Exploring the solvation behaviour of L-valine in aqueous solutions of some carbohydrates through thermophysical properties at 293.15 to 313.15 K

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ABSTRACT

Density and speed of sound of L-valine (0.025 to 0.2 mol kg^{-1}) in water and in aqueous saccharides viz 0.1 M glucose, 0.1 M sucrose and 0.1 M lactose were obtained at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. From the density and speed of sound data, the limiting apparent molar volume, limiting apparent molar compressibility and their corresponding transfer parameters have been evaluated. Positive values of transfer parameters suggest the predominance of solute-solvent (hydrophilic-ionic group and hydrophilic-hydrophilic group) interactions over solute-solute (hydrophobic-hydrophilic group) interactions in the solution. The results have been discussed in terms of solute-solute and solute-solvent interactions in these systems. Moreover, modulation of volumetric properties of L-valine in aqueous saccharides solutions has also been discussed in relation to the increase in the complexity of saccharides and temperature.

Keywords: Density, Speed of sound, L-valine, Saccharides, Transfer volume, Transfer compressibility

I.INTRODUCTION

Proteins play an important role in the biological processes of nearly all living organisms. In order to understand the role played by the biological molecules in the living organism, it is necessary to study the interactions of proteins with their surrounding environment. These interactions are mainly between the protein molecules and the solvent ions. The study of these interactions provides important insight into the conformational stability and folding/unfolding of globular proteins. The complex conformational and configurational factors determining the structure of proteins in sugar solution make the study of protein-sugar interactions difficult. Since amino acids are the model compounds of protein molecules, their thermodynamic properties in aqueous and aqueous-saccharide solutions provide valuable information on solute-solute and solute-solvent interactions that are useful in studying the stability of proteins. Although, an extensive study on physicochemical properties of amino acids has been known, however, to the best of our knowledge, no approach has been made on volumetric and speed of sound for L-valine in various aqueous–saccharides solution. This prompted us to study the density and speed of sound of L-valine (0.025 to 0.2 mol kg^{-1}) in water and three carbohydrates (0.1 glucose, 0.1 sucrose and 0.1 lactose) mol dm^{-3} have been measured at T = (293.15, 298.15, 303.15, 308.15 and 313.15

II.EXPERIMENTAL SECTION

L-valine, α-lactose monohydrate (all >99.8%), D-(+)-glucose, sucrose (both >99.5%) was used as such without further purification. Freshly prepared triple distilled water was used for preparing solutions of amino acid and saaccharides. An electronic single pan five digit analytical balance (Mettler; Model AE-240) with a precision of ±0.00001 g was used for weighing. All the solutions were prepared with care and stored in special airtight bottles to avoid the exposure of solution to air and evaporation. The density of solutions was measured using vibrating tube density meter (Model: DMA 5000M, Anton Paar, Austria) with an uncertainty of ±0.00005 g cm^{-3}. Before each series of measurement, it was calibrated using doubly distilled water and dry air at atmospheric pressure. The temperature was automatically kept constant within ± 0.03K with the help of in-built Peltier system. The speed of sound in the solutions was measured using a single-crystal variable-path multi-frequency ultrasonic interferometer (Model: M-82S, Mittal Enterprises, India) operating at a fixed frequency of 2 MHz. The uncertainty in speed measurement was found to be within ±0.5 m s^{-1}. The temperature of the sample solution was maintained to an accuracy of ±0.02 K using an electronic controlled thermostatic water bath (Model: TIC-4000N, Thermotech, India).

III.RESULTS AND DISCUSSION

The present work measures density and ultrasonic speeds (Table 1) of solutions of L-valine in water, 0.1 M glucose, 0.1 M sucrose and 0.1 M lactose were obtained at temperatures of (293.15, 298.15, 303.15, 308.15 and 313.15) K. We have calculated several thermodynamic parameters by using the following equations:

