Thermophysical studies of protonated and deprotonated glycine in aqueous sodium acetate buffer solutions at different temperatures

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Interactions of glycine in water and in (0.10, 0.50 and 1.00) mol kg^{-1} aqueous sodium acetate buffer solutions of pH (1.00 and 12.40) have been investigated at different temperatures, T(K) = (298.15-318.15). Densities, ρ and viscosities, η of glycine in water and in aqueous sodium acetate buffer solutions have been measured. The obtained density data have been used to calculate apparent molar volume, ϕ_v, limiting partial molar volume, ϕ_v^o, limiting partial molar volumes of transfer, $\Delta_{tr}\phi_v$. Viscosity B-coefficient, viscosity B-coefficient of transfer, $\Delta_{tr}B$, activation free energies per mole of the solute, $\Delta\mu_2^{o\#}$ and solvent, $\Delta\mu_1^{o\#}$ have been calculated from viscosity data. Further, second order derivative of partial molar expansion coefficient and dependence of dB/dT coefficients on temperature is useful in measuring the structure making and breaking behaviour of solute in these systems. Pair and triplet interaction coefficients for both the properties were also calculated. Thus, the results obtained from volumetric and viscometric studies are of considerable importance to identify different type of interactions (*i.e.* H-bonding, van der Waals interactions) in these systems.

Keywords: Acetate buffer, pH, Glycine, Density, Viscosity

Protein hydration plays an important role in proper functioning of the native conformational stability of proteins which contributes to the formation of most stable folded structure of protein molecule[1-2]. Due to the complex structure of proteins, it is challenging to resolve different types of interactions involving protein hydration. In order to obtain more insight into the conformational stability of proteins, it is necessary to study simple model compounds *i.e.* amino acids (AA) and peptides[3]. AA being the basic components of protein is considered to be one of the most important model compounds that participate mainly in all physiochemical processes of living organisms. AA are sensitive to external conditions such as pH of the solution as AA dissociate into different ionic forms in aqueous media *i.e.*, cations, zwitterions and anions[2]. Variation in pH results into overall modification of conformational stability of protein molecules. Thus, pH plays an important role in various biochemical reactions occurring in living environments. pH of the solution can be maintained with the addition of buffers[4]. Biological buffers such as phosphate, citrate and acetate etc. are of immense importance for research in pharmaceutical industry, biomedicine and clinical chemistry. Therefore, it is of enormous significance to study the effects of various biological buffer solutions on the stability of protein model compounds. Sodium acetate buffer (NaAcB) is one such biological buffer used in various biochemical studies of enzymes (*i.e.* cytochemical reactions), as pickling agent in chrome tanning and also helps to prevent vulcanization of chloroprene in synthetic rubber production[5]. Hence, interactions between NaAcB and AA are very important to understand the conformational stability of protein molecule in aqueous medium.

A survey of literature reveals that volumetric and viscometric studies of AA in aqueous sodium acetate at different temperatures have been determined by various authors[6-11]. Recently, studies on AA in biological buffer solutions at physiological conditions have drawn much attention. Till now, no study on interactions of AA in aqueous NaAcB of different pH has been reported. Thus, in light of above picture, it will be worthwhile to study systematically the effect of NaAcB on AA by varying pH and temperature. In the wake of our study on the thermodynamic properties of amino acids in different buffer solutions of pH (1.00 (protonated), 7.40 (zwitterionic) and 12.40 (deprotonated)) at T(K) = (288.15, 293.15, 298.15, 303.15, 308.15, 310.15, 313.15, 318.15, 323.15 and 328.15), in the present article we have

reported the volumetric and viscometric properties of glycine in water and in (0.10, 0.50 and 1.00) $mol\,kg^{-1}$ aqueous NaAcB solutions of pH (1.00 and 12.40) at T(K) = 298.15, 308.15, 310.15 and 318.15.

The derived parameters such as limiting partial molar volume, ϕ_v^o, viscosity B-coefficients, corresponding transfer values, $\Delta_{tr}\phi_v$ and $\Delta_{tr}B$, partial molar expansion coefficient, $(\partial\phi_v^o/\partial T)_P$ and their second order derivative, $(\partial^2\phi_v^o/\partial T^2)_P$, and free energies of activation of viscous flow $\Delta\mu_1^{o\#}$ and $\Delta\mu_2^{o\#}$ were obtained by using experimental density and viscosity data. Moreover, volumetric and viscometric studies were found to be very useful for the interpretation of different interactions in these systems.

Material and Methods

Glycine was procured from S.D. Fine Chem. Ltd., India, and anhydrous sodium acetate and glacial acetic acid were procured from Loba Chemie Pvt. Ltd., India, and used without any purification. Detailed information of the chemicals used for the experimental work is given in Table S1 in Supplementary Data. All the chemicals were dried under vacuum for 24 h at 373.15 K over anhydrous $CaCl_2$ before use. Deionised, doubly distilled and degassed water was used for the preparation of experimental solutions. The specific conductance of water used for the preparation of solutions was $<1.3\times10^{-6}$ S cm^{-1}. Conductance of water was checked by using SYSTRONICS conductivity meter-306, India with cell constant 0.12 cm^{-1}. Accuracy and precision in the measurement of conductance of water is found to be ±1% and ±2%, respectively.

All ternary solutions (*i.e.* glycine + water or glycine+aqueous NaAcB) were prepared on molality basis. Weighing was done on electronic digital balance METTLER TOLEDO ME204, India precised upto ±0.1 mg. The standard uncertainty in molality, $u(m)$ for the studied system lies between $\pm2\times10^{-4}\,mol\,kg^{-1}$. pH of the prepared solutions was checked by using SYSTRONICS digital pH meter-335, India with repeatability and accuracy of ±0.01 and ±0.02, respectively. pH meter was calibrated with standardized buffer solutions (*i.e.* pH 7.00 and pH 9.20). Further, pH 1.00 and pH 12.40 were attained by using equimolar concentrations of hydrochloric acid (HCl) and sodium hydroxide (NaOH), respectively. pH 14.00 was not attained, thus the present work has been carried out at 12.40.

Densities, ρ of the studied system were measured by using a vibrating tube digital density meter (DMA 4500M, Anton Paar, Austria) at T(K) = (298.15-318.15) with the interval of 10 K including physiological temperature (*i.e.* 310.15 K). Density meter was calibrated by measuring the densities of double distilled water and dry air at 298.15 K. After calibration, the performance of density meter was checked by measuring the densities of aqueous NaCl solutions, which agree well with the literature values[12]. Comparative plots of experimental densities of NaCl with literature values[13] are given as Fig. S1, Supplementary Data. Reproducibility and precision in triplicate density measurements were found to be ±4× 10^{-5} g cm^{-3} and ±2× 10^{-5} g cm^{-3}, respectively. Density meter has built in thermostat to maintain the desired temperature within ±0.03 K over the temperature range, T(K) = (273.15-363.15).

Viscosity, η measurements of the studied system have been carried out at T(K) = (298.15-318.15) with the interval of 10 K including physiological temperature *i.e.* 310.15 K, by using Ubbelhode type viscometer with flow time of nearly 300 s for water at T(K) = 298.15. The viscometer was calibrated with deionised, double distilled and degassed water. Flow time of the experimental solutions was measured with RACER digital stopwatch with the resolution of ±0.01 s. Average of at least four flow time readings were taken for further calculations. Viscometer containing the experimental solution was allowed to stand for 20 min to minimize the thermal variations in viscobath (SISKIN PROFICHILL, India) having accuracy of ±0.01 K. The measured viscosities were accurate to ±1%. The uncertainties calculated from triplicate measurements were ±0.3%.

