

This article was downloaded by:

On: 28 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

### Effect of temperature on partial molar volumes and viscosities of aqueous solutions of $\alpha$ -dl-Aminobutyric acid, dl-Norvaline and dl-Norleucine

Carmen M. Romero<sup>a</sup>; Faustino Negrete<sup>b</sup>

<sup>a</sup> Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá, Colombia

<sup>b</sup> Departamento de Química, Facultad de Ciencias, Universidad de Córdoba, Córdoba, Montería

**To cite this Article** Romero, Carmen M. and Negrete, Faustino(2004) 'Effect of temperature on partial molar volumes and viscosities of aqueous solutions of  $\alpha$ -dl-Aminobutyric acid, dl-Norvaline and dl-Norleucine', *Physics and Chemistry of Liquids*, 42: 3, 261 – 267

**To link to this Article:** DOI: 10.1080/00319100410001659596

**URL:** <http://dx.doi.org/10.1080/00319100410001659596>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## EFFECT OF TEMPERATURE ON PARTIAL MOLAR VOLUMES AND VISCOSITIES OF AQUEOUS SOLUTIONS OF $\alpha$ -DL-AMINO BUTYRIC ACID, DL-NORVALINE AND DL-NORLEUCINE

CARMEN M. ROMERO<sup>a,\*</sup> and FAUSTINO NEGRETE<sup>b</sup>

<sup>a</sup>*Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá, Colombia;* <sup>b</sup>*Departamento de Química, Facultad de Ciencias, Universidad de Córdoba, Córdoba, Montería*

(Received 26 October 2003)

In this work, we present experimental results for partial molar volumes and viscosities of aqueous solutions of  $\alpha$ -DL-aminobutyric acid, DL-norvaline and DL-norleucine at 288.15, 293.15, 298.15 and 303.15 K. The thermodynamic behavior of aqueous amino acid solutions is compared with that reported for glycine and  $\alpha$ -alanine in water and is discussed in terms of group additivity and electrostriction.

The temperature dependence of the infinite dilution partial molar volumes and the *B* viscosity coefficients are interpreted in terms of amino acid hydration. According to the usual hydrophobicity criteria, the amino acids considered do not have a hydrophobic character and their behavior is dominated by the polar groups.

*Keywords:* Amino acid; Hydrophobicity; Solute–solvent interactions; Viscosity

### INTRODUCTION

Amino acids have been considered model compounds that can give useful information to understand the behavior of proteins and the role of solvent structure in the denaturation process. In fact, volumetric and viscometric properties of these compounds have been used to provide an insight into hydrophobicity, hydration properties and solute–solvent interactions.

Most studies have been done on naturally occurring amino acids at 298.15 K [1–13]. However, very few data are reported in literature for amino acids such as norvaline and norleucine in spite of their linear hydrocarbon chain, especially at temperatures different from 298.15 K [14–20]. For this reason, in this work we present a study of the temperature effect on apparent molar volumes and viscosities of aqueous solutions of DL- $\alpha$ -aminobutyric acid, norvaline and norleucine at 288.15, 293.15, 298.15 and 303.15 K.

---

\*Corresponding author. E-mail: cmromeroi@unal.edu.co

The experimental results are analyzed in terms of group additivity [1,3,12,13, 15,20,23] expressing the experimental values as the contribution of polar groups and number of CH<sub>2</sub> units. The electrostrictive effect or the solute-solvent interaction associated with electrostatic interactions between the charged groups and water [3,11,24-26] is used to evaluate the electrostriction volume and the number of hydrated water molecules based on the simple model proposed by Millero [3]. According to this model, the infinite dilution partial molar volume can be described as the sum of two contributions: the intrinsic volume and the electrostriction volume

$$\bar{V}^o = \bar{V}_{\text{int}}^o + \bar{V}_{\text{elect}}^o \quad (1)$$

The temperature dependence of the partial molar volume at infinite dilution and the viscosity  $B$  coefficient are used to interpret the effect of the hydrocarbon chain on water structure using the general hydrophobicity criteria proposed by Hepler [16,22,23,27,28]. According to his criteria, the behavior of the second derivative of the infinite dilution partial molar volume with temperature is related to the hydrophobic or hydrophilic character of the solute. In this way if  $(\partial V^o/\partial T) > 0$  and  $(\partial^2 V^o/\partial T^2) < 0$  the solute has hydrophilic character, but if the behavior shows that  $(\partial V^o/\partial T) < 0$  and  $(\partial^2 V^o/\partial T^2) > 0$  the solute has hydrophobic character [27].

