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The Specific Heat Capacities of D-Glucose and D-Xylose in Water–Ethanol System

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Using an isoperibol twin calorimeter the specific heat capacities of solutions of D-glucose and D-xylose dissolved in water–ethanol mixtures (10, 20, 30, and 50 wt% of ethanol) have been measured at temperature close to 30 °C and the apparent molar heat capacity of te solutes ϕ_{C_p} has been calculated. Dependence of ϕ_{C_p} upon solute concentration varied markedly with the solvent composition but the variation was similar for both solutes. The infinite dilution values of $\phi_{C_p}^{\circ}$ *i.e.* $C_{p,2}^{\infty}$ are higher for D-glucose than for D-xylose at any compositions of the solvent system. The $C_{p,2}^{\infty}$ decreased first noticeably with the amount of ethanol in the solvent, reaching a minimum value at approximately 20 wt% of ethanol, then it increased. Values of the parameter $\Delta C_{p,2}^{\infty}=C_{p,2}^{\infty}-C_{p,2}^{*}$, where $C_{p,2}^{*}$ is the specific heat capacity of the solute in the solid state, are negative in 10, 20, and 30 wt% of ethanol, while it is positive in 50 wt%. The values of $\Delta C_{p,2}^{\infty}$ have been discussed in its connection with the degree of structuring of the solvents.

To date we have measured the specific heat capacity, C_p, of aqueous solutions of hexose (D-fructose, D-galactose, D-glucose, and D-mannose,[1]) pentose (D-xylose, D-arabinose, D-ribose, and L-arabinose),[2]) as well as several kinds of commercial samples of dextran[3]) which is an anhydroglucose polymer. The solute-solvent interaction between these saccharide molecules and solvent water has been discussed on the basis of the partial molar heat capacity at infinite dilution, $C_{p,2}^{\infty}$, calculated from our experimental results.

As a continuation of the above-mentioned measurements we will describe in this paper the results of determination of the specific heat capacities of solutions of D-glucose and D-xylose in the mixed solvent consisting of water and ethanol (10, 20, 30, and 50 wt% of ethanol).

Addition of ethanol to the aqueous solution of saccharides will result in the precipitation of saccharides. This phenomenon can be considered as a result of removal of hydrated water by the added ethanol. In fact, compressibility measurements[4,5]) have shown that in pure water the partial specific compressibility, $\bar{\kappa}_2^{\circ}$, of D-glucose and dextran is negative, showing the hydration of these solutes, but that the $\bar{\kappa}_2^{\circ}$ increases with increasing content of ethanol and it becomes a constant positive value in the solvents containing more than 20 wt% of ethanol. In such solvents water molecules preferentially hydrated to saccharides are completely removed by the action of ethanol, then the values of $\bar{\kappa}_2^{\circ}$ correspond to the compressibility of the solutes themselves. Measurements of specific heat capacity and those of compressibility are complementary in elucidating the solute-solvent interaction. The former results seem to give more direct information on the structural change of solvent caused by the addition of solutes.[1–3])

Experimental

Materials. Commercially available guaranteed grade D-glucose and D-xylose were dried in an electric vacuum oven and used without further purification. The ethanol used for preparation of the mixed solvents was obtained by drying by anhydrous $CaSO_4$ and then distilling the guaranteed pure-grade reagents.

Calibration of the Calorimeter and Measurements. Specific heat capacities of solutions were determined using an isoperibol twin calorimeter of dry-shield type. Details concerning this calorimeter and procedures of measurements have been reported earlier.[1]) However, the manipuration has been modified slightly. Preliminary experiment of this work demonstrated that introduction of 100 g each of solution to be examined and a reference liquid into each Dewar vessel does not give a successful result. This is due to the large variation of density with the composition of the water–ethanol mixture. The difference in the volume of two liquids leads immediately to the difference in the surface area not immersed in liquids in the two Dewar vessels. To reduce the relative magnitude of the heat leak through the inner surface of the vessels, we have increased the amount of sample solution and reference liquid in each Dewar vessel to 150 g. Following the

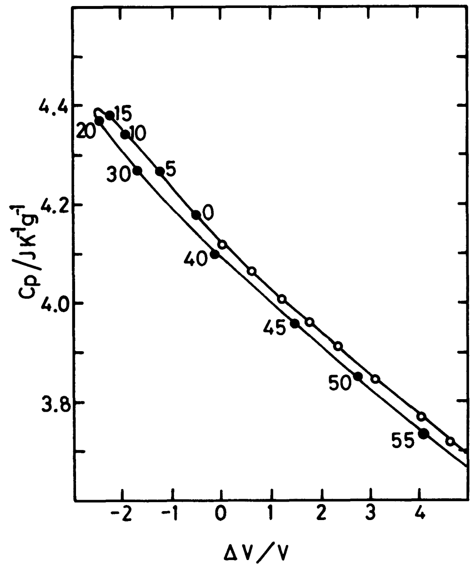

Fig. 1. Calibration curve of the twin calorimeter using 150 g of aqueous solutions of sodium chloride and of ethanol. ΔV is the change of potential of the thermistor bridge during 5 min. ○: sodium chloride, ●: ethanol.
The rotational rate of the stirring system is at 450 min.$^{-1}$ The numeral in the figure refers to the weight per cent of ethanol in the solvent.

