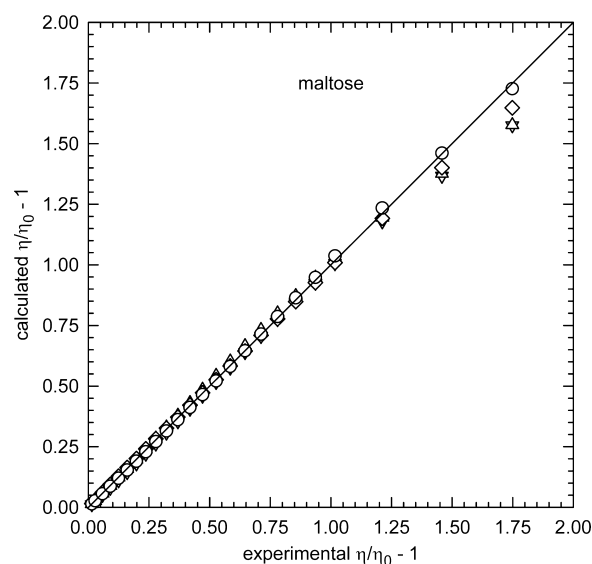

Figure 15. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for maltose at 20 °C, up to 351.0 g in 1000 g of water and $V/V_0 = 0.3537$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated by eq 3. $H_T = 5.1$ for eqs 5–7, and the hydration number is 10 for eq 3. The line is drawn with a slope of unity.

linear regression on the eq 5 circles (line not shown) yields slope = 1.006 and correlation coefficient = 0.9998.

More recent measurements of Hagen and Kaatze are available at 25 °C for maltose solutions at three concentrations.[26] They are plotted in Figure 16. Equation 5 matches
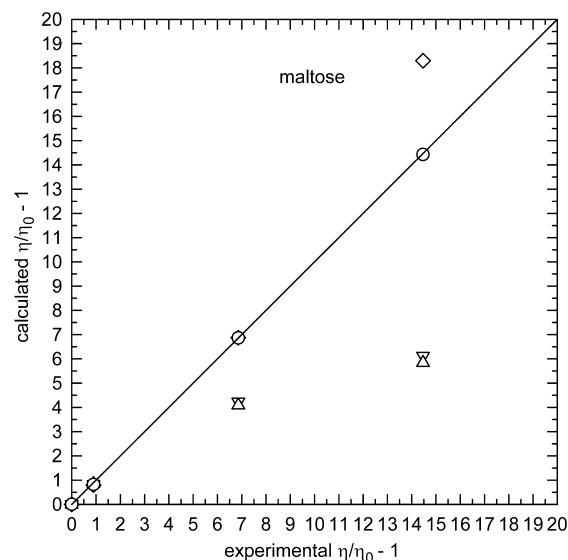

Figure 16. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for maltose at 25 °C, to 1056.31 g in 1000 g of water and $V/V_0 = 1.3638$. (O) Calculated by eq 5. (∇) Calculated by eq 6. ($\triangle$) Calculated by eq 7. ($\diamond$) Calculated by eq 3. $H_T = 5.22$ for eqs 5–7, and the hydration number is 9.9 for eq 3. The line is drawn with a slope of unity.

the experiment accurately with $H_T = 5.22$ to the highest concentration reported of 51.37 wt %, $m = 3.086$, and a noteworthy high concentration of 1056.31 g in 1000 g of H_2O. While the results of eq 5 start deviating from the older measurements beyond 26 wt % (351 g kg^{-1} of H_2O) in Figure 15, eq 5 is successful for over three times the molality of the

solute in Figure 16. Equation 3 is successful up to $(\eta/\eta_0 - 1) = 6.86$, but it fails badly at the highest available point of 14.47.

Available measurements at 25 °C for the disaccharide lactose extend to 23.38 wt % of the anhydrous substance, $m = 0.8915$, 305.14 g in 1000 g of water.[24] Solution densities were obtained from the data of McDonald and Turcote.[27] In the domain $(\eta/\eta_0 - 1) < 0.75$, eqs 5–7 yield good agreement with $H_T = 4.92$; eq 3 requires a hydration number of 9.90. The plot is shown in Figure 17. Linear regression on the circles (line not shown)
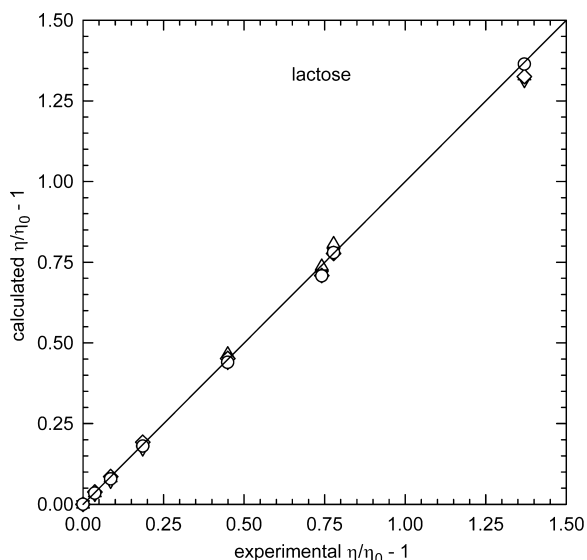

