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Viscosity *B*-Coefficients and Thermodynamics of Viscous Flow of *l*-arginine /*l*-histidine in Aqueous-Gentamicin Sulphate at Temperatures from 298.15 to 318.15 K

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Abstract

The viscosities, η of l-arginine and l-histidine in aqueous-gentamicin sulphate (1% and 2% gentamicin sulphate in water) solvents have been measured at temperatures from 293.15 K to 318.15 K and at pressure, p= 101 kPa. The η data have been used to calculate Falkenhagen coefficient, *A*, Jones-Dole coefficient, *B*, transfer values of B-coefficients, B_{tr}, free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{o\#}$ and solute, $\Delta\mu_2^{o\#}$, enthalpies, $\Delta H^{o\#}$ and entropies, $\Delta S^{o\#}$ of activation of viscous flow per mole of solute. The results have been interpreted in terms of prevailing solute-solute and solute-solvent interactions. These amino acids act as structure maker in aqueous-gentamicin sulphate solvents.

Keywords: Viscosity; Amino acids; Gentamicin sulphate; B-coefficients; molecular interactions; Thermodynamic of viscous flow

Introduction

Drug-macromolecule interactions in aqueous medium are of great significance in view of thermodynamic behaviour in biochemical processes such as transport of drug to target, binding with other molecules, etc. in the physiological media [1,2]. The interactions between drugs and proteins play a major role in all metabolic pathways which are occurring in the interior of human body and this phenomenon involves a complex mechanism [3]. Due to complex conformational structure of proteins, aqueous solutions of amino acids are of great interest for better understanding of drug-protein interactions because their structures can be altered easily and the contribution of side chain groups of amino acid/peptide chain can be a leading factor in deciding the type and extent of interactions [4]. Therefore, to have deeper knowledge of the mechanism of drug action, here we have measured the viscosities of *l*-arginine and *l*-histidine in aqueous gentamicin sulphate solutions.

Gentamicin sulphate is a complex mixture of broad-spectrum aminoglycoside antibiotic produced by Micromonospora purpurea, is widely used in treatment of serious life-threatening bacterial infections, especially in burns wounds, as it possesses good spectrum of activity against gram-negative bacteria. It inhibits bacterial growth by constraining protein synthesis [5,6]. The use of gentamicin is associated with toxic side-effects and great risk of human health as it can cause damage to cranial nerves, resulting in permanent hearing loss [7]. *l*-histidine, an essential amino acid and a semi-essential or conditionally essential amino acid namely *l*-arginine [8]. *l*-arginine is an amino acid which is capped by positively charged guanidinium group even in most basic environments and consists of a 3-carbon aliphatic straight chain [9]. The imidazole ring, as a histidine moiety, functions as a ligand towards transition metal ions in a variety of biologically important iron-heme systems and some metalloproteins [10]. Many workers have reported the thermodynamics data of amino acids + drug in water [11-14] but no work has been reported on the systems under investigation.

In continuation of our ongoing research work on physicochemical studies of amino acids in aqueous-drug media [15-19], here we present the study on the transport behaviour of amino acids in aqueous-gentamicin sulphate by measuring viscosities, η of solutions of *l*-arginine/*l*-histidine in aqueous-gentamicin sulphate (1% and 2% gentamicin sulphate in water) solvents at temperatures, 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15

K and at pressure, p = 101 kPa. Using the experimental data, The η data have been used to calculate Falkenhagen coefficient, A, Jones-Dole coefficient, B, transfer values of B-coefficients, B_{tr}, free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^{o\#}$ and solute, $\Delta\mu_2^{o\#}$, enthalpies, $\Delta H^{o\#}$ and entropies, $\Delta S^{o\#}$ of activation of viscous flow per mole of solute. The results have been interpreted in terms of prevailing solute-solute and solute-solvent interactions. The sign of dB/dT are used to infer the structure-making and structure breaking ability of the amino acids.

