



Solution thermodynamics of sodium pyruvate in aqueous glycine solutions at T 298.15–313.15 K

BIJAN KUMAR PANDIT¹, ABHIJIT SARKAR¹ and BISWAJIT SINHA^{1*}

¹Department of Chemistry, University of North Bengal, Darjeeling-734013, India

(Received 31 October, revised 31 December 2015, accepted 17 February 2016)

Abstract: In this study, the effects of sodium pyruvate on the solution thermodynamics of glycine were investigated in terms of the solute–solute and solute–solvent interactions in aqueous solutions. The measured density and viscosity were used to derive the apparent molar volumes (ϕ_V), partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients at 298.15, 303.15, 308.15 and 313.15 K under ambient pressure. The interactions are further discussed in terms of ion–dipolar, hydrophobic–hydrophobic, hydrophilic–hydrophobic group interactions. The activation parameters of viscous flow are also discussed in terms of the transition state theory. The overall results indicated that ion–hydrophilic and hydrophilic–hydrophilic group interactions are predominant in the ternary solutions.

Keywords: partial molar volumes; viscosity *B*-coefficients; glycine; sodium pyruvate.

INTRODUCTION

Amino acids are the fundamental building blocks of proteins. Salt-induced electrostatic forces are known to play vital roles in modifying the protein structure by denaturation and affecting properties such as solubility and activity of enzymes.¹ The physicochemical properties of amino acids and salts in the aqueous phase provide valuable information on solute–solute and solute–solvent interactions. These interactions are important in understanding the stability of proteins and are informative for several biochemical and physiological process in a living cell. Therefore in order to gain more insight into the hydration of proteins and non-covalent forces stabilizing their native structure, it is necessary to determine the effect of salts on model compound of proteins, such as amino acids. Although a large number of studies have been realized regarding the volumetric properties of amino acids,^{1–9} less attention has been given to organic salts with considerable significance in biological processes and industry.^{2,3}

*Corresponding author. E-mail: abhijitslg4@gmail.com
doi: 10.2298/JSC151031034P

Among organic salts, sodium pyruvates have significance in the body being converted into acetyl coenzyme A, which enters into a process designated to provide energy for the cell.

The present study reports the experimentally measured values of density and viscosity of sodium pyruvate in aqueous glycine solutions as a function of concentration and temperature at ambient pressure. Using the experimentally measured data, the apparent molar volume, limiting apparent molar volume, Jones–Dole coefficients, *etc.* were calculated. These parameters were used to discuss solute–solute and solute–solvent interactions in the aforementioned systems. Information regarding the solution thermodynamics of sodium pyruvate in aqueous glycine solutions is still rare in the literature.

EXPERIMENTAL

Materials

Sodium pyruvate (Sigma–Aldrich, mass fraction purity > 99.5 %,) and glycine (S.D Fine Chemicals, India, mass fraction purity > 98.5 %) were used for the present study. Deionised, doubly distilled, degassed water with a specific conductance of 1×10^{-6} S cm⁻¹ was used for the preparation of different aqueous solutions. Sodium pyruvate was used as received from the vendor and its melting point was found to be 300 °C. The physical properties of different aqueous solutions of glycine are reported in Table S-I of the Supplementary material to this paper. No comparable data were found in the literature for the densities (ρ_0) and viscosities (η_0) of the aqueous glycine solutions used as solvents in this work. Glycine was purified by dissolving it in distilled water at 90–95 °C and recrystallizing. After filtration, the salt was dried *in vacuo* for a few hours and its melting point was measured as 233 °C. Stock solutions of sodium pyruvate in different aqueous solutions of glycine were prepared by mass and then further diluted to obtain the different working solutions. Molalities (m) were converted into molarities (c) by using the experimental densities. All solutions were prepared fresh before use and adequate precautions were taken to avoid evaporation losses during the measurements.

Methods

The mass measurements were realized on a digital electronic analytical balance (Mettler, AG 285, Switzerland) with a precision of ± 0.01 mg. The densities were measured with a vibrating-tube densitometer (Anton Paar DMA 4500M) that was maintained at ± 0.01 K of the desired temperatures and calibrated with doubly distilled water and dry air. The uncertainty in density was estimated to be ± 0.00001 g cm⁻³. The viscosities were measured by means of a suspended Ubbelohde type viscometer. It was calibrated at the experimental temperatures with doubly distilled water and purified methanol.²⁹ A thoroughly cleaned and perfectly dried viscometer was filled with the experimental solutions and placed vertically in a glass-walled thermostated bath maintained at ± 0.01 K of the desired temperatures. After attainment of thermal equilibrium, the efflux times of flow were recorded with a digital stopwatch that measured time correct to ± 0.01 s. At least three repetitions of each data (reproducible to ± 0.02 s) were taken to average the flow times. Based on experimental work on several pure liquids, the precision of the viscosity measurements was evaluated to be within ± 0.003 mPa s and the total uncertainty of the viscosity measurements was 0.30 %. Details of the methods and techniques of the density and viscosity measurements were described elsewhere.^{10–12}

