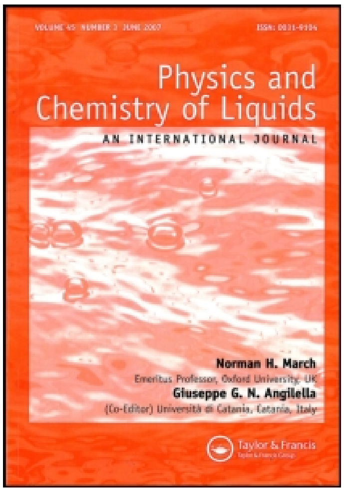

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Physics of glycine interactions with halide salts of alkali metals (group I) determined with density, viscosity, and activation energy in aqueous solutions at 310.15 K

Man Singh[a]; Maneesha Pandey[a]
[a] Chemistry Research Lab., Deshbandh College, University of Delhi, New Delhi-110 019, India

To cite this Article Singh, Man and Pandey, Maneesha(2008) 'Physics of glycine interactions with halide salts of alkali metals (group I) determined with density, viscosity, and activation energy in aqueous solutions at 310.15 K', Physics and Chemistry of Liquids, 46: 2, 119 — 139

To link to this Article: DOI: 10.1080/00319100600682599

URL: http://dx.doi.org/10.1080/00319100600682599

Physics and Chemistry of Liquids
Vol. 46, No. 2, April 2008, 119–139

Taylor & Francis
Taylor & Francis Group

Physics of glycine interactions with halide salts of alkali metals (group I) determined with density, viscosity, and activation energy in aqueous solutions at 310.15 K

MAN SINGH* and MANEESHA PANDEY

Chemistry Research Lab., Deshbandh College, University of Delhi,
New Delhi – 110 019, India

(*Received 22 February 2006; in final form 10 March 2006*)

Density, ρ (10^3 kg m^{-3}) and viscosity, η (10^{-1} kg m^{-1} s^{-1}) for 0.01–0.33 mol kg^{-1} aqueous lithium to cesium chloride and iodide salts, and of 0.01–0.10 mol kg^{-1} glycine (Gly) in 0.01 mol kg^{-1} aqueous salts have been measured at pH 7. The apparent molal volume ($V_\phi/10^{-6}$ m^3 mol^{-1}) was calculated from the ρ values, and the η values were fitted in the extended Jones–Dole equation for B (kg mol^{-1}) and D (kg mol^{-1})^2, and Jones–Dole coefficients at infinite dilution ($m \rightarrow 0$). The limiting apparent molal volume V_ϕ^0, referred to as the partial molal volume ($\bar{V}_2^0$, binary) of the solute at $m \rightarrow 0$, was obtained from the regression of the V_ϕ values, illustrates the solute–solvent and solute–solute interactions. The $\bar{V}_1^0$ of water was calculated from ρ, and $\bar{V}_3^0$ for Gly in aqueous salts from ρ values for Gly systems. The free energy of activation of the viscous flow ($\Delta\mu_1^{0*}$ (kJ mol^{-1})) per mol of water was calculated from $\bar{V}_1^0$ and η^0; and $\Delta\mu_2^{0*}$ (for aqueous salts) from their B coefficients, $\bar{V}_2^0$, and $\bar{V}_1^0$; while $\Delta\mu_3^{0*}$ (for Gly in aqueous salts) from their B coefficients, $\bar{V}_3^0$, and $\bar{V}_2^0$ values respectively. The $\Delta\mu_1^{0*}$, $\Delta\mu_2^{0*}$, and $\Delta\mu_3^{0*}$ are the activation energies for structural changes, and the B coefficients associated with transition state theory explain the positive transitions of interacting molecules in the systems. The B and $\Delta\mu_2^{0*}$ values are negative, inferring the water structure breaking action, the limiting density ρ^0, and the viscosity η^0 which elucidates ion–water, ion–Gly, and ion–water–Gly interactions. S_d and D elucidate the ion–ion interactions and the composition effect, and B the size of hydrated ion and the ion–Gly associations. The ρ^0 and B values increase with composition except for RbCl, and B of Gly are higher for RbCl and CsI and ρ^0 for RbCl and NaI have been rationalized with the shell size and the filled and the unfilled 'd' orbital. Excess viscosity (η^E) and excess viscosity function (Y^E) were calculated from η for compositional effects on ion–ion–water, Gly–ion–ion, Gly–ion–water, Gly–Gly–ion, and Gly–Gly–water interactions.

Keywords: Limiting constants; Structure breaker and maker; Ion–water interaction; Gly–water interaction; Electrostatic interaction

1. Introduction

Physicochemical properties of amino acids in aqueous salt solutions are of current interest for understanding the complexity of biomolecules in the biological processes. Thus, the salts of metals of group IA are of great importance to monitor the processes.

---

*Corresponding author. Email: mansingh50@hotmail.com

Physics and Chemistry of Liquids
ISSN 0031-9104 print/ISSN 1029-0451 online © 2008 Taylor & Francis
DOI: 10.1080/00319100600682599

Although enormous studies on the density and the viscosity of glycine (Gly) for aqueous NaCl and KCl have been made, only a limited number of work on halide salts of Rb^+ and Cs^+ is reported. However, the halide salts are of biophysical, physiological [1], and industrial interests [2,3] and are chosen, while the densities of some salts have been reported but not their viscosities. Long ago, Traube [4] measured the partial molal volumes [5,6] of biomolecules from the densities of sodium and potassium chlorides [7–12]. More so Landolt-Bornstein [3] and Pitzer [5] reviewed the structural interactions of aqueous salts [13–21] from 1976 to 1988. Notably, the $^+NH_3$–CH_2–COO^- of Gly due to N^+ and O^- ionic atoms induce the intra/intermolecular interactions causing torsional forces and disruption of electron distribution forming dipoles, which can stress or strain the solutions depicted by ρ and η data, and thus salt–amino acid interactions are of fundamental significance [22,23] for biochemical sciences. Further, the treatment of transition state theory for such solutions including the partial molal volumes and the viscosity coefficient B together is meant to resolve the structure breaking and making tendencies of the ions and the amino acids. The treatment of activation energies for the structure breaking and making effects of Gly in aqueous salts systems have been of thermodynamic uses to elucidate the linkage with the medium.

2. Experimental

Salts and Gly (AR, Sigma, Merck or Fluka) were used after drying at 110°C for 12 h and then dried *in vacuo* over P_2O_5 at room temperature for a minimum of 24 h, and the dryness was checked with anhydrous $CuSO_4$ salt. Triple distilled water deionized by passing through two Cole-Parmer mixed bed ion exchange column of conductivity less than $6 \times 10^{-7}\,S\,cm^{-1}$, and was used for preparation of solutions w/w.

The densities and the viscosities were measured with a bicapillary pyknometer of $20 \times 10^{-3}\,dm^3$ capacity and a survismeter [24] thermostated to better than ±0.01°C, read by a Beckman thermometer. The temperature was maintained by an electric relay encircuited with a contact thermometer and a 25 W immersion rod along with circulation of cold water by a circulatory pump through a copper coil immersed in the water bath. The solutions in the pyknometer and the survismeter were thermostated for about 30 min and the instruments were calibrated with water and aqueous sodium chloride solutions prepared w/w with 0.01 mg Dhona balance, model 100DS, Indian make. An absolutely dried empty pyknometer was weighed several times for reproducibility in weights with a similar treatment for the flow time with survismeter. The errors in the densities and the viscosities were calculated from the weights and the flow times.

3. Theory

The ρ values were calculated from $w/w_0 + 0.0012(1-(w/w_0))$ relation, where, w and w_0 are weights of the solution and the solvent-filled pyknometer, and the ρ, ρ_0, and 0.0012 are the solution, solvent, and air densities respectively, and $(1-(w/w_0))$ is the buoyancy correction. The V_ϕ is calculated from ρ data as:

$$V_\phi = 1000(\rho_0 - \rho)/m\rho_0\rho + M/\rho \tag{1}$$

where M is the molar mass of the solute; an error in V_ϕ is calculated from $\pm\Delta\rho 1000/m$. The ρ is regressed against m for ρ^0 and slope constant S_d, and V_ϕ *versus* $m^{1/2}$ for salts, V_ϕ *versus* m for Gly, were fitted in the Masson's equation [20] for limiting the apparent molal volume V_ϕ^0, at $m \rightarrow 0$. The ρ^0 and V_ϕ^0 values denote the solute–solvent, while the S_d and S_v slope constants denote the solute–solute interactions [25]. The η is calculated from $\eta = (\rho t)/(\rho_0 \mathrm{t}_0)\eta_0$ and the relative viscosity $\eta_\mathrm{r} = \eta/\eta_0$ relations, where t is the flow time of solution and t_0 of solvent, ρ_0 the density, and η_0 the viscosity of the solvent. Jones–Dole showed a concentration dependence of η_r for dilute electrolytic solutions expressed by empirical equation,

$$\eta = \frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm. \tag{2}$$

Falkenhagen *et al.*, demonstrated large interionic forces with $m^{1/2}$ term, and coefficient A could be calculated from the Deby–Hückel–Onsager equation, and measured the molecular interactions, Jones–Dole coefficient B for solute–solvent interactions. For Gly solutions, a nonelectrolyte, this equation was modified by Phang [30], Martin and Tyrell [31] for aqueous salts, the and coefficient A for nonelectrolyte is almost zero. Thus, an extended Jones–Dole equation is applicable for Gly systems as

$$\eta = \frac{\eta}{\eta_0} = 1 + Bm + Dm^2. \tag{3}$$

Excess viscosity (η^E) were calculated from

$$\eta^\mathrm{E} = \eta - \exp(x_1 \ln \eta_1 + x_2 \ln \eta_2). \tag{4}$$

The x_1 and x_2 mole fractions of the solute and the solvent, the η_1 and η_2 viscosities, and the excess viscosity function (Y^E) was calculated by Redlich–Kister relation [27],