Experimental

Chemicals

The specifications (Table 1) of the chemicals used in the present work are: *l*-arginine (mass fraction purity > 0.99), *l*-histidine (mass fraction purity > 0.99) procured from SRL India were used after recrystallization from ethanol-water mixture and dried in vacuum over P_2O_5 at room temperature (308.15 K) for 72 h. The drug gentamicin sulphate (SRL, India, mass fraction purity > 0.99) was used as received, i.e., without further purification except for drying in oven for 24 h. The purity of the purified chemicals was checked by performing gas chromatography analysis using Shimadzu Gas Chromatograph (Model: GC-2010 Plus). The triply distilled water with specific conductance less than 1×10−6 S·cm^{-1} was used for preparing different concentrations of gentamicin sulphate solutions (1% and 2% gentamicin sulphate in water, w/w) and these solutions were used as solvents to prepare amino acid solutions of different concentrations. The solutions were prepared afresh on molality basis, for which an electronic balance (Model: GR-202R, AND, Japan) with a precision of ±0.01 mg was used and stored in special airtight bottles to avoid exposure to air and evaporation. The uncertainty in the molality of the solutions was estimated within ±1×10−4 mol·kg^{-1}.

Table 1: Specification of chemicals.

Chemical Name (CAS number)	Provenance	Initial Purity	Purification Method	Final Mass Fraction Purity	Analysis Method
l-Arginine (74-79-3)	SRL, India	> 0.99	Re-crystallization	> 0.998	GC[a]
l-Histidine (71-00-1)	SRL, India	> 0.99	Re-crystallization	> 0.996	GC
Gentamicin sulphate (1405-41-0)	SRL, India	> 0.99[b]	Used as received	> 0.99[b]	–

[a]GC: Gas chromatography; [b]As stated by the manufacturer

Viscosity measurements

The viscosity measurements have been done by using a Microviscometer (Anton Paar, Lovis 2000M) at different temperatures (T/K= 293.15, 298.15, 303.15, 308.15, 313.15 and 318.15), and atmospheric pressure, p=101 kPa. The rolling ball principle is used in the measurement of viscosities, and the viscosity values are calculated using the following relation

$$\eta = \mathrm{K}\left(\rho_{ball} - \rho\right)t \quad (1)$$

where K is a constant of the viscometer, ρ_{ball} is the density of rolling ball, ρ is the density of the sample, and t is the averaged rolling time of the sample. The standard uncertainty in viscosity measurements was found within ± 1%. A detailed description of the instrument had been mentioned in our earlier study [15].

Results

The experimental values of viscosity, η of solutions of *l*-arginine and *l*-histidine in aqueous-gentamicin sulphate solvents as functions of amino acid concentration and temperature have been listed in Table 2. A close persual of the Table 2 shows that the values of viscosity decrease with rise in temperature at a particular concentration but increases with increase in concentration for all the systems studied.

Table 2: Viscosities, 103·η/N·s·m^{-2} of solutions of *l*-arginine/*l*-histidine in aqueous-gentamicin sulphate (1% and 2% gentamicin sulphate in water, w/w) solvents as functions of molality, m of *l*-arginine/*l*-histidine at temperatures T=(293.15-318.15) K and at pressure, p = 101 kPa.

m (mol·kg^{-1})	T/K					
	293.15	298.15	303.15	308.15	313.15	318.15
***l*- Arginine in 1% Aqueous-Gentamicin Sulphate**						
0	1.0265	0.9112	0.8151	0.7343	0.6658	0.6086
0.025	1.0385	0.9216	0.8242	0.7423	0.6729	0.615
0.0499	1.0503	0.9317	0.8327	0.7496	0.679	0.6202
0.075	1.0622	0.9417	0.8412	0.7567	0.685	0.6253
0.1	1.074	0.9517	0.8495	0.7637	0.6909	0.6302
0.1251	1.0858	0.9616	0.8579	0.7707	0.6968	0.6351
0.15	1.0976	0.9715	0.8662	0.7776	0.7025	0.6399