RESULTS AND DISCUSSION

The apparent molar volumes (ϕ_V) of sodium pyruvate in different aqueous solutions of glycine were determined from the solution densities using the following equation:^{13,32,33}

$$\phi_V = (M / \rho_0) - 1000(\rho - \rho_0) / (m\rho\rho_0) \quad (1)$$

where M and m are the molar mass and molality of sodium pyruvate in the aqueous solutions of glycine; ρ_0 and ρ are the densities of the solvent and the solution, respectively. Experimental densities (ρ), viscosities (η) and derived parameters at different temperatures are reported in Table S-II of the Supplementary material. As the ϕ_V values are independent of the concentration of sodium pyruvate for extremely dilute solutions, it could be assumed that the ϕ_V values are equal to the partial molar volume (ϕ_V^0) at infinite dilution. The plots of ϕ_V values against the square root of molal concentrations of sodium pyruvate were found to be linear. Hence the partial molar volumes (ϕ_V^0) at infinite dilution and the slopes (S_V^*) from Eq. (2) were determined using least squares fitting of the ϕ_V values to the Masson equation:¹⁴

$$\phi_V = \phi_V^0 + S_V^* \sqrt{m} \quad (2)$$

The ϕ_V^0 and S_V^* values are reported in Table I, which shows that the ϕ_V^0 values are positive and increase with increasing molarity of glycine in the mixtures and with increasing temperature of the respective mixtures. These trends in the ϕ_V^0 values indicate the presence of strong solute–solvent interactions and that such interactions further strengthen at higher concentrations of glycine in the ternary solutions. The increase of ϕ_V^0 with temperature may be the result of the following effects: at higher temperatures the thermal energy of the water molecule increase causing fast movement of the bulk electrostricted water molecules from the interaction region of Na^+ and $-\text{COO}^-$ groups, resulting in a positive volume change. These trends in the ϕ_V^0 values are clear manifestations of the trends in the ϕ_V values (as listed in Table S-II).

The parameter S_V^* is a volumetric virial coefficient and characterizes the pair-wise interactions between the solvated species^{15–17,29} in the solution. Its sign is determined by the interactions between solute species. Table I shows that the S_V^* values are positive for all the ternary solutions and the values decrease both when the experimental temperature and the glycine concentration in the ternary solutions increases. For ionic species such as sodium pyruvate or zwitter-ionic glycine, the positive S_V^* values suggest that the pair-wise interactions (between solute–solute or solute–cosolute) is dominated by the charged end groups or ions and the S_V^* values just reciprocate the trends in the ϕ_V^0 values for the studied aqueous solutions.

TABLE I. Partial molar volumes (ϕ_V^0) and the slope (S_V^*) of Eq. (2) for sodium pyruvate in aqueous glycine solutions with corresponding standard deviations (σ) at different temperatures; c is the glycine concentration in water

T / K	$\phi_V^0 \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	$S_V^* \times 10^6 / \text{m}^3 \text{ kg}^{1/2} \text{ mol}^{-3/2}$	$\sigma \times 10^6 / \text{m}^3 \text{ mol}^{-1}$
Water			
298.15	67.48	15.93	0.02
303.15	69.18	15.36	0.02
308.15	71.02	14.58	0.01
313.15	72.10	13.75	0.03
$c = 0.005 \text{ mol dm}^{-3}$			
298.15	58.48	21.06	0.07
303.15	59.93	19.08	0.05
308.15	62.50	18.34	0.02
313.15	63.55	18.09	0.04
$c = 0.010 \text{ mol dm}^{-3}$			
298.15	59.88	19.42	0.01
303.15	61.71	17.19	0.01
308.15	63.77	16.94	0.03
313.15	64.66	16.55	0.09
$c = 0.015^a$			
298.15	61.28	18.76	0.04
303.15	63.61	16.79	0.09
308.15	64.23	16.59	0.06
313.15	65.82	16.17	0.08
$c = 0.020 \text{ mol dm}^{-3}$			
298.15	62.80	18.09	0.02
303.15	64.59	16.33	0.05
308.15	65.88	15.14	0.01
313.15	67.02	14.40	0.01

Apparent molar volumes (ϕ_V) and densities (ρ) were used to derive the apparent molar expansibilities (ϕ_E) of glycine solutions using the relation:¹⁸

$$\phi_E = \alpha \phi_V + 1000(\alpha - \alpha_0)/(m\rho_0) \quad (3)$$

where α and α_0 are the coefficients of isobaric thermal expansion of the solvent and solution, respectively, and the other symbols have their usual significance.

