

Ultrasonic studies of interactions in ternary solutions containing sorbitol and sodium carboxylate solution at 308 K

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Abstract. Ultrasonic velocities and densities of sorbitol in aqueous alkali carboxylate solutions of different concentrations: 0.5 M, 1.0 M and 1.5 M at 308 K have been measured. Adiabatic compressibility, β_s ; apparent molar volume, Φ_v , apparent molar compressibility, Φ_{β_s} , and hydration number, H_n were deduced from their measured data. Results show that there are short range weak interactions.

Keywords. Ultrasonic velocity; adiabatic compressibility; apparent molar volume; apparent molar compressibility; hydration number.

1. Introduction

Sorbitol–water–alkali carboxylates are biologically, industrially and physicochemically important. Vishnu and Singh (1977) have conductometrically studied the interactions of sodium carboxylates with sucrose in water and formamide and interpreted their results in terms of the effect of the hydrocarbon chain in H-bonding in a saturated solution of sucrose. They conclude that the hydrophobicity of long alkyl chains causes increased H-bonding of the solvent. The apparent molal compressibility (Φ_{β_s}), is a sensitive function of the solute–solvent and solute–solute interactions (Kaulgud and Rao 1976). It is a useful parameter for elucidating the structural interactions in systems. Several aspects of the hydration of solutes with large hydrophobic molecules have been studied (Mohanty *et al* 1983; Bhowmick and Mohanty 1986). Apparent molar volume (Φ_v) and apparent molar compressibility (Φ_{β_s}) studies of sodium salts in water through sound velocity measurements are interpreted (Bhowmick *et al* 1985). In the present work, the result of experimental measurements of density and ultrasonic velocity for ternary solutions are reported. These have been studied as binary systems, treating sorbitol as a solute and the respective aqueous carboxylate solution as solvent. The effect of electrolytic concentration and the length of the hydrophobic alkyl chain of the carboxylate has been investigated.

2. Experimental

The chemicals in the present investigation, sorbitol (IR, SM, extra pure) and CH_3COONa (Analar BDH, Min Assay 99%), were used as such without further purification.

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2.1 Solution compositions

Ultrasonic velocity and density of freshly prepared solutions of sorbitol in aqueous sodium formate, acetate, propionate, butyrate and valerate solutions at different molalities 0.5 M, 1.0 M & 1.5 M were prepared by weight-dilution method using double distilled water at 308 K.

2.2 Method

Ultrasonic velocities and densities of freshly prepared solutions of sorbitol in aqueous sodium carboxylate solution were measured at a constant temperature of 308 K by ultrasonic interferometer and a bicapillary pycnometer respectively. A large double-walled and properly insulated tank with a transparent wall was filled with water of a constant temperature (thermostat). The thermo-regulator used was a conventional mercury-filled toluene regulator. This was connected through an electric relay (Annu Vidyut type) to an immersion heater (1.5 kW) in the water bath and a thermostat to maintain a constant temperature correct of ± 0.1 K. The scientific balance (Balman, Mfg Co. model No. 8-2 M, Varanasi, India) was used for weighing. The accuracy of weight measurement is ± 0.1 g.

3. Theoretical considerations

Various ultrasonic and solutions parameters were computed from the velocity and density data using the following equations.

Adiabatic compressibility (β_s)

$$\beta_s = 1/u^2 \rho. \quad (1)$$

Apparent molar compressibility (Φ_{β_s})

$$\Phi_{\beta_s} = 1000/C\rho\rho^0 * (\beta_s\rho^0 - \beta_s^0\rho) + \bar{M} \beta_s\rho^0. \quad (2)$$

Apparent molar volume (Φ_v)

$$\Phi_v = \frac{1000(\rho^0 - \rho)}{C\rho^0} + \frac{\bar{M}}{\rho^0}. \quad (3)$$

Hydration number (H_n)

$$H_n = \frac{n}{n^0} \times \left(1 - \frac{\beta_s}{\beta_s^0} \right), \quad (4)$$

where, u is the ultrasonic velocity, ρ is density of solutions, β_s and β_s^0 are the compressibilities of solution and solvent, n and n^0 are the number of moles of solute and solvent respectively, \bar{M} is the effective molecular weight of ternary solutions given by

$$\bar{M} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3}{n_1 + n_2 + n_3} \quad (5)$$

where, n_1 , n_2 , and n_3 are the number of moles of components—(1) water, (2) sodium carboxylate and (3) sorbitol, and M_1 , M_2 and M_3 are the respective molecular weights.

