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Thermodynamic Properties of Aqueous Carbohydrate Solutions

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Densities of binary mixtures of carbohydrates + water at (278.15, 288.15, 298.15, and 308.15) K have been determined. The carbohydrates investigated were: D-xylose, D-fructose, α-D-glucose, and D-sucrose. These results along with literature data of other thermodynamic properties have been used to test the Nitta−Chao model.

Introduction

This work is part of our investigation of the thermodynamics of aqueous solutions of the following carbohydrates: D-xylose, D-fructose, α-D-glucose, and D-sucrose. Water activity a_w is a property of interest, but it is difficult to measure. For this reason, use of the Nitta−Chao group contribution model (Nitta *et al.*, 1977) for the prediction of the water activity at 298.15 K has been considered.

Because of the existence of Nitta−Chao parameters which reflect the temperature dependence of the thermodynamic properties, we have needed values of the same property at several temperatures. Due to difficulties of finding this in the literature we have opted to determine experimental densities ρ for these systems at (278.15, 288.15, 298.15, and 308.15) K. Molar volumes of the mixtures V_m are obtained from density values.

Experimental Section

Products. The carbohydrates used in our measurements have been supplied from Aldrich: α-D-glucose ACS Reagent, D-fructose (puriss, >99 mol %), D-xylose (puriss, >99 mol %), and D-sucrose (puriss, >99 mol %). The solutions were prepared using double-distillated water passed through an ionic exchange resin and finally degassed: the specific conductance was less than 6×10^{-8} $\mathrm{ohm^{-1}\cdot cm^{-1}}$. The precision on the mole fractions x was estimated to be ±0.000 002.

Apparatus and Procedure. Densities of the mixtures were obtained with a Kyoto Electronics vibrating tube densimeter. With this procedure, the precision of the measurements is $\pm 0.000\,01\ \mathrm{g\cdot cm^{-3}}$. The temperature of the tube was controlled to ±0.005 K using a Hetotherm PFCBIIe thermostat.

Results and Discussion

Data Treatment. The experimental results are shown in Table 1. These values have been fitted as a function of the mole fractions and temperature to a polynomial of the form

$$\rho/\mathrm{g\cdot cm^{-3}} = \sum_{i=1}^{n}\sum_{j=1}^{3}10^{-(j-1)}A_{ij}x^{i-1}\,(T/K - 278.15)^{j-1} \qquad (1)$$

The coefficients A_{ij} of the polynomial and the standard deviations (Table 2) have been obtained using the Marquardt algorithm (Marquardt, 1963) and are not valid for mole fractions below those shown in Table 1. The comparison between our results fitted with eq 1 and some literature values is expressed in terms of percentage mean deviations, defined by

$$\mathrm{PMS} = \frac{100}{N_y}\sum\frac{|Y - Y_{\mathrm{lit}}|}{|Y|} \qquad (2)$$

where Y and Y_{lit} are respectively the data of this work and literature data and N_y is the number of points; for α-D-glucose + water at 298.15 K (Taylor and Rowlinson, 1955) PMS is about 0.050%, 0.059% for D-xylose + water at 298.15 K (Uedaira and Uedaira, 1969), and 0.041% for D-sucrose + water at 278.15 K (Garrod and Herrington, 1970).

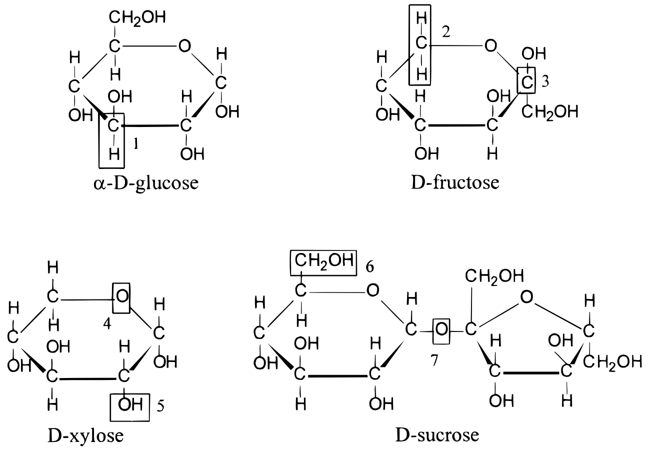

Figure 1. Group decomposition of carbohydrate molecules: (1) CH_r; (2) CH_{2r}; (3) C_r; (4) O_r; (5) OH; (6) CH_2OH; (7) O_u.