- **Apparent molar volume,** $V_\phi = \dfrac{1000(\rho_o - \rho)}{m\rho\rho_o} + \dfrac{M}{\rho}$
- $V_\phi = V^o_\phi + S_v m$
- **Limiting apparent molar transfer volume,** $V^\circ_{\phi,tr} = V^\circ_{\phi,aq\text{-}MM} - V^\circ_{\phi,water}$
- The variation of apparent molar volume V_ϕ against molality, m of L-valine in various in water and aqueous saccharides are shown in Figure 1.
- The V°_ϕ, S_v and $V^\circ_{\phi,tr}$ values for L-valine from water to aqueous-saccharides, shown in Table 2, are positive and increases with increase in the complexity of saccharides.
- This may be interpreted by co-sphere overlap model, based on which the effect of overlap of hydration co-sphere is decisive in determining the nature of interaction between the solute species. The different types of interactions occurring between L-valine and saccharides may be classified as follows: (a) the hydrophilic-ionic interactions between OH groups of saccharides and ($NH_3^+$and COO^-) zwitterionic centres of L-valine molecules; (b) the hydrophilic-hydrophilic interactions through the hydrogen bonding between the OH groups of saccharides and OH groups of L-valine molecules; (c) the hydrophilic-hydrophobic interactions between the OH groups of saccharides and alkyl chain ($-CH_2$) of L-valine molecules, and (d) the

hydrophobic-hydrophobic interactions between the alkyl chain (-CH_2) of saccharides molecule and alkyl chain (-CH_2) of L-valine molecule.

- Interactions of types (a) and (b) result in net increase in volume due to the overlap of the hydration co-sphere of the ion (COO^- and NH_3^+) and hydrophilic OH group and due to the overlap of the hydration co-sphere of NH_2 and OH groups leading to increase in the magnitude of hydrogen bonding interaction, respectively.
- On the other hand, interactions of types (c) and (d) result in net decrease in transfer volume.
- The isentropic compressibility, apparent molar compressibility and limiting apparent molar transfer compressibility is given by the following equation:
- $\boldsymbol{\kappa_s = (u^2\rho)^{-1}}$
- $$K_{s,\phi} = \frac{1000(\kappa_s\rho_o - \kappa^o{}_s\rho)}{m\rho\rho_o} + \frac{M}{\rho}$$
- $\boldsymbol{K_{s,\phi} = K^o{}_{s,\phi} + S_k m}$
- The variation of against molal concentration of L-valine in various aqueous-saccharides sovents are presented in Plot 2. The values of $K^o{}_{s,\phi}$ and S_k along with the standard deviation, σ, (Table 2) for L-valine in water as also aqueous-saccharides at different temperatures are negative and positive, respectively.
- The negative values of $K°_{s,\phi}$ reaffirm that the water molecules surrounding the ionic charged groups of amino acid molecules provide great resistance to compression than water molecules present in bulk of solution, thereby, advocating the existence of strong solute-solvent interactions than weak solute-solvent interactions.
- $\boldsymbol{K°_{s,\phi,tr} = K°_{s,\phi,aq\text{-}MM} - K°_{s,\phi,water}}$
- The $K°_{s,\phi,tr}$ values for L-valine from water to aqueous-saccharides, shown in Table 3, are positive which decreases with increase in temperature but increases with increase in complexity of saccharides.
- The decrease in $V°_{\phi,tr}$ and $K°_{s,\phi,tr}$ values with increase in temperature indicate that release of water molecules from the secondary solvation layer of L-valine zwitterions into the bulk becomes difficult with addition of saccharides in the solution due to greater hydrophilic–ionic group and hydrophilic–hydrophilic group interactions as compared to those in water.

IV.TABLES AND FIGURES

Table 1 Densities (ρ) and speeds of sound (u) of L-valine of different molalities in water and aqueous saccharides solutions at different temperatures.

m (mol kg^{-1})	*T* (K)										
	293.15				293.15				293.15		
	ρ (kg m^{-3})		ρ (kg m^{-3})		ρ (kg m^{-3})		ρ (kg m^{-3})		ρ (kg m^{-3})		
L-valine + water											
0.000	998.212	0.000	998.212	0.000	998.212	0.000	998.212	0.000	998.212	0.000	
0.025	998.8	0.025	998.89	0.025	998.8	0.025	998.89	0.025	998.8	0.025	