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0.1752	1.1095	0.9814	0.8744	0.7846	0.7083	0.6447
0.1999	1.1214	0.9913	0.8827	0.7915	0.714	0.6495
***l*-Arginine in 2% Aqueous-Gentamicin Sulphate**						
0	1.0592	0.9391	0.8391	0.7547	0.6835	0.6243
0.025	1.0701	0.9485	0.8473	0.7619	0.6899	0.63
0.05	1.082	0.9585	0.8559	0.7691	0.6961	0.6353
0.075	1.0942	0.9688	0.8646	0.7764	0.7023	0.6405
0.1	1.1064	0.9791	0.8733	0.7837	0.7084	0.6456
0.125	1.1188	0.9894	0.8819	0.7909	0.7145	0.6506
0.15	1.1312	0.9999	0.8907	0.7982	0.7206	0.6557
0.175	1.1435	1.0102	0.8993	0.8056	0.7266	0.6608
0.2	1.1562	1.0207	0.908	0.8128	0.7326	0.6657
***l*-Histidine in 1% Aqueous-Gentamicin Sulphate**						
0	1.0265	0.9112	0.8151	0.7343	0.6658	0.6086
0.02	1.037	0.9203	0.8231	0.7414	0.6721	0.6143
0.0399	1.0476	0.929	0.8302	0.7474	0.6772	0.6185
0.06	1.0584	0.9379	0.8376	0.7533	0.682	0.6223
0.0799	1.0691	0.9465	0.8448	0.7592	0.6867	0.6259
0.1	1.08	0.9554	0.8519	0.765	0.6912	0.6294
0.1201	1.0906	0.9642	0.859	0.7706	0.6957	0.633
0.14	1.1013	0.973	0.866	0.7762	0.7001	0.6364
0.1601	1.1122	0.9817	0.873	0.7818	0.7045	0.6399
***l*-Histidine in 2% Aqueous-Gentamicin Sulphate**						
0	1.0592	0.9391	0.8391	0.7547	0.6835	0.6243
0.02	1.0694	0.948	0.8469	0.7616	0.6897	0.6299
0.04	1.0805	0.9571	0.8546	0.768	0.695	0.6343
0.0599	1.0915	0.9662	0.8622	0.7741	0.6999	0.6383
0.08	1.1027	0.9755	0.8698	0.7803	0.7049	0.6422
0.0999	1.114	0.9847	0.8773	0.7864	0.7098	0.646
0.12	1.1253	0.994	0.8847	0.7923	0.7146	0.6497
0.1399	1.137	1.0034	0.8922	0.7983	0.7193	0.6534
0.16	1.1484	1.0126	0.8997	0.8043	0.7239	0.6571

Analysis of viscosity data

The relative viscosities of *l*-arginine and *l*-histidine in aqueous-gentamicin sulphate solutions were analyzed by using Jones-Dole equation [20], which is used to calculate *A*- and *B*-coefficients of viscosity

$$\eta_r = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad (2)$$

where η_r is the relative viscosity of the solution, η and η_o are the viscosities of solution and the solvent (aqueous-gentamicin sulphate), respectively; and *A* and *B* are the Falkenhagen [21,22] and Jones-Dole coefficients, respectively. The intercept *A* is an indicative of solute-solute interactions [23] while *B*-coefficient delivers information regarding the solvation of ions and their effects on the solvent structure in the environment of solute particles [24]. The values of *A* can be calculated theoretically but are every so often ignored in case of non-electrolytes due to their very small magnitude. The coefficients, *A* and *B* have been obtained as the intercept and slope, respectively from plots of $[(\eta_r - 1)/m^{1/2}]$ *vs.* $m^{1/2}$, which will be conferred in terms of solute-solute and solute-solvent interactions. The plots were found almost linear for amino acids in water and in aqueous gentamicin sulphate (Figures 1&2) and the values of *A*- and *B*-coefficients for amino acids in water and in aqueous gentamicin sulphate along with the standard deviations of linear regression, σ are reported in Table 3.

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Table 3: Falkenhagen coefficient, *A*, Jones-Dole coefficient, *B*, standard deviations of linear regression, *σ*, free energies of activation of viscous flow per mole of solvent, $\Delta\mu_1^{\circ\#}$, and per mole of solute, $\Delta\mu_2^{\circ\#}$ for *l*-arginine/*l*-histidine in aqueous and aqueous-gentamicin sulphate (1% and 2 % gentamicin sulphate in water, w/w) solvents at different temperatures.

