

Physico-Chemical Studies of Some Bio-active Solutes in Pure Methanoic Acid

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Abstract

The apparent molar volume (ϕ_V), viscosity B -coefficient, adiabatic compressibility (ϕ_K) and molar refraction (R) of L-Glycine, L-Alanine, L-Valine and L-Leucine have been determined in methanoic acid at 298.15 K from density (ρ), viscosity (η), speed of sound (u) and refractive index (n_D) respectively. The apparent molar volumes have been extrapolated to zero concentration to obtain the limiting values at infinite dilution using Masson equation. The limiting apparent molar volume (ϕ_V^0) and experimental slopes (S_V^*) obtained from the Masson equation have been interpreted in terms of solute-solvent and solute-solute interactions, respectively. The viscosity data were analyzed using the Jones-Dole equation, and the derived parameters A and B have also been interpreted in terms of solute-solute and solute-solvent interactions, respectively in the solutions. Molar refraction (R) have been calculated using the Lorentz-Lorenz equation. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) of these amino acids at infinite dilution were evaluated.

Keyword: Solute-Solvent and Solute-Solute Interactions, Methanoic Acid, Amino Acids

1. Introduction

Amino acids, particularly important in biochemistry, are critical to life, and have many functions in metabolism. One particularly important function is to serve as the building blocks of proteins. Due to their central role in biochemistry; amino acids are important in nutrition and are commonly used in food technology and industry.

Methanoic acid is an essential chemical industry material. It is widely used in the textile industry, tanning industry, rubber processing industry, and pharmaceutical industry. In addition, methanoic acid is used as a preservative and antibacterial agent in livestock feed.^{1,2}

The volumetric, viscometric and interferometric behavior of solutes have been proved to be very useful in elucidating the various interactions occurring in pure solvents. Studies on the effect of concentration (molality) the

apparent molar volumes of solutes have been extensively used to obtain information on ion-ion, ion-solvent, and solvent-solvent interactions.³⁻⁷

Here, we have attempted to report the limiting apparent molar volume (ϕ_V^0), experimental slopes (S_V^*), and viscosity B -coefficients, limiting apparent molar adiabatic compressibility (ϕ_K^0) and molar refraction (R) for the cited amino acids in methanoic acid.

2. Experimental

2.1. Chemicals

Methanoic acid (Thomas Baker, > 98%) are used after purification using standard methods.⁸ L-Glycine, L-Alanine, L-Valine and L-Leucine were procured from (Sigma Aldrich > 99 %) and were used as such without

Table 1. Densities (ρ), Viscosities (η), Refractive Index (n_D) and Speed of sound (u) of Methanoic acid at 298.15 K

Expt.	$\rho/\text{g cm}^{-3}$		$\eta/\text{mPa s}$		n_D		$u/\text{m s}^{-1}$	
	Lit	Expt.	Lit	Expt.	Lit	Expt.	Lit	
1.21401	1.21405 ²⁰	1.532	1.51 ²¹	1.3697	1.3694 ²¹	1276.8	1283.0 ²²	

further purification. The physical properties of the pure solvent were in good agreement with values found in the literature, as reported in Table 1.

2. 2. Measurements

The density, ρ , was measured with an Anton Paar density meter (DMA 4500M). The uncertainty in the density measurements is within $5 \times 10^{-5} \text{ g cm}^{-3}$. It was calibrated by double-distilled water and dry air. The viscosity, η , was measured by means of suspended Ubbelohde type viscometer, calibrated at 298.15 K with triply distilled water and purified methanol using density and viscosity values from literature. A thoroughly cleaned and perfectly dried viscometer filled with experimental solution was placed vertically in a glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to 0.01 K. After attainment of thermal equilibrium, efflux times of flow were recorded with a stop watch. The flow times were accurate to $\pm 0.1 \text{ s}$, and the uncertainty in the viscosity measurements was $\pm 2 \times 10^{-3} \text{ mPas}$. The mixtures were prepared by mixing known volume of pure liquids in airtight-stopper bottles and each solution thus prepared was distributed into three recipients to perform all the measurements in triplicate, with the aim of determining possible dispersion of the results obtained. Adequate precautions were taken to minimize evaporation losses during the actual measurements. Mass measurements were done on a Mettler AG-285 electronic balance with a precision of $\pm 0.01 \text{ mg}$. The precision of density measurements was $\pm 3 \times 10^{-4} \text{ g cm}^{-3}$. Refractive index was measured with the help of Abbe-Refractometer (U.S.A). The accuracy of refractive index measurement was ± 0.0002 units. The refractometer was calibrated twice using distilled and deionized water, and calibration was checked after every few measurements.