α and α_0 are defined as: $\alpha_0 = -\rho_0^{-1}(d\rho_0/dT)_p$ and $\alpha = -\rho^{-1}(d\rho/dT)_p$, respectively. The uncertainty of α and α_0 values was $\pm 5 \times 10^{-6} \text{ K}^{-1}$. The uncertainty of the apparent molar expansibilities (ϕ_E) was within $\pm 0.001 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$. The partial molar expansibilities (ϕ_E^0) were derived from the relation:¹⁸

$$\phi_E = \phi_E^0 + S_E \sqrt{m} \quad (4)$$

The ϕ_E^0 values for the experimental solutions at different temperatures are reported in Table II, which shows that the ϕ_E^0 values are positive and further increase when the temperatures increase but decrease when the concentration of

glycine increases. Such trend in the ϕ_E^0 values may be attributed to the absence of caging or packing effects.^{19,20} According to Heplar,²¹ the long-range structure making or breaking ability of solutes in solutions can be better characterized by the sign of the $(d\phi_E^0/dT)_p$ terms. If the sign of $(d\phi_E^0/dT)_p$ is slightly negative or positive, the solute is a structure maker, and if it is large negative, the solute is a structure breaker. The $(d\phi_E^0/dT)_p$ values were obtained from the slopes of the linear fits of the ϕ_E^0 values against the experimental temperatures (T), with the standard deviation values lying within the range of 0.00001–0.00002. From the values of $(d\phi_E^0/dT)_p$, reported in Table II, it is evident that sodium pyruvate acts as a mild structure maker and its structure making ability decreases to some extent when the glycine concentrations in the studied solutions increase.

TABLE II. Limiting partial molar expansibilities (ϕ_E^0) for sodium pyruvate in aqueous glycine solutions at different temperatures

c mol dm^{-3}	$\phi_E^0 \times 10^4 / m^3 mol^{-1} K^{-1}$					$S_E \times 10^4 / m^3 mol^{-1} K^{-1}$			$(d\phi_E^0/dT)_p$ $cm^3 mol^{-1} K^{-2}$	
	T / K									
	298.15	303.15	308.15	313.15	298.15	303.15	308.15	313.15		
0	2.903 ±0.001	2.917 ±0.001	2.932 ±0.001	2.946 ±0.002	1.523 ±0.001	1.528 ±0.001	1.534 ±0.001	1.542 ±0.001	0.282 ±0.001	
0.005	3.351 ±0.001	3.365 ±0.001	3.383 ±0.001	3.399 ±0.001	2.024 ±0.001	2.035 ±0.002	2.042 ±0.001	2.049 ±0.001	0.328 ±0.001	
0.010	3.079 ±0.001	3.093 ±0.002	3.108 ±0.001	3.122 ±0.003	1.854 ±0.001	1.865 ±0.001	1.869 ±0.001	1.877 ±0.001	0.287 ±0.001	
0.015	2.631 ±0.001	2.646 ±0.002	2.656 ±0.001	2.670 ±0.001	1.676 ±0.001	1.686 ±0.001	1.692 ±0.002	1.699 ±0.001	0.258 ±0.001	
0.020	2.568 ±0.001	2.581 ±0.001	2.594 ±0.001	2.606 ±0.001	2.530 ±0.002	2.542 ±0.001	2.554 ±0.001	2.566 ±0.001	0.252 ±0.001	

The partial molar volumes of transfer ($\Delta\phi_V^0$) from water to an aqueous solution of glycine were determined from the relation:^{17,22}

$$\Delta\phi_V^0 = \phi_V^0[\text{Aqueous solution of glycine}] - \phi_V^0[\text{Water}] \quad (5)$$

The $\Delta\phi_V^0$ values are depicted in Fig. 1 as a function of molarity of glycine in aqueous solutions. The $\Delta\phi_V^0$ values are free from solute–solute interactions and therefore provide valuable information about solute–cosolute interactions.²² Figure 1 shows that the $\Delta\phi_V^0$ values are negative at all the experimental temperatures and increase monotonically with increasing glycine concentration in the ternary solutions. According to the cosphere model,²³ while the overlap of hydration cospheres of two ionic species results in a volume increase, those of hydration cospheres of hydrophobic–hydrophobic and ion–hydrophobic groups result in a net volume decrease. The negative $\Delta\phi_V^0$ values indicate that ion–hydrophobic and hydrophobic–hydrophobic group interactions are predominant over ion–hydrophilic, hydrophilic–hydrophilic and hydrophobic–hydrophilic interactions.

