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RESEARCH ARTICLE

Comparative Physiochemical Analysis Of Phenylalanine, Tryptophan & Methionine in Aqueous Solutions Of Nitrates In terms of Linear, Exponential, Second Order Polynomial and Third Order polynomial Using Volumetric Approach

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Abstract: Volumetric properties of phenylalanine ($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) in aqueous solutions of Nitrates at T =298.15K, in terms of Linear, Exponential, Second Order Polynomial and Third Order polynomial has been calculated using volumetric approach. The densities, Partial molar volumes and transfer partial molar volumes have been calculated on the basis of density measurements of phenylalanine, tryptophan and methionine, respectively. The results have been compared using mathematical operations like exponential behavior, second and up to third order polynomials. Interesting observations were found on the basis of comparisons in between these mathematical operations. However it has been found that phenylalanine and tryptophan in water has positive slope linearly so considered has structure makers in water while methionine has negative slope in water, considered as structure breakers. However with the intermission of nitrates, the value of slope becomes reverse except at 1.0 mol·kg^{-1}. This suggests that solution thermodynamics has been played major role in protein/amino acids stability.

Case Description: Phenylalanine, Tryptophan, Methionine amino acids have taken and attempt has been made to correlate the molar volumes calculated in terms of densities change with the change in the concentration of cosolute (sodium nitrate) and then identifies the curves or behvaior in terms of various mathematical operations so as to reach conclusion about strucutre making/ breaking behavior of these amino acids.

Discussion and Evaluation: Phenylalanine and tryptophan in water has positive slope (linearly) so considered has structure makers in water while methionine has negative slope in water, considered as structure breakers. However with the addition of nitrates, the value of slope becomes reverse except at 1.0 mol·kg^{-1}. While on the basis of third order polynomial which seems to be more accurate as they have higher R^2 (Regression) values near to 1.0; which proves the fact that trivalent interactions (3rd order) are more important as compared to divalent and monovalent.

Conclusions: Amino acids are very much affected by the addition of cosolute like in our case (sodium nitrate) and therefore there behavior as well as properties changes very significantly with the change in the concentration effect of colsolute. Thus, concentration effect is an important parameter for slating in/ salting out of amino acids.

Introduction

The use of protein model compounds is a very important tool in the hand of a biochemist (Archer 1992, Bondi 1968, Basumallick et al. 1986, Franks et al.1976). Volumetric and viscometric properties of amino acids are helping us to

better understanding of proteins bahavior and hydration properties (Franks et al. 1970, Hakin et al. 1994, Hepler 1969, Kharakoz 1989, Kishore et al. 1995, Murphy et al. 1998, McMillan et al. 1995, Millero 1972). Complete physiochemical analysis of phenylalanine ($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) in aqueous solutions of nitrates in terms of linear, exponential, second order polynomial and third Order polynomial using volumetric approach is not found in literature. However some workers did few work for calculating the effect of sodium nitrate over molar volumes but in case of neutral/lower amino acids(Soto et al. 1999).

Consequently, in the present paper, the apparent molar volumes, $V_{2,\phi}$ of phenylalanine; tryptophan; methionine in water and in aqueous sodium nitrate solutions (0.25, 0.5, 0.75, 1.0, 1.5, 2.0) mol·kg^{-1} have been determined by measuring the densities using a vibrating-tube digital densimeter at T= 298.15K. From these data, the partial molar volumes at infinite dilution, V_2^0, In terms of linear, exponential, second order polynomial and third order polynomial using volumetric approach has been determined. These parameters have been rationalized in terms of various interactions occurring in these solutions. The concentration effect of sodium nitrate on these parameters has also been discussed.

Materials and Methods

Phenylalanine ($C_9H_{11}NO_2$), Tryptophan($C_{11}H_{12}N_2O_2$) & Methionine ($C_5H_{11}NO_2S$) from Sigma Chemical Co. and sodium nitrate (AR, Thomas Baker, India), were used without further purification, however these were dried over anhydrous $CaCl_2$ in a vacuum desiccator before use. Deionized, doubly distilled degassed water with a specific conductance less than 1.3 ×10^{-6} Ω^{-1}·cm^{-1} was used for the measurements. All solutions were prepared by mass using a Mettler balance with an accuracy of ±0.01 mg.

Table 1: Solutions densities, ρ, and apparent molar volumes, $V_{2,\phi}$ for the phenylalanine($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & Methionine ($C_5H_{11}NO_2S$) in aqueous solutions of $NaNO_3$ at different concentrations