Table 3. Molality (m), apparent molar volume (ϕ_V), $(\eta/\eta_0-1)m^{1/2}$, molar refraction (R), adiabatic compressibility (β) and apparent molal adiabatic compressibility (ϕ_K) of Glycine, Alanine, Valine and Leucine in Methanoic acid at 298.15 K

molality /mol kg ⁻¹	$\phi_V 10^6 /\text{m}^3 \text{mol}^{-1}$	$(\eta/\eta_0-1)/\text{m}^{1/2} /\text{kg}^{1/2} \text{mol}^{-1/2}$	$R /\text{cm}^3 \text{mol}^{-1}$	$\beta 10^{10} / \text{Pa}^{-1}$	$\phi_K 10^{10} / \text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$
L-Glycine + Methanoic acid mixture					
0.0082	54.43	0.095	13.9930	5.0208	-2.92
0.0206	55.25	0.110	14.2240	4.9588	-3.48
0.0330	55.82	0.121	14.4040	4.8848	-3.92
0.0454	56.28	0.129	14.5360	4.8034	-4.25
0.0579	56.66	0.137	14.6650	4.7129	-4.57
0.0704	57.09	0.145	14.7722	4.6177	-4.83
L-Alanine + Methanoic acid mixture					
0.0082	65.55	0.096	16.6254	5.0223	-2.72
0.0206	66.13	0.112	16.9900	4.9589	-3.42
0.0330	66.60	0.125	17.2330	4.8829	-3.91
0.0455	66.97	0.136	17.4400	4.7960	-4.33
0.0579	67.30	0.145	17.6170	4.7042	-4.64
0.0704	67.57	0.153	17.7790	4.6030	-4.95
L-Valine + Methanoic acid mixture					
0.0082	87.38	0.097	21.8826	5.0232	-2.52
0.0206	87.82	0.116	22.4601	4.9575	-3.37
0.0331	88.15	0.131	22.8803	4.8786	-3.91
0.0455	88.45	0.142	23.2302	4.7851	-4.42
0.0580	88.68	0.153	23.5401	4.6854	-4.80
0.0705	88.91	0.164	23.7802	4.5743	-5.18
L-Leucine + Methanoic acid mixture					
0.0082	97.29	0.098	24.5187	5.0244	-2.35
0.0206	97.63	0.121	25.2700	4.9585	-3.28
0.0331	97.88	0.137	25.7900	4.8739	-3.98
0.0456	98.11	0.151	26.2700	4.7780	-4.50
0.0581	98.27	0.163	26.6500	4.6694	-4.98
0.0706	98.43	0.176	27.0086	4.5532	-5.38

Table 2. Experimental values of Densities (ρ), Viscosities (η), Refractive Index (n_D) and Speed of sound (u) of Glycine, Alanine, Valine and Leucine in Methanoic acid at 298.15 K

molality /mol kg ⁻¹	$\rho 10^{-3} / \text{kg cm}^{-3}$	$\eta / \text{mPa s}$	n_D	$u / \text{m s}^{-1}$
L-Glycine + Methanoic acid mixture				
0.0082	1.21410	1.545	1.3702	1280.8
0.0206	1.21421	1.556	1.3771	1288.7
0.0330	1.21430	1.566	1.3825	1298.4
0.0454	1.21438	1.574	1.3865	1309.3
0.0579	1.21445	1.583	1.3904	1321.8
0.0704	1.21450	1.591	1.3936	1335.3
L-Alanine + Methanoic acid mixture				
0.0082	1.21411	1.545	1.3707	1280.6
0.0206	1.21423	1.557	1.3799	1288.7
0.0330	1.21434	1.567	1.3860	1298.6
0.0455	1.21444	1.576	1.3913	1310.3
0.0579	1.21453	1.585	1.3958	1323.0
0.0704	1.21461	1.594	1.3999	1337.4
L-Valine + Methanoic acid mixture				
0.0082	1.21412	1.545	1.3711	1280.5
0.0206	1.21427	1.558	1.3821	1288.9
0.0331	1.21442	1.568	1.3903	1299.2
0.0455	1.21455	1.578	1.3970	1311.7
0.0580	1.21467	1.589	1.4031	1325.5
0.0705	1.21479	1.599	1.4078	1341.5
L-Leucine + Methanoic acid mixture				
0.0082	1.21414	1.546	1.3714	1280.3
0.0206	1.21433	1.559	1.3842	1288.7
0.0331	1.21450	1.570	1.3932	1299.8
0.0456	1.21467	1.581	1.4016	1312.6
0.0581	1.21484	1.592	1.4082	1327.7
0.0706	1.21500	1.603	1.4145	1344.5