Results and Discussion

Volumetric properties

Apparent molar volumes, ϕ_v of glycine in (0.10, 0.50 and 1.00) $mol\cdot kg^{-1}$ aqueous NaAcB solutions of pH (1.00 and 12.40) have been obtained from experimental measured densities at different temperatures, T(K) = (298.15-318.15) by using the following equation:

$$\phi_v = \frac{M}{\rho}\left[\frac{1000(\rho-\rho_0)}{m\rho\rho_0}\right] \qquad\qquad \dots (1)$$

where M (g mol^{-1}) and m (mol kg^{-1}) is the molecular mass and molalities of glycine, ρ_o (g cm^{-3}) and ρ (g cm^{-3}) are the densities of solvent (water or aqueous

NaAcB) and solution (water/ aqueous NaAcB + glycine), respectively. The ρ, ρ_o and ϕ_v values of glycine in water and in (0.10, 0.50 and 1.00) mol kg^{-1} aqueous NaAcB solutions of pH (1.00 and 12.40) are given in Tables 1 and S2, Supplementary Data. Standard uncertainty in apparent molar volume, $u\,(\phi_v)$ is ± 0.10 cm^3 mol^{-1}. Strong solute-solvent interactions are represented by positive ϕ_v values whereas delicate solute-solvent interactions are represented by negative ϕ_v values. Presently, positive ϕ_v values obtained for glycine in water and in aqueous NaAcB solutions of different pH may attribute due to the presence of strong solute-solvent interactions among NH_4^+ and COO^- groups of glycine and ions of NaAcB $(CH_3COO^-, Na^+, H^+, Cl^-)$ at different pH values. Further, these solute-solvent interactions result into formation of hydrogen bonds in the present system and ϕ_v values increase with increase in concentration of co-solute (*i.e.* NaAcB) at different pH values. Representative plots of ϕ_v versus m of glycine in aqueous NaAcB solutions at studied pH (1.00 and 12.40) and at T(K) = 310.15 are illustrated in Figs. S2 and S3, Supplementary Data. It

can be seen from these figures that ϕ_v values decrease with increase in the concentration of glycine. Decrease in ϕ_v values at extreme pH values may attribute due to the presence of common ions in these solutions (presence of H^+ ions in acetate buffer as well as in HCl used to attain pH 1.00 and also presence of Na^+ both in acetate buffer as well as in NaOH to attain pH 12.40), which may lead to repulsion among the ions accompanied by conformational changes that does not allow the formation of hydrogen bonds between the ions.

Apparent molar volume, ϕ_v at infinite dilution becomes equal to limiting partial molar volume, ϕ_v^o. The ϕ_v^o values reflect the exact volume of the solute and volume change arising from solute-solvent interactions. The ϕ_v^o values have been determined by using least square fit of the following equation to the corresponding ϕ_v data and are summarized in Table 1:

$$\phi_v = \phi_v^0 + S_v m \qquad \qquad \dots (2)$$

$$\phi_v = \phi_v^0 + \alpha m + \beta m^2 \qquad \dots (3)$$

where ϕ_v^o (cm^3 mol^{-1}) is the partial molar volume, S_v is the experimental slope, α and β are the fitting

Table 1 — Densities, ρ, and apparent molar volumes, ϕ_v, of glycine in (0.10, 0.50 and 1.00) mol kg^{-1} aqueous sodium acetate buffer (NaAcB) solutions of pH (1.00 and 12.40) at different temperatures, T(K) = (298.15 to 318.15).

m (mol · kg^{-1})	ρ (g · cm^{-3})	ϕ_v (cm^3· mol^{-1})	ρ (g · cm^{-3})	ϕ_v (cm^3· mol^{-1})	ρ (g · cm^{-3})	ϕ_v (cm^3· mol^{-1})	ρ (g · cm^{-3})	ϕ_v (cm^3· mol^{-1})
	T(K) = 298.15		T(K)= 308.15		T(K)= 310.15		T(K) = 318.15	
			Glycine in 0.10 mol · kg^{-1}NaAcB of pH 1.00					
0.0000	1.00284		0.99970		0.99897		0.99580	
0.0981	1.00581	44.63	1.00262	45.18	1.00188	45.30	0.99867	45.76
0.2035	1.00906	44.20	1.00582	44.73	1.00507	44.84	1.00184	45.19
0.2976	1.01201	43.82	1.00874	44.30	1.00798	44.41	1.00473	44.73
0.3954	1.01514	43.40	1.01182	43.89	1.01106	43.98	1.00779	44.28
0.4937	1.01834	42.97	1.01497	43.48	1.01421	43.55	1.01092	43.83
0.6121	1.02216	42.65	1.01875	43.13	1.01797	43.22	1.01466	43.49
0.7026	1.02523	42.23	1.02178	42.71	1.02100	42.79	1.01767	43.05
0.7801	1.02795	41.81	1.02447	42.28	1.02368	42.36	1.02033	42.63
0.8921	1.03165	41.55	1.02813	42.01	1.02733	42.09	1.02396	42.35
0.9890	1.03514	41.06	1.03158	41.52	1.03078	41.59	1.02740	41.84
			Glycine in 0.10 mol · kg^{-1}NaAcB of pH 12.40					
0.0000	1.00701		1.00382		1.00310		0.99989	
0.0851	1.00775	65.93	1.00456	66.11	1.00383	66.27	1.00062	66.45
0.1991	1.00962	61.46	1.00642	61.67	1.00568	61.80	1.00245	62.06
0.3070	1.01285	55.47	1.00959	55.81	1.00885	55.90	1.00560	56.15
0.3986	1.01563	52.77	1.01233	53.15	1.01158	53.24	1.00831	53.50
0.4991	1.01860	51.06	1.01526	51.45	1.01450	51.55	1.01121	51.80
0.6005	1.02159	49.88	1.01820	50.30	1.01744	50.38	1.01413	50.64
0.6960	1.02434	49.15	1.02091	49.57	1.02015	49.65	1.01682	49.90
0.7962	1.02719	48.58	1.02373	49.00	1.02295	49.09	1.01960	49.34
0.8845	1.02969	48.18	1.02619	48.60	1.02541	48.69	1.02204	48.95
0.9986	1.03280	47.85	1.02930	48.24	1.02847	48.37	1.02508	48.62

(*Contd.*)