$$Y^\mathrm{E} = x_1 x_2 \sum \eta^\mathrm{E} (1 - 2x_1)^{j-1}. \tag{5}$$

Further, the η data are examined for transition state theory of η_r as per Feakins *et al.*, the B coefficient is fitted as,

$$B = \left(\bar{V}_1^0 - \bar{V}_2^0\right)/1000 - \bar{V}_1^0\left[\left(\Delta\mu_2^{0*} - \Delta\mu_1^{0*}\right)/RT\right]/1000 \tag{6}$$

where the $\bar{V}_1^0$ and $\bar{V}_2^0$ are the partial molal volumes of the solvent and the solute respectively, $\Delta\mu_2^{0*}$ and $\Delta\mu_1^{0*}$ are the contributions per mole of the solute and the solvent to the free energies of activation for the viscous flow. The $\Delta\mu_1^{0*}$ was calculated from

$$\Delta\mu_1^{0*} = RT \ln\left(\frac{\eta_0 \bar{V}_1^0}{hN}\right). \tag{7}$$

The $\Delta\mu_2^{0*}$ from the values of $\Delta\mu_1^{0*}$ as

$$\Delta\mu_2^{0*} = \Delta\mu_1^{0*} - \left(\frac{RT}{\bar{V}_1^0}\right)\left[1000B - \left(\bar{V}_1^0 - \bar{V}_2^0\right)\right]. \tag{8}$$

The $\Delta\mu_2^{0*}$ values are higher than that of $\Delta\mu_1^{0*}$ and tend to vary. An increase in $\Delta\mu_2^{0*}$ predicts the viscous flow and an erratic complex behaviour of the solutes due to the solute–solvent interactions.

4. Results

The ρ^0 values for aqueous NaCl and KCl were compared with literature in table 1 and found a close agreement, regression constants of ρ and η, and η^E values are given in table 3, the constants of Jones–Dole equation along with Y^E in table 5. The differences of ρ^0 and η^0 between the chloride and iodide salts are given in table 2 and the plots of ρ and η in figures 1 and 2 while η^E *versus* x_2 and Y^E *versus* x_2 in figures 3 and 4, respectively.

Table 1. Densities, viscosities, reduced viscosities, and excess viscosities of aqueous salt systems and Gly therein at 310.15 K.

M (mol kg^{-1})	ρ (10^3 kg m^{-3} $\pm 10^{-5}$)	η (10^{-3} kg m^{-1} s^{-1} $\pm 10^{-5}$)	η_r (10^{-3} kg mol^{-1})	η^E (10^{-3} kg m^{-1} s^{-1})
Salt systems				
		Chlorides		
LiCl				
0	0.99338 ± 5.243	0.69470 ± 19.91		
0.0114	0.99448 ± 5.260	0.71788 ± 20.90	2.94015	0.02282
0.0699	0.99565 ± 5.260	0.70258 ± 21.17	0.16242	0.00724
0.1100	0.99634 ± 5.250	0.70356 ± 21.16	0.11596	0.00780
0.1500	0.99712 ± 5.240	0.67723 ± 21.15	−0.16764	−0.01490
0.2050	0.99816 ± 5.230	0.64921 ± 21.13	−0.31939	−0.03598
0.2900	0.99977 ± 5.225	0.57919 ± 20.45	−0.57335	−0.07987
0.3344	1.00062 ± 5.220	0.55736 ± 20.04	−0.59119	−0.08805
NaCl				
0.0050	0.99424 ± 5.260	0.69882 ± 21.21	1.19351	0.00400
0.0101	0.99441 ± 5.260	0.70004 ± 21.19	0.76435	0.00518
0.0506	0.99711 ± 5.250	0.70395 ± 21.16	0.26300	0.00869
0.0988	0.99796 ± 5.250	0.70834 ± 21.10	0.19888	0.01221
0.5115	1.01351 ± 5.170	0.73509 ± 20.85	0.11366	0.01998
1.0398	1.03341 ± 5.090	0.77560 ± 20.47	0.11199	−0.00337
KCl				
0.0105	0.99405 ± 5.260	0.69441 ± 21.28	−0.04011	−0.00039
0.0521	0.99607 ± 5.250	0.69855 ± 21.24	0.10635	0.00355
0.1073	0.99867 ± 5.240	0.70251 ± 21.20	0.10473	0.00689
0.1500	1.00072 ± 5.230	0.70624 ± 21.04	0.11077	0.00974
0.2050	1.00334 ± 5.220	0.71081 ± 19.56	0.11311	0.01276
0.2900	1.00739 ± 5.210	0.71786 ± 19.14	0.11498	0.01646
0.3344	1.00951 ± 5.200	0.72155 ± 19.98	0.11558	0.01793
RbCl				
0.0102	0.99445 ± 5.260	0.69473 ± 21.28	0.00401	−0.00007
0.0468	0.99562 ± 5.260	0.69430 ± 21.31	−0.01243	−0.00048
0.1839	0.99999 ± 5.250	0.69372 ± 21.32	−0.00771	−0.00088
0.1500	0.99891 ± 5.240	0.69370 ± 21.13	−0.00956	−0.00093
0.2050	1.00067 ± 5.230	0.69377 ± 20.13	−0.00653	−0.00081
0.2900	1.00339 ± 5.220	0.69439 ± 20.02	−0.00154	−0.00028
0.3344	1.00480 ± 5.210	0.69497 ± 19.92	0.00114	0.00013
CsCl				
0.0101	0.99524 ± 5.260	0.69964 ± 21.21	0.70655	0.00479
0.0504	1.00060 ± 5.230	0.70020 ± 21.26	0.15720	0.00513
0.1014	1.00728 ± 5.200	0.70607 ± 21.24	0.16134	0.01014
0.1500	1.01369 ± 5.120	0.70892 ± 21.13	0.13644	0.01202
0.2050	1.02093 ± 5.110	0.71290 ± 20.72	0.12777	0.01443
0.2900	1.03213 ± 4.950	0.71904 ± 20.37	0.12083	0.01730
0.3344	1.03798 ± 4.910	0.72225 ± 2012	0.11861	0.01840

(*Continued*)

Table 1. Continued.

M (mol kg^{-1})	ρ (10^3 kg m^{-3} ± 10^{-5})	η (10^{-3} kg m^{-1} s^{-1} ± 10^{-5})	η_r (10^{-3} kg mol^{-1})	η^E (10^{-3} kg m^{-1} s^{-1})
		Iodides		
LiI				
0.0114	0.99585 ± 5.260	0.69720 ± 20.90	0.31515	0.00236
0.0699	1.00095 ± 5.260	0.69984 ± 21.17	0.10591	0.00469
0.1100	1.00445 ± 5.250	0.70166 ± 21.16	0.09105	0.00611
0.1500	1.00793 ± 5.240	0.70347 ± 21.14	0.08414	0.00738
0.2050	1.01272 ± 5.230	0.70596 ± 21.01	0.07904	0.00889
0.2900	1.02012 ± 5.220	0.70980 ± 20.24	0.07496	0.01069
0.3344	1.02399 ± 5.210	0.71181 ± 20.05	0.07366	0.01138
NaI				
0.0103	0.99589 ± 5.260	0.70032 ± 21.21	0.78490	0.00546
0.0516	1.00020 ± 5.240	0.69779 ± 21.30	0.08620	0.00283
0.1020	1.00549 ± 5.210	0.69926 ± 21.34	0.06441	0.00401
0.1500	1.01052 ± 5.200	0.70533 ± 21.09	0.10199	0.00896
0.2050	1.01628 ± 5.190	0.71786 ± 20.76	0.16262	0.01840
0.2900	1.02519 ± 5.180	0.74896 ± 20.14	0.26932	0.03888
0.3344	1.02984 ± 5.178	0.77087 ± 19.98	0.32787	0.05151
KI				
0.0509	0.99998 ± 5.240	0.69418 ± 21.36	−0.01481	−0.00059
0.1013	1.00573 ± 5.210	0.69759 ± 21.37	0.04110	0.00251
0.1016	1.00576 ± 5.200	0.70473 ± 21.25	0.14218	0.00893
0.1500	1.01128 ± 5.190	0.70791 ± 21.05	0.12673	0.01116
0.2050	1.01755 ± 5.180	0.71553 ± 20.76	0.14629	0.01653
0.2900	1.02725 ± 5.170	0.72732 ± 20.24	0.16194	0.02325
0.3344	1.03231 ± 5.160	0.73348 ± 20.11	0.16694	0.02599
RbI				
0.0101	0.99298 ± 5.270	0.68108 ± 21.51	−1.94744	−0.01358
0.0504	0.99959 ± 5.240	0.68998 ± 21.43	−0.13463	−0.00458
0.1010	1.00744 ± 5.200	0.70246 ± 21.31	0.11065	0.00689
0.1500	1.01529 ± 5.120	0.71385 ± 21.11	0.18377	0.01623
0.2050	1.02403 ± 4.990	0.72682 ± 20.91	0.22552	0.02558
0.2900	1.03754 ± 4.920	0.74686 ± 20.22	0.25889	0.03736
0.3344	1.04460 ± 4.800	0.75732 ± 20.10	0.26957	0.04222
CsI				
0.0101	0.99588 ± 5.260	0.69576 ± 21.28	0.15157	0.00095
0.0507	1.00371 ± 5.220	0.69707 ± 21.35	0.06723	0.00215
0.1017	1.01359 ± 5.180	0.69336 ± 21.54	−0.01898	−0.00129
0.1500	1.02292 ± 5.130	0.68436 ± 21.23	−0.09920	−0.00886
0.2050	1.03355 ± 5.010	0.66762 ± 21.09	−0.19017	−0.02151
0.2900	1.04998 ± 4.910	0.62812 ± 20.64	−0.33046	−0.04663
0.3344	1.05857 ± 4.810	0.60092 ± 20.12	−0.40368	−0.06094
Gly in aqueous 0.01 M LiCl				
0	0.99447 ± 5.215	0.73882 ± 21.02	–	–
0.0101	0.99512 ± 5.260	0.67634 ± 21.22	−2.62642	0.00162
0.0313	0.99575 ± 5.260	0.67780 ± 21.20	−0.77790	0.00301
0.0501	0.99671 ± 5.260	0.67765 ± 21.22	−0.49011	0.00281
0.0699	0.99715 ± 5.250	0.68140 ± 21.16	−0.27389	0.00624
0.0993	0.99945 ± 5.240	0.68849 ± 21.06	−0.08994	0.01244
0.01 M NaCl				
0	0.99469 ± 5.250	0.70029 ± 21.04	–	–
0.0050	0.99417 ± 5.260	0.69389 ± 21.21	−0.23262	0.00091
0.0101	0.99432 ± 5.260	0.69038 ± 21.27	−0.61803	−0.00257
0.0152	0.99448 ± 5.250	0.69328 ± 21.21	−0.13499	0.00030
0.0202	0.99463 ± 5.246	0.69580 ± 21.18	0.07814	0.00277
0.0266	0.99482 ± 5.243	0.69506 ± 21.20	0.01940	0.00203
0.0503	0.99554 ± 5.242	0.69514 ± 21.20	0.01272	0.00206

