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## Electrolytic Studies Of Glycine And DL- $\alpha$ Alanine In 1:1 Electrolytic Aqueous Solutions Of Halide Salts Of Alkali Metals At 308.15 K



**Man Singh**  
Chemistry Research Lab,  
Deshbandhu College, University of Delhi,  
New Delhi – 110 019 (INDIA)  
Ph: 011-26217579  
E-mail: mansingh50@hotmail.com



**Maneesha Pandey**  
Chemistry Research Lab,  
Deshbandhu College, University of Delhi,  
New Delhi – 110 019 (INDIA)

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### ABSTRACT

Electromotive force (EMF) of concentration cell with transference number ( $t_+$ ) has been obtained for glycine and DL- $\alpha$  alanine in 1:1 electrolyte (NaCl, KCl, RbCl and NaI, KI, RbI) solutions at 308.15 K. The cell electrodes work of Ag-AgCl type have been prepared from Ag<sub>2</sub>O paste in water and based on the liquid-liquid junction potential. The activity coefficient data are derived from the measured EMF values and are discussed in terms of pairwise interactions to interpret the amino acid interactions with salts in aqueous solutions. The effect of the -CH<sub>3</sub> of the alanine is noted to weaken the activity of the acids due the hydrophobic interactions and the iodide ion I<sup>-</sup> has depicted its induced potential impact on the interactions.

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### KEYWORDS

Concentration cell;  
Bias potential;  
Activity coefficient;  
Induced potential;  
Pair wise interactions;  
Hydrophobic interactions;  
Junction potential.

### INTRODUCTION

The ion-molecular interactions of the salt-biomolecules have drawn the focus of the physico-chemical investigations in aqueous solutions. Thus electrolytic studies of salts and amino acids, peptides and proteins have been of great use for various newly emerging biosciences and biotechnology. The

salts in general monitor the molecular interactions and activities of biomolecules and biopolymers. Especially of alkali and alkali earth metal cations are interesting as they are much weaker as compared to complex forming interaction with transition metal ions<sup>[1,2]</sup>. Mechanism of salt actions on complex biomolecules elucidates their effect on small and structurally less complex model compounds, which

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is of great help. Thus the thermodynamic studies of ionic interaction of salts with molecular interactions of model compounds of proteins, nucleic acids and membranes are chosen for investigation. Reportedly very few efforts have been put up in this direction<sup>[3-6]</sup>, the illustration of such affects is not complete in itself hence more and more investigations are intuitively imperative. Reportedly no work is undertaken on amino acids in iodide salts of alkali metals. Thus activity coefficients ( $\gamma_{\pm}$ ) of amino acids in chosen salt systems at 308.2 K have been obtained from the measured EMF values with the cells with transference of the type (I) of the electrode as is give below. The AA represents amino acids.

**Ag/AgCl/MCl( $m_1$ )/MCl( $m_2$ ), AA( $m_2$ )/AgCl/Ag (I)**

McMillian Mayer theory has found some relevance to elaborate the salt-amino acid interactions in terms of pairwise intermolecular forces. The pairwise interaction coefficient for amino acids in mixed solvents of nonelectrolyte from the volumetric data<sup>[7]</sup> rationalizes the behavior of interactions of acids mixed solvents and present complete picture of acid's interaction mechanism.

### EXPERIMENTAL

#### Material

On the pattern of stokes and Levin<sup>[8]</sup> device, the concentration cells were made with extra precautions to avoid mixing of solutions in the two electrodes. The EMF of the cell was stabilized to within few microvolts in about 30-40 min after the cell attains thermal equilibrium. The cell EMF which was measured with Leads & Northrup 7554 Type K4 attached to potentiometer a Keinthley 155 micro voltmeter as null detector with 1V to 1000V range with 0.05 $\mu$ V resolution. Its measuring range was 0.016V with 0.01 $\mu$ V resolution, the potentiometer was guarded with cooper wire of 1mm id to prevent its fluctuations, guarding was extended to thermostat too. Prior to measurements the potentiometer was calibrated against NPL (New Delhi) certified Cadmium standard cell of 1.01745V (Toshiniwal). Though this arrangement allowed the EMF to be read

with a precision of 1 $\mu$ V, the final EMF values were stable to within  $\pm 10\mu$ V. Thus the usual correction<sup>[9]</sup> for the bias potentials, which were always less than 50 $\mu$ V, was made. Ag-AgCl electrodes were of the thermal electrolytic type<sup>[10]</sup>.

#### Concentration cell

The two electrodes of 1.5x18cm in inner diameter (id) and length respectively of glass were prepared separately with B5\$ cone. The 99.9% pure silver was fused in the cone crossing the full length of the electrode with extrusion at both the top and bottom of it. The extruded wire at the top was used for electrical connection with the potentiometer and bottom for fusing with 100% pure Pt spiral (platinum metal) measuring the liquid-liquid junction potential of the concentration cell. The electrodes were termed as Ag-AgCl and assembled in the in glass vessels of 1x14cm in inner diameter and length respectively with \$ ground glass joints  $J_1$  and  $J_2$ . The vessels were having side tubes of glass of 1cm id, one of the side tubes has a bulb of 15ml with ground glass joint of B10, and the working diagram of it is drawn in figure 1. The cell assembly was kept in a double walled thermostat with cooling and heating provisions, a 25L paraffin oil was used as thermostatic liquid. A Jume mercury contact thermometer with solid state relay was used for temperature control  $\pm 0.1^\circ$ C.

Chloride and iodide salts of sodium, potassium and rubidium (E. Merck) were dried at 420K and glycine and DL- $\alpha$  alanine (Sigma) at 320.15K under vacuum for three days, stored over  $P_2O_5$  in a desiccators and redried before use. Other chemicals of analytical grade were used without further purification except drying and demineralized distilled over acidified potassium dichromate and then alkaline permanganate was used. Its conductivity was found to be  $10^{-6}\Omega^{-1}cm^{-1}$  and used, after boiling off the dissolved air, for solution prepared w/w by same day to avoid errors due to possible fermentation of the amino acids. Vacuum corrections were applied to all weighing. The stock solutions of salts were prepared w/w and were used as solvent for amino acid solutions.

