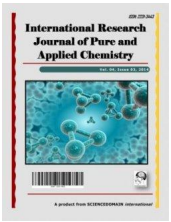

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Phase Diagrams, Molal Volumes and Polarizabilities of (Lysine, Methionine Amino Acids-Alcohol-Water) Tri-Component Systems

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Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

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ABSTRACT

The molal solubility, density and refractive index of DL-Methionine (as a nonpolar neutral amino acid) and L-Lysine (as polar basic amino acid) in water–methanol and water–ethanol mixed solvents with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) at 298.15 K were determined experimentally. From the values of the measured refractive indices, molal solubilities and densities, the apparent molal volumes, the excess refractive indices, the molar refractions and the polarizabilities, of the amino acids under study were calculated and discussed. The solvation of the amino acids under study was discussed in terms of their molal solubility, apparent molar volume and refractive index. The molal solubility data were modeled according to Setchenow equation.
The phase diagram of the tri-component systems under study (amino acid-alcohol-water) were also determined and discussed. The effect of the solvent on the solubility of neutral amino acids (DL-Methionine), basic amino acid (L-Lysine) was discussed. The results indicate that the molal solubility of L-Lysine is higher than that of DL-Methionine in the solvents under study.

Keywords: Solvation; refractive index; apparent molar volumes; L-lysine; Dl-methionine; setchenow.

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1. INTRODUCTION

As reported earlier [1-4], many interactions in solutions can be considered depending on the solvation process of the substance. Also refractive index and density measurements of solutions are expected to shed some light on the solute-solvent interaction and configuration of their mixtures [5-8]. The refractive index and density have been used to study the structure and solvent-solvent interaction of binary mixtures with water, aliphatic alcohols and cyclic ethers [9-14]. The separation of amino acids from the excess reagents, and other impurities in the aqueous solution, is often done by crystallization or precipitation methods. The separation cost accounts for about 50% of the total production cost [15].

L-Lysine plays the major role in calcium absorption; building muscle protein; recovering from surgery or sports injuries; and the body production of hormones, enzymes, and antibodies [16]. DL-Methionine is an essential amino acid in humans. Methionine is important in angiogenesis and growth of new blood vessels. Supplementation may benefit those suffering from Parkinson, drug withdrawal, schizophrenia, and radiation. Methionine is found in meat, fish, and dairy products, and it is play an important role in many cell functions. Overconsumption of methionine, as in the standard American diet but not vegan diet [17] is related to cancer growth in a number of studies [18-20].

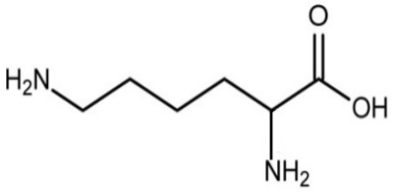
Studying of the solvation of amino acids in different solvents is useful for rational design of the separation processes. Neutral amino acids such as DL-Methionine have an amino group and carboxyl group, which give rise to zwitterionic amino acid molecules in the neutral pH range. Basic amino acids such as lysine have two amino groups and one carboxyl group, which also give rise to zwitterionic amino acid molecules with basic amino group.

The present study aims to report the solvation behavior of the zwitterionic amino acids: DL-Methionine and L-Lysine in aqueous solutions of methanol and ethanol at 298.15 K.

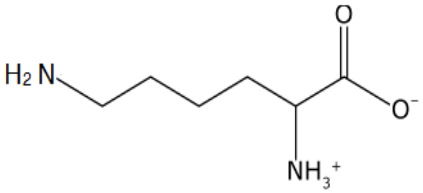
2. EXPERIMENTAL

2.1 Materials

Amino acids; L-Lysine and D-L-Methionine of 99.5% & 99% purity respectively, were obtained from LOBA Chemie Company (India) (Scheme 1).

