



(RESEARCH ARTICLE)



To investigate the thermodynamic parameters of Li, Na and K salt of L leucinate at various temperature and concentration by conductometric measurement

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International Journal of Science and Research Archive, 2023, 09(01), 294–302

Publication history: Received on 07 April 2023; revised on 20 May 2023; accepted on 23 May 2023

Article DOI: <https://doi.org/10.30574/ijrsra.2023.9.1.0386>

Abstract

Recently in this laboratory the conductometric measurement of aqueous solutions of Li, Na and K salt of L-leucine were studied at different temperature and molar concentration to investigate the solute-solvent, ion-solvent interactions (solute means drug) and also the effect of dilution was investigated. During this work the thermodynamic parameters (change in free energy, change in entropy and change in enthalpy) were investigated at concentrations range (0.01 to 0.15) M and at various temperature 298.15, 303.15, 308.15, and 313.15 K. The thermodynamic parameters helps to understand a solute-solute, solute-solvent and solvent-solvent interaction and this information will also be helpful to understand pharmacokinetics and pharmacodynamics of these drug salts.

Keywords: LSL; SSL; PSL; Conductometric thermodynamic parameters.

1. Introduction

Metal salts of amino acids received more attention of researchers at global level. These salts have various applications in various field of sciences. These salts are effectively used as CO₂ absorbents. Climatic change is a result of excessively changes atmospheric background. Day by day carbon dioxide (CO₂) emissions is increasing which is most concerning environmental issue, a global warming. The salt solution of the amino acids is developing into an absorbent for CO₂ capture[1-2] for evaluation and thorough characterization of the solvent for CO₂ collection and other industrial applications, the physicochemical properties of absorbents are required [3-6]. Solubility, ionisation and mobilization of metal salt closely related to their conductivity. Ionisation and solubility strongly influence by molecular interaction like solute-solute interaction, solute-solvent and solvent-solvent interactions, intra and intermolecular interaction effect on the conductivity. Conductometric measurements are one of the unique non-destructive, environmentally friendly and simple to handle research techniques.

The thermodynamic parameters obtained in conductometric measurements will become a useful tool to predict drug activity and drug effect in medicinal and drug chemistry. Leucine has its own importance in medicinal sciences and pharmaceutical sciences due to their significant application. Metal salt of this amino acid affects the solubility and conductivity. Conductometric investigation received more attention of researchers for molecular interactions investigation at various concentration and different temperatures by using different types of molecules [7-13].

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Navarro *et al.* [14] reported the densities, refractive indices, electrical conductivity and viscosities of aqueous potassium and sodium salt solutions containing serine at normal air pressure and at various temperatures. Tirona *et al.* [15] used experimental validation to correlate the density, refractive index, and electrical conductivity of the amino acid salt solutions with temperature and amino acid salt concentration. In the study of densities, viscosities, refractive indexes, and electrical conductivities of aqueous alkali (potassium or sodium) salts of the amino acid α -alanine at various temperatures and concentrations gave average absolute deviation values of 0.03%. In the studied densities, viscosity, refractive index and electrical conductivity of aqueous alkali (potassium or sodium) salts of the amino acid α -alanine at various temperatures and concentrations for that an empirical equation was applied to correlate the density, refractive index and electrical conductivity of the amino acid salt solutions with temperature gave average absolute deviation values of 0.03%, 0.01% and 0.6% respectively.

Ionic behavior of lithium salt of L-leucine (LSL), sodium salt of L-leucine (SSL) and potassium salt of L-leucine (PSL) were not yet been discussed in the literature at a lower concentration by conductometrically. Therefore, the present investigation designed in the direction to understand effect of low concentrations on thermodynamic parameters of LSL, SSL and PSL at concentration range (0.01 to 0.15) mol L⁻¹ and at different temperatures 298.15, 303.15, 308.15 and 313.15 K appraise ionic behavior of lithium sodium and potassium salt of leucinate. The thermodynamic parameters like ΔH^0 , ΔS^0 and ΔG^0 for the formation have been studied from the values of ion association constant at various temperatures. The computed values have been used to discuss qualitatively the nature of different interactions.