Water Activity: Nitta−Chao Model. In 1977 Nitta *et al.* developed a group contribution molecular model which predicts thermodynamic properties of polar and nonpolar pure liquids and their solutions. This model adopts the cell theory for the liquid state. The repulsive forces are taken into account from the Carnahan−Starling equation of state for hard spheres (Carnahan and Starling, 1969), and the attractive ones are expressed through the lattice energy. Making use of the quasichemical approximation (Guggenheim, 1944) and supposing group pair aditivity, we calculate the lattice energy. Thus, the configurational partition function of the liquid is expressed as follows:

$$\ln Q = \ln g_0 + \ln g_1 + Nc\left[\ln \tilde{v} - \frac{(4\tilde{v} - 3)}{(\tilde{v} - 1)^2}\right] - \sum_i\sum_{j\geq i}\frac{N_{ij}\phi_{ij}}{kT} \qquad (3)$$

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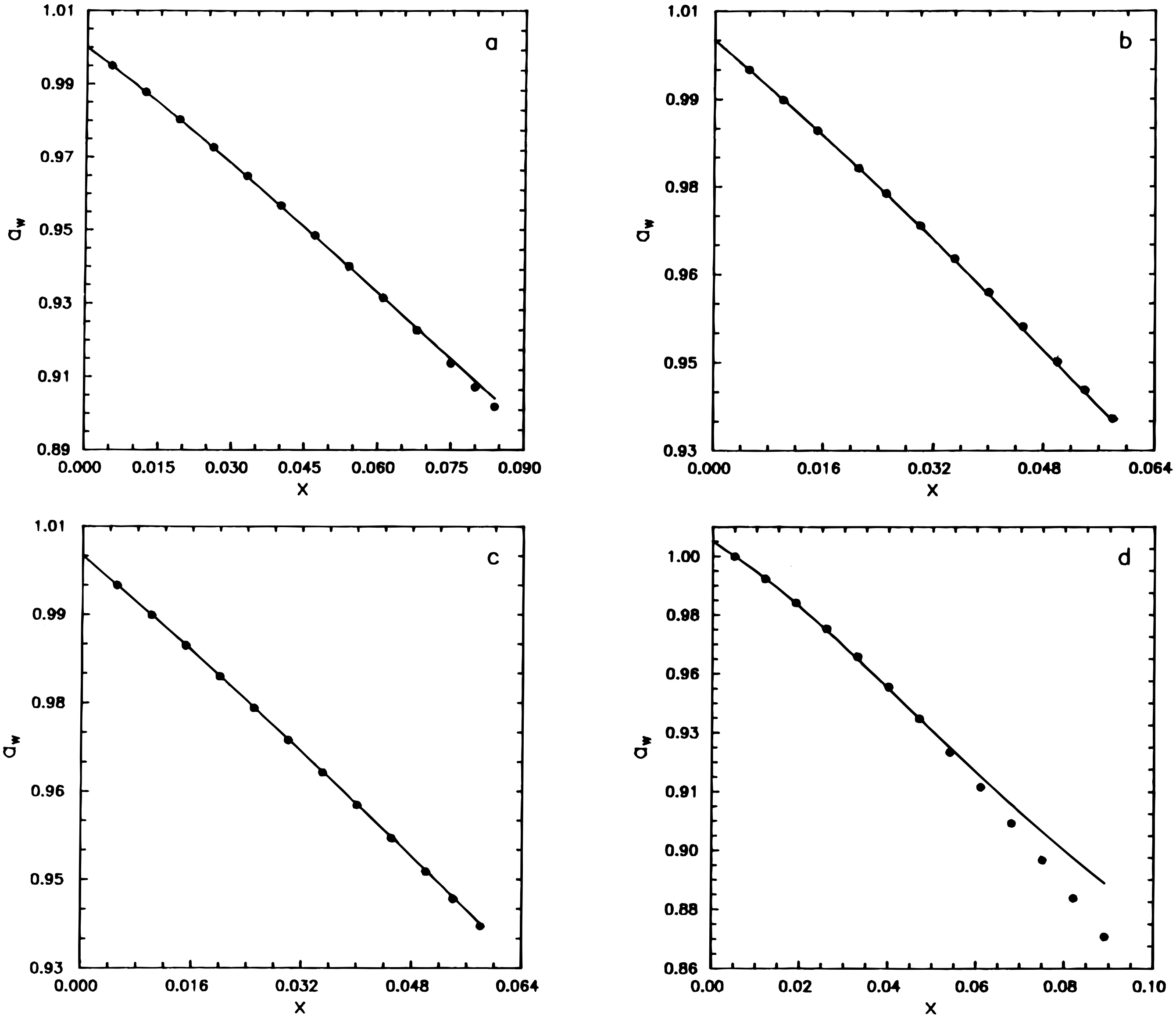