Figure 17. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for lactose at 25 °C, to 305.15 g in 1000 g of water and $V/V_0 = 0.2983$. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. $H_T = 4.92$ for eqs 5–7; the hydration number for eq 3 is 9.90. The line is drawn with a slope of unity. The point at experimental $(\eta/\eta_0 - 1) = 0.7412$ is from ref 26.

yields slope = 0.9988 and correlation coefficient = 0.9999. At the highest available concentration, eq 5 again demonstrates better agreement with experiment than the other three approaches. Viscosity measurements are also available[21] at 20 °C up to 18 wt % and yield $H_T = 5.10$ for eqs 5–7 and 10.2 for eq 3. The hydration numbers at 20 °C are marginally higher than those at 25 °C, as would be expected. The plot is given in the Supporting Information, Figure S10.

Available data for the trisaccharide raffinose at 0 °C extend only up to 8.5960 wt %, $m = 0.1864$, 94.02 g in 1000 g of water on the basis of the anhydrous material.[17] $H_T = 11.9$ for eqs 5–7. Equation 3 requires a hydration number of 19.5. The results are shown in Figure 18. In this limited viscosity range, eqs 6 and 7 yield fairly good agreement with experiment; eqs 5 and 3 show excellent agreement. Linear regression on the eq 5 circles (line not shown) yields slope = 0.9972 and correlation coefficient = 0.9994.

Measurements are also available for raffinose solutions at 25 °C, up to 8.5959 wt %, $m = 0.1863$, 94.02 g in 1000 g of water on the basis of the anhydrous material.[17] Figure 19 shows the results of values calculated by eqs 5–7 with a common $H_T = 8.8$ and a hydration number of 15 by eq 3. A significant decrease in the value of H_T is observed relative to that at 0 °C. Linear regression on the circles (line not shown) yields slope = 0.9991 and correlation coefficient = 0.9999. Measurements of Dunlop at 25 °C[28] used up to 3.46 wt %, $m = 0.07111$, and yield a
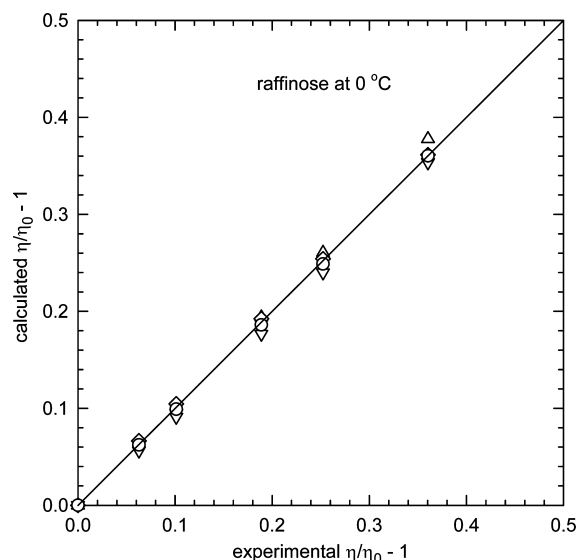

Figure 18. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for raffinose at 0 °C for all available data; maximum $V/V_0 = 0.1036$. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. $H_T = 11.9$ for eqs 5–7; the hydration number for eq 3 is 19.5. The line is drawn with a slope of unity.
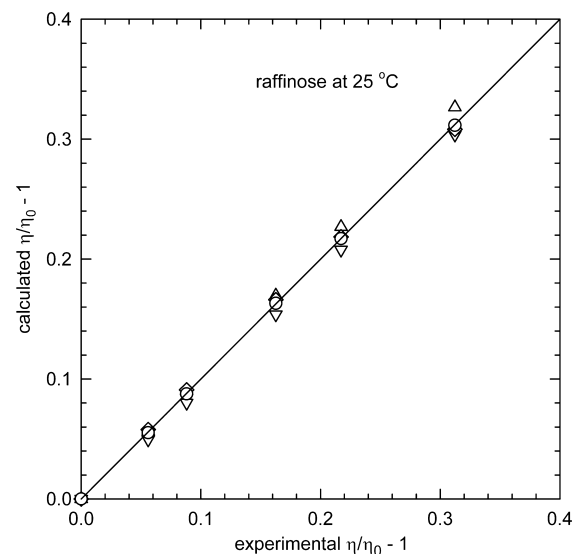

Figure 19. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for raffinose at 25 °C for all available data; maximum $V/V_0 = 0.0913$. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. $H_T = 8.8$ for eqs 5–7, and the hydration number is 15 for eq 3. The line is drawn with a slope of unity.

similar value of $H_T = 8.7$. The plot is given in the Supporting Information, Figure S11.

Available measurements of raffinose solutions at 50 °C extend to 8.596 wt %, $m = 0.1864$, 94.91 g in 1000 g of water on the basis of the anhydrous material.[17] Figure 20 shows the performance of eqs 5–7 with a common $H_T = 6.2$ and that of eq 3 with a hydration number of 11.5. Linear regression on the eq 5 circles (line not shown) yields slope = 0.9976 and correlation coefficient = 0.9999. The hydration number continues to decrease as the temperature increases.