2. Material and methods

All the chemicals used are of AR grade. L-leucine (Leu CAS No. 61-90-5, 99% purity) were supplied by S D Fine-Chem Ltd, India. Alkali hydroxides viz., lithium hydroxide (LiOH, CAS No. 1310-65-2, GR, % purity) was purchased from Sigma Aldrich, while sodium hydroxide (NaOH, CAS No. 1310-73-2, GR, 98 % purity) and potassium hydroxide (KOH, CAS No. 1310-58-3, GR, 98 % purity) were purchased from Merck. All the solutions during investigations were used freshly prepared. Concentrations of solutions varied from 0.01 to 0.15 ml. By neutralizing the amino acid with an equimolar quantity of base (KOH, NaOH, and LiOH), LSL, SSL and PSL solutions were prepared.

A digital conductivity meter was used to measure electrical conductivity. To measure the conductivity, a conductivity cell was submerged in a sample solution. A thermostat was used to maintain the thermal stability of the water bath within ± 0.01 K. A standard KCl solution from Merck was used to calibrate the conductivity meter. Solution's temperature was regulated by placing the sample tube in a water bath. The conductivities were measured for their concentrations range (0.01 to 0.15) M and at 298.15, 303.15, 308.15 and 313.15 K.

The conductivity cell was cleaned with deionised water and ethanol after each test to get rid of any adhering material, and it was then dried before being used for the next measurement. Three repeats of each measurement were made, and the average reading was used. The calculated overall measurement uncertainty was $\pm 1.0\%$.

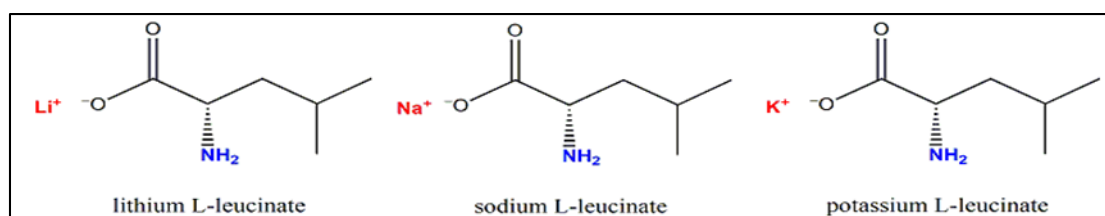


Figure 1 Structure of LSL, SSL and PSL

3. Results and discussion

The observe conductance for each concentration solutions of SSL, LSL and PSL were recorded at temperature 298.15 K, 303.15 K, 308.15 K and 313.15 K. From the data of observed conductance (G), specific conductance (k) and molar conductance (μ) were determined by known literature method and tabulated in Table-1 and Table-2 at 298.15 K, 303.15 K, 308.15 K and 313.15 K respectively.

Table-1, Table-2, Figure 2, Figure 3 and Figure 4 revealed that as concentrations increases the observe conductance and specific conductance also increases while molar conductance decrease for SSL, LSL and PSL solutions. When

temperature increase from 298 K to 313 K observe conductance, specific conductance and molar conductance increases for SSL, LSL and PSL solutions.

Specific conductance and molar conductance were calculated from observe conductance by following equations,

$$K = k \cdot G$$

$$\mu = (K \cdot 1000) / M$$

Where k is cell constant and M is molarity.

Observed conductance (G), specific conductance (k) and molar conductance (μ) values of PSL are greater than SSL and LSL solution.

During this investigation it was observed that the molar conductance of PSL is more than SSL and LSL which is clearly indicates that as ionic size of metal ion increases the conductivity increases. This would be due to formation of hydration sphere around metal ions depending on the size, smaller the size higher is the hydration hence restricts the mobility of ions in solution. Thus PSL has good conductivity and mobility in solution among all three salts which is helpful for diffusion of ions or good drug effect of PSL is comparatively good than SSL and LSL. The absorption, transformation and metabolism of PSL are better than SSL and LSL will show good drugs activity than SSL and LSL. In molar conductance of PSL solutions the values are greater than SSL and LSL.

From Figure 5 it reveals that observed conductance (G) increases in the following increasing order for LSL, SSL and PSL,

$$LSL(G) < SSL(G) < PSL(G).$$

This is because, as the Lewis acidity of alkali cations rises ($Li^+ > Na^+ > K^+$), water molecules clump together more and the sacrificial reduction of counter anions is less effective. Increased H_2O aggregation around Li^+ reduces its mobility and hence conductivity. As the alkali cation's Lewis acidity decreases from Li^+ to K^+ , cation- H_2O and cation-anion interactions become weaker[16].