4. Results and discussion

Experimental data on ultrasonic velocity and density have been used to deduce various thermodynamic and solution parameters such as adiabatic compressibility (β_s), apparent molar volume (Φ_v), apparent molar compressibility (Φ_{β_s}) and hydration number (H_n) using (1) to (5).

Different parameters computed from the ultrasonic velocity and density measurements can be employed to understand solute-solvent (*ss*) and solute-cosolute (*scs*) interactions in aqueous ternary systems, consisting of electrolyte-water-nonelectrolyte, as well the structural properties of solutes. Sorbitol molecules are therefore expected to be structure breakers because of the fact that as soon as sorbitol molecules occupy the interstitial spaces of water due to their large molecular size, ion-solvent interactions weaken. There occurs however a structural rearrangement as a result of hydration (sorbitol), leading to a comparatively more ordered state. Sorbitol therefore behaves as a structure maker and there is increase in the ultrasonic velocity in aqueous

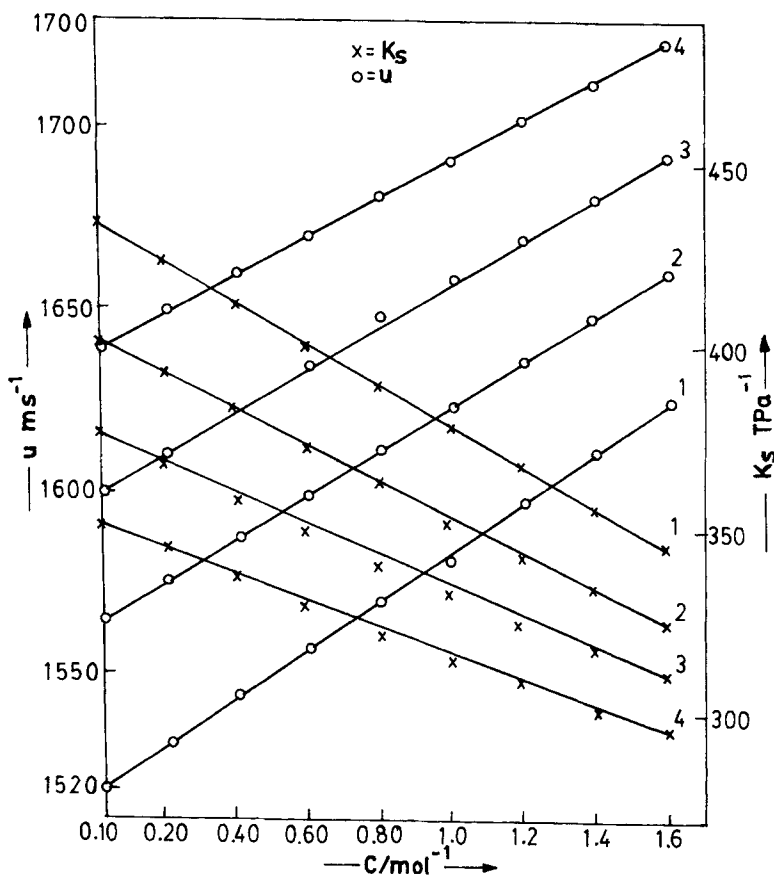


Figure 1. Variation of ultrasonic velocity (u) and adiabatic compressibility (β_s) of sorbitol at different molar concentrations in pure water and in various concentrations of sodium acetate in water at 308 K. (1—water, 2—0.5 M NaAc, 3—1.0 M NaAc, 4—1.5 M NaAc.)