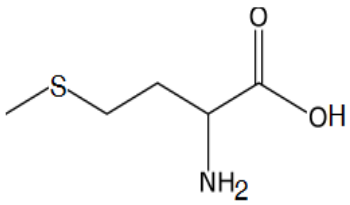


L-Lysine amino acid

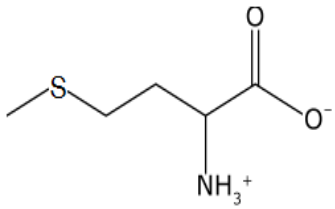


Zwitterion of L-Lysine

(S)-2, 6-Diaminohexanoic acid



DL-Methionine



Zwitterion of DL-Methionine

2-amino-4-(methylthio) butanoic acid

(Scheme 1)

Methanol and Ethanol of 99% purity were obtained from Fisher Scientific Company (England).

2.2 Solutions, Apparatus and procedure

Alcoholic solutions with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) were prepared using bi-distilled water, with a conductivity of ~0.02 μS cm^{-1}. All solutions were prepared on a volume basis. 15ml test tubes were used as sample tubes. The amino acids were added in excess of the amount required for saturation. Then, 10-mL solvent was added into the sample tubes. The sample tubes were sealed using plastic cover and kept in a thermostatic water bath at 25±0.1°C. The solutions were agitated for 48 h using Teflon-coated magnetic stir bars. The mixing was then stopped, and the solutions were allowed to settle for one hour. Samples were taken of the supernatant liquid phase using a micro-pipit (1 ml). Glass dish was weighed empty and with the solution. The dish was put into an oven for one hour at about 70-80°C and put the dish into desiccator for half hour then weighed again with the dry sample. Repeat the pervious step for half hour and weight again for confirmation of the constant weight. The solubility of the sample was calculated from knowledge of the mass of the empty dish, the mass of the dish with the solution, the dry mass of the solid. To test the accuracy of the above experimental procedure, the solubility of the amino acids under study was measured in pure water and compared with literature values [21]. The values reported in this work are the average of at least three replicates. The results were found to differ by <0.5% molal. The refractive indices of the prepared systems were measured using Abbe`s refractometer connected with ultra–thermostat of type Kottermann 4130.

3. RESULTS AND DISCUSSION

3.1 Density and Molal Solubility

The determined density and molal solubility of L-Lysine and DL-Methionine in methanol-water and ethanol-water mixtures with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) at 298.15 K are reported in Table 1.

The obtained data show that the molal solubility of L-Lysine and D-L-Methionine are decreased in presence of different mole fractions of methanol and ethanol (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) indicating a salting-out effect of the studied salts on the molal solubility of L-Lysine and D-L-Methionine. The effect was increase as the mole fraction of methanol and ethanol increase.

Table 1. The molal solubility of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol-water and ethanol-water mixtures at 298.15 K

x_1	Molal Solubility, m (mol kg^{-1})			
	In Ethanol-water		In Methanol-water	
	Lys	***Meth***	***Lys***	***Meth***
0.0	4.72090	0.27501	4.72090	0.27501
	4.73390	**0.27491**	**4.73390**	**0.27491**
0.1	3.21807	0.18754	3.20417	0.22247
0.3	2.66855	0.10876	1.97386	0.12271
0.5	1.42637	0.09471	1.85765	0.12174
0.7	0.75556	0.08124	0.78165	0.03707
0.9	0.17746	0.03412	0.09994	0.01245
1.0	0.02607	0.00851	0.05217	0.01148
	Density ρ ($g.cm^{-3}$)			
0.0	1.1225	0.9972	1.1225	0.9972
	1.1245	**0.9962**	**1.1245**	**0.9962**
0.1	1.1165	0.9923	1.1200	1.0119
0.3	1.0623	0.9598	1.1303	0.9856
0.5	0.9712	0.9270	0.9785	0.9022
0.7	0.9108	0.8942	0.8878	0.8766
0.9	0.8566	0.8181	0.7133	0.8565
1.0	0.7849	0.7681	0.7131	0.7885

** Values in Bold are from ref. [21]*

The obtained data show that the density of L-Lysine and DL-Methionine are decreased in presence of different mole fractions of methanol and ethanol. This may be due to the decrease of the molal solubility of L-Lysine and DL-Methionine as the mole fraction of methanol and ethanol increase. Also, this may be due to the decrease density of methanol and ethanol compared to that of water at the same temperature.