Viscosity and density measurements of aqueous solutions of triethanolamine, $N(CH_2CH_2OH)_3$, are available up to 3.0 molar at 30 and 40 °C.[29] The molar volume of pure
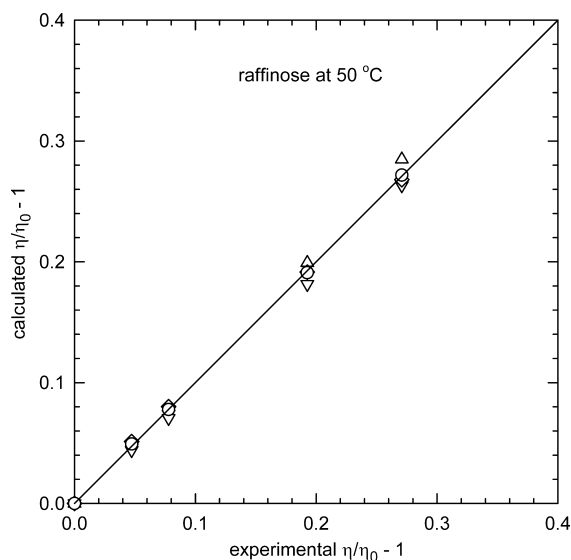
Figure 20. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for raffinose at 50 °C for all available data; maximum $V/V_0 = 0.0749$. (O) Calculated by eq 5. (◇) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. $H_T = 6.2$ for eqs 5–7, and the hydration number is 11.5 for eq 3. The line is drawn with a slope of unity.

triethanolamine is the molar mass divided by the density,[30] $149.17/1.124 = 132.71$ cm^3. For the three most dilute data at 30 and 40 °C, eq 5 can be approximated as $(\eta/\eta_0 - 1) \times V_{tot}/2.9 = V$ because the second-order term would not be very significant. Plots of $(\eta/\eta_0 - 1) \times V_{tot}/(2.9 \times m)$ versus m extrapolated to infinite dilution provide an estimate of V, the hydrodynamic effective molar volume. The two plots are in Figure 21. At 30 °C, the zero intercept is 137.9 cm^3 mol^{-1}, and at 40 °C, it is 133.7 cm^3 mol^{-1}. These effective molar volumes are very nearly equal to the molar volume of the pure compound and indicate a hydration number, H_T, near 0.

Accurate determination of the extent of hydration of triethanolamine is obtained by using all available measure-
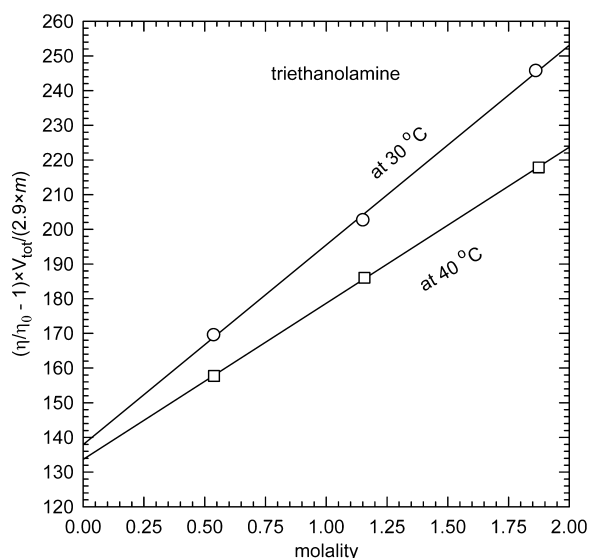

Figure 21. Plot of $(\eta/\eta_0 - 1) \times V_{tot}/(2.9 \times m)$ versus m for tiethanolamine at 30 and 40 °C, with the experimental values of $(\eta/\eta_0 - 1)$, V_{tot}, m, and $k = 2.9$. The zero intercepts indicate the hydrodynamic effective molar volume of solute at infinite dilution.

ments.[30] A plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values is shown in Figure 22 for solutions at 30 °C for all
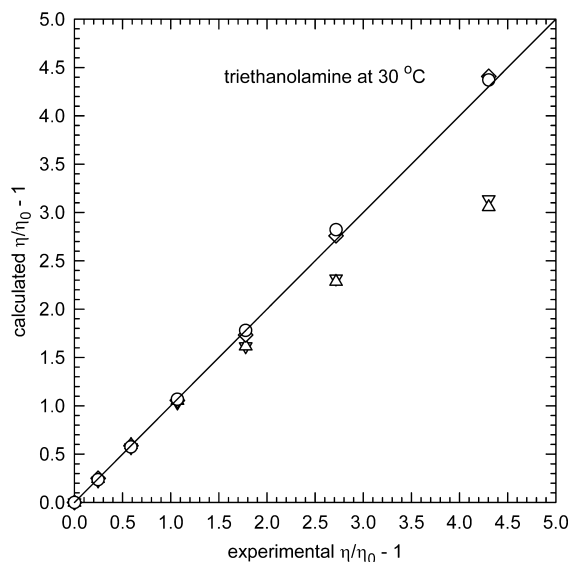

