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Calorimetric Study of the Glucose + Ethanol + Water System at High Ethanol Concentrations at 45 °C

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Enthalpies of mixing of 50% (w/w) glucose + water solutions with ethanol and aqueous ethanol solutions have been measured at 45 °C. These results have been combined with the enthalpy of dilution in water, partial molar excess enthalpies of water, and the enthalpy of solution of anhydrous glucose in water to obtain the differential enthalpy of solution of glucose in ethanol solutions containing up to 4.5% (w/w) glucose and 15% water. The standard enthalpy of solution in ethanol is considerably more endothermic than in water and is decreased by increasing concentrations of either water or glucose.

As part of a larger study of the thermodynamic properties of sugars in ethanol and ethanol + water mixtures, the differential enthalpy of solution of D-glucose has been determined in ethanol and ethanol-rich aqueous solutions. The rate of solution of anhydrous glucose in these solutions is too slow for accurate calorimetric measurements with the equipment available, so a more complex route to these values was used. A similar technique was used earlier to determine enthalpies of solution of HCl and NaOH in ethanol-rich solutions (*1*). Differential enthalpies of mixing of small amounts of 50% (w/w) aqueous glucose with larger quantities of ethanol, water, and glucose were measured at 45 °C. Final concentrations of glucose were between 0.1 and 4.5%, and final concentrations of water were between 0.1 and 15% (calculated as though the glucose were not present). Combination of these data with partial molar excess enthalpies of water, and the enthalpy of dilution of the glucose solution in water, provides the enthalpy of transfer of glucose from an infinitely dilute state in water to states within the range of compositions given. Further combination with the enthalpy of solution of anhydrous glucose in pure water gives differential enthalpies of solution in the glucose + ethanol + water solutions.

Experimental Section

Materials. D-Glucose was Fisher Certified ACS Dextrose and was used without further purification. Samples for enthalpies of solution were dried for 12 h at 110 °C, but there were no significant differences in measurements on these samples and undried samples. Ethanol was U. S. Industrial Chemicals Punctilious Grade. Singly distilled water in equilibrium with atmospheric carbon dioxide was used for all measurements.

Table I. Enthalpy of Solution of Anhydrous D-Glucose in Water at 45 °C

wt of glucose, g	wt of water, g	ΔH_{soln}, kJ/mol
0.1296	91.24	13.9
0.2027	93.93	13.8
0.3144	91.97	13.5
0.3328	93.10	14.0
0.3582	93.53	13.5
0.3997	92.38	14.0
		av 13.8

Calorimetry. Mixing and dilution measurements were made on a Tronac Model 550 titration calorimeter operating in the isoperibol mode at 45.0 ± 0.1 °C. Titrant solutions of water or 50.0 ± 0.1% glucose were manually injected into weighed solvent mixtures (approximately 95 mL) in increments of 0.1 to 0.5 mL with a 2.5-mL Gilmont micrometer syringe with an accuracy of 0.0002 mL. After delivery of 2.0 mL, the syringe was refilled and the incremental titration continued until a total of 4.0 mL of pure water or 6.0 mL of glucose solution had been injected. At least three heat capacity measurements were performed for each 2-mL series, and calculations of the incremental heats of mixing were based on linear regression of heat capacity vs. volume added. Individual measurements of enthalpy per unit volume are considered to be accurate to 1%. These measurements were converted to a molar basis by using the density of water (0.9902 g/mL) and the measured density (1.206 ± 0.001 g/mL) of the glucose solution.

Enthalpies of solution of anhydrous glucose were measured on a Tronac Model 450 isoperibol titration calorimeter with an ampule adapter. Samples of 0.1–0.4 g were sealed in 1–1.5-mL glass ampules, weighing to within 0.1 mg. Breaking of the ampule into approximately 95 mL of water was bracketed by heat capacity determinations agreeing to within 0.5%. Most of the thermal effect was compensated by using the calibration heater such that the measurements were essentially isothermal. Values were reproducible to within about 1.5%, as has generally been the case for this calorimeter with other sugar samples.

