Viscometric properties of L-valine in aqueous glucose/sucrose/lactose solutions at T = (293.15 to 313.15) K

Ashwani Kumar[1], **Asha Sharmhal**[2] **and Rajinder K. Bamezai***[1]
[1]Department of Chemistry, University of Jammu, Jammu-180 006, India
[2]Department of Chemistry, Govt. Degree College, Basholi, Kathua, India

ABSTRACT

Viscosity of (L-valine + 0.1 mol dm^{-3} aqueous glucose/sucrose/lactose) systems have been measured as a function of molal concentration of L-valine at different temperatures: (293.15, 298.15, 303.15, 308.15 and 313.15) K. The viscosity data has been utilized to determine viscosity B-coefficients employing Jones-Dole equation. The viscosity B-coefficients of transfer ($\Delta_{tr}B$) and variation of B with temperature (dB/dT) of L-valine have been obtained using the experimental viscosity values. The results have been discussed in terms of solute-solvent interactions; and structure making tendency of L-valine molecules in aqueous saccharides solutions.

Keywords: Viscosity, L-valine, Saccharides, Viscosity B-coefficients, Structure maker

1. INTRODUCTION

Amino acid, as a basic unit of protein has been in use for studies on the solvation and conformation of proteins which in turn provides valuable information on molecular interactions [1-4]. The polyhydroxy compounds, for example saccharides, are widely distributed in various forms of life as essential moieties and play significant role in many biological processes [5-7]. They also play a key role in stabilizing the native conformations of proteins/enzymes [8-10]. The stabilization of native conformations of proteins has been related to various non-covalent interactions like hydrogen bonding, electrostatic, hydrophobic, etc. [11,12]. The study of these interactions provides important insight into the conformational stability and folding/unfolding of globular proteins [13-15]. The complex conformational and configurational factors determining the structure of proteins in sugar solution makes the study of protein-sugar interactions difficult and interesting. One of the useful approaches involves studying the model components of proteins, i.e., amino acids in aqueous and mixed aqueous saccharides solutions. Jones-Dole or viscosity B-coefficients values is considered to be a vital parameter to describe the structure maker or structure breaker nature of solute in various solvents. By means of the researches on the transport properties of amino acids in the solutions of aqueous saccharides, one can gather useful information about the solute-solute and solute-solvent interactions, which turns to be helpful in understanding the mechanism of protein stabilization through saccharides [2, 16-17].

No doubt the literature survey shows a comprehensive study on transport properties of amino acids [18-23], however, viscometric work of the interactions between L-valine in aqueous solutions of different saccharides and their comparative behaviour seem to be scarce. One of the reasons of studying viscometric properties in conjunction with volumetric properties is that L-valine and their derivatives are known as compensatory or compatible solutes in stabilizing proteins and enhancing enzyme activity [24-26]. So, this prompted us to evaluate the transport behaviour of L-valine with three saccharides (glucose, sucrose and lactose) in aqueous medium. Hence, in continuation to our previous work [27,28], we are reporting the nature of L-valine in aqueous saccharides depending upon viscosity *B*-coefficients and viscosity *B*-coefficients of transfer from T = (293.15 to 313.15) K and 1 atmospheric pressure.

2. EXPERIMENTAL

2.1. Source and purity of chemicals

The specifications of the chemicals used in the present work are: L-valine and α-lactose monohydrate (all >99.8%), D-(+)-glucose and sucrose (both >99.5%). All these chemicals are obtained from Sigma Aldrich, India and used after storing them over anhydrous calcium chloride in a vacuum desiccator overnight at room temperature, except α-lactose monohydrate which was used as such. Freshly prepared triple distilled water was used for preparing solutions of L-valine and saccharides.