(*Continued*)

Table 1. Continued.

M (mol kg^{-1})	ρ (10^{3} kg m^{-3} $\pm$ 10^{-5})	η (10^{-3} kg m^{-1} s^{-1} $\pm$ 10^{-5})	η_r (10^{-3} kg mol^{-1})	η^E (10^{-3} kg m^{-1} s^{-1})
0.01 M KCl				
0	0.99404 ± 5.240	0.69462 ± 21.08	–	–
0.0101	0.99363 ± 5.260	0.69770 ± 21.23	0.42723	0.00011
0.0304	0.99423 ± 5.260	0.70062 ± 21.19	0.28072	0.00294
0.0507	0.99473 ± 5.260	0.70041 ± 21.20	0.16219	0.00268
0.0711	0.99540 ± 5.250	0.70395 ± 21.14	0.18725	0.00591
0.1009	0.99623 ± 5.250	0.70734 ± 21.10	0.18034	0.00878
0.01 M RbCl				
0	0.99444 ± 5.250	0.69472 ± 21.11	–	–
0.0100	0.99617 ± 5.260	0.70691 ± 21.45	1.75802	0.00004
0.0299	0.99690 ± 5.260	0.70973 ± 21.06	0.72384	0.00278
0.0502	0.99747 ± 5.250	0.71142 ± 21.04	0.47928	0.00433
0.0705	0.99804 ± 5.250	0.71650 ± 20.97	0.44514	0.00896
0.1011	0.99957 ± 5.240	0.71882 ± 20.95	0.34350	0.01076
0.01 M CsCl				
0	0.99525 ± 5.255	0.69879 ± 21.01	–	–
0.0101	0.99723 ± 5.260	0.69869 ± 21.17	0.56979	−0.00042
0.0302	0.99796 ± 5.250	0.70214 ± 21.12	0.35427	0.00293
0.0504	0.99872 ± 5.250	0.70324 ± 21.11	0.24405	0.00392
0.0714	0.99923 ± 5.250	0.70538 ± 21.08	0.21525	0.00582
0.1002	0.99958 ± 5.240	0.70872 ± 21.03	0.20150	0.00865
0.01 M LiI				
0	0.99447 ± 5.234	0.69713 ± 19.65	–	–
0.0101	0.9971766 ± 5.260	0.69168 ± 21.22	−0.43046	0.00005
0.0313	0.9981351 ± 5.260	0.69351 ± 21.20	−0.05495	0.00182
0.0501	0.998985 ± 5.260	0.69512 ± 21.22	0.01219	0.00333
0.0699	0.9998802 ± 5.250	0.69683 ± 21.16	0.04384	0.00484
0.0993	1.0012094 ± 5.240	0.69936 ± 21.06	0.06756	0.00698
0.01 M NaI				
0	0.99585 ± 5.220	0.70035 ± 19.45	–	–
0.0100	0.99637 ± 5.260	0.69233 ± 21.25	−0.34153	−0.00043
0.0300	0.99697 ± 5.260	0.69640 ± 21.19	0.08135	0.00353
0.0501	0.99782 ± 5.250	0.69450 ± 21.23	−0.00561	0.00165
0.0701	0.99889 ± 5.250	0.69902 ± 21.17	0.08872	0.00582
0.0992	0.99976 ± 5.240	0.70106 ± 21.14	0.09231	0.00748
0.01 M KI				
0	0.99531 ± 5.210	0.69849 ± 19.34	–	–
0.0101	0.99558 ± 5.260	0.69327 ± 21.28	−0.20371	−0.00063
0.0303	0.99606 ± 5.260	0.69686 ± 21.22	0.10235	0.00287
0.0502	0.99660 ± 5.250	0.69746 ± 21.22	0.07917	0.00338
0.0708	0.99751 ± 5.250	0.70049 ± 21.18	0.11761	0.00613
0.1011	0.99862 ± 5.240	0.70244 ± 21.16	0.11017	0.00768
0.01 M RbI				
0	0.99304 ± 5.265	0.68084 ± 21.22	–	–
0.0301	0.99323 ± 5.270	0.70860 ± 21.27	0.66442	0.00216
0.0504	0.99437 ± 5.260	0.71084 ± 21.25	0.46108	0.00425
0.0704	0.99493 ± 5.260	0.71468 ± 21.19	0.40880	0.00773
0.1004	0.99596 ± 5.250	0.71681 ± 21.29	0.31709	0.00940
0.1006	0.99571 ± 5.250	0.71698 ± 21.16	0.31882	0.00955
0.01 M CsI				
0	0.99586 ± 5.250	0.69372 ± 21.03	–	–
0.0100	0.99352 ± 5.260	0.69185 ± 21.30	−0.40988	0.00054
0.0299	0.99408 ± 5.260	0.69349 ± 21.28	−0.05836	0.00212
0.0503	0.99450 ± 5.250	0.69567 ± 21.25	0.02762	0.00415
0.0704	0.99527 ± 5.250	0.69696 ± 21.24	0.04622	0.00526
0.1002	0.99638 ± 5.250	0.70217 ± 21.16	0.10734	0.00979

Table 2. Density of aqueous NaCl and KCl systems calculated from our regression constants of primary data and literature values at 310.15 K.

	ρ ($10^3\,\mathrm{kg\,m^{-3}}$), NaCl			ρ ($10^3\,\mathrm{kg\,m^{-3}}$), KCl		
M ($\mathrm{mol\,kg^{-1}}$)	Exp.	Lit.	Δ	Exp.	Lit.	Δ
0.1	0.99807	0.99735	0.00072	0.99833	0.99796	0.00037
0.5	1.01310	1.01296	0.00013	1.01741	1.01578	0.00163
1.0	1.03188	1.03177	0.00011	1.04126	1.03711	0.00415

Literature: Reference [2]. Δ = Exp.-lit.

Table 3. The $\Delta\rho^0 = [\rho^0(\text{iodide} - \rho^0(\text{chloride})]$ and $\Delta\eta = [\eta(\text{iodide}) - \eta(\text{chloride})]$ for iodide salts in aqueous medium.

	Aqueous salts		Gly in salts	
Systems	$\Delta\rho$	$\Delta\eta$	$\Delta\rho$	$\Delta\eta$
LiI–LiCl	0.00336	−0.04745	0.00234	0.01739
NaI–NaCl	0.0005	0.00191	0.00188	0.00069
KI–KCl	0.00061	−0.00669	0.00175	−0.00364
RbI–RbCl	−0.00027	−0.01639	−0.00337	−0.00032
CsI–CsCl	−0.00001	−0.00322	−0.00404	−0.00787

5. Discussion

The experimental ρ^0 values of NaCl [22] and Gly [4, 26] are in agreement with the literature and the densities of aqueous CsCl and CsI increase with the composition having the maximum values among the salt systems (figure 1). An order of ρ^0 for aqueous chloride salts is noted as NaCl > LiCl > RbCl > CsCl > KCl and iodides as LiI > NaI > KI > CsI > RbI. The Li^+ and Na^+ due to the small size and high charge density form a long-range, ordered, large-sized hydration sphere, and the void volume is occupied by free water molecules resulting in high ρ^0 values. The KCl has an exceptionally low value due to its polarizability. With I^-, a trend is in accordance with charge density except Rb^+ that may be due to the comparable sizes between Cs^+ and Rb^+ and thus, the charge density fails to monitor the size of the hydration sphere. The higher ρ^0 of iodides than the chlorides except RbCl > RbI and CsCl > CsI signifies an enhancement in the packing strength of I^- than Cl^- with large-sized cations only.

Likewise, B values (table 5) for salts are listed as LiCl > NaCl > CsCl > RbCl > KCl and NaI > LiI > CsI > KI > RbI, and they signify the size of the hydrated molecules/ions. The B values are positive for Li^+, Na^+, and Cs^+ while negative for the K^+ and Rb^+ system. This strengthens the ρ^0 trend proving Li^+, Na^+, and Cs^+ as the water breakers while K^+ and Rb^+ as the makers. Although Li^+ is small sized, its effective nuclear charge has a greater influence on the water molecules with effective hydration spheres; Na^+ has a similar behaviour. The Cs^+ acts as water breaker due to its large size effect that dominates over the effective nuclear charge. As is given in table 5, the B values for chlorides are higher than that of the iodide salts by ±2.2 to 0.07 $\mathrm{kg\,mol^{-1}}$ except CsCl.

Table 4. Regression constants of densities and viscosities; data for systems at 310.15 K.