The molal solubility of L-Lysine and DL-Methionine in methanol-water and ethanol-water mixtures with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, 1.0 by volume) at 298.15 K was also analyzed in term of the Setchenow relationship[22] (converted to a molality basis) as in the following equation:

$$\log_{10}(m_o/ m) = k. x_1 \quad (1)$$

Where m_o and m is the molal solubility of the amino acid in water in the absence and in the presence of alcohols respectively, x_1 is the mole fraction of alcohols (by volume). Examination of the plots in the present study for the amino acids under study, in water and in the presence of different mole fraction of alcohols, suggest that a quadratic term was added, leading to the following extended Setchenow equation:

$$\log_{10}(m_o/ m) = k_2 x_1^2 + k_1 x_1 + k_0 \quad (2)$$

The relation of $\log_{10}(m_o/ m)$ versus x_1 for the studied systems are shown in Fig. 1. The parameters; k_o, k_1 and k_2 of equation 2 were presented in Table 2 and Fig. 1. The higher values of Setchenow coefficients in case of L-Lysine than that for DL-Methionine, indicate a salting-in effect of the solvents under study on the molal solubility of L- Lysine. Also, the higher values of Setchenow coefficients of L-Lysine and DL-Methionine in ethanol-water solvents than that in methanol-water solvents, indicate a salting-in effect of the ethanol-water than that of methanol-water.

The determined parameters were examined to see whether they are additive. It was found that the difference between the parameters, are not sensibly constant. This indicates that the determined parameters are not additives.

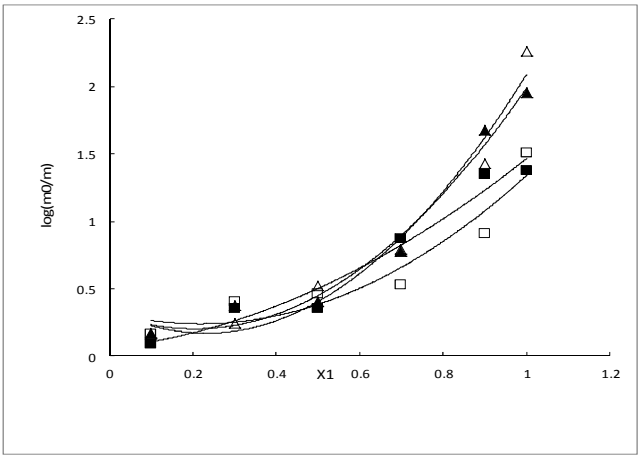


Fig. 1. The Setchenow relation of L-Lysine and DL-Methionine in methanol-water (▲ Lys and ■ Meth), ethanol-water (Δ Lys and □ Meth) with alcohol mole fractions

Table 2. The Setchenow coefficients of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol-water and ethanol-water mixtures at 298.15 K

	Molal solubility, m (mol kg^{-1})			
	In ethanol-water		In methanol-water	
	Lys	***Meth***	***Lys***	***Meth***
$k_\cdot$	0.3451	0.3258	0.3211	0.0590
k_1	-1.5059	-0.7827	-1.1540	0.3663
k_2	3.2497	1.7972	2.8214	1.0393
R^2	0.9705	0.9015	0.9805	0.9655

3.2 Phase Diagram

Depending on the molal solubility data, the phase diagram of L-Lysine and DL-Methionine in both ethanol-water and methanol-water mixed solvents were obtained as presented in Figs. 2 and 3. The phase diagrams for L-Lysine and DL-Methionine in methanol are similar to that in ethanol with very small difference. As shown from Figs 2 and 3, the molal solubility of L-Lysine is higher than that of DL-Methionine in ethanol-water and methanol-water mixed solvents.