m_s (mol·kg^{-1})	$\rho\times10^{-3}$ (kg·m^{-3})	$V_{2,\phi}\times10^{6}$ (m^3·mol^{-1})	m_s (mol·kg^{-1})	$\rho\times10^{-3}$ (kg·m^{-3})	$V_{2,\phi}\times10^{6}$ (m^3·mol^{-1})	m_s (mol·kg^{-1})	$\rho\times10^{-3}$ (kg·m^{-3})	$V_{2,\phi}\times10^{6}$ (m^3·mol^{-1})
		T =298.15K						
		Phenylalanine($C_9H_{11}NO_2$)						
		$^a m_s$=0.00 mol·kg^{-1}						
0.00000	0.997047		0.09899	1.001116	123.82	0.20343	1.003172	134.56
0.07865	1.000445	121.8	0.10232	1.001683	119.54			
0.08986	1.000689	124.45	0.15689	1.002985	126.85			
		$^a m_s$=0.25 mol·kg^{-1}						
0.00000	1.01174		0.14567	1.012565	157.61	0.28982	1.01432	154.18
0.19891	1.012068	161.61	0.2454	1.012898	158.48			
0.2323	1.012343	160.64	0.25452	1.013454	156.43			
		$^a m_s$=0.50 mol·kg^{-1}						
0.00000	1.025077		0.21232	1.026787	153.23	0.30212	1.030434	143.52
0.20322	1.02698	151.96	0.24545	1.028982	145.45	0.34544	1.032453	139.82
		$^a m_s$=0.75 mol·kg^{-1}						
0.00000	1.037864		0.38983	1.03999	153.78	0.41232	1.041232	151.09
0.32343	1.039892	153.04	0.40323	1.04012	153.63	0.48984	1.041389	151.97
		$^a m_s$=1.0 mol·kg^{-1}						
0.00000	1.050713		0.11454	1.052767	140.7	0.22343	1.053101	147.2
0.10989	1.052321	143.74	0.20323	1.052898	147.17	0.24545	1.053454	146.72
		$^a m_s$=1.5 mol·kg^{-1}						
0.00000	1.075983		0.14545	1.077121	146.61	0.20323	1.079121	139.78
0.12122	1.076898	146.88	0.18981	1.078101	143.6	0.28982	1.080212	140.37
		$^a m_s$=2.0 mol·kg^{-1}						
0.00000	1.099888		0.30434	1.102891	141.64	0.38987	1.108978	129.84
0.29892	1.102124	143.71	0.32143	1.10545	135.2	0.39232	1.10909	129.71

		Tryptophan($C_{11}H_{12}N_2O_2$)						
		$^{a}m_s$=0.25 mol·kg^{-1}						
0.00000	1.01174		0.20323	1.012865	196.23	0.30434	1.014789	191.49
0.18791	1.012278	198.95	0.21343	1.01298	195.94			
0.19121	1.012843	196.01	0.28928	1.014654	191.46			
		$^{a}m_s$=0.5 mol·kg^{-1}						
0.00000	1.025077		0.20323	1.029077	179.8	0.24787	1.031434	173.74
0.19891	1.02898	179.87	0.24545	1.030439	177.51	0.25465	1.031653	173.54
		$^{a}m_s$=0.75 mol·kg^{-1}						
0.00000	1.037864		0.38983	1.03999	191.32	0.41232	1.041232	188.58
0.32343	1.039892	190.58	0.40323	1.04012	191.16	0.48984	1.041389	189.45
		$^{a}m_s$=1.0 mol·kg^{-1}						
0.00000	1.050713		0.11454	1.052767	177.78	0.22343	1.053101	184.27
0.10989	1.052321	180.84	0.20323	1.052898	184.25	0.24545	1.053454	183.77
		$^{a}m_s$=1.5 mol·kg^{-1}						
0.00000	1.075983		0.14545	1.077121	182.85	0.20323	1.079121	175.95
0.12122	1.076898	183.13	0.18981	1.078101	179.81	0.28982	1.080212	176.51
		$^{a}m_s$=2.0 mol·kg^{-1}						
0.00000	1.099888		0.30434	1.102891	177.04	0.38987	1.108978	165.04
0.29892	1.102124	179.13	0.32143	1.10545	170.51	0.39232	1.10909	164.91

		Methionine ($C_5H_{11}NO_2S$)						
		$^{a}m_s$=0.00 mol·kg^{-1}						
0.00000	0.997047		0.18981		183.74		1.003436	182.17
0.10232	0.999187	183.4	0.20343	1.001174	183.66			
0.14565	1.000434	180.82	0.25656	1.001592	186.16			
		$^{a}m_s$=0.25 mol·kg^{-1}						
0.00000	1.011740		0.20323	1.012865	141.92	0.30434	1.014789	137.28
0.18791	1.012278	144.61	0.21343	1.01298	141.63			
0.19121	1.012843	141.69	0.28928	1.014654	137.24			
		$^{a}m_s$=0.50 mol·kg^{-1}						
0.00000	1.025077		0.20323	1.029077	126.34	0.24787	1.031434	120.41
0.19891	1.02898	126.41	0.24545	1.030439	124.12	0.25465	1.031653	120.21
		$^{a}m_s$=0.75 mol·kg^{-1}						
0.00000	1.037864		0.38983	1.03999	138.42	0.41232	1.041232	135.74
0.32343	1.039892	137.68	0.40323	1.04012	138.27	0.48984	1.041389	136.62
		$^{a}m_s$=1.0 mol·kg^{-1}						
0.00000	1.050713		0.11454	1.052767	125.52	0.22343	1.053101	132.03
0.10989	1.052321	128.56	0.20323	1.052898	132	0.24545	1.053454	131.55
		$^{a}m_s$=1.5 mol·kg^{-1}						
0.00000	1.075983		0.14545	1.077121	131.78	0.20323	1.079121	124.97
0.12122	1.076898	132.04	0.18981	1.078101	128.78	0.28982	1.080212	125.58
		$^{a}m_s$=2.0 mol·kg^{-1}						
0.00000	1.099888		0.30434	1.102891	127.16	0.38987	1.108978	115.43
0.29892	1.102124	129.21	0.32143	1.10545	120.75	0.39232	1.10909	115.31

