



## MATHEMATICAL INTERPRETATION OF STRUCTURE MAKING AND STRUCTURE BREAKING PROPERTIES OF SOLUTES BY USING VISCOMETRIC AND VOLUMETRIC METHODS

Shaukat A. Shah<sup>1</sup>, Ratnakar B. Lanjewar<sup>2</sup> and Ashish P. Wakulkar<sup>3</sup>

<sup>1,3</sup>Department Of Chemistry, Anand Niketan College, Anandwan, Warora (M.S)

<sup>2</sup>Department of Chemistry, Dharampeth M.P. Deo Memorial Science College, Nagpur

Communicated : 23.01.2023

Revision : 28.02.2023 & 08.03.2023

Published : 30.05.2023

Accepted : 03.04.2023

### ABSTRACT:

From Experimental data of densities and viscosities of solvent and solutions is used to predict solute-solvent interactions. From density data, apparent molar volume ( $\Phi_V$ ), intercept value ( $\Phi_{V0}$ ), (partial molar volume), slope of the graph ( $S_V$ ) were calculated and viscosity coefficient B (slope) and A (intercept) were calculated from the viscosity data using Jones-Dole equation. How signs (positive and negative) of intercepts and slopes attribute solute-solvent and solute-solute interactions of hydrated or solvated solute is explained in this paper.

**Keywords :-** Apparent molar volume, Partial molar volume, Jone-Dole equation, salvation or hydration.

### INTRODUCTION :

Hydrated solutes (in case of non-electrolytes) or ions (in case of electrolytes) have basic applications in chemical and biological processes [1]. Most biochemical processes take place in aqueous media. This involves hydration of molecular species or ions and contraction or expansion of volume which depends on the nature of solutes. Hydration of solutes or ions is of great interest to understand the influence of studied molecular species on the water structure in an aqueous solution in relation to their participation in the stability and biological functions [2]. Hydration is one of the most important interactions which are responsible for the secondary structure of molecular species/ ions through non-covalent bonding and other physicochemical properties of solutes [3]. The ability of solute to change the properties of solvent or cosolvent in solution depends on their molecular characteristics such as size, shape, conformation and configuration [4]. Intracellular and extracellular environment of cell depends on the structure of water molecules. Due to

addition of solute in water, water's hydrogen bond strength is supposed to be changed many physicochemical properties [5]. Water play central role in the study of biochemical processes. After dissolution, solute becomes less or more hydrated. Nature of hydrated molecules (solutes) governs shape, size, stereochemistry and physicochemical properties. Molecular volumes of hydrated molecules are also related to apparent molar volume, partial molar volume, hydrophobicity, hydrophilicity, compressibility and other thermo acoustic parameters [6]. Volume of any molecules is important in biological context. Viscometric and volumetric methods are easy to measure these parameters.

### EXPERIMENTAL :

Solute (electrolytes or non-electrolytes) is used. It should be very pure (purity of > 99%). The water/ any solvent used for the preparation of solution were double distilled. The molar / molal solution of solute was prepared by using digital electronic balance with great accuracy

Densities ( $\rho$ ) and viscosities ( $\eta$ ) of studied solutions was measured by using specific gravity

bottle by relative measurement method or digital densitometer with accuracy of  $\pm 0.1 \text{ kg.m}^{-3}$  and An Ostwald's viscometer or Digital viscometer was used for the measurement of viscosity of liquid mixtures with an accuracy of  $0.0001 \text{ Nsm}^2$  respectively. The viscometer was calibrated before used.

## RESULTS AND DISCUSSION :

### Apparent, partial molar/molal Volume, Slope and Intercept

When a solute added into solvent, solute molecules get hydrated or solvated and its volume changed. This volume of hydrated or solvated solute is called apparent molar/ molal volume. At very dilute (infinite dilution) solution, more number of solvent molecules is available per solute molecules, this leads to greater size of the solute. Hydrated/solvated volume of solute at infinite dilution is called partial molar/molal volume [7,8,9].

Apparent molar or molal volume can be calculated from the density data by using eq. (1.1)

$$\Phi_V = \frac{M}{\rho_0} - \frac{1000(\rho - \rho_0)}{C\rho_0} \quad (1.1)$$

Or equation ... (1.2) is also rearranged as

$$\Phi_V = \frac{M}{\rho_0} + \frac{1000(\rho_0 - \rho)}{C\rho_0} \quad (1.2)$$

Where,  $\Phi_V$ ,  $C$ ,  $\rho$ ,  $\rho_0$  and  $M$  are the apparent molar volume, molarity, density of the solution, density of solvent (water or other solvent) and molar mass of solute respectively.

If concentration unit is molality, then  $C$  the molarity of solution is replaced with 'm' in the above example as follows

$$\Phi_V = \frac{M}{\rho_0} + \frac{1000(\rho_0 - \rho)}{m\rho_0} \quad (1.3)$$

There is another formula to calculate apparent molar/molal volume from same data available as follows.

$$\Phi_V = \frac{M}{\rho} + \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} \quad (1.4)$$

Main changes in the formula is density at denominator in both part in left hand side of the equation (1.4) molar mass of solute is divided by

density of solution instead of density of solvent and additionally in second part of the equation solution density is multiplied at denominator.