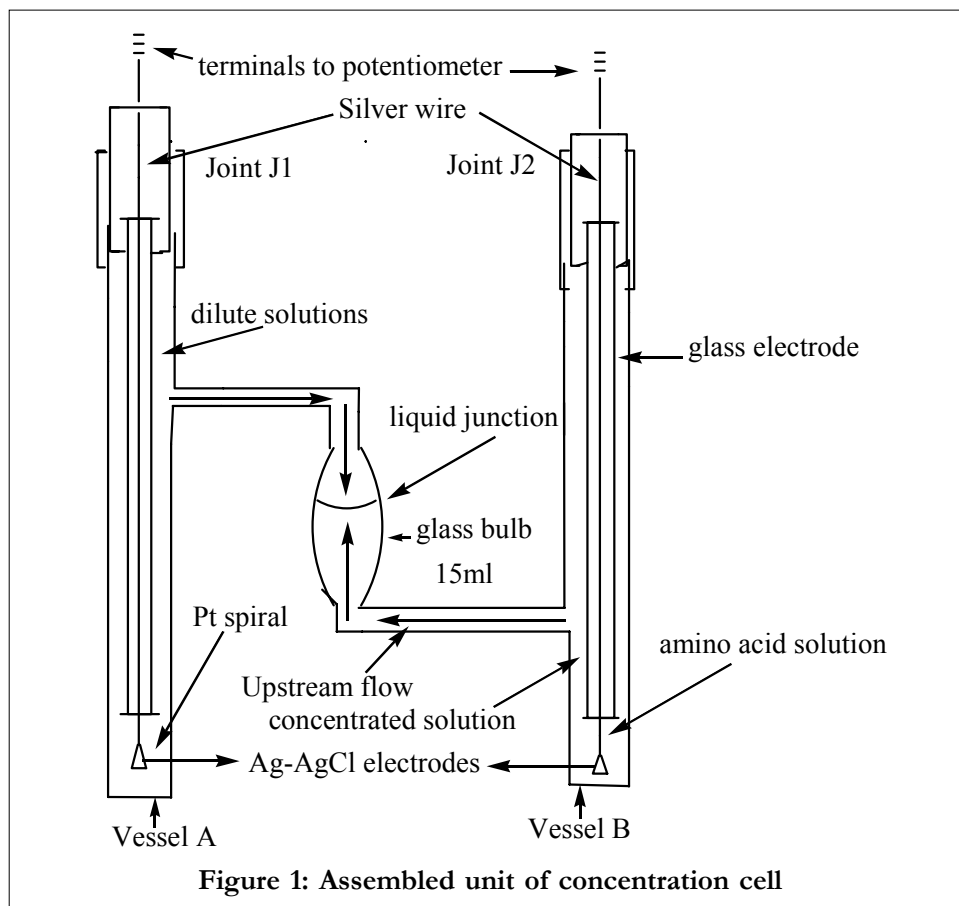


Figure 1: Assembled unit of concentration cell

### Preparation of Ag-AgCl electrode:

A silver oxide ( $\text{Ag}_2\text{O}$ ) precipitated from the aqueous  $\text{AgNO}_3$  solution by  $\text{NaOH}$  washed with conductivity water till no free  $\text{NaOH}$  was found. A specific conductance of the water from final washing was  $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  at lab temperature. The  $\text{Ag}_2\text{O}$  was dried at  $95^\circ\text{C}$  and stored in  $\text{P}_2\text{O}_5$  filled desiccator. The Pt (Sigma, USA) spiral was cleaned by boiling in concentrated  $\text{HNO}_3$  with repeated rinsing in distilled and boiling in conductance waters. The paste of  $\text{Ag}_2\text{O}$  was made in water and applied to the treated Pt spirals with spatula to make bead of 4-5mm size around spirals and suspended in the furnace for thermal reduction in steps. Firstly to prevent sputtering due to the rapid formation of steam, the temperature of the furnace was maintained below  $100^\circ\text{C}$  for 30min allowing superficial drying. Afterwards the temperature was raised at uniform @ to  $400\text{-}450^\circ\text{C}$  for 30min and cooled within the furnace to prevent thermal shock after switching the furnace off. Second coat of the paste was made much thinner from

a gravity point of view followed by similar heat treatments to reduce  $\text{Ag}_2\text{O}$  to Ag metal.

### Chloridization

It was chloridized in 0.05N  $\text{KCl}$  and 0.1N  $\text{HCl}$  (highly pure AR) making it as anode and Pt spiral of 100% platinum metal as cathode by passing a current of 10miliampere. A 10-20% Ag was assumed to be converted to  $\text{AgCl}$  with dark brown colour.

### Testing

Were tested with filling aqueous 0.01N  $\text{NaCl}$  solutions in both the vessels and measured the potential difference which was found to be  $50\text{-}60\mu\text{V}$ .

### Measurement

The electrodes and vessels were rinsed with concerned solutions, amino acid solution in aqueous salt was filled in B vessel avoiding downward streaming of it while of salt in A. The filled cell was placed in oil bath for thermal equilibrium for 20min and EMF was measured at an interval of 30min until steady

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values are obtained. Approximately after 1.30 to 2.00hr, cell gave almost stable values. The subsequent lot of solutions was filled after emptying the previous and after adequate rinsing with the subsequent solutions, the later were filled in the vessels. The measurements were repeated in similar manner and the cell was calibrated with NaCl solutions.

### RESULT AND DISCUSSION

The concentration cell was standardized with ac-

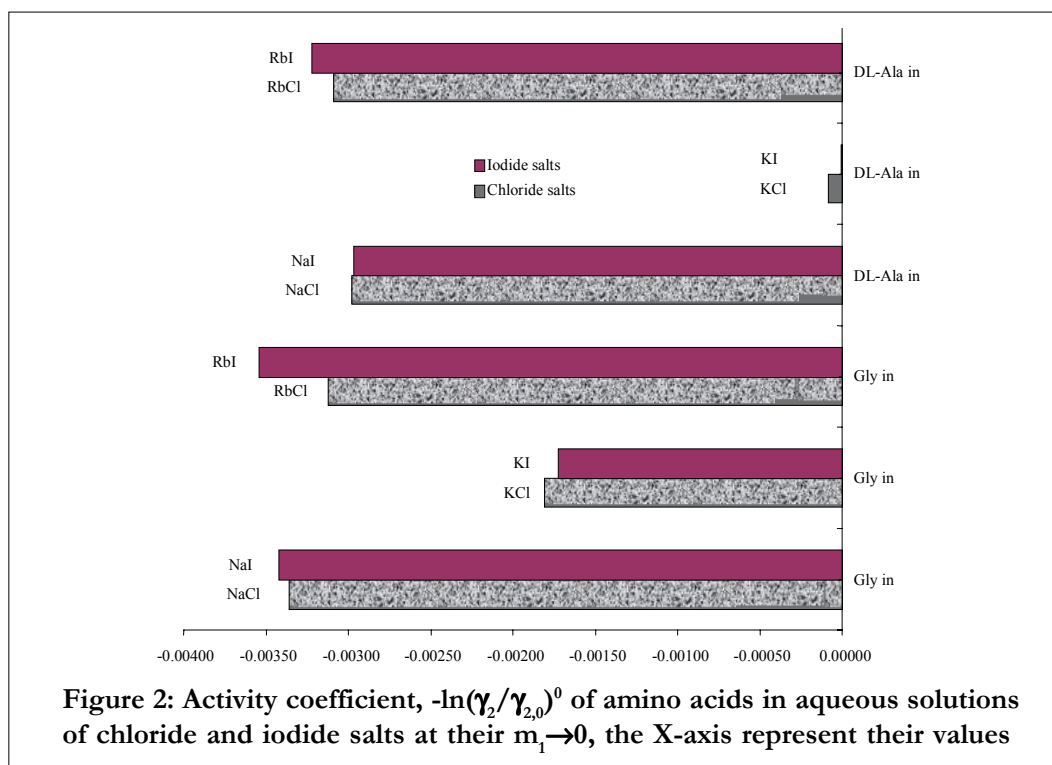
tivity coefficients<sup>[11]</sup> of NaCl at 308.15K from the measured EMF on the cell II.