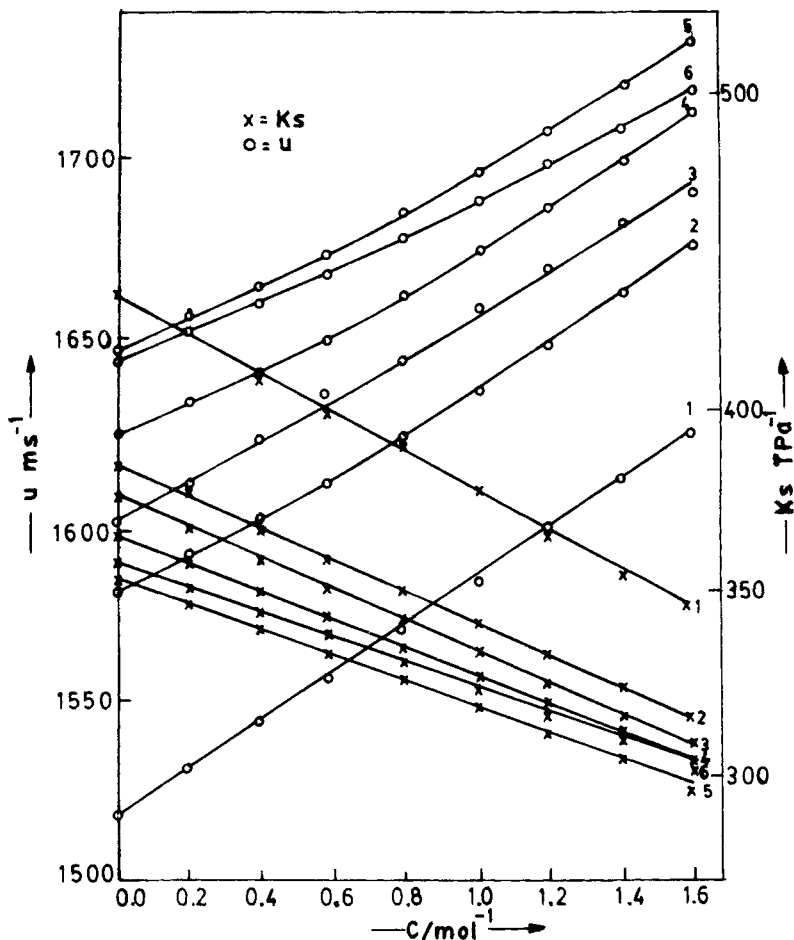
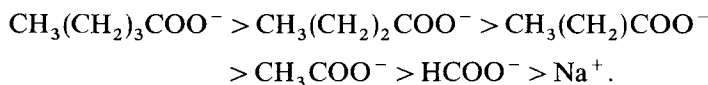


Figure 2. Variation of ultrasonic velocity (u) and adiabatic compressibility (β_s) of sorbitol at different molar concentrations (C) in pure water and of different sodium carboxylate solutions at 308 K. (1—water; 2—1.0 M NaFr, 3—1.0 M NaAc, 4—1.0 M NaPr, 5—1.0 M NaBu and 6—1.0 M NaVa; see table 1 for the abbreviations used.)

sodium carboxylate solutions with increasing sorbitol concentrations which indicates greater ion-solvent interactions.

Plots of ultrasound velocity vs sorbitol concentrations at 308 K for aqueous sodium acetate solutions of different concentrations and for 1.00 M aqueous sodium carboxylate solutions are depicted in figures 1 and 2. The slight nonlinearity of the plots in the case of sorbitol-water-alkali carboxylate systems show that the interactions in the present systems are weak. The hydrophobic and hydrophilic characteristics of solutes in aqueous solutions can also be understood in terms of ultrasound velocity. It has been found that ultrasound velocity increases in all carboxylate solutions (figures 1 and 2). This indicates that sodium carboxylates behave as hydrophobic solutes in sorbitol. It is well known that large monovalent ions generally have a hydrophilic structure (SB)

effect. Moreover, the results also show that hydrophobic character increases with decreasing size of ions and may be expressed in the order:



Ultrasonic velocity of sorbitol increases with sodium carboxylate concentration which indicates greater solute–solvent interaction. Thus, they behave as structure-makers. Figures 1 and 2 also show that ultrasound velocity of sorbitol increases with increasing size/length of carboxylate ions up to butyrate and begins to decrease with size from valerate. Apparent molar volume (Φ_v) and the apparent molar isentropic compressibility (Φ_{β_s}) are useful parameters for studying structure interactions. They are sensitive functions of solute–solvent and solute–cosolute interactions. Values of Φ_v and Φ_{β_s} of sorbitol in aqueous sodium carboxylate solutions at 308 K are given in table 1. Values for all sodium carboxylates at different concentrations are found to be positive while Φ_{β_s} for sorbitol has both positive and negative signs in different sodium carboxylate solutions. Φ_{β_s} of sorbitol is positive in aqueous sodium carboxylate of different concentrations viz. (0.5 M–1.5 M) NaF, (1.0 M–1.5 M) NaAc, (0.5 M–1.5 M) NaPr, NaBu and NaVal, while negative in water at 0.5 M NaAc only. Values of limiting apparent molar volume (Φ_v^0) and limiting apparent molar compressibility ($\Phi_{\beta_s}^0$) of sorbitol in different sodium carboxylate solutions are shown in table 2. Limiting apparent molar volume has been worked out with the help of apparent molar volume, at infinite dilution,

$$\Phi_v = \Phi_v^0 + S_v C^{1/2}, \quad (6)$$

S_v is the experimental slope. The S_v of sorbitol in water and in 0.5 M has both positive and negative values as shown in table 3. This reveals the weak interactions at low concentrations of electrolyte and the moderately stronger ones at higher concentration of carboxylate.

The partial molar compressibility $\Phi_{\beta_s}^0$ has been found with the help of the equation:

$$\Phi_{\beta_s} = \Phi_{\beta_s}^0 + S_{\beta_s} C^{1/2}. \quad (7)$$

The gradients S_{β_s} were found to be negative for sorbitol–water–alkali carboxylate systems. The negative values of S_{β_s} for sorbitol in table 3 show that the solute–solvent interaction in water is relatively stronger. The change of the sign of S_{β_s} from positive to negative shows that weak interaction may become relatively strong in long-chain carboxylate solutions. The positive and negative Φ_{β_s} values can be explained in the light of structural and geometrical compressibility. The positive and negative slopes (S_{β_s}) of the curve Φ_{β_s} vs $C^{1/2}$ can be explained in terms of solute–solvent interactions and occupation of cavities by solute molecules. The positive and negative character of Φ_{β_s} can be discussed in the light of the equation,

$$\Phi_{\beta_s} = \frac{1000}{C} (\beta_s - \beta_s^0) + \beta_s \Phi_v. \quad (8)$$

Negative or positive values of Φ_{β_s} would be obtained depending on whether $1000(\beta_s - \beta_s^0)/C$ is greater or less than $\beta_s \Phi_v$, respectively. Hall (1948) has discussed compressibility in terms of its division into structural, β_{struct} , and geometrical β_g . β_{struct} has been defined as that part of compressibility resulting from the

Table 1. Apparent molar volume $\Phi_v \times 10^3 \text{m}^3/\text{mol}$ and apparent molar compressibility $\Phi_{\beta_s} \times 10^{15} \text{m}^5/\text{Nmol}$ of sorbitol in aqueous sodium carboxylate solutions at 308 K.