2.2. Apparatus and procedure

The solutions were prepared on molality basis using an electronic single pan five digit analytical balance (Model: Mettler AE-240) with a precision of ±0.01 mg. The aqueous solutions of glucose, sucrose and lactose (each being 0.1 mol dm^{-3}) were used as solvent to prepare L-valine solutions of eight different molal concentrations (ranging from 0.025 to 0.2) mol kg^{-1}. The solutions were prepared with utmost care and stored in special airtight bottles to avoid their exposure to air and evaporation. The viscosity of the solutions was measured by using an Ubbelohde viscometer, calibrated at 298.15 K with distilled water and pure methanol. In order to avoid the thermal fluctuation of solutions in viscometer, the solution was immersed for about half an hour in a thermostatic water bath. The time of flow was noticed using an electronic watch with the resolution of 0.01 s. An Average of at least five sets reproducible within ±0.1 s was used with sufficient care. The accuracy in measurements of viscosity was within $\pm 1 \times 10^{-6}$ N s m^{-2}. An electronic controlled thermostatic water bath (Model: TIC-4000N, Thermotech, India) was used to maintain the temperature of the solutions to an accuracy of ±0.02 K.

3. RESULTS AND DISCUSSION

3.1. Viscometric studies

The experimental values of viscosity of different molalities of L-valine in pure water and aqueous solutions of saccharides (0.1 glucose, 0.1 sucrose and 0.1 lactose) mol dm^{-3} as a function temperature are calculated using the density data already reported in the literature [38] and are displayed in Table 1. It is evident that viscosity continually increases with increasing molal concentration of L-valine and decreases with increasing temperature in all the investigated systems. A representative 3-D plot of viscosity, η, versus molality, m, of L-valine in aqueous 0.1 mol dm^{-3} lactose solution is displayed in Fig. 1. With an increase in temperature, there is typically an increase in the molecular interchange as molecules move faster at higher temperature. In liquid state, there will be molecular interchange similar to those developed in a gas, but there are additional substantial attractive, cohesive forces between the molecules of a liquid (which are much closer together than those of a gas). Both cohesion and molecular interchange factors contribute to liquid viscosity. The impact of increasing the temperature of a liquid is to reduce the cohesive forces while simultaneously increasing the rate of molecular interchange. The former effect causes a decrease in the shear stress while the latter causes it to increase. Thus, the lowering of viscosity as a result of impact of increasing temperature may be due to the accelerated molecular motion in the system.

The relative viscosity, η_r, which is related to the molality, m, may be expressed using Jones-Dole equation [29]:

$$\eta_r = \frac{\eta}{\eta_o} = 1 + Am^{1/2} + Bm \qquad (1)$$

where η_o and η are viscosities of solvent (aqueous saccharide) and solution (L-valine + water + saccharide), respectively. *A,* called as Falkenhagen coefficient, is a constant which arises from ion-ion or solute–solute interactions. *B,* called also as viscosity *B*-coefficients or Jones-Dole coefficient, which measures the size, shape, charge and structural effects is regarded as an important parameter to study solute-solvent interactions [30-32]. The *A*-coefficients (values not given) for L-valine is found to be much smaller in magnitude as compared to *B*-coefficients and, hence, can be considered negligible in case of non-electrolytes [33].

The values of reduced viscosity, $(\eta_r\text{-}1)/m^{1/2}$, of solutions of different molalities of L-valine in water and aqueous saccharides are presented in Table 1 and plotted in Fig. 2, respectively. Accordingly, viscosity *B*-coefficients, found to be linear at all concentrations and temperatures, are estimated using a plot between reduced viscosity and square root of molality by least squares analysis method. An analysis of Table 2 reveals that the values of viscosity *B*-coefficients for L-valine in water show a reasonable agreement with literature value [30]. The positive *B*-coefficients for L-valine at all temperatures show the dominance of solute-solvent interactions over solute-solute interactions. As is evident from Table 2, *B*-coefficients of L-valine in aqueous saccharides are larger than in water indicating that in presence of co-solute (saccharide), the structure of solution gets strengthened. The values of *B*-coefficients increase with the increase in the complexity of saccharide solutions in the order: glucose < sucrose < lactose. An increase in *B*-coefficients values from glucose to lactose may be attributed to the formation of structure that allows the solute to act on solvent and reinforce its structure by hydrogen bonding [34]. Thus, the inference drawn from *B*-coefficients supports the behaviour of an existence of strong solute-solvent interactions which further advocates the existence of strong ionic-hydrophillic and hydrophilic-hydrophillic interactions.