#### Ag/AgCl/NaCl(m<sub>1</sub>)/NaCl(m<sub>2</sub>)/AgCl/Ag

Here  $m=0.09 \text{ mol kg}^{-1}$  and  $0.055 \leq m^1/\text{mol kg}^{-1} \leq 0.1$  and values compared with the reported<sup>[12]</sup> ones to within  $\pm 0.13\%$  and given in TABLE1. The EMF values of the cell I obtained at electrolyte and amino acid concentrations are given in TABLE 2 and expressed<sup>[6]</sup> as E in terms of the electrolyte molality  $m_1$  and of acids as  $m_2$ . Thus the E values were fitted

**TABLE 1: The E for cell (1) for a fixed  $m_1=0.09037 \text{ mol kg}^{-1}$  of NaCl in one side and  $m_2/\text{mol kg}^{-1}$  on the other at 308.15K.**

NaCl $m_2$	E/volt	$\log \gamma_2/\gamma_1$	$\log \gamma_2/\gamma_1 +$ $(0.5107\sqrt{m_2})/(1+1.350\sqrt{m_2})$	$m_2, \text{NaCl}$	$\gamma_2, \text{Exp.}$	$\gamma_2, \text{lit.}$
0.00876	0.0469	0.06111	0.10352	0.067	0.9483	0.936
0.01098	0.0440	0.05780	0.10358	0.095	0.9219	0.912
0.01101	0.0439	0.05776	0.10358	0.130	0.8916	0.884
0.01346	0.0408	0.05422	0.10364	0.150	0.8757	0.869
0.02333	0.0294	0.04114	0.10389	0.177	0.8558	0.851
0.06548	0.0044	0.00676	0.10497	0.212	0.8327	0.829
0.07688	0.0042	0.00343	0.10526	0.232	0.8208	0.818
0.08988	0.0075	0.00273	0.10559	0.250	0.8110	0.809
0.09897	0.0119	0.00420	0.10582	0.268	0.8021	0.800
0.10099	0.0131	0.00475	0.10587	0.295	0.7901	0.789



**Figure 2: Activity coefficient,  $-\ln(\gamma_2/\gamma_{2,0})^0$  of amino acids in aqueous solutions of chloride and iodide salts at their  $m_1 \rightarrow 0$ , the X-axis represent their values**

**TABLE 2:** The  $m_1$  of salt solutions and  $m_2$  of the amino acids in the salt solutions used as solvents, the  $E/mv$  cell potential,  $\delta E/mv$  biased potential and  $\ln(\gamma_2/\gamma_{2,0})$  activity coefficient of the amino acids in salt systems. The  $m_1$  for both the chloride and iodide salts were maintained the same values and the transport number,  $t_+$  of the cation also taken same value for iodide salts

NaCl		Gly				NaI		Gly	
$m_1$	$m_2$	$t_+$	$E/mv$	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2,0})$	$m_2$	$E/mv$	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2,0})$
0.01016	0.09954	0.3958	0.400	-0.034	0.0174	0.09984	0.419	-0.034	0.0182
	0.30472		1.065	-0.012	0.0500	0.30452	1.028	-0.012	0.0485
	0.51779		1.645	0.024	0.0794	0.51979	1.669	0.024	0.0804
0.02393		0.3938				0.53122	1.703	0.021	0.0821
						0.57754	1.840	0.024	0.0889
	0.09867		0.345	-0.012	0.0158	0.09967	0.368	-0.012	0.0166
	0.19945		0.675	-0.024	0.0310	0.19845	0.646	-0.024	0.0298
	0.50703		1.510	-0.024	0.0710	0.50803	1.519	-0.024	0.0710
0.04025		0.3926				0.53122	1.585	0.009	0.0741
	0.09897		0.326	-0.018	0.0147	0.09807	0.354	-0.018	0.0158
	0.19907		0.600	-0.002	0.0286	0.19807	0.599	-0.002	0.0281
	0.30111		0.915	-0.043	0.0418	0.30011	0.849	-0.043	0.0406
	0.40016		1.091	0.024	0.0535	0.40002	1.094	0.024	0.0529
	0.50577		1.325	0.025	0.0647	0.50477	1.351	0.025	0.0658
0.06239		0.391				0.53122	1.416	0.025	0.0691
						0.56754	1.505	0.043	0.0735
	0.09947		0.290	-0.007	0.0135	0.09907	0.289	-0.007	0.0146
	0.20069		0.510	0.037	0.0263	0.20002	0.521	0.037	0.0258
	0.30044		0.780	0.007	0.0379	0.30014	0.752	0.007	0.0369
	0.40218		0.975	0.035	0.0486	0.40118	0.985	0.035	0.0480
0.09096		0.3895				0.50425	1.222	-0.011	0.0594
						0.54222	1.310	0.034	0.0636
	0.09956		0.240	0.013	0.0122	0.09856	0.245	0.013	0.0132
	0.19924		0.465	0.021	0.0235	0.19824	0.459	0.021	0.0229
	0.29904		0.685	0.013	0.0337	0.29504	0.667	0.013	0.0323
	0.40032		0.885	0.006	0.0431	0.40202	0.897	0.006	0.0427
KCL 0.01004		0.4886				0.50345	1.114	-0.047	0.0526
						0.53022	1.172	0.032	0.0552
	0.09851		0.415	0.012	0.0154	0.09751	0.444	0.012	0.0164
	0.20314		0.856	0.001	0.0330	0.20031	0.833	0.001	0.0318
	0.29988		1.265	-0.028	0.0476	0.29958	1.208	-0.028	0.0467
	0.38995		1.535	0.035	0.0605	0.38695	1.538	0.035	0.0598
0.03008		0.48847				0.49389	1.942	0.014	0.0758
						0.50104	1.969	0.023	0.0769
	0.09946		0.370	0.014	0.0148	0.09846	0.379	0.014	0.0150
	0.20120		0.767	0.009	0.0292	0.20012	0.748	0.009	0.0286
	0.29956		1.113	0.015	0.0422	0.29906	1.106	0.015	0.0417
	0.40134		1.468	-0.040	0.0550	0.40104	1.476	-0.040	0.0553
0.05028		0.4885				0.48705	1.788	0.041	0.0668
						0.50688	1.860	0.024	0.0694
	0.09930		0.355	-0.002	0.0136	0.09093	0.342	-0.002	0.0136
	0.19926		0.705	-0.017	0.0264	0.19906	0.675	-0.017	0.0262
	0.30125		0.960	0.046	0.0388	0.30105	0.988	0.046	0.0381
	0.40200		1.315	-0.013	0.0501	0.4002	1.292	-0.013	0.0497

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TABLE 2 cont...