Property	T/K					
	293.15	298.15	303.15	308.15	313.15	318.15
***l*-Arginine in water [17]**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	0.0133 ± 0.0005	0.0135 ± 0.0002	0.0144 ± 0.0003	0.0156 ± 0.0003	0.0174 ± 0.0003	0.0202 ± 0.0003
B /(kg·mol^{-1})	0.4305 ± 0.0014	0.4029 ± 0.0006	0.3724 ± 0.0008	0.3406 ± 0.0008	0.3069 ± 0.0008	0.2718 ± 0.0008
10·σ for equation (2)	0.0037	0.0016	0.0019	0.0022	0.0022	0.0021
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.29	9.16	9.04	8.93	8.83	8.74
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	590.68	561.91	527.77	490.48	448.9	403.86
***l*-Arginine in 1% aqueous-gentamicin sulphate**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	0.0013 ± 0.0003	0.0046 ± 0.0002	0.0080 ± 0.0002	0.0118 ± 0.0003	0.0158 ± 0.0004	0.0208 ± 0.0002
B /(kg·mol^{-1})	0.4587 ± 0.0008	0.4294 ± 0.0008	0.3969 ± 0.0007	0.3630 ± 0.0009	0.3269 ± 0.0004	0.2894 ± 0.0005
10·σ for equation (2)	0.002	0.002	0.0019	0.0023	0.0011	0.0013
B_{tr} /(kJ·mol^{-1})	0.0282	0.0265	0.0245	0.0223	0.02	0.0176
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.37	9.24	9.11	9	8.9	8.81
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	624.65	594.38	558.25	518.57	474.48	426.71
***l*-Arginine in 2% aqueous-gentamicin sulphate**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	-0.0116 ± 0.0003	-0.0087 ± 0.0003	-0.0046 ± 0.0003	-0.0011 ± 0.0002	0.0040 ± 0.0003	0.0087 ± 0.0004
B /(kg·mol^{-1})	0.4829 ± 0.0009	0.4537 ± 0.0008	0.4213 ± 0.0008	0.3874 ± 0.0007	0.3510 ± 0.0010	0.3130 ± 0.0012
10·σ for equation (2)	0.0024	0.0022	0.0021	0.0018	0.0026	0.0031
B_{tr} /(kg·mol^{-1})	0.0524	0.0508	0.0489	0.0467	0.0441	0.0412
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.46	9.33	9.2	9.09	8.98	8.89
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	653.03	623.53	588.35	549.49	505.67	457.88
***l*-Histidine in water [17]**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	0.0128 ± 0.0002	0.0159 ± 0.0004	0.0196 ± 0.0003	0.0237 ± 0.0002	0.0285 ± 0.0002	0.0340 ± 0.0005
B /(kg·mol^{-1})	0.5016 ± 0.0008	0.4515 ± 0.0012	0.3975 ± 0.0011	0.3404 ± 0.0008	0.2819 ± 0.0006	0.2204 ± 0.0018
10·σ for equation (2)	0.0018	0.0029	0.0026	0.0018	0.0015	0.0042
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.29	9.16	9.04	8.93	8.83	8.74
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	686.73	628.57	562.78	490.14	413.04	329.15
***l*-Histidine in 1% aqueous-gentamicin sulphate**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	-0.0022 ± 0.0003	0.0030 ± 0.0003	0.0096 ± 0.0006	0.0173 ± 0.0005	0.0251 ± 0.0007	0.0332 ± 0.0006

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B /(kg·mol^{-1})	0.5268 ± 0.0009	0.4756 ± 0.0011	0.4203 ± 0.0019	0.3618 ± 0.0015	0.3015 ± 0.0023	0.2380 ± 0.0019
10·σ for equation (2)	0.0021	0.0027	0.0045	0.0035	0.0055	0.0045
B_{tr} /(kg·mol^{-1})	0.0252	0.0241	0.0228	0.0214	0.0196	0.0176
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.37	9.24	9.11	9	8.9	8.81
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	716.02	657.26	590.68	516.9	438.31	352.5
***l*-Histidine in 2% aqueous-gentamicin sulphate**						
A /(kg$^{1/2}$·mol$^{-1/2}$)	-0.0099 ± 0.0006	-0.0038 ± 0.0003	0.0036 ± 0.0005	0.0109 ± 0.0005	0.0189 ± 0.0006	0.0275 ± 0.0006
B /(kg·mol^{-1})	0.5500 ± 0.0019	0.4986 ± 0.0011	0.4431 ± 0.0017	0.3844 ± 0.0018	0.3239 ± 0.0020	0.2601 ± 0.0021
10·σ for equation (2)	0.0046	0.0026	0.004	0.0042	0.0047	0.005
B_{tr} /(kg·mol^{-1})	0.0483	0.0471	0.0455	0.044	0.042	0.0398
$\Delta\mu_1^{\circ\#}$ /(kJ·mol^{-1})	9.46	9.33	9.2	9.09	8.98	8.89
$\Delta\mu_2^{\circ\#}$ /(kJ·mol^{-1})	742.41	684.29	618.23	545.27	467.24	382.1