## EXPERIMENTAL SECTION

The materials used were the following: DL- $\alpha$ -aminobutyric acid, DL- $\alpha$ -norvaline and DL- $\alpha$ -norleucine Merck, analytical reagents which were dried under vacuum for 48 h before use. Water was bidistilled, treated according to literature and degassed before use. All solutions were prepared by weight using a Mettler balance AT 261 dual range with sensitivity of  $10^{-5}$  g in the lower range. The concentration range in which solutions were prepared was 0.003–0.100 molal for aminobutyric acid and norvaline and 0.003–0.080 molal for norleucine solutions.

Density of solutions was measured using a magnetic float densimeter described elsewhere [29] with a sensitivity of  $\pm 2 \times 10^{-6}$  g cm<sup>-3</sup>. Viscosity was determined using two Ubbelohde viscometers with efflux times near 300 s for water. Reproducibility of efflux times was in all cases better than 0.05%.

Density and efflux times were determined at 288.15, 293.15, 298.15 and 303.15 K for the amino acid solutions. All measurements were carried out in a constant temperature bath with temperature controlled to  $\pm 0.005$  K.

The density data obtained for each solution were used to calculate the apparent molar volume  $\phi_v$  using the equation:

$$\phi_v = M/d + 1000(d_o - d)/mdd_o \quad (2)$$

where  $M$  is the molecular weight of the solute,  $m$  its molal concentration,  $d$  and  $d_o$  are the densities of the solution and the solvent respectively.

The viscosity data were obtained from the relation:

$$\eta = \alpha dt - \beta d/t \quad (3)$$

where  $\alpha$  and  $\beta$  are the viscometer constants,  $d$  is the density and  $t$  the efflux time. The relative viscosities  $\eta_r = \eta/\eta_o$  were calculated from the solution and solvent viscosities respectively.

## RESULTS

For each amino acid, the apparent molar volumes were fitted by least-squares to a linear equation of the type

$$\phi_v = \phi_v^o + S_v m \quad (4)$$

where  $\phi_v^o$  is the infinite dilution apparent molar volume and  $S_v$  is the experimental slope. At infinite dilution  $\phi_v^o$  equals  $\bar{V}^o$  the infinite dilution partial molar volume.

The relative viscosity values were adjusted by least-squares to a second-order equation as proposed by Tsangaris–Martin [30].

$$\eta_r = 1 + Bm + Dm^2 \quad (5)$$

In this equation  $B$  and  $D$  are empirical coefficients. The  $B$  coefficient depends on the size, shape and charge of the solute molecule.

Electrostriction volumes were calculated according to Eq. (1) which assumes that the partial molar volume at infinite dilution can be expressed as the sum of a contribution due to the intrinsic molar volume and a contribution due the electrostriction volume. In this work we adopt the proposal of Millero to calculate the intrinsic molar volumes from the crystal volume [31–33], considering the corrections due to the packing densities for organic crystals and for random packing spheres [3,34].

$$V_{\text{int}}^o = \left( \frac{0.7}{0.634} \right) \bar{V}_{\text{crystal}}^o \quad (6)$$

In this way, the electrostriction volumes are evaluated and the hydration numbers are calculated from the equation:

$$\bar{V}_{\text{electr}}^o = n_H (\bar{V}_E^o - \bar{V}_B^o) \quad (7)$$

where  $\bar{V}_E^o$  is the partial molar volume of electrostricted water,  $\bar{V}_B^o$  is the molar volume of bulk water and  $n_H$  is the hydration number. The difference  $(\bar{V}_E^o - \bar{V}_B^o)$  taken as  $-3.3 \text{ cm}^3/\text{mol}$  from Millero is assumed to be constant in the temperature range considered in this work [16].

## DISCUSSION

The dependence of the apparent molal volume on concentration is linear in the concentration range considered. For all amino acids the slope  $(d\bar{V}/dX_2)$  was positive. Table I shows the partial molar volume at infinite dilution and the viscosity  $B$  coefficient for

TABLE I Partial molar volume at infinite dilution and viscosity  $B$  coefficient for  $\alpha$ -DL-aminobutyric acid, DL-norvaline and DL-norleucine at 288.15, 293.15, 298.15 and 303.15 K

Amino acid	$T$ (K)	$\bar{V}^\circ$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$B$ ( $\text{kg mol}^{-1}$ )
Aminobutyric acid	288.15	74.44	0.3130
	293.15	74.98	0.3103
	298.15	75.64	0.2950
	303.15	75.89	0.2793
Norvaline	288.15	90.53	0.4063
	293.15	91.03	0.3993
	298.15	91.77	0.3710
	303.15	92.21	0.3519
Norleucine	288.15	106.20	0.5011
	293.15	106.88	0.4925
	298.15	107.58	0.4543
	303.15	108.22	0.4342