Table 1 — Densities, ρ, and apparent molar volumes, ϕ_v, of glycine in (0.10, 0.50 and 1.00) mol $\cdot$ kg^{-1} aqueous sodium acetate buffer (NaAcB) solutions of pH (1.00 and 12.40) at different temperatures, T(K) = (298.15 to 318.15) (*Contd.*)

m (mol $\cdot$ kg^{-1})	ρ (g $\cdot$ cm^{-3})	ϕ_v (cm$^3\cdot$ mol^{-1})	ρ (g $\cdot$ cm^{-3})	ϕ_v (cm$^3\cdot$ mol^{-1})	ρ (g $\cdot$ cm^{-3})	ϕ_v (cm$^3\cdot$ mol^{-1})	ρ (g $\cdot$ cm^{-3})	ϕ_v (cm$^3\cdot$ mol^{-1})
	T(K) = 298.15		T(K)= 308.15		T(K)= 310.15		T(K) = 318.15	
Glycine in 0.50 mol $\cdot$ kg^{-1}NaAcB of pH 1.00								
0.0000	1.01232		1.00891		1.00813		1.00479	
0.2939	1.02079	45.65	1.01726	46.11	1.01646	46.19	1.01305	46.49
0.3965	1.02382	45.34	1.02023	45.84	1.01943	45.91	1.01600	46.19
0.4878	1.02649	45.18	1.02287	45.66	1.02206	45.73	1.01862	45.99
0.6067	1.02992	45.07	1.02626	45.53	1.02545	45.59	1.02199	45.85
0.7141	1.03299	44.99	1.02930	45.44	1.02847	45.52	1.02500	45.76
0.7843	1.03494	45.01	1.03123	45.44	1.03040	45.52	1.02691	45.77
0.9099	1.03838	45.05	1.03462	45.49	1.03378	45.57	1.03028	45.80
Glycine in 0.50 mol $\cdot$ kg^{-1}NaAcB of pH 12.40								
0.0000	1.02621		1.02271		1.02193		1.01854	
0.2043	1.02762	66.51	1.02411	66.76	1.02333	66.81	1.01994	67.01
0.3960	1.03091	61.60	1.02735	61.92	1.02656	61.98	1.02318	62.13
0.4922	1.03361	58.45	1.03002	58.78	1.02922	58.86	1.02580	59.06
0.6016	1.03685	55.78	1.03322	56.12	1.03242	56.19	1.02898	56.40
0.6956	1.03924	54.67	1.03558	55.02	1.03478	55.08	1.03132	55.30
0.7962	1.04207	53.41	1.03837	53.77	1.03756	53.84	1.03410	54.04
0.8895	1.04460	52.58	1.04087	52.94	1.04006	53.00	1.03657	53.22
0.9963	1.04745	51.84	1.04369	52.20	1.04287	52.26	1.03937	52.48
Glycine in 1.00 mol $\cdot$ kg^{-1}NaAcB of pH 1.00								
0.0000	1.01917		1.01559		1.01479		1.01133	
0.2002	1.02463	47.15	1.02097	47.61	1.02016	47.67	1.01666	47.94
0.2971	1.02749	46.32	1.02380	46.75	1.02298	46.83	1.01946	47.09
0.4005	1.03051	45.89	1.02678	46.32	1.02596	46.38	1.02242	46.65
0.5803	1.03571	45.48	1.03192	45.90	1.03109	45.96	1.02756	46.14
0.6961	1.03897	45.39	1.03514	45.81	1.03430	45.88	1.03073	46.10
0.8133	1.04217	45.41	1.03831	45.81	1.03747	45.87	1.03387	46.11
0.9052	1.04469	45.38	1.04080	45.78	1.03995	45.85	1.03634	46.08
1.0095	1.04743	45.45	1.04351	45.84	1.04266	45.91	1.03903	46.14
Glycine in 1.00 mol $\cdot$ kg^{-1}NaAcB of pH 12.40								
0.0000	1.04476		1.04091		1.04007		1.03651	
0.1064	1.04412	77.41	1.04027	77.72	1.03943	77.79	1.03587	78.07
0.2020	1.04371	76.69	1.03986	77.00	1.03902	77.06	1.03525	78.33
0.2874	1.04380	74.98	1.03995	75.27	1.03910	75.37	1.03554	75.64
0.4015	1.04437	72.77	1.04051	73.07	1.03966	73.15	1.03611	73.38
0.5103	1.04535	70.75	1.04151	70.99	1.04067	71.05	1.03711	71.29
0.6019	1.04678	68.65	1.04294	68.87	1.04210	68.93	1.03854	69.15
0.6988	1.04766	67.86	1.04383	68.07	1.04299	68.12	1.03943	68.34
0.8005	1.04968	65.91	1.04577	66.21	1.04491	66.28	1.04136	66.48
0.9059	1.05118	64.96	1.04730	65.21	1.04636	65.36	1.04277	65.60
0.9953	1.05423	62.57	1.05029	62.86	1.04944	62.91	1.04582	63.15

m (mol $\cdot$ kg^{-1})is the molality of solute (glycine) in aqueous NaAcB solutions; Standard uncertainty in $u(m)$ = (0.03-0.41) mol $\cdot$ kg^{-1}; $u(\phi_v)$ = (0.33-0.76) cm$^3\cdot$ mol^{-1}; $u(p)$ = 0.05 MPa

parameters and m (mol kg^{-1}) is the molality of solution. At extreme pH conditions (*i.e.* at pH 1.00 and pH 12.40) of aqueous NaAcB solutions for glycine second order polynomial was used to fit the data (Eqn 3) except for glycine in 0.10 mol kg^{-1} NaAcB of pH 1.00, where Eqn (2) is used. At infinite dilution, the aqueous NaAcB molecules surrounding glycine ion shows the presence of strong solute-solvent interactions. From Table 2, it can be evident that ϕ_v^0 values for glycine in water and in aqueous NaAcB follow the order: pH 1.00 > pH 12.40. The observed behaviour of glycine in water and in aqueous NaAcB solutions of different pH can be attributed due to alteration in pH which may change the (i) possibility of forming hydrogen bonds, (ii) modification of the binding properties of glycine and

Table 2 — Limiting partial molar volumes, ϕ_v^o, of glycine in water and in (0.10, 0.50 and 1.00) mol $\cdot$ kg^{-1} aqueous NaAcB solutions of pH (1.00 and 12.40) and at different temperatures, T(K) = (298.15 to 318.15)

T(K) ↓	pH→ 1.00					12.40				
	ϕ_v^o (cm$^3\cdot$mol^{-1})	R^2	α	β	SD	ϕ_v^o (cm$^3\cdot$mol^{-1})	R^2	α	β	SD
					Glycine in water					
298.15	50.36±0.01	0.99	-1.06±0.02	-	0.02	67.32±0.32	0.99	-14.50±0.52	-	0.46
308.15	50.56±0.02	0.99	-1.07±0.03	-	0.02	67.52±0.31	0.99	-14.36±0.51	-	0.45
310.15	50.69±0.02	0.99	-1.11±0.03	-	0.02	67.64±0.32	0.99	-14.41±0.51	-	0.46
318.15	50.85±0.02	0.99	-0.97±0.03	-	0.02	67.82±0.25	0.99	-14.42±0.41	-	0.36
				Glycine in 0.10 mol $\cdot$ kg^{-1} NaAcB						
298.15	45.00±0.04	0.99	-3.96±0.07		0.06	69.92±0.98	0.98	-53.21±4.13	32.03±3.70	0.87
308.15	45.53±0.04	0.99	-4.05±0.07		0.06	70.01±0.97	0.98	-52.29±4.06	31.41±3.64	0.86
310.15	45.65±0.05	0.99	-4.10±0.08		0.07	70.19±0.97	0.98	-52.64±4.06	31.69±3.64	0.86
318.15	46.05±0.06	0.99	-4.28±0.10		0.09	70.38±0.96	0.98	-52.42±4.05	31.52±3.63	0.85
				Glycine in 0.50 mol $\cdot$ kg^{-1} NaAcB						
298.15	46.71±0.09	0.99	-4.61±0.34	3.07±0.28	0.03	74.47±0.80	0.99	-41.78±2.87	19.15±2.32	0.39
308.15	47.18±0.04	0.99	-4.53±0.14	2.94±0.12	0.01	74.65±0.82	0.99	-41.36±2.91	18.91±2.35	0.40
310.15	47.29±0.04	0.99	-4.66±0.13	3.06±0.11	0.01	74.68±0.81	0.99	-41.23±2.89	18.81±2.33	0.40
318.15	47.64±0.06	0.99	-4.90±0.22	3.17±0.18	0.02	74.87±0.77	0.99	-41.23±2.76	18.85±2.23	0.38
				Glycine in 1.00 mol $\cdot$ kg^{-1} NaAcB						
298.15	48.35±0.26	0.97	-7.86±0.99	5.03±0.81	0.14	79.55±0.31	0.99	-16.87±0.50		0.45
308.15	48.82±0.27	0.97	-7.96±1.03	5.05±0.84	0.14	79.85±0.32	0.99	-16.92±0.51		0.46
310.15	48.90±0.26	0.97	-7.99±1.00	5.08±0.82	0.14	79.92±0.33	0.99	-16.91±0.53		0.48
318.15	49.23±0.26	0.97	-8.32±0.99	5.31±0.82	0.14	80.52±0.47	0.99	-17.39±0.76		0.69