Figure 22. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for triethanolamine at 30 °C, to 727.14 g in 1000 g of water and $V/V_0 = 0.6616$. (O) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. $H_T = 0.00$ for eqs 5–7, and the hydration number is 2.21 for eq 3. The line is drawn with a slope of unity.

available experimental values that go up to 42.10 wt %, $m = 4.874$, 727.14 g in 1000 g of water. A common $H_T = 0.00$ satisfies eqs 5–7 up to $(\eta/\eta_0 - 1) = 1.1$; similarly, a hydration number of 2.2 is obtained for eq 3. Equations 6 and 7 fail beyond $(\eta/\eta_0 - 1) = 1.5$. Linear regression on the eq 5 circles (line not shown) yields slope = 1.023 and correlation coefficient = 0.9998. Both eqs 5 and 3 agree with experiment up to a high value of 727.14 g in 1000 g of H$_2$O. It is particularly noteworthy that, despite $H_T = 0.00$, these solutions exhibit a contraction in volume. The molar volume of the solute is $(149.17$ g$)/(1.124$ g cm$^3) = 132.71$ cm^3. At the highest concentration, the volume of pure solute is $4.874 \times 132.71 = 646.83$ cm^3, and the volume of 1000 g of water is 1004.35 cm^3, for a sum of 1651.18 cm^3, while the experimental volume of this solution is 1624.53 cm^3. There is a volume contraction of 26.65 cm^3. This point will be addressed further in the Discussion section.

Additional measurements of viscosities and densities are available for triethanolamine solutions at 20 °C expressed in terms of polynomial analytical functions.[31] The measurements extend to 33.986 wt %, $m = 3.4513$, 514.83 g in 1000 g of H$_2$O. This set of data is satisfied with $H_T = 0.14$ for eq 5 and a hydration number of 2.35 for eq 3. The small increase in H_T at 20 °C relative to $H_T = 0.0$ at 30 °C is in the expected direction. The relevant plot is given in the Supporting Information, Figure S12.

Density and viscosity measurements of solutions of diisopropanolamine, bis(2-hydroxypropyl)amine, are available at temperatures between 25 and 70 °C for mole fractions of 0.000–1.000 amine.[32] Measurements at 25 °C are compared to those calculated by eqs 3 and 5 in Figure 23 up to a concentration of 6.175 m, 822.4 g in 1000 g of water. The results of eq 5 with $H_T = 1.47$ adhere to the slope of unity fairly well up to the concentration limit plotted, up to a high value of
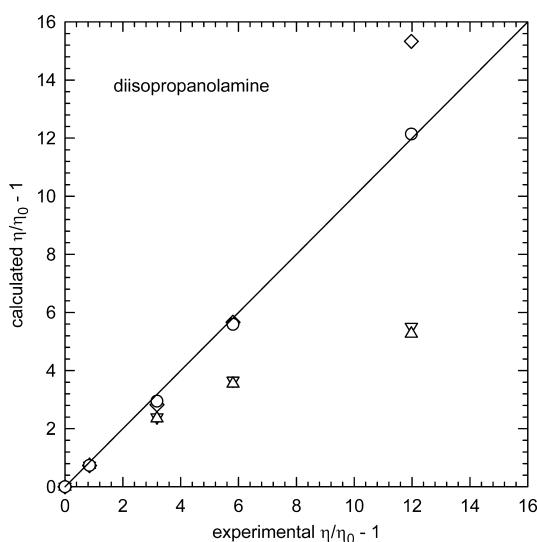
10064

dx.doi.org/10.1021/jp306248a | J. Phys. Chem. B 2012, 116, 10055–10069

Figure 23. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for diisopropanolamine at 25 °C, up to 822.32 g in 1000 g of H_2O and $V/V_0 = 1.2359$. (○) Calculated by eq 5. (▽) Calculated by eq 6. (△) Calculated by eq 7. (◇) Calculated by eq 3. For eqs 5–7, $H_T = 1.47$; for eq 3, the hydration number is 4.0. The line is drawn with a slope of unity.

822.32 g in 1000 g of H_2O. Equation 3 does well up to $(\eta/\eta_0 - 1) = 5.809$ with a hydration number of 4.0 but fails badly beyond this point. Equations 6 and 7 with $H_T = 1.47$ match only the most dilute point.

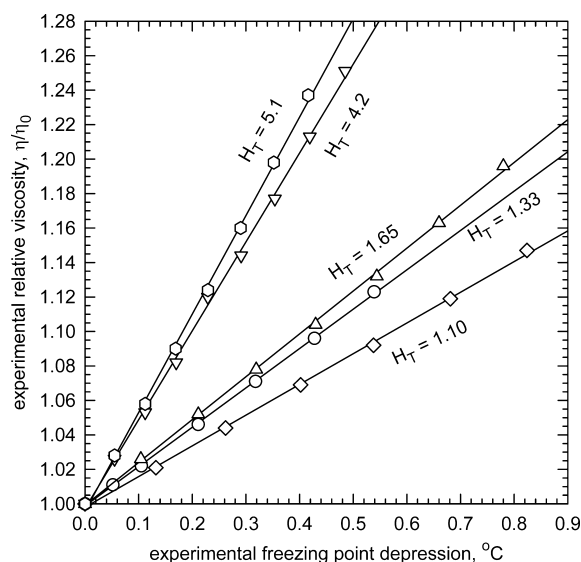Figure 24 shows the relationship between experimental viscosities and experimental freezing point depressions, ΔT,[21]