Aqueous systems	ρ^0 ($10^3\,\mathrm{kg\,m^{-3}}$)	S_d ($10^3\,\mathrm{kg^2\,m^{-3}\,mol^{-1}}$)	η ($10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}}$)	$S\eta$ ($10^{-6}\,\mathrm{kg\,m^{-1}\,s^{-1}\,mol^{-1}}$)	$S\eta^1$ ($10^{-6}\,\mathrm{kg\,m^{-1}\,s^{-1}mol^{-1}})^2$
Binary systems					
LiCl	0.99334	0.02413	0.74413	−0.53123	
NaCl	0.99431	0.03984	0.69956	0.07256	
KCl	0.99333	0.04636	0.69379	0.08302	
RbCl	0.99333	0.08694	0.69487	−0.01435	−0.04378
CsCl	0.99331	0.12744	0.69807	0.07232	
LiI	0.99763	0.04624	0.69668	0.04525	
NaI	0.99339	0.10478	0.11182	−0.12221	0.98608
KI	0.99329	0.11926	0.68710	0.13869	
RbI	0.99347	0.15752	0.67848	0.23577	
CsI	0.99353	0.19602	0.69485	0.10169	−1.14412
Ternary systems					
Gly in–					
LiCl	0.99349	0.03029	0.67342	0.13271	
NaCl	0.99347	0.03065	0.69120	0.20757	−2.51617
KCl	0.99332	0.03068	0.69661	0.10254	
RbCl	0.99352	0.03045	0.70555	0.13617	
CsCl	0.99553	0.03060	0.69811	0.10531	
LiI	0.99672	0.04521	0.69081	0.08611	
NaI	0.99361	0.03036	0.69189	0.09197	
KI	0.99508	0.03412	0.69297	0.09783	
RbI	0.99303	0.03053	0.70523	0.11863	
CsI	1.01329	0.03121	0.69024	0.11092	

Table 5. Falkenhagen constant $A \pm 10^{-4}$, and viscosity coefficient $B \pm 10^{-4}$, slope constant $D \pm 10^{-4}$ of regression of $(\eta_r - 1)/m^{1/2}$ *vs.* $m^{1/2}$ for aqueous salts and $(\eta_r - 1)/m$ *vs.* m for Gly for aqueous salts fitted to Jone–Dole equation and excess viscosity function Y^E.

Systems	A $(10^{-3}\,\mathrm{kg\,mol})^{-1/2}$	B $(10^{-3}\,\mathrm{kg\,mol^{-1}})$	D $(10^{-3}\,\mathrm{kg\,mol^{-1}})^{3/2}$	Y^E $(10^{-3}\,\mathrm{kg\,m^{-1}\,s^{-1}})$
Binary systems				
LiCl	5.4963	−117.3178	241.1505	0.11740
NaCl	1.4549	−9.7192	7.2433	−0.02449
KCl	−0.0228	5.2321	−11.6399	−0.04319
RbCl	0.0002	−0.4672	1.4797	0.00218
CsCl	1.1804	−19.5763	43.8155	−0.05292
LiI	0.6001	−9.0421	19.7427	−0.03342
NaI	1.2778	−26.0152	69.5619	−0.08377
KI	−0.1728	7.8878	−14.9149	−0.05776
RbI	−3.2285	76.0003	−167.4250	−0.07087
CsI	0.3155	−6.7449		0.08765
	B $(10^{-3}\,\mathrm{kg\,mol^{-1}})$	D $(10^{-3}\,\mathrm{kg\,mol^{-1}})^{2}$	D^1 $(10^{-3}\,\mathrm{kg\,mol^{-1}})^{3}$	
Ternary systems				
Gly in–				
LiCl	−3.2142	81.4868	513.9732	0.02588
NaCl	−0.5933	35.7506	−467.1321	0.00376
KCl	0.5101	−9.4113	61.7941	0.02038
RbCl	2.0776	−46.7671	299.4460	0.02670
CsCl	0.6719	−12.0951	74.7880	0.02080
LiI	−0.5560	17.0652	−110.7306	0.01688
NaI	−0.4127	14.4045	−96.2392	0.01783
KI	−0.2704	11.6061	−79.3147	0.01936
RbI	0.9955	−13.3241	65.7835	0.03996
CsI	−0.5167	15.6370	−96.2326	0.02168

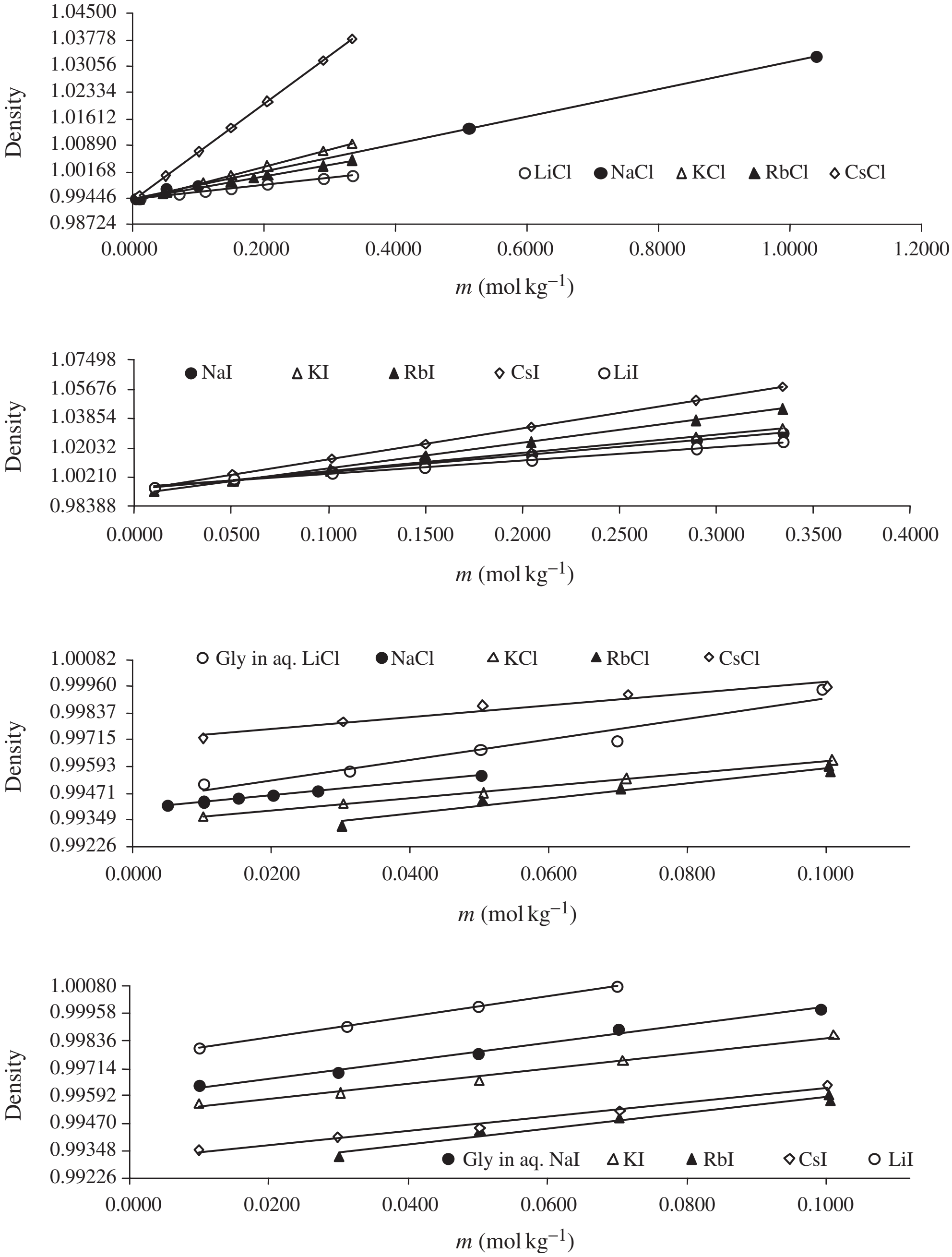

Figure 1. y-axis densities (1×10^3 kg m^{-3}) of salt and Gly systems at 310.15 K, x-axis m (mol kg^{-1}) of salts and Gly.

