© INNOVATIVE RESEARCH THOUGHTS | Refereed | Peer Reviewed | Indexed
ISSN : 2454 – 308X | Volume : 04 , Issue : 02 | January – March 2018

ISOTHERMAL COMPRESSIBILITY STUDIES OF DIPEPTIDE IN AQUEOUS SODIUM CHLORIDE SOLUTION

Subhash[a], and Dheeraj Kumar[b]
a Department of Chemistry, D.S.College, Aligarh (UP), India
b Department of Chemistry, K.R.(PG) College, Mathura(UP), India
Email: dh2107@gmail.com[2]

ABSTRACT

Protein hydration plays a crucial role in stabilizing the native structure of globular proteins in aqueous solutions. The specific interactions of water with various functional groups on the proteins as well as other solvent-related effects contribute to the formation of the stable folded structure of proteins in solutions. Thus, it is of immense importance to study the low-molecular –weight model compounds such as amino acids, peptides, and their derivatives, which represent the building blocks of proteins in a variety of media. The conformational transitions of biopolymers are extremely sensitive to subtle changes in solvent medium. Therefore, in order to understand the behavior of proteins in aqueous salt solutions, we have studied the isothermal compressibility and their derived parameters of glycylglycine in aqueous electrolyte solutions.

KEY WORDS: Isothermal Compressibility, Internal Pressure, Dipeptide

INTRODUCTION

Isothermal compressibility is a sensitive measure of solute-solvent interactions and as such, can be used to monitor solute hydration in an aqueous solution[1, 2]. The isothermal compressibility has been well utilized to study the equilibrium as well as transport properties of various systems[3, 4]. Though, it is not an easy task to determine isothermal compressibility directly[2] but, through ultrasonic velocity, density and heat capacity at constant pressure measurements, it can be determined indirectly[5, 6]. It has been widely evaluated by several workers [6-10] to elucidate the intermolecular / interionic interactions in aqueous and mixed aqueous solutions of amino acids, peptides and proteins. These data have been interpreted in terms of intermolecular / interionic interactions operative in the systems.

Internal pressure is known to be a measure of overall cohesion (dispersion, repulsion, ionic and dipolar interactions) in liquid systems. It has been widely used [11-14] to investigate the intermolecular interactions in liquid systems. Suryanarayana[11] suggested an indirect method for evaluating internal pressure using the viscosity, density and ultrasonic velocity data. This method has been used[12] to study the internal pressure of pure liquids, binary liquid mixtures and solutions of electrolytes and non-electrolytes[12]. Pandey et al.[15] extended the proposed method for evaluating the internal pressure values of multi-component systems.

Hildebrand et al introduced the concept of cohesive energy density, which is the energy of isothermal vaporization from the liquid to the ideal-gas state. The square root of the cohesive energy density is known as solubility parameter (δ). The Solubility parameter has been found to be useful for assessing the compressibilities of various substances. It has served as an efficient guide in the selection of proper compounding ingredients and solvents for polymeric substances[16, 17]. The pseudo-gruneisen parameter, which accounts for the molecular association in solutions, has been evaluated by a

number of researchers[18, 23]. It is a dimensionless constant governed by the molecular order and structure.

In this chapter, an attempt has been made to evaluate the isothermal compressibility values employing the McGowan's relations, the internal pressure, the solubility parameter and the pseudo-gruneisen parameter values using the experimental ultrasonic velocity and density data for ternary systems glycylglycine + (2.0M) NaCl + water. The computed values have been used to study the intermolecular / interionic interactions in the systems under investigation.

EXPERIMENTAL:

The di-peptide glycylglycine used in this work were obtained from SRL (Mumbai). The salts namely, sodium chloride was purchased from E. Merck (India). All the chemicals were of ≥99% purity. The di-peptide was used as such without further purification. They were dried at ~110°C and kept in vacuum desiccator over P_2O_5 for several hours before use. The salts sodium chloride was recrystalysed twice in triply distilled water dried in a vacuum oven and then kept over P_2O_5 in a vacuum desiccator at room temperature for a minimum of 24 hours. All the solutions were made by weight using a balance having an accuracy of ±0.1 mg. Stock solutions of 2.0M sodium chloride were prepared in triply distilled water and used as solvents for the preparation of various molal solutions of di-peptide.

A Pyknometer of approximately 8.5 ml capacity, consisting of a small bulb with flat bottom and a graduated stem, was used for the density measurements. The pyknometer was calibrated with the triple distilled water using the literature values of density of pure water at required temperature [24]. The reproducibility of density values was found to be within ±0.0002 gm/cm^3.

