



Volumetric analysis of L-arginine hydrochloride in aqueous and aqueous tetrahydrofuran solution at 303.15 K

Balwinder Saini, Bindu Rani and R. K. Bamezai*

Department of Chemistry, University of Jammu, Jammu - 180 006

ABSTRACT

The apparent molal volume and adiabatic compressibility of L-arginine hydrochloride in water and aqueous tetrahydrofuran has been determined at 303.15 K from precise density and sound measurements. The experimental data has been used to evaluate various thermodynamic and acoustic parameters, like, partial molal volume at infinite dilution, partial molal adiabatic compressibility at infinite dilution, relative association, etc. The data has further been investigated in terms of relative viscosity and B- coefficient of Jones – Dole equation.

Key words: Ultrasonic velocity, density, viscosity, apparent molal volume, compressibility

INTRODUCTION

The study of thermodynamic stability of the native structure of proteins has proved quite challenging and still remains a subject of extensive investigation [1]. Due to the complexities arising from direct thermodynamic study on proteins, investigations on the behavior of model compounds of proteins like amino acids and peptides in aqueous and mixed aqueous solvents make one to understand the factors governing the stability of the biopolymers [2, 3]. The interpretation of behavior of amino acids is quite helpful in understanding the water-protein interactions in solutions. Moreover volumetric, viscometric and ultrasonic studies of amino acids in aqueous and mixed aqueous solutions of organic solvents can provide valuable information for understanding protein unfolding [4-7]. Mixed aqueous solvents are extensively used in chemistry and other fields to control factors like stability, reactivity and solubility of systems [8, 9]. In this paper, we present the volumetric and thermodynamic studies of L-arginine hydrochloride in aqueous and mixed aqueous solution containing THF. L-Arginine hydrochloride is an essential amino acid with anabolic and immune system supportive effects. The water and THF has proved to be most interesting solution due to hydrogen bond interaction of water with THF [10-12].

Additionally, THF is a widely used solvent which can dissolve a wide range of non-polar and polar chemical compounds [13, 14]. It is an aprotic solvent with a dielectric constant of 7.6. As one of the most polar cyclic ethers it is a useful solvent, much less potent anesthetic and more ecologically friendly than diethyl ether. Moreover, a literature survey indicates that no physiochemical study on this system has been reported using THF as solvent. Therefore, an attempt has been made to understand the behavior of arginine hydrochloride with water and water/THF mixed solution at 303.15 K using ultrasonic velocity technique.

MATERIALS AND METHODS

L-Arginine-hydrochloride used in the present work was an analytical reagent having a minimum assay of 99.9%. The triply distilled degassed water with specific conductance less than $10^{-6} \Omega^{-1} \text{ cm}^{-1}$ was used for preparation of solutions. The measured density of water was compared with the literature values [15, 16]. All solutions were made on weight basis using an Analytical balance, Mettler (AE240), with an accuracy of $1.0 \times 10^{-5} \text{ g}$.

The density was measured using a 20 ml specific gravity bottle which was precalibrated using conductivity water. Each reported density data was an average of at least five measurements. The ultrasonic velocity of solutions at 5 MHz was measured with the help of multi frequency ultrasonic interferometer (M-82, Mittal Enterprises, India) having maximum uncertainty of 0.5 ms^{-1} in velocity. The temperature around the cell was controlled within $\pm 0.05 \text{ K}$ by circulating water from a constant temperature bath. The viscosity was measured using an Ostwald type viscometer, which was also calibrated using conductivity water at the desired temperature. The velocity and viscosity measurements, performed at least three times for each composition, were found to be repeatable within the precision limits.

THEORY, RESULTS AND DISCUSSION

The apparent molal volumes (Φ_V) for L-arginine hydrochloride in aqueous and mixed aqueous solution using THF at 303.15 K was calculated from density and speed of sound using Equation 1.

$$\Phi_V = M/d - [(d - d_0) 1000 / mdd_0] \quad (1)$$

where M is the molecular weight of solute, d_0 and d refer to the densities of solvent and solution, respectively and m is the concentration of amino acid expressed usually as molality. Making use of Equation 2, the apparent molal adiabatic compressibility (Φ_K) can be calculated as follows.

$$\Phi_K = MK_s / d - [(K_s^0 d - K_s d_0) / mdd_0] \quad (2)$$

where K_s^0 and K_s are the adiabatic compressibility of solvent and solution, respectively given by Equations 3a and 3b.

$$K_s^0 = 1/u_0^2 d_0 \quad (3a)$$

$$K_s = 1/u^2 d \quad (3b)$$

where u is the ultrasonic velocity and d is the density in their respective mediums.

