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Thermodynamic (volume and compressibility) and spectral investigations of the glycine, diglycine and triglycine in aqueous α- and β-cyclodextrin solutions at T = 298.15 K

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ABSTRACT

Apparent molar volumes and apparent molar adiabatic compressibilities have been determined for glycine, diglycine, and triglycine in aqueous α- and β-cyclodextrin (0.002–0.008 mol kg^{-1}) solutions by measurements of densities and speeds of sound at 298.15 K. The limiting apparent molar volume, limiting apparent molar adiabatic compressibilities, and their corresponding slopes were computed using the density and speed of sound data. These data were used to calculate the transfer values of partial molar volumes and partial molar adiabatic compressibilities at infinite dilution. Transfer parameters have been interpreted from the point of view of concentration dependence of solute–solute and solute–solvent interactions. These transfer parameters have further been used to calculate the group contribution of a peptide backbone $(-CH_2CONH-)_n$ unit. The experimental results have also been discussed on the basis of ^{1}H NMR measurements.

1. Introduction

Cyclodextrins (CD) are oligosaccharides containing 6 to 12 α-(1,4)-linked glycopyranose units. Due to the lack of free rotation about the glycosidic bonds, these molecules form a cylindrical cavity which is hydrophobic from inside and hydrophilic (due to the primary and secondary −OH) from outside [1]. α- and β-Cyclodextrin containing six and seven glycopyranose units are most common. Literature values of the depth and cavities of α- and β-CD are not consistent [2–4]. However cavity depth of 8 Å approximately, independent of the type of CD and cavity diameter of 5 and 7 Å for α- and β-CD respectively, seems reasonable. Due to the ability of CDs to form inclusion complexes with a variety of guest molecules in solution these offers many interesting applications both chemistry and industry [5–8]. It has also been seen from X-ray structural studies that crystalline α-CD contains two water molecules situated at well defined sites in the cavity [9]. During complex formation with a guest molecule, the water molecules are fully or partially expelled from the cavity and conformation changes into a low-energy symmetrical conformation [10]. Similar studies show that β-CD molecule contains 6.5 water molecules distributed statistically between eight possible bonding sites. Numerous hypotheses have been proposed to account for the stability of these complexes, but it is clear that the formation of these complexes must involve extensive desolvation and resolvation of the host, guest, and complex.

The thermodynamic properties of solutes like volumetric and compressibility are known to be sensitive to the nature and degree of the solute solvation [11,12]. In the case of complex formation with CDs, the transfer of a guest molecule from water to the nonpolar cavity of a CD is expected to give rise to significant changes in its partial molar compressibility and/or volume. In recent years, a number of workers have determined the various thermodynamic properties of CDs in aqueous solutions containing organic and surfactant molecules [13–25].

This paper presents the result of a study of the apparent molar volume and apparent molar adiabatic compressibility at infinite dilution in ternary glycine/diglycine/triglycine – α-cyclodextrin and β-cyclodextrins (CD) – water (w) solutions. Measurements of density and speed of sound at 298.15 K was used to determine the apparent molar volume and apparent molar adiabatic compressibility at infinite dilution of glycine/diglycine/triglycine in the binary water (w + CD) solvent as a function of both the CD concentration and the glycine/diglycine/triglycine concentration. Further, transfer partial molar volume and adiabatic compressibilities at infinite dilution, pair, and triplet interaction coefficients, and hydration numbers results are discussed in terms of solute–solute and solute–solvent occurring in the ternary solution of present study. To determine the specific interactions between amino acid/peptides and α- and β-cyclodextrins at molecular level ^{1}H NMR spectroscopy has been used, which is a direct molecular approach.