	95		5		95		5		95	
0.050	999.570	0.050	999.570	0.050	999.570	0.050	999.570	0.050	999.570	0.050
0.075	1000.237	0.075	1000.237	0.075	1000.237	0.075	1000.237	0.075	1000.237	0.075
0.100	1000.897	0.100	1000.897	0.100	1000.897	0.100	1000.897	0.100	1000.897	0.100
0.125	1001.548	0.125	1001.548	0.125	1001.548	0.125	1001.548	0.125	1001.548	0.125
0.150	1002.190	0.150	1002.190	0.150	1002.190	0.150	1002.190	0.150	1002.190	0.150
0.175	1002.823	0.175	1002.823	0.175	1002.823	0.175	1002.823	0.175	1002.823	0.175
0.200	1003.450	0.200	1003.450	0.200	1003.450	0.200	1003.450	0.200	1003.450	0.200
L-valine + 0.1 M aqueous-glucose										
0.000	1005.255	0.000	1005.255	0.000	1005.255	0.000	1005.255	0.000	1005.255	0.000
0.025	1005.892	0.025	1005.892	0.025	1005.892	0.025	1005.892	0.025	1005.892	0.025
0.050	1006.521	0.050	1006.521	0.050	1006.521	0.050	1006.521	0.050	1006.521	0.050
0.075	1007.141	0.075	1007.141	0.075	1007.141	0.075	1007.141	0.075	1007.141	0.075
0.100	1007.753	0.100	1007.753	0.100	1007.753	0.100	1007.753	0.100	1007.753	0.100
0.125	1008.359	0.125	1008.359	0.125	1008.359	0.125	1008.359	0.125	1008.359	0.125
0.150	1008.952	0.150	1008.952	0.150	1008.952	0.150	1008.952	0.150	1008.952	0.150
0.175	1009.541	0.175	1009.541	0.175	1009.541	0.175	1009.541	0.175	1009.541	0.175
0.200	1010.119	0.200	1010.119	0.200	1010.119	0.200	1010.119	0.200	1010.119	0.200
L-valine + 0.1 M aqueous-sucrose										
0.000	1011.	0.000	1011.4	0.000	1011.	0.000	1011.4	0.000	1011.	0.000

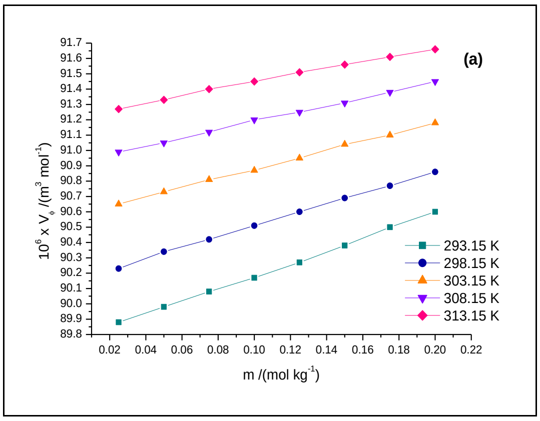
	404		04		404		04		404	
0.025	1012.000	0.025	1012.000	0.025	1012.000	0.025	1012.000	0.025	1012.000	0.025
0.050	1012.587	0.050	1012.587	0.050	1012.587	0.050	1012.587	0.050	1012.587	0.050
0.075	1013.165	0.075	1013.165	0.075	1013.165	0.075	1013.165	0.075	1013.165	0.075
0.100	1013.737	0.100	1013.737	0.100	1013.737	0.100	1013.737	0.100	1013.737	0.100
0.125	1014.295	0.125	1014.295	0.125	1014.295	0.125	1014.295	0.125	1014.295	0.125
0.150	1014.848	0.150	1014.848	0.150	1014.848	0.150	1014.848	0.150	1014.848	0.150
0.175	1015.393	0.175	1015.393	0.175	1015.393	0.175	1015.393	0.175	1015.393	0.175
0.200	1015.929	0.200	1015.929	0.200	1015.929	0.200	1015.929	0.200	1015.929	0.200
L-valine + 0.1 M aqueous-lactose										
0.000	1011.810	0.000	1011.810	0.000	1011.810	0.000	1011.810	0.000	1011.810	0.000
0.025	1012.404	0.025	1012.404	0.025	1012.404	0.025	1012.404	0.025	1012.404	0.025
0.050	1012.989	0.050	1012.989	0.050	1012.989	0.050	1012.989	0.050	1012.989	0.050
0.075	1013.565	0.075	1013.565	0.075	1013.565	0.075	1013.565	0.075	1013.565	0.075
0.100	1014.131	0.100	1014.131	0.100	1014.131	0.100	1014.131	0.100	1014.131	0.100
0.125	1014.691	0.125	1014.691	0.125	1014.691	0.125	1014.691	0.125	1014.691	0.125
0.150	1015.241	0.150	1015.241	0.150	1015.241	0.150	1015.241	0.150	1015.241	0.150
0.175	1015.782	0.175	1015.782	0.175	1015.782	0.175	1015.782	0.175	1015.782	0.175
0.200	1016.313	0.200	1016.313	0.200	1016.313	0.200	1016.313	0.200	1016.313	0.200