Figure 24. Plots of experimental relative viscosity (η/η_0) versus experimental freezing point depressions. (◇) Tartaric acid. (○) Citric acid. (△) Fructose. (▽) Sucrose. (○) Maltose. The H_T values from viscosities are shown for each.

of relatively dilute solutions for five typical solutes. Even though viscosity is not a colligative property, the linear relation between η/η_0 at 20 °C and ΔT is evident. Both quantities plotted are purely experimental measurements, devoid of interpretation.

The proposal put forth here that volume ratios in equations relating to viscosities must be expressed in terms of V/V_0 and not V/V_{tot} is supported strongly by examining the relation between each of them and experimental freezing point depressions, ΔT.[21] A linear relationship between V/V_0 and ΔT holds over extended ranges of concentration. Figures 25–27 show some typical plots. The straight lines are the result of linear regression on the circles of eq 5. Linearity is present only with V/V_0.
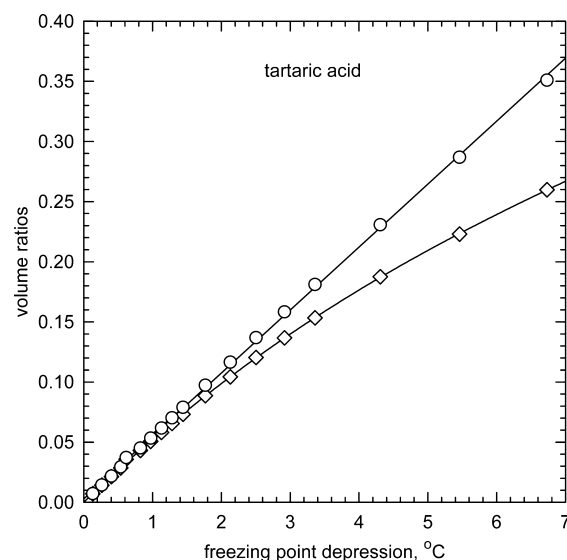

Figure 25. Plot of volume ratios of tartaric acid solutions up to 32 wt % (470.7 g in 1000 g of H_2O and $V/V_0 = 0.3510$) at 20 °C versus freezing point depressions. (○) Volume ratio = V/V_0. (◇) Volume ratio = V/V_{tot}.

Conspicuous by their absence among the solutes treated above are some well-studied relatively small molecules, such as methanol, ethanol, 1-propanol, urea, ethylene glycol (1,2-
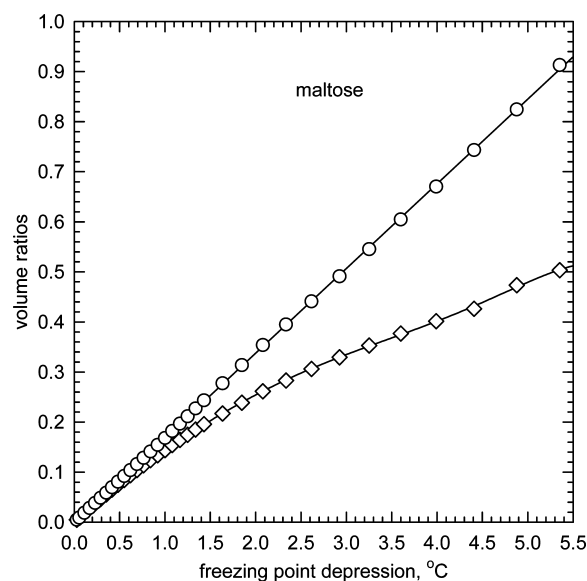

Figure 26. Plot of volume ratios of maltose solutions up to 44 wt % (785.3 g in 1000 g of H_2O and $V/V_0 = 0.9132$) at 20 °C versus freezing point depressions (all available data[21]). (○) Volume ratio = V/V_0. (◇) Volume ratio = V/V_{tot}.
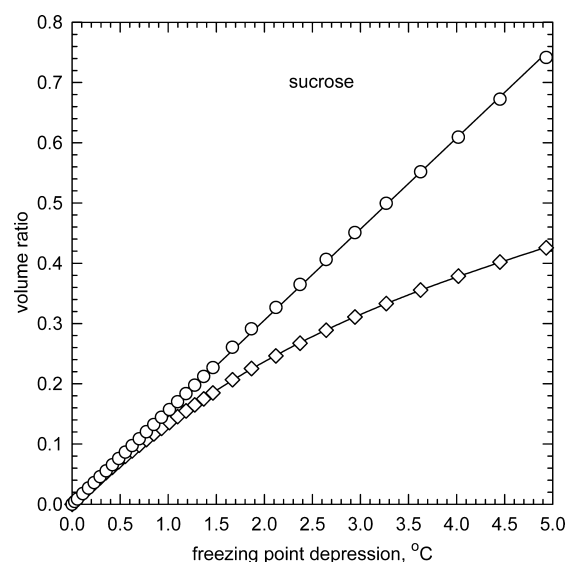
Figure 27. Plot of volume ratios of sucrose solutions up to 42 wt % (742.1 g in 1000 g of H_2O and $V/V_0 = 0.7414$) at 20 °C versus freezing point depressions (all available data[21]). (○) Volume ratio = V/V_0. (◇) Volume ratio = V/V_{tot}.