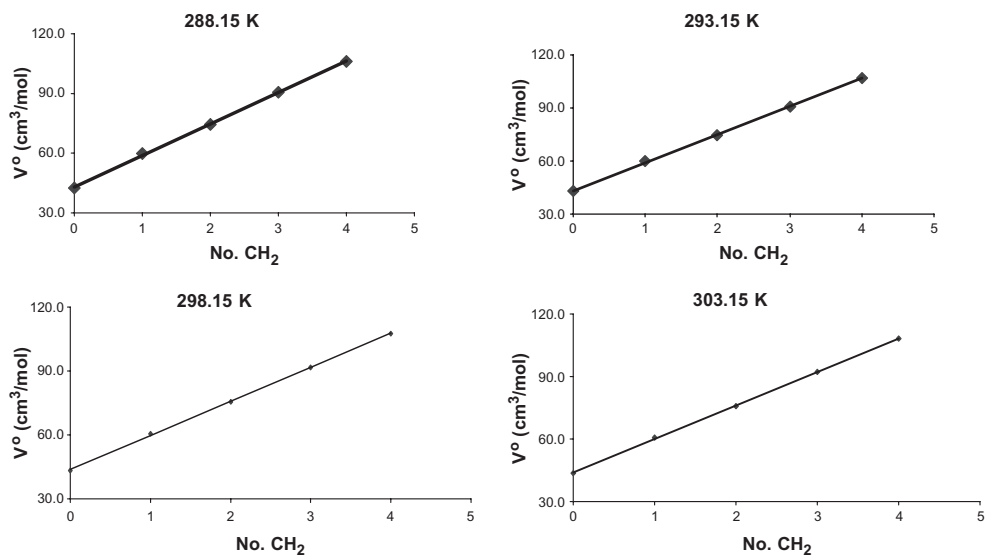


FIGURE 1 Partial molar volume at infinite dilution as a function of the number of  $\text{CH}_2$  groups at 288.15 K, 293.15, 298.15 and 303.15 K.

$\alpha$ -DL-aminobutyric acid, DL-norvaline and DL-norleucine at 288.15, 293.15, 298.15 and 303.15 K.

Figure 1 shows the behavior of the partial molar volume at infinite dilution with the number of  $\text{CH}_2$  groups and Fig. 2 shows the behavior of the viscosity  $B$  coefficient as a function of the number of  $\text{CH}_2$  groups. In both cases, data for glycine and alanine from literature have been included. At all temperatures, the infinite dilution partial molar volume and the  $B$  coefficient of viscosity increase linearly with number of  $\text{CH}_2$  groups. This is a very important result because up to the moment, most additivity studies in amino acids have not considered norvaline and norleucine but have been done with valine and leucine which do not have a linear chain.

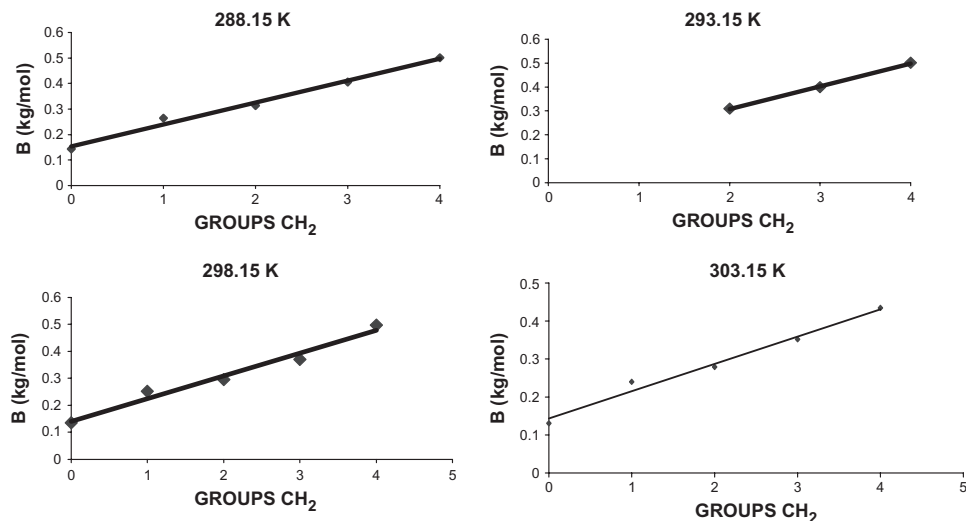


FIGURE 2 Viscosity  $B$  coefficient as a function of the number of  $\text{CH}_2$  groups at 288.15, 293.15, 298.15 and 303.15 K.

