

Einstein's Theory of Viscosity – Applicability to Amino Acid Solutions with Urea (Aq)

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Abstract: To determine the effective hydrodynamic radii of small uncharged molecules in dilute aqueous solution, Einstein's classical theory of viscosity can be employed. The radii thus obtained are considered as hypothetical sphere whose hydrodynamic behavior is the same as that of the solute molecule along with that solvent which is too firmly bound to the solute in viscous shearing process. Einstein's formula is recuperated as a first-order asymptotic extension of the effective viscosity in the volume fraction. The formula is applied to molecules having comparable size to that of water. Determining the viscometric radii of Glycine in solution with Urea(aq) from Einstein's equation, an attempt has been carried out to obtain empirical correction for Stokes-Einstein diffusion equation.

Keywords:

Viscosity, Einstein's equation, solute-solvent interactions, hydrodynamic radius, temperature dependence

INTRODUCTION:

The methods such as molecular model or crystallographic studies available for determining size of small uncharged molecules in solution using do not allow for solvation of molecules in solution. Electrostriction between solute and solvent molecules introduces an additional theoretical drawback to calculations based on the partial molal volume of solute in aqueous solution. Einstein's effective viscosity relation has been proved by Minton and Grupi[1] for a dilute suspension of binary and ternary mixtures of Non-associating proteins[2].

MATERIAL AND METHOD:

0.01M aqueous solution of Urea (minimum assay 99%, Qualigens) was prepared by w/v. Solutions of Glycine 0.103m to 1.012 m (precision of $\pm 1 \times 10^{-4}$ g on electronic digital balance) were prepared with Urea(aq). Density was measured by precalibrated bicapillary pycnometer (error $\pm 0.06\%$), viscosity by precalibrated Ostwald's viscometer(error $\pm 0.07\%$), sound speed by Ultrasonic interferometer (Mittal Enterprises, New Delhi, Model F-81) working at a fixed frequency of 2 MHz up to an accuracy of $\pm 0.04\%$ were measured at constant temperature in a refrigerated water bath maintaining temperature up to $\pm 0.1^\circ\text{C}$ [1-3]. The experimentation is carried out at temperature 298 K, 308 K and 318K in order to have precise information on the interactions in the solution.

Einstein's classical hydrodynamic treatment of viscosity has been employed for the determination of the effective

hydrodynamic radii of small amino acid Glycine molecules in dilute aqueous solution of Urea (urea in aqueous is considered as solvent). Einstein's theory proposes the effect of solute particles in viscous flow of to distort the stream-lines of solvent flow, thereby introducing a rotational quality. This obstructing action increases the energy dissipated at constant shear velocity and also the coefficient of internal friction or viscosity.

The viscosities (η) of the solutions of Glycine with Urea(aq) enhances with the increase in concentration of amino acids at all temperatures and lessen with the ascending temperature (Table 1). The increase with concentration can be explained as the molecular association between solute and solvent. Thermal energy influences the bond strength, hence η decline with the rise of temperature.

When rigid uncharged spheres are randomly dispersed in an incompressible medium, the viscosity of the pure solvent is increased according to the relationship:

$$\eta = \eta_0 (1 + 2.5\phi) \quad \dots\dots\dots(1)$$

Where η = the viscosity of the solution, η_0 = the viscosity of the pure solvent,

and ϕ = the volume fraction of the solvated solute molecules.

Einstein states for very small rigid spheres suspended in a liquid, the coefficient of viscosity increases by a fraction that is equal to 2:5 times the total volume of the spheres suspended in a unit volume, provided that this total volume is very small[3].

Einstein's theory was developed on the assumption that the solute molecule is large compared to the solvent molecules. The application of this treatment to molecules whose sizes are comparable to that of water represents a considerable extrapolation to infinite dilution.

The formula above should be interpreted as a first-order calculation in an infinite asymptotic expansion of the true effective viscosity in powers of the volume fraction[4].