procedures described in our early work,[1] we have carried out calibration of the calorimeter using aqueous solutions of ethanol and sodium chloride, whose specific heat capacities are given in the literature.[6] Results of calibration are illustrated schematically in Fig. 1. In principle, the calibration based on the C_p data of aqueous solutions of ethanol and sodium chloride should give an identical curve. This is not the case in Fig. 1. It may be noted here, however, that the calibration using 100 g of sample and reference liquids led to much larger differences between the two sets of calibration than those shown in Fig. 1. Increase of the rotational rate of the stirrer from 450 to 600 min^{-1} resulted in a minor effect on the general features illustrated in Fig. 1.

Dissolution of D-glucose and D-xylose in the solvent system concerned in this work always results in the lowering of the C_p value of the solutions. We, therefore, used the upper curve for the measurements in 10 wt% of ethanol, while the lower calibration curve was adopted for the determination of C_p in 20, 30, and 50 wt% of ethanol. Measurement was not done in 40 wt% of ethanol, for in this mixed solvent the potential difference ΔV to be detected is very small (see, Fig. 1) and desired precision of the measurement could not be attained. On the other hand, measurements in ethanol-rich solvents are also difficult owing to the limited solubility of the solutes D-glucose and D-xylose.

TABLE 1. SPECIFIC HEAT CAPACITY AND APPARENT MOLAR HEAT CAPACITY OF D-GLUCOSE IN WATER–ETHANOL SYSTEM AS FUNCTIONS OF MOLALITY m

wt% of EtOH	$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{C_p}{\text{J}\cdot\text{g}^{-1}\,\text{K}^{-1}}$	$\frac{\phi_{C_p}}{\text{J}\cdot\text{mol}^{-1}\,\text{K}^{-1}}$
10	0	4.342	—
	0.5001	4.077	205
	0.6501	4.017	224
	0.8003	3.961	238
	1.000	3.890	250
	1.200	3.837	258
	1.300	3.810	277
	1.500	3.767	295
20	0	4.371	—
	0.5001	4.090	175
	0.6499	4.021	186
	0.8000	3.964	205
	1.001	3.897	228
	1.200	3.831	240
	1.351	3.792	254
	1.500	3.758	269
30	0	4.271	—
	0.4000	4.074	242
	0.6002	3.989	249
	0.8000	3.910	253
	1.000	3.832	251
	1.119	3.788	251
	1.201	3.765	257
50	0	3.848	—
	0.1001	3.820	408
	0.2000	3.785	367
	0.2541	3.764	347
	0.3000	3.743	324
	0.3302	3.732	321
	0.3603	3.721	318
	0.4001	3.707	315
	0.5030	3.655	275

Measurements of C_p have been done at six to eight different concentrations of solute at temperature close to 30 °C and the infinite dilution values of the partial molar heat capacity $C^{\infty}_{p,2}$ have been determined.

Results and Discussion

C_p Data and Determination of $C^{\infty}_{p,2}$. In view of the paucity of the C_p data of solutions in general, and especially in mixed solvent system, presentation of our experimental results in an original numerical form seems worthy. All the C_p values determined in this study are summarized in Tables 1 and 2. From these data the apparent molar heat capacity of solute, ϕ_{C_p}, at solute concentration of molality m was calculated using the equation,

$$\phi_{C_p} = \frac{1}{m}[(1000+mM_2)C_p - 1000C_{p,1}], \tag{1}$$

where $C_{p,1}$ is the specific heat capacity of the solvent system and M_2 is the molar mass of the solute. The values of ϕ_{C_p} at infinite dilution, $\phi_{C_p}{}^{\circ}=C^{\infty}_{p,2}$, were deter-