R^2 = Regression coefficient; α and β = fitting parameters; SD= standard deviation; ± are the respective errors

ions of NaAcB and (iii) alteration of hydration behaviour of protein due to difference between the hydration states of charged glycine in aqueous NaAcB solution of pH (1.00 and 12.40). Further, ϕ_v^o values of glycine in water and in aqueous NaAcB increase with increase with temperature at studied pH values. This increase in ϕ_v^o values with temperature may be due to the fact that heat energy of the solvent molecule increase, causes fast movement of the bulk electrostricted solvent molecules from loose solvation layer of the charged glycine in these systems[14]. The obtained trend of ϕ_v^o values for the present system also specifies that the solvation behaviour of glycine in NaAcB is pH, concentration and temperature dependent.

Limiting partial molar volumes of transfer, $\Delta_{tr}\phi_v$ of glycine from water to aqueous NaAcB solutions have been calculated by using the following equation and are summarized in Table S3:

$$\Delta_{tr}\phi_v(water \rightarrow aqueous\ NaAcB\ solutions) = \phi_v^0(in\ aqueous\ NaAcB\ solutions) - \phi_v^0(in\ water)$$

… (4)

The representative plots of $\Delta_{tr}\phi_v$ values for the studied system of different pH values have been given in Fig. 1 (only at T(K) = 310.15). Both positive and
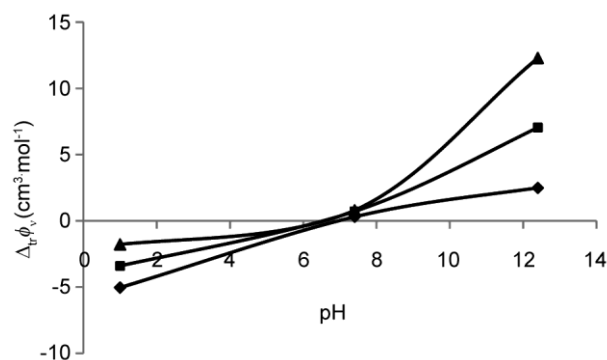

Fig. 1 — Representative plots of limiting partial molar volume of transfer, $\Delta_{tr}\phi_v$ for glycine versus pH in (♦0.10, ■0.50, ▲ 1.00) mol $\cdot$ kg^{-1} aqueous NaAcB solutions at T(K) = 310.15

negative $\Delta_{tr}\phi_v$ values have been observed for glycine in aqueous NaAcB solutions. At pH 1.00, the $\Delta_{tr}\phi_v$ values are negative for glycine whereas at pH 12.40, positive $\Delta_{tr}\phi_v$ values have been observed in aqueous NaAcB solutions at all temperatures studied.

In accordance to co-sphere overlap model[15,16], the overlap of co-sphere of two polar ions or with that of hydrophilic group always result into positive $\Delta_{tr}\phi_v$ values. On the other hand, overlap of two non-polar ions or with that of hydrophilic group results into negative $\Delta_{tr}\phi_v$ values. Following type

of interactions may be probable in ternary system: (a) ion-dipolar interactions among zwitterionic centres of glycine (NH_4^+ and COO^-) and ions of NaAcB (CH_3COO^-, Na^+, H^+, Cl^-); (b) ion-hydrophobic interactions among ions of NaAcB and non polar part of glycine (hydrocarbon part); (c) hydrophobic-hydrophobic interactions among non polar groups of glycine and non polar groups of NaAcB. Positive $\Delta_{tr}\phi_v$ values indicate the dominance of type (a) interactions whereas negative $\Delta_{tr}\phi_v$ values indicate the dominance of type (b) and type (c) interactions. In present system, negative $\Delta_{tr}\phi_v$ values at pH 1.00 for glycine indicate the dominance of type (b) and type (c) interactions and positive $\Delta_{tr}\phi_v$ values at pH 12.40, for indicate the dominance of type (a) interactions. The obtained $\Delta_{tr}\phi_v$ values further strengthen the point that solvation behaviour of glycine in these systems is pH, concentration and temperature dependent.

The magnitude of ϕ_v^0 values of glycine in NaAcB can be explained by considering the modified equation of Shahidi and Farell[17] as:

$$\phi_v^0 = V_{v,w} + V_{void} - V_{shrinkage} \qquad \ldots (5)$$

where $V_{v,w}$ is the van der Waals volume, V_{void} is the volume associated with voids and $V_{shrinkage}$ is the volume owed to shrinkage that arises from electrostriction of solvent molecules caused by hydrophilic groups present in solute. It is assumed that $V_{v,w}$ and V_{void} are not significantly affected by the presence of aqueous NaAcB solutions. So, negative $\Delta_{tr}\phi_v$ values can be ascribed due to enhancement in $V_{shrinkage}$ i.e. electrostriction of neighbouring solvent molecules due to these charged

centres will be increased, whereas positive $\Delta_{tr}\phi_v$ can be ascribed owing to decrease in volume owed to shrinkage, resulting from the stronger interactions occurring in these systems. No regular trend has been observed for $\Delta_{tr}\phi_v$ values for glycine in aqueous NaAcB solutions of pH (1.00 and 12.40). This may be due to increased thermal disturbance and deteriorating of interactions that result into electrostriction of solvent molecules from mutually interacting ions.