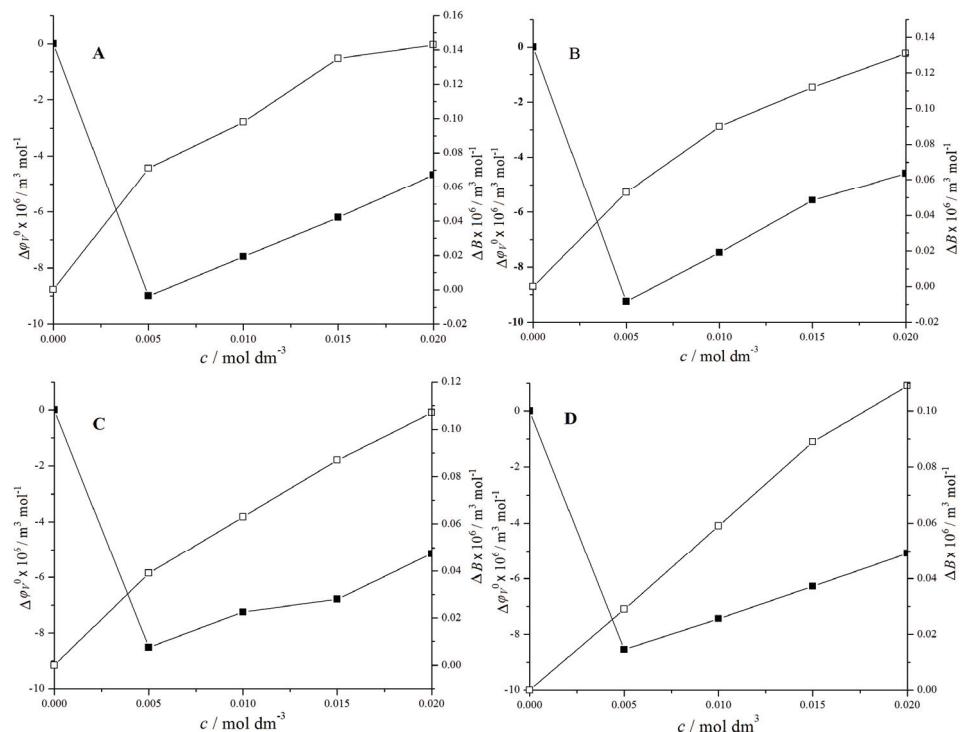


Fig. 1. Plots of partial molar volumes of transfer ($\Delta\phi_V^0$) and viscosity B -coefficients of transfer (ΔB) from water to aqueous solutions of glycine for sodium pyruvate at different temperatures: A, $T = 298.15$ K; B, $T = 303.15$ K; C, $T = 308.15$ K; D, $T = 313.15$ K.

Symbols: ■, $\Delta\phi_V^0$; □, ΔB .

The partial molar volumes (ϕ_V^0) of a solute can also be explained by a simple model^{15,24} given by the relation:

$$\phi_V^0 = \phi_{vw} + \phi_{void} - \phi_S \quad (6)$$

where ϕ_{vw} , ϕ_{void} and ϕ_S are the van der Waals volumes, the volumes associated with voids or empty spaces and the shrinkage volumes due to electrostriction. Assuming the ϕ_{vw} and ϕ_{void} values are of the same magnitude in water and in aqueous solutions of glycine for the same solute, the observed negative $\Delta\phi_V^0$ for sodium pyruvate indicates an increase in the shrinkage volume in the presence of glycine. As glycine exists in a zwitterionic form, the possible interactions (Fig. 2) could roughly be summarized as follows: i) polar $-\text{NH}_3^+$ group of zwitterionic glycine and $-\text{COO}^-$ of pyruvate and HO^- ions, ii) polar $-\text{COO}^-$ group (through both the O-atoms) of zwitterionic glycine and Na^+ and H^+ , iii) ionic-hydrophobic interaction between ions of sodium pyruvate and the non polar part of the zwitterionic glycine molecules. According to the cosphere overlap model developed by Friedman and Krishnan,²³ the overlap of hydration cospheres of two

ionic species results in an enhanced volume as some electrostricted water molecules return to the bulk water with a higher volume contribution $\Delta\phi_V^0$ values. Thus, the negative $\Delta\phi_V^0$ values for sodium pyruvate indicate that ion–hydrophobic and hydrophobic–hydrophobic interactions predominate over the ion–hydrophilic, hydrophilic–hydrophobic and hydrophilic–hydrophilic interactions and favour the bulk structure of water.