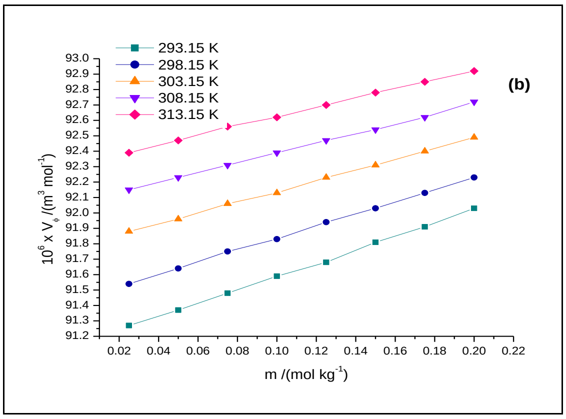
Table 2 Limiting apparent molar volume (V°_ϕ), standard deviation (σ), slope (S_v), transfer volume ($V^\circ_{\phi,tr}$), limiting apparent molar compressibility ($K^\circ_{s,\phi}$), standard deviation (σ), slope (S_k) and transfer compressibility, ($K^\circ_{s,\phi,tr}$) of L-valine and L-valine in water and aqueous saccharides solutions at different temperatures.

Property	*T* (K)				
	293.15	298.15	303.15	308.15	313.15
L-valine + water					
$10^6 \times V^\circ_\phi$ (m^3mol^{-1})	89.77(±0.01)	90.15(±0.01)	90.57(±0.01)	90.93(±0.01)	91.23(±0.01)
	(90.54)[47]	(90.87)[47]	(90.22)[47]	(91.48)[47]	-
σ	0.01	0.01	0.01	0.01	0.01
$10^6 \times S_v$ ($m^3mol^{-2}kg$)	4.12(±0.05)	3.54(±0.03)	3.03(±0.03)	2.59(±0.04)	2.20(±0.04)
$10^{14} \times K^\circ_{s,\phi}$ ($Pa^{-1}m^3mol^{-1}$)	-4.00(±0.02)	-3.62(±0.02)	-3.28(±0.02)	-2.92(±0.02)	-2.63(±0.02)
σ	0.03	0.02	0.03	0.02	0.02
$10^{14} \times S_k$ ($Pa^{-1}m^3mol^{-2}kg$)	9.80(±0.19)	9.17(±0.13)	8.70(±0.18)	8.35(±0.13)	8.10(±0.15)
L-valine + 0.1 M aqueous glucose					
$10^6 \times V^\circ_\phi$ (m^3mol^{-1})	91.15(±0.01)	91.45(±0.01)	91.79(±0.01)	92.07(±0.01)	92.32(±0.01)
σ	0.01	0.01	0.01	0.01	0.01
$10^6 \times S_v$ ($m^3mol^{-2}kg$)	4.34(±0.04)	3.89(±0.03)	3.52(±0.04)	3.23(±0.05)	3.01(±0.04)
$10^6 \times V^\circ_{\phi,tr}$ (m^3mol^{-1})	1.38	1.30	1.22	1.14	1.09
$10^{14} \times K^\circ_{s,\phi}$ ($Pa^{-1}m^3mol^{-1}$)	-3.05(±0.02)	-2.96(±0.02)	-2.83(±0.01)	-2.51(±0.02)	-2.44(±0.02)

σ	0.02	0.03	0.02	0.02	0.02
$10^{14}\times S_k$ (Pa^{-1}m^{3}mol^{-2}kg)	10.03(±0.15)	9.53(±0.16)	9.16(±0.10)	8.90(±0.12)	8.80(±0.13)
$10^{14}\times K^{\circ}_{s,\phi,tr}$ (Pa^{-1}m^{3}mol^{-1})	0.95	0.66	0.45	0.41	0.19
L-valine + 0.1 M aqueous sucrose					
$10^{6}\times V^{\circ}_{\phi}$ (m^{3}mol^{-1})	92.35(±0.01)	92.64(±0.01)	92.87(±0.01)	93.06(±0.01)	93.21(±0.01)
σ	0.01	0.01	0.01	0.01	0.01
$10^{6}\times S_v$ (m^{3}mol^{-2}kg)	4.72(±0.06)	4.28(±0.06)	3.98(±0.03)	3.78(±0.04)	3.65(±0.03)
$10^{6}\times V^{\circ}_{\phi,tr}$ (m^{3}mol^{-1})	2.58	2.49	2.30	2.13	1.98
$10^{14}\times K^{\circ}_{s,\phi}$ (Pa^{-1}m^{3}mol^{-1})	-2.61(±0.01)	-2.52(±0.02)	-2.41(±0.01)	-2.34(±0.01)	-2.28(±0.01)
σ	0.02	0.02	0.01	0.02	0.02
$10^{14}\times S_k$ (Pa^{-1}m^{3}mol^{-2}kg)	10.06(±0.11)	9.75(±0.14)	9.42(±0.08)	9.07(±0.10)	8.78(±0.10)
$10^{14}\times K^{\circ}_{s,\phi,tr}$ (Pa^{-1}m^{3}mol^{-1})	1.39	1.10	0.87	0.58	0.35
L-valine + 0.1 M aqueous lactose					
$10^{6}\times V^{\circ}_{\phi}$ (m^{3}mol^{-1})	92.40(±0.01)	92.69(±0.01)	92.92(±0.01)	93.09(±0.01)	93.22(±0.01)
σ	0.01	0.01	0.01	0.01	0.01