According to Masson [17], Φ_V is the linear function of molal concentration represented by Equation 4.

$$\Phi_V = \Phi_V^0 + S_v m \quad (4)$$

where Φ_V^0 is the partial molal volume at infinite dilution or limiting apparent molal volume which is a measure of solute-solvent interaction. S_v is the experimental slope, also known as volumetric pair wise interaction coefficient [18, 19], represents a measure of solute-solute interaction. According to Gucker [20] and Debye – Huckel [21], Φ_K is the linear function of molal concentration shown by Equation 5.

$$\Phi_K = \Phi_K^0 + S_K m \quad (5)$$

where Φ_K^0 is the limiting apparent molal adiabatic compressibility and S_K is the experimental slope. Both these values are obtained from linear plot of Φ_K v/s m using least square method.

The relative viscosity (η_r) is calculated as the ratio of viscosity of solution (η) and corresponding solvent (η_0), i.e., $\eta_r = \eta/\eta_0$. In order to evaluate viscosity B-coefficient, the value of η_r is fitted by the method of least square fit using Equation 6.

$$\eta_r = 1 + Bc \quad (6)$$

where c is the molarity of solution. The value of viscosity B-coefficient depends upon the size of solute and nature of solute-solvent interactions which is definite for solute-solvent system.

Relative association (R_A) is the measure of non-ideality of solution which has been calculated by Equation 7.

$$R_A = (d/d_0) (u_0/u)^{1/3} \quad (7)$$

where u_0 and u are the ultrasonic velocities of solvent and solution, respectively.

The values of density, ultrasonic velocity, apparent molal volume, apparent molal adiabatic compressibility and relative association are presented in Table 1. The values of density increase with the increase in concentration of L-arginine hydrochloride in aqueous as well as in different concentration of aqueous THF which may be attributed to an increase in hydrophilic interaction. However, increasing the concentration of THF in water (zero molality), referred herein as solvent, results in the decrease in the density of solution. The Table 1 also reveals that ultrasonic velocity increases with increase in the concentration of solute (L-arginine hydrochloride) as well as on increasing the THF content. The increase of ultrasonic velocity in solutions may be attributed to the cohesion brought about by the ionic hydration. When the amino acid dissolves in THF/water solution, the cations NH_3^+ and anions COO^- are formed. The water molecules are attached to the ions strongly by the electrostatic forces, which introduce greater cohesion in the solution. Thus, cohesion increases with the increasing amino acid concentration in the solution. The increased association observed in these solutions may also be due to water structure enhancement brought about by an increase in electrostriction in presence of THF.

The values of apparent molal volume, Φ_v , and apparent molal compressibility, Φ_K , are also shown in Table 1. The former shows an increasing trend, becoming more positive as the concentration of solute is increased. The later displays a negative trend which may be attributed to the loss of compressibility of surrounding solvent molecules, hence less compressible. As per the hypothesis of dissolution, the large and negative values of Φ_K may also indicate the presence of packing or caging effect [22, 23].

Shown in Figure 1 are plots of Φ_v against molality for the said solute. The Φ_v of L-arginine hydrochloride is a linear function of the molal concentration with a positive slope. The large positive slopes are found for amino acids having aromatic rings and terminal carboxyl group. Also, shown in Figure 2 are plots of Φ_K versus molality. These curves too show a linear variation and the slopes for the compressibility data behave similar to the slopes of volume data.

Equations 4 and 5 are used to calculate the partial molal volume at infinite dilution or limiting apparent molal volume (Φ_v°) and limiting apparent molal adiabatic compressibility (Φ_K°), respectively. The graphically evaluated values of Φ_v° and corresponding slope S_v along with Φ_K° and its slope S_K is presented in Table 2. The Φ_v° value for L-arginine hydrochloride is positive and higher in THF/water combination when compared with aqueous solution only. This is an indicative of stronger interaction in the presence of THF. The support towards stronger interaction also comes from the values of slope S_v which remain positive for L-arginine hydrochloride in water and THF/water solution.