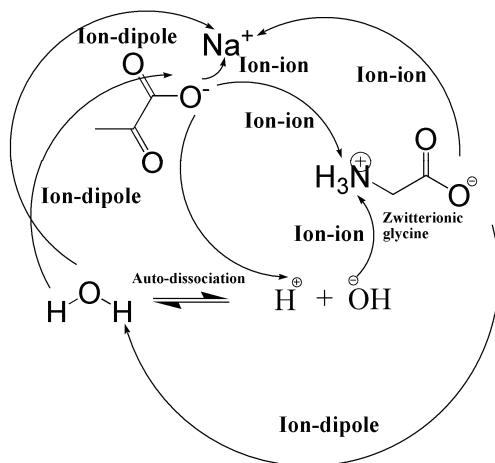


Fig. 2. Schematic representation of different possible ionic group interactions for sodium pyruvate in aqueous glycine solutions.

The viscosities (η) of the different experimental aqueous solutions were analyzed by the Jones–Dole equation:²⁵

$$(\eta/\eta_0 - 1)/\sqrt{m} = (\eta_r - 1)/\sqrt{m} = A + B\sqrt{m} \quad (7)$$

where $\eta_r = \eta/\eta_0$ is the relative viscosity; η_0 and η are the viscosities of the solvent and solution, respectively. A and B are two adjustable parameters that are obtained by a least squares analysis and their values are reported in Table III. The viscosity B -coefficient³¹ reflects the effects of solute–solvent interactions on the solution viscosity and provides information about the solvation of a solute and the structure of the solvent in the local vicinity of the solute molecules. Table III shows that the viscosity B -coefficients for sodium pyruvate in the studied solvent systems are positive and thus suggest the presence of strong solute–solvent interactions in the studied solutions. These interactions further increase when both the molarity of the sodium pyruvate in the ternary solutions and the temperatures increase. The A -coefficients values are indicative of solute–solute or ion–ion interactions and in the present study their values support the results obtained from viscosity B -coefficients discussed earlier. The viscosity B -coefficients of transfer (ΔB) from water to aqueous solutions of glycine were determined using the relation:^{17,22}

$$\Delta B = B[\text{Aqueous solution of glycine}] - B[\text{Water}] \quad (8)$$

The ΔB values are depicted in (Fig. 1) as a function of molarity of glycine in aqueous solutions and support the results obtained from the $\Delta\phi_V^0$ values discussed earlier.

TABLE III. Values of viscosity A - and B -coefficients for sodium pyruvate in aqueous glycine solutions at different temperatures; c : glycine concentration in water

Viscosity coefficient	T / K			
	298.15	303.15	308.15	313.15
Water				
$A \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	-0.001	-0.015	-0.0318	-0.019
$B \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	0.410	0.540	0.620	0.670
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	0.001	0.001	0.001	0.001
$c = 0.005 \text{ mol dm}^{-3}$				
$A \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	-0.016	-0.023	-0.051	-0.021
$B \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	0.481	0.593	0.659	0.699
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	0.001	0.001	0.001	0.001
$c = 0.010 \text{ mol dm}^{-3}$				
$A \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	-0.033	-0.029	-0.031	-0.037
$B \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	0.508	0.630	0.683	0.729
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	0.001	0.001	0.001	0.001
$c = 0.015 \text{ mol dm}^{-3}$				
$A \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	-0.034	-0.034	-0.060	-0.051
$B \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	0.545	0.652	0.707	0.759
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	0.001	0.001	0.001	0.001
$c = 0.020 \text{ mol dm}^{-3}$				
$A \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	-0.036	-0.039	-0.071	-0.061
$B \times 10^{-6} / \text{m}^3 \text{ mol}^{-1}$	0.553	0.671	0.727	0.777
$\sigma \times 10^{-6} / \text{m}^{3/2} \text{ mol}^{-1/2}$	0.002	0.002	0.002	0.002