Where,  $\Phi_V$ ,  $m$ ,  $\rho$ ,  $\rho_0$  and  $M$  are the apparent molal volume, molality, density of the solution, density of solvent (water or other solvent) and molar mass of solute respectively.

From the above formulae, apparent molar/molal volumes are working out from density and concentration data of given system. Graph is plotted between apparent molar/molal volume on Y-axis and root of concentration on X-axis. Relation obtained from the graph is called Messon's relation given by equation (1.5)

This relation is also derived from least square fit method [9-10].

$$\Phi_V = \Phi_V^0 + S_V C \quad (1.5)$$

Where,  $\Phi_V^0$ , is partial molar volume, intercept of (graph) linear fit and known as partial molar volume and  $S_V$  is the slope of graph.

### INTERPRETATION:

**Intercept ( $\Phi_V^0$ ):** At infinite dilution, solutes get more hydrated due to availability of more number of water or solvent molecules and hence, hydrated solute has bigger size (apparent molar volume has greater value). As the concentration of solute increased, size of the hydrated molecules reduced (apparent molar volume lower value). At higher concentration, solute-solvent interaction decreased and solute-solute interaction increased.

**Slope ( $S_V$ ):** Slope ( $S_V$ ) may be positive (+ve) or negative (-ve) which is depend on the partial molar volume, at infinite dilution, whether the solute is more hydrated or less hydrated. At very dilute solution as  $c$  tends to zero, solute is more hydrated and  $\Phi_V = \Phi_V^0$  (apparent molar volume becomes partial molar volume). Then, with concentration, apparent molar volume values decreases. If we calculate the slope of such system, then slope is always negative ( $S_V = y_2 - y_1 / x_2 - x_1$ ) because  $y_2 < y_1$  &  $x_2 > x_1$ . Negative value of slope indicates structure maker

properties of solute with water molecules it means that solute molecules and solvent molecules has greater affinity toward each other compared to itself.

### Viscosity, Viscosity Coefficient $B$ and Intercept $A$

The structure making and structure breaking properties of solute is also understood by considering

*Jone-Dole* Equation (1.6) in term of viscosity coefficient  $B$  and intercept  $A$

$$\eta/\eta_0-1=A+B\sqrt{C} \quad (1.6)$$

Where,  $\eta / \eta_0$  is the relative viscosity,  $C$  is molar concentration of solute,  $A$  and  $B$  are constants for the studied solute.  $A$ -coefficient contributes for electrostatic forces (inter ionic) and the  $B$ -coefficient reveals about disorder produced by cations and anions in case of electrolyte and solutes in case of non-electrolyte in the water/ solvent structure [11].

### Interpretation of Viscosity Coefficient $B$ (slope) and Intercept $A$

#### Graph:

$(\eta / \eta_0 - 1) / \sqrt{C}$  values were plotted against  $\sqrt{C}$  shows linearity for solute solution with slope  $B$  and intercept  $A$ . The *Jone-Dole* equation is more useful for ionic solute because  $A$  gives information about ion-ion interactions. In our present study, dextrose is covalent (non-electrolytes). Therefore, the values of  $A$  for solute at all the studied temperatures are very small because the interionic interaction is weak in case of non-electrolytes. The very small values of intercept  $A$  may be due to non-covalent interactions.

### Interpretation of Viscosity Coefficient $B$ (slope)

The values of coefficients  $B$ , decides structure making and structure breaking properties of the solute molecules. More positive value indicates structure making (solute-solvent affinity

strengthen) property. As the values of coefficients  $B$  decrease structure making property become weak (solute-solvent affinity weakens).

### Interpretation of Intercept $A$

The values of coefficients  $A$ , decides solute-solute intermolecular interactions in case of non-electrolytes and anion-cation (inter-ionic) interaction of the solute in case of electrolytes. More positive value indicates greater solute-solute or cation-anion (solute-solvent affinity weaken) interactions. As the values of coefficients  $A$  decrease solute-solute or cation-anion interaction become weak (solute-solvent affinity strengthen). The very small values of intercept  $A$  may be due to non-covalent interactions.

### REFERENCES:

- Bushra Naseem et al, Arabian Journal of Chemistry (2021) 14,103405]
- Sudhakar S. Dhhondge and et al, J.Chem. Thermodynamics 67 (2013) 217-226].
- Anwar Ali, et al, Acta Physico-chemica Sinica, 2007, 23(1),79-83
- Sudhakar S.D., et al, J.Chem. Thermodynamics,67 (2013),217-226
- Muhammad A.J., et al, Food Chemistry 173(2015) 551-556
- Gordon G. Birch and et al., Pure & Appl. Chem., Vol.69,No.4, pp. 685-692, 1997.
- S. A. Galema and H.Hoiland, J. Phys. Chem.,95 (1991) 5321-5326
- C. Klofufar, C. Horvat, and R.D.Tasic, J. Acta Chimica Slovenica,53(2006) 274-283
- D.O. Masson, Philosophical magazine 8(1929) 218-235,
- Millard E.B., (1953), Physical Chemistry for College, McGraw-Hill book Company: 150
- S. Nishikawa, N. Kuramoto and T. Uchiyama, Bull. Chem. Soc. Japan, 67 (1994) 287