NaCl		Gly				NaI			
$m_1$	$m_2$	$t_+$	E/mv	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2.0})$	$m_2$	E/mv	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2.0})$
	0.50481		1.607	-0.026	0.0609	0.50281	1.608	-0.026	0.0617
0.0702		0.4886				0.54321	1.732	0.042	0.0664
	0.09891		0.293	0.034	0.0125	0.09801	0.303	0.034	0.0132
	0.20092		0.608	0.033	0.0247	0.20062	0.591	0.033	0.0241
	0.50365		1.440	0.099	0.0558	0.50265	1.442	0.099	0.0562
						0.54024	1.547	0.032	0.0602
						0.55654	1.593	0.032	0.0619
0.0903		0.4887							
	0.09911		0.325	-0.020	0.0117	0.09811	0.343	-0.020	0.0124
	0.19833		0.589	0.000	0.0227	0.19633	0.583	0.000	0.0220
	0.29833		0.872	-0.027	0.0325	0.29833	0.833	-0.027	0.0319
	0.50315		1.315	0.021	0.0514	0.50315	1.334	0.021	0.0519
						0.52132	1.379	0.023	0.0537
						0.57643	1.514	0.041	0.0591
RbCl						RbI			
0.01014	0.10020	0.5032	0.531	-69.000	0.0172	0.10022	0.478	-69.000	0.0187
	0.19866		0.750	0.016	0.0333	0.19846	0.877	0.016	0.0335
	0.30069		1.400	-0.086	0.0491	0.30049	1.292	-0.086	0.0488
	0.40229		1.663	0.044	0.0639	0.40129	1.701	0.044	0.0639
	0.50570		2.135	-0.050	0.0780	0.50057	2.105	-0.050	0.0788
						0.51232	2.153	0.032	0.0805
						0.53212	2.233	0.032	0.0835
0.02001		0.5032							
	0.09987		0.439	-0.005	0.0162	0.09947	0.453	-0.005	0.0172
	0.19960		0.810	0.031	0.0315	0.19906	0.816	0.031	0.0312
	0.30162		1.226	0.009	0.0462	0.30132	1.189	0.009	0.0456
	0.40351		1.573	0.030	0.0600	0.40321	1.560	0.030	0.0599
	0.50756		1.915	0.038	0.0731	0.50706	1.939	0.038	0.0745
						0.52321	1.997	0.023	0.0768
						0.55002	2.095	0.042	0.0806
0.04027		0.0532							
	0.10072		0.410	-0.012	0.0148	0.10012	0.420	-0.012	0.0160
	0.19983		0.755	0.010	0.0286	0.19903	0.747	0.010	0.0283
	0.30115		1.110	0.007	0.0417	0.30105	1.083	0.007	0.0411
	0.50612		1.763	-0.009	0.0655	0.50602	1.760	-0.009	0.0668
	0.40173		1.392	0.050	0.0539	0.40113	1.414	0.050	0.0536
						0.51123	1.777	0.032	0.0674
						0.52319	1.817	0.023	0.0689
0.06041		0.0532							
	0.09903		0.382	-0.019	0.0135	0.09603	0.391	-0.019	0.0143
	0.19897		0.706	-0.002	0.0262	0.19877	0.702	-0.002	0.0260
	0.30068		1.031	-0.004	0.0383	0.30028	1.008	-0.004	0.0375
	0.40173		1.329	-0.005	0.0494	0.40133	1.314	-0.005	0.0490
	0.50623		1.608	-0.006	0.0597	0.50623	1.631	-0.006	0.0610
						0.55011	1.764	0.024	0.0660
0.08054		0.0532							
	0.09887		0.332	0.004	0.0125	0.09847	0.352	0.004	0.0135
	0.19991		0.670	-0.013	0.0244	0.19941	0.641	-0.013	0.0241
	0.29994		0.915	0.034	0.0354	0.29494	0.915	0.034	0.0342
	0.40004		1.240	-0.021	0.0454	0.40014	1.217	-0.021	0.0452
	0.50343		1.493	-0.021	0.0548	0.50343	1.513	-0.021	0.0561
						0.51177	1.536	0.042	0.0569
NaCl						NaI			
	DL-Ala					DL-Ala			
0.00997	0.1003	0.3958	0.326	0.000	0.0155	0.1023	0.346	0.000	0.0166
	0.2042		0.642	-0.001	0.0304	0.2092	0.647	-0.001	0.0309
	0.3058		0.924	-0.001	0.0439	0.30501	0.916	-0.001	0.0436
	0.4093		1.195	-0.006	0.0565	0.4063	1.200	-0.006	0.0571

TABLE 2 cont...