Figure 2. Water activity a_w at 298.15 K. (a) xα-D-glucose + (1 − x)water: (●) experimental data (Stokes and Robinson, 1966). (b) xD-fructose + (1 − x)water: (●) experimental data (Barone *et al.*, 1986). (c) xD-xylose + (1 − x)water: (●) experimental data (Uedaira and Uedaira, 1969). (d) xD-sucrose + (1 − x)water: (●) experimental data (Robinson and Stokes, 1961). (—) Nitta−Chao model.

g_0 and g_1 being combinatorial factors given by the quasichemical approximation, N the total number of molecules, c the average external degrees of freedom per molecule, $\tilde{v} = V/V^\circ$ the reduced volume with V and V° the actual volume and the hard core volume of the liquid, respectively, k the Boltzmann constant, T the absolute temperature, N_{ij} the number of ij pairs in the liquid calculated from the quasichemical approximation by means of the introduction of the contacts of a group i (Q_i), and ϕ_{ij} the pairwise interaction energy.

The hard core volume of a group i (V_i°) is represented by the empirical expression

$$V_i^\circ = V_{io}^\circ \exp\left[a_i\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \qquad (4)$$

where V_{io}° denotes the hard core volume at the base temperature T_0 (normally 298.15 K) and a_i is the V_i° temperature dependence parameter.

The pairwise interaction energy, ϕ_{ij}, is given by

$$\phi_{ij} = -\frac{\epsilon_{ij}}{\tilde{v}}\exp\left[\frac{\kappa}{\tilde{v}}\right] - \sigma_{ij} \qquad (5)$$

where κ is a constant whose value is 0.7, ϵ_{ij} is the dispersive interaction energy parameter, and σ_{ij} is the chemical association interaction energy expressed by

$$\frac{\sigma_{ij}}{T} = \frac{\sigma_{ij}^0}{T_0} + \sigma'_{ij}\left[\frac{1}{T} - \frac{1}{T_0}\right] \qquad (6)$$

σ_{ij}^0 and σ'_{ij} being respectively the base associative interaction energy parameter and the associative temperature parameter.

The expressions for the thermodynamic properties of the pure liquids and the mixtures are derived from eq 3 by the standard methods of statistical thermodynamics.

An initial guess using a group decomposition of the molecules in well-defined groups, given in previous works (Eckart *et al.*, 1986), results in large deviations from experimental data for the quantities to be reproduced. For this reason, we have proposed a new group decomposition of the molecules and, in some cases, a reparametrization of well-defined groups (i.e. CH_2) has been necessary. In Figure 1 the definition of the groups which characterize the carbohydrate molecules is given. Water molecules are considered a group. The decomposition of the molecules to its constituent groups is given in Table 3.