The solution densities were measured using a vibrating-tube digital densimeter (model DMA 60/602, Anton paar), having a precision of ± 1×10^{-3} kg·m^{-3} and an accuracy of ± 3 x10^{-3} kg·m^{-3}. The temperature of water around the densimeter cell was controlled within ± 0.01K. The densimeter was calibrated by using pure water and dry air. All the density measurements were made with reference to pure water. Working of the densimeter was checked by measuring the densities of aqueous sodium chloride solutions, which agreed well with the literature values (Archer, 1992)

Results and discussion

The densities, ρ, and apparent molar volumes, $V_{2,\phi}$, of phenylalanine; tryptophan; methionine in water and in aqueous sodium nitrate solutions of various molalities (m_s, molality of sodium nitrate solutions, mol·kg^{-1}) at T=298.15K are given in Table 1. Apparent molar volumes

of amino acids have been calculated as follows:

$$V_{2,\phi} = M/\rho - [(\rho - \rho_0)/m\cdot\rho\cdot\rho_0], \quad (1)$$

where M is the molar mass of the amino acid, m (mol·kg^{-1}) is the molality of amino acid, and ρ and ρ_0 are the densities of solution and solvent (water or water + sodium nitrate), respectively. The values of uncertainty in apparent molar volumes arising from various experimental measured quantities are of the order of 0.041×10^{-6} and 0.087×10^{-6} at low and high concentrations respectively of amino acids studied.

Table 2(a): Standard Partial molar volumes, $V_2^{0}{}_{,\phi}$ at infinite dilution phenylalanine($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) in water and in aqueous sodium nitrate solutions at (288.15-318.15) K

$V_2^{0}{}_{,\phi}$ x 10^6 /m^3·mol^{-1} at various m_s /mol·kg^{-1}[a]							
Amino acids	**Water**	**[a]m_s = 0.25**	**m_s = 0.5**	**m_s = 0.75**	**m_s = 1.0**	**m_s = 1.5**	**m_s = 2.0**
			T=288.15K				
Phenylalanine($C_9H_{11}NO_2$)	113.30 ±0.05[b] (97.14) 42.84[c], 42.40[d]	164.22 ± 0.05 (-26.52)	170.0 ±0.07 (-89.0)	156.1 ±0.05 (-8.45)	138.0 ±0.03 (39.52)	151.70 ±0.12 (-43.47)	181.66 ±0.04 (-133.7)
Tryptophan($C_{11}H_{12}N_2O_2$)	181.90 ±0.05[b] (6.71) 42.84[c], 42.40[d]	207.60 ± 0.04 (-54.52)	201.10 ±0.03 (-105.2)	193.70 ±0.09 (-8.85)	175.10 ±0.04 (39.28)	188.0 ±0.18 (-44.16)	217.70 ±0.14 (-135.9)
Methionine ($C_5H_{11}NO_2S$)	131.90 ±0.05[b] (-27.46) 42.84[c], 42.40[d]	153.10 ± 0.05 (-53.46)	147.10 ±0.13 (-102.9)	140.70 ±0.10 (-8.387)	122.80 ±0.06 (39.60)	136.80 ±0.08 (-43.18)	166.90 ±0.09 (-132.8)

Table 2(b): Standard Transfer Partial molar volumes, $\Delta V_{tr}^{0}{}_{,\phi}$ at infinite dilution phenylalanine($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) from aqueous sodium nitrate solutions to Water at T =298.15 K.

	$V_2^{0}{}_{,\phi}$ x 10^6 /m^3·mol^{-1} at various m_s /mol·kg^{-1}[a]					
Amino acids	**[a]m_s = 0.25**	**m_s = 0.5**	**m_s = 0.75**	**m_s = 1.0**	**m_s = 1.5**	**m_s = 2.0**
		T = 298.15K				
Phenylalanine($C_9H_{11}NO_2$)	50.92	56.70	42.80	24.70	38.40	68.36
Tryptophan($C_{11}H_{12}N_2O_2$)	25.70	19.20	11.80	-6.80	6.10	35.80
Methionine ($C_5H_{11}NO_2S$)	21.20	15.20	8.80	-9.10	4.90	35.0

Table 3: Comparison in terms of Linear, Exponential, Second Order Polynomial and Third Order polynomial for Partial molar volumes of phenylalanine($C_9H_{11}NO_2$), in water and in aqueous sodium nitrate solutions at T =298.15 K.