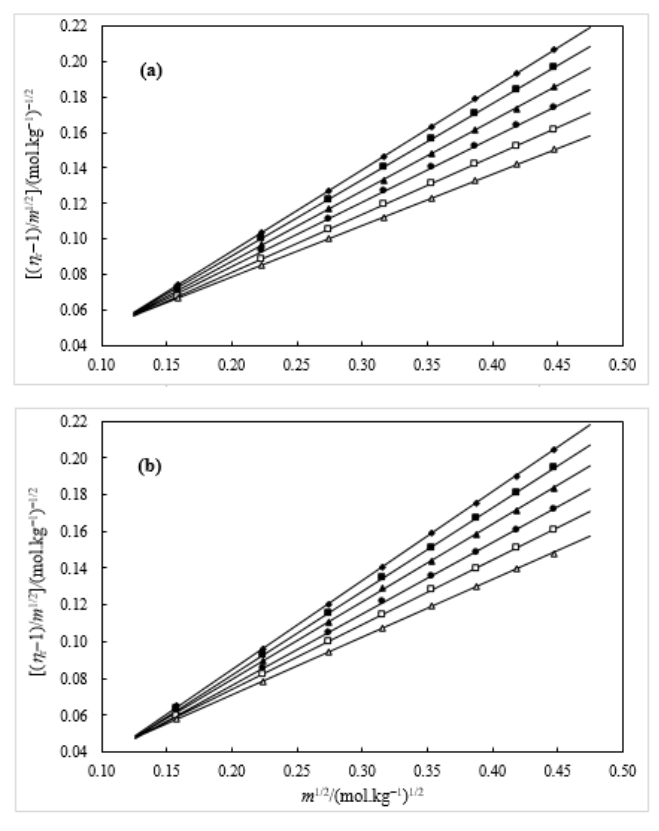

Figure 1: Variations of $[(\eta_r-1)/m^{1/2}]$ *vs.* $m^{1/2}$ of l-arginine in (a) 1% aqueous-gentamicin sulphate and (b) 2% aqueous-gentamicin sulphate at temperatures, T/K = 293.15, ♦; T/K = 298.15, ■; T/K = 303.15, ▲; T/K = 308.15, ●; T/K = 313.15, □; T/K = 318.15, Δ. The points represent experimental values and lines represent values calculated from equation (2).

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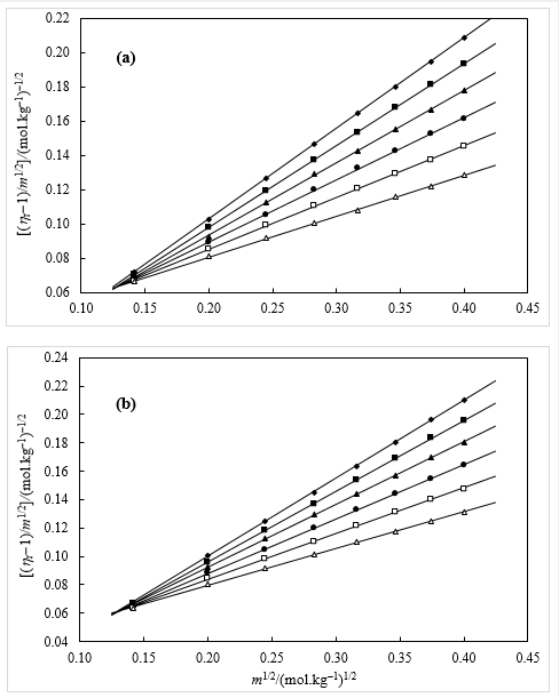

Figure 2: Variations of $[(\eta_r-1)/m^{1/2}]$ *vs.* $m^{1/2}$ of l-histidine in (a) 1% aqueous-gentamicin sulphate and (b) 2% aqueous-gentamicin sulphate at temperatures, T/K = 293.15, ♦; T/K = 298.15, ■; T/K = 303.15, ▲; T/K = 308.15, ●; T/K = 313.15, □; T/K = 318.15, Δ. The points represent experimental values and lines represent values calculated from equation (2).