Table 1 G and K values of LSL, SSL and PSL different temperatures

m (kg.mol ⁻¹)	G 10 ⁻³ (S.cm ⁻¹)				m (kg.mol ⁻¹)	K.10 ⁻³ (S.cm ⁻¹)			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
LSL					LSL				
0.00999	0.74	0.84	0.92	1.01	0.00999	0.7252	0.8232	0.9016	0.9898
0.02975	1.82	2.02	2.25	2.54	0.02975	1.7836	1.9796	2.2060	2.4892
0.04951	2.79	3.12	3.45	3.84	0.04951	2.7342	3.0576	3.3810	3.7632
0.06957	3.64	4.04	4.49	4.97	0.06957	3.5672	3.9592	4.4002	4.8706
0.08957	4.41	4.89	5.42	5.97	0.08957	4.3169	4.7873	5.3067	5.8506
0.10957	5.13	5.73	6.34	6.97	0.10957	5.0274	5.6154	6.2132	6.8306
0.13147	5.89	6.56	7.28	7.99	0.13147	5.7722	6.4239	7.1344	7.8302
0.15336	6.62	7.38	8.16	9.01	0.15336	6.4876	7.2324	7.9968	8.8298
SSL					SSL				
0.01002	0.76	0.85	0.93	1.02	0.01002	0.7448	0.8330	0.9114	0.9996
0.03050	2.05	2.29	2.48	2.72	0.03050	2.0090	2.2442	2.4304	2.6656
0.05098	3.25	3.63	3.98	4.34	0.05098	3.1850	3.5574	3.9004	4.2532

0.06973	4.29	4.8	5.28	5.77	0.06973	4.2042	4.704	5.1744	5.6546
0.08976	5.44	6.05	6.67	7.27	0.08976	5.3312	5.9290	6.5366	7.1246
0.10979	6.52	7.27	8.00	8.61	0.10979	6.3896	7.1246	7.8400	8.4378
0.13074	7.55	8.42	9.25	10.01	0.13074	7.3990	8.2516	9.0650	9.8098
0.15169	8.42	9.35	10.31	11.29	0.15169	8.2516	9.1630	10.1040	11.0640
PSL					PSL				
0.01007	0.83	0.91	0.99	1.08	0.01007	0.8134	0.8879	0.9712	1.0574
0.03010	2.25	2.46	2.67	2.94	0.03010	2.2050	2.4108	2.6166	2.8812
0.05014	3.51	3.86	4.27	4.72	0.05014	3.4398	3.7828	4.1875	4.6256
0.07199	4.79	5.30	5.90	6.50	0.07199	4.6942	5.1940	5.7820	6.3700
0.09103	5.96	6.57	7.29	7.985	0.09103	5.8457	6.4386	7.1442	7.8253
0.11007	7.13	7.87	8.60	9.35	0.11007	6.9874	7.7126	8.4280	9.1630
0.12977	8.25	9.07	9.88	10.71	0.12977	8.0850	8.8886	9.6824	10.496
0.14947	9.32	10.22	11.15	12.07	0.14947	9.1336	10.016	10.927	11.829

Similar trend is observed for (k) and (μ) values as; LSL < SSL < PSL

The (Ksp), log (Ksp) and thermodynamics parameter viz. change in free energy (ΔG), change in entropy (ΔS) and change in enthalpy (ΔH) of LSL, SSL and PSL were determined by known literature method at various molar concentration and temperatures. The values of Ksp, ΔG , ΔH and ΔS are presented in **Table 2**, **Table-3** and **Table-4**, respectively.