The Φ_K° value for L-arginine hydrochloride at all concentrations is found to be negative. The large negative values of Φ_K° may also indicate hydrophobic interaction [24]. Additionally, the limiting apparent molal compressibility Φ_K° is a measure of protection against compression, which the solute molecule imparts to water. The values of S_K are positive for L-arginine hydrochloride in various concentrations of THF. The positive value of S_K suggests that solute-solvent interactions are relatively stronger.

Equation 6, expressing Jones – Dole equation [25] has been used to calculate viscosity B coefficients. It may be pointed here that c is molarity of solution calculated from molality. The values of relative viscosity and B-coefficients are tabulated in Table 3. The B-coefficient values are positive which shows strong alignment of THF with the solute causing strong alignment of L-arginine hydrochloride. The strong interaction immobilizes the neighboring solvent molecules and presents large obstruction to viscous flow of solution thereby increasing its viscosity. The plot of relative viscosity and concentration is presented in Figure 3. The hydrated solutes can be classified in two types, namely, kosmotropes (structure makers) while weakly hydrated ones are chaotropes (structure breakers). For ionic solids, it has been established that strong kosmotropic anions stabilize proteins and strong kosmotropic cations destabilize them. The kosmotropicity of ions can be quantified by viscosity B coefficients, hydration entropies, hydration volumes, heat capacities, ion mobilities, etc. In general, positive B coefficients suggest kosmotropic behavior since strongly hydrated solutes exhibit a large change in viscosity with concentration. As observed from Equation 7, the relative association (R_A) is a function of ultrasonic velocity. The relative association is influenced by two factors (i) the breaking up of the solvent structure on addition of solute to it, and (ii) the solvation of solute. The first parameter results in decrease while the later results in increase in R_A . The increase in R_A with concentration (Table 1) suggests the solvation of L-arginine hydrochloride predominating over the breaking-up of the solvent structure.

Table 1: Molalities, densities, ultrasonic velocities, adiabatic compressibilities, apparent molal volumes, apparent molal adiabatic compressibilities and relative association of L-arginine hydrochloride at 303.15 K in aqueous and in mixed aqueous solution of THF

m (mol kg ⁻¹)	d (kg m ⁻³)	U (m s ⁻¹)	K _s x 10 ¹⁰ (Pa ⁻¹)	Φ _v x 10 ⁶ (m ³ mol ⁻¹)	Φ _K x 10 ¹⁵ (m ³ mol ⁻¹ Pa ⁻¹)	R _A
L-Arginine hydrochloride in aqueous solution						
0.0	995.65	1510	4.40			
0.1	1004.95	1526	4.27	116.69	-82.52	1.00580
0.2	1013.09	1532	4.20	121.45	-49.01	1.01263
0.3	1020.22	1537	4.14	125.83	-33.43	1.01865
0.4	1025.48	1542	4.10	132.38	-21.99	1.02279
L-Arginine hydrochloride in 5% aqueous THF						
0.0	992.73	1532	4.29			
0.1	1001.72	1548	4.16	119.87	-76.98	1.00557
0.2	1008.48	1553	4.11	130.20	-37.38	1.01127
0.3	1015.24	1558	4.05	133.05	-24.62	1.01695
0.4	1021.47	1564	4.00	135.37	-18.78	1.02188
L-Arginine hydrochloride in 10% aqueous THF						
0.0	990.76	1545	4.22			
0.1	998.27	1557	4.13	135.05	-41.39	1.00499
0.2	1004.03	1566	4.06	143.11	-26.21	1.00884
0.3	1009.47	1575	3.99	146.31	-20.64	0.01238
0.4	1014.50	1584	3.92	148.59	-17.27	0.01549
L-Arginine hydrochloride in 15% aqueous THF						
0.0	987.37	1560	4.16			
0.1	993.27	1574	4.06	152.00	-37.49	1.00298
0.2	998.31	1583	3.99	155.53	-21.08	1.00616
0.3	1002.94	1595	3.91	157.65	-20.08	1.00828
0.4	1007.46	1606	3.84	158.61	-18.29	1.01051
L-Arginine hydrochloride in 20% aqueous THF						
0.0	985.20	1572	4.10			
0.1	990.97	1586	4.01	153.48	-35.57	1.00289
0.2	995.90	1595	3.94	157.01	-19.49	1.00598
0.3	1000.12	1606	3.87	160.16	-16.00	1.00793
0.4	1004.51	1615	3.81	160.93	-12.32	1.01047
L-Arginine hydrochloride in 25% aqueous THF						
0.0	983.55	1590	4.02			
0.1	988.54	1604	3.93	161.74	-27.81	1.00214
0.2	992.71	1615	3.86	165.31	-17.24	1.00408
0.3	996.16	1628	3.78	168.57	-15.49	1.00488
0.4	999.42	1641	3.71	170.42	-14.48	1.00550