An ultrasonic interferometer (Mittal's model: M-77, India**)** was used for the measurement of ultrasound velocity at a frequency of 4 MHz in the temperature range: 303.15 – 323.15 K. The ultra-thermostat (Type U-10) was used to maintain the desired temperature.

RESULTS AND DISCUSSION

The measured density and ultrasonic velocity values for Lglycylglycine 2.0M aqueous NaCl system have been used to determine the isothermal compressibility employing the following McGowan's expression (κ_T)[25],

$$\kappa_T = 1.33\times10^{-8} / (6.4\times10^{-4}\, u^{3/2}\, \rho)^{3/2} \qquad [1].$$

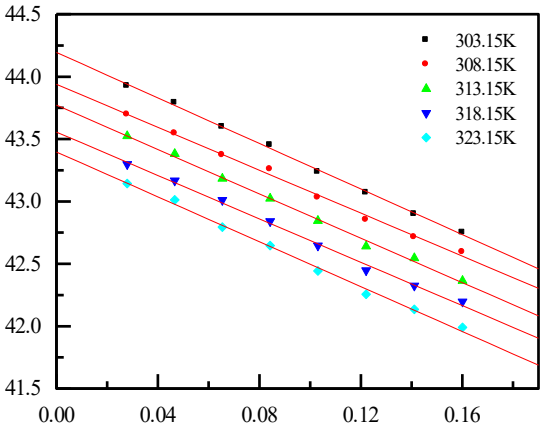
The computed isothermal compressibility values glycylglycine -aqueous NaCl system have been listed in Table 1.

Table 1: Isothermal compressibility values ($\kappa_T/10^{-12}$ m^{2}N^{-1}) of Glycylglycine in 2.0M aqueous NaCl solution as functions of concentration and temperature

Conc / mol kg^{-1}	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
0.0000	44.27	44.05	43.88	43.64	43.48
0.0279	43.92	43.69	43.52	43.30	43.14
0.0466	43.79	43.54	43.38	43.17	43.01
0.0654	43.60	43.37	43.18	43.01	42.79
0.0842	43.45	43.26	43.02	42.84	42.65
0.1031	43.24	43.03	42.85	42.65	42.44

0.1221	43.07	42.85	42.64	42.45	42.26
0.1411	42.89	42.71	42.54	42.32	42.14
0.1601	42.75	42.59	42.36	42.20	41.99

The κ_T values obtained have been further utilized to calculate the internal pressure, solubility parameter and specific heat ratio values for the systems under investigation. The κ_T values have been found to be decreasing with increase in concentration of di-peptide in aqueous NaCl solutions. The trends of variation of κ_T with variations in solute concentration and in temperature are similar to those of trends of variations of isentropic compressibility values for the systems. The trends of variation of κ_T values with solute concentration at different temperature have been plotted in the Figures 1.



Figures1: Isothermal compressibility vs concentration of glycylglycine in 2.0M aqueous NaCl solution

The decrease in isothermal compressibility values with increase in di-peptide concentration may be attributed to a corresponding increase in electrostriction of water with successive increase in the solute concentration in solutions. This increase in electrostriction of bulk water may cause a decrease in the amount of water, which in turn, may cause the corresponding decrease in the isothermal compressibility values of solutions[26, 27]. An observation of Table 1 also reveals that the κ_T values show a decreasing trend of variation with increase in temperature. This decrease in isothermal compressibility values of di-peptide - aqueous electrolyte systems may be explained in terms of two structural types of water aggregates (a structured form and a non-structured or less structured form) present in solutions.

The internal pressure values (P_i) for the systems under investigation have been computed by using following relation,

$$P_i = \frac{\alpha_T T}{\kappa_T} - P \qquad [2]$$

where P is the external pressure at a given temperature and it may be considered negligible in comparison to P_i value. Therefore, the term P can be neglected in the above expression and it may be written as follows,

$$P_i = \frac{\alpha_T T}{\kappa_T} \qquad [3]$$

α_T, the coefficient of thermal expansion, has been computed from the temperature dependent data of density, employing the following relation,

$$\alpha_T = -1/\rho\ (\partial\rho/\partial T)_P \qquad [4]$$

The calculated values internal pressure has been listed in Tables 2. The observed values of internal pressure have been found to be increasing with increase in solute concentration as may be envisaged from the plots of internal pressure versus solute concentration at different temperatures Figures 2.