The values of Ksp, (ΔG), (ΔH) and (ΔS) were calculated using following equations,

$$\Delta G = -2.303 * 8.314 * T * \log k_{sp}$$

$$\Delta H = (2.303 * R * T_1 * T_2 * \log k_{sp1}) / [\log k_{sp2} * (T_1 - T_2)]$$

$$\Delta S = (\Delta H - \Delta G) / T_1$$

These tables shows that along with increasing concentration, Ksp, ΔH and ΔS values increases continuously while ΔG decreases for PSL solutions. While temperature increases from 298 K to 313K Ksp, ΔH and ΔS decreases continuously while ΔG increases for LSL, SSL and PSL solutions. PSL shows greater values of thermodynamic parameter as well as Ksp than SSL and LSL. Both the systems have positive ΔG values suggest that in the solvent, the dissociation process is favoured over the association process. The negative values of ΔH and ΔS suggest the dissociation process is exothermic and decrease in randomness in the solvent, respectively [17].

Table 2 μ and Ksp of LSL, SSL and PSL at different temperatures

M (mol.L ⁻¹)	μ (S.cm ² .mol ⁻¹)				M (mol.L ⁻¹)	Ksp.10 ⁻³			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
LSL					LSL				
0.00996	72.808	82.647	90.518	99.373	0.00996	0.1033	0.1030	0.1027	0.1023
0.02966	60.131	66.739	74.371	83.919	0.02966	0.9161	0.9135	0.9106	0.9072
0.04936	55.389	61.941	68.492	76.235	0.04936	2.5372	2.5301	2.5219	2.5127
0.06936	51.427	57.079	63.437	70.218	0.06936	5.0097	4.9957	4.9795	4.9613

0.08930	48.339	53.607	59.423	65.513	0.08930	8.3041	8.2808	8.2540	8.2238
0.10924	46.020	51.402	56.874	62.526	0.10924	12.4264	12.3916	12.3515	12.3063
0.13108	44.036	49.008	54.428	59.736	0.13108	17.8902	17.8400	17.7822	17.7171
0.15290	42.429	47.300	52.300	57.748	0.15290	24.3435	24.2752	24.1966	24.1080
SSL					SSL				
0.00999	74.552	83.380	91.228	100.056	0.00999	0.1039	0.1036	0.1033	0.1029
0.03041	66.064	73.799	79.922	87.656	0.03041	0.9629	0.9602	0.9571	0.9536
0.05083	62.661	69.988	76.736	83.677	0.05083	2.6901	2.6826	2.6739	2.6641
0.06952	60.472	67.661	74.427	81.334	0.06952	5.0328	5.0187	5.0024	4.9841
0.08949	59.571	66.251	73.040	79.610	0.08949	8.3393	8.3159	8.2890	8.2587
0.10946	58.372	65.086	71.622	77.083	0.10946	12.4763	12.4414	12.4011	12.3557
0.13035	56.762	63.303	69.543	75.257	0.13035	17.6920	17.6424	17.5852	17.5209
0.15124	54.560	60.587	66.807	73.157	0.15124	23.8161	23.7493	23.6724	23.5857
PSL					PSL				
0.01004	81.053	88.474	96.775	105.368	0.01004	0.1049	0.1046	0.1042	0.1038
0.03001	73.471	80.328	87.186	96.002	0.03001	0.9378	0.9352	0.9322	0.9288
0.04999	68.812	75.674	83.771	92.534	0.04999	2.6018	2.5945	2.5861	2.5767
0.07177	65.402	72.366	80.558	88.750	0.07177	5.3640	5.3489	5.3316	5.3121
0.09076	64.411	70.943	78.718	86.223	0.09076	8.5764	8.5524	8.5247	8.4935
0.10974	63.673	70.281	76.800	83.498	0.10974	12.5393	12.5041	12.4636	12.4180
0.12938	62.490	68.701	74.836	81.123	0.12938	17.4298	17.3810	17.3247	17.2613
0.14902	61.289	67.208	73.324	79.374	0.14902	23.1238	23.0590	22.9843	22.9002