From Table 2 it is also evident that *B*-coefficients show a decreasing trend with rise in temperature. The information regarding structure-making or structure-breaking capability of the solute is well documented by considering the temperature derivative of *B*-coefficients, *dB/dT* [29]. The negative values of *dB/dT* (Table 2) suggest that nature of L-valine is that of structure-maker in aqueous saccharides. The structure-making ability of L-serine in aqueous d-xylose/l-arabinose and L-valine in aqueous sorbital solutions has also been observed by Nain *et al*. [30] and Ren *et al*. [35], respectively.

3.2. TRANSFER VISCOSITY

The viscosity B-coefficients of transfer, $\Delta_{tr}B$, of L-valine from water to aqueous glucose/sucrose/lactose solutions has been evaluated using the relation:

$$\Delta_{tr}B = B_{aq\text{-}saccharides} - B_{water} \tag{2}$$

where B_{water} is B-coefficients of L-valine in water. Further, for L-valine, increase in $\Delta_{tr}B$ values in the order of glucose < sucrose < lactose (Fig. S2) may be due to greater dehydration effect of lactose than sucrose which is again greater than glucose i.e., the higher $\Delta_{tr}B$ value is due to interactions of solute in solvent which cause the release of electrostrictive water molecules into the bulk water. Glucose molecule is a monosaccharide, whereas both sucrose and lactose has two monosaccharide units with the difference that the lactose molecule has galactose and glucose subunits whereas the sucrose molecule consists of glucose and fructose subunits. The lactose and sucrose has equal number of OH groups but the former consisting of galactose and glucose subunits has the most moderate and disturbed hydration layers [36] than sucrose molecule which consists of glucose and fructose subunits. Therefore, lactose molecule does not fit well into the structure of water, or one can say that it has poor compatibility with the three-dimensional hydrogen-bonded structure of water. Hence, it interacts strongly with L-valine and resulting dehydration contributes more positive values to $\Delta_{tr}B$ than sucrose molecule. In other words, the main contribution to B-coefficients of transfer values comes from the interactions between charged centres of L-valine and saccharides molecules, rather than from interactions between R groups of L-valine and saccharides molecules. The above trend is due to strong ionic-hydrophilic and hydrophilic-hydrophilic interactions of L-valine in aqueous lactose and sucrose solutions than in glucose one. $\Delta_{\text{tr}}B$ values show a decreasing trend with increasing temperature for the current system. Similar results are reported by Banipal et al. [37].

4. CONCLUSIONS

The viscosities of solutions of L-valine in water and in aqueous (0.1 glucose, 0.1 sucrose and 0.1 lactose) mol dm^{-3} are measured at different temperatures. From the experimental results, viscosity B-coefficients, its temperature derivative and transfer parameters are evaluated. The obtained values of B-coefficients and its transfer counterpart are positive which signifies that amino acid-saccharide-water interactions are stronger than amino acid-amino acid interactions. The negative values of dB/dT have been argued for the structure-making behaviour of L-valine in aqueous-saccharides solutions.

ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry, University of Jammu, Jammu, for providing the necessary facilities for the completion of this work.

REFERENCES

[1] R. Bhat, and J. C. Ahluwalia, J. Phys. Chem. **89**, 1099 (1985).

[2] H. Zhao, Biophys. Chem. **122**, 157 (2006).

[3] P. H. Von Hippel, and T. Schleich, in *Structure and Stability of Biological Macromolecules* ed. By S.N. Timasheff, and G.D. Fasman (Marcel Dekker, New York, 1969), p. 417.

[4] G. R. Hedwig, and H. Hoiland, J. Chem. Thermodyn. **23**, 1029 (1991).

[5] D. P. Miller, and J. J. de Pablo, J. Phys. Chem. B **104**, 8876 (2000).

[6] K. Zhuo, H. Liu, H. Zhang, Y. Liu, and J. Wang, J. Chem. Eng. Data **53**, 57 (2008).

[7] G. O. Hernandez-Segura, M. Campos, M. Costas, and L. A. Torres, J. Chem. Thermodyn. **41**, 17 (2009).

[8] J. F. Back, D. Oakenfull, and M. B Smith, Biochem. **18**, 5191 (1979).

[9] H. Uedaira, and H. Uedaira, Bull. Chem. Soc. Jpn. **53**, 2451 (1980).