Table 1. Densities ρ for Carbohydrate + Water

x	ρ/g·cm^{-3} T = 278.15 K	x	ρ/g·cm^{-3} T = 288.15 K	ρ/g·cm^{-3} T = 298.15 K	x	ρ/g·cm^{-3} T = 308.15 K
			xα-D-Glucose + (1 − x)Water			
0.005 13	1.019 57	0.005 13	1.018 34	1.016 04	0.005 13	1.012 92
0.009 97	1.036 93	0.009 97	1.035 42	1.032 89	0.009 97	1.029 48
0.015 05	1.054 13	0.015 05	1.052 41	1.049 65	0.015 05	1.046 34
0.019 84	1.069 70	0.019 84	1.067 61	1.064 66	0.019 84	1.061 33
0.025 26	1.086 30	0.025 26	1.083 94	1.080 74	0.025 26	1.077 13
0.029 90	1.099 81	0.029 90	1.097 06	1.093 86	0.029 90	1.090 11
0.034 98	1.113 72	0.034 98	1.110 86	1.107 48	0.034 98	1.103 62
0.040 05	1.126 97	0.040 05	1.123 97	1.120 41	0.040 05	1.116 37
0.045 04	1.139 38	0.045 04	1.136 08	1.132 45	0.045 04	1.128 19
0.049 97	1.151 14	0.050 03	1.147 79	1.144 09	0.050 24	1.140 14
0.054 98	1.162 27	0.055 13	1.159 23	1.155 37	0.055 13	1.150 80
0.060 00	1.173 15	0.060 14	1.169 68	1.165 87	0.060 14	1.161 31
0.065 02	1.183 56	0.065 17	1.180 06	1.176 00	0.065 17	1.171 40
0.070 22	1.193 87	0.070 26	1.189 89	1.185 69	0.070 26	1.181 12
0.075 19	1.203 15	0.075 04	1.198 38	1.194 59	0.075 04	1.189 92
0.080 14	1.212 21	0.080 01	1.207 86	1.203 40	0.080 01	1.198 61
0.085 13	1.221 09	0.085 03	1.216 27	1.211 96	0.085 03	1.207 19
0.089 96	1.228 95	0.090 23	1.225 10	1.220 48	0.090 23	1.215 62
0.095 04	1.237 11	0.094 96	1.232 42	1.227 92	0.094 96	1.222 95
			xD-Fructose + (1− x)Water			
0.004 10	1.016 12		1.014 96	1.012 58		1.009 41
0.010 00	1.038 01		1.036 43	1.033 63		1.030 14
0.016 00	1.058 78		1.056 75	1.053 73		1.049 89
0.022 05	1.078 48		1.075 63	1.072 60		1.068 63
0.028 09	1.096 89		1.094 31	1.090 43		1.086 17
0.034 02	1.114 00		1.110 94	1.106 92		1.102 44
0.039 95	1.130 13		1.126 95	1.122 67		1.117 78
0.045 93	1.145 44		1.141 93	1.137 51		1.132 39
0.052 11	1.160 31		1.156 63	1.151 95		1.146 75
0.058 02	1.173 76		1.169 72	1.165 07		1.159 57
0.063 66	1.185 72		1.181 92	1.176 92		1.171 43
			xD-Xylose + (1 − x)Water			
0.070 00	1.198 66		1.194 59	1.189 44		1.183 81
0.006 33	1.019 39		1.018 01	1.015 82		1.012 46
0.011 90	1.035 38		1.033 59	1.031 27		1.027 67
0.017 99	1.052 10		1.050 02	1.047 36		1.043 57
0.023 99	1.067 67		1.065 27	1.062 46		1.058 39
0.030 13	1.082 68		1.080 08	1.076 93		1.072 88
0.036 06	1.096 42		1.093 61	1.090 36		1.085 98
0.042 22	1.110 05		1.106 98	1.103 60		1.098 96
0.047 96	1.122 14		1.118 85	1.115 28		1.110 96
0.054 00	1.134 18		1.130 78	1.127 03		1.122 28
0.060 24	1.145 99		1.142 45	1.138 54		1.133 72
0.066 06	1.156 70		1.152 94	1.148 89		1.143 98
			xD-Sucrose + (1 − x)Water			
0.072 07	1.167 14		1.163 23	1.159 03		1.153 99
0.004 02	1.028 90		1.027 50	1.025 08		1.021 87
0.010 00	1.066 93		1.065 09	1.062 25		1.058 82
0.016 00	1.100 88		1.098 63	1.095 26		1.090 96
0.022 21	1.131 96		1.129 32	1.125 71		1.121 68
0.028 04	1.158 04		1.154 97	1.151 15		1.147 05
0.034 31	1.183 23		1.179 91	1.175 62		1.171 38
0.040 25	1.204 71		1.201 04	1.196 67		1.192 19
0.046 12	1.223 98		1.220 11	1.215 59		1.210 93
0.051 89	1.241 16		1.237 15	1.232 47		1.227 89
0.057 98	1.257 99		1.253 74	1.248 88		1.244 10
0.063 86	1.272 96		1.268 40	1.263 51		1.258 41
0.070 21	1.287 52		1.282 90	1.278 08		1.272 84

The parametrization of these new groups has been performed so that convergence between model predictions and experimental data was reached. In addition to the density data of this work literature values of the following properties were used: (excess molar enthalpies at 298.15 K) α-D-glucose and D-sucrose (Savage and Wood, 1976), D-fructose and D-xylose (Barone *et al.*, 1981); (excess molar Gibbs energies at 298.15 K) α-D-glucose (Stokes and Robinson, 1966), D-fructose (Barone *et al.*, 1986), D-xylose (Uedaira and Uedaira, 1969), and D-sucrose (Robinson and Stokes, 1961).

