

Viscometric studies on the interactions of L-arginine with maltose monohydrate in aqueous solutions at T = (298.15 to 308.15 K)

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ABSTRACT

Viscosities of L-arginine (0.025 to 0.2 mol kg⁻¹) in varying concentrations of aqueous maltose monohydrate (0 to 6 mass % of maltose monohydrate in water) have been measured at different temperatures, viz., 298.15 K, 303.15 K and 308.15 K. The experimental results are analysed in accordance with viscosity B-coefficients, viscosity B-coefficients of transfer, B_{tr}, and variation of B with temperature, dB/dT. The Gibbs free energy of activation of viscous flow per mole of solvent, $\Delta\mu_1^\ddagger$, as well as per mole of solute, $\Delta\mu_2^\ddagger$, along with activation enthalpy, ΔH_2^\ddagger , and activation entropy, ΔS_2^\ddagger , using different concentrations of maltose monohydrate in aqueous medium are also evaluated using Feakin's transition-state theory. The results are discussed in terms of intermolecular interactions and that the solute acts as structure maker in the solvent system under study.

Keywords: Viscosity; L-arginine; maltose monohydrate; Viscosity B-coefficients; Activation parameters

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 viscometric for L-arginine in various aqueous–maltose monohydrate solutions. This prompted us to study the viscosity of L-arginine (0.025 to 0.2 mol kg⁻¹) in varying concentrations of aqueous maltose monohydrate (0 to 6 mass % of maltose monohydrate in water) at T = (298.15, 303.15 and 308.15) K.

II EXPERIMENTAL SECTION

D-Maltose monohydrate (abbreviated as MM) and L-arginine (both having a mass fraction purity of >99.8%) 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 viscosity of the solutions was measured by using an Ubbelohde viscometer, calibrated at 298.15 K with distilled water and pure methanol. The time of flow was noticed using an electronic watch with the resolution of 0.01s. 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).

IV RESULTS AND DISCUSSION

The present work measures viscosity (Table 1) of solutions of L-arginine in various aqueous-MM solutions. We have calculated several transport parameters by using the following equations:

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

- The values of viscosity, η are reported in Table 1.
- Reduced viscosity, $(\eta_r-1)/m^{1/2}$, of solutions of different molalities of L-arginine in water and aqueous MM solutions are presented in Table 1 and plotted in Fig.1 respectively.
- The lowering of viscosity as a result of impact of increasing temperature may be due to the accelerated molecular motion in the system.
- 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.
- The positive B -coefficients (Table 2) for L-arginine at all temperatures show the dominance of solute-solvent interactions over solute-solute interactions.

- As is evident from Table 2, B -coefficients of L-arginine in aqueous MM solutions are larger than in water indicating that in presence of co-solute (maltose), the structure of solution gets strengthened.
- The negative values of dB/dT (Table 2) suggest L-arginine is acting as structure-maker in aqueous solutions of MM.
- The viscosity B -coefficients of transfer, $\Delta_{tr}B$, (Table 2) of L-arginine from water to aqueous MM solutions has been evaluated using the relation:

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

- Further, for L-arginine, $\Delta_{tr}B$ values increases with increase in concentration is due to interactions of MM with either R groups or charged centers of L-arginine 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.
- The Gibbs free energy of activation or chemical potential per mole of solvent, $\Delta\mu_1^{\circ\#}$, is obtained from the following relation:

$$\Delta\mu_1^{\circ\#} = RT \ln \left(\frac{\eta_0 V_1}{h N_A} \right)$$

$$\Delta\mu_2^{\circ\#} = \Delta\mu_1^{\circ\#} + \left(\frac{RT}{V^{\circ_2}} \right) [1000B - (V_1^{\circ} - V_2^{\circ})]$$