TABLE 2. SPECIFIC HEAT CAPACITY AND APPARENT MOLAR HEAT CAPACITY OF D-XYLOSE IN WATER–ETHANOL SYSTEM AS FUNCTIONS OF MOLALITY m

wt% of EtOH	$\frac{m}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{C_p}{\text{J}\cdot\text{g}^{-1}\,\text{K}^{-1}}$	$\frac{\phi_{C_p}}{\text{J}\cdot\text{mol}^{-1}\,\text{K}^{-1}}$
10	0	4.342	—
	0.2000	4.229	70
	0.5000	4.100	132
	0.7000	4.005	120
	1.000	3.926	173
	1.300	3.826	178
	1.500	3.775	189
20	0	4.371	—
	0.1999	4.265	110
	0.5995	4.072	113
	0.7992	3.993	127
	0.9925	3.940	157
	1.200	3.865	159
	1.400	3.833	191
30	0	4.271	—
	0.2000	4.178	162
	0.4000	4.081	138
	0.6000	3.983	118
	0.8000	3.899	120
	1.000	3.816	118
	1.200	3.733	112
50	0	3.848	—
	0.1000	3.827	365
	0.2000	3.791	284
	0.2700	3.765	258
	0.3300	3.738	228
	0.4000	3.708	207
	0.5000	3.664	182

mined from the least-squares fitting of the experimental data.[1,2]

Concentration Dependence of ϕ_{C_p}. The coefficient related with concentration dependence of ϕ_{Cp} of a nonelectrolyte has significances physically similar to the first order parameter, B_c, of the following expression used in the case of ϕ_{C_p} of electrolytic solutes:

$$\phi_{C_p} = C^{\infty}_{p,2} + A_c m^{1/2} + B_c m, \tag{2}$$

where A_c is a parameter derived from the Debye-Hückel theory. In numerous papers describing the determination of C_p and ϕ_{C_p} of solutions which have hitherto been published, those making reference to the concentration dependence of ϕ_{C_p} are rather few in number.[7-10] The concentration dependence coefficient of ϕ_{C_p} should not be treated as a mere adjustable parameter to reproduce the experimental results. More attention must be paid to this coefficient, as it can serve as a clue in elucidating the nature of solute-solute-solvent interactions. Unfortunately, no theoretical prediction of this coefficient has been put forth. Experiments have shown that it is positive or negative, depending on the circumstances. The values of the coefficients listed in Table 3 are those obtained as first-order coefficients of the function $\phi_{C_p}(m)$ with respect to the molality m. The purpose of this work is chiefly the determination of $C^{\infty}_{p,2}$ rather than that of the concentration dependence of ϕ_{C_p}. Although the values shown in Table 3 are not so precise as to deserve a detailed discussion of these values, the general trend of the concentration dependence of ϕ_{C_p} in the aqueous mixed solvent system is clearly seen in Table 3; solute concentration dependence of ϕ_{C_p} varies remarkably with the solvent system but the variation is qualitatively the same for D-glucose and D-xylose. Table 3 suggests that with variation of the media surrounding the solute, the degree of solute-solute-solvent interactions varies in a similar fashion for D-glucose and D-xylose dissolved in the water–ethanol mixture.

TABLE 3. CONCENTRATION DEPENDENCE COEFFICIENT OF ϕ_{C_p} OF D-GLUCOSE AND D-XYLOSE IN WATER–ETHANOL SYSTEM

wt% of EtOH	D-glucose	D-xylose
0	26±7	−1±2
10	86±4	66±9
20	91±2	89±11
30	12±3	−24±5
50	−284±16	−346±24

$C^{\infty}_{p,2}$ and $\Delta C^{\infty}_{p,2}$. The values of $\phi_{C_p}{}^{\circ}=C^{\infty}_{p,2}$ determined in this work and those in pure water obtained in our previous work,[1,2] are presented in Table 4. It is noteworthy in Table 4 that the $C^{\infty}_{p,2}$'s of D-glucose are always higher than those of D-xylose in any compositions of the solvent system, showing the positive contribution of $C^{\infty}_{p,2}$ (–CH(OH)–) in water–ethanol system. Variation of $C^{\infty}_{p,2}$ with the content of ethanol in the solvent given in Table 4 is more easily understood by the aid of Fig. 2. Here again similar variation can be observed for both solutes and the minimum appears at about 20 wt% of ethanol. This behavior differs

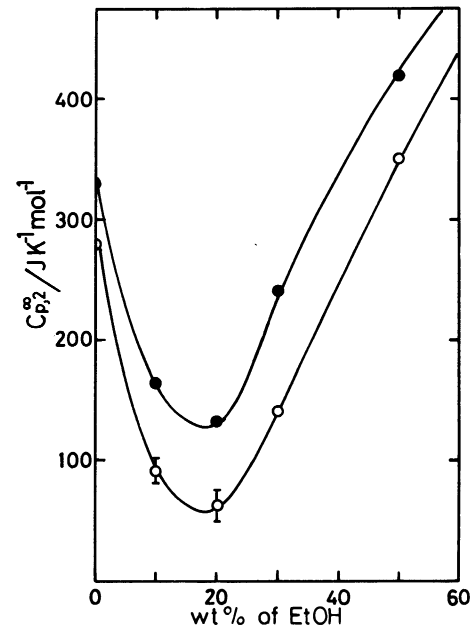

Fig. 2. Variation of $C_{p,2}$ with the ethanol content in the solvent system. ●: D-glucose, ○: D-xylose.