Results and Discussion

The enthalpy of solution of anhydrous D-glucose in water at 45 °C is given in Table I. Any concentration dependence of

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Table II. Partial Molar Excess Enthalpies of Water in Ethanol + Water Mixtures at 45 °C

10^2W_w[a]	$-L_w$, J/mol	10^2W_w[a]	$-L_w$, J/mol
0.198	1066	6.419	165
0.660	946	6.782	178
0.792	928	7.263	158
1.053	893	7.755	138
1.314	860	8.108	148
1.637	743	8.459	120
2.150	646	8.865	124
2.531	563	9.324	119
2.836	502	9.722	114
3.024	505	10.232	122
3.399	463	10.692	137
3.894	403	11.148	145
4.323	358	11.655	159
4.869	298	12.100	158
5.186	231	13.095	181
5.559	255	13.580	181
6.052	196	14.171	199

[a] Average weight fraction of water over the incremental addition.

Table III. Observed Differential Enthalpies of Mixing of 50% (w/w) Glucose/Water with Aqueous Ethanol Solutions at 45 °C, and Derived Partial Molar Enthalpies of Transfer from Infinite Dilution in Water

$100W_w$[a]	$100W_g$	ΔH^{mix}, kJ/mol	$-L_w$,[b] kJ/mol	$\bar{H}_g - \bar{H}_{g,w}$,[c] kJ/mol
0.13	0.131	3.71	1.114	16.3
0.38	0.378	4.26	1.046	16.2
0.67	0.664	4.85	0.971	16.0
0.95	0.946	5.25	0.901	15.7
1.28	1.265	5.68	0.826	15.4
1.56	1.540	6.03	0.765	15.1
1.85	1.790	6.14	0.707	14.7
2.01	1.945	6.36	0.676	14.6
2.21	2.136	6.67	0.639	14.5
2.45	2.364	6.78	0.596	14.2
2.65	2.553	6.44	0.563	13.5
2.81	2.702	7.17	0.538	14.0
3.00	2.888	6.87	0.508	13.4
3.24	3.109	7.13	0.474	13.3
3.59	3.336	7.41	0.426	13.1
3.75	3.480	7.06	0.407	12.6
3.94	3.660	7.21	0.384	12.5
4.17	3.874	6.87	0.358	11.9
4.44	4.120	6.95	0.330	11.7
4.66	4.330	6.71	0.308	11.2
4.89	4.537	7.00	0.287	11.3
5.11	0.112	11.10	0.270	15.2
5.22	0.234	11.00	0.260	15.1
5.34	0.355	10.73	0.251	14.7
5.45	0.458	11.04	0.243	14.9
5.61	0.636	10.50	0.232	14.3
5.84	0.873	10.83	0.217	14.4
6.03	1.070	10.55	0.205	14.1
6.22	1.265	10.37	0.195	13.8
6.41	1.458	10.34	0.185	13.6
6.52	1.573	10.30	0.180	13.6
6.82	1.769	9.70	0.167	12.8
7.00	1.958	9.82	0.159	12.9
7.15	2.108	9.63	0.153	12.6
7.34	2.295	9.10	0.149	12.0
7.49	2.443	8.80	0.145	11.7
7.67	2.628	9.00	0.141	11.9
7.89	2.847	8.74	0.137	11.6
8.07	3.028	8.54	0.135	11.3
8.58	3.270	9.00	0.129	11.7
8.76	3.448	8.18	0.128	10.9
8.90	3.589	8.00	0.127	10.7
9.15	3.834	7.98	0.126	10.7
9.40	4.077	7.86	0.126	10.6
9.69	4.351	7.55	0.127	10.3
10.08	0.086	11.46	0.129	14.2
10.19	0.210	10.76	0.129	13.5
10.34	0.375	10.44	0.131	13.2
10.56	0.620	10.03	0.133	12.8
10.82	0.903	9.50	0.136	12.3
11.04	1.143	9.38	0.139	12.2
11.30	1.420	8.88	0.142	11.8
11.82	1.781	8.42	0.151	11.4
12.04	2.013	8.56	0.155	11.6
12.29	2.280	8.02	0.160	11.1
12.54	2.544	7.72	0.165	10.8
12.75	2.769	7.54	0.169	10.7
13.00	3.028	7.16	0.174	10.4
13.76	3.370	7.04	0.191	10.4
14.03	3.659	7.16	0.197	10.6
14.34	3.979	6.61	0.204	10.1
14.68	4.329	6.27	0.212	9.8
14.92	4.571	5.96	0.217	9.6