Table 3 ΔG and ΔH of LSL, SSL and PSL at different temperatures

M (mol.L⁻¹)	ΔG(J.mol⁻¹)				M (mol.L⁻¹)	ΔH(J.mol⁻¹)			
	298.15 K	303.15 K	308.15 K	313.15 K		298.15 K	303.15 K	308.15 K	313.15 K
LSL					LSL				
0.00996	22754.35	23143.02	23533.04	23924.44	0.00996	-346013.92	-357602.24	-369381.52	-
0.02966	17343.40	17641.32	17940.60	18241.25	0.02966	-345980.92	-357562.84	-369335.56	-
0.04936	14817.80	15073.37	15330.30	15588.60	0.04936	-345957.28	-357534.61	-369302.64	-
0.06936	13131.13	13358.41	13587.05	13817.07	0.06936	-345936.42	-357509.72	-369273.62	-
0.08930	11878.19	12084.46	12292.09	12501.09	0.08930	-345917.10	-357486.66	-369246.73	-
0.10924	10878.84	11068.35	11259.22	11451.46	0.10924	-345898.50	-357464.46	-369220.86	-
0.13108	9975.34	10149.70	10325.42	10502.51	0.13108	-345878.48	-357440.57	-369193.02	-
0.15290	9211.69	9373.25	9536.16	9700.44	0.15290	-345858.50	-357416.73	-369165.24	-
SSL					SSL				

0.00999	22739.49	23127.90	23517.68	23908.82	0.00999	-346013.85	-357602.16	-369381.42	-
0.03041	17219.94	17515.80	17813.01	18111.59	0.03041	-345979.93	-357561.66	-369334.18	-
0.05083	14672.73	14925.86	15180.36	15436.22	0.05083	-345955.67	-357532.70	-369300.41	-
0.06952	13119.74	13346.84	13575.29	13805.11	0.06952	-345936.27	-357509.53	-369273.40	-
0.08949	11867.69	12073.78	12281.24	12490.06	0.08949	-345916.92	-357486.45	-369246.48	-
0.10946	10868.90	11058.25	11248.95	11441.03	0.10946	-345898.30	-357464.22	-369220.58	-
0.13035	10002.96	10177.78	10353.96	10531.51	0.13035	-345879.14	-357441.37	-369193.94	-
0.15124	9265.99	9428.46	9592.28	9757.47	0.15124	-345860.02	-357418.56	-369167.36	-
PSL					PSL				
0.01004	22717.15	23105.20	23494.60	23885.36	0.01004	-346013.75	-357602.03	-369381.27	-
0.03001	17285.25	17582.20	17880.51	18180.18	0.03001	-345980.46	-357562.29	-369334.91	-
0.04999	14755.45	15009.97	15265.85	15523.10	0.04999	-345956.59	-357533.80	-369301.69	-
0.07177	12961.72	13186.17	13411.97	13639.14	0.07177	-345934.03	-357506.86	-369270.29	-
0.09076	11798.17	12003.10	12209.39	12417.05	0.09076	-345915.73	-357485.02	-369244.82	-
0.10974	10856.43	11045.57	11236.06	11427.93	0.10974	-345898.04	-357463.92	-369220.23	-
0.12938	10039.96	10215.41	10392.21	10570.38	0.12938	-345880.03	-357442.42	-369195.17	-
0.14902	9339.12	9502.82	9667.87	9834.28	0.14902	-345862.06	-357420.98	-369170.19	-

Table 4 ΔS values of LSL, SSL and PSL different temperatures

M(mol.L⁻¹)	$\Delta S(J.mol^{-1} K^{-1})$			
	298.15 K	303.15 K	308.15 K	313.15 K
LSL				
0.00996	-1236.85	-1255.96	-1275.08	-
0.02966	-1218.60	-1237.68	-1256.78	-
0.04936	-1210.05	-1229.12	-1248.20	-
0.06936	-1204.32	-1223.38	-1242.45	-
0.08930	-1200.05	-1219.10	-1238.16	-
0.10924	-1196.64	-1215.68	-1234.72	-
0.13108	-1193.54	-1212.57	-1231.60	-
0.15290	-1190.91	-1209.93	-1228.95	-
SSL				
0.00999	-1236.80	-1255.91	-1275.03	-
0.03041	-1218.18	-1237.27	-1256.36	-
0.05083	-1209.55	-1228.63	-1247.71	-
0.06952	-1204.28	-1223.34	-1242.41	-
0.08949	-1200.02	-1219.07	-1238.12	-
0.10946	-1196.60	-1215.64	-1234.69	-

0.13035	-1193.63	-1212.66	-1231.70	-
0.15124	-1191.10	-1210.12	-1229.14	-
PSL				
0.01004	-1236.73	-1255.84	-1274.95	-
0.03001	-1218.40	-1237.49	-1256.58	-
0.04999	-1209.83	-1228.91	-1247.99	-
0.07177	-1203.74	-1222.80	-1241.87	-
0.09076	-1199.78	-1218.83	-1237.88	-
0.10974	-1196.56	-1215.60	-1234.65	-
0.12938	-1193.76	-1212.79	-1231.83	-
0.14902	-1191.35	-1210.37	-1229.39	-