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Table 1
Densities, ρ, and speeds of sound, u of glycine, glycylglycine, and glycylglycylglycine in aqueous α-cyclodextrin and β-cyclodextrin solutions at 298.15 K.

m/ (mol kg^{-1})	$\rho\cdot10^{-3}$ / (kg m^{-3})	u/ (m s^{-1})	m/ (mol kg^{-1})	$\rho\cdot10^{-3}$ / (kg m^{-3})	u/ (m s^{-1})	m/ (mol kg^{-1})	$\rho\cdot10^{-3}$ / (kg m^{-3})	u/ (m s^{-1})
Glycine								
0.00213 mol kg^{-1} α-cyclodextrin			0.00415 mol kg^{-1} α-cyclodextrin			0.00610 mol kg^{-1} α-cyclodextrin		
0.00000	0.997756	1497.36	0.00000	0.998432	1497.76	0.00000	0.999118	1497.94
0.05792	0.999586	1500.34	0.05074	1.000041	1500.66	0.05192	1.000764	1500.86
0.11081	1.001240	1503.27	0.12223	1.002294	1504.80	0.10332	1.002384	1503.49
0.15355	1.002567	1505.99	0.15875	1.003438	1506.99	0.16746	1.004392	1506.76
0.20706	1.004219	1508.75	0.21053	1.005054	1509.80	0.19596	1.005281	1508.31
0.25547	1.005702	1511.25	0.25963	1.006576	1512.18	0.25309	1.007050	1511.36
0.32173	1.007711	1514.44	0.30771	1.008058	1514.50	0.30286	1.008585	1513.81
Glycine								
0.00838 mol kg^{-1} α-cyclodextrin			0.00210 mol kg^{-1} β-cyclodextrin			0.00394 mol kg^{-1} β-cyclodextrin		
0.00000	0.999758	1498.35	0.00000	0.997831	1497.23	0.00000	0.998522	1497.62
0.05409	1.001475	1501.28	0.05847	0.999682	1500.28	0.06075	1.000463	1500.86
0.10156	1.002972	1503.81	0.10391	1.001111	1502.67	0.09880	1.001667	1502.86
0.16004	1.004804	1506.98	0.15464	1.002698	1505.34	0.13963	1.002950	1504.98
0.20803	1.006299	1509.40	0.19128	1.003837	1507.23	0.20526	1.004991	1508.36
0.25462	1.007741	1511.66	0.25550	1.005822	1510.57	0.25457	1.006509	1510.92
0.29156	1.008878	1513.57	0.29735	1.007106	1512.90	0.28262	1.007360	1512.41
Glycine						*Glycylglycine*		
0.00609 mol kg^{-1} β-cyclodextrin			0.00807 mol kg^{-1} β-cyclodextrin			0.00207 mol kg^{-1} α-cyclodextrin		
0.00000	0.999376	1497.99	0.00000	1.000474	1498.73	0.00000	0.997740	1497.36
0.05760	1.001207	1501.03	0.06472	1.002514	1502.05	0.05402	1.000737	1501.86
0.10841	1.002807	1503.77	0.10803	1.003872	1504.39	0.10125	1.003328	1505.75
0.15629	1.004301	1506.14	0.15323	1.005281	1506.80	0.15256	1.006107	1509.85
0.21146	1.006008	1509.08	0.19819	1.006678	1509.18	0.19529	1.008396	1513.31
0.25307	1.007281	1511.19	0.25390	1.008398	1512.05	0.25748	1.011691	1518.17
0.30574	1.008887	1513.92	0.29881	1.009776	1514.33	0.29621	1.013719	1521.27
Glycylglycine								
0.00395 mol kg^{-1} α-cyclodextrin			0.00627 mol kg^{-1} α-cyclodextrin			0.00785 mol kg^{-1} α-cyclodextrin		
0.00000	0.998459	1497.70	0.00000	0.999295	1498.08	0.00000	0.999789	1498.33
0.05555	1.001536	1502.41	0.06179	1.002699	1503.31	0.05470	1.002803	1502.94