3.3 Molal Volumes

From the molal solubility and density values, the apparent molal volumes, φV of L-Lysine and DL-Methionine in methanol-water and ethanol-water with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) at 298.15 K, were calculated using the following equation [23]:

$$\varphi V = \frac{M}{\rho} - \frac{1000}{m}\left[\frac{1}{\rho^{\circ}} - \frac{1}{\rho}\right] \quad (3)$$

where M and m are the molecular weight, and the molality of L-Lysine and DL-Methionine, respectively. ρ and ρ° are the densities of solution and solvent, respectively. The calculated apparent molal volumes, φV of L-Lysine and DL-Methionine in methanol-water, ethanol-water with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) at 298.15 K, are given in Table 3.

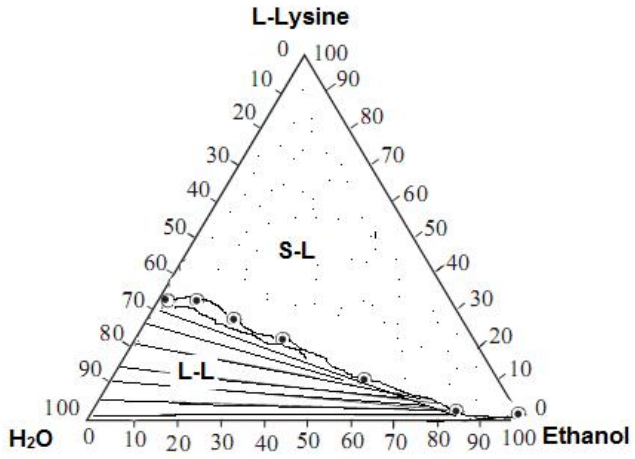


Fig. 2. The phase diagram of L-lysine-ethanol-water system

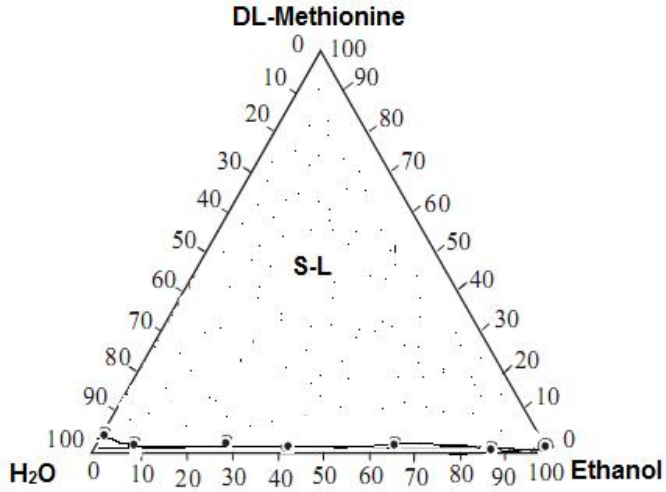


Fig. 3. The phase diagram of DL-Methionine-ethanol-water system

The apparent molal volume of L-Lysine and DL-Methionine in water and in methanol-water and ethanol-water solutions, is increase as the mole fraction of methanol and ethanol increase. This may be due to the decrease of the solution density in the same direction, where the volume has inverse proportion change with the density (d=m/v).

The solvated radii of the amino acids under study were calculated using the following equation by considering spherical form of the solvated molecules [24] and their values are given in Table 3.

$$\varphi V = \frac{4}{3}\pi r^3 \quad (4)$$

The packing density (P) (the relation between the Van der Waals volume and the partial molal volume of relatively large molecules is found to be constant [25, 26]). Therefore, it is possible to calculate the Van der Waals volumes (V_w) of the amino acids under study by apply the following equation [26].

Packing density (P) =

$$V_w / V\varphi = 0.661 \pm 0.017 \quad (5)$$

The electrostriction volume (V_e) which is the volume compressed by the solvent [25-28], can be calculated using the following equation.

$$V_e = V_w - \varphi V \quad (6)$$

The values of the solvated radius, Van Der Waals volume and the electrostriction volume are reported in Table 4.