Sorbitol aqueous sodium carboxylate solution $\Phi_v \times 10^3 (\Phi_{\beta_s}^* 10^{15})$								
(mol)	0.0 M	0.5 M	1.0 M	1.5 M	0.0 M	0.5 M	1.0 M	1.5 M
Sodium formate (NaFr)								
0.447	122.71	122.10	122.71	123.32	-61.58	10.25	45.41	48.81
0.632	122.71	122.83	123.02	123.42	-63.83	11.52	41.78	54.79
0.775	122.54	122.75	123.12	123.48	-58.47	6.92	43.19	54.89
0.894	122.46	123.08	123.31	123.48	-50.30	7.39	39.37	54.44
1.000	122.30	123.22	123.49	123.57	-37.33	6.07	41.99	52.76
1.095	122.21	123.49	123.67	123.64	-37.33	6.61	43.23	53.48
1.183	121.99	123.57	123.74	123.68	-40.93	5.71	42.98	52.92
1.265	121.89	123.82	123.85	123.68	-24.70	4.66	42.84	51.13
Sodium acetate (NaAc)								
0.447	122.71	122.31	122.34	122.04	-61.57	-31.16	-31.03	16.01
0.632	122.71	122.31	122.82	122.04	-63.82	-18.79	-7.67	29.01
0.775	122.54	122.15	123.99	122.20	-58.47	-12.45	4.69	40.57
0.894	122.46	121.94	123.19	122.40	-50.30	-5.28	17.2	46.02
1.000	122.30	121.82	123.50	122.42	-37.33	-0.88	28.14	55.46
1.095	122.21	121.80	123.54	122.52	-40.93	3.14	33.82	61.53
1.183	121.99	121.75	123.65	122.59	-31.71	7.18	44.43	67.86
1.265	121.89	121.63	123.67	122.70	-24.70	16.98	57.85	70.39
Sodium propionate (NaPr)								
0.447	122.71	122.76	123.25	120.68	-61.57	17.79	66.34	94.23
0.632	122.71	122.32	123.25	120.22	-63.82	9.32	66.84	85.61
0.775	122.54	122.43	123.25	119.26	-58.47	13.81	65.5	74.36
0.894	122.46	121.89	123.61	122.11	-50.30	18.31	70.17	92.47
1.000	122.30	121.97	123.82	122.40	-37.33	14.64	63.37	88.66
1.095	122.21	121.85	123.49	122.83	-40.93	20.76	64.22	95.19
1.183	121.99	121.49	123.94	123.06	-31.71	13.09	65.88	100.47
1.265	121.89	121.22	124.03	123.54	-24.70	11.2	60.35	98.89
Sodium butyrate (NaBu)								
0.447	122.71	122.81	124.74	124.40	-61.57	70.29	109.82	161.52
0.632	122.71	123.04	124.48	124.74	-63.82	65.04	101.47	158.96
0.775	122.54	123.24	124.41	124.98	-58.47	58.84	97.76	155.74
0.894	122.46	123.31	124.28	125.09	-50.30	56.95	82.84	150.63
1.000	122.30	123.47	124.22	125.32	-37.33	54.26	83.04	150.35
1.095	122.21	123.63	124.10	125.37	-400.93	55.64	80.18	150.05
1.183	121.99	123.66	124.00	125.65	-31.97	48.42	76.13	148.71
1.265	121.89	123.84	123.93	125.82	-24.1	45.1	72.3	146.11
Sodium valerate (NaVa)								
0.447	122.71	121.75	126.20	125.27	-61.57	31.94	106.60	141.56
0.632	122.71	122.27	125.58	125.48	-63.82	33.37	107.36	143.85
0.775	122.54	122.50	125.07	125.23	-58.47	40.67	104.13	141.90
0.894	122.46	122.70	124.77	125.58	-50.30	32.45	102.00	143.87
1.000	122.30	122.85	124.49	125.60	-37.33	38.30	97.74	145.73
1.095	122.21	123.34	124.26	125.32	-40.93	38.08	99.90	146.96
1.183	121.99	123.50	124.05	125.68	-31.71	38.08	99.90	146.49
1.265	121.89	123.74	125.74	123.74	-24.7	40.47	94.16	146.52

Table 2. Limiting apparent molar volume $\Phi_v^0 \times 10^3/\text{m}^3/\text{mol}$ and limiting apparent molar compressibility $\Phi_{\beta_s}^0 \times 10^{15}\text{m}^5/\text{N mol}$ of sorbitol in aqueous sodium carboxylate solution at 308 K and at different concentrations.

Sodium carboxylate	$\Phi_v^0 \times 10^3(\text{m}^3/\text{mole})$				$\Phi_{\beta_s}^0 \times 10^{15}(\text{m}^5/\text{N mol})$			
	0.0 M	0.5 M	1.0 M	1.5 M	0.0 M	0.5 M	1.0 M	1.5 M
Sodium formate	123.54	121.10	122.04	123.12	-10.30	15.00	39.05	58.00
Sodium acetate	123.54	123.02	121.96	121.52	-10.30	-50.60	-60.80	-70.70
Sodium propionate	123.54	123.58	122.60	119.35	-10.30	21.00	73.50	95.50
Sodium butyrate	123.54	122.28	125.16	123.68	-10.30	84.00	128.00	170.00
Sodium valerate	123.54	120.80	127.50	125.10	-10.30	26.00	115.00	139.00

Table 3. Experimental slopes $S_v \times 10^{9/2}(\text{m}^{9/2}/\text{mol}^{-3/2})$ and $S_{\beta_s} \times 10^{3/2}(\text{N}^{1/2}\text{mol}^{3/2})$ 1.5 M of sorbitol in aqueous sodium carboxylate solutions at 308 K and at different concentrations.