Volumetric pair and triplet interaction coefficients, V_{AB} and V_{ABB}, respectively, have been calculated by using McMillan Mayer theory of solutions[18] in order to study different types of solute-solute and solute-solvent interactions in these systems. According to this theory $\Delta_{tr}\phi_v$ values can be represented as:

$$\Delta_{tr}\phi_v = 2V_{AB}m + 3V_{ABB}m^2 \qquad \ldots (6)$$

where A denotes glycine, B denotes aqueous NaAcB solutions and m (mol kg^{-1}) is the molality of co-solute (i.e. NaAcB solutions). V_{AB} and V_{ABB} are volumetric pair and triplet interaction coefficients, respectively. The values of V_{AB} and V_{ABB} of glycine in aqueous NaAcB solutions at studied pH values and at different temperatures are reported in Table 3. In case of glycine in aqueous NaAcB of pH (1.00 and 12.40), V_{AB} values are positive whereas V_{ABB} values are found to be negative at all temperatures studied. The higher magnitude of V_{AB} values over V_{ABB} values indicates that interactions between glycine and NaAcB solutions are mainly pairwise. Overall, the positive values of volumetric pair interaction coefficients suggest that interactions between glycine and NaAcB solutions are strong and further support the conclusion drawn from co-sphere overlap model.

Table 3 — Pair, V_{AB} and Triplet, V_{ABB} interaction coefficients for glycine in (0.10, 0.50 and 1.00) mol · kg^{-1} NaAcB solutions of pH (1.00 and 12.40) at different temperatures, T (K) = (298.15 to 318.15)

T (K) ↓	pH→ 1.00		12.40		pH→ 1.00		12.40	
	V_{AB} (cm^3·mol^{-2}·kg)	V_{ABB} (cm^3·mol^{-2}·kg^2)	V_{AB} (cm^3·mol^{-2}·kg)	V_{ABB} (cm^3·mol^{-2}·kg^2)	η_{AB} (dm^3·mol^{-2}·kg)	η_{ABB} (dm^3·mol^{-3}·kg^2)	η_{AB} (dm^3·mol^{-2}·kg)	η_{ABB} (dm^3·mol^{-3}·kg^2)
Glycine								
298.15	2.44	-0.37	6.00	-0.52	0.030	0.058	-0.054	-0.099
308.15	2.33	-0.32	6.12	-0.52	0.045	0.073	-0.080	-0.124
310.15	2.33	-0.33	5.80	-0.37	0.047	0.071	-0.084	-0.120
318.15	2.24	-0.30	5.57	-0.10	0.055	0.077	-0.088	-0.120

To study the temperature dependence of ϕ_v^o, partial molal expansibilities, $(\partial\phi_v^o/\partial T)_P$ and their second order derivative, $(\partial^2\phi_v^o/\partial T^2)_P$ have been expressed by using the following equation:

$$\phi_v^0 = a + bT + cT^2 \qquad \ldots (7)$$

where $\phi_v^o\,(\text{cm}^3\cdot\text{mol}^{-1})$ is the limiting partial molar volume, (a, b and c) are constants and T(K) is the absolute temperature. The $(\partial\phi_v^o/\partial T)_P$ and $(\partial^2\phi_v^o/\partial T^2)_P$ values are summarized in Table 4. At pH 1.00, in case of glycine, $(\partial\phi_v^o/\partial T)_P$ value decreases in (0.10 and 1.00) mol·kg⁻¹ NaAcB whereas increases in water and 0.50 mol kg⁻¹ aqueous NaAcB. At pH 12.40, $(\partial\phi_v^o/\partial T)_P$ values for glycine almost increase with increase in temperature. As recommended by Hepler[19] a thermodynamic relation by whom qualitative information concerning hydration of solute could be assessed from heat expansion is as per the following:

$$(\partial C_P^0/\partial P)_T = -T(\partial^2\phi_v^0/\partial T^2)_P\ldots \qquad \ldots (8)$$

where $C_P^o\,(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ is the partial molar heat capacity. According to Eqn. (8)[19], the structure breaking solute should have negative $(\partial^2\phi_v^o/\partial T^2)_P$ values, whereas structure making solute have positive $(\partial^2\phi_v^o/\partial T^2)_P$ values. It can be easily seen from Table 4 that at pH (1.00 and 12.40), glycine act as structure maker in water and in (0.50 and 1.00) mol·kg⁻¹NaAcB whereas in 0.10 mol·kg⁻¹NaAcB glycine acts as structure breaker. The obtained results further reflect major difference in the nature of solvation behaviour of these solutes in aqueous NaAcB solutions at different pH values and all temperatures studied.

Viscometric studies

Viscosities, η of glycine in (0.10, 0.50 and 1.00) mol kg⁻¹ aqueous NaAcB solutions of pH (1.00 and 12.40) at different temperatures, T(K) = (298.15-318.15) with the interval of 10 K, including physiological temperature i.e. 310.15 K by using the following equation and are summarized in Table 5:

$$\eta = \left(at - \frac{b}{t}\right)\rho \times 100 \qquad \ldots (9)$$

where a and b are the viscometric constants ($a = 0.00002873\ \text{mPa m}^3\ \text{kg}^{-1}$ and $b = 0.0075959\ \text{mPa s}^2\ \text{m}^3\ \text{kg}^{-1}$), t (s) is the flow time, $\rho\,(\text{g cm}^{-3})$ is the density. Relative viscosities, η_r [$(\eta_r = \eta/\eta_o)$ where η (mPa s) and η_o (mPa s) are the viscosities of solution and solvent, respectively, and are presented as Table 5. η_r values vary linearly as the concentration of glycine in water and in aqueous NaAcB increases (Table 5) and follow the order as pH 12.40>pH 1.00 which may be due to the destruction of solvent structure due to the interaction of zwitterions of glycine with the anions of NaAcB solutions.

The viscosity B-coefficients provide information regarding solute-solute interactions and also the degree of solvent structuring introduced by ions. The calculated values of viscosity B-coefficient of glycine in different concentrations of aqueous NaAcB solutions of different pH at different temperatures have been summarized in Table 6 and follow the order as pH 1.00> pH 12.40. The high values of viscosity B-coefficient for the studied system at pH 1.00, may attribute due to weak repulsions among these systems which led to the formation of hydrogen bonds. With the increase in pH values i.e.

Table 4 — Partial molar expansion coefficients, $(\partial\phi_v^o/\partial T)_P$ and $(\partial^2\phi_v^o/\partial T^2)_P$ of glycine in water and in (0.10, 0.50 and 1.00) mol·kg⁻¹aqueous NaAcB of pH (1.00 and 12.40) at different temperatures, T(K) = (298.15 to 318.15)

pH ↓	$(\partial\phi_v^o/\partial T)_P$ (cm³·mol⁻¹·K⁻¹)				$(\partial^2\phi_v^o/\partial T^2)_P$ (cm³·mol⁻¹·K⁻²)
	T(K) =298.15	T(K) =308.15	T(K) =310.15	T(K) =318.15	
			Glycine in water		
1.00	0.0213	0.0219	0.0225	0.0232	0.0001
12.40	0.0243	0.0250	0.0256	0.0262	0.0001
		Glycine in 0.10 mol·kg⁻¹NaAcB			
1.00	0.063	0.058	0.052	0.047	-0.0011
12.40	-0.415	-0.418	-0.422	-0.426	-0.0007
		Glycine in 0.50 mol·kg⁻¹NaAcB			
1.00	0.045	0.057	0.068	0.080	0.0023
12.40	0.019	0.020	0.021	0.022	0.0002
		Glycine in 1.00 mol·kg⁻¹NaAcB			
1.00	0.055	0.050	0.045	0.040	0.0009
12.40	0.024	0.034	0.044	0.054	0.0020