NaCl						NaI			
$m_1$	Gly $m_2$	$t_+$	E/mv	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2.0})$	Gly $m_2$	E/mv	$\delta E/mv$	$\ln(\gamma_2/\gamma_{2.0})$
0.02043		0.3943				0.4511	1.326	-0.042	0.0631
	0.1009		0.305	-0.001	0.0144	0.1029	0.324	-0.001	0.0155
	0.2051		0.596	-0.002	0.0283	0.2021	0.575	-0.002	0.0274
	0.3068		0.852	0.000	0.0406	0.30608	0.838	0.000	0.0398
	0.4023		1.066	0.008	0.0513	0.34041	0.924	0.005	0.0440
						0.4023	1.081	0.008	0.0514
0.0402		0.3926							
	0.1017		0.275	0.001	0.0131	0.10102	0.287	0.001	0.0133
	0.2053		0.527	0.001	0.0253	0.20501	0.516	0.001	0.0245
	0.3069		0.758	-0.003	0.0362	0.3059	0.739	-0.003	0.0354
	0.4131		0.960	0.006	0.0463	0.41021	0.969	0.006	0.0466
						0.42321	0.998	0.054	0.0480
						0.50112	1.169	0.008	0.0564
0.06061		0.3912				0.52311	1.218	0.005	0.0588
	0.1008		0.245	0.001	0.0118				
	0.2049		0.476	-0.001	0.0229	0.1018	0.258	0.001	0.0984
	0.3064		0.672	0.004	0.0325	0.2029	0.459	-0.001	0.1926
	0.4027		0.845	0.001	0.0407	0.3034	0.658	0.004	0.2864
						0.4047	0.859	0.001	0.3809
						0.45323	0.955	0.004	0.4261
						0.48765	1.024	0.006	0.4582
0.08066		0.3900							
	0.1007		0.224	0.001	0.0108	0.1067	0.241	0.001	0.0121
	0.2043		0.426	0.006	0.0208	0.20402	0.417	0.006	0.0206
	0.3067		0.617	-0.003	0.0296	0.3097	0.609	-0.003	0.0298
	0.4116		0.785	-0.008	0.0374	0.41036	0.791	-0.008	0.0385
						0.43212	0.830	0.006	0.0404
						0.47862	0.914	0.007	0.0445
KCl						KI			
0.01024	0.10152	0.4886	0.408	0.004	0.0158	0.10252	0.432	0.004	0.0164
	0.20419		0.825	-0.014	0.0312	0.20319	0.798	-0.014	0.0307
	0.3074		1.185	0.046	0.0458	0.30014	1.150	0.046	0.0445
	0.41276		1.543	0.015	0.0600	0.41176	1.555	0.015	0.0603
						0.42313	1.597	0.004	0.0620
						0.45634	1.717	0.004	0.0667
						0.4898	1.839	0.008	0.0714
0.02012		0.4885							
	0.10087		0.381	-0.007	0.0143	0.10187	0.418	-0.007	0.0148
	0.20327		0.735	-0.001	0.0282	0.20227	0.719	-0.001	0.0276
	0.30565		1.101	-0.027	0.0413	0.30265	1.020	-0.027	0.0404
	0.41031		1.289	-0.021	0.0540	0.41081	1.344	-0.021	0.0542
						0.42313	1.381	0.003	0.0558
						0.43288	1.410	0.003	0.0570
						0.49874	1.608	0.005	0.0654
0.03016		0.48846							
	0.10336		0.378	-0.024	0.0136	0.10236	0.375	-0.024	0.0150
	0.20803		0.676	0.014	0.0266	0.20503	0.671	0.014	0.0262
	0.31825		0.998	0.026	0.0394	0.31725	0.994	0.026	0.0384
	0.42019		1.289	0.023	0.0468	0.41019	1.262	0.023	0.0485
						0.45643	1.395	0.003	0.0535
						0.56434	1.706	0.007	0.0653
0.04000		0.48846							
	0.1313		0.357	0.057	0.0159	0.13013	0.389	0.057	0.0186
	0.2078		0.654	-0.012	0.0247	0.2058	0.614	-0.012	0.0262
	0.31238		0.954	-0.020	0.0360	0.31038	0.926	-0.020	0.0367
	0.41997		1.226	-0.011	0.0468	0.41997	1.252	-0.011	0.0477
						0.45368	1.352	-0.004	0.0511

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TABLE 2 cont...

NaCl		Gly				NaI Gly				
$m_1$	$m_2$	$t_+$	E/mv	$\delta E$ /mv	$\ln(\gamma_2/\gamma_{2,0})$	$m_2$	E/mv	$\delta E$ /mv	$\ln(\gamma_2/\gamma_{2,0})$	
RbCl						RbI				
0.01007	0.10187	0.5032	0.376	0.003	0.0142	0.10107	0.389	0.003	0.0148	
	0.20389		0.724	0.004	0.0272	0.20289	0.710	0.004	0.0267	
	0.30697		1.056	-0.004	0.0393	0.30607	1.035	-0.004	0.0387	
	0.41259		1.354	-0.004	0.0504	0.41209	1.370	-0.004	0.0510	
					0.45321	1.499	0.005	0.0558		
					0.48797	1.609	0.005	0.0599		
0.02007		0.5032				0.10204	0.362	0.004	0.0141	
	0.10224		0.348	0.004	0.0131	0.10204	0.362	0.004	0.0141	
	0.20395		0.659	0.013	0.0251	0.20195	0.649	0.013	0.0245	
	0.30671		0.975	-0.010	0.0361	0.30471	0.945	-0.010	0.0352	
	0.40265		1.203	0.006	0.0452	0.40205	1.225	0.006	0.0453	
					0.45354	1.373	0.004	0.0506		
					0.4898	1.478	0.004	0.0544		
					0.52312	1.573	0.003	0.0578		
0.04028		0.5032				0.10105	0.318	0.005	0.0123	
	0.10185		0.305	0.005	0.0116	0.10105	0.318	0.005	0.0123	
	0.20447		0.586	0.005	0.0221	0.20403	0.573	0.005	0.0217	
	0.30695		0.845	-0.002	0.0315	0.30605	0.825	-0.002	0.0309	
	0.41008		1.064	0.000	0.0398	0.41018	1.082	0.000	0.0404	
					0.45304	1.187	0.003	0.0443		
					0.48765	1.273	0.005	0.0474		
					0.56455	1.463	0.004	0.0544		
0.06043		0.5032				0.10101	0.308	-0.001	0.0111	
	0.10171		0.280	-0.001	0.0104	0.10101	0.308	-0.001	0.0111	
	0.20346		0.558	-0.300	0.0197	0.20316	0.520	-0.300	0.0192	
	0.30603		0.742	0.004	0.0279	0.30403	0.729	0.004	0.0273	
	0.4115		0.932	0.008	0.0352	0.41015	0.949	0.008	0.0358	
					0.45342	1.039	0.004	0.0393		
					0.47657	1.087	0.006	0.0411		
					0.59898	1.341	0.007	0.0509		
0.08035		0.5032				0.10181	0.263	0.007	0.0102	
	0.10081		0.243	0.007	0.0093	0.10181	0.263	0.007	0.0102	
	0.20359		0.475	0.000	0.0178	0.20259	0.458	0.000	0.0172	
	0.30468		0.665	0.001	0.0249	0.30268	0.651	0.001	0.0241	
	0.40126		0.825	0.000	0.0307	0.40106	0.842	0.000	0.0309	
					0.45654	0.949	-0.005	0.0347		
					0.57654	1.182	0.008	0.0430		

to equation 1.

$$-E = \frac{2RT}{F} m_2 t_+ (A + Bm_1^{1/2} + Cm_2 + Dm_1) \quad (1)$$

The A, B, C and D are the coefficients of the equation, their values are given TABLE 4 and constant A is salt-amino acid pair interaction coefficient and  $t_+$  is the cationic transference number in the absence of amino acids. The values of coefficients A, B, C and D are put in eq. (2) for the power series determination of logarithm of electrolyte activity coefficient.