Table 2: Internal pressure values ($P_i/10^9$ Nm^{-2}) of Glycylglycine in 2.0M aqueous NaCl solution as functions of concentration and temperature

Conc / mol kg^{-1}	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
0.0283	3.725	3.816	3.904	3.998	4.087
0.0473	3.733	3.826	3.913	4.007	4.095
0.0663	3.747	3.839	3.928	4.017	4.113
0.0853	3.756	3.845	3.939	4.030	4.123
0.1044	3.772	3.862	3.952	4.045	4.140
0.1235	3.783	3.875	3.968	4.060	4.154
0.1427	3.795	3.884	3.973	4.068	4.162
0.1620	3.805	3.892	3.986	4.077	4.173

This increasing trend of variation of P_i with solute concentration may be due to an increase in cohesive forces in systems.

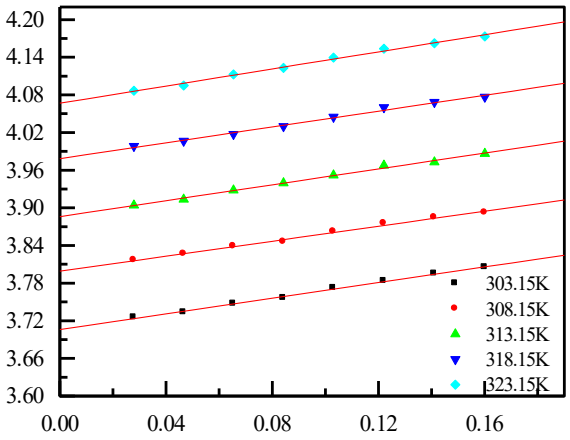


Figure.2: Internal pressure versus concentration of glycylglycine in 2.0M aqueous NaCl solution.

The trends of variation of internal pressure values for glycylglycine - aqueous electrolyte systems have also been found be increasing with increase in temperature, which may apparently be attributed to a decrease in the repulsive forces among the constituents of the system. It seems that the increase in the values of internal pressure is closely associated with the expansivity of the system with temperature, as a consequence of which the molecular / ionic species or clusters get closer to the extent envisaged by the expansivity of the system under investigation. This will, therefore, account for the increase in the internal pressure values with successive increases in temperature.

The square root of the cohesive energy density of the internal pressure, referred as the solubility parameter (δ) has been computed employing the following expression,

$$\delta = \left(\frac{\alpha_T T}{\kappa_T}\right)^{1/2} = (Pi)^{1/2} \qquad [5]$$

The computed values of solubility parameter for all the systems under investigation have been listed in Table 3.

Table 3: Solubility parameter values, δ /10^4(Nm^{-2})$^{1/2}$ of Glycylglycine in 2.0M aqueous NaCl solution as functions of concentration and temperature

Conc / mol kg^{-1}	Temperature / K				
	303.15	308.15	313.15	318.15	323.15
0.0279	-5.349	-5.248	-5.150	-5.055	-4.963
0.0466	-5.355	-5.253	-5.156	-5.061	-4.968
0.0654	-5.359	-5.258	-5.160	-5.066	-4.973
0.0842	-5.365	-5.263	-5.165	-5.071	-4.978
0.1031	-5.369	-5.269	-5.171	-5.075	-4.983
0.1221	-5.375	-5.273	-5.176	-5.081	-4.988
0.1411	-5.380	-5.278	-5.181	-5.085	-4.992
0.1601	-5.385	-5.283	-5.186	-5.091	-4.997

The trend of variation of δ values has been found to be increasing with increase in temperature. Such an increase may be attributed to an increase in the cohesive energy density. In the view of the fact that the solubility parameter happens to be the square root of the internal pressure, similar trend in the variation of its values is envisaged as that in those of the internal pressure values with variation in temperature and solute concentration.

The pseudo-gruneisen parameter (Γ) value has been evaluated by using the following relation[28],

$$\Gamma = \frac{\gamma - 1}{\alpha_T T} \qquad [6]$$

where γ is the specific heat ratio while α_T and T have their usual meaning. The values of γ have been computed employing the following expression[29],

$$\gamma = C_P / C_V = \kappa_T / \kappa_s. \qquad [7]$$

The calculated values of Γ have been summarized in the Tables 4. An examination of the Table 4 shows that the Γ values are negative in all the systems under investigation. The Γ values exhibit a decreasing trend of variation with increase in di-peptide concentration in aqueous NaCl solutions while an increasing trend of variation with increase in temperature.