[a] Calculated as if glucose were not present. [b] Calculated from smoothing equation. [c] Enthalpies of transfer from the solid state, $\bar{H}_g - \bar{H}_{g,s}$, may be calculated by adding the enthalpy of solution of anhydrous glucose (13.8 kJ/mol) to these values.

the enthalpy of solution was below the sensitivity of these measurements. The average value at 45 °C is linear with six values determined previously (*2*) with a different calorimeter (*1*) in the range of 25–33 °C, obeying the equation

$$\Delta H^{soln}\ (\mathrm{kJ/mol}) = 7.1 + 0.15t \pm 0.1$$

The heat capacity change on solution, 150 J/(mol K), is considerably larger than the value of approximately 107 J/(mol K) reported by Kawaizumi et al. (*3*) at 30 °C.

Partial molar excess enthalpies of water (represented as L_w) are given in Table II. These are the result of incrementally adding up to 4 mL of water, first to pure ethanol then to a solution of 5% water, and then to a solution of 10% water. One measurement, in which there was a definite operator error, has been excluded from the data set. Taylor and Bertrand (*4*) have shown that the molar enthalpy of mixing of a small increment of one component with a much larger quantity of a solution closely approximates the partial molar excess enthalpy of that component at the average of the solution compositions before and after the addition. Results are therefore reported at the average of the initial and final weight fractions of water for the addition of an increment (W_w). These values obey the equation

$$L_w\ (\mathrm{J/mol}) = -1132 + 2.72 \times 10^4 W_w - 2.34 \times 10^5 W_w^2 + 6.2 \times 10^5 W_w^3 \quad (2)$$

with a standard deviation of 16 J/mol, the larger deviations occurring at low weight fractions of water. Partial molar excess enthalpies of ethanol were calculated from eq 2 and the Gibbs–Duhem equation and were combined with the values for water to obtain excess enthalpies of mixing for water concentrations up to 0.3 mole fraction. These values are consistently about 9% less exothermic than values extrapolated to 45 °C from the equation given by Larkin (*5*) for measurements at 50 °C and higher.

The enthalpy of dilution of 50% aqueous glucose to final concentrations between 0.5 and 2% in pure water was measured as −1450 J/mol with a standard deviation of 20 J/mol. Table III lists differential enthalpies of mixing of small amounts of 50% aqueous glucose solution with larger amounts of glucose, ethanol, and water. Values are reported at the average weight fraction of glucose for the addition, and the average weight fraction of water, calculated as if the glucose were not present. The actual average weight fraction of water in the solution may be calculated as $W_w(1 - W_g)$. Observed enthalpies of mixing contain contributions from both the glucose and the water, so the effect of water is removed by subtracting a quantity (RL_w), in which R represents the number of moles of water per mole of glucose in the 50% solution (in this case, R = 10.00) from the enthalpy of mixing per mole of glucose. For these calculations, smoothing equations for L_w over narrower ranges of composition were used instead of eq 2. The remaining quantity represents the difference between the partial molar enthalpy of glucose in the solution ($\bar{H}_g$) and the apparent partial molar enthalpy of glucose in the 50% solution. The enthalpy of dilution in pure water represents the difference between the partial molar enthalpy of glucose at infinite dilution in water ($\bar{H}_{g,w}$) and the apparent partial molar enthalpy of glucose in the 50% solution. This quantity was also subtracted from the enthalpy of mixing to give values of the partial molar enthalpy of transfer of glucose from the infinitely dilute (standard) state in water to the solution of interest ($\bar{H}_g - \bar{H}_{g,w}$), listed in column 5 of Table III. The enthalpy of solution of anhydrous glucose in water (13.8 kJ/mol) may be added to these values to obtain differential enthalpies of solution of solid glucose ($\bar{H}_g - \bar{H}_{g,s}$).