A close perusal of Table 3 points out that the values of *A*-coefficients are very close to zero which specifies weak solute-solute interactions. However, the positive *B*-coefficients indicate the presence of strongly hydrated solutes known as kosmotropes and presence of strong solute-solvent interactions in these solutions. Large and positive *B*-coefficients values, which increase with increasing concentration of gentamicin sulphate at investigated temperatures, promotes the structure making effect of the drug, i.e., contraction of solvent molecules around solute molecules (amino acid). *B*-coefficients increases with increasing concentration of gentamicin sulphate, the purpose may be that the friction increases to inhibit water flow at increased gentamicin sulphate concentration.

Thus, the inference drawn from the values of coefficients *A* and *B* recommend existence of stronger solute-solvent interactions which further advocates the existence of strong ionic-hydrophilic and hydrophilic-hydrophilic interactions. Further, the values of *B* in 1% aqueous-gentamicin sulphate solution are smaller than those in 2% aqueous-gentamicin sulphate solution. In higher composition of hydrotropic agents, the increase in *B* might be due to formation of clathrates by liquid aggregates of water + gentamicin sulphate solvent around amino acid molecules. This brings about a strong association of the molecules and growth of van der Waals forces into significant factors which lead to the formation of clathrate [25].

To gather more information about the structure-making or structure-breaking tendency of the solute in different solvent media another important property, the temperature derivatives of *B*-coefficient, (dB/dT) can be taken into consideration [21,22,26]. According to Eyring's theory of viscosity [27], if $dB/dT < 0$ the viscous flow activation energy for the solution is greater than for the solvent, i.e., the solute is kosmotrope and in the other case the solute is chaotrope. One property for characterizing the effect of ion hydration is kosmotropicity [24]. The sign of dB/dT shows that a net balance occurs between the structure stabilization carried out by the hydrophobic groups and the disruption by hydrophilic groups. In general, the dB/dT is negative for structure-maker and positive for structure-breaker solutes in solution. The negative dB/dT values in the present system specify that all these amino acids act as structure-maker in these aqueous-gentamicin sulphate solvents.

The transfer values of *B*-coefficients, B_{tr} from water to aqueous-gentamicin sulphate have also been calculated using the following relation [28,29].

$$B_{\mathrm{tr}} = B_{\text{Aqueous-gentamicin sulphate}} - B_{\mathrm{Water}} \quad (3)$$

The values B_{water} of have been taken from our earlier study [17]. The B_{tr} values are included in Table 3. A perusal of Table 3 reveals that values are positive for both the amino acids in aqueous-gentamicin sulphate solvents and increase with increase in the concentration of gentamicin sulphate. The positive B_{tr} values indicate the dominance of ionic-hydrophilic interactions between zwitterionic center (NH_3^+ and COO^-) of *l*-arginine/*l*-histidine molecules and the polar sites of gentamicin sulphate molecules

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[29,30]. The B_{tr} values increase with a rise of temperature which may be due to filling of cavities of water by amino acid molecules to a profound extent [31]. The B_{tr} values are greater in case of *l*-histidine than those in *l*-arginine (Table 3). It can be said that as the size of the solute (amino acid) increases or its structure becomes more complex, therefore it is increasingly difficult to accommodate larger solute molecule (*l*-histidine in this case) in an ordered solvent environment [31].