TABLE II Group contribution to partial molar volume and viscosity  $B$  coefficient at 288.15, 293.15, 298.15 and 303.15 K

$T$ (K)	$\bar{V}_{\text{CH}_2}^{\infty}$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$B_{\text{CH}_2}$ ( $\text{kg mol}^{-1}$ )
288.15	15.83	0.086
293.15	15.93	0.095
298.15	16.00	0.084
303.15	16.08	0.072

The behavior of volumetric and viscometric group contributions with temperature is presented in Table II. The volumetric contribution was evaluated from the slope of the curve and it increases with temperature. In the case of the group contribution to the viscosity coefficient the change is very small and does not follow a defined tendency. We will not attempt an explanation about this fact because the lack of viscosity data at temperatures different from 298.15 K is noticeable and data dispersion is high.

The partial molar volume at infinite dilution increases with temperature while the  $B$  coefficient decreases with temperature. The volumetric behavior with temperature is characteristic of solutes showing hydrophilic hydration. In both cases the behavior can be described well by a polynomial second-order equation. In Table III the first derivative at 298.15 K and second derivative of partial molar volume at infinite dilution with temperature are reported. The second derivative is negative for the three amino acids considered in this work. According to Hepler hydrophobicity criteria this means that hydrophilic interactions predominate over hydrophobic interactions, thus confirming the previous result. The second derivative becomes less negative with increasing chain length showing that the hydrophobic character becomes more important. A similar conclusion can be obtained from the analysis of the behavior of the viscosity coefficient with temperature.

TABLE III First derivative at 298.15 K and second derivative of partial molar volume at infinite dilution and viscosity  $B$  coefficient with temperature

Amino acid	$dV^o/dT$ at 298.15 K	$d^2V/dT^2/10^3$	$dB^o/dT$ at 298.15 K	$d^2B/dT^2/10^4$
Aminobutyric acid	0.086	-5.8	-1.68	-2.6
Norvaline	0.113	-1.2	-3.22	-2.4
Norleucine	0.133	-0.8	-4.2	-2.3

TABLE IV Electrostriction volume and hydration numbers for  $\alpha$ -DL-aminobutyric acid, DL-norvaline and DL-norleucine at 288.15, 293.15, 298.15 and 303.15 K

$T$ (K)	Amino acid	$d$ (g cm <sup>-3</sup> )	$V_{crystal}^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\phi_2^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$V_{int}^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$V_{electr}^o$ (cm <sup>3</sup> mol <sup>-1</sup> )	$n_H$
288.15	Abu	1.2300	83.84	74.30	92.56	-18.26	5.6
	Nval	1.1950	98.30	90.42	108.53	-18.11	5.5
	Nleu	1.1720	111.93	106.15	123.57	-17.42	5.3
293.15	Abu	1.2300	83.84	74.96	92.56	-17.60	5.3
	Nval	1.1950	98.30	91.11	108.53	-17.42	5.3
	Nleu	1.1720	111.93	106.88	123.57	-16.69	5.1
298.15	Abu	1.2300	83.84	75.64	92.56	-16.92	5.6
	Nval	1.1950	98.30	91.77	108.53	-16.76	5.5
	Nleu	1.1720	111.93	107.58	123.57	-15.99	5.3
303.15	Abu	1.2300	83.84	75.87	92.56	-16.69	5.1
	Nval	1.1950	98.30	92.16	108.53	-16.37	5.0
	Nleu	1.1720	111.93	108.13	123.57	-15.44	4.7

In Table IV electrostriction volumes and hydration numbers are presented. It can be seen that at all temperatures and for the amino acids studied, electrostriction volumes and hydration numbers become smaller with temperature increase and with increasing chain length. This shows that electrostrictive effect decreases with temperature and chain length and so the number of water molecules hydrated predominantly by polar groups.

### Acknowledgments

This work was supported by the Universidad Nacional de Colombia and the Universidad de Córdoba. We would like to express our appreciation to the reviewer for his comments and suggestions for improving the manuscript.