- The calculated values of $\Delta\mu_1^{\circ\#}$, V_1° and $\Delta\mu_2^{\circ\#}$ at various temperatures are summarized in Table 3.
- The values of $\Delta\mu_2^{\circ\#}$ signify the capability to form the transition state via the solute-solvent interactions from the ground state of the solvent. The values of $\Delta\mu_2^{\circ\#}$ are large and positive than those of $\Delta\mu_1^{\circ\#}$ for L-arginine in aqueous and aqueous- MM solutions reflecting that interactions between L-arginine and aqueous MM solutions in the ground state are stronger than in the transition state.
- The activation entropy, $\Delta S_2^{\circ\#}$, and activation enthalpy, $\Delta H_2^{\circ\#}$ values for the viscous flow of L-arginine in water and aqueous-MM solutions are obtained using the following equations:

$$\Delta S_2^{\circ\#} = - \left(\frac{d\Delta\mu_2^{\circ\#}}{dT} \right)$$

$$\Delta H_2^{\circ\#} = \Delta\mu_2^{\circ\#} + T\Delta S_2^{\circ\#}$$

- The values reported in Table 3 shows that for L-arginine values of $\Delta H_2^{\circ\#}$ and $T\Delta S_2^{\circ\#}$ are negative which indicates that the formation of the transition state is associated with bond making and the increase in order of the system.

TABLES AND FIGURES

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

m (mol kg ⁻¹)	T (K)					
	298.15		303.15		308.15	
	$\eta \times 10^3$ (N s m ⁻²)	$(\eta_r-1)/m^{1/2}$ (mol ^{-1/2} kg ^{1/2})	$\eta \times 10^3$ (N s m ⁻²)	$(\eta_r-1)/m^{1/2}$ (mol ^{-1/2} kg ^{1/2})	$\eta \times 10^3$ (N s m ⁻²)	$(\eta_r-1)/m^{1/2}$ (mol ^{-1/2} kg ^{1/2})
L-arginine + water						
0.000	0.8903		0.7973		0.7190	
0.025	0.9005	0.0727	0.8053	0.0633	0.7257	0.0588
0.050	0.9108	0.1029	0.8133	0.0899	0.7324	0.0832
0.075	0.9210	0.1260	0.8214	0.1103	0.7391	0.1022
0.100	0.9313	0.1458	0.8294	0.1275	0.7459	0.1183
0.125	0.9416	0.1629	0.8375	0.1425	0.7527	0.1326
0.150	0.9519	0.1787	0.8456	0.1565	0.7594	0.1451
0.175	0.9623	0.1934	0.8537	0.1690	0.7662	0.1568
0.200	0.9727	0.2071	0.8618	0.1809	0.7730	0.1679
L-arginine + 2% aqueous-MM						
0.000	0.9355		0.8343		0.7459	
0.025	0.9486	0.0886	0.8450	0.0810	0.7549	0.0765
0.050	0.9618	0.1257	0.8556	0.1140	0.7639	0.1078
0.075	0.9750	0.1541	0.8663	0.1402	0.7729	0.1322
0.100	0.9883	0.1784	0.8771	0.1622	0.7820	0.1531
0.125	1.0015	0.1997	0.8878	0.1813	0.7911	0.1714
0.150	1.0148	0.2190	0.8986	0.1991	0.8002	0.1880
0.175	1.0282	0.2369	0.9094	0.2152	0.8093	0.2032
0.200	1.0415	0.2534	0.9202	0.2303	0.8183	0.2171
L-arginine + 4% aqueous-MM						
0.000	0.9838		0.8711		0.7698	
0.025	1.0008	0.1094	0.8852	0.1025	0.7815	0.0961
0.050	1.0179	0.1552	0.8993	0.1449	0.7932	0.1360
0.075	1.0350	0.1899	0.9134	0.1774	0.8049	0.1665
0.100	1.0521	0.2195	0.9276	0.2052	0.8167	0.1926
0.125	1.0693	0.2458	0.9418	0.2296	0.8284	0.2152
0.150	1.0865	0.2696	0.9560	0.2517	0.8402	0.2363
0.175	1.1037	0.2914	0.9702	0.2721	0.8521	0.2556
0.200	1.1209	0.3117	0.9844	0.2909	0.8638	0.2730
L-arginine + 6% aqueous-MM						
0.000	1.0365		0.9112		0.7962	
0.025	1.0580	0.1309	0.9290	0.1233	0.8113	0.1202
0.050	1.0796	0.1860	0.9469	0.1753	0.8264	0.1695
0.075	1.1012	0.2278	0.9647	0.2143	0.8415	0.2077

0.100	1.1229	0.2638	0.9827	0.2483	0.8567	0.2404
0.125	1.1446	0.2950	1.0006	0.2774	0.8719	0.2689
0.150	1.1663	0.3233	1.0186	0.3044	0.8872	0.2951
0.175	1.1881	0.3497	1.0367	0.3292	0.9025	0.3191
0.200	1.2100	0.3743	1.0548	0.3524	0.9128	0.3415

Table 2 Viscosity B -coefficients and viscosity B -coefficients of transfer ($\Delta_r B$) of L-arginine in aqueous MM solutions at different temperatures and temperature coefficient (dB/dT).