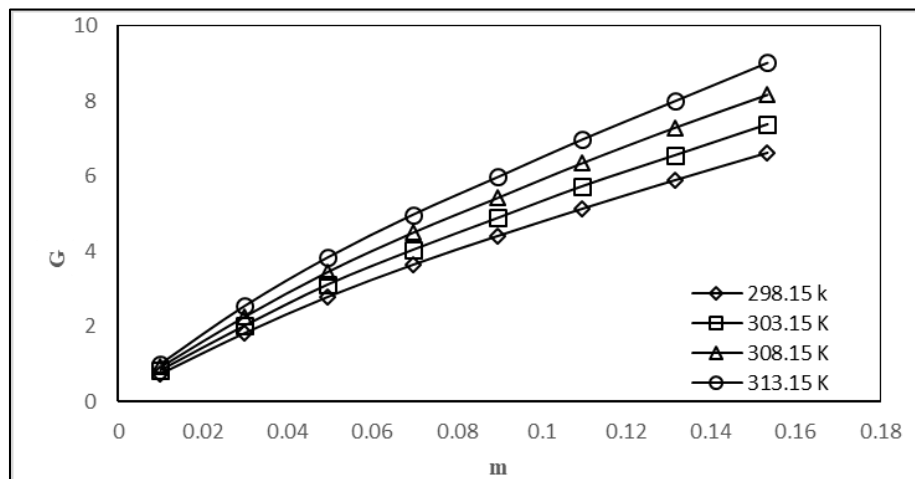


Figure 2 Graph of (G) vs concentration of LSL in water at different temperatures (T).

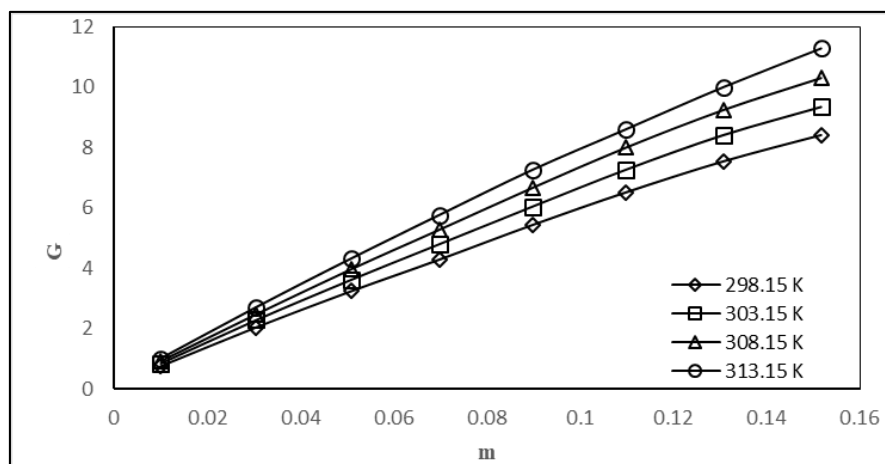


Figure 3 Graph of (G) vs concentration of SSL in water at different temperatures (T).