The parameters which characterize the new groups have been obtained by an optimization iterative process (Christensen, 1982) which employed the Marquardt algorithm.

Table 2. Coefficients A_{ij} of Eq 1 and Standard Deviations s

	A_{ij}		
i	j = 1	j = 2	j = 3
	xα-D-Glucose + (1 − x)Water (s = 0.000 13)		
1	1.000 41	-0.000 39	−0.000 53
2	3.854 09	−0.083 48	0.010 93
3	−19.475 8	0.702 66	−0.125 48
4	54.175 5	−2.873 57	0.636 80
	xD-Fructose + (1 − x)Water (s = 0.000 13)		
1	1.000 34	−0.000 25	−0.000 59
2	3.951 10	−0.118 38	0.018 09
3	−19.687 9	1.610 61	−0.459 93
4	53.188 1	−9.186 85	3.463 84
	xD−Xylose + (1 − x)Water (s = 0.000 13)		
1	1.000 09	−0.000 37	−0.000 52
2	3.130 79	−0.076 21	0.005 88
3	−14.174 9	0.729 53	−0.049 11
4	40.153 8	−3.868 38	0.195 25
	xD−Sucrose + (1 − x)Water (s = 0.000 12)		
1	1.000 52	−0.000 73	−0.000 40
2	7.348 09	−0.062 65	−0.014 97
3	−75.584 4	−1.163 91	1.158 80
4	551.635	31.174 7	−21.248 6
5	−1942.91	−180.473	121.263

Table 3. Group Decomposition of This Work for Binary Mixtures of Carbohydrate + Water

substance	CH_r	CH_{2r}	C_r	O_r	OH	CH_2OH	O_u	H_2O
α-D-glucose	5	0	0	1	4	1	0	0
D-fructose	3	1	1	1	4	1	0	0
D-xylose	4	1	0	1	4	0	0	0
D-sucrose	8	0	1	2	4	3	1	0
water	0	0	0	0	0	0	0	1

Table 4. Parameters for the Nitta−Chao Model Calculated in This Work

group	V^o/cm^3·mol^{-1}	a	c	Q
CH_{2r}	9.76	21.20	0.113	0.219
CH_r	6.09	21.30	−0.107	0.118
C_r	3.20	21.20	−0.329	0
CH_2OH	14.25	23.70	0.344	1.927
OH	7.01	39.60	0.245	3.234
O_r	4.10	55.10	0.128	2.367
H_2O	9.98	102.6	0.814	6.450
O_u	4.24	28.64	0.436	1.831

groups	CH_{2r}	CH_r	C_r	CH_2OH	OH	O_r	H_2O	O_u
				ϵ_{ij}/J·mol^{-1}				
CH_{2r}	163							
CH_r	368	314						
C_r	0	0	0					
CH_2OH	6736	1954	0	11305				
OH	3351	2912	0	7920	6017			
O_r	1644	1397	0	7682	9594	6531		
H_2O	908	238	0	8017	9050	9314	12908	
O_u	6468	4134	0	10920	11632	9255	9176	10071
				σ_{ij}°/J·mol^{-1}				
CH_{2r}	0							
CH_r	0	0						
C_r	0	0	0					
CH_2OH	0	0	0	569				
OH	0	0	0	1469	6757			
O_r	0	0	0	1674	8389	6540		
H_2O	0	0	0	870	3979	6159	628	
O_u	0	0	0	6908	6117	5054	7757	10435
				σ_{ij}'/J·mol^{-1}				
CH_{2r}	0							
CH_r	0	0						
C_r	0	0	0					
CH_2OH	0	0	0	10983				
OH	0	0	0	12301	15246			
O_r	0	0	0	5753	5627	9163		
H_2O	0	0	0	11071	8297	13125	2925	
O_u	0	0	0	3690	28773	6887	12188	1715

The derived parameters are given in Table 4. The fitting process resulted in PMS about 2.4% for the density ρ and 0.06% for the water activity a_w. Finally, Figure 2 shows how the theory fits the experimental data in the case of the water activity.

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