Table 2: Values of limiting apparent molal volumes, limiting apparent molal compressibilities, constants S_v and S_K for L-arginine hydrochloride at 303.15 K at different concentrations

Concentration	Φ ⁰ _v x 10 ⁶ (m ³ mol ⁻¹)	S _v x 10 ⁶ (m ³ mol ⁻² kg)	Φ ⁰ _K x 10 ⁶ (m ³ mol ⁻¹ Pa ⁻¹)	S _K x 10 ¹⁵ (m ³ mol ⁻² Pa ⁻¹ kg)
0%	111.22 (±0.92)	51.4 (±3.36)	-96.03 (±9.92)	197.17 (±36.23)
5%	117.28 (±3.72)	49.35 (±13.58)	-86.28 (±15.12)	187.36 (±55.21)
10%	132.31 (±2.62)	43.82 (±9.55)	-45.86 (±5.31)	77.93 (±19.39)
15%	150.45 (±1.11)	21.95 (±4.07)	-38.88 (±7.06)	58.60 (±25.80)
20%	151.52 (±1.26)	25.50 (±4.59)	-39.16 (±5.91)	73.24 (±21.59)
25%	159.18 (±0.77)	29.30 (±2.83)	-29.19 (±4.42)	41.74 (±16.16)

(Values in the parenthesis indicate error)

Table 3. Molarities, viscosities, relative viscosities and viscosity B-coefficient of Jones-Dole equation

c (mol L ⁻¹)	$\eta \times 10^3$ (Pa s)	η_r	Viscosity B-coefficient (L mol ⁻¹)
L-Arginine hydrochloride in aqueous solution			
0.00000	0.8007		0.3721
0.08301	0.8299	1.0365	
0.19443	0.8574	1.0708	
0.28788	0.8867	1.1074	
0.37832	0.9129	1.1401	
L-Arginine hydrochloride in 5% aqueous THF solution			
0.00000	0.8891		0.2601
0.08274	0.9140	1.0280	
0.19354	0.9366	1.0534	
0.28647	0.9544	1.0734	
0.37684	0.9744	1.0959	
L-Arginine hydrochloride in 10% aqueous THF solution			
0.00000	0.9481		0.2938
0.08246	0.9751	1.0285	
0.19269	1.0007	1.0555	
0.28484	1.0267	1.0829	
0.37426	1.0526	1.1102	
L-Arginine hydrochloride in 5% aqueous THF solution			
0.00000	1.0263		0.9384
0.08204	1.0975	1.0694	
0.19159	1.2172	1.1860	
0.28300	1.3121	1.2785	
0.37167	1.3726	1.3374	
L-Arginine hydrochloride in 20% aqueous THF solution			
0.00000	1.1230		0.7315
0.08185	1.1528	1.0265	
0.19113	1.2628	1.1245	
0.28220	1.3658	1.2162	
0.37058	1.4362	1.2789	
L-Arginine hydrochloride in 25% aqueous THF solution			
0.00000	1.1921		0.9987
0.08165	1.3290	1.1148	
0.19052	1.4325	1.2017	
0.28109	1.5022	1.2601	
0.36870	1.6340	1.3707	