[10] S. Li, W. Sang, and R. Lin, J. Chem. Thermodyn. **34**, 1761 (2002).

[11] P. H. Von Hippel, and T. Schleich, Acc. Chem. Res. **2**, 257 (1969).

[12] F. Franks, Biophys. Chem. **96**, 117 (2002).

[13] Z. Yan, J. Wang, W. Kong, and J. Lu, Fluid Phase Equilib. **215**, 143 (2004).

[14] C. M. Romero, E. Moreno, and J. L. Rojas, Thermochim. Acta **328**, 33 (1999).

[15] K. Kuwajima, Proteins: Struct. Funct. Genet. **6**, 87 (1989).

[16] K. Gekko, J. Biochem. **90**, 1633 (1981).

[17] T. C. Bai, and G. B. Yan, Carbohydr. Res. **338**, 2921 (2003).

[18] A. Pal, and N. Chauhan, Ind. J. Chem. **48A**, 1069 (2009).

[19] G. A. Kulikova, and E. V. Parfenyuk, J. Solut. Chem. **37**, 835 (2008).

[20] A. Ali, S. Hyder, S. Sabir, D. Chand, and A. K. Nain, J. Chem. Thermodyn. **38**, 136 (2006).

[21] R. Rani, A. Kumar, T. Sharma, B. Saini, and R. K. Bamezai, Acta Chim. Slov. **63**, 589 (2016).

[22] R. Rani, A. Kumar, and R. K. Bamezai, J. Mol. Liq. **224**, 1142 (2016).

[23] A. Soto, A. Arce, and M. K. Khoshkbarchi, Biophys. Chem. **76**, 73 (1999).

[24] H. Zhao, J. Mol. Catal. B: Enzym. **37**, 16 (2005).

[25] A. Pollard, and R. G. W. Jones, Planta **144,** 291 (1979).

[26] M. E. Clark, *The Osmotic Role of L-valine: Discovery and Function*, in *Transport Processes-Iono and Osmoregulation*, ed. By R. Gilles, and M. Gilles-Baillien (Springer Verlag, Berlin, 1985), p. 412-423.

[27] A. Kumar, R. Rani, A. Gupta, B. Saini, and R. K. Bamezai, Phys. Chm. Liq. **54**, 602 (2016).

[28] A. Kumar, R. Rani, B. Saini, and R. K. Bamezai, J. Solut. Chem. **46**, 931 (2017).

[29] G. Jones, and M. Dole, J. Am. Chem. Soc. **51**, 2950 (1929).

[30] A. K. Nain, and M. Lather, Phys. Chem. Liq. **53**, 599 (2015).

[31] A. K. Nain, R. Pal, and R. K. Sharma, J. Mol. Liq. **165**, 154 (2012).

[32] T. S. Banipal, H. Singh, P. K. Banipal, and V. Singh, Thermochim. Acta **553**, 31 (2013).

[33] H. D. B. Jenkins, and Y. Marcus, Chem. Rev. **95 (8)**, 2695 (1995).

[34] K. Kumar, B. S. Patial, and S. Chauhan, J. Chem. Eng. Data **60**, 47 (2015).

[35] X. Ren, C. Zhu, and Y. Ma, J. Chem. Thermodyn. **93**, 179 (2016).

[36] P. K. Banipal, A. K. Chahal nee Hundal, and T. S. Banipal, Carbohydr. Res. **345**, 2262 (2010).

[37] P. K. Banipal, V. Singh, and T. S. Banipal, J. Chem. Eng. Data **58**, 2355 (2013).

[38] A. Kumar, R. Rani, B. Saini, and R. K. Bamezai, J. Mol. Liq. **241**, 237 (2017).