Table 5 — Relative viscosities, η_r of glycine in water and in (0.10, 0.50 and 1.00) mol $\cdot$ kg^{-1} aqueous NaAcB solutions of pH (1.00 and 12.40) at T(K)= (298.15 to 318.15)

c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r
Glycine in water of pH 1.00							
T(K)= 298.15		T(K) = 308.15		T(K) = 310.15		T(K) = 318.15	
η_o= 0.8964		η_o=0.7245		η_o=0.6968		η_o=0.6009	
0.0975	1.0107	0.9720	1.0133	0.0972	1.0140	0.0969	1.0157
0.2000	1.0220	0.1994	1.0244	0.1994	1.0252	0.1988	1.0282
0.2975	1.0325	0.2966	1.0350	0.2966	1.0358	0.2957	1.0395
0.3905	1.0445	0.3893	1.0471	0.3893	1.0482	0.3882	1.0505
0.4848	1.0535	0.4833	1.0556	0.4833	1.0565	0.4819	1.0607
0.5785	1.0656	0.5768	1.0673	0.5768	1.0679	0.5751	1.0710
0.6761	1.0765	0.6741	1.0779	0.6741	1.0785	0.6721	1.0856
0.7766	1.0884	0.7743	1.0911	0.7743	1.0916	0.7720	1.0962
0.8546	1.0981	0.8521	1.1002	0.8521	1.1009	0.8496	1.1087
0.9486	1.1094	0.9458	1.1118	0.9458	1.1121	0.9430	1.1226
Glycine in water of pH 12.40							
η_o=0.9071		η_o=0.7329		η_o=0.7093		η_o=0.6075	
0.1042	1.0100	0.1039	1.0072	0.1038	1.0070	0.1035	1.0064
0.2006	1.0201	0.1999	1.0186	0.1997	1.0173	0.1991	1.0162
0.2976	1.0275	0.2966	1.0308	0.2963	1.0299	0.2954	1.0280
0.3989	1.0408	0.3976	1.0387	0.3972	1.0381	0.3960	1.0397
0.4942	1.0522	0.4925	1.0502	0.4920	1.0498	0.4906	1.0477
0.5891	1.0634	0.5871	1.0617	0.5865	1.0611	0.5848	1.0557
0.6782	1.0757	0.6757	1.0738	0.6751	1.0733	0.6731	1.0685
0.7736	1.0847	0.7707	1.0842	0.7699	1.0835	0.7677	1.0803
0.8686	1.0989	0.8653	1.0956	0.8644	1.0945	0.8619	1.0886
0.9569	1.1068	0.9531	1.1069	0.9522	1.1062	0.9494	1.1021
Glycine in 0.10 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 1.00							
η_o=0.9039		η_o= 0.7335		η_o=0.7035		η_o= 0.6066	
0.1017	1.0114	0.1014	1.0122	0.1013	1.0128	0.1010	1.0153
0.1997	1.0249	0.1991	1.0273	0.1989	1.0278	0.1983	1.0313
0.2962	1.0330	0.2953	1.0379	0.2950	1.0385	0.2942	1.0406
0.3938	1.0475	0.3927	1.0477	0.3923	1.0491	0.3911	1.0508
0.5872	1.0717	0.5855	1.0774	0.5849	1.0785	0.5832	1.0807
0.7782	1.0987	0.7759	1.1029	0.7752	1.1068	0.7729	1.1119
0.8712	1.1094	0.8687	1.1159	0.8678	1.184	0.8653	1.1244
0.9615	1.1200	0.9588	1.1247	0.9578	1.1262	0.9550	1.1366
Glycine in 0.10 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 12.40							
η_o=0.9307		η_o=0.7525		η_o=0.7215		η_o=0.6232	
0.1036	1.0072	0.1033	1.0112	0.1032	1.0090	0.1029	1.0138
0.2022	1.0163	0.2016	1.0190	0.2013	1.0196	0.2007	1.0246
0.2974	1.0268	0.2966	1.0295	0.2962	1.0304	0.2953	1.0358
0.3940	1.0374	0.3928	1.0400	0.3922	1.0422	0.3911	1.0469
0.4876	1.0498	0.4861	1.0521	0.4854	1.0524	0.4840	1.0582
0.5893	1.0623	0.5876	1.0641	0.5867	1.0645	0.5849	1.0694
0.6771	1.0712	0.6751	1.0779	0.6740	1.0785	0.6720	1.0832
0.7740	1.0833	0.7717	1.0917	0.7704	1.0913	0.7681	1.0922
0.8647	1.0952	0.8622	1.1009	0.8606	1.0992	0.8581	1.1064
0.9609	1.1044	0.9581	1.1090	0.9562	1.1150	0.9534	1.1209
Glycine in 0.50 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 1.00							
η_o=0.9649		η_o=0.7836		η_o=0.7537		η_o=0.6499	
0.1141	1.0210	0.1045	1.0215	0.1044	1.0212	0.1040	1.0270
0.2212	1.0371	0.2028	1.0374	0.2026	1.0381	0.2018	1.0271

(*Contd.*)

Table 5 — Relative viscosities, η_r of glycine in water and in (0.10, 0.50 and 1.00) mol $\cdot$ kg^{-1}aqueous NaAcB solutions of pH (1.00 and 12.40) at T(K)= (298.15 to 318.15) (*Contd.*)

c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r	c (mol$\cdot$ dm^{-3})	η_r
Glycine in 0.50 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 1.00							
η_o=0.9649		η_o=0.7836		η_o=0.7537		η_o=0.6499	
0.4348	1.0652	0.3987	1.0656	0.3983	1.0664	0.3968	1.0713
0.6425	1.0911	0.5895	1.0915	0.5890	1.0923	0.5867	1.0962
0.8461	1.1125	0.7767	1.1131	0.7759	1.1132	0.7729	1.1162
0.9423	1.1294	0.8651	1.1309	0.8643	1.1310	0.8610	1.1387
1.0416	1.1400	0.9566	1.1432	0.9557	1.1443	0.9520	1.1478
Glycine in 0.50 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 12.40							
η_o=1.0575		η_o=0.8484		η_o=0.8144		η_o=0.6979	
0.1039	1.0100	0.1035	1.0100	0.1034	1.0119	0.1031	1.0152
0.2010	1.0184	0.2002	1.0204	0.2000	1.0184	0.1994	1.0227
0.3967	1.0404	0.3952	1.0459	0.3948	1.0420	0.3935	1.0502
0.5888	1.0660	0.5865	1.0692	0.5859	1.0684	0.5839	1.0707
0.7863	1.0892	0.7833	1.0928	0.7825	1.0946	0.7796	1.0965
0.9642	1.1169	0.9605	1.1183	0.9596	1.1171	0.9560	1.1224
Glycine in 1.00 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 1.00							
η_o=1.0460		η_o=0.8459		η_o=0.8128		η_o=0.7053	
0.1963	1.0324	0.1955	1.0349	0.1953	1.0350	0.1947	1.0384
0.3981	1.0549	0.3964	1.0598	0.3961	1.0602	0.3949	1.0625
0.5014	1.0725	0.4992	1.0786	0.4987	1.0792	0.4972	1.0840
0.6823	1.0994	0.6792	1.1140	0.6786	1.1147	0.6766	1.1161
0.7903	1.1182	0.7867	1.1259	0.7859	1.1265	0.7836	1.1324
0.8745	1.1332	0.8704	1.1382	0.8696	1.1383	0.8670	1.1455
0.9704	1.1459	0.9658	1.1492	0.9649	1.1497	0.9621	1.1566
Glycine in 1.00 mol $\cdot$ kg^{-1} aqueous NaAcB of pH 12.40							
η_o=1.1834		η_o=0.9543		η_o=0.9155		η_o=0.7834	
0.1042	1.0119	0.1043	1.0131	0.1037	1.0137	0.1032	1.0150
0.2069	1.0221	0.2072	1.0281	0.2059	1.0292	0.2050	1.0333
0.4010	1.0505	0.4018	1.0563	0.3992	1.0565	0.3976	1.0619
0.6045	1.0821	0.6061	1.0898	0.6020	1.0903	0.5998	1.0928
0.7918	1.1095	0.7943	1.1168	0.7886	1.1143	0.7860	1.1242
0.6969	1.1019	0.6990	1.1095	0.6941	1.1103	0.6917	1.1153
0.8873	1.1291	0.8905	1.1319	0.8839	1.1324	0.8812	1.1438
0.9751	1.1466	0.9788	1.1511	0.9713	1.1513	0.9686	1.1620