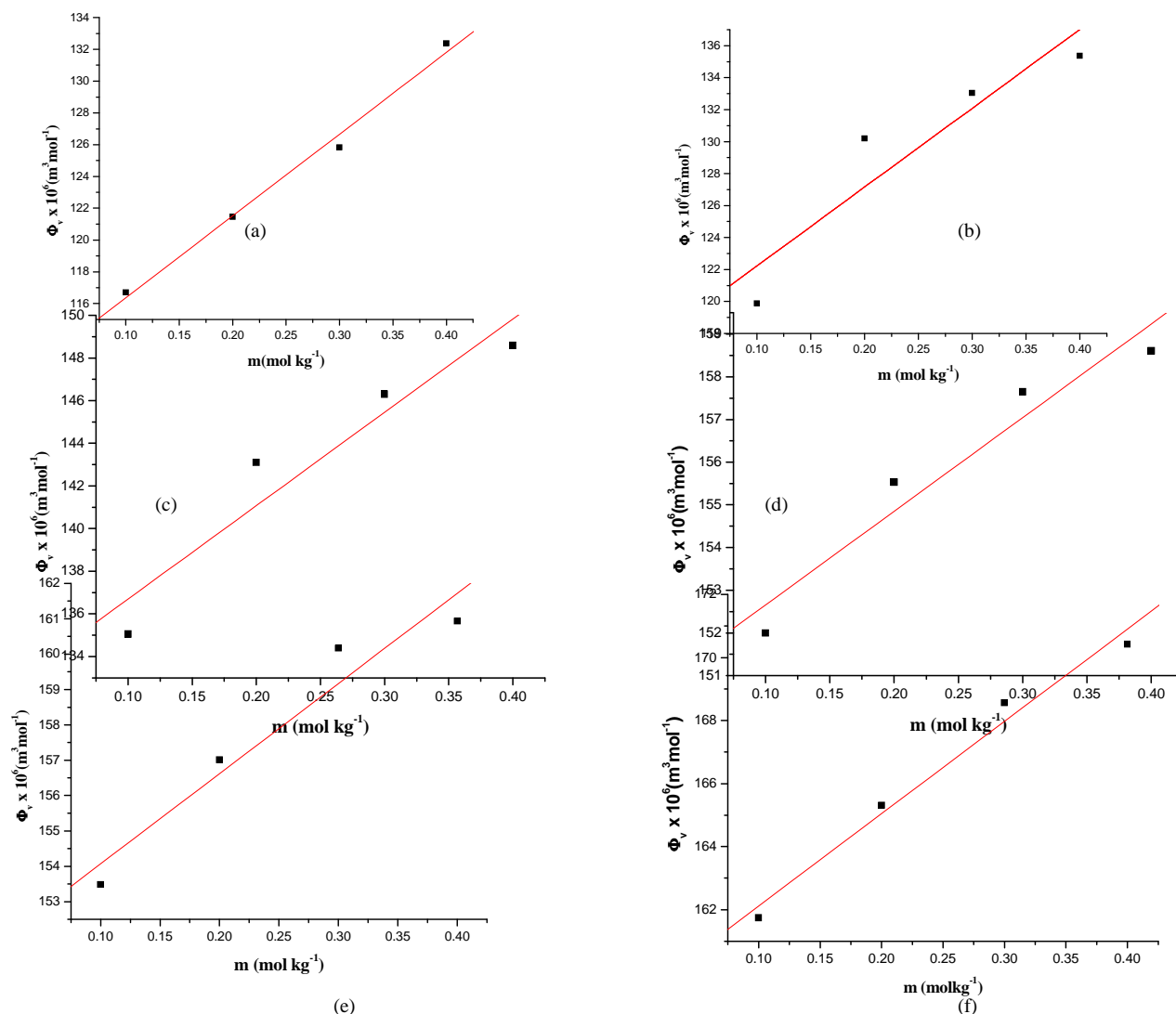


Fig. 1: Plot of apparent molar volume (Φ_v) v/s molality (m) at 303.15 K (a) L-Arginine hydrochloride in aqueous solution (b) L-Arginine hydrochloride in 5% aqueous THF (c) L-Arginine hydrochloride in 10% aqueous THF (d) L-Arginine hydrochloride in 15% aqueous THF (e) L-Arginine hydrochloride in 20% aqueous THF (f) L-Arginine hydrochloride in 25% aqueous THF.