Einstein used this method in his original paper to determine the radius and hydration of sucrose, a molecule whose radius is only three times greater than that of water. The validity of Einstein's theory has been experimentally confirmed for

suspended particles with radii as small as 50 Å [5]. Several modifications have been developed for more concentrated solutions[6]. Mooney realized that, at higher concentrations, the empirical data for relative viscosity appear to follow more of an exponential function of concentration. Correlations between relative viscosity η_r and volume fraction were modified accordingly and various empirical relations were given by Krieger and Dougherty, Mooney, Eilers, Quemada and Robinson[7].

The effective hydrodynamic radius may be defined as the radius of a rigid uncharged sphere which exhibits the same hydrodynamic behavior as the solvated molecule in solution, thus including that water of hydration which is too firmly bound to participate in the viscous shearing process.

In the present experiments, the problem of concentration dependence has been avoided by extrapolation of the reduced viscosity to infinite dilution. At very low concentrations an average value of the reduced viscosity has been used[8].

The equation then becomes

$$\lim_{c \rightarrow 0} \left[\frac{(\eta/\eta_0) - 1}{C} \right] = 2.5\phi / C \quad \dots\dots(2)$$

Where C is the concentration of solute in molar units.

The effective hydrodynamic radius (r, in cm) is thus expressed as

$$r = \left[\frac{300}{\pi N} \lim_{c \rightarrow 0} \left\{ \frac{(\eta/\eta_0) - 1}{C} \right\} \right]^{1/3} \quad \dots\dots(3)$$

Where N is Avogadro's number

RESULTS AND DISCUSSIONS:

Viscosities measured over the concentration range from 0.01M to 1.02 M are given in Table 1 together with the calculated hydrodynamic radii.

As can be seen from our data, the effective hydrodynamic radii show very little dependence on concentration.

S. No.	Conc. mol kg ⁻¹	Viscosity [η/(x10 ⁻³ Ns m ⁻²)] at	Effective Hydrodynamic radius in Å
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		298 K	
1	0.0000	0.8799	----
2	0.1030	0.8925	2.804
3	0.2060	0.9028	2.716
4	0.3090	0.9131	2.685
5	0.4119	0.9203	2.605
6	0.5149	0.931	2.615
7	0.6179	0.9445	2.661
8	0.7209	0.9668	2.79
9	0.8239	0.9892	2.881
10	0.9269	1.0044	2.893
11	1.0298	1.0193	2.9
S. No.	Conc. mol kg ⁻¹	Viscosity [η/(x10 ⁻³ Ns m ⁻²)] at 308 K	Effective Hydrodynamic radius in Å
1	0.0000	0.715	----
2	0.1030	0.7324	3.3498
3	0.2060	0.7442	3.156
4	0.3090	0.7522	2.9888
5	0.4119	0.7638	2.9729
6	0.5149	0.775	2.9565
7	0.6179	0.7863	2.9468
8	0.7209	0.8051	3.0263
9	0.8239	0.8239	3.0833
10	0.9269	0.8347	3.0595
11	1.0298	0.8456	3.0411
S. No.	Conc. mol kg ⁻¹	Viscosity [η/(x10 ⁻³ Ns m ⁻²)] at 318 K	Effective Hydrodynamic radius in Å

1	0.0000	0.6019	----
2	0.1030	0.6231	3.8017
3	0.2060	0.6336	3.4542
4	0.3090	0.6434	3.3046
5	0.4119	0.6533	3.2282
6	0.5149	0.6647	3.2071
7	0.6179	0.6764	3.1983
8	0.7209	0.6918	3.2379
9	0.8239	0.7076	3.2722
10	0.9269	0.7152	3.2233
11	1.0298	0.7228	3.1836

The effective hydrodynamic radii also depend on temperature (Table 1).

To conclude the increase in the effective hydrodynamic radii with increasing temperature is consistent with a increased degree of molecular hydration. Second, the relatively small magnitude of the temperature effect on the effective hydrodynamic radii suggests that long range solute-solvent interactions are of second order importance for this compound.

The increasing hydrodynamic radius with higher temperatures can be explained as the solvent structure disrupted by increased thermal agitation and neglected or minimum disordering effect of the solute particle[9,10]. The increasing values with temperature also suggest that long range solute-solvent interactions are also important in the parameter we have computed.

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