Table 6 — Viscosity B-coefficient of glycine in water and in (0.10, 0.50 and 1.00) mol $\cdot$ kg^{-1}aqueous NaAcB solutions of pH (1.00 and 12.40) at different temperatures, T(K)= (298.15 to 318.15)

pH ↓	B-coefficient (dm$^3\cdot$ mol^{-1})			
	T(K) = 298.15	T(K) = 308.15	T(K) = 310.15	T(K) = 318.15
Glycine in water				
1.00	0.113±0.002	0.117±0.004	0.118±0.004	0.127±0.006
12.40	0.110±0.004	0.108±0.006	0.107±0.006	0.102±0.007
Glycine in 0.10 mol $\cdot$ kg^{-1} NaAcB				
1.00	0.124±0.006	0.131±0.007	0.134±0.007	0.142±0.007
12.40	0.106±0.005	0.113±0.005	0.115±0.004	0.123±0.003
Glycine in 0.50 mol $\cdot$ kg^{-1} NaAcB				
1.00	0.137±0.010	0.151±0.011	0.152±0.010	0.158±0.036
12.40	0.115±0.007	0.119±0.005	0.119±0.011	0.125±0.012
Glycine in 1.00 mol $\cdot$ kg^{-1} NaAcB				
1.00	0.149±0.007	0.158±0.010	0.159±0.010	0.167±0.010
12.40	0.143±0.008	0.150±0.007	0.151±0.008	0.162±0.006

where ± are the respective errors.

from pH 1.00 to pH 12.40, the association among the solute particles is destroyed because of increased electrostatic repulsions, H-bonds break, hence the values of viscosity B-coefficient decreases. Overall, the values of viscosity B-coefficient for glycine in aqueous NaAcB increases with increase in concentration of aqueous NaAcB as well as with increase in temperature which may be due to (a) possibility of forming hydrogen bonds (b) modification of the binding properties of glycine and ions of NaAcB. The results obtained from viscosity B-coefficients are in line with the results obtained from ϕ_v^o values.

The values of viscosity B-coefficient of glycine in aqueous NaAcB solutions of pH (1.00 and 12.40) at different temperatures have been used to calculate corresponding transfer values by using the following equation as:

$\Delta_{tr}B = B - coefficient(in\ aqueous\ NaAcB\ solutions)$
$-B - coefficient(in\ water)$ ... (10)

The obtained values of $\Delta_{tr}B$ of glycine in aqueous NaAcB of different pH values have been reported in Table S4. Representative plots of $\Delta_{tr}B$ of glycine in water and in aqueous NaAcB are given as Fig. 2 at 310.15 K. At pH (1.00 and 12.40), the positive $\Delta_{tr}B$ values of glycine in aqueous NaAcB solutions may attribute due to more structured environment of co-solute around the solute (except for glycine in $0.10\ mol \cdot kg^{-1}$ aqueous NaAcB of pH 12.40). It may be noted that the variation of $\Delta_{tr}\phi_v$ and $\Delta_{tr}B$ of glycine in aqueous NaAcB solutions is not similar, which reveals that the dependence of these parameters for studied system is somewhat different. The first derivative of viscosity B-coefficient with temperature $i.e.\ dB/dT$ has been used to indicate the effect of solute particles on solvent molecule. The negative sign of dB/dT indicates structure making behaviour whereas positive sign of dB/dT indicate structure breaking behaviour[20]. For present system, dB/dT values have been reported in Table S5. Negative values of dB/dT for glycine in water indicates that glycine act as structure maker whereas positive dB/dT values for glycine in aqueous NaAcB solution at studied pH values indicate that glycine acts as structure breaker in these solutions. The obtained dB/dT values of glycine in aqueous NaAcB solutions are very small and do not follow a definite trend which further suggests that behaviour of glycine in aqueous NaAcB solutions is pH, temperature and concentration dependent.

The viscosity B-coefficient of transfer, $\Delta_{tr}B$ for glycine in aqueous NaAcB solutions of pH (1.00 and 12.40) can also be expressed by McMillan-Mayer theory[18], by using the following equation as:

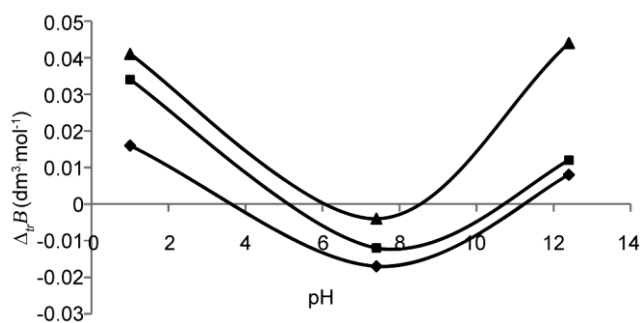$\Delta_{tr}B = 2\eta_{AB}m + 3\eta_{ABB}m^2 + \cdots$ ... (11)

Fig. 2 — Representative plots of viscosity B-coefficient of transfer, $\Delta_{tr}B$ for glycine versus pH in ($\blacklozenge$0.10, $\blacksquare$ 0.50, $\blacktriangle$ 1.00) $mol \cdot kg^{-1}$ aqueous NaAcB solutions at T(K) = 310.15

where η_{AB} and η_{ABB} are respectively the viscometric pair and triplet interaction coefficients and m (mol^{-1} kg) is the molality of co-solute (*i.e.* aqueous NaAcB). The values of η_{AB} and η_{ABB} for the studied system have been compiled in Table 3. η_{AB} values for glycine are positive whereas η_{ABB} values are found to be negative at studied pH values. Overall, positive values of η_{AB} for glycine reveal that pair interactions are more dominating than triplet interactions in these studied systems. The positive η_{AB} values occur due to the overlap of hydration sphere of glycine and aqueous NaAcB molecules which again supports the conclusion drawn from volumetric studies. Further, the obtained behaviour of η_{AB} and η_{ABB} values for glycine in aqueous NaAcB solutions are in-line with volumetric results which may attribute due to the difference in the stereochemistry of dominant conformations in present system at different pH and over the entire range of temperatures studied.

