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J. Chem. Thermodynamics 38 (2006) 1385–1395
JCT
www.elsevier.com/locate/jct

Partial molar volumes and adiabatic compressibilities at infinite dilution of aminocarboxylic acids and glycylglycine in water and aqueous solutions of sodium sulphate at (288.15, 298.15 and 308.15) K

Ponnadurai Ramasami [a,*], Rita Kakkar [b]

[a] Department of Chemistry, University of Mauritius, Réduit, Mauritius
[b] Department of Chemistry, University of Delhi, Delhi 110007, India

Received 16 August 2005; received in revised form 31 January 2006; accepted 31 January 2006
Available online 15 March 2006

Abstract

The partial molar volume and partial molar adiabatic compressibilities at infinite dilution of DL-aminobutanoic acid, DL-norvaline, β-alanine, 4-aminobutanoic acid, 5-aminopentanoic acid, 6-aminohexanoic acid and glycylglycine have been obtained in water and aqueous solutions of (0.5, 1.0 and 1.5) mol · kg^{-1} sodium sulphate at (288.15, 298.15 and 308.15) K from measurements of density and ultrasonic velocity. A qualitative interpretation of the results has been given using the Kirkwood model and nature of the interactions in solutions. A model, derived from Scaled Particle Theory, has been used for quantitative explanation of partial molar volumes and for the understanding the volumes of interaction. The results distinguish the behaviour of α-amino acids from that of α,ω-amino acids, and of the "less polar" 5-aminopentanoic acid from that of the analogous, but "more polar", glycylglycine in solution. These findings are in agreement with previous studies in aqueous solutions and they support the water-structure making ability of sodium sulphate.

Keywords: Amino acids; Glycylglycine; Aqueous sodium sulphate; Partial molar volumes; Partial molar adiabatic compressibilities

1. Introduction

The properties and behaviour of amino acids in solutions have always been a matter of interest mainly because amino acids are, among other compounds, the basic structural building units of biomolecules [1–3]. Elucidating and predicting the effect of solvent on the structure and reactivity of solutes have been challenging tasks since long and although no definite principle has been laid down, much progress has been achieved [4,5]. Different techniques have been adopted for the understanding of the behaviour of amino acids in solutions [6–9]. However, it appears that volumetric properties of a solute, such as partial molar volume [10] and, particularly compressibility [3,10], still remain powerful tools for probing the hydrational state of the solute in the solution. During the last 15 years there have been various partial molar volume studies involving amino acids in water [10–13] and mixed solvents [4,5,14–20] but surprisingly there have been less compressibility studies [10–13,21,22].

In a previous communication [13], the partial molar volumes and partial adiabatic compressibilities at infinite dilution of glycine and DL-alanine were reported in water and aqueous solutions of sodium sulphate. Analysis of the experimental data allowed one only to differentiate between "pure" hydrophilic hydration of the simplest amino acid, glycine, and that of the hydrophobic hydration of DL-alanine because of the introduction of methyl group in glycine. However, in DL-alanine the $-CH_3$ group should not be considered as totally independently hydrated because the $-CH_3$ group will be almost enclosed in the overlapping shells of the charged terminal groups [12]. In

* Corresponding author. Tel.: +2302570315; fax: +2304656928.
E-mail addresses: p.ramasami@uom.ac.mu, ramchemi@intnet.mu (P. Ramasami), rita_kakkar@vsnl.com (R. Kakkar).

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doi:10.1016/j.jct.2006.01.014

view of this, a better understanding will be obtained if the investigation is extended to a homologous series of solutes and systematically varying the number of carbon atoms in the chain. Only few workers [11,23–26] did comprehensive work of this kind taking aminocarboxylic acids as a homologous series but their studies were restricted to water.

α,ω-Aminocarboxylics are suitable for partial molar volume studies [11] and, once they are chosen, it becomes advantageous to consider the α-aminocarboxylic acids so that the effect of branching can also be viewed. In order to extend the understanding of the behaviour of amino acids from water to electrolytic solutions and in continuation with the previous work [13], this paper reports the partial molar volumes, partial molar adiabatic compressibilities at infinite dilution and their variations with temperature for a series of some α-aminocarboxylic acids with non-branched aliphatic chains, α,ω-aminocarboxylic acids and a dipeptide namely glycylglycine. The study has been carried out in water and aqueous solutions of sodium sulphate at (288.15, 298.15 and 308.15) K. Sodium sulphate has been chosen because of its structure making ability [13]. The resulting data are interpreted in terms of Kirkwood model [27] and the modified Scale Particle Theory [11,28,29]. The latter is being used in estimating the volume of interaction, an important parameter to understand solute–solvent interactions [30].