dihydroxyethane), glycine, and so forth. A typical plot for such species is Figure 28, showing the results with eqs 5 and 3 for
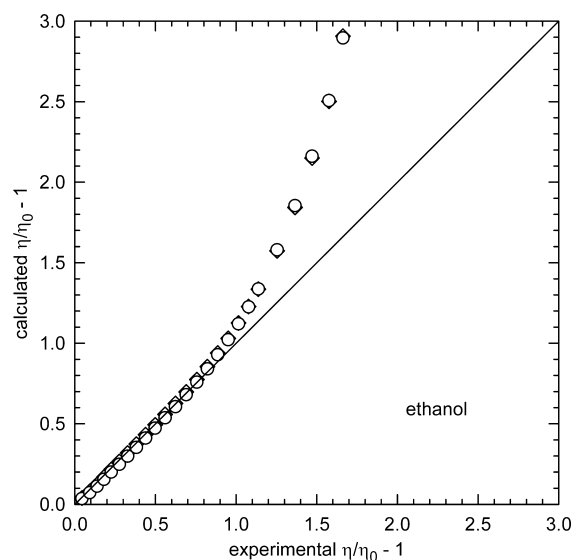

Figure 28. Plot of calculated $(\eta/\eta_0 - 1)$ versus experimental values for ethanol solutions at 20 °C, up to 30 wt % and $V/V_0 = 0.5052$. (○) Calculated by eq 5. (◇) Calculated by eq 3. $H_T = -0.24$ for eq 5, and the hydration number is 0.70 for eq 3. The line is drawn with a slope of unity.

viscosities of ethanol solutions.[21] For all such small-volume species, negative H_T values are needed to match the experimental measurements at $(\eta/\eta_0 - 1) \approx 0.75$ and show upward curvatures as does ethanol. Even though freezing point depression measurements show positive H_T values, negative H_T values with viscosity measurements seem to indicate that the solutes are producing water! Another example of similar nonsense results is obtained with methanol solutions at 20 °C,[21] for which H_T is negative at −0.63. A plot similar to that of Figure 5 with this H_T value yields a molar volume at infinite

dilution of 2.33 cm³ with $k = 2.5$ and of 2.45 cm³ with $k = 2.9$, rather than the minimum of 40.49 cm³ of pure liquid methanol. Similarly, viscosities of glycine solutions[25] have $H_T = 0.0$ and a molar volume of 0.0 cm³ at infinite dilution. The plots for methanol and for glycine solutions are in the Supporting Information, Figures S13 and S14. Such strange results will be discussed in the following section.

■ **DISCUSSION**

In plots of calculated versus experimental viscosities that extend beyond the relatively dilute domain of up to $(\eta/\eta_0 - 1) \approx 1.0$, the values calculated by eq 5, $(\eta/\eta_0 - 1) = 2.9 \times (V/V_0) + 5.6 \times (V/V_0)^2$, match experiment better than any of the other alternatives to which eq 5 has been compared. The single exception at high concentrations is the case of Figure 22 for solutions of triethanolamine, where eqs 5 and 3 perform equally well. This is also the only case where $H_T = 0.00$, no bound water.

The overall performance of eq 3 is better than that of eqs 6 and 7, but the hydration numbers that it requires to match experiment bear no relation to hydration numbers obtained from colligative properties and other phenomena.[10−12] It has been noted that eq 3 is not derivable from Einstein's work and that it is an empirical relation.[33]

Using volume ratios expressed as V/V_0 results in H_T values consistent with those from freezing point depressions. The average number of strongly bound waters is the same, irrespective of what measurements are being performed of colligative properties or of viscosities. As Figures 25−27 have shown, plots of V/V_0 versus freezing point depressions are linear to very high concentrations, while those of V/V_{tot} are not.

Deviations of calculated viscosities from experimental values at very high concentrations indicate the onset of effects other than those accounted for by eq 5. What these effects might be would constitute conjectures at this point. One known effect that is not accounted for is that, at high concentrations, hydrogen-bonding solutes start bonding strongly to each other,[11] rather than only to the solvent water, and thus cause changes in H_T and in the volume of solute particles.