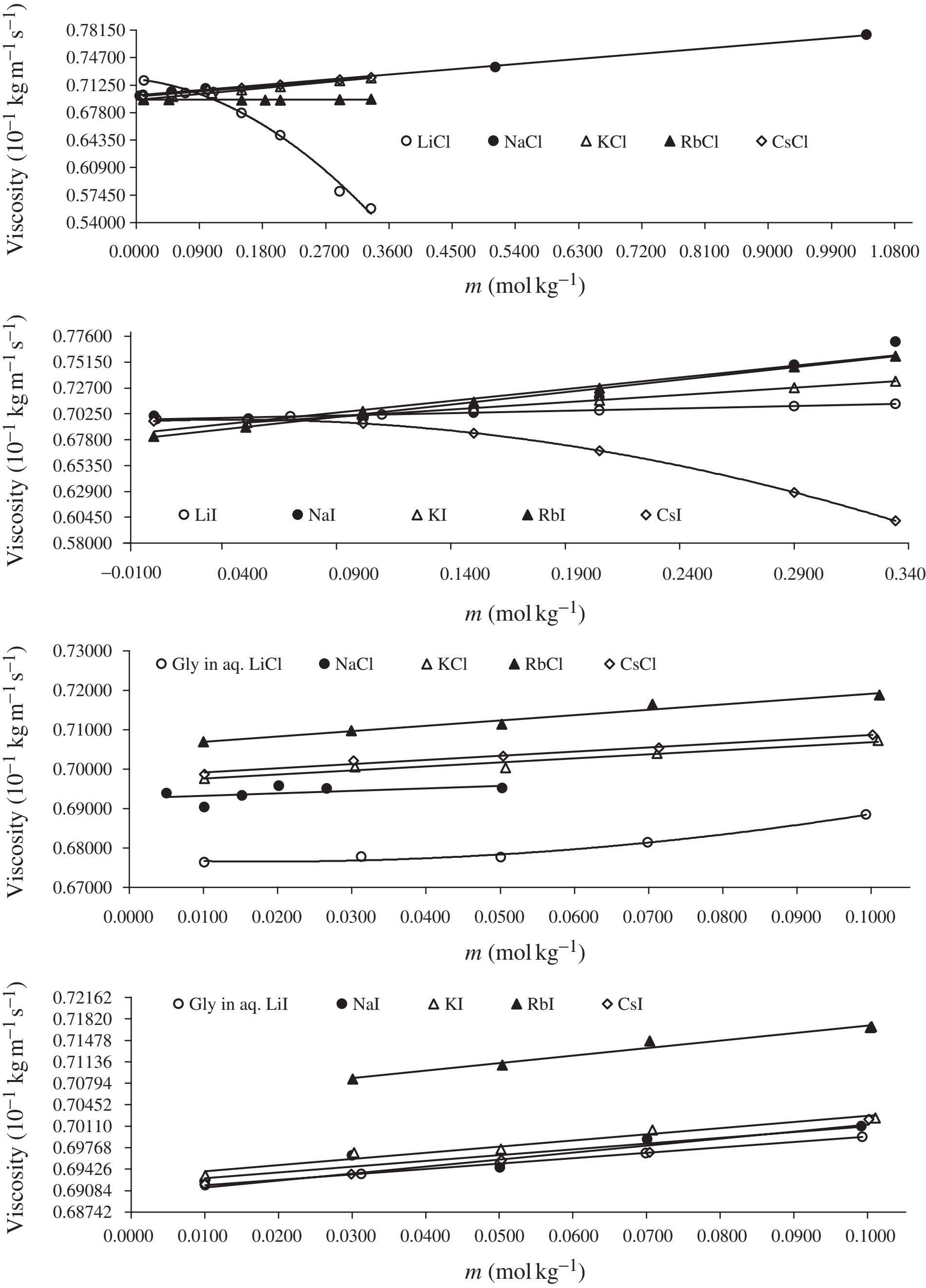

Figure 2. Viscosities of salt (in 10^{-1} kg m^{-1} s^{-1}) and Gly systems at 310.15 K, the m of salts (in mol kg^{-1}) and Gly is plotted on x-axis.

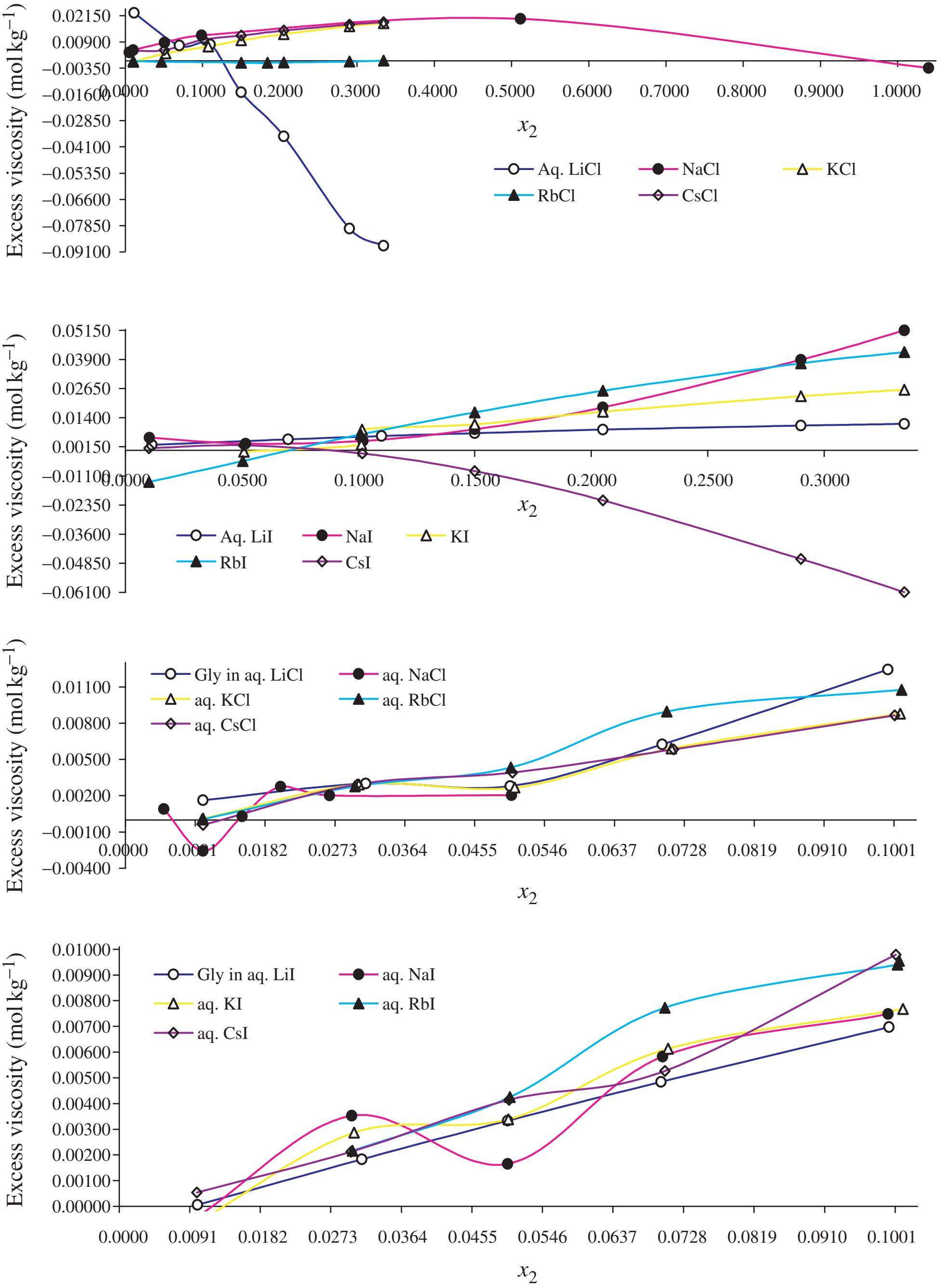

Figure 3. y-axis, excess viscosity (in mol kg^{-1}) of Gly in aqueous chloride and iodide salts systems at 37°C, x-axis mole fraction of system.

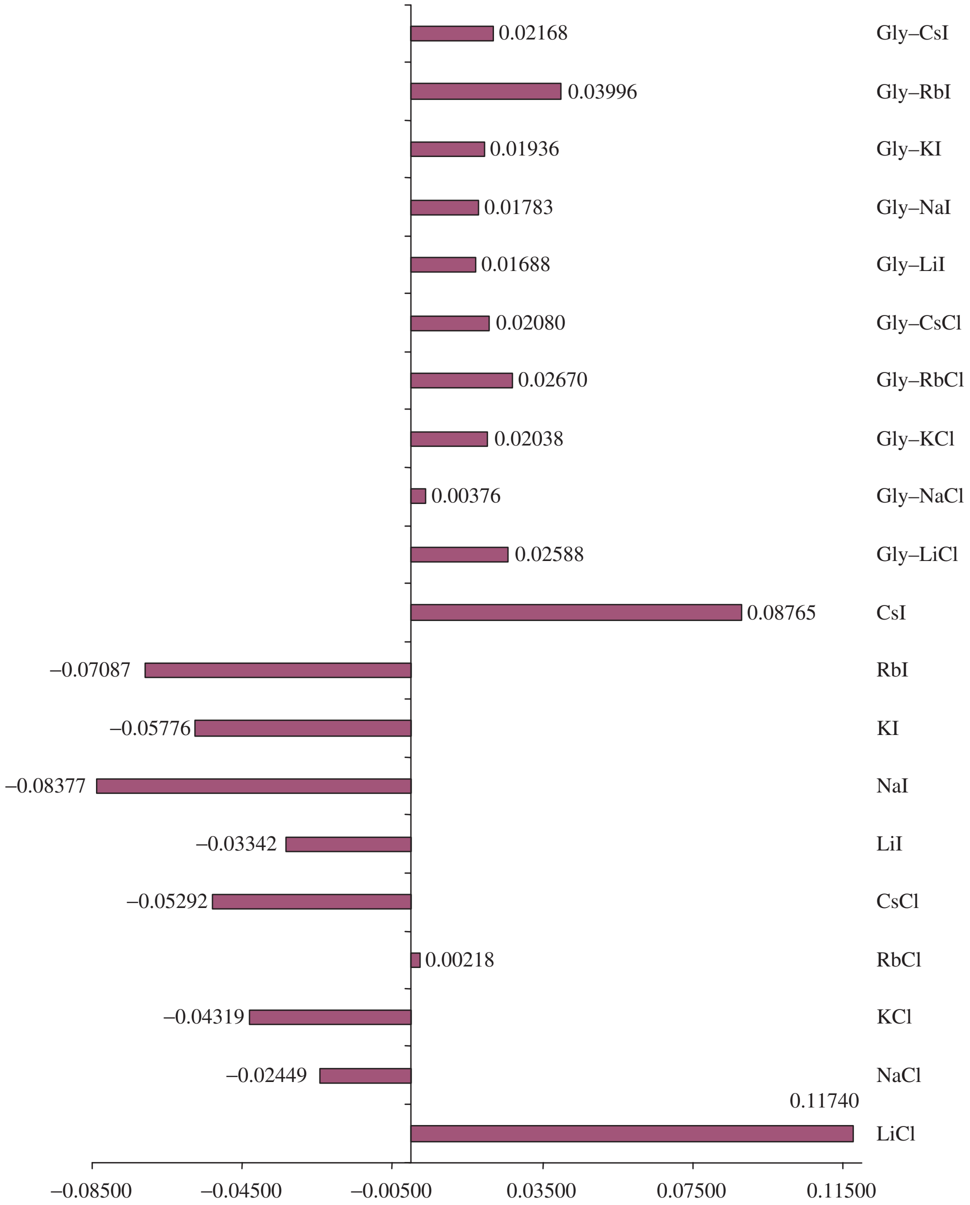

Figure 4. *y*-axis, salt and Gly systems and *x* axis excess function (Y^E), the Y^E values are shown along the bars.