$10^6 \times S_v$ ($m^3 mol^{-2} kg$)	4.85(±0.04)	4.37(±0.03)	4.03(±0.03)	3.81(±0.04)	3.68(±0.03)
$10^6 \times V^\circ_{\phi,tr}$ ($m^3 mol^{-1}$)	2.63	2.54	2.35	2.16	1.99
$10^{14} \times K^\circ_{s,\phi}$ ($Pa^{-1} m^3 mol^{-1}$)	-2.37(±0.02)	-2.28(±0.01)	-2.19(±0.01)	-2.11(±0.02)	-2.06(±0.01)
σ	0.03	0.01	0.02	0.02	0.02
$10^{14} \times S_k$ ($Pa^{-1} m^3 mol^{-2} kg$)	10.16(±0.18)	9.84(±0.09)	9.49(±0.10)	9.13(±0.12)	8.84(±0.11)
$10^{14} \times K^\circ_{s,\phi,tr}$ ($Pa^{-1} m^3 mol^{-1}$)	1.63	1.34	1.09	0.81	0.57





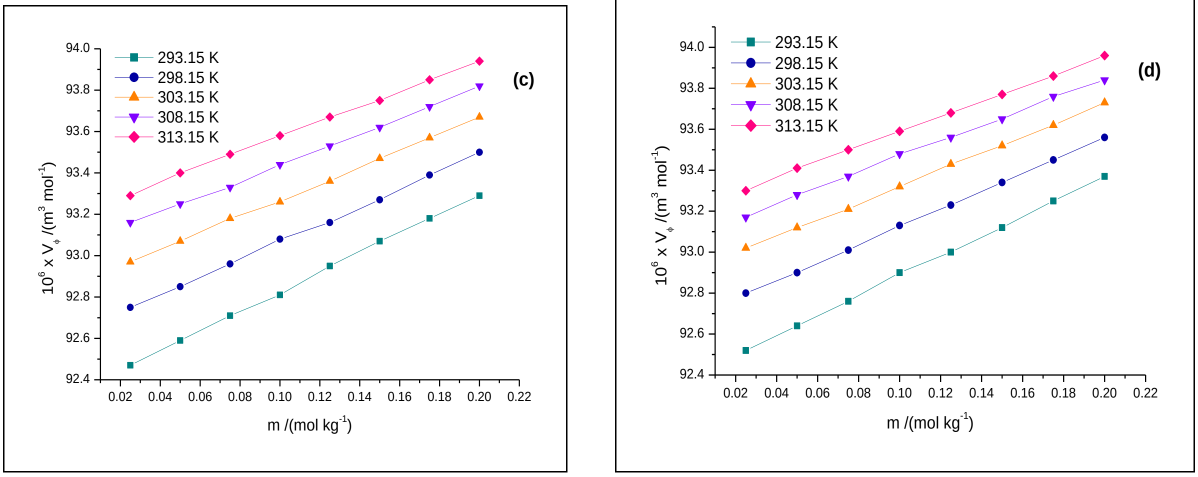


Fig. 1 Variation of apparent molar volume (V_ϕ) with molality (m) for L-valine in water, and saccharides + water solutions: (a) water, (b) 0.1 M glucose, (c) 0.1 M sucrose, (d) 0.1 M lactose at different temperatures