According to transition state theory of relative viscosity,²⁶ the contribution per mole of a solute to the free energy of activation for viscous flow of the solution ($\Delta\mu_2^{\theta*}$) is related to the viscosity B -coefficients by the following relation:

$$\Delta\mu_2^{\theta*} = \Delta\mu_1^{\theta*} + RT(1000B + \varphi_{V,2}^0 - \varphi_{V,1}^0)/\varphi_{V,1}^0 \quad (9)$$

where $\varphi_{V,1}^0$ and $\varphi_{V,2}^0$ are the partial molar volumes of the solvent and solute, respectively. The free energy of activation of viscous flow per mole of the pure solvent or solvent mixture ($\Delta\mu_1^{\theta*}$) is given by the relation:^{27,28}

$$\Delta\mu_1^{\theta*} = \Delta G_1^{\theta*} = \frac{RT \cdot \ln(\eta_0 \varphi_{V,1}^0)}{hN_A} \quad (10)$$

where N_A is the Avogadro's number and the other symbols have their usual significances.²⁷



The entropy of activation for viscous flow per mole of the solute in ternary solutions ($\Delta S_2^{\theta*}$) can be obtained from the negative slope of the plots of $\Delta\mu_2^{\theta*}$ against T :

$$\Delta S_2^{\theta*} = \frac{-d(\Delta\mu_2^{\theta*})}{dT} \quad (11)$$

and the activation enthalpy for viscous flow ($\Delta H_2^{\theta*}$) can be obtained from the relation:

$$\Delta H_2^{\theta*} = \Delta\mu_2^{\theta*} + T\Delta S_2^{\theta*} \quad (12)$$

The parameters ($\varphi_{V,2}^0 - \varphi_{V,1}^0$), $\Delta\mu_1^{\theta*}$, $\Delta\mu_2^{\theta*}$, $\Delta H_2^{\theta*}$ and $T\Delta S_2^{\theta*}$ are reported in Table IV. Table IV shows that the $\Delta\mu_1^{\theta*}$ values are almost invariant of the solvent compositions and temperatures, which implies that the $\Delta\mu_2^{\theta*}$ values are dependent mainly on the viscosity B -coefficients and ($\varphi_{V,2}^0 - \varphi_{V,1}^0$) deviations. The $\Delta\mu_2^{\theta*}$ values contain the change in the free energy of activation of the solute in the presence of solvent and contributions from the movement of solute molecules. The $\Delta\mu_2^{\theta*}$ values were found to be positive at all the experimental temperatures, which suggest the process of viscous flow becomes difficult with increasing temperature and molality of glycine in the solution. Hence, the formation of the transition state becomes less favourable in the presence of glycine but becomes somewhat more favourable at lower temperatures. According to Feakins *et al.*²⁷, $\Delta\mu_2^{\theta*} > \Delta\mu_1^{\theta*}$ for solutes with positive viscosity B -coefficients indicates stronger solute–solvent interactions in the ground state than in the transition state, *i.e.*, the formation of the transition state is accompanied by the rapture and distortion of the intermolecular forces in the solvent structure.²⁷ The larger are the values of $\Delta\mu_2^{\theta*}$, the greater is the structure making tendency of the solute, and the positive values of $\Delta\mu_2^{\theta*}$ for sodium pyruvate in the different aqueous glycine solutions suggests sodium pyruvate is a net structure promoter in the ternary mixtures. The values of $T\Delta S_2^{\theta*}$ and $\Delta H_2^{\theta*}$ listed in Table IV are negative for all experimental solutions at all temperatures, suggesting that the transition state is associated with bond making and an increase in order.

TABLE IV. Values of ($\varphi_{V,2}^0 - \varphi_{V,1}^0$), $\Delta\mu_1^{\theta*}$, $\Delta\mu_2^{\theta*}$, $\Delta H_2^{\theta*}$ and $T\Delta S_2^{\theta*}$ for sodium pyruvate in different aqueous glycine solutions at different temperatures; c : glycine concentration in water

Parameter	T / K			
	298.15	303.15	308.15	313.15
Water				
$(\varphi_{V,2}^0 - \varphi_{V,1}^0) \times 10^6 / \text{m}^3 \text{ mol}^{-1}$	49.36	51.01	52.79	52.79
$\Delta\mu_1^{\theta*} / \text{kJ mol}^{-1}$	9.180	9.060	8.960	8.860
$\Delta\mu_2^{\theta*} / \text{kJ mol}^{-1}$	101.04	117.50	129.55	141.05
$T\Delta S_2^{\theta*} / \text{kJ mol}^{-1}$	-850.2	-864.4	-878.7	-893.0
$\Delta H_2^{\theta*} / \text{kJ mol}^{-1}$	-819.3	-832.0	-844.5	-857.3