$$\ln(\gamma_1/\gamma_{1,0}) = Am_2 + Bm_2^{1/2}m_2 + Cm_2^2 + Dm_1m_2 \quad (2)$$

Being the mean ionic activity coefficient in the

absence of nonelectrolyte, the cation transference numbers are required at each molality of the salt for the analysis of experimental results. Their values were obtained from literature<sup>[12]</sup> and given in TABLE 2, due to the non-availability of the transference numbers of  $Rb^+$  these were assumed to be equal to that of  $K^+$  at 0.04m and independent of concentration. Only those parameters the numerical values of whose estimates were greater than their respective 95% confidence limits were used in the final regression. It was found that A, B and C parameters were sufficient for the analysis of the present data  $t_+$  and estimates along with their 95% confidence limits, and their values are given in TABLE 3. The A val-



**TABLE 3:** The regression constants of the  $E/mv$  vs  $m_2$  and the  $\ln(\gamma_2/\gamma_{2,0})$  vs  $m_2$  of the amino acids for the fixed  $m_1$  of salt systems. The  $E/mv, m_2 \rightarrow 0$  is intercept represented as  $E^0/mv$  and  $S_E$  slope value likewise  $\ln(\gamma_2/\gamma_{2,0}), m_2 \rightarrow 0$ , intercept represented as  $\ln(\gamma_2/\gamma_{2,0})^0$  and  $S_A$  slope value

NaCl $m_1$	$t_+$	Gly				Gly NaI			
		$E^0/mv$	$S_E$	$\ln(\gamma_2/\gamma_{2,0})^0$	$S_A$	$E^0/mv$	$S_E$	$\ln(\gamma_2/\gamma_{2,0})^0$	$S_A$
0.01016	0.3958	0.122	2.975	0.0034	0.1482	0.122	2.975	0.0034	0.1481
0.02393	0.3938	0.086	2.821	0.0033	0.1340	0.086	2.820	0.0034	0.1331
0.04025	0.3926	0.113	2.452	0.0036	0.1231	0.113	2.452	0.0037	0.1230
0.06239	0.3910	0.061	2.305	0.0036	0.1106	0.060	2.302	0.0037	0.1106
0.09096	0.3895	0.033	2.146	0.0036	0.0973	0.034	2.146	0.0036	0.0973
		DL-Ala				DL-Ala			
		NaCl				NaI			
0.00997	0.3958	0.056	2.809	0.0028	0.1327	0.056	2.809	0.0030	0.1333
0.02043	0.3943	0.064	2.526	0.0032	0.1196	0.064	2.526	0.0032	0.1197
0.04020	0.3926	0.064	2.206	0.0028	0.1074	0.064	2.206	0.0024	0.1078
0.06061	0.3912	0.056	1.983	0.0031	0.9363	0.056	1.983	0.0034	0.9326
0.08066	0.3900	0.050	1.810	0.0027	0.0861	0.050	1.810	0.0029	0.0869
		Gly				Gly			
		KCL				KI			
0.01004	0.4886	0.076	3.780	0.0019	0.1492	0.076	3.779	0.0018	0.1498
0.03008	0.4885	0.022	3.626	0.0020	0.1331	0.022	3.627	0.0019	0.1332
0.05028	0.4885	0.063	3.071	0.0028	0.1167	0.063	3.072	0.0029	0.1167
0.07020	0.4886	0.027	2.814	0.0026	0.1060	0.027	2.815	0.0028	0.1063
0.09030	0.4887	0.103	2.448	0.0028	0.0975	0.103	2.448	0.0028	0.0977
		DL-Ala				DL-Ala			
		KCl				KI			
0.01024	0.4886	0.059	3.630	0.0018	0.1419	0.059	3.630	0.0019	0.1420
0.02012	0.4885	0.113	2.996	0.0018	0.1275	0.113	2.996	0.0018	0.1276
0.03016	0.4885	0.079	2.880	0.0038	0.1083	0.079	2.880	0.0039	0.1087
0.04000	0.4885	0.001	2.975	0.0051	0.1003	0.001	2.975	0.0055	0.1004
		Gly				Gly			
		RbCL				RbI			
0.01014	0.5032	0.071	4.064	0.0031	0.1500	0.071	4.064	0.0037	0.1500
0.02001	0.5032	0.091	3.644	0.0031	0.1402	0.091	3.644	0.0032	0.1406
0.04027	0.0532	0.089	3.301	0.0031	0.1251	0.090	3.301	0.0034	0.1252
0.06041	0.0532	0.101	3.022	0.0032	0.1136	0.101	3.023	0.0033	0.1139
0.08054	0.0532	0.069	2.865	0.0031	0.1046	0.070	2.866	0.0032	0.1050
		DL-Ala				DL-Ala			
		RbCl				RbI			
0.01007	0.5032	0.069	3.154	0.0029	0.1166	0.070	3.154	0.0030	0.1166
0.02007	0.5032	0.067	2.872	0.0033	0.1036	0.068	2.878	0.0035	0.1038
0.04028	0.5032	0.068	2.469	0.0030	0.0908	0.069	2.469	0.0031	0.0910
0.06043	0.5032	0.098	2.072	0.0029	0.0798	0.099	2.074	0.0030	0.0800
0.08035	0.5032	0.064	1.933	0.0030	0.0688	0.065	1.936	0.0032	0.0690

ues are plotted in figure 3. In general the values of A, B and C coefficients are slightly lower for iodide salts than of chlorides. It could be amounted to the induced potential of the  $I^-$  anion present solutions

perhaps  $I^-$  strengthen the salt-amino acid interactions. The values for DL- $\alpha$  alanine in aqueous NaCl at 298.15K from references 6 and 13 and  $\ln(\gamma_2/\gamma_{2,0})$  values for chosen systems are listed in TABLE 2.