3.4 Refractive Index, Molar refraction and Polarizability

The refractive indices of L-Lysine and DL-Methionine in water and in methanol-water and ethanol-water with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume) were measured at 298.15 K, and their values are reported in Table 5.

As shown from Table 5, the refractive indices of L-Lysine in methanol-water and ethanol-water are decrease as the mole fraction of methanol or ethanol increase. This may be to the decrease of the molal solubility of L-Lysine in the same direction. On the other hand the excess refractive indices of DL-Methionine in methanol-water and ethanol-water are increase as the mole fraction of methanol or ethanol increase. This may be to the increase of the refractive index of alcohol than that of water.

The excess refractive indices (n^E) as a result of the presence of L-Lysine and DL-Methionine in solutions can be calculated according to the following equation.

$$n^E = n - (x_1.n_1 + x_2.n_2) \quad (7)$$

Table 3. The apparent molal volume, φV and the solvated radius, r of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol-water and ethanol-water mixtures at 298.15 K

x_1	Apparent molal volumes, φV ($cm^3 mol^{-1}$)			
	In Ethanol-water		In Methanol-water	
	Lys	***Meth***	***Lys***	***Meth***
0.0	129.517	132.651	129.517	132.651
0.1	130.448	133.612	129.997	147.447
0.3	137.298	140.446	128.868	151.383
0.5	150.459	153.63	149.225	165.383
0.7	160.485	163.821	164.634	170.213
0.9	170.657	174.188	204.957	174.208
1.0	186.253	190.101	205.009	189.233
	Solvated radius, (r, cm)			
0.0	3.139	3.164	3.067	3.148
0.1	3.147	3.172	3.143	3.278
0.3	3.201	3.225	3.134	3.307
0.5	3.300	3.323	3.291	3.406
0.7	3.372	3.395	3.401	3.438
0.9	3.441	3.465	3.658	3.465
1.0	3.543	3.567	3.6585	3.562

Table 4. The Van der Waals and the electrostriction volume of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol-water and ethanol-water mixtures at 298.15 K

x_1	Van der Wall, (V_w, cm^3mol^{-1})			
	In Ethanol-water		In Methanol-water	
	Lys	*Meth*	*Lys*	*Meth*
0.0	85.610	87.682	79.856	86.312
0.1	86.226	88.318	85.928	97.462
0.3	90.754	92.835	85.182	100.064
0.5	99.453	101.549	98.638	109.318
0.7	106.081	108.285	108.823	112.511
0.9	112.804	115.137	135.476	115.151
1.0	123.113	125.656	135.511	125.083
	Electrostriction volume, (V_e, cm^3mol^{-1})			
0.0	-43.906	-44.968	-40.955	-44.265
0.1	-44.222	-45.295	-44.069	-49.984
0.3	-46.544	-47.611	-43.686	-51.318
0.5	-51.005	-52.081	-50.587	-56.064
0.7	-54.404	-55.535	-55.811	-57.702
0.9	-57.853	-59.049	-69.480	-59.056
1.0	-63.139	-64.444	-69.498	-64.149

Table 5. The refractive indices, (n) and excess refractive indices (n^E) of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol-water and ethanol-water mixtures at 298.15 K

x_1	Refractive indices, n			
	In Ethanol-water		In Methanol-water	
	Lys	*Meth*	*Lys*	*Meth*
0.0	1.4215	1.3415	1.4215	1.3415
0.1	1.4200	1.3435	1.4205	1.3419
0.3	1.4105	1.3535	1.3895	1.3450
0.5	1.3870	1.3610	1.3495	1.3480
0.7	1.3755	1.3650	1.3485	1.3490
0.9	1.3685	1.3645	1.3445	1.3445
1.0	1.3610	1.3650	1.3390	1.3380
	Excess refractive indices (n^E)x10^{-3}			
0.0	0.00	0.00	0.00	0.00
0.1	4.55	-3.50	7.25	0.75
0.3	7.15	4.95	-7.25	4.55
0.5	-4.25	7.75	-30.75	8.25
0.7	-3.65	7.05	-15.25	9.95
0.9	1.45	1.85	-2.75	6.15
1.0	0.00	0.00	0.00	0.00