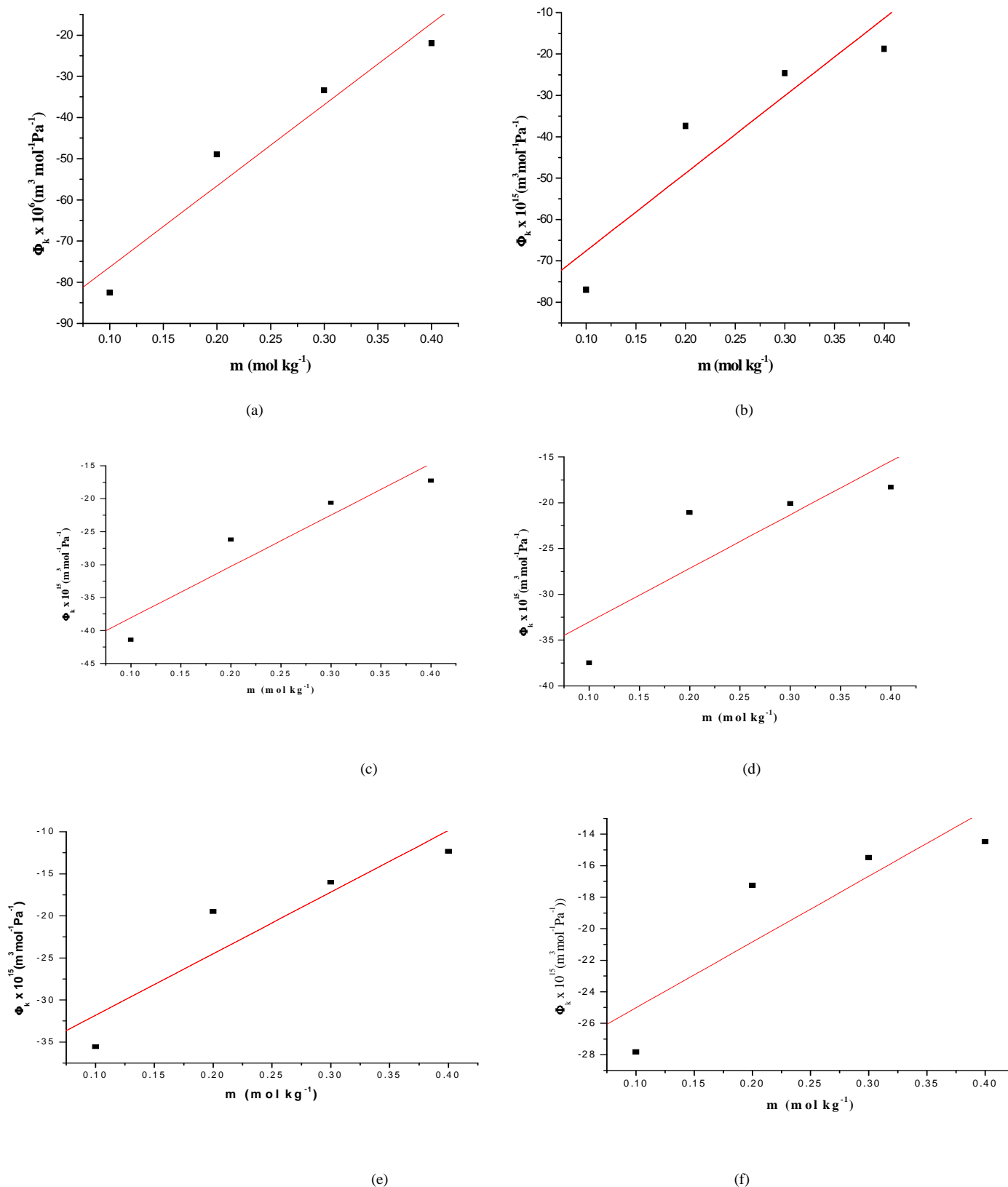


Fig. 2: Plot of apparent molal adiabatic compressibility (Φ_k) v/s molality (m) at 303.15 K (a) L-Arginine hydrochloride in aqueous solution (b) L-Arginine hydrochloride in 5% aqueous THF (c) L-Arginine hydrochloride in 10% aqueous THF (d) L-Arginine hydrochloride in 15% aqueous THF (e) L-Arginine hydrochloride in 20% aqueous THF (f) L-Arginine hydrochloride in 25% aqueous THF.