TABLE IV. Continued

Parameter	T / K			
	298.15	303.15	308.15	313.15
<i>c</i> = 0.005 mol dm ⁻³				
($\phi_{V,2}^0 - \phi_{V,1}^0$) × 10 ⁶ / m ³ mol ⁻¹	40.33	41.75	44.30	45.21
$\Delta\mu_1^{\theta*}$ / kJ mol ⁻¹	9.190	9.070	8.970	8.880
$\Delta\mu_2^{\theta*}$ / kJ mol ⁻¹	80.39	97.09	107.94	114.52
$T\Delta S_2^{\theta*}$ / kJ mol ⁻¹	-821.2	-835.0	-848.8	-862.5
$\Delta H_2^{\theta*}$ / kJ mol ⁻¹	-740.8	-737.9	-740.8	-748.0
<i>c</i> = 0.010 mol dm ⁻³				
($\phi_{V,2}^0 - \phi_{V,1}^0$) × 10 ⁶ / m ³ mol ⁻¹	41.74	43.54	45.58	46.33
$\Delta\mu_1^{\theta*}$ / kJ mol ⁻¹	9.220	9.090	8.990	8.910
$\Delta\mu_2^{\theta*}$ / kJ mol ⁻¹	84.31	102.51	111.56	119.02
$T\Delta S_2^{\theta*}$ / kJ mol ⁻¹	-812.3	-825.4	-839.6	-853.2
$\Delta H_2^{\theta*}$ / kJ mol ⁻¹	-728.0	-723.4	-728.0	-734.1
<i>c</i> = 0.015 mol dm ⁻³				
($\phi_{V,2}^0 - \phi_{V,1}^0$) × 10 ⁶ / m ³ mol ⁻¹	43.15	45.45	46.04	47.49
$\Delta\mu_1^{\theta*}$ / kJ mol ⁻¹	9.220	9.110	8.980	8.940
$\Delta\mu_2^{\theta*}$ / kJ mol ⁻¹	89.60	105.89	115.01	120.63
$T\Delta S_2^{\theta*}$ / kJ mol ⁻¹	-757.7	-770.4	-783.1	-795.8
$\Delta H_2^{\theta*}$ / kJ mol ⁻¹	-668.1	-664.5	-668.1	-675.2
<i>c</i> = 0.020 mol dm ⁻³				
($\phi_{V,2}^0 - \phi_{V,1}^0$) × 10 ⁶ / m ³ mol ⁻¹	44.66	46.43	47.69	48.79
$\Delta\mu_1^{\theta*}$ / kJ mol ⁻¹	9.238	9.130	9.000	8.951
$\Delta\mu_2^{\theta*}$ / kJ mol ⁻¹	90.91	108.71	118.12	126.93
$T\Delta S_2^{\theta*}$ / kJ mol ⁻¹	-811.1	-824.7	-838.3	-851.8
$\Delta H_2^{\theta*}$ / kJ mol ⁻¹	-720.2	-716.0	-720.2	-725.0

CONCLUSIONS

In summary, partial molar volumes (ϕ_V^0) and viscosity *B*-coefficients of sodium pyruvate in aqueous solutions of glycine indicate the presence of strong solute–solvent interactions and such interactions further strengthen at higher glycine concentrations and increase at higher temperatures. These facts may be attributed to the predominance of ion–hydrophilic and hydrophilic–hydrophilic group interactions over ion–hydrophobic, hydrophobic–hydrophobic and hydrophilic–hydrophobic interactions. In addition, the trends in $(d\phi_E^0 / dT)_p$ and $\Delta\mu_2^{\theta*}$ for sodium pyruvate in the aqueous solutions of glycine suggest that sodium pyruvate is a net structure promoter in the studied aqueous solutions.

SUPPLEMENTARY MATERIAL

Additional thermodynamic data are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.



Acknowledgement. The authors are grateful to the Departmental Special Assistance Scheme under the University Grants Commission, New Delhi (SAP-DRS-III, No. 540/12/DRS/2013) for financial support.

ИЗВОД

ТЕРМОДИНАМИКА РАСТВАРАЊА У ВОДЕНИМ РАСТВОРИМА ГЛИЦИНА СА НАТРИЈУМ-ПИРУВАТОМ У ТЕМПЕРАТУРНОМ ОПСЕГУ 298,15–313,15 К

BIJAN KUMAR PANDIT, ABHIJIT SARKAR AND BISWAJIT SINHA

Department of Chemistry, University of North Bengal, Darjeeling-734013, India

Проучавана је термодинамика растварања натријум-пирувата у воденим растворима глицина са становишта интеракција типа растворак–растворак и растворак–растварач. Измерене вредности густине и вискозности раствора су коришћене за процену привидних моларних запремина (ϕ_V^0), парцијалних моларних запремина при бесконачном разблажењу (ϕ_V^0) и *V* коефицијената Jones–Dole једначине, на температурама 298,15, 303,15, 308,15 и 318,15 К и на атмосферском притиску. Присутне интеракције су разматране на следећи начин: преко јон–диполарних интеракција, као и интеракција хидрофобних–хидрофобних и хидрофилних–хидрофобних група. Теорија прелазног стања је примењена у разматрању активационих параметара вискозног тока. Сви приказани резултати указују да су интеракције група типа: јон–хидрофилне и хидрофилне–хидрофилне доминантне у тернарним растворима.