Phenylalanine($C_9H_{11}NO_2$)							
Mathematical Operations	$^a m_s$ = 0.0	$^a m_s$ = 0.25	m_s = 0.5	m_s = 0.75	m_s = 1.0	m_s = 1.5	m_s = 2.0
Linear	y = 97.14x +113.3 R^2 = 0.808	y = -26.52x + 164.2 R^2 = 0.235	y = -89.00x + 170.0 R^2 = 0.905	y = -8.454x + 156.1 R^2 = 0.191	y = 39.52x + 138.0 R^2 = 0.763	y = -43.47x + 151.7 R^2 = 0.712	y = -133.7x + 181.6 R^2 = 0.899
Exponential	$y = 114.0e^{0.760x}$ R^2 = 0.801	$y = 164.3e^{-0.16x}$ R^2 = 0.238	$y = 172.0e^{-0.60x}$ R^2 = 0.910	$y = 156.1e^{-0.05x}$ R^2 = 0.191	$y = 138.1e^{0.273x}$ R^2 = 0.760	$y = 151.9e^{-0.30x}$ R^2 = 0.710	$y = 190.1e^{-0.98x}$ R^2 = 0.906
Second Order Polynomial	$y = 1017.x^2 - 190.4x + 131.3$ R^2 = 0.886	$y = -920.8x^2 + 369.7x + 123.6$ R^2 = 0.866	$y = 426.8x^2 - 321.9x + 200.5$ R^2 = 0.931	$y = -38.71x^2 + 23.13x + 149.7$ R^2 = 0.207	$y = -396.2x^2 + 176.2x + 127.5$ R^2 = 0.814	$y = 342.4x^2 - 185.4x + 165.1$ R^2 = 0.839	$y = 3249.x^2 - 2394.x + 569.2$ R^2 = 0.999
Third Order Polynomial	$y = -2703.x^3 + 2166.x^2 - 344.4x + 137.7$ R^2 = 0.886	$y = 10087x^3 - 7590.x^2 + 1793.x + 26.12$ R^2 = 0.949	$y = -9084.x^3 + 7915.x^2 - 2339.x + 378.1$ R^2 = 0.947	$y = 15740x^3 - 19173x^2 + 7669.x - 854.4$ R^2 = 0.745	$y = -31288x^3 + 17196x^2 - 2978.x + 304.1$ R^2 = 0.912	$y = 13951x^3 - 8147.x^2 + 1444.x + 66.47$ R^2 = 0.950	$y = -15064x^3 + 18514x^2 - 7516.x + 1138.$ R^2 = 0.999

Table 4: Comparison in terms of Linear, Exponential, Second Order Polynomial and Third Order polynomial for Partial molar volumes of tryptophan($C_{11}H_{12}N_2O_2$) in water and in aqueous sodium nitrate solutions at T =298.15 K.

Tryptophan($C_{11}H_{12}N_2O_2$)							
Mathematical Operations	$^a m_s$ = 0.0	$^a m_s$ = 0.25	m_s = 0.5	m_s = 0.75	m_s = 1.0	m_s = 1.5	m_s = 2.0
Linear	y = 6.708x + 181.9 R^2 = 0.072	y = -54.52x + 207.6 R^2 = 0.900	y = -105.2x + 201.1 R^2 = 0.811	y = -8.850x + 193.7 R^2 = 0.201	y = 39.28x + 175.1 R^2 = 0.759	y = -44.16x + 188.0 R^2 = 0.715	y = -135.9x + 217.7 R^2 = 0.900
Exponential	$y = 181.9e^{0.036x}$ R^2 = 0.071	$y = 208.0e^{-0.28x}$ R^2 = 0.903	$y = 202.8 e^{-0.59x}$ R^2 = 0.809	$y = 193.8 e^{-0.04x}$ R^2 = 0.200	$y = 175.2 e^{0.216x}$ R^2 = 0.756	$y = 188.2 e^{-0.24x}$ R^2 = 0.714	$y = 224.5 e^{-0.79x}$ R^2 = 0.905
Second Order Polynomial	$y = -96.97x^2 + 45.76x + 178.4$ R^2 = 0.129	$y = 367.2x^2 - 235.6x + 229.0$ R^2 = 0.915	$y = -4132.x^2 + 1759.x - 6.845$ R^2 = 0.870	$y = -39.83x^2 + 23.65x + 187.2$ R^2 = 0.217	$y = -400.3x^2 + 177.3x + 164.5$ R^2 = 0.811	$y = 344.1x^2 - 186.8x + 201.5$ R^2 = 0.840	$y = 3286.x^2 - 2422.x + 609.7$ R^2 = 0.999
Third Order Polynomial	$y = -7970.x^3 + 4676.x^2 - 843.1x + 229.2$ R^2 = 0.963	$y = 952.6x^3 - 318.9x^2 - 73.69x + 216.5$ R^2 = 0.915	$y = -27334x^3 + 14823x^2 - 2602.x + 326.0$ R^2 = 0.871	$y = 16003x^3 - 19494x^2 + 7798x - 833.7$ R^2 = 0.749	$y = -31501x^3 + 17312x^2 - 2998.x + 342.3$ R^2 = 0.911	$y = 14056x^3 - 8209.x^2 + 1455.x + 102.1$ R^2 = 0.951	$y = -14871x^3 + 18354x^2 - 7478.x + 1172$ R^2 = 0.999

Table 5: Comparison in terms of Linear, Exponential, Second Order Polynomial and Third Order polynomial for Partial molar volumes of methionine ($C_5H_{11}NO_2S$) in water and in aqueous sodium nitrate solutions at T =298.15 K.