The negative H_T values found with small molecules can be understood in terms of their molar volumes. Einstein's equation was derived for and is applicable only to solute particles that have molar volumes "significantly greater" than the molar volume of the solvent, water in the present case. All solutes examined with molar volumes smaller than about 85 cm³ were found to produce negative H_T values. Then, the question arises as to what is the hydrodynamic effective volume of water itself, an aspect not addressed by Einstein. It certainly is not 18 cm³ because now it is well established that water forms some rather stable clusters. Spectroscopic studies have shown that liquid water contains ice nanoparticles.[34] Relative abundances up to the water pentamer indicate that the trimer is the most abundant but that there are also many clusters large enough to resemble amorphous ice.[34] The water hexamer is the crossover point beyond which noncyclic structures become more stable than the cyclic structures found up to the pentamer.[35] As cluster size increases, the O−O distances converge toward the corresponding distance in ice Ih.[36] A minimum estimate of the hydrodynamic effective volume of water would be that of the trimer, $3 \times 18 = 54$ cm³. The average strongly bound cluster size of water near room temperature cannot be greater than 85 cm³ because Einstein's viscosity relationship would then fail, but it does not. Dividing 85 cm³ by the molar volume of

monomeric H_2O indicates $85/18 \approx 4.7$ as the maximum possible average clustering of water. This conclusion is consistent with the report of Yethiraj et al.[37] of a coarse-grained model for water consisting of cluster units of four water molecules, the volume of which would be approximately $4 \times 18 = 72$ cm^3. This model describes known experimental properties of water quite successfully. Additional waters will hydrogen bond to such water clusters, but likely with binding energies lower than 13.3 kcal mol^{-1} and with small residence times. Evidently, solutes with molar volumes greater than about 85 cm^3 have volumes "significantly greater" than the hydrodynamic effective volume of water near room temperature.

In further support of the validity of the volume ratio being expressed as V/V_0, Figure 29 shows a plot of volume
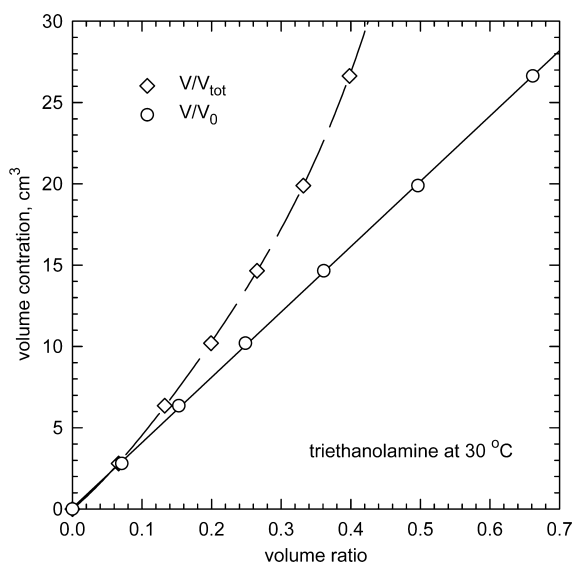

Figure 29. Plot of volume contractions of solutions of triethanolamine at 30 °C versus volume ratios. (○) Versus V/V_0. (◇) Versus V/V_{tot}.

contractions of solutions of triethanolamine at 30 °C versus V/V_0 and versus V/V_{tot}. Volume contractions are common with solutions of nonelectrolytes, as they are with solutions of electrolytes, where contractions of the latter are explained by electrostriction caused by the electric field effects of ions.[38] For nonelectrolytes, volume contractions are often ascribed to a shrinking of the volume of water bound to solute.[22,39] Because triethanolamine solutions have $H_T = 0.00$, volume contractions cannot be ascribed to a decrease in the volume of bound water molecules, there being none. The experimental total volumes are smaller than the sum of the volumes of the pure solute and of the water. The difference at each molality is the volume contraction. Figure 29 shows that the amount of volume contraction of triethanolamine solutions at 30 °C is linearly related to V/V_0, not to V/V_{tot}, up to a high concentration of 4.874 m. This fact supports the use made of the molar volume of monomeric water in calculating molar volumes of strongly hydrated solutes.

One possible explanation of the facts found with triethanolamine is that the water molecules surrounding the solute, even though not tightly bound to it, are incapable of participating in forming water clusters because they are not surrounded by other water molecules. Ice has a density of 0.92, or about 8% lower than that of liquid water near room temperature. By the law of mass action, the decrease in the concentration of water

capable of forming clusters will decrease the fraction of water residing in larger, ice-like clusters of lower density.[34−36] This will cause an increase in the density of bulk water with a concomitant decrease in its volume. At the highest solute concentration of triethanolamine, the total volume decrease is 26.63 cm^3, which is only a 1.6% decrease of the density of the free, bulk water. Triethanolamine has a molar volume of 133 cm^3, and several water molecules can fit around it, solvating it and thus becoming incapable of participating in the formation of clusters. The statistics of hydrogen-bond strengths are only weakly modified beyond the first solvation shell even with ionic solutes.[40] The small 1.6% change in the density of bulk water and associated characteristics will be difficult to detect experimentally. Volume contractions of other solutes are complicated by the existence of bound waters and interpretation of such volume contractions no longer is straightforward.