System	T (K)			dB/dT ($\text{dm}^3\text{mol}^{-1}\text{K}^{-1}$)
	298.15	303.15	308.15	
	Viscosity B -coefficients ($\text{dm}^3\text{mol}^{-1}$)/ Viscosity B -coefficients of transfer ($\text{dm}^3\text{mol}^{-1}$)			
L-arginine + water	0.465(± 0.001)	0.407(± 0.001)	0.378(± 0.001)	- 0.009(± 0.001)
L-arginine + 2% aqueous-MM	0.570(± 0.002)/ 0.105	0.517(± 0.001)/ 0.110	0.488(± 0.001)/ 0.110	- 0.008(± 0.001)
L-arginine + 4% aqueous-MM	0.700(± 0.001)/ 0.235	0.652(± 0.002)/ 0.245	0.613(± 0.001)/ 0.235	- 0.009(± 0.001)
L-arginine + 6% aqueous-MM	0.841(± 0.001)/ 0.376	0.792(± 0.001)/ 0.385	0.766(± 0.002)/ 0.388	- 0.008(± 0.002)

Table 3 Apparent (partial) molar volume of solvent (V_1°), Gibbs free energy of activation for solvent ($\Delta\mu_1^\ddagger$), Gibbs free energy of activation for solute, ($\Delta\mu_2^\ddagger$), $T\Delta S_2^\ddagger$, activation enthalpy (ΔH_2^\ddagger) for L-arginine in water and aqueous MM solutions at different temperatures.

T (K)	$V_1^\circ \times 10^6$ ($\text{m}^3\text{mol}^{-1}$)	$\Delta\mu_1^\ddagger$ (kJmol^{-1})	$\Delta\mu_2^\ddagger$ (kJmol^{-1})	$T\Delta S_2^\ddagger$ (kJmol^{-1})	ΔH_2^\ddagger (kJmol^{-1})
L-arginine + water					
298.15	18.07	9.16	87.30	-300.83	-213.53
303.15	18.09	9.04	80.35	-305.88	-225.53
308.15	18.12	8.93	77.21	-310.92	-233.71
L-arginine + 2% aqueous-MM					
298.15	18.29	9.32	100.99	-265.06	-164.07
303.15	18.30	9.19	95.04	-269.50	-174.46
308.15	18.32	9.05	92.10	-273.95	-181.85
L-arginine + 4% aqueous-MM					
298.15	18.51	9.47	117.38	-266.55	-149.17
303.15	18.53	9.33	112.48	-271.02	-158.54
308.15	18.55	9.17	108.44	-275.49	-167.05
L-arginine + 6% aqueous-MM					

298.15	18.72	9.63	135.11	-200.06	-64.95
303.15	18.74	9.47	130.24	-203.41	-73.17
308.15	18.77	9.28	128.40	-206.77	-78.37