0.09794	1.003859	1505.93	0.10141	1.004863	1506.51	0.10999	1.005821	1507.45
0.15006	1.006685	1510.06	0.14890	1.007435	1510.35	0.14584	1.007762	1510.35
0.20545	1.009652	1514.65	0.19894	1.010119	1514.38	0.19626	1.010471	1514.44
0.24397	1.011695	1517.60	0.25214	1.012953	1518.63	0.24855	1.013258	1518.60
0.29623	1.014446	1521.84	0.30216	1.015584	1522.62	0.29264	1.015587	1522.12
Glycylglycine								
0.00197 mol kg^{-1} β-cyclodextrin			0.00402 mol kg^{-1} β-cyclodextrin			0.00593 mol kg^{-1} β-cyclodextrin		
0.00000	0.997856	1497.41	0.00000	0.998726	1497.90	0.00000	0.999566	1498.20
0.04903	1.000575	1501.55	0.05063	1.001532	1502.01	0.05881	1.002802	1503.30
0.10172	1.003463	1506.02	0.10283	1.004390	1506.29	0.10028	1.005066	1506.53
0.14532	1.005827	1509.65	0.15693	1.007321	1510.77	0.15142	1.007836	1511.06
0.20083	1.008803	1514.18	0.19946	1.009591	1514.07	0.19788	1.010330	1514.93
0.24961	1.011385	1517.86	0.24748	1.012128	1517.96	0.24600	1.012897	1518.60
0.29599	1.013818	1521.50	0.29266	1.014494	1521.34	0.29730	1.015610	1522.49
Glycylglycine			*Glycylglycylglycine*					
0.00807 mol kg^{-1} β-cyclodextrin			0.00207 mol kg^{-1} α-cyclodextrin			0.00395 mol kg^{-1} α-cyclodextrin		
0.00000	1.000474	1498.73	0.00000	0.997740	1497.36	0.00000	0.998459	1497.70
0.05521	1.003526	1503.39	0.03882	1.000725	1501.36	0.04065	1.001598	1501.92
0.10651	1.006332	1507.46	0.04909	1.001508	1502.41	0.04954	1.002279	1502.75
0.15156	1.008767	1511.35	0.06058	1.002380	1503.58	0.06044	1.003110	1503.87
0.20589	1.011669	1515.49	0.07060	1.003138	1504.53	0.07220	1.004002	1505.01
0.24904	1.013960	1518.93	0.07771	1.003674	1505.23	0.07944	1.004549	1505.75
0.30178	1.016721	1523.06	0.08910	1.004530	1506.41	0.09054	1.005388	1506.90
Glycylglycylglycine								
0.00627 mol kg^{-1} α-cyclodextrin			0.00785 mol kg^{-1} α-cyclodextrin			0.00197 mol kg^{-1} β-cyclodextrin		
0.00000	0.999295	1498.08	0.00000	0.999789	1498.33	0.00000	0.997856	1497.41
0.04209	1.002517	1502.40	0.03982	1.002844	1502.41	0.04609	1.001401	1502.40
0.04924	1.003057	1503.12	0.04944	1.003577	1503.38	0.05705	1.002235	1503.57
0.06227	1.004034	1504.45	0.05993	1.004375	1504.45	0.06338	1.002716	1504.20
0.07203	1.004758	1505.42	0.06867	1.005037	1505.39	0.06974	1.003197	1504.88
0.08219	1.005513	1506.53	0.07638	1.005619	1506.13	0.08152	1.004086	1506.08
0.09445	1.006418	1507.75	0.08649	1.006382	1507.16	0.09321	1.004965	1507.27
Glycylglycylglycine								
0.00402 mol kg^{-1} β-cyclodextrin			0.00593 mol kg^{-1} β-cyclodextrin			0.00807 mol kg^{-1} β-cyclodextrin		
0.00000	0.998726	1497.90	0.00000	0.999566	1498.20	0.00000	1.000474	1498.73
Glycylglycylglycine								