(Примљено 31. октобра, ревидирано 31. децембра 2015, прихваћено 17. фебруара 2016)

REFERENCES

1. B. Sinha, A. Sarkar, P. K. Roy, D. Brahman, *Int. J. Thermophys.* **32** (2011) 2062
2. B. Sinha, P. K. Roy, M. N. Roy, *Acta Chim. Slov.* **57** (2010) 651
3. A. K. Nain, R. Pal, R. K. Sharma, *J. Mol. Liq.* **165** (2012) 154
4. A. K. Nain, R. Pal, *J. Mol. Liq.* **60** (2013) 98
5. A. K. Nain, D. Chand, *J. Chem. Thermodyn.* **41** (2009) 243
6. R. Sadeghi, B. Goodarzi, *J. Mol. Liq.* **141** (2008) 62
7. A. Ali, S. Hyder, S. Sabir, D. Chand, A. K. Nain, *J. Chem. Thermodyn.* **38** (2006) 136
8. Riyazuddin, M. A. Usmani, *Thermochim. Acta* **532** (2012) 36
9. R. Palani, Y. Reeginal, *J. Indian Chem. Soc.* **87** (2010) 265
10. D. Brahman, B. Sinha, *J. Chem. Eng. Data* **56** (2011) 3073
11. M. N. Roy, B. Sinha, *J. Chem. Eng. Data* **51** (2006) 590
12. M. N. Roy, B. Sinha, *J. Mol. Liq.* **133** (2007) 89
13. B. Sinha, V. K. Dakua, M. N. Roy, *J. Chem. Eng. Data* **52** (2007) 1768
14. D. O. Masson, *Philos. Mag.* **8** (1929) 218
15. R. K. Wadi, P. Ramasami, *J. Chem. Soc. Faraday Trans.* **93** (1997) 243
16. T. S. Banipal, D. Kaur, P. K. Banipal, *J. Chem. Eng. Data* **49** (2004) 1236
17. K. Belibagli, E. Agrancı, *J. Solution Chem.* **19** (1990) 867
18. H. S. Harned, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd ed., Reinhold Publishing Corporation, New York, 1964
19. F. J. Millero, in *Water and Aqueous Solutions: Structure, Thermodynamics, and Transport Processes*, R. A. Horne, Ed., Wiley–Interscience, New York, 1972
20. M. L. Parmer, D. S. Banyal, *Indian J. Chem., A* **44** (2005)
21. L. G. Hepler, *Can. J. Chem. Thermodyn.* **47** (1969) 4617
22. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **37** (2005) 37



23. H. L. Friedman, C. V. Krishnan, in *Water: A Comprehensive Treatise*, F. Franks, Ed., Vol. 3, Plenum Press, New York, 1973, Ch. 1
24. R. Bhatt, J. C. Ahluwalia, *J. Phys. Chem.* **89** (1985) 1099
25. G. Jones, M. Dole, *J. Am. Chem. Soc.* **51** (1929) 2950
26. B. Sinha, P. K. Roy, B. K. Sarkar, D. Brahman, M. N. Roy, *J. Chem. Thermodyn.* **42** (2010) 380
27. D. Feakins, D. J. Freemantle, K. J. Lawrence, *J. Chem. Soc., Faraday Trans.* **70** (1974) 795
28. S. Glasstone, K. Laidler, H. Eyring, *The Theory of Rate Processes*, McGraw–Hill, New York, 1941
29. A. Chatterjee, B. Das, *J. Chem. Eng. Data* **51** (2006) 1352
30. M. Natarajan, R. K. Wahi, H. C. Gour, *J. Chem. Eng. Data* **35** (1990) 87
31. R. H. Stokes, R. Miles, *International Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon, New York, 1965
32. S. S. Dhondge, D. W. Deshmukh, L. J. Paliwal, *J. Chem. Thermodyn.* **58** (2013) 140
33. C. Zhao, P. Ma, J. Li, *J. Chem. Thermodyn.* **37** (2005) 37.