TABLE 4. LIMITING PARTIAL MOLAR HEAT CAPACITIES $C^{\infty}_{p,2}$ AND INCREMENT $\Delta C^{\infty}_{p,2}(=C^{\infty}_{p,2}-C^{*}_{p,2})$ FOR D-GLUCOSE AND D-XYLOSE IN WATER–ETHANOL SYSTEM

wt% of EtOH	D-glucose		D-xylose	
	$C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}	$\Delta C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}	$C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}	$\Delta C^{\infty}_{p,2}$ / J K^{-1} mol^{-1}
0	331±7[a]	107[a]	281±2[b]	97[b]
10	164±5	−60	92±11	−92
20	132±3	−92	63±13	−121
30	241±3	17	141±5	−43
50	419±6	195	350±10	166

$C^{*}_{p,2}=224\pm3$ J K^{-1} mol^{-1} for D-glucose[a]
$=184$ J K^{-1} mol^{-1} for D-xylose[b]
a) Ref. 1. b) Ref. 2.

significantly from the case of the partial specific compressibility $\bar{\kappa}_2^{\circ}$ which, as stated in the introductory part of this paper, takes a constant positive value at above 20 wt% of ethanol.[4,5] In this connection it is remembered that in water the $\bar{\kappa}_2^{\circ}$ gave the hydration number of saccharides which is not proportional to the number of monomer unit contained in the saccharides, whereas the $\Delta C_{p,2}^{\infty}$, a quantity which will be mentioned immediately below, increases linearly with the molecular dimension from mono- to trisacharides.[1] According to the Kirkwood-Buff solution theory[11] the isothermal compressibility of a binary solution is describable in terms of the pair correlation function. On the other hand, an extended treatment of the Kirkwood-Buff theory[12] has proved that the specific heat capacity of pure liquids at constant volume contains contributions from three- and four-particle distribution function. Differences in adiabatic and isothermal compressibility, or heat capacity at constant pressure and at constant volume are essentially indifferent in the present consideration. Hence, it seems reasonable to consider that the $\bar{\kappa}_2^{\circ}$ reflects predominantly the interaction in the vicinity of solute molecules, while the partial molar heat capacity is concerned with the long range molecular interaction in solutions and is pertinent to the discussion of the structural change of the solvent system.

Ben-Naim[13] proposed a theory to analyse the relation between ϕ_{C_p} of non-polar gases and the equilibrium species in the two-state model of water. However, his theory was unsuccessful even to predict the definite sign of the quantity ϕ_{C_p}. As before,[1–3] we prefer to use the quantity $\Delta C_{p,2}^{\infty}$ in discussing the structural change of the solvent system. The $\Delta C_{p,2}^{\infty}$ is defined as

$$\Delta C_{p,2}^{\infty} = C_{p,2}^{\infty} - C_{p,2}^{*}, \tag{3}$$

where $C_{p,2}^{*}$ in the specific heat capacity of the pure solute. In water we have classified the "structure-forming" and "structure-breaking" effects of solute according to the sign of the $\Delta C_{p,2}^{\infty}$. With the same criteria as in water, D-glucose and D-xylose are working as structure-breaking solutes in solvents containing 10, 20, and 30 wt% of ethanol, while they are structure-forming solutes in water and 50 wt% (presumably also at 40 wt%, see Fig. 2) of ethanol. This conclusion is simple but is not persuasive. Rather, the following interpretation seems more plausible; the structure of solvent is different for each solvent system and we are observing a structuring of the respective solvent systems through the parameter $\Delta C_{p,2}^{\infty}$. Consequently, the positive value of $\Delta C_{p,2}^{\infty}$ at 50 wt% of ethanol does not correspond straightfowardly to the structure promotion by the added solutes D-glucose or D-xylose, but it shows that the promoted structure exists even before addition of the solutes. The promoted structure in the water–ethanol system is expected, for example, from viscosity data of this mixture which shows the very high peak at *ca.* 45 wt% of ethanol. Values of the concentration dependence of ϕ_{C_p} in water–ethanol system as shown in Table 3 may also be related to the structure promotion in this aqueous mixed solvent.

Combination of the results of $\bar{\kappa}_2^{\circ}$ and $C_{p,2}^{\infty}$ leads to the following conclusion; addition of ethanol in the aqueous solutions of D-glucose and D-xylose gives rise to the removal of preferentially hydrated water molecules and at the same time the structuring of the solvent system as a whole decreases. With increasing ethanol content in the solvent, the structure promotion in water-ethanol system becomes progressively predominant up to certain ethanol content. Owing to this process the minimum appears and $\Delta C_{p,2}^{\infty}$ again takes a positive value at 50 wt% of ethanol.

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