### References

- [1] C. Jolicoeur, B. Riedl, D. Desrochers, L.L. Lemelin, R. Zamojska and O. Enea (1986). *J. Solution Chem.*, **15**, 109.
- [2] K.B. Belibagli and E. Ayrancy (1990). *J. Solution Chem.*, **19**, 867.
- [3] F.J. Millero, A. Lo Surdo and C. Shin (1978). *J. Phys. Chem.*, **82**, 784.
- [4] F. Shahidi and P.G. Farrell (1981). *J. Chem. Soc., Faraday Trans. 1*, **77**, 963.
- [5] K. Tamaki and M. Asada (1988). *Yu Kagaku*, **37**, 437.
- [6] J.S. Sandhu and U. Kashyap (1986). *J. Electrochem. Soc. India*, **35**, 283.
- [7] W.D. Devine and B.M. Lowe (1971). *J. Chem. Soc., (A)*, 2113.

- [8] R.K. Wadi, A. Gupta and D.V.S. Jain (1981). *Ind. J. Chem.*, **20A**.
- [9] A.K. Mishra and J.C. Ahluwalia (1983). *Biopolymers.*, **22**, 2397.
- [10] B.S. Lark, K. Bala and A.S. Bhui (1981). *J. Chem. Sci.*, **7**, 35.
- [11] C.M. Romero and R.E. Munar (1998). *Phys. and Chem. of Liquids*, **36**, 83.
- [12] T. Ogawa, K. Mizutani and M. Yasuda (1984). *Bull. Chem. Soc. of Japan*, **57**, 2064.
- [13] T.H. Lilley (1985). In: C. Barret (Ed.), *The Chemistry and Biochemistry of Aminoacids*. Chapman, Hall–Methuen, London.
- [14] T.V. Chalikian, A.P. Sarvazyan and K.J. Breslauer (1993). *J. Phys. Chem.*, **97**, 13017.
- [15] B.K. Abrosimov and G.K. Sibrina (1989). *Izv. Acad. Nauk. SSSR, Ser. Khim.*, **6**, 1256.
- [16] D.P. Kharakoz (1989). *Biophysical Chem.*, **34**, 115.
- [17] A.W. Hakin, M.M. Duke, S.A. Klassen, R.M. McKay and K.E. Preuss (1994). *Can. J. Chem.*, **72**, 362.
- [18] L.S. Mason, P.M. Kampmeyer and A.L. Robinson (1952). *J. Am. Chem. Soc.*, **74**, 1287.
- [19] M. Kikuchi, M. Sakurai and K. Nitta (1995). *J. Chem. Eng. Data*, **40**, 935
- [20] J. Wang, Z. Yan, W. Liu and J. Lu (1997). *Physikalische Chemie*, Bd. **199S**, 25.
- [21] J.L. Neal and D.A.I. Goring (1970). *J. Phys. Chem.*, **74**, 658
- [22] R.G. Clarke and P.R. Tremaine (1999). *J. Phys. Chem. B*, **103**, 5131.
- [23] R.K. Wadi and P. Ramasami (1997). *J. Chem. Soc., Faraday Trans.*, **93**(2), 243.
- [24] T.H. Lilley (1986). In: G.Q. Nilson and J.E. Enderby (Eds.), *Water and Aqueous Solutions*. Adam Hilger, Bristol.
- [25] M. Abbate, G. Castronuovo, V. Elia and S. Puzziello (1993). *Can J. Chem.*, **71**, 2150.
- [26] E.J. Cohn and J.T. Edsall (1943). *Proteins, Amino Acids and Peptides*. Reinhold Publishing Corporation, New York.
- [27] F. Franks (Ed.) (1978). *Water a Comprehensive Treatise*, Vols. II and IV. Plenum Press, New York.
- [28] F. Franks (2000). *Water. A Matrix of Life*, 2nd Edn. Royal Society of Chemistry, Cambridge.
- [29] C.M. Romero and R.E. Munar (1997). *Rev. Academia Colombiana de Ciencias Exactas Físicas y Naturales*, **21**, 535.
- [30] J.M. Tsangaris and R.B. Martin (1965). *Arch. Biochem. Biophys.*, **112**, 267.
- [31] D.R. Lide (Ed.) (1993). *Hanbook of Chemistry and Physics*, 73rd Edn. CRC Press, Inc Boca Raton.
- [32] NIST Chemistry WEB Book. <http://webbook.nist.gov/chemistry/>
- [33] Amino acid repository. IMB Jena Image Library of Biological Macromolecules, [http://www.imb-jena.de/IMAGE\\_AA.html](http://www.imb-jena.de/IMAGE_AA.html)
- [34] J.V. Leyendekkers (1986). *J. Phys. Chem.*, **90**, 5449.