Thermodynamic parameters of activation of viscous flow

Thermodynamic parameters of the viscous flow can be obtained from the viscosity *B*-coefficients. The viscosity data were analyzed on the basis of extended Eyring transition state theory for relative viscosity of amino acid solutions as suggested by Feakins et al. [32,33], using equation (4) to calculate the various thermodynamic activation parameters (Gibbs energy, enthalpy and entropy) of viscous flow for the amino acids

$$B = \frac{[(\overline{V}_1^{\circ} - \overline{V}_2^{\circ}) + \overline{V}_1^{\circ}(\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#})/RT]}{1000} \quad (4)$$

where $\overline{V}_1^{\circ}$ is the apparent (partial) molar volume of the solvent (aqueous-gentamicin sulphate) and $\overline{V}_2^{\circ}$ $(=V_{\phi}^{\circ})$ is the limiting apparent (partial) molar volume of the solute, respectively, $\Delta\mu_1^{\circ\#}$ and $\Delta\mu_2^{\circ\#}$ are the free energies per mole for the solvent and solute, respectively, and R is the universal gas constant. The values of $\overline{V}_1^{\circ}$ and $\overline{V}_2^{\circ}$ have been calculated from density data reported in our earlier study [17]. According to Eyring viscosity model [27], free energy per mole of activation of viscous flow of solvent, $\Delta\mu_1^{\circ\#}$ can be calculated using the viscosity relation

$$\Delta\mu_1^{\circ\#} = RT\ln(\eta\overline{V}_1^{\circ}/hN) \quad (5)$$

where h is Planck's constant and N is Avogadro number and R is the universal gas constant. On rearranging equation (4) $\Delta\mu_2^{\circ\#}$, can be calculated by

$$\Delta\mu_2^{\circ\#} = \Delta\mu_1^{\circ\#} + \left(\frac{RT}{\overline{V}_1^{\circ}}\right)\left[1000B - (\overline{V}_1^{\circ} - \overline{V}_2^{\circ})\right] \quad (6)$$

The calculated values of $\Delta\mu_1^{\circ\#}$ and $\Delta\mu_2^{\circ\#}$ are specified in Table 3 and will be discoursed in terms of solute-solute and solute-solvent interactions.

The values of $\Delta\mu_1^{\circ\#}$ and $\Delta\mu_2^{\circ\#}$ (Table 3) are positive and decrease with increasing temperature. According to transition state theory of relative viscosity, $(\Delta\mu_2^{\circ\#} - \Delta\mu_1^{\circ\#})$ values indicate the change in activation energy when at infinite dilution one mole of solvent is replaced by one mole of solute. Therefore, if $\Delta\mu_2^{\circ\#} > \Delta\mu_1^{\circ\#}$, as observed, the interactions between *l*-arginine/*l*-histidine and solvent (water and aqueous-gentamicin sulphate) molecules in the ground state are stronger than in the transition state, i.e., ground state is the favored state from the free energy point of view [34]. Hence in the transition state, the solvation of the solute molecules is less preferred in free energy terms. The values of $\Delta\mu_2^{\circ\#}$ signify the capability to form the transition state via the solute-solvent interactions from the ground state of the solvent. Decrease in $\Delta\mu_2^{\circ\#}$ with increase in temperature shows that higher temperature is more suited for the formation of transition state. Also, the values of $\Delta\mu_1^{\circ\#}$ and $\Delta\mu_2^{\circ\#}$ for these amino acids in aqueous-gentamicin sulphate solvents are larger than those in water and these values increase with increase in concentration of gentamicin sulphate in solution (Table 3).

It has been reported [22,26], $\Delta\mu_2^{\circ\#} > \Delta\mu_1^{\circ\#}$ for solutes with positive viscosity *B*-coefficients indicates that in ground state, interactions between amino acids and solvent molecules are much stronger than those in the transition state, i.e., due to cleavage and distortion of the intermolecular bonds, the formation of transition state is much less favored in the presence of the drug molecule. Also, the higher the $\Delta\mu_2^{\circ\#}$ value, the higher the structure-making tendency of the solute. Our results indicate that the *l*-arginine in aqueous drug solvent is the best structure making. Thus, the conclusions drawn from $\Delta\mu_2^{\circ\#}$ are in agreement with those drawn from the trends of *B* and B_{tr} values and further supports our earlier results from volumetric and ultrasonic properties of these systems [35]. The enthalpies per mole, $\Delta H^{\circ\#}$ and entropies per mole, $\Delta S^{\circ\#}$ of activation of viscous flow of solute have been calculated using the following relation