Table 1. Viscosity (η) and reduced viscosity $\{(\eta_r\text{-}1)/m^{1/2}\}$ of solutions of L-valine of different molalities in water and aqueous saccharides at different temperatures.

m (mol kg^{-1})	T (K)									
	293.15		298.15		303.15		308.15		313.15	
	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)	$\eta \times 10^3$ (N s m^{-2})	$(\eta_r\text{-}1)/m^{1/2}$ (mol$^{-1/2}$ kg$^{1/2}$)
L-valine + water										
0.000	1.0019		0.8903		0.7973		0.7190		0.6526	
0.025	1.0092	0.0458	0.8968	0.0464	0.8025	0.0411	0.7231	0.0361	0.6557	0.0303
0.050	1.0163	0.0644	0.9028	0.0628	0.8073	0.0560	0.7274	0.0525	0.6589	0.0434
0.075	1.0236	0.0790	0.9089	0.0762	0.8122	0.0684	0.7318	0.0649	0.6623	0.0543
0.100	1.0313	0.0929	0.9146	0.0864	0.8173	0.0792	0.7359	0.0742	0.6658	0.0638
0.125	1.0382	0.1024	0.9211	0.0977	0.8221	0.0881	0.7396	0.0810	0.6691	0.0716
0.150	1.0450	0.1112	0.9267	0.1057	0.8270	0.0962	0.7436	0.0884	0.6723	0.0778
0.175	1.0520	0.1196	0.9336	0.1162	0.8324	0.1053	0.7480	0.0965	0.6751	0.0825
0.200	1.0587	0.1268	0.9386	0.1214	0.8369	0.1111	0.7517	0.1016	0.6785	0.0888
L-valine + 0.1 mol dm^{-3} aqueous-glucose										
0.000	1.1705		0.9613		0.8295		0.7637		0.7629	
0.025	1.1823	0.0639	0.9707	0.0618	0.8380	0.0648	0.7702	0.0541	0.7680	0.0421
0.050	1.1936	0.0882	0.9802	0.0878	0.8459	0.0883	0.7769	0.0774	0.7734	0.0614
0.075	1.2061	0.1109	0.9890	0.1053	0.8538	0.1071	0.7841	0.0978	0.7794	0.0788
0.100	1.2179	0.1281	0.9991	0.1242	0.8614	0.1217	0.7901	0.1092	0.7848	0.0907
0.125	1.2294	0.1423	1.0085	0.1388	0.8689	0.1345	0.7966	0.1218	0.7908	0.1036
0.150	1.2409	0.1553	1.0175	0.1509	0.8765	0.1464	0.8035	0.1347	0.7965	0.1137
0.175	1.2537	0.1699	1.0265	0.1621	0.8847	0.1591	0.8094	0.1432	0.8014	0.1207
0.200	1.2651	0.1807	1.0357	0.1730	0.8927	0.1704	0.8150	0.1501	0.8071	0.1295
L-valine + 0.1 mol dm^{-3} aqueous-sucrose										
0.000	1.1088		0.9907		0.8873		0.7939		0.7054	
0.025	1.1225	0.0782	1.0019	0.0717	0.8965	0.0653	0.8022	0.0665	0.7119	0.0585
0.050	1.1362	0.1107	1.0137	0.1040	0.9057	0.0927	0.8110	0.0963	0.7185	0.0828

0.075	1.1496	0.1345	1.0260	0.1301	0.9150	0.1140	0.8195	0.1178	0.7253	0.1031
0.100	1.1635	0.1561	1.0380	0.1509	0.9258	0.1372	0.8276	0.1344	0.7319	0.1186
0.125	1.1769	0.1738	1.0495	0.1678	0.9348	0.1515	0.8354	0.1480	0.7384	0.1323
0.150	1.1917	0.1930	1.0608	0.1827	0.9445	0.1665	0.8438	0.1623	0.7446	0.1435
0.175	1.2062	0.2099	1.0724	0.1971	0.9543	0.1804	0.8523	0.1757	0.7511	0.1547
0.200	1.2208	0.2258	1.0839	0.2103	0.9640	0.1932	0.8599	0.1859	0.7577	0.1657
L-valine + 0.1 mol dm^{-3} aqueous-lactose									
0.000	1.1243		0.9768		0.8676		0.7923		0.7497	
0.025	1.1387	0.0810	0.9887	0.0773	0.8778	0.0740	0.8004	0.0648	0.7569	0.0609
0.050	1.1535	0.1162	1.0006	0.1090	0.8874	0.1019	0.8094	0.0965	0.7640	0.0852
0.075	1.1688	0.1444	1.0125	0.1334	0.8974	0.1256	0.8185	0.1205	0.7714	0.1059
0.100	1.1840	0.1679	1.0256	0.1581	0.9078	0.1464	0.8265	0.1365	0.7778	0.1184
0.125	1.1984	0.1864	1.0370	0.1742	0.9180	0.1643	0.8348	0.1517	0.7853	0.1344
0.150	1.2135	0.2049	1.0492	0.1915	0.9283	0.1805	0.8431	0.1657	0.7927	0.1482
0.175	1.2268	0.2180	1.0611	0.2064	0.9391	0.1969	0.8512	0.1777	0.7998	0.1597
0.200	1.2411	0.2325	1.0732	0.2206	0.9486	0.2088	0.8593	0.1890	0.8073	0.1719