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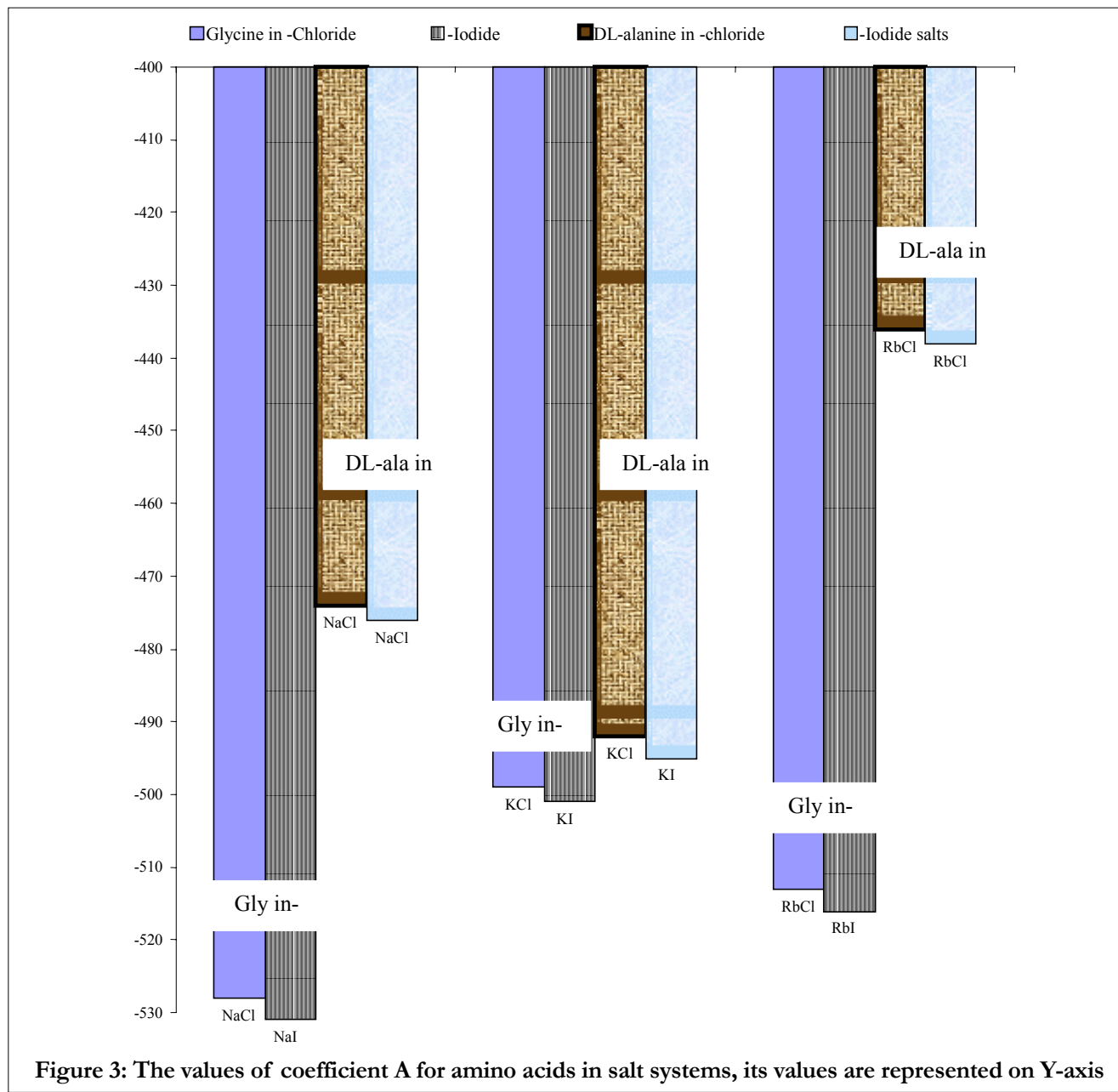


TABLE 4: the coefficients of the equation obtained for the amino acids in salt systems, the values of coefficient A are negative for systems. The term D is very negligible for nonelectrolytes hence are omitted. The units of the coefficients A/kg mol<sup>-1</sup>, B/kg<sup>3/2</sup>mol<sup>3/2</sup>, C/kg<sup>2</sup>mol<sup>-2</sup>.

salts	Gly in salt systems						
	A	B	C	A	B	C	
NaCl	-528	659	131	NaI	-531	661	132
KCl	-499	618	102	KI	-501	620	103
RbCl	-513	653	102	RbI	-516	655	104
DL- $\alpha$ -alanine in salt systems							
NaCl	-474	653	135	NaI	-476	654	137
KCl	-492	569	105	KI	-495	571	107
RbCl	-436	648	138	RbI	-438	650	139

However these values for glycine are higher than those DL- $\alpha$  alanine, probably it happens due to the hydrophobic effect of the  $-\text{CH}_3$  group of DL- $\alpha$  alanine. Further the  $\ln(\gamma_2/\gamma_{2,0})$  values of acids in iodide salts are slightly higher than those of chlorides, although like chloride salts the higher values are found for glycine than those of DL- $\alpha$  alanine. The  $\delta E$  values defined  $\delta E = E(\text{expt}) - E(\text{calc, eqn 1})$  are indicative of the scatter of the data and are included in TABLE 2 and remain almost same for the salts. Applying the cross differential relation<sup>[13]</sup> to equation (2), the expression for the activity coefficient of amino acids<sup>[3]</sup> can be obtained as a power series in  $m_1$  and  $m_2$ .

$$\ln(\gamma_2/\gamma_{2,0}) = m_1(2A + \frac{4}{3}Bm_1^{1/2} + Dm_1) + 4Cm_1m_2 \quad (3)$$

Here  $\gamma_2$  and  $\gamma_{2,0}$  are the activity coefficients of amino acids in the presence and absence of electrolyte, respectively. With molalities of amino acids these values do not increase linearly and are slightly higher for iodide salts than those of the chlorides. This proves that concentrations of amino acids the  $\ln\gamma_2/\gamma_{2,0}$  values however salt concentration decrease the values. The concentrations of acids perhaps break the water structure that enhances the solubilization of the acids while of salt strengthen the cation-zwitterion interactions along with cage formation around the  $-\text{CH}_2-$  of glycine and  $-\text{CH}_3-\text{CH}-$  of DL- $\alpha$  alanine (TABLE 2). Perhaps this action mechanism may be very effective to monitor the activities of salt-amino acids solutions of biophysical and biotechnological significance<sup>[16]</sup>. Although the similar trend of  $\ln\gamma_2/\gamma_{2,0}$  values for amino acids is observed in iodide salt systems but their values are higher (TABLE 3). No definite trend with salt is found and glycine produced

higher  $\ln\gamma_2/\gamma_{2,0}$  values than those of KCl and RbCl, noticeably KCl gives lowest values for acids. It could be rationalized to the fact that the 3d empty sub-orbital cause some induced potential in the  $\text{K}^+$  ion causing stronger ion hydration formation. This structure of  $\text{K}^+$  ion influences the activity of amino acids. Further the  $\ln\gamma_2/\gamma_{2,0}$  values for DL- $\alpha$  alanine are found lower by  $\pm 0.005$  than those of glycine with both categories of the salts, this is evident due to the hydrophobic effect of  $-\text{CH}_3$  of alanine. A rough linear regression of the  $\ln\gamma_2/\gamma_{2,0}$  data of acids against their molalities is made and its coefficient is noted as  $\ln(\gamma_2/\gamma_{2,0})^0$  and slope  $S_A$ , the values are listed in TABLE 3 and plotted in figure 2. It is noted that the  $S_A$  values decrease with salt concentrations that shows a net decrease in the activity of the acids. For higher salts concentrations though the trend remains same but higher  $S_A$  values for iodide salts are noted. Similarly the  $E/\text{mv}$  values are regressed against acid's molalities, the coefficient  $E^0/\text{mv}$  is intercept and  $S_E$  is slope, the values are noted in TABLE 3. With both the categories of the salts these values decrease with their concentrations, it could be attributed the stronger amino acid-salt interactions and pair wise interaction both for salts as well as acids. The values of the A, B and C coefficients are found slightly higher for iodide salts than those of chlorides, it depicts that  $\text{I}^-$  contributes larger share to the  $\ln(\gamma_2/\gamma_{2,0})$  than those of the chlorides and these parameters are noted higher for glycine than those of alanine (TABLE 4). Further the  $\ln(\gamma_2/\gamma_{2,0})$  data of acids are regressed against the salts molality  $m_1$  and their intercept is resented as  $\ln(\gamma_2/\gamma_{2,0})_{m_1 \rightarrow 0}$  and slope as  $S_{\text{activity coefficient}}$  in TABLE 5. These values do not reflect any definite effect of the size of cation, for the types of