2. Experimental

DL-aminobutanoic acid, DL-norvaline, β-alanine, 4-aminobutanoic acid, 6-aminohexanoic acid and glycylglycine were purchased from Sigma Chemicals Limited. 5-Aminopentanoic acid was purchased from Aldrich Chemicals Limited. β-Alanine and 4-aminobutanoic acid were used after drying for 24 h at 353 K. The other aminocarboxylic acids and glycylglycine were dried at room temperature under vacuum in the presence of phosphorus pentoxide for 72 h and then used. Anhydrous sodium sulphate (GR, Sarabhai Merck and S. D. Fine-Chem Pvt Ltd., India) was used after vacuum drying for 24 h at 413 K. Within the experimental accuracy of our measurements, no difference was detected between the same compound from the two sources. All solutions were prepared by weight using Mettler AE 163 balance precise to ±0.1 mg. Bi-distilled, water deionised by passing through an ion exchanger, was degassed by boiling and was then used to prepare all solutions. The densities were measured with an Anton Paar vibrating tube digital densitometer (DMA 601/60). The experimental details for density measurements and calibration procedures are given in literature [31]. The maximum uncertainty in density is $1 \times 10^{-5}\ \mathrm{g \cdot cm^{-3}}$. The apparent molar volumes $V_{\phi,2}$ were calculated from:

$$V_{\phi,2} = M/d - (d - d_o)/(d \times d_o \times m), \quad (1)$$

where M is the molecular mass of the solute, m is its molality, d and d_o are the densities of the solvent and the solution, respectively.

The ultrasonic velocities, u, were measured using an ultrasonic interferometer (Model M-83) from Mittal enterprises. The experimental details for density measurements and calibration procedures are given in the literature [13]. The maximum uncertainty in velocity of sound is $\pm 0.5\ \mathrm{m \cdot s^{-1}}$. The temperature was controlled within ±0.01 K using LAUDA thermostat (model M20) for velocity measurements.

The apparent molar adiabatic compressibilities, $K_{\phi,2}$, were determined from the densities and the adiabatic compressibities, β_s, of the solutions using the equation:

$$K_{\phi,2} = \beta_s \times M/d + (\beta_s \times d_o - \beta_s^\circ \times d)/(d \times d_o \times m). \quad (2)$$

The adiabatic compressibilities, β_s, were calculated from the solution sound velocities, u, and densities, d, using the equation:

$$\beta_s = 1/(d \times u^2) \quad (3)$$

and β_s° is the compressibility of the solvent.

3. Results and discussion

The densities and sound velocities used for (0.5, 1.0 and 1.5) $\mathrm{mol \cdot kg^{-1}}$ sodium sulphate are those reported earlier [13]. Limiting values of molar volume and molar adiabatic compressibilities of glycine and DL-alanine are those reported earlier [13]. Measurements were performed at different concentrations ranging form 0.1 $\mathrm{mol \cdot (kg \cdot solvent)^{-1}}$ to 1.0 $\mathrm{mol \cdot (kg \cdot solvent)^{-1}}$ for all solvents including mixed solvents, except for DL-norvaline for which the range was from 0.1 $\mathrm{mol \cdot (kg \cdot solvent)^{-1}}$ to 0.7 $\mathrm{mol \cdot (kg \cdot solvent)^{-1}}$ due to its low solubility. The apparent molar volumes and apparent molar adiabatic compressibilities were calculated from equations (4) and (5), respectively. These values were then fitted to the equations:

$$V_{\phi,2} = V_{\phi,2}^\circ + S_v m, \quad (4)$$

$$K_{\phi,2} = K_{\phi,2}^\circ + S_k m, \quad (5)$$

which were weighted according to the errors associated with them, to obtain the limiting values of $V_{\phi,2}^\circ$ and $K_{\phi,2}^\circ$ as intercepts at zero concentrations. These are reported in tables 1 and 2. In those cases where the error associated with the slope was greater than the slope itself, the required limiting value was obtained by weighted average and the slope was taken to be zero. The $V_{\phi,2}^\circ$ and $K_{\phi,2}^\circ$ values of the aminocarboxylic acids and glycylglycine were fitted linearly to temperature, and then by analytically differentiating the obtained functions, the expansibilities and variations of the partial molar adiabatic compressibilities with temperature were obtained. These are also included in tables 1 and 2.

The accuracy of our instruments was tested by comparing the obtained $V_{\phi,2}^\circ$, $K_{\phi,2}^\circ$, expansibilities and temperature slopes of partial molar adiabatic compressibilities for the amino acids and glycylglycine in water with the literature values. They are given in tables 3 and 4 and it is interesting to note the agreement between these values. However it is