Methionine ($C_5H_{11}NO_2S$)							
Mathematical Operations	$^{a}m_s$ = 0.0	$^{a}m_s$ = 0.25	m_s = 0.5	m_s = 0.75	m_s = 1.0	m_s = 1.5	m_s = 2.0
Linear	y = -27.46x + 131.9 R^2 = 0.082	y = -53.46x + 153.1 R^2 = 0.898	y = -102.9x + 147.1 R^2 = 0.809	y = -8.387x + 140.7 R^2 = 0.190	y = 39.60x + 122.8 R^2 = 0.764	y = -43.18x + 136.8 R^2 = 0.709	y = -132.8x + 166.9 R^2 = 0.899
Exponential	$y = 132.4e^{-0.23x}$ R^2 = 0.088	$y = 153.7e^{-0.38x}$ R^2 = 0.902	$y = 149.5e^{-0.83x}$ R^2 = 0.805	$y = 140.7\ e^{-0.06x}$ R^2 = 0.190	$y = 122.9\ e^{0.306x}$ R^2 = 0.761	$y = 137.0\ e^{-0.33x}$ R^2 = 0.708	$y = 176.4\ e^{-1.09x}$ R^2 = 0.906
Second Order Polynomial	$y = -2710x^2 + 1353.x - 36.92$ R^2 = 0.791	$y = 366.5x^2 - 234.2x + 174.5$ R^2 = 0.913	$y = -4081.x^2 + 1738.x - 58.17$ R^2 = 0.869	$y = -38.52x^2 + 23.04x + 134.4$ R^2 = 0.206	$y = -397.0x^2 + 176.5x + 112.3$ R^2 = 0.815	$y = 342.0x^2 - 185.0x + 150.2$ R^2 = 0.838	$y = 3233.x^2 - 2382.x + 552.6$ R^2 = 0.999
Third Order Polynomial	$y = -34190x^3 + 23882x^2 - 5417.x + 526.1$ R^2 = 0.911	$y = 924.8x^3 - 299.5x^2 - 77.02x + 162.3$ R^2 = 0.913	$y = -27699x^3 + 15128x^2 - 2681.x + 279.1$ R^2 = 0.870	$y = 15687x^3 - 19109x^2 + 7643.x - 866.4$ R^2 = 0.744	$y = -31292x^3 + 17198x^2 - 2978.x + 288.9$ R^2 = 0.912	$y = 13948x^3 - 8145.x^2 + 1444.x + 51.60$ R^2 = 0.950	$y = -14326x^3 + 17750x^2 - 7253.x + 1094.$ R^2 = 0.999

Figure-1. Apparent molar volumes on (y axis) with change in molality (x axis) of Phenylalanine ($C_9H_{11}NO_2$) in aqueous solutions of sodium nitrate at T=298.15K; (a) 0.25mol·kg^{-1} ; (b) 0.5mol·kg^{-1} ; (c) 0.75mol·kg^{-1} ; (d) 1.0mol·kg^{-1} (e) 1.5mol·kg^{-1} (f) 2.0mol·kg^{-1} .