5.1. *Slope constant* S_d

The influence of the salt composition on the ion–ion interactions with RbCl > CsCl > KCl > NaCl > LiCl and CsI > RbI > KI > NaI > LiI order of values show a decrease in the size of the cations except Rb^+ with no influence of size of anion on the interactions, however, the S_d values from CsI to LiI decrease. Iodide salts have considerably higher values than that of chlorides but RbCl has higher S_d than of CsCl, probably a stronger screening on Rb^+ causes stronger Rb^+–Rb^+ interactions. It leads to a higher composition effect on them, but the fully filled 4d weakens the screening and Cs^+–water–Cs^+ interactions. But from KCl to LiCl, the S_d values are noted to decrease by about ±0.05.

5.2. *Ternary systems*

The ρ^0 order of Gly–salt system is found as CsCl > RbCl > LiCl > KCl > NaCl and LiI > NaI > KI > CsI > RbI (figure 1). Like aqueous salt, Gly–salt systems have higher values for iodides than chlorides except RbCl, which may be attributed to the effective hydration of Cl^- when compared to I^- due to its small size. The trend of ρ^0 of iodide system (figure 1) is same in the binary and the ternary systems which may be due to the compact ion-hydration complex preventing I^- interaction with Gly, thus, the zwitterion may remain on the outer surface of the complex. Hence, the electrostatic interactions of Gly seem incompetent to break ion-hydration structure favoring the formation of primary hydration sphere resulting into the formation of larger hydrosphere. Moreover, ρ^0 values, seems to be constituted of four factors as $(\rho_{vw}+\rho_v)+(\rho_s+\rho_h)$, the ρ_{vw} represents intrinsic interactions (at $m=0$) or Van der Waals attraction force, ρ_v void volume, ρ_s contribution of solute–solvent interactions and ρ_h, the hydrophobic hydration. The $(\rho_{vw}+\rho_v)$ is approximately the same in water and aqueous salts thus change in $(\rho_s+\rho_h)$ must explain a trend of ρ^0 and ρ^0_{tr} (density transfer from binary to ternary systems). From the trend of ρ^0 values it can be concluded that I^- has a larger composition effect on ion–ion interactions than of Cl^-, especially for the small-sized cations, if the size of the cations is increased like Rb^+ and Cs^+, the I^- does not remain so effective and Cl^- dominates over the interactions. Notably a difference in ρ^0 values is larger for Gly strengthening Gly–salt interactions, optionally ion-hydration may make an effective linkage with zwitterion-hydration resulting in a larger volume for Cs^+ and Rb^+. The ρ^0 values of aqueous CsCl are lower than RbCl–water, but Gly in aqueous CsCl produces higher values by $0.0005\times10^3\,\mathrm{kg\,m^{-3}}$ than of RbCl–water (table 3). It proves Gly to strengthen the Cs^+–water interaction due to large size of Cs^+, but the decrease in ρ^0 values (figure 1) of Gly for LiCl to KCl with size predicts a decrease in the screening effect and concludes that I^- protects the size effect of the cations. The probably filled and unfilled 'd' or 'p' orbital stabilizes ion–water interactions.

The S_d values of Gly for salts are noted as LiCl > RbCl > NaCl > KCl > CsCl and LiI > NaI > KI > CsI > RbI. Here, RbCl produces higher values than NaCl, KCl, and CsCl but lower than LiCl, this depicts that Gly due to empty 4d orbital of Rb^+, strengthens Rb^+–water interactions breaking the water structure and strengthening the Rb^+–water and Rb^+–O^-OCCH_2–N^+H_2 interactions. These factors cause a higher packing influence on Gly for salts; also Na^+, K^+, and Cs^+ form Na^+–$^-OOCCH_2$–N^+H_2, K^+–$^-OOCCH_2$–N^+H_2, and Cs^+–$^-OOCCH_2$–N^+H_2 interactions. However, with composition of Gly for salts, an order of S_d is found as LiCl > RbCl > NaCl > KCl > CsCl and LiI > NaI > KI > CsI > RbI. It confirms a contribution of polarization of I^- and integrates the size with minor deviations for CsI and RbI, due to, screening, a remarkable shift in behaviour of halide salts of alkali metals and regulates Gly–Gly interactions. Unlike aqueous salts, the B values for Gly therein are almost of opposite trends conceptualizing the fact that Gly weakens the ion–water interactions of Li^+ and Na^+ with similar effect as that of Cl^- and I^-. Although the ion–water interaction from KCl to CsCl including RbI seems to be strengthened, for KI and CsI it weakens and such trends of B values denote that $–NH_3^+$ and $–COO^-$ groups disrupt the bulk water strengthening, and the water–Gly and salt–water–Gly interactions. Notably, a decrease in B values by $5.973\,kg\,mol^{-1}$ of Gly for LiCl and NaCl proves a breaking down interaction due to a greater affinity for the water molecules repelling from the hydrophilic polar ends or the hydrophobic water of $–CH_2–$. Although an increase in values proves that cations get associated with the hydrated water of polar groups instead of the repelling water molecule. Here, the Gly–water–cation interactions may not be denied illustrating the Gly effects on KCl–water interactions, as B values of aqueous KCl are lower than that of Gly. The Gly has a remarkable influence on Rb^+ interactions as it reports maximum B values among Gly–salt systems for both anions, however, larger values are for Cl^- by 0.0012. Thus B values of Gly for RbCl prove that it has a stronger affinity for water and get incorporated in the hydrated water repelling to another phase developing the microphase of aqueous RbCl. It further deepens when Rb^+ is taken with I^- of RbI, as B values for its system are higher than CsI with negative B values for Gly, thus it depicts a mild effect on Gly–water interactions. However, like ρ^0 there is regularity in the order of B values of Gly in iodide salts (table 4).

5.3. *Viscosity*

Contribution of size of Li^+ is assessed from difference of ρ^0 values between the chloride and iodide salts with noticeable difference due to I^- with Li^+. It concludes that I^- polarization is more effective for stronger screening effect and weaker for Cs^+, as a result the η values of aqueous iodide salts are found to be lower than the chlorides, except the NaI and NaCl pair (figure 2). It proves that chloride salts on flow may not follow Newtonian motion and hence cause maximum torsional forces, while due to polarized I^-, the iodide salts may stick to the laminar flow. The difference in ρ^0 and η values of iodide and chloride salts and of Gly therein is given in table 5. This shows that $\Delta\rho$ values are higher and $\Delta\eta$ lower except for LiI–LiCl with Gly and weighs contribution of Gly on I^- polarization, due to the strengthening effect of Gly on ion–water interactions by breaking the water structure. It favors the action as structure breaker for aqueous salts and higher ρ^0 values of Gly for iodide salts due to stronger $I^-–N^+H_3CH_2COO^-$ interaction. It causes structuredness and hence ρ^0 values of Gly system are higher than that of binary salts and η values for iodides are lower than that of chlorides. The I^-–water and $I^-–N^+H_3CH_2COO^-$ interactions are stronger, and the hydration sphere of I^- is seen to be small sized with Newtonian flow. However, the slope values for η did not follow a particular pattern but for KI, RbI, and CsI are noted to have higher η values than of chloride counterparts (figure 2). Here, the presence of 'd' orbital seems to make difference, perhaps due to the screening pattern. In general, S_d values for Gly are noted higher for iodide salts except for RbI, which has lower S_d than others in the series.

5.4. *Excess viscosity η^E and function (Y^E)*

In general, the η^E values of chloride salts are lower than that of the iodides by ±0.005 and seems to facilitate the ion–water interactions slightly stronger than that of chlorides via the hydrogen bonding. The η^{E} values for LiCl after 0.15 to $0.3344\,\mathrm{mol\,kg^{-1}}$ are negative that decrease with composition (figure 3) and infer a decrease in the interactions between ion and water, with negative values for Rb^+ and positive for CsCl; this shows the weakening of the Rb^+–water and the strengthening of CsCl water interactions. The η^{E} positive values for the iodide salts support the Rb^+–water interactions due to the hydrogen bonding, and also η^{E} positive values of Gly for salts with stronger Gly–ion–water, Gly–Gly–ion, Gly–ion–ion, and Gly–water–water interactions (figure 3). Although η^{E} values for Gly are slightly lower by 0.002 than salts (table 4) and positive Y^{E} function of salts indicating a mutual loss of ion–water interactions with positive values for Gly inferring an enhancement of $\mathrm{N^+H_3CH_2COO^-}$–cations interactions. The values for $\mathrm{Cl^-}$ are higher by 0.005 than $\mathrm{I^-}$ salts, and cast weakening in the ion–water interactions than of $\mathrm{I^-}$. Figure 4 clearly depicts the Y^{E} for salts and Gly–salt systems; the Gly–salt systems including LiCl and CsI have positive values while others are negative. It infers that Gly strengthens the ion–water interactions while the other systems mildly weaken the hydrogen bonding involved in the ion–water interactions. It is proven that the iodide salts behave as structure breakers, RbCl as a mild maker, NaCl, KCl, and CsCl as slightly less structure breakers than the iodides.