Table4: Pseudo-gruneisen parameter values of Glycylglycine in 2.0M aqueous NaCl solution as functions of concentration and temperature

	Temperature / K				
Conc / mol kg^{-1}	303.15	308.15	313.15	318.15	323.15
0.0279	-5.349	-5.248	-5.150	-5.055	-4.963
0.0466	-5.355	-5.253	-5.156	-5.061	-4.968
0.0654	-5.359	-5.258	-5.160	-5.066	-4.973
0.0842	-5.365	-5.263	-5.165	-5.071	-4.978
0.1031	-5.369	-5.269	-5.171	-5.075	-4.983

0.1221	-5.375	-5.273	-5.176	-5.081	-4.988
0.1411	-5.380	-5.278	-5.181	-5.085	-4.992
0.1601	-5.385	-5.283	-5.186	-5.091	-4.997

The trend of variation of pseudo-gruneisen parameter may also be expressed in terms of expansivity of the system. In the view of the fact that the pseudo-gruneisen parameter is inversely proportional to the coefficient of expansion, the trend in its behavior will be opposite of that recorded for internal pressure, which has direct dependence on coefficient of expansion.

REFERENCES

1. J.G. Mathieson and B.E. Conway, *J. Solution Chem.*, 1974, 3, 455.
2. H. Høiland, in *Thermodynamic Data for Biochemistry and Biotechnology*, H. -J. Hinz (ed.), Springer -Verlag: Berlin, 1986, ch 4.
3. J.D. Pandey, B.R. Chaturvedi and N. Pant, *Acoust. Lett*.,1981, 4, 128.
4. K. J. Patil and D. N. Raut, *Ind. J. Pure and Appl. Phys.*, 1980, 18, 499.
5. G.R. Hedwig and H. Høiland, *Phys. Chem. Chem. Phys.*, 2004, 6, 2440.
6. F.J. Millero, G.K. Ward and P. Chetirkin, *J. Biol. Chem.*, 1976, 251,4001.
7. G.R. Hedwig, *J. Phys. Chem.*, 1995, 99, 12063.
8. A.A. Yayanos, *J. Phys. Chem*., 1993, 97, 13027.
9. A. F. S. S. Mendonca, S. M. A. Dias, F. A. Dias, B. A. S. Barata and I. M. S. Lampreia, *Fluid Phase Equilib*., 2003, 212, 67.
10. A.W. Hakin, H. Høiland and G.R. Hedwig, *Phys. Chem. Chem Phys*., 2000, 2, 4850.
11. C.V. Suryanarayana, *Indian J. Pure App. Phys*., 1989, 27, 751.
12. I.L. Acevedo, G.C. Pedrosa and M. Katz, *J. Solution Chem.*, 1990, 19, 11.
13. J.D. Pandey and V. Tiwari, *Z. Phys. Chem. (Leipzig)*, 1981, S 53, 262.
14. D. R. Rossensky, *J. Phys. Chem*., 1977, 81, 1578.
15. J. D. Pandey, A. K. Shukla, N. Tripathi and G. P. Dubey, *Pramana- J. Phys.*, 1993, 40, 81.
16. J.A. Brydson, *Plastics*, *London*, 1961, 26, 107.
17. H. Burrell, *J. Paint Technol*., 1958, 40, 197.
18. B.P. Shukla, V.N. Mishra and S.N. Dubey, *Curr. Sci*., 1983, 52, 721.
19. J.N.C. Lopes, L.P.N. Rebelo and G. Jancso, *J. Mol. Liq*., 1992, 54, 115.
20. J. Amoros, J.R. Solana and E. Villar, *Mat. Chem. Phys*., 1988, 20, 255.
21. B. K. Sharma, *Ultrasonics*, 1987, 25, 365.
22. B. K. Sharma, *Phys. Lett. A,* 1984, 101, 405.
23. S.K. Kor and S.K. Pandey, *Ultrasonics*, 1973, 29, 63.
24. G.S. Kell, *J. Chem. Eng. Data*, 1975, 20, 97.
25. J.G. McGowan, *Nature (London)*, 1966, 210, 1255.
26. F.J. Millero, R.W. Curry, W. Drost-Hansen, *J. Chem. Eng. Data*, 1969, 14, 422.
27. F. J. Millero, G. K. Ward, F. K. Lepple and E. V. Hoff, *J. Phys. Chem.*, 1974,78, 1636.
28. J. N. Shapiro and L. Knopoff, *Phys. Rev. B*3, 1970, 10, 3990.
29. M. R. Islam and S.K. Quadri, *Acoust. Lett.,* 1988, 11, 219.