The ultrasonic velocities, $u/m\ s^{-1}$, were measured using an ultrasonic interferometer (Model M-83) from Mittal enterprises. The interferometer working at 2 MHz is based on the same principle as was used by Freyer et al.⁹ and Kiyoharo et al.^{10,11} The obtained velocities were corrected for diffraction errors as given by Subrahmayan et al.¹² The maximum uncertainty in the velocity is $\pm 0.5\ m\ s^{-1}$. The temperature was controlled within $\pm 0.01\ K$ using a Lauda thermostat for velocity measurements.

Viscosity of the solution, η , is given by the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

Where K and L are the viscometer constants and t and ρ are the efflux time of flow in seconds and the density of the experimental liquid respectively. The uncertainty in viscosity measurements is within $\pm 0.003\ mPas$.

The solutions studied here were prepared by mass and the conversion of molarity into molality was accomplished⁵ using experimental density values. The experimental values of densities (ρ), viscosities (η), refractive index (n_D) and speed of sound (u) of solution mixtures are reported in Table 2 and the derived parameters are reported in Table 3.

3. Results and Discussion

Apparent molar volumes (ϕ_V) were determined from the solution densities using the following equation:

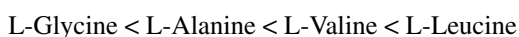
$$\phi_V = M/\rho - 1000(\rho - \rho_0)/m\rho\rho_0 \quad (2)$$

where M is the molar mass of the solute, m is the molality of the solution; ρ_0 and ρ are the densities of the solvent and the solution respectively. The limiting apparent molar volume ϕ_V^0 was calculated using a least-square treatment to the plots of ϕ_V versus \sqrt{m} using the Masson equation.¹³

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \quad (3)$$

where ϕ_V^0 is the limiting apparent molar volume at infinite dilution and S_V^* is the experimental slope. The plots of ϕ_V against square root of molal concentration (\sqrt{m}) were found to be linear with slopes. Values of ϕ_V^0 and S_V^* are reported in Table 4.

A perusal of Table 4 shows that ϕ_V^0 values are positive and the trend in the solute-solvent interaction is



This shows that with increases in the number of carbon atoms in the studied amino acids, the solute-solvent interaction also increases.

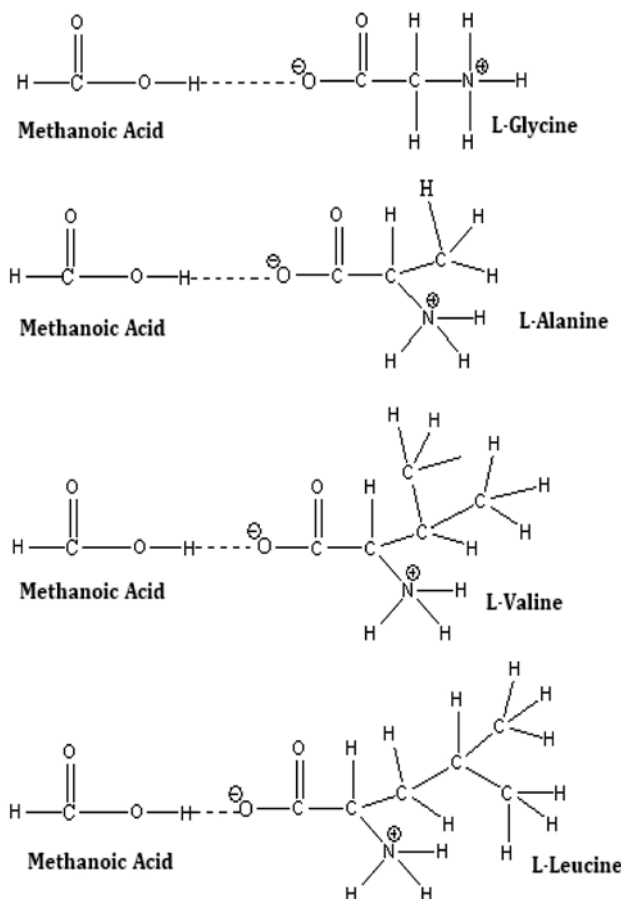
It is known that the amino acids remain in zwitterionic form in solid and in liquid. Hence the negatively char-

Table 4. Limiting apparent molar volumes (ϕ_V^0), experimental slopes (S_V^*), A , B coefficients, limiting partial adiabatic compressibility (ϕ_K^0), and experimental slope (S_K^*) of Glycine, Alanine, Valine and Leucine in Methanoic acid at 298.15 K