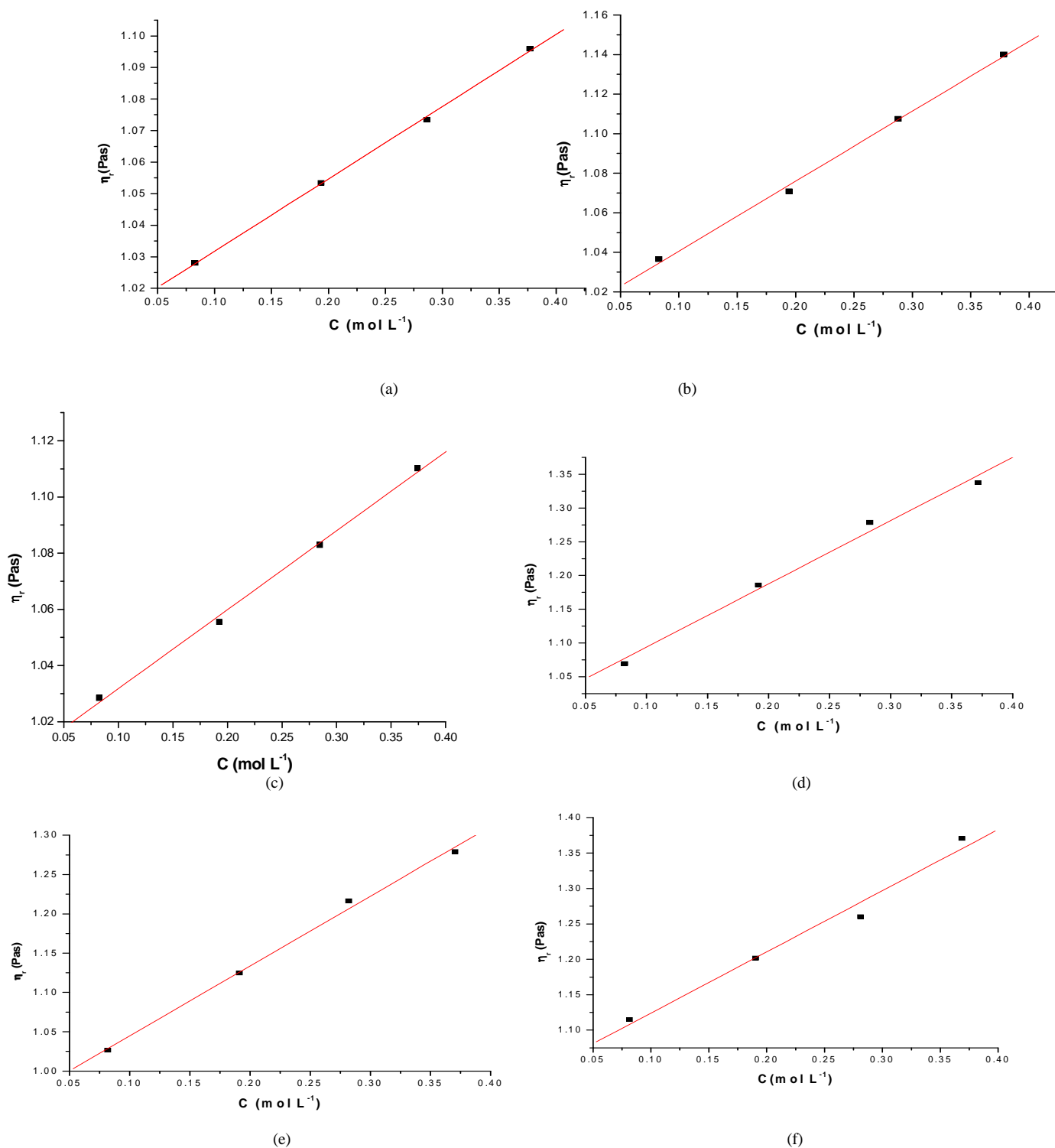


Fig. 3: Plot of relative viscosity (η_r) v/s molarity (C) at 303.15 K (a) L-Arginine hydrochloride in aqueous solution (b) L-Arginine hydrochloride in 5% aqueous THF (c) L-Arginine hydrochloride in 10% aqueous THF (d) L-Arginine hydrochloride in 15% aqueous THF (e) L-Arginine hydrochloride in 20% aqueous THF (f) L-Arginine hydrochloride in 25% aqueous THF.

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