5.5. *Molar volume*

Moreover, $\bar{V}_2^0$ value seems to be constituted of four factors as $(\bar{V}^0_{2\,\mathrm{vw}} + \bar{V}^0_{2\,\mathrm{v}}) + (\bar{V}^0_{2\,\mathrm{s}} + \bar{V}^0_{2\,\mathrm{h}})$, where the ρ_{vw} represents the intrinsic interactions (at $m = 0$) or Van der Waal's attraction force, $\bar{V}_2^0$ the void volume, $\bar{V}_2^0$ the contribution of solute–solvent interactions, and $\bar{V}^0_{2\,\mathrm{h}}$ the hydrophobic hydration. The $(\bar{V}^0_{2\,\mathrm{vw}} + \bar{V}^0_{2\,\mathrm{v}})$ is approximately the same in water and aqueous salts. Thus, a change in $(\bar{V}^0_{2\,\mathrm{s}} + \bar{V}^0_{2\,\mathrm{h}})$ must explain a trend of $\bar{V}_2^0$ and $\bar{V}^0_{2\,\mathrm{tr}}$ (density transfer from binary to ternary systems). Thus $(\bar{V}^0_{2\,\mathrm{s}} + \bar{V}^0_{2\,\mathrm{h}})$ of Gly for salt is taken as:

$$\left(\bar{V}^0_{2\,\mathrm{s}} + \bar{V}^0_{2\,\mathrm{v}}\right)_{\mathrm{aq.\ salt}} = \bar{V}^0_{2\,\mathrm{sg}} + \bar{V}^0_{2\,\mathrm{ss}} + \bar{V}^0_{2\,\mathrm{sw}} + \bar{V}^0_{2\,\mathrm{ww}}. \tag{9}$$

The $\bar{V}^0_{2\,\mathrm{sg}}$, $\bar{V}^0_{2\,\mathrm{ss}}$, $\bar{V}^0_{2\,\mathrm{sw}}$, and $\bar{V}^0_{2\,\mathrm{ww}}$ are the contributions from salt–Gly, salt–salt, salt–water, and dipole–dipole interactions respectively, $\bar{V}^0_{2\,\mathrm{tr}}$ is calculated as:

$$\bar{V}^0_{2\,\mathrm{tr}} = \left(\bar{V}^0_{2\,\mathrm{sg}} + \bar{V}^0_{2\,\mathrm{ss}}\right) - \left(\bar{V}^0_{2\,\mathrm{sw}} + \bar{V}^0_{2\,\mathrm{ww}}\right). \tag{10}$$

The $\bar{V}^0_{2\,\mathrm{sg}}$ is prominent due to salt–polar group ($\mathrm{N^+H_3}$ and $-\mathrm{COO^-}$) interactions than due to salt $-\mathrm{CH_2}-$, as salts decrease electrostriction of water with a decrease in $\bar{V}^0_{2\,\mathrm{sw}}$ and increase in $\bar{V}^0_{2\,\mathrm{ss}}$ while $\bar{V}^0_{2\,\mathrm{ww}}$ remains the same which explains an increase in $\bar{V}_2^0$ with the salt concentrations. From the trend of $\bar{V}_2^0$ values, it concludes that $\mathrm{I^-}$ has a larger composition effect on the ion–ion interactions than that of $\mathrm{Cl^-}$, for small-sized cations. If size of cations is increased like $\mathrm{Rb^+}$ and $\mathrm{Cs^+}$, the $\mathrm{I^-}$ does not remain so effective and $\mathrm{Cl^-}$ dominates over the interactions.

The positive V_{s} due to a predominance of salt–polar group over salt–nonpolar group interactions decreases the electrostriction with salts i.e., decrease in V_{sw} and increase in V_{ss} with constancy in V_{ww} jointly explains an increase in $\bar{V}_2^0$ with salt concentration.

However, a gradual decrease in $V_{ss} - V_{sw}$ with the salt concentration is responsible for the leveling effect of $\bar{V}_2^0$ curves. Thus $\bar{V}_2^0$ values of salts have been compared with the values obtained by Krumgalz and Pogorelsky [10,13] in 1995 at 210.15 K, and match the trends of our values at 310.15 K with $\pm 0.900–1.00 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$.

The $\bar{V}_2^0$ values for LiCl to aqueous CsCl are found in an increasing order with higher values for aqueous LiI to CsI systems than that of chloride. Thus, the numerical values for chloride and iodide systems demarcate an influence of iodide on the $\bar{V}_2^0$ values of aqueous salts. The $\bar{V}_2^0$ values increase from Li^+ to Cs^+ with shell number from $2s^1$ to $6s^1$, so that the size of cation is noted to weaken the cation–water interactions. Perhaps, the shielding/screening effect on the nuclear charge distribution on the larger orbital of cations may be functional for such effect to be strengthened by iodide anion (table 5).

A decrease in $\bar{V}_2^0$ values with concentration was reported for aqueous NaCl, KCl, RbCl, and their iodide salts along with CsI. The slope S_v values were found in range of -0.038 to -2.072 for chloride and 0.868 to -4.316 from NaI to CsI salts with higher concentration effect for iodide salts than chloride. The I^- is large sized with substantial ionization potential causing ion–ion interaction with the composition and viewed in the light of a single ion contribution, as chloride and iodide anions remain common. Thus, larger influence of iodide on ion–ion interaction is noted for Na^+, but with the size of cation, the S_v values were lowered weakening the structure breaking action of cations.

5.6. *Ternary system*

The $\bar{V}_2^0$ values of Gly for aqueous salts are noted higher than that of water, while the S_v values are lower. The $\bar{V}_2^0$ of Gly is slightly higher for LiCl, NaCl, RbCl, LiI, NaI, and CsI inferring Gly as a weaker structure breaker and for salts with negative S_v values structure maker (table 6). A continuous decrease in $\bar{V}_2^0$ values from LiI to CsI by $0.88 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$ depicts that the cations in association with I^- induce the structure making action. An order of S_v values is listed as RbCl > CsCl > NaCl > KCl > LiCl and iodide salts as KI > RbI > NaI > LI > CsI showing that the Rb^+ and Cs^+ ions with 'd' orbital produce larger S_v values causing a stronger Gly–Gly and Gly–water interactions that of the Na^+, K^+ and Li^+ ions. LiCl has minimum S_v values with almost a nil influence on the Gly–water and Gly–Gly interactions, Gly in CsI with 0.114 value illustrating a weaker interaction of Cs^+ and I^- with $-COO^-$ and $-NH_3^+$ polar groups. The values of Falkenhagen constant A have been found to be negative for KCl, KI, RbI signifying a weaker structure breaking under the action of water. The negative A value for LiCl (table 5) predicts a strong destabilization with water as compared to other salts due to the larger nuclear charge on its outer shell electron. The negative B values for binary salt systems propose a stronger and spontaneous ion–ion interaction, except KCl, KI, and RbI. The latter do not show much stronger ion–ion interactions with compositions, and hence not much significance is attached with D values except the composition effect on the ion–ion interactions. The B coefficient with positive or negative values is an adjustable parameter measuring an effective hydrodynamic volume of the solvated ions and the Gly–ion–water interactions. The B values for salt systems are negative, indicating a weaker ion–solvent interaction with a mild structure breaker action.

Table 6. Regression constants of molal volumes and free energies of activation for solvent ($\Delta\mu_1^{0*}$), binary ($\Delta\mu_2^{0*}$), and ternary solutions ($\Delta\mu_3^{0*}$).

Systems	V_2^0 ($1 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$)	S_v ($\mathrm{m^3\,mol^{-1}}$)	$\Delta\mu_1^{0*}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta\mu_2^{0*}$ ($\mathrm{kJ\,mol^{-1}}$)	$\Delta\mu_2^{0*} - \Delta\mu_1^{0*}$
Binary systems					
LiCl	17.774	0.636	62.300	16686.16	−16.74
NaCl	17.843	−0.038	62.300	1382.46	−1.42
KCl	27.945	−0.760	62.300	−745.49	2.14
RbCl	33.400	−2.072	62.300	64.34	2.11
CsCl	40.637	5.841	62.300	2781.19	0.42
LiI	36.230	0.637	62.300	1283.54	1.29
NaI	36.591	−0.868	62.300	3697.56	−1.07
KI	46.765	−6.755	62.300	−1125.89	5.20
RbI	51.417	−0.489	62.300	−10814.15	15.55
CsI	59.283	−4.316	62.300	953.53	4.90
Ternary systems					
Gly in–					
LiCl	44.046	0.029	16748.40	479017.69	3.23
NaCl	43.917	0.197	1444.70	83377.91	3.59
KCl	43.883	0.128	−683.26	−49199.23	3.74
RbCl	43.987	0.462	126.58	−161010.19	3.97
CsCl	43.891	0.299	2843.42	−39977.19	3.76
LiI	44.120	0.350	1345.78	40338.81	3.62
NaI	44.059	0.409	3759.80	32302.90	3.63
KI	43.872	0.632	−1063.65	13998.23	3.62
RbI	43.874	0.560	−10751.92	−60274.47	3.80
CsI	43.070	0.114	1015.77	24184.27	3.48

5.7. *Activation energy*

An activation energy, $\Delta\mu_2^{0*}$, for salts is acquired from the solution itself readying them for the interaction and its redistribution from the intermolecular nonreacting bonds. The values of $\Delta\mu_1^{0*}$, $\Delta\mu_2^{0*}$, and $\Delta\mu_3^{0*}$ (for Gly in salt systems) given in table 6 where $\Delta\mu_1^{0*}$ for water is positive and predicts a weakly favored formation of transition state as per the transition state theory. The $\Delta\mu_2^{0*}$ values are negative for KCl, KI, and RbI that states the formation of a transition state at the cost of breaking and distortion of heteromolecular bonds with a stronger structure breaking under the action of water. The positive $\Delta\mu_2^{0*}$ values with an order of LiCl > NaI > CsCl > NaCl > LiI > CsI illustrate a weakly favored transition state formation at 310.15 K. High thermal energy contents seem to destabilize the water structure and acts as facilitating factor, and thus $\Delta\mu_2^{0*}$ values categorize salts as structure makers, although at 298.15 K the salts are reported to behave as a structure breaker. Thus an order of $\Delta\mu_2^{0*}$ reinforces a contention of strong solute–solvent interactions, Feakins *et al.* [28] has shown that if $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$, the solute behaves as a structure maker.