Sodium carboxylate	$S_v(\text{mol}/\text{dm}^3)$				$S_{\beta_s}(\text{mol}/\text{dm}^3)$			
	0.0 M	0.5 M	1.0 M	1.5 M	0.0 M	0.5 M	1.0 M	1.5 M
Sodium formate	-1.32	2.16	1.44	0.44	60.20	-9.00	3.00	-4.00
Sodium acetate	-1.32	-1.08	1.44	0.88	60.20	56.00	94.00	36.00
Sodium propionate	-1.32	-1.80	1.10	3.10	60.20	8.00	10.00	-6.00
Sodium butyrate	-1.32	1.24	-0.96	1.68	60.20	30.00	-44.00	-18.00
Sodium valerate	-1.32	2.30	-3.00	0.40	60.20	10.00	-16.00	8.00

breakdown of intermolecular bonds accompanying the destruction of the open water structure with compressional sound waves, and β_g is the instantaneous compressibility arising due to the decrease in the average intermolecular distances. Initially, both β_{struct} and β_g decrease with increasing temperature, β_{struct} attains a constant value, while β_g increases. Variations of β_{struct} and β_g result from shift in equilibrium between network (ice-like or Frank-Wen clusters) molecules and free water molecules, either in Frank-Wen cavities or outside. The effect of solutes on β_{struct} and β_g can be explained in the following way.

Structure-making solutes, which are not too small, tend to be accommodated in Frank-Wen cavities with the free water molecules between the structured regions literally forced, if necessary, to provide a cavity of suitable size and shape, i.e. existing

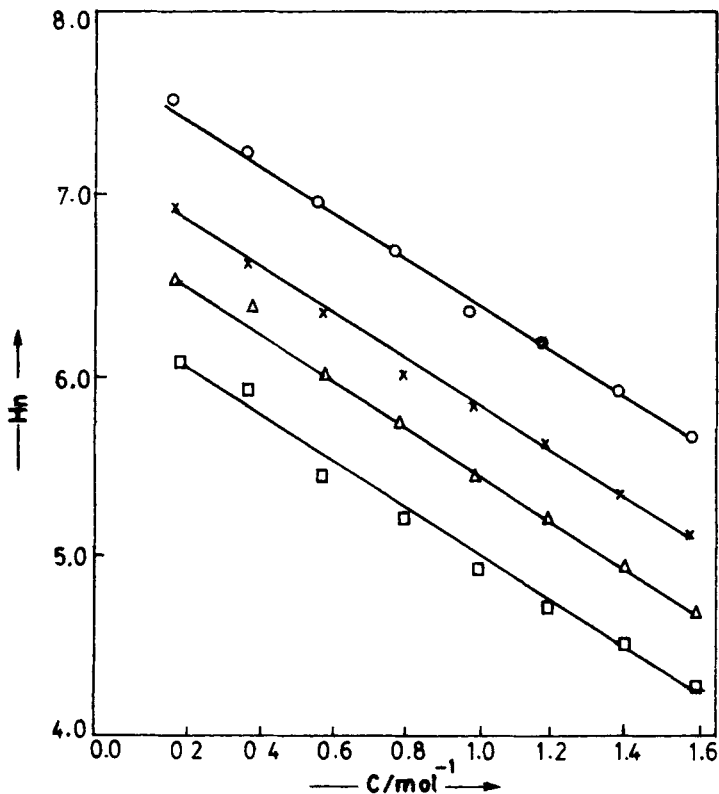


Figure 3. Variation of hydration number (H_n) of sorbitol at different molar concentrations (c) in water and in sodium acetate solution at 308 K. (○— H_2O , ×—0.5 M NaAc, Δ—1.0 M NaAc and □—1.5 M NaAc.)

cavity is modified and enlarged with the help of free or monomeric water molecules. Thus, β_{struct} is not enhanced, resulting in small positive $\partial\beta_{\text{struct}}/\partial C$, whereas the loss of free water molecules leads to a negative $\partial\beta_{\text{struct}}/\partial C$. Likewise, structure-breaking solutes (destroying either the ice or Frank–Wen clusters) would show a large negative value of β_{struct} , as a result of which free water molecules would be generated and we could expect positive values for $\partial\beta_{\text{struct}}/\partial C$.