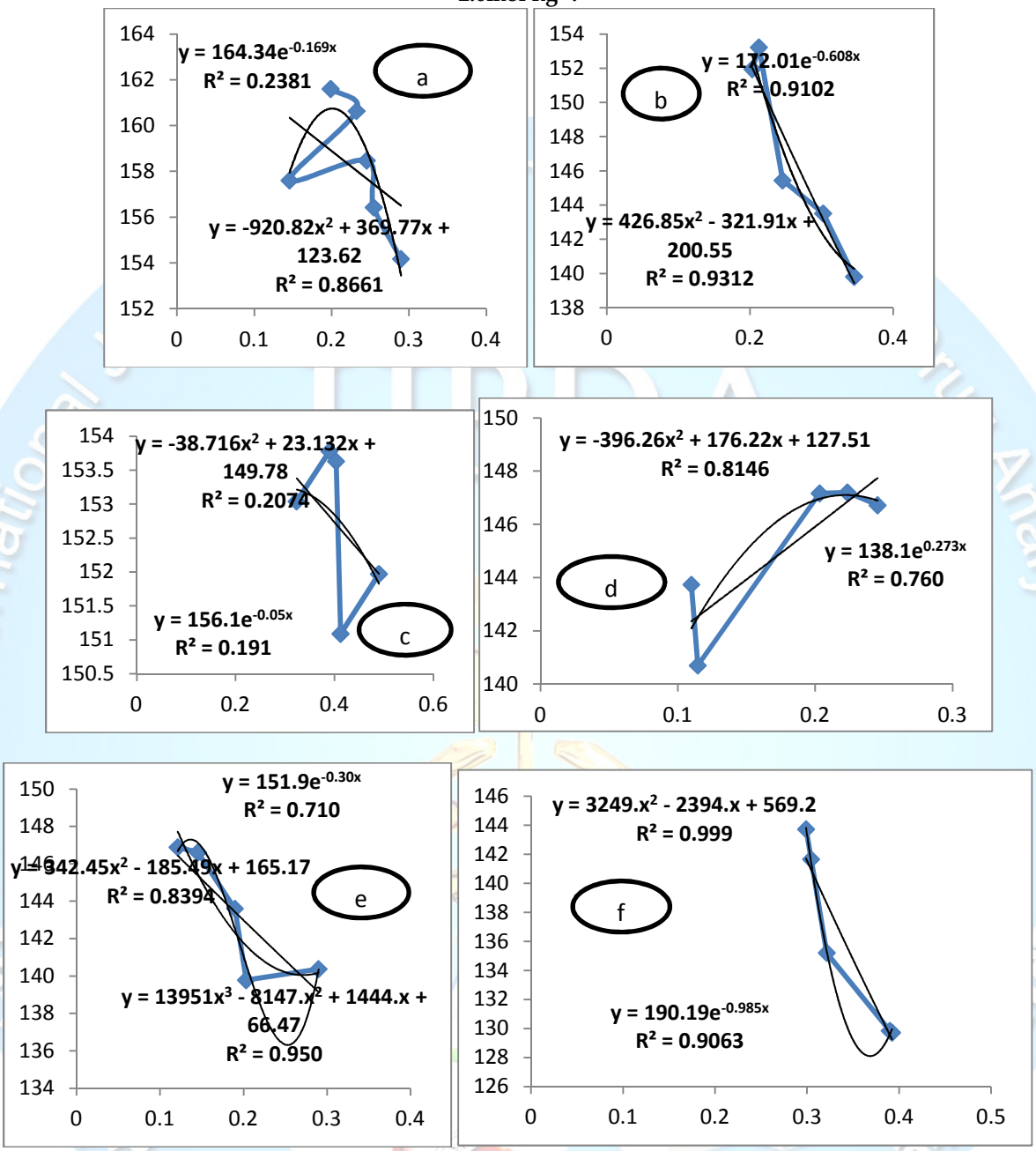


Figure 2. Apparent molar volumes on (y axis) with change in molality (x axis) of Tryptophan($C_{11}H_{12}N_2O_2$) in aqueous solutions of sodium nitrate at T=298.15K; (g)0.25mol·kg^{-1} ; (h)0.5mol·kg^{-1} ; (i)0.75mol·kg^{-1} ; (j)1.0mol·kg^{-1} (k)1.5mol·kg^{-1} (l)2.0mol·kg^{-1}.

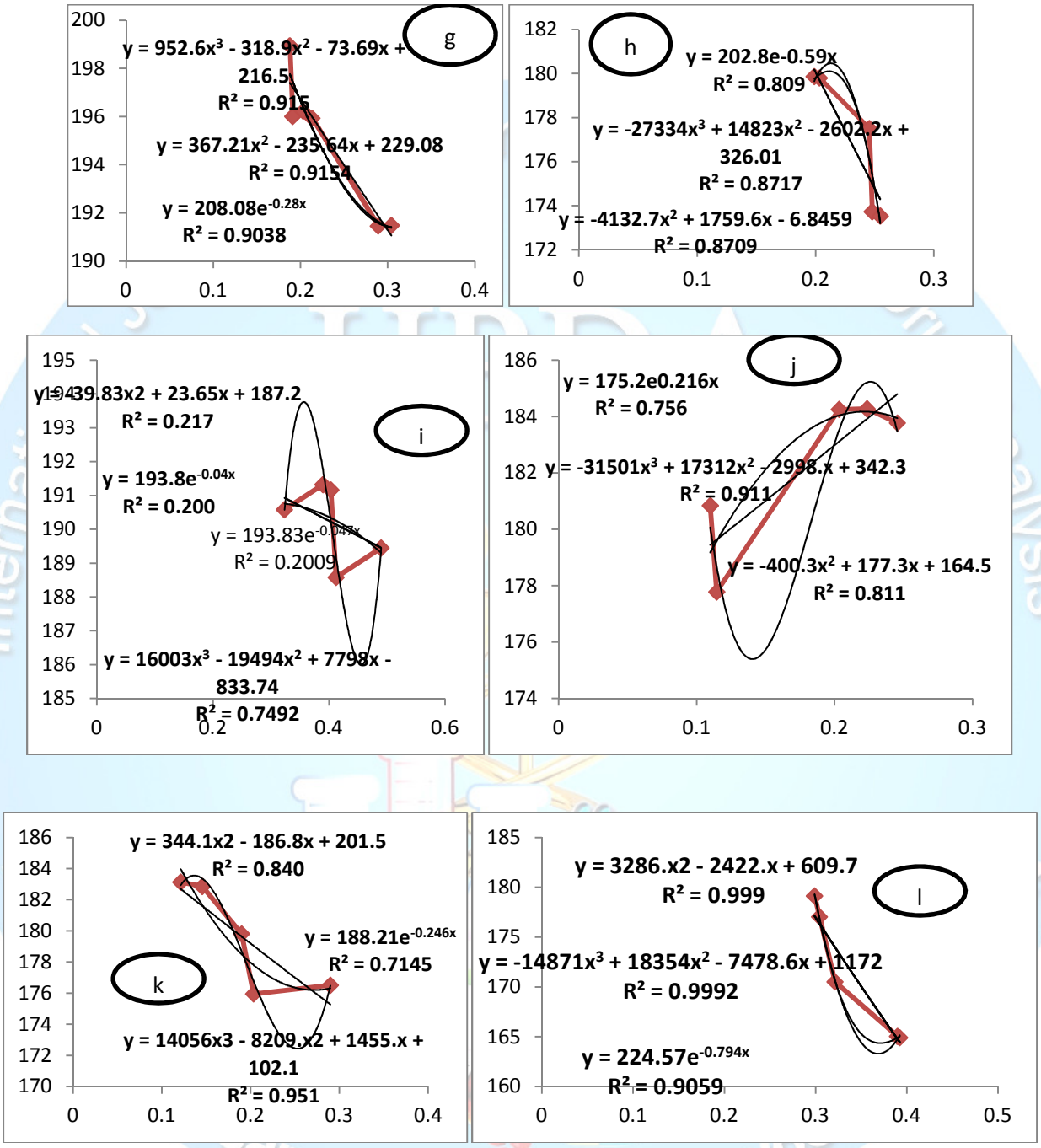


Figure 3. Apparent molar volumes on (y axis) with change in molality (x axis) of Methionine ($C_5H_{11}NO_2S$) in aqueous solutions of sodium nitrate at T=298.15K; (m)0.25mol·kg^{-1} ; (n)0.5mol·kg^{-1} ; (o)0.75mol·kg^{-1} ; (p)1.0mol·kg^{-1} (q)1.5mol·kg^{-1} (r)2.0mol·kg^{-1}.