Table 2. Viscosity *B*-coefficients and viscosity *B*-coefficients of transfer ($\Delta_{tr}B$) of L-valine in aqueous saccharides at different temperatures and temperature coefficient (*dB/dT*).

System	T (K)					*dB/dT* ($dm^3mol^{-1}K^{-1}$)
	293.15	298.15	303.15	308.15	313.15	
	Viscosity *B*-coefficients (dm^3mol^{-1})/ Viscosity *B*-coefficients of transfer (dm^3mol^{-1})					
L-valine + water	0.282(±0.004)	0.264(±0.004)	0.245(±0.002)	0.225(±0.004)	0.203(±0.003)	-0.004 (±0.001)
L-valine + 0.1 mol dm^{-3} aqueous glucose	0.407(±0.004)/ 0.125	0.386(±0.004)/ 0.122	0.362(±0.003)/ 0.117	0.335(±0.008)/ 0.110	0.305(±0.005)/ 0.102	-0.005(±0.001)
L-valine + 0.1 mol dm^{-3} aqueous sucrose	0.509(±0.006) 0.227	0.479(±0.005)/ 0.215	0.446(±0.005)/ 0.201	0.410(±0.005)/ 0.185	0.370(±0.003)/ 0.167	-0.007(±0.001)
L-valine + 0.1 mol dm^{-3} aqueous lactose	0.526(±0.007)/ 0.244	0.498(±0.004)/ 0.234	0.473(±0.005)/ 0.228	0.425(±0.008)/ 0.200	0.382(±0.005)/ 0.179	-0.007(±0.001)

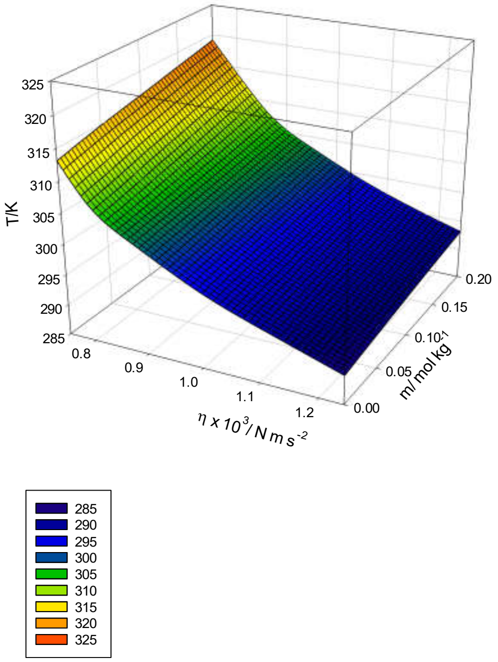
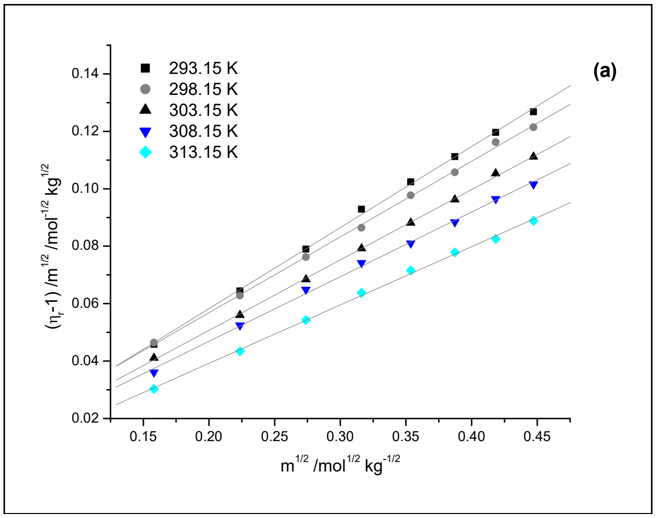


Fig. 1. Variation of viscosity (*η*) with molality (*m*) for L-valine in 0.1 mol dm^{-3} aqueous lactose at (293.15, 298.15, 303.15, 308.15 and 313.15) K.