TABLE 5: The regression analysis of  $\ln(\gamma_2/\gamma_{2,0})^0$  of amino acids vs  $m_1$  of salts in solution, the  $\ln(\gamma_2/\gamma_{2,0})_{m_1 \rightarrow 0}$  is intercept and  $S_{\text{activity coefficient}}$  the slope value.

	$(\gamma_2/\gamma_{2,0})_{m_1 \rightarrow 0}$	$S_{\text{activity coefficient}}$		$(\gamma_2/\gamma_{2,0})_{m_1 \rightarrow 0}$	$S_{\text{activity coefficient}}$
Gly in NaCl	0.0034	0.00297	Gly in NaI	0.0034	0.00295
Gly in KCl	0.0018	0.01212	Gly in KI	0.0017	0.01403
Gly in RbCl	0.0031	0.00011	Gly in RbI	0.0035	-0.00413
DL-Ala in NaCl	0.0030	-0.00154	DL-Ala in NaI	0.0030	-0.00004
DL-Ala in KCl	0.0001	-0.12110	DL-Ala in KI	0.0000	0.01310
DL-Ala in RbCl	0.0031	-0.00159	DL-Ala in RbI	0.0032	-0.01275

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**TABLE 6:** The data of trace activity coefficient ( $-\ln\gamma_2^{\text{tr}}$ ) of amino acids in salt solutions with concentration ( $m_1/\text{molkg}^{-1}$ ) at 308.15K.

$-\ln\gamma_2^{\text{tr}}$ of glycine in aqueous salts								
NaCl, $m_1$	NaCl $-\ln\gamma_2^{\text{tr}}$	NaI $-\ln\gamma_2^{\text{tr}}$	KCl $m_1$	KCl $-\ln\gamma_2^{\text{tr}}$	KI $-\ln\gamma_2^{\text{tr}}$	RbCl $m_1$	RbCl $-\ln\gamma_2^{\text{tr}}$	RbI $-\ln\gamma_2^{\text{tr}}$
0.01016	0.0038	0.0043	0.01004	0.0035	0.0043	0.01014	0.0037	0.0041
0.02393	0.0085	0.0084	0.03008	0.0100	0.0100	0.02012	0.0071	0.0071
0.04025	0.0138	0.0133	0.05028	0.0159	0.0158	0.04027	0.0135	0.0132
0.06239	0.0203	0.0199	0.07020	0.0214	0.0215	0.06041	0.0194	0.0192
0.09096	0.0280	0.0285	0.09030	0.0264	0.0272	0.08054	0.0249	0.0253
$-\ln\gamma_2^{\text{tr}}$ of DL- $\alpha$ alanine								
0.00977	0.0033	0.0037	0.01024	0.0037	0.0075	0.01007	0.0030	0.0035
0.02043	0.0065	0.0065	0.02012	0.0070	0.0108	0.02007	0.0058	0.0058
0.04020	0.0121	0.0118	0.03016	0.0103	0.0140	0.04028	0.0109	0.0106
0.06061	0.0174	0.0172	0.04000	0.0134	0.0173	0.06043	0.0155	0.0154
0.08066	0.0221	0.0225				0.08035	0.0196	0.0201

salts the alanine has lower values of them. Likewise trace activity coefficients  $\gamma_2^{\text{tr}}$  of the amino acid are obtained by putting  $m_2=0$ , where  $\gamma_{2,0}=1$ , in eqn (3), thus  $\gamma_2^{\text{tr}}$  is represented as.

$$\ln \gamma_2^{\text{tr}} = \{2A + (4/3)Bm_1^{1/2} + Dm_1\}m_1 \quad (4)$$

The  $\ln \gamma_2^{\text{tr}}$  values are given in TABLE 6 and can be seen that the variation of electrolyte activity coefficient is not linear with amino acid concentration. Though the contrary observations have been made in the case of relatively concentrated solution of other salt + amino acid systems<sup>[4]</sup>. This indicates a decrease in the salt's activity coefficient with increase in amino acid concentration and the decrease becomes less pronounced with concentrations of them. It indicates that salting out effects tend to be predominant at around higher salt concentrations and similar conclusions about amino acid activity coefficient can be drawn from the variation of  $\ln \gamma_2^{\text{tr}}$  with electrolyte. The iodide salts have got larger values than those of the chlorides (TABLE 6) have. The leading term in the activity coefficient expansion, eqn (2), arises from the pair wise interactions between the salts and the acids. The coefficient A, a measure of pair wise interaction illustrates contributions from the cation as well as the anion. It can be seen from TABLE 4 that A values for the two systems are negative which indicates, in agreement with the earlier conclusions, a net attractive interac-

tion between salts and acids. As far as we are aware, no data are available in literature for these systems at 308.15K for comparison purposes. However DL- $\alpha$  alanine in aqueous NaCl has been studied at 298.15K by Kelley and Cilley and phang<sup>[15]</sup> (TABLE 2). The higher A value reported by phang<sup>[15]</sup> is not unexpected, as a value obtained from data on concentrated solutions contains, in addition to the pairwise interactions, the contributions from triplet and higher order solute-solute interactions<sup>[7]</sup>. In view of this the value of the pair wise interaction coefficient A obtained from dilute solutions seems to be more reliable. The values for KCl and RbCl are of same order of magnitude as for NaCl and it is true for iodide salts. No correlation could be found between A values and the cation size.

## CONCLUSION

The studies have denoted that the larger the chain length weaker is the activity coefficient of the amino acids. Also the iodide ion cause strengthens the salt-amino acid interactions and  $-\text{CH}_3$  group of the alanine weakens the salt-amino acid interactions. The KCl/I produces lower activity and potential values while NaCl/I and RbCl/I salts slightly higher values.

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