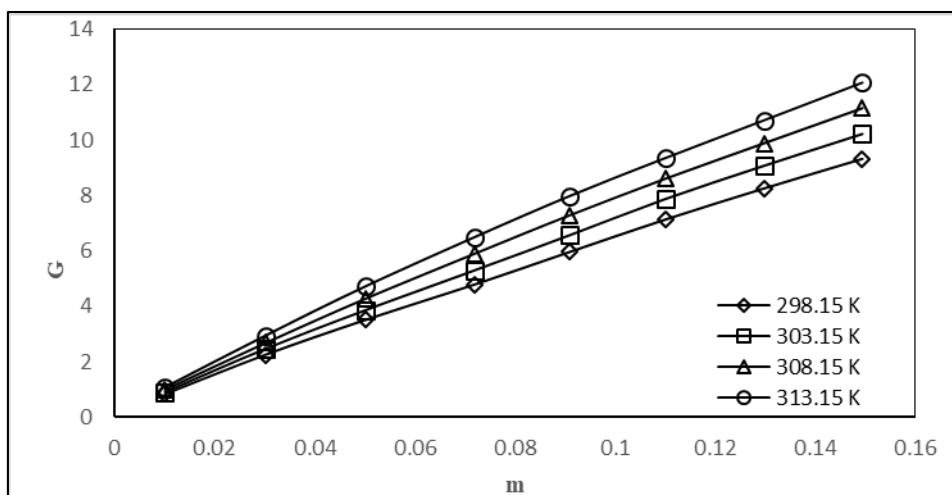


Figure 4 Graph of (G) vs concentration of PSL in water at different temperatures (T).

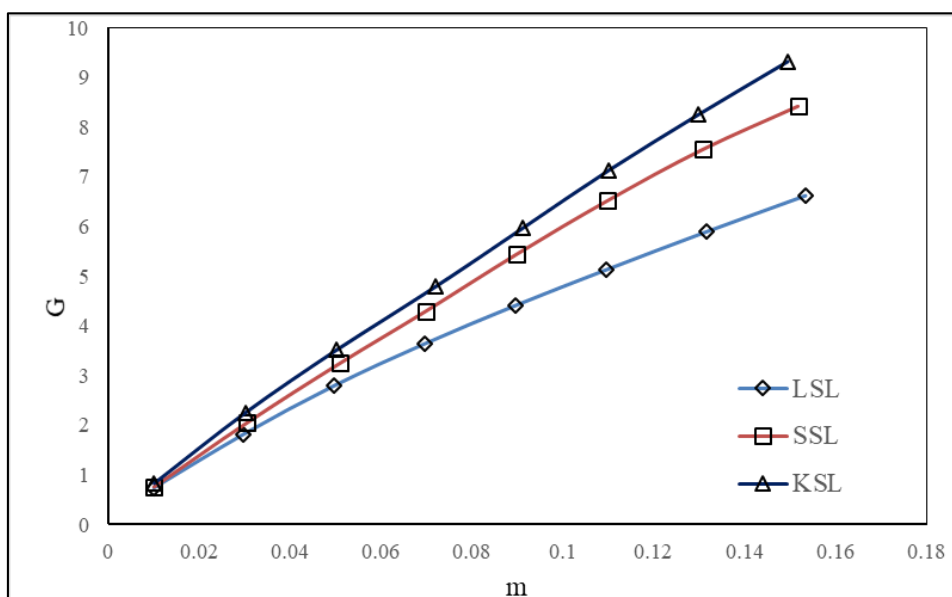


Figure 5 Graph of comparison of (G) vs concentration of LSL, SSL and KSL in water at 298.15 K (T).

4. Conclusion

The conductivity was measured for LSL, SSL and PSL solutions at concentrations range (0.01 to 0.15) M and at various temperature 298.15, 303.15, 308.15 and 313.15 K. All studied salt solution showed good conductivity at all temperatures, the conductivity of the PSL was found to be greater than SSL and LSL. Li^+ have shorter ionic size than other cations (K^+ and Na^+), which results in more water molecules surrounding them and forming larger hydrated spheres in solution, which reduces their mobility in aqueous solutions. This hydration affects the mobility and conductivity of solution. While the potassium was slowly crystallizing with water. Metal hydration and crystallization affects the ionisation and mobilisation of metal salts. Lithium ion react with water molecules and this fact affect LSL's ionisation and conductivity.

The temperature, molar concentrations and percentage compositions are also responsible for change in the values of these parameters. The solute-solvent interactions, solvent-solvent interactions and solute-solute interactions are another factor which directly hampers these parameters. The internal geometry as well as internal and intra hydrogen bonding affect these parameters. The molar conductance of PSL is higher than SSL and LSL this fact support to good ionisation and mobility of PSL. Thus PSL would also show good pharmacodynamics than SSL and LSL.

Compliance with ethical standards

Acknowledgments

The authors thank to the Director of G.V.I.S.H., Amravati for granting permission for research facility and also express their gratitude to the Principal of HPT Arts and Science College, Nashik for kind cooperation.

Disclosure of conflict of interest

The authors declare that they have no known financial or personal conflicts that would have appeared to have an impact on the research presented in this study.

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