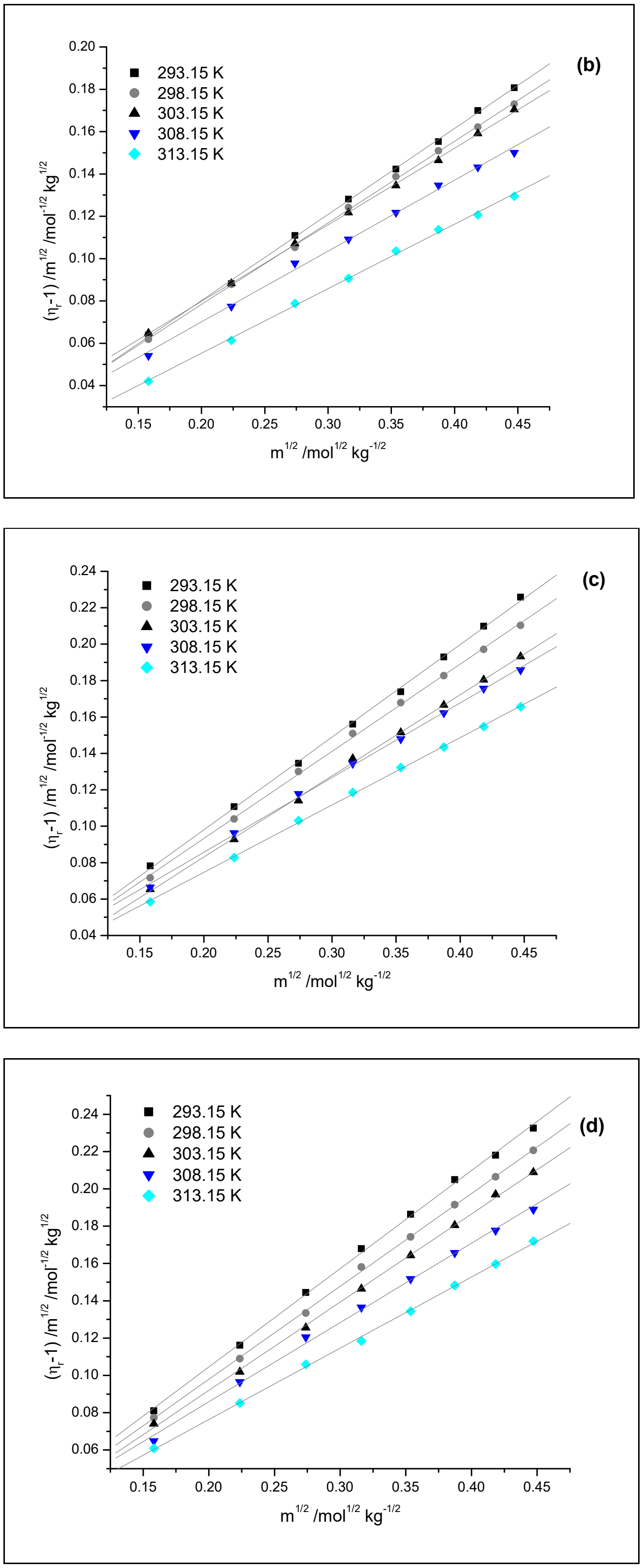


Fig. 2. Variation of reduced viscosity $\{(\eta_r-1)/m^{1/2}\}$ with molality ($m^{1/2}$) of L-valine in (a) water, (b) 0.1 mol dm^{-3} glucose, (c) 0.1 mol dm^{-3} sucrose, (d) 0.1 mol dm^{-3} lactose, at different temperatures.