$$\Delta\mu_2^{\circ\#} = \Delta H^{\circ\#} - T\Delta S^{\circ\#} \quad (7)$$

The values of $\Delta S^{\circ\#}$ and $\Delta H^{\circ\#}$ are calculated from the slopes and intercepts of linear fit of $\Delta\mu_2^{\circ\#}$ *vs.* T and the results are included in Table 4. The process of dissolution of solute in the ground state solvent to form a solution is accompanied by free energy changes along with entropy and enthalpy changes [27,33,34]. The positive values for both $\Delta H^{\circ\#}$ and $\Delta S^{\circ\#}$ of activation viscous flow (Table 4) demonstrates that the association process is endothermic in nature and more energy consuming. The parameter $\Delta H^{\circ\#}$ gives information about the solute-solvent interactions, whereas $\Delta S^{\circ\#}$ provides evidence of structural order of the species in solution [35,36]. When a solute is introduced into the solvent, the interaction between solvent molecules (aqueous-gentamicin sulphate, in this case) must be broken to accommodate the former, which is found to be an endothermic process. Once the encounter complex has been formed, the interacting partners essentially rearrange their relative orientations in pursuit of the optimal binding configuration.

Moreover, *l*-arginine -gentamicin sulphate interaction is more ordered than *l*-histidine-gentamicin sulphate system as pointed out by $\Delta S^{\circ\#}$ values. The sign of $\Delta S^{\circ\#}$ reproduces the field-effect on various molecular processes ensuing in the liquid. It is interesting to note that for the amino acids under study, the enthalpies of activation $\Delta H^{\circ\#}$ and entropies of activation $\Delta S^{\circ\#}$ of viscous flow are positive signifying that the formation of the transition state is linked with solute-solvent bond making in transition state, as a result the formation of activated complex becomes easier. The results can be also viewed in terms of the geometrical fit of solute species in an ordered solvent [37]. The values of both $\Delta H^{\circ\#}$ and

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$\Delta S^{\circ\#}$ are greater in case of *l*-histidine than those in *l*-arginine (Table 4). It can be argued that as the size of the solute (amino acid) increases or its structure becomes more complex, therefore it is increasingly difficult to accommodate larger solute molecule (*l*-histidine in this case) in an ordered solvent environment. These results are in the accordance of the conclusion drawn earlier.

Table 4: Enthalpies, $\Delta H^{\circ\#}$ and entropies, $\Delta S^{\circ\#}$ of activation of viscous flow for *l*-arginine//*l*-histidine in water and aqueous-gentamicin sulphate (1% and 2% gentamicin sulphate in water, w/w) solvents.

System	$\Delta H^{\circ\#}$ (kJ·mol^{-1})	$\Delta S^{\circ\#}$ (kJ·mol^{-1}K^{-1})	R^2
l-Arginine in water [17]	2792.7	7.49	0.994
l-Arginine in 1% aqueous-gentamicin sulphate	2958.97	7.94	0.994
l-Arginine in 2% aqueous-gentamicin sulphate	2952.57	7.82	0.993
l-Histidine in water [17]	4897.3	14.33	0.996
l-Histidine in 1% aqueous-gentamicin sulphate	4995.92	14.56	0.996
l-Histidine in 2% aqueous-gentamicin sulphate	4984.5	14.43	0.996

Conclusion

In the present article, from the experimental η data of the solutions of *l*-arginine /*l*-histidine in aqueous-gentamicin sulphate (1% and 2% of gentamicin sulphate, w/w in water), different viscometric parameters, *viz*., Falkenhagen Coefficient, *A*, Jones-Dole coefficient, *B*, d*B*/d*T*, transfer values of *B*-coefficients, B_{tr}, Gibbs energy of activation per mole of the solvent, $\Delta\mu_1^{\circ\#}$ and solute, $\Delta\mu_2^{\circ\#}$; enthalpies, $\Delta H^{\circ\#}$ and entropies, $\Delta S^{\circ\#}$ of activation of viscous flow of solute per mole were calculated, with an objective to understand the solute-solute and solute-solvent interactions. The analysis and interpretation of the obtained results indicate that there exist strong solute-solvent interactions in these systems, which increase with increase in gentamicin sulphate concentration. The predominance of solute-solvent interactions in *l*-arginine and aqueous-gentamicin sulphate system can be related to its high capacity to donate hydrogen bonds. The negative sign of d*B*/dT confirmed that *l*-arginine /*l*-histidine act as structure-makers in these aqueous-gentamicin sulphate solvents.

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