Where n, is the refractive index of the amino acid in mixed methanol-water and ethanol-water solvents, n_1 is the refractive index of the amino acid in pure methanol or ethanol solvent and n_2 is the refractive index of the amino acid in pure water. The values of the excess refractive indices are tabulated in above Table 5 and represented in Fig. 4.

Also from the values of the measured refractive indices, of L-Lysine and DL-Methionine in methanol-water and ethanol-water, the molar

refraction (R_m) can be calculated [29] using the following equation.

$$R_m = \frac{n^2-1}{n^2+2}\varphi V = P_A + P_E = P_D + P_T \quad (8)$$

Where φV is the apparent molal volume of L-Lysine and DL-Methionine in solution, n is the refractive index of L-Lysine and DL-Methionine solution. The right hand side of equation (3) is equal to the total molar polarization or the distortion polarization which equal to the summation of both the electron polarization (P_E) and the atomic polarization (P_A). The atomic polarization (P_A) was calculated [30] from the following equation.

$$P_A = 1.05\, n^2 \quad (9)$$

The mean value of the molecular dipole polarizability (α ; dipole moment induced by electric field) can be calculated from the optical refractive index (n) of a material containing N molecules per unit volume. The refractive index is related to the polarizability (α) of the molecules by Lorenz-Lorenz formula [31] as shown in the following equation.

$$\frac{n^2-1}{n^2+2} = \frac{4\pi\hat{n}\alpha}{3} \quad (10)$$

Where $\hat{n} = \frac{N}{\varphi V}$, ($N$) is the Avogadro's number and (φV) is the apparent molal volume. From equation (10), the polarizabilities of L-Lysine and DL-Methionine in methanol-water and ethanol-water with alcohol mole fractions (0.0, 0.10, 0.30, 0.50, 0.70, 0.90, and 1.0, by volume), were calculated. The values of the calculated molar refraction (R_m), polarizability (α) and the atomic polarization were recorded in Table 6.

The molar refraction and the polarizability are directly proportional to the apparent molal volume. The molar refraction and the polarizability of L-Lysine and DL-Methionine in methanol-water and ethanol -water is increase as the mole fraction of ethanol and methanol increase.

This increase in the molar refraction and the polarizability of L-Lysine and DL-Methionine with the mole fraction of ethanol and methanol may be related to the increase in the apparent molar volume of L-Lysine and DL-Methionine with the mole fraction of ethanol and methanol respectively.