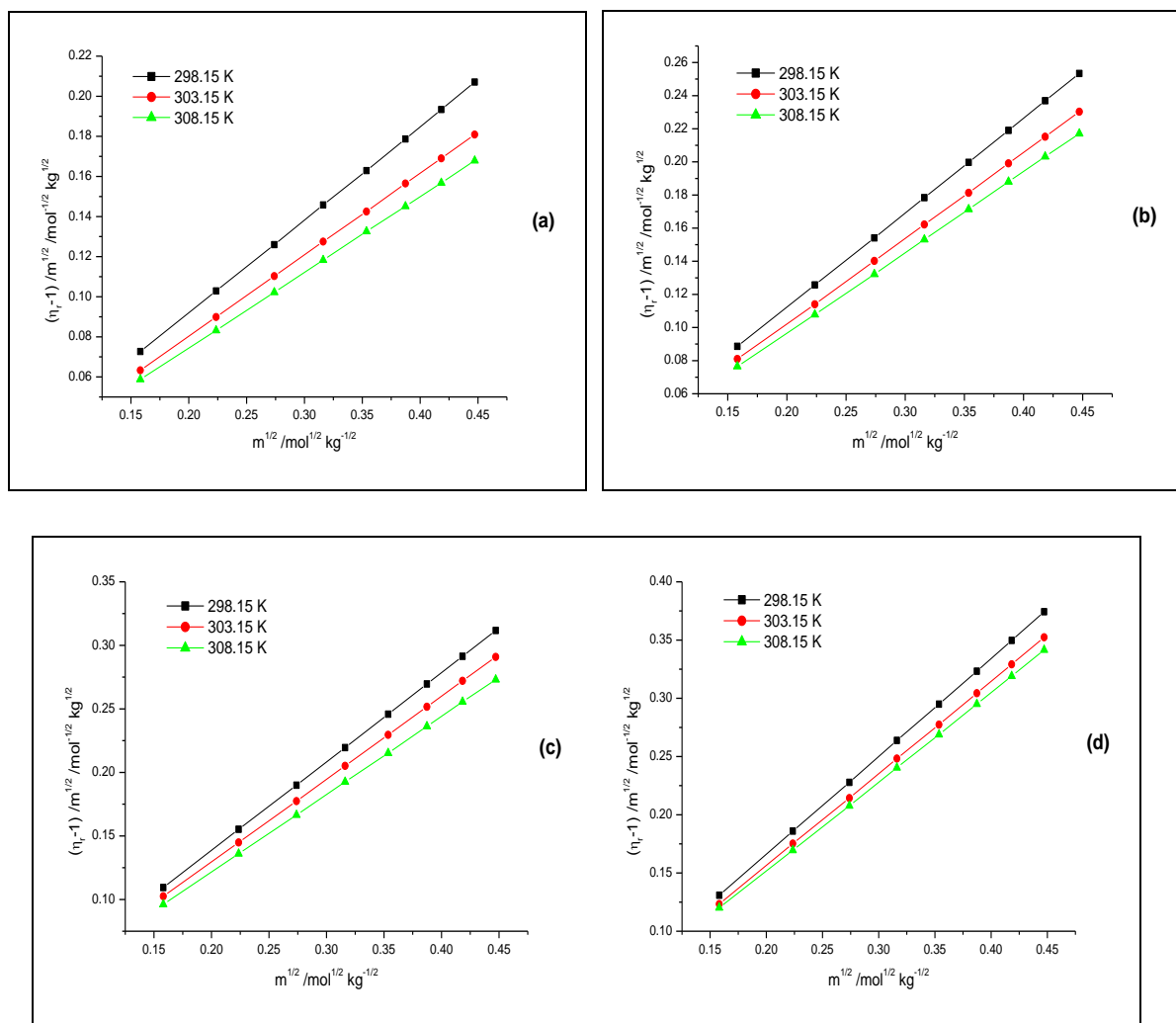


Fig. 1 Variation of $[(\eta_r - 1) / m^{1/2}]$ with molality ($m^{1/2}$) of L-arginine in water and MM + water solutions: (a) water, (b) 2% MM, (c) 4% MM, (d) 6% MM at different temperatures

CONCLUSION

The viscosities, η , of solutions using different molalities L-arginine in water and in aqueous-maltose monohydrate at various concentrations as 2%, 4% and 6% are measured and are reported at different temperatures. Using the experimental viscometric data various transport and activation parameters, viz., The viscosity B-coefficients, viscosity B-coefficients of transfer, variation of B with temperature, the Gibbs free energy of activation of viscous flow per mole of solvent as well as per mole of solute, activation entropy and activation enthalpy, were calculated and reported. The observed positive viscosity B-coefficients values for various L-arginine solutions show that the interactions get strengthened in presence of MM indicating the

presence of strong solute-solvent interactions. The temperature dependence of coefficient data (dB/dT) values come out to be negative which shows that L-arginine act as structure-maker in aqueous MM solution. The data is supported by considering the thermodynamic parameters.