There is a possibility that salts in thermally destabilized water do not require much $\Delta\mu_2^{0*}$ for the transition state and develop hydration at a cost of less $\Delta\mu_2^{0*}$. Thus, LiCl make least distortions followed by NaI and other salts having positive $\Delta\mu_2^{0*}$ (table 6). Likewise, a negative $\Delta\mu_3^{0*}$ (for Gly) for aqueous KCl, RbCl, CsCl, and RbI predicts the process as spontaneous and is positive for other salts with an order of LiCl > NaCl > LiI > NaI > CsI > KI proposing a favorable transition state formation for them. Comparatively higher $\Delta\mu_3^{0*}$ values predict the process of viscous flow as difficult with concentrations of Gly, due to the stronger ion–solvent interactions. Thus LiCl and NaCl cause much hindrance in the viscous flow due to their ion-hydration complex or cationic or anionic interactions with respective polar groups of Gly. The $\Delta\mu_2^{0*} - \Delta\mu_1^{0*} < 0$ for LiCl, NaCl, NaI, while $\Delta\mu_2^{0*} - \Delta\mu_1^{0*} > 0$ for KCl, RbCl, CsCl, LiI, KI, RbI, and CsI systems. The value < 0 indicates structure breaker and > 0 maker; Feakins *et al.* [28] support our results. The dielectric constant, caused by the salts, plays a key role in monitoring the interactions; the role of dielectric constant has been explained by Rohdewald and Moldner [29]. Among the binary systems, the $\Delta\mu_2^{0*} - \Delta\mu_1^{0*} > 15$ and for CsI = 4.90 indicating RbI and CsI to strengthen the structure, making an effect on water. The $\Delta\mu_3^{0*} - \Delta\mu_2^{0*} > 0$ for Gly in salt systems has a structure making influence with almost the same values for chloride and iodide salts proving a similar structure making effect of Gly on salt–water interactions.

6. Conclusion

The chloride salts have a higher density and S_d than the iodides, but higher B values for chlorides than those of the iodides except CsCl, but RbCl has higher S_d than that of CsCl, due to, Cs^+–water–Cs^+ interactions. Gly–salt systems have higher ρ^0 values for iodides than the chlorides. Gly does not break ion-hydration, however, I^- illustrates a larger composition effect on ion–ion interactions than that of the Cl^-. The higher S_d values of Gly in salts than NaCl, KCl, and CsCl but lower than LiCl, depicts that Gly strengthens the Rb^+–water and the Rb^+–O^-OCCH_2–N^+H_2 interactions. The B values of Gly predict the weakening of ion–water and favoring the water–Gly and the salt–water–Gly interactions. A decrease in the B values of Gly for LiCl and NaCl, Gly in RbI has *B* higher than that of CsI depicting a mild effect on Gly–water interactions. The higher η values for KI, RbI, and CsI than that of the chlorides predict a stronger I^- –water and I^- –$N^+H_3CH_2COO^-$ interactions. The η^E values of chloride salts are lower than that of iodides, and are positive for iodide salts and Gly in salts. The positive Y^E values for Gly in salts indicate a mutual loss of ion–water interactions due to the weakening electrostriction of water. Higher $\bar{V}_2^0$ values for aqueous iodide salts than that of the chlorides, increase from Li^+ to Cs^+ with shell number from $2s^1$ to $6s^1$. The slope S_v values were found to vary from -0.038 to -2.072 for chlorides and 0.868 to -4.316 for iodides, with higher concentration effect for iodides. The $\bar{V}_2^0$ of Gly in aqueous salts are higher than that of water and lower S_v values prove Gly to be a weaker structure breaker and salts maker due to negative S_v. The larger S_v values for Rb^+ and Cs^+ denote a stronger Gly–Gly and Gly–water interactions, and LiCl has minimum S_v values. Falkenhagen constant *A* is negative for KCl, KI, and RbI due to the weaker structure breaking action. The negative *B* values for binary salts propose stronger and spontaneous ion–ion interactions with not much significance for *D* values except for the composition effect on the interactions. The $\Delta\mu_1^{0*}$ for water is positive with weakly favored formation of transition state and $\Delta\mu_2^{0*}$ is negative for KCl, KI, and RbI with the transition at a cost of breaking and distortion of the heteromolecular bonds. The positive $\Delta\mu_2^{0*}$ values for LiCl, NaI, CsCl, NaCl, LiI, and CsI illustrate the weakly favored transition state with salts as the structure maker. The $\Delta\mu_2^{0*} > \Delta\mu_1^{0*}$, defines the solute to behave as a structure maker. Negative $\Delta\mu_3^{0*}$ for Gly in aqueous salts predicts spontaneous process. Higher $\Delta\mu_3^{0*}$ values of Gly predict the viscous flow as difficult with concentrations due to stronger ion–solvent interactions. The $\Delta\mu_2^{0*} - \Delta\mu_1^{0*} < 0$ for LiCl, NaCl, NaI, and $\Delta\mu_2^{0*} - \Delta\mu_1^{0*} > 0$ for KCl, RbCl, CsCl, LiI, KI, RbI, and CsI prove the structure breaker and maker actions respectively, and the $\Delta\mu_3^{0*} - \Delta\mu_2^{0*} > 0$ for Gly for salts enhances the structure making effect.

Acknowledgement

M.P. is highly thankful to CSIR (Council for Scientific and Industrial Research), Govt. of India, New Delhi, for the financial assistance.

References

[1] M.L. Parmar, D.K. Dhiman. *J. Indian Chem. Soc.*, **79**, 729 (2002).
[2] A. Apelblat, E. Manzurola. *J. Chem. Thermodynamics*, **31**, 869 (1999).
[3] J.L. Fauchere Pliska, V. Eur. *J. Med. Chem.*, **18**, 369 (1983).
[4] J. Traube. *Samm. Chem. Vortr.*, **4**, 255 (1899).
[5] P.S. Rogers, K.S. Pitzer. *J. Phys. Chem. Ref. Data*, **11**, 15 (1982).
[6] F. Vaslow. *J. Phys. Chem.*, **70**, 2286 (1966).
[7] F. Franks, H.T. Smith. *Trans. Faraday Soc.*, **63**, 2586 (1967).
[8] F. Vaslow. *J. Phys. Chem.*, **73**, 3745 (1969).
[9] L.F. Silvester, K.S. Pitzer. *J. Phys. Chem.*, **81**, 1822 (1977).
[10] B.S. Krumgalz, R. Pogorelsky, Ya.A. Iosilevskii, A. Weiser, K.S. Pitzer. *J. Solution Chem.*, **23**, 849 (1994).
[11] Landolt-Bornstein. *Numerical Data and Fundamental relationship in Science and Technology*, New Series, K.H. Hellwege (Ed.), pp. 47–48 and 80–81, Springer-Verlag, Berlin (1977).

[12] V.M.M. Lobo. *Handbook of Electrolyte*, part A, pp. 798–918; part B, pp. 1602–1691, Elsevier, Amsterdam (1999).
[13] B.S. Krumgalz, R. Pogorelsky, K.S. Pitzer. *J. Phys. Chem. Ref. Data*, **25**, 663 (1996).
[14] F.T. Gucker, C.L. Chernick, P. Roy-Chowdhury. *Proc. Natl. Acad. Sci. USA*, **55**, 12 (1966).
[15] J.L. Fortier, P.A. Leduc, J.E. Desnoyers. *J. Solution Chem.*, **3**, 323 (1974).
[16] F.T. Gucker, D. Stubley, D.J. Hill. *J. Chem. Thermodynamics*, **7**, 865 (1975).
[17] F.J. Millero, G.K. Ward, P.V. Chetirkin. *J. Acoust. Soc. Am.*, **61**, 1492 (1977).
[18] I.V. Olofsson. *J. Chem. Thermodynamics*, **11**, 1005 (1979).
[19] M.A. Simard, J.L. Fortier. *Can. J. Chem.*, **59**, 3208 (1981).
[20] J.A. Gates, R.H. Wood. *J. Chem. Eng. Data*, **30**, 44 (1985).
[21] F. Kawalzumi, F. Nakao, H. Nomura. *J. Chem. Eng. Data*, **33**, 204 (1988).
[22] P.S. Roger, K.S. Pitzer. *J. Phys. Chem. Ref. Data*, **11**, 15 (1982).
[23] A. Ben-Naim. *J. Chem. Phys.*, **90**, 7412 (1989).
[24] M. Singh. *J. Inst. Exp. Tech.*, **48**(2), 270 (2005).
[25] A.W. Hakin, D.C. Daisley, L. Delgado, J.L. Liu, R.A. Marriott, J.L. Marty, G. Tompkins. *J. Chem. Thermodynamics*, **30**, 583 (1998).
[26] K. Mishra, J.C. Ahluwalia. *J. Phys. Chem.*, **88**, 86 (1984).
[27] O. Redlich, A.T. Kister. *Ind. Eng. Chem.*, **40**, 427 (1960).
[28] D. Feakins, D.J. Freemantle, K.G. Lawrence. *J. Chem. Soc. Faraday Trans. I*, **70**, 795 (1974).
[29] P. Rohdewald, M. Moldner. *J. Phys. Chem.*, **77**, 373 (1973).
[30] S. Phang. *Aust. J. Chem.*, **30**, 1605 (1977).
[31] N.J.V. Tyrrell, M. Kennerley. *J. Chem. Soc., A-Inorg. Phys. Theo.*, **11**, 2724 (1968).