The hydration numbers (H_n) of sorbitol at 308 K are shown in figures 3 and 4. These plots indicate that the hydration number (H_n) of sorbitol linearly decreases with increasing molarity. This decrease is more distinct and pronounced with increasing molarity of sodium carboxylate at fixed sorbitol concentration. The hydration number of sorbitol in water is maximum and generally decreases with increasing concentration of sodium carboxylate. The hydration number of the ion is most significant for understanding the structural properties of solutions. The hydration of ions occurs as a result of ion–solvent interactions. The water molecules form a symmetrical tetrahedron or octahedron around the ion with the appropriate end of the dipole pointing towards the charge.

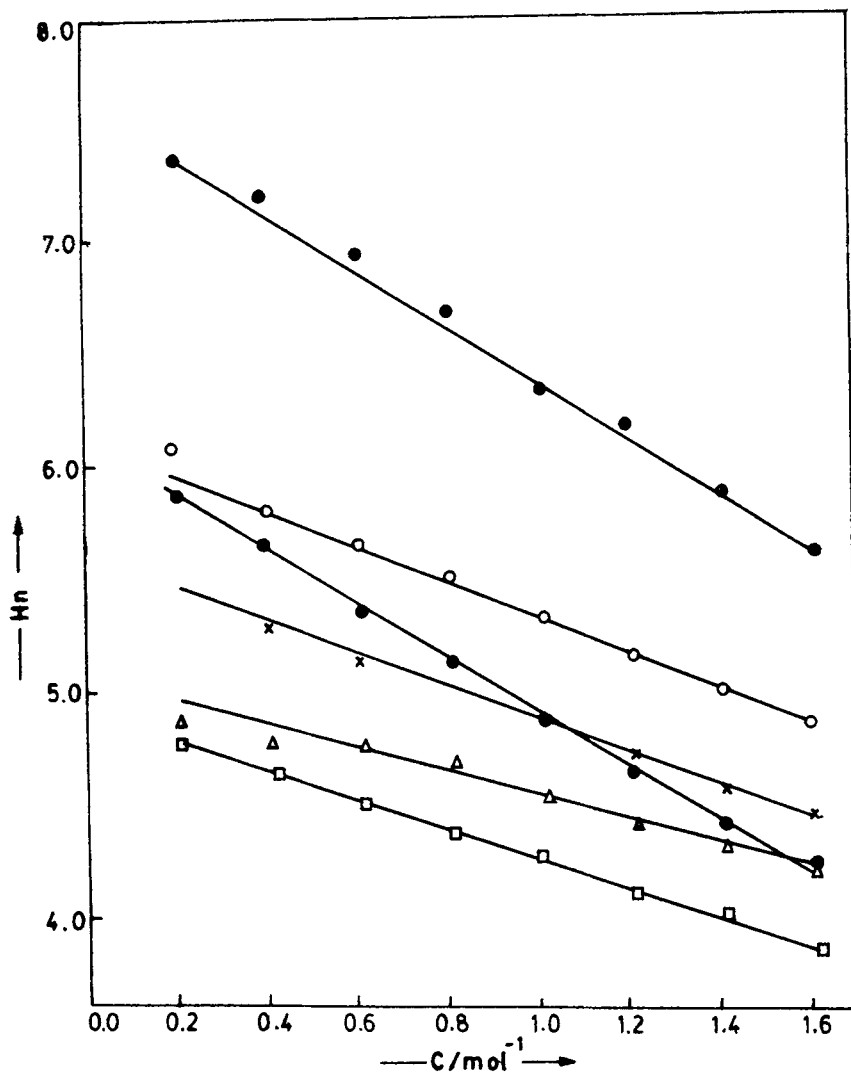


Figure 4. Variation of hydration number (H_n) of sorbitol at different molar concentrations (c) in water and in aqueous sodium carboxylate solution at 308 K. (O— H_2O , \oplus —1.0 M NaFr, \bullet —1.0 M NaAc, \times —1.0 M NaPr, Δ —1.0 M NaBu, \square —1.0 M NaVa); abbreviations as in table 1 and figure 2.)

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