Estimation of uncertainties in derived values is complicated by the necessity of interpolating values of L_w between observed values. Values of ΔH^{mix} have an uncertainty of the order of 1%, and values of L_w have an uncertainty of 1% or 0.005 kJ/mol, whichever is greater. This latter uncertainty is multiplied by a factor of 10 in calculating the uncertainty in $\bar{H}_g - \bar{H}_{g,w}$. On this basis, an uncertainty of 0.2 kJ/mol is assigned to the calculated values for solutions containing less than 3% water, decreasing to 0.1 kJ/mol for solutions containing more than 10% water. An additional uncertainty of 0.2 kJ/mol is assigned to calculated values of $\bar{H}_g - \bar{H}_{g,s}$.

This differential enthalpy of solution of glucose in ethanol is considerably more endothermic than in water, and the value is lowered by the presence of both glucose and water. The effect of added glucose is considerably greater than the effect of added water.

Glossary

L_w	partial molar excess enthalpy of water in an ethanol + water mixture
W_w	weight fraction of water, calculated as if glucose were not present
W_g	weight fraction of glucose
$\bar{H}_g$	partial molar enthalpy of glucose in a mixture of ethanol, water, and glucose
$\bar{H}_{g,w}$	partial molar enthalpy of glucose at infinite dilution in water
$\bar{H}_{g,s}$	molar enthalpy of solid anhydrous glucose

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Calorimetric Study of the Xylose + Ethanol + Water System at High Ethanol Concentrations at 45 °C

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Enthalpies of mixing of 50% (w/w) xylose + water solutions with ethanol and aqueous ethanol solutions have been measured at 45 °C. These results have been combined with the enthalpy of dilution in water, partial molar excess enthalpies of water, and the enthalpy of solution of anhydrous xylose in water to obtain the differential enthalpy of solution of xylose in ethanol solutions containing up to 4.5% (w/w) xylose and 15% water. The standard enthalpy of solution in ethanol is considerably more endothermic than in water and is decreased by increasing concentrations of either water or xylose.

As a continuation of a study of the thermodynamic properties of sugars in ethanol and ethanol + water mixtures (*1*), the differential enthalpy of solution of D-xylose in ethanol and ethanol-rich aqueous solutions has been determined. As was the case with glucose, the rate of solution of anhydrous xylose in these solutions is too slow for accurate calorimetric measurements with the equipment available. Differential enthalpies of mixing of small amounts of 50% (w/w) xylose in water with larger quantities of ethanol, water, and xylose at 45 °C were combined with partial molar excess enthalpies of water and the enthalpy of dilution of the xylose solution in water to obtain the enthalpy of transfer of xylose from an infinitely dilute state in water to states within the range of compositions given. These data were combined with the enthalpy of solution of anhydrous xylose in pure water, yielding differential enthalpies of solution in the xylose + ethanol + water solutions. Final concentrations of xylose were between 0.1 and 4.5%, and final concentrations of water were between 0.1 and 15% (calculated as though the xylose were not present).

Table I. Enthalpy of Solution of Anhydrous Xylose in Water at 45 °C

wt of xylose, g	wt of water, g	ΔH_{soln}, kJ/mol
0.6904	93.40	15.09
0.9419	93.00	15.60
1.0166	92.82	15.15
1.3357	92.96	15.10
		av 15.2

Experimental Section

Materials. Fisher Purified D-xylose was dried for 12 h at 90 °C. Ethanol was U. S. Industrial Chemicals Punctilious Grade. Singly distilled water in equilibrium with atmospheric carbon dioxide was used for all measurements.

Calorimetry. Calorimetric techniques were the same as those in the preceding work. On addition of the concentrated aqueous xylose solution to ethanol-rich solvents a slow endothermic process, usually lasting 2–4 min, was observed after the rapid initial temperature change. To facilitate extrapolations on the thermogram, the calibrating heater was operated to

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