$\phi_V^0\ 10^6/\ m^3\ mol^{-1}$	$S_V^*\ 10^6/\ m^3\ mol^{-3/2}\ kg^{1/2}$	$A/kg\ mol^{-1}$	$B/kg^{1/2}\ mol^{-1/2}$	$\phi_K^0\ 10^{10}/\ m^3\ mol^{-1}\ Pa^{-1}$	$S_K^*\ 10^4/\ m^3\ mol^{-3/2}\ Pa^{-1}\ kg^{1/2}$
L-Glycine + Methanoic acid mixture					
53.07	15.07	0.070	0.278	-1.913	-11.001
L-Alanine + Methanoic acid mixture					
64.48	11.68	0.066	0.328	-1.578	-12.774
L-Valine + Methanoic acid mixture					
86.57	8.76	0.062	0.382	-1.165	-15.146
L-Leucine + Methanoic acid mixture					
96.67	6.55	0.057	0.443	-0.786	-17.381

ged oxygen atom in the carboxylic group of amino acids probably interacts with the acidic hydrogen of methanoic acid rendering higher solute-solvent interaction in comparison with solute-solute interaction as evident from ϕ_V^0 values. The order of solute-solvent interaction mentioned in Table 4 may be due to the following reason:

As the higher amino acids contain more alkyl groups (electron releasing group), the carboxylate oxygen



becomes more negative rendering to stronger H-bonding, i.e. stronger solute-solvent interaction. A plausible mechanism of interaction between methanoic acid and different amino acids as evident from the experimental observation explained and discussed above is given below:

The S_V^* values of the amino acid solution given in Table 4 decreases with increases in the number of carbon atoms of the studied amino acids rendering minimum solute-solute interaction in the higher analogs.

The magnitude of ϕ_V^0 values is much greater than those of S_V^* for all the solutions as seen in Figure 1 and suggests that solute-solvent interactions dominate over solute-solute interactions.

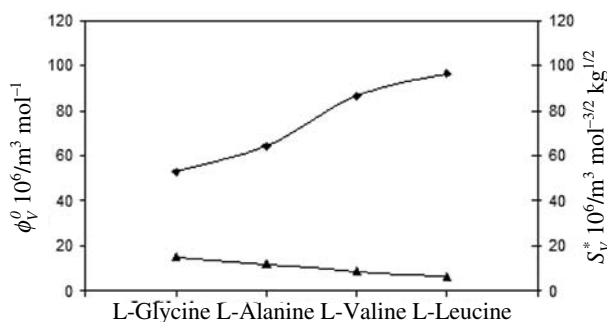


Figure 1. Plot of ϕ_V^0 $10^6/\text{m}^3 \text{mol}^{-1}$ (—◆—) and S_V^* $10^6/\text{m}^3 \text{mol}^{-3/2} \text{L}^{1/2}$ (—▲—) of the studied amino acids in Methanoic acid at 298.15K

The viscosity data has been analyzed using Jones-Dole¹⁴ equation:

$$(\eta / \eta_0 - 1) / m^{1/2} = A + Bm^{1/2} \quad (4)$$

where η_0 and η are the viscosities of the solvent and solution respectively. A and B are the constants estimated by a least-squares method and are reported in Table 4. The values of the A -coefficient are found to decrease with the increase in the number of carbon atoms of amino acids. These results indicate the presence of very weak solute-solute interactions. These results are in excellent agreement with those obtained from S_V^* values.

The effects of solute-solvent interactions on the solution viscosity can be inferred from the B -coefficient.^{15,16} The viscosity B -coefficient is a valuable tool to provide information concerning the solvation of the solutes and their effects on the structure of the solvent. From Table 4 it is evident that the values of the B -coefficient are positive, thereby suggesting the presence of strong solute-solvent interactions, and strengthened with an increase the number of carbon atoms of amino acids. Similar results are obtained from ϕ_V^0 values discussed earlier.

The adiabatic compressibility (β) was evaluated from the following equation:

$$\beta = 1 / u^2 \rho \quad (5)$$

Where ρ is the density of solution and u is the speed of sound in the solution. The apparent molal adiabatic compressibility (ϕ_K) of the solutions was determined from the relation,

$$\phi_K = M\beta / \rho + 1000(\beta \rho_0 - \beta_0 \rho) / m \rho \rho_0 \quad (6)$$

Where β_0 , β are the adiabatic compressibility of the solvent and solution respectively and m is the molality of the solution. Limiting partial molal adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were obtained by fitting ϕ_K against the square root of molality of the electrolyte (\sqrt{m}) using the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{m} \quad (7)$$

The values of β and ϕ_K are reported in Table 3. The values of ϕ_K^0 and S_K^* are presented in Table 4. Since the values of ϕ_K^0 and S_K^* are measures of solute-solvent and solute-solute interactions respectively, a perusal of Table 4 and Figure 2 shows that the values are in agreement with those drawn from the values of ϕ_V^0 and S_V^* discussed earlier.