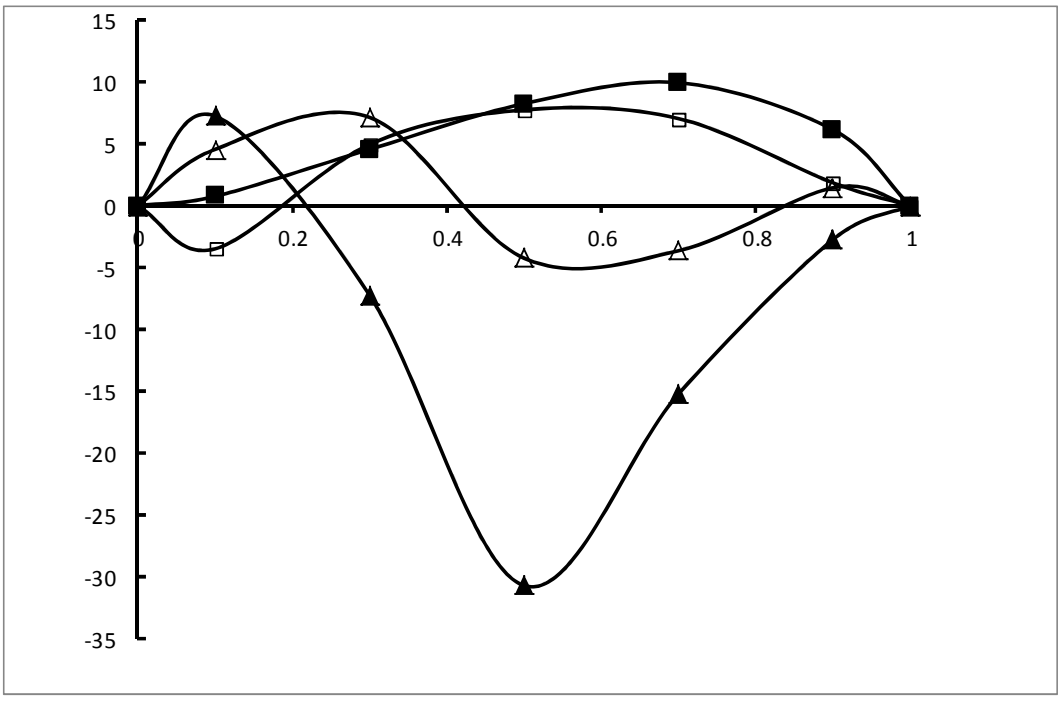


Fig. 4. The excess refractive index of L-Lysine and DL-Methionine in methanol-water (▲ Lys and ■ Meth) and ethanol-water (Δ Lys and □ Meth) with alcohol mole fractions

Table 6. The molar refraction, polarizability (α) and the atomic polarization of L-Lysine (*Lys*) and DL-Methionine *(Meth)* in methanol and ethanol-water mixtures at 298.15 K

x_1	Molar refraction, (R_m, cm^3)			
	In Ethanol-water		In Methanol-water	
	Lys	*Meth*	*Lys*	*Meth*
0.0	32.878	27.256	32.878	27.148
0.1	33.011	27.597	33.046	27.416
0.3	34.053	29.809	32.509	29.161
0.5	35.422	33.288	32.333	32.207
0.7	36.781	35.859	34.398	34.443
0.9	38.460	38.085	36.199	36.199
1.0	41.208	41.617	38.936	38.832
	polarizability (α, cm/molecule)			
0.0	1.303	1.080	1.303	1.076
0.1	1.308	1.0942	1.310	1.087
0.3	1.350	1.181	1.289	1.156
0.5	1.404	1.319	1.282	1.277
0.7	1.458	1.421	1.363	1.365
0.9	1.524	1.510	1.435	1.435
1.0	1.633	1.650	1.543	1.539
	Atomic polarization, P_A			
0.0	2.121	1.889	1.303	1.076
0.1	2.117	1.895	1.310	1.087
0.3	2.088	1.923	1.289	1.156
0.5	2.019	1.945	1.282	1.277
0.7	1.986	1.956	1.363	1.365
0.9	1.966	1.955	1.435	1.435
1.0	1.945	1.956	1.543	1.539

4. CONCLUSIONS

The results indicate that the molal solubility of L-Lysine is higher than that of DL-Methionine in the solvents under study. The density of L-Lysine and DL-Methionine are decreased in presence of different mole fractions of methanol and ethanol. This may be due to the decrease of the molal solubility of L-Lysine and DL-Methionine as the mole fraction of methanol and ethanol increase. The apparent molal volume of L-Lysine and DL-Methionine is increase as the mole fraction of methanol and ethanol increase.

The refractive indices of L-Lysine are decrease as the mole fraction of methanol or ethanol increase. On the other hand the refractive indices of DL-Methionine are increase as the mole fraction of methanol or ethanol increase. This may be to the increase of the refractive index of alcohol than that of water. The molar refraction and the polarizability of L-Lysine and DL-Methionine are increase with the increase of the mole fraction of ethanol and methanol.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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