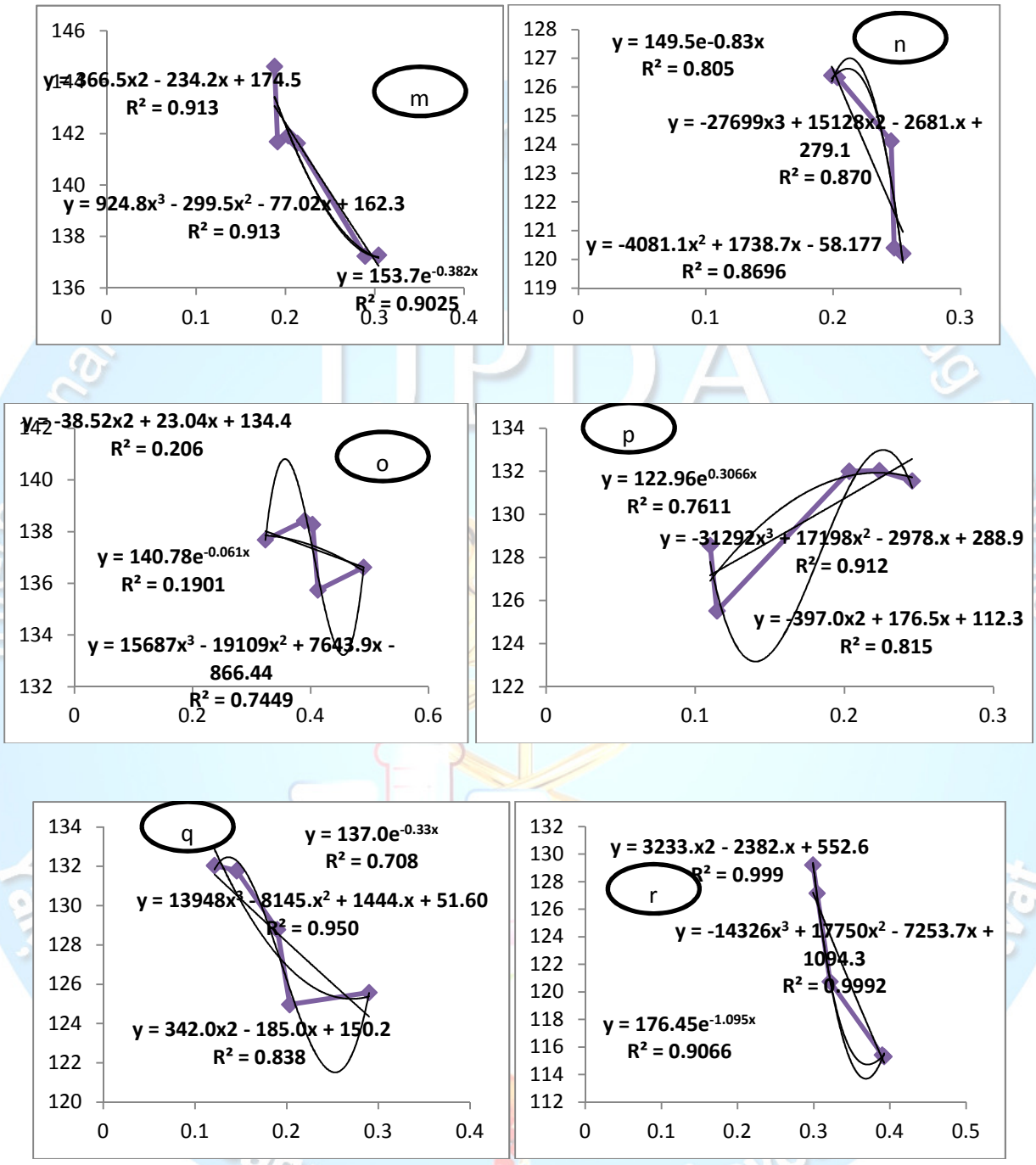
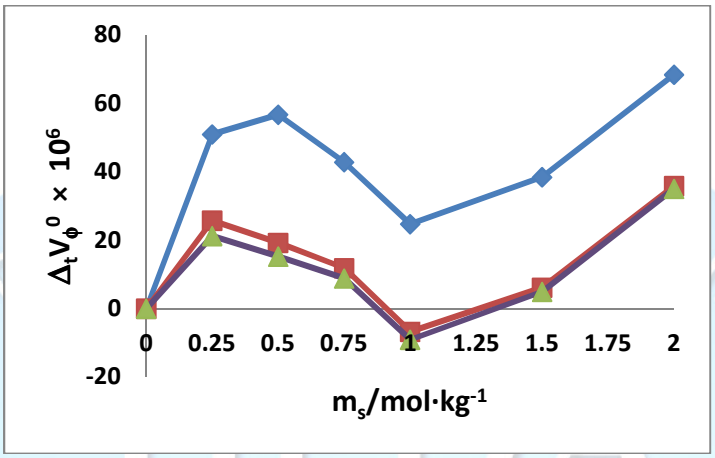