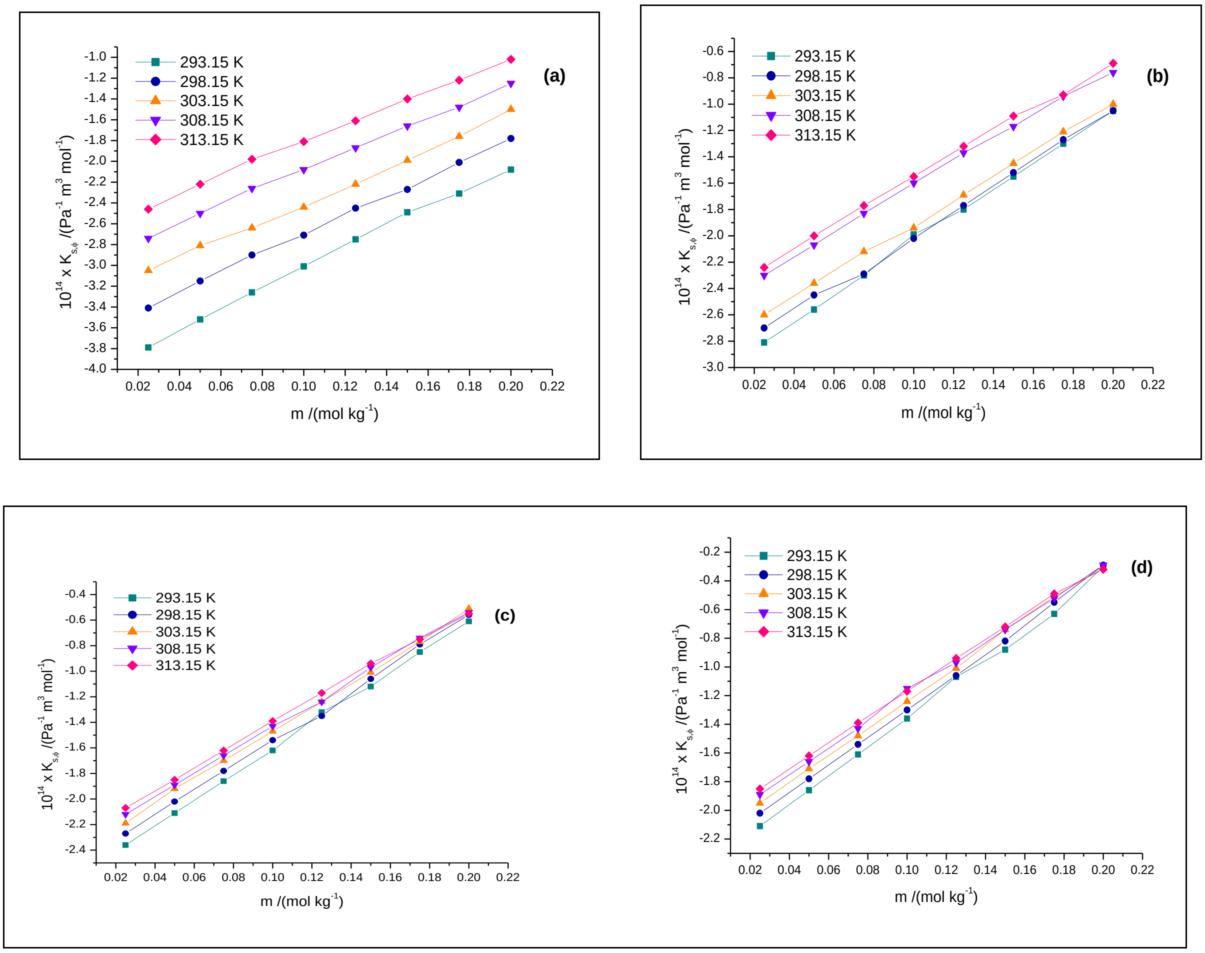


Fig. 2 Variation of apparent molar compressibility ($K_{s,\phi}$) with molality (m) for L-valine in water, and saccharides + water solutions: (a) water, (b) 0.1 M glucose, (c) 0.1 M sucrose, (d) 0.1 M lactose, at different temperatures

V.CONCLUSIONS

The densities and speeds of sound of solutions of L-valine in water and in aqueous saccharides (0.1 mol dm^{-3} glucose, 0.1 mol dm^{-3} sucrose and 0.1 mol dm^{-3} lactose) are measured at different temperatures. From the experimental density and speed of sound results, several thermodynamic parameters are calculated. The degree of interactions increases with an increase in the molar mass of amino acid and an increase in the complexity of saccharides. The positive values of $\Delta_{tr}V°_{\phi}$ and $\Delta_{tr}K°_{s,\phi}$ show that solute-solvent interactions are prominent over solute-solute interactions and this overpowering effect decreases with the increase in temperature for all the systems under study..