On the basis of gas-phase ion−water cluster measurements of sequential binding energies, water molecules were considered "bound" to solute if their binding energy was greater than about 13.3 kcal mol^{-1}.[10] One may question whether the same value is appropriate for the nonelectrolytes treated in this work. Recent theoretical calculations of sequential binding energies of a water molecule to other waters provide support for this value with neutral species.[41] For $H_2O + (H_2O)_n \rightarrow (H_2O)_{n+1}$, the sequential binding energies are 4.9 kcal mol^{-1} for $n = 1$, 10.0 kcal mol^{-1} for $n = 2$, 11.3 kcal mol^{-1} for $n = 3$, and 13.0 kcal mol^{-1} for $n = 4$ (for forming the pentamer). Energetically, a water molecule will be more stabilized by binding to other waters if its binding energy to solute is smaller than 13.0 kcal mol^{-1}. The required binding energy for a water molecule to become "bound" to solute is not dependent on the solute. It depends on the binding energy of water to other waters. If a water molecule can bind to solute with more than 13.3 kcal mol^{-1}, it will bind to solute; if not, it will be more stable by binding to other waters to form clusters.

The value of H_T obtained in this work may be misinterpreted as an empirical constant derived from experimental data so as to fit the data from which it was derived. That this is not the case, but that H_T has physical meaning, is demonstrated by the classic experiments of Rais et al.,[42] Motomizu et al.,[43] and Osakai et al.[44] In two-phase mixtures of water and nitrobenzene containing bases soluble in the organic phase, they analyzed the numbers of various cations extracted from the water layer into the organic layer and the number of water molecules, n, coextracting with the cations at 25 °C. The values of n so measured are shown in Table 1, along with the H_T values of the cations reported from freezing point depression measurements.[11] The coextraction measurements have nothing to do with either colligative properties or viscosities. Despite the difference in temperature, the correspondence between the experimentally determined n and the H_T values is unmistakable. H_T is not an empirical constant but quantifies the average number of water molecules that are more strongly bound to the solute and are extracted into the organic layer with it, rather than remaining bound to other waters and staying in the aqueous layer.

Finally, Einstein's stated reasoning for the viscosity relationship of eq 2 is examined. He concluded that the solute "together with the bound water held by it" is impeding the mobility of the water.[1] Which water? Is it the bound water, the unbound free water, or the total water that is being impeded? It is clear that what was meant was not the bound water stuck to the solute that is being impeded. It is the rest of the water, the

Table 1. Numbers of Water Molecules, n, Coextracting with Cations from the Aqueous Layer into Nitrobenzene Compared to H_T Values from Freezing Point Depression Measurements

cation	n	H_T
Li$^+$	6.3,[a] 5.7,[b] 4.2,[c] 5.5[d]	6.7 (2)[e]
Na$^+$	4.0,[a] 3.6,[b] 3.6,[c] 3.5[d]	3.5 ± 0.2 (5)[e]
K$^+$	1.0,[b] 1.0,[c] 1.3[d]	1.1 ± 0.2 (8)[e]
Rb$^+$	0.7,[b] 0,[c] 0.7[d]	0.6 (1)[e]
Cs$^+$	0.4,[b] 0,[c] 0.7[d]	0.4 (1)[e]
Ca^{2+}	15,[a] 12,[b] 13[d]	12.1 ± 0.1 (2)[e]
Ba^{2+}	10,[a] 11,[b] 9.4[d]	9.4 ± 0.1 (3)[e]

[a]Reference 44; the organic anion was tetraphenylborate. [b]Reference 44; the organic anion was the anion of bis(2,4,6-trinitrophenyl)amine. [c]Reference 42. [d]Reference 43. [e]Reference 11; the numbers in parentheses designate the number of salts of chlorides, bromides, iodides, and thiocyanates from which the H_T values were obtained.

free water V_0, whose mobility is being impeded by the hydrated solute particles. The volume ratio meant is V/V_0. Einstein seems to have simplified the notation *at infinite dilution* as V/V_{tot}, which is equal to V/V_0 at infinite dilution. It appears that Einstein's viscosity relationship, using V/V_{tot}, is being misapplied to real solutions. Use of V/V_0 has been shown here to produce more accurate descriptions of viscosities to quite high concentrations and to be consistent with H_T values from colligative properties that have been shown to correlate with many other, some apparently unrelated, phenomena.[10−12] The interpretation given here to the volume ratio of Einstein's eq 2 is consistent with Einstein's explicitly stated reasoning.

CONCLUSIONS

The appropriate volume ratio to be used with Einstein's viscosity relationship is V/V_0 for the solutes treated in this work at realistic concentrations. V denotes the hydrodynamic effective molar volume of solute along with the water bound to it sufficiently strongly as to become part of the solute and act as a single particle with it. V_0 denotes the volume of the rest of the water, the free water that constitutes the solvent. The proportionality constant of 2.5 for the relationship between $(\eta/\eta_0 - 1)$ and volume ratios of perfect spheres is not valid for the many hydrophilic compounds treated in this work. A value of 2.9 is operative. The equation $(\eta/\eta_0 - 1) = 2.9(V/V_0) + 5.6(V/V_0)^2$ describes experimental measurements accurately for wide ranges of concentration and volume fraction. The hydrodynamic effective volume of water near room temperature is likely greater than 54 cm^3 but definitely less than 85 cm^3; the best estimate is that of the tetramer cluster of about 72 cm^3.

ASSOCIATED CONTENT

S Supporting Information

Additional plots of calculated versus experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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