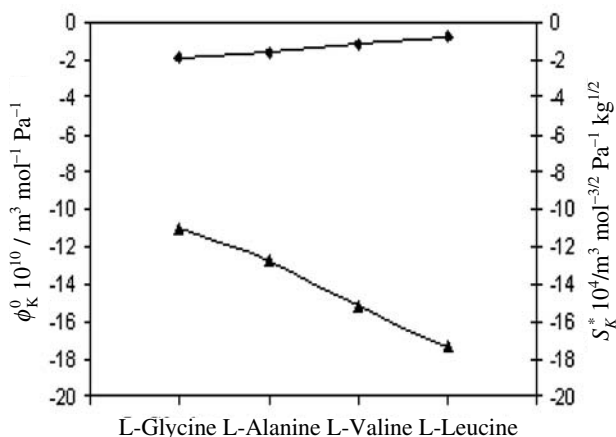


Figure 2. Plot of ϕ_K^0 $10^{10} / \text{m}^3 \text{mol}^{-1} \text{Pa}^{-1}$ (—◆—) and S_K^* $10^4 / \text{m}^3 \text{mol}^{-3/2} \text{Pa}^{-1} \text{kg}^{1/2}$ (—▲—) of the studied amino acids in Methanoic acid at 298.15K

The molar refraction, R can be evaluated from the Lorentz-Lorenz relation¹⁷

$$R = \left\{ (n_D^2 - 1) / (n_D^2 + 2) \right\} (M / \rho) \quad (8)$$

Where R , n_D , M and ρ are the molar refraction, the refractive index, the molar mass and the density of solution respectively. The refractive index of a substance is defined as the ratio c_0/c , where c is the speed of light in the medium and c_0 the speed of light in vacuum. Stated more simply, the refractive index of a compound describes its ability to refract light as it moves from one medium to another and thus, the higher the refractive index of a com-

pound, the more the light is refracted.¹⁸ As stated by Deetlefs et al.¹⁹ the refractive index of a substance is higher when its molecules are more tightly packed or in general when the compound is denser. Hence a perusal of Tables 3 and 4 we found that the refractive index and the molar refraction values respectively are higher for L-leucine indicating to the fact that the molecules are more tightly packed in the solution. The interaction in the solution is basically solute-solvent interaction and a small amount of solute-solute interaction. The trend in the package of the studied molecules in methanoic acid is L-Glycine < L-Alanine < L-Valine < L-Leucine.

4. Conclusion

The values of the limiting apparent molar volume (ϕ_V^0), viscosity B -coefficients and limiting partial isentropic compressibility (ϕ_K^0) indicates the presence of strong solute-solvent interactions which increases with the increase of in the number of carbon atoms of the studied amino acids in methanoic acid. The refractive index and the molar refraction values suggest that L-leucine molecules are more tightly packed in the solution leading to higher solute-solvent interaction than the other studied amino acids.

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Povzetek

Raztopinam L-glicina, L-alanina, L-valina in L-levcina v metanojski kislini smo izmerili gostoto (ρ), viskoznost (η), hitrost zvoka (u) in lomni koeficient (n_D). Iz eksperimentalnih podatkov smo izračunali navidezne molske volumne (ϕ_V), viskoznostne B -koeficiente, adiabatne kompresibilnosti (ϕ_K) in molsko refrakcijo (R). Z uporabo Massonove enačbe smo z ekstrapolacijo določili limitne vrednosti navideznih molskih volumnov (ϕ_V^0) in naklona (S_V^*). Oba parametra smo uporabili v interpretaciji interakcij topilo-topljenec in topljenec-topljenec. Eksperimentalne podatke viskoznosti preiskovanih sistemov smo obravnavali z Jones-Dolejevo enačbo, dobljena koeficienta A in B pa smo prav tako uporabili pri obravnavi interakcij v raztopinah. Molsko refrakcijo (R) smo izračunali z Lorentz-Lorenzovo zvezo in določili tudi limitne vrednosti navidezne molske adiabatne kompresibilnosti (ϕ_K^0) proučevanih sistemov.