Figure 4. Standard partial molar volumes of transfer, $\Delta_t V^0$, of phenylalanine($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) vs. different molalities, m_s, of sodium nitrate solutions: ◊, phenylalanine($C_9H_{11}NO_2$); ■, tryptophan($C_{11}H_{12}N_2O_2$) ; ▲, methionine ($C_5H_{11}NO_2S$) T= 298.15 K



Apparent molar volumes on (y axis) with change in molality (x axis) of phenylalanine ($C_9H_{11}NO_2$), tryptophan($C_{11}H_{12}N_2O_2$) & methionine ($C_5H_{11}NO_2S$) in aqueous solutions of sodium nitrate at T=298.15K; with the concentration range (0.25-2.0) mol·kg^{-1} are illustrated in Figs. 1-3. At infinite dilution, the apparent molar volumes, $V_{2,\phi}^0$ and partial molar volumes, V_2^0 are identical ($V_{2,\phi}^0 = V_2^0$). In the case of negligible concentration dependence of $V_{2,\phi}$, V_2^0 was determined by taking the average of all the data points. However, where finite concentration dependence was observed, V_2^0 was determined by least-squares fitting of the data using the following equation.

$$V_{2,\phi} = V_2^0 + S_v m, \quad (2)$$

where S_v is the experimental slope. The V_2^0 values along with their standard deviations are summarized in Table 2. The experimental values of V_2^0 for the amino acids in water agreed well with those reported in the literature.

The standard partial molar volumes of transfer, $\Delta_t V^0$, at infinite dilution from water to aqueous sodium nitrate solutions have been evaluated as follows:

$$\Delta_t V^0 = V_2^0 \text{(in aqueous sodium nitrate)} - V_2^0 \text{(in water)} \quad (3)$$

The $\Delta_t V^0$ values for the phenylalanine, tryptophan, methionine are illustrated in Fig. 4. The values first decrease with the increase in concentration of sodium nitrates in the range (0.25-1.0)mol·kg^{-1} and then increases in the range (1.0-2.0)mol·kg^{-1}. The reason is due to hydrophobic character of these amino acids which are dominating initially but later ion-ion interactions overcome the hydrophobic character of these amino acids. However, the transfer molar volumes values for tryptophan ($C_{11}H_{12}N_2O_2$) and methionine ($C_5H_{11}NO_2S$) found to be negative at 1.0 mol·kg^{-1}. This may be due to the phenomenon of electrostriction.

Using mathematical operations in terms of linearly, second and third order polynomial we obtained the following mathematical equations;

Phenylalanine ($C_9H_{11}NO_2$):
$^a m_s$ = 0.0 mol·kg^{-1} (Water)
y = 97.14x +113.3, R^2 = 0.808 (Linearly)
$y = 114.0e^{0.760x}$, R^2 = 0.801 (Exponentially)
$y = 1017.x^2 - 190.4x + 131.3$, R^2 = 0.886 (Second Order Polynomial)
$y = -2703.x^3 + 2166.x^2 - 344.4x + 137.7$, R^2 = 0.886 (Third Order Polynomial)

$^a m_s$ = 0.25 mol·kg^{-1}
y = -26.52x + 164.2, R^2 = 0.235 (Linearly)
$y = 164.3e^{-0.16x}$, R^2 = 0.238 (Exponentially)
$y=-920.8x^2+369.7x+123.6$, R^2 = 0.866 (Second Order Polynomial)
$y = 10087x^3 - 7590.x^2 + 1793.x + 26.12$, R^2 = 0.949 (Third Order Polynomial)

In the continuation of this, similar data for these respective amino acids are shown in Tables 3,4 & 5.

Conclusion

On comparing these tables, an interesting observation was found that found on the basis of comparisons in between these mathematical operations; phenylalanine and tryptophan in water has positive slope (linearly) so considered

has structure makers in water while methionine has negative slope in water, considered as structure breakers. However with the addition of nitrates, the value of slope becomes reverse except at 1.0 mol·kg^{-1}. While on the basis of third order polynomial which seems to be more accurate as they have higher R^2 (Regression) values near to 1.0; which proves the fact that trivalent interactions(3rd order) are more important as compared to divalent and monovalent. This is similar to the concept of ABB interactions as compared to AB and AA interactions. However on noticed these polynomial one can suggest the bahavior of structure breaking /making on the basis of positive and negative slopes while the intercept values in positive and negative strengthen the fact that partial molar volumes can be negative also. Thus proves revolutionary methodologies in studying solution thermodynamics.

Authors' contributions

All authors contributed in process of manuscript writing. We confirm that the manuscript has been submitted solely to this journal and is not published, in press, or submitted elsewhere. All authors agree to the terms and conditions. We confirm that all the research meets the ethical guidelines, including adherence to the legal requirements of the study country. VD(Vaneet Dhir) designed, performed the experimental work and wrote the manuscript. RPSG(RP Singh Grewal) contributed for investigating comparative trend in terms of different mathematical operations and interpretations in terms of polynomial approach. All authors read and approved the final manuscript.

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Competing interests

The authors (Vaneet Dhir and R.P. Singh Grewal) declare that they have no competing interest.

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