The activation free energy of a single solute particle, $\Delta\mu_1^{o\#}$ in a solvent molecule can be calculated in accordance to Eyring's simple model[21] by using the following equation as:

$$\eta_0 = \left({hN_A}/{V_1^0} \right) exp \left({\Delta\mu_1^{0\#}}/{RT} \right)   \text{... (12)}$$

where η_o ($mPa \cdot s$) is the viscosity of pure solvent, h ($J \cdot s$) is the Planck's constant, N_A (mol^{-1}) is Avogadro's number, R ($J\ mol^{-1}\ K^{-1}$) is the universal gas constant, $T(K)$ is the absolute temperature, respectively and V_1^o ($cm^3\ mol^{-1}$) is the average molar volume of glycine in water and in (0.10, 0.50 and 1.00) $mol \cdot kg^{-1}$ aqueous NaAcB solutions of pH (1.00 and 12.40) at T(K)= (298.15-318.15). The values of $\Delta\mu_1^{o\#}$ and V_1^o have been summarized in Table S6. According to Feakins *et al.*[22,23] the activation free energy, $\Delta\mu_2^{o\#}$ for the viscous flow of glycine in aqueous NaAcB solutions is related to viscosity B-coefficient as follows:

$$\Delta\mu_2^{0\#} = \Delta\mu_1^{0\#} + \left({RT}/{V_1^0} \right) \left[1000B - \left(V_1^0 - \phi_v^0 \right) \right]   \text{... (13)}$$

where ϕ_v^o ($cm^3 \cdot mol^{-1}$)is the limiting partial molar volume of glycine in aqueous NaAcB solutions of pH (1.00 and 12.40). $\Delta\mu_2^{o\#}$ values for the present system have been reported in Table S7. It is evident from Table S6 and Table S7, that the values of $\Delta\mu_1^{o\#}$ and $\Delta\mu_2^{o\#}$ are positive and the values of $\Delta\mu_2^{o\#}$ are higher than that of $\Delta\mu_1^{o\#}$, reveals the existence of stronger

Table 7 — Thermodynamic activation parameters, ΔG_2^o of glycine in water and in (0.10, 0.50 and 1.00) mol kg^{-1}aqueous NaAcB solutions of pH (1.00 and 12.40) at different temperatures, T(K)= (298.15 to 318.15)

pH ↓	ΔG_2^o (kJ· mol^{-1})			
	T(K) = 298.15	T(K) = 308.15	T(K) = 310.15	T(K) = 318.15
	Glycine in water			
1.00	22.72	21.17	21.44	23.26
12.40	22.23	22.63	22.62	22.41
	Glycine in 0.10 mol kg^{-1}NaAcB			
1.00	20.59	22.28	22.83	24.57
12.40	21.64	23.29	23.73	25.45
	Glycine in 0.50 mol kg^{-1}NaAcB			
1.00	21.52	24.11	24.40	25.82
12.40	22.48	23.72	23.86	25.25
	Glycine in 1.00 mol kg^{-1}NaAcB			
1.00	22.07	23.93	24.20	25.84
12.40	25.58	27.42	27.57	29.74

Table 8— Activation parameters enthalpy, $\Delta H^{o\#}$ and entropy, $\Delta S^{o\#}$of glycine in water and in (0.10, 0.50 and 1.00) mol · kg^{-1}aqueous NaAcB solutions of pH (1.00 and 12.40)

pH ↓	$\Delta H^{o\#}$ (kJ· mol^{-1})	$\Delta S^{o\#}$ (kJ· mol^{-1})
	Glycine in water	
1.00	31.85±26.56	0.002±0.09
12.40	34.69±4.38	0.011±0.01
	Glycine in 0.10 mol kg^{-1}NaAcB	
1.00	-23.27±3.94	-0.178±0.01
12.40	-19.30±3.78	-0.168±0.01
	Glycine in 0.50 mol kg^{-1}NaAcB	
1.00	-27.46±5.68	-0.197±0.02
12.40	- 2.42±3.83	-0.116±0.012
	Glycine in 1.00 mol kg^{-1}NaAcB	
1.00	-20.96±3.18	-0.177±0.01
12.40	-19.62±6.39	-0.185±0.02

solute-solvent interactions among glycine and water or aqueous NaAcB solutions. Further, the values of $\Delta \mu_2^{o\#}$ reflects the capability to form transition state from ground state through solute-solvent interactions. According to Transition state theory[23], each solvent molecule present in 1 mol of solution must pass through the transition state and should interact more or less strongly with the solute particles. Hence, Gibb's free energy of transfer of solute provide first contribution from ground state to transition state, $\Delta G_2^o(1-1')$ and $\Delta G_2^o(2-2')$ give second contribution to $\Delta \mu_2^{o\#}$. The $\Delta G_2^o(1-1')$ values thus obtained for glycine in aqueous NaAcB solution of different pH values and at different temperatures have been reported in Table 7. The $\Delta G_2^o(1-1')$ values of glycine in present system increase with increase in concentration of aqueous NaAcB as well as with increase in temperature. $\Delta \mu_2^{o\#}$ and $\Delta G_2^o(1-1')$ values are higher than $\Delta \mu_2^{o\#}$ suggest the formation of transition state which is less favored in presence of glycine. This may be attributed due to the breaking and distortion of H-bonds among these systems. $\Delta G_2^o(1-1')$ values for glycine in water and in aqueous NaAcB solutions of different pH follow the order as pH 12.40> pH 1.00 (except for glycine in water). Decrease in $\Delta G_2^o(1-1')$ values with change in pH indicates that structure destroying property is increased as the pH of the system changes.

Activation parameters entropy, $\Delta S^{o\#}$and enthalpy, $\Delta H^{o\#}$ for the viscous flow have been calculated by using the following equation and are summarized in Table 8.

$$\Delta S^{0\#} = -\frac{d\left(\Delta \mu_2^{0\#}\right)}{dT} \qquad \dots (14)$$

$$\Delta H^{0\#} = \Delta \mu_2^{0\#} + T\Delta S^{0\#} \qquad \dots (15)$$

The obtained positive values of $\Delta S^{o\#}$ and $\Delta H^{o\#}$ for glycine in water indicate that the transition state is disorganized due to the breaking of solute-solvent bonds as compared to the ground state whereas the reverse is true for the negative values of $\Delta S^{o\#}$ and $\Delta H^{o\#}$ for the studied system. It may be concluded from $\Delta S^{o\#}$ and $\Delta H^{o\#}$ values that solute-solvent bonds are relatively stronger than solvent-solvent bonds, which further indicate a less favourable transition state in the presence of solute whereas the ground states are in the ordered region.

Conclusions

Negative $\Delta_{tr}\phi_v$ values for glycine at pH 1.00 indicate the dominance of hydrophobic-hydrophobic interactions whereas positive $\Delta_{tr}\phi_v$ values at pH 12.40 indicate the dominance of ion-dipolar interactions. Results obtained are in-line with $\phi_v$and ϕ_v^o values. Viscosity B-coefficient for glycine increases with increase in temperature, indicating the increase of the solute-solvent interactions. Pair interactions dominate over triplet interactions. Positive values of $\Delta H^{o\#}$ and $\Delta S^{o\#}$ indicate that the formation of transition state is assisted by decrease in order whereas reverse is true when the values are negative. Overall, the results obtained from volumetric, viscometric, and spectroscopic studies provide valuable information on intermolecular interactions, which can further influence their efficacy in biological applications.

Supplementary Data

Acknowledgment

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