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

100W_w[a]	100W_x	ΔH^{mix}, kJ/mol	$-L_w$,[b] kJ/mol	$\bar{H}_x - \bar{H}_{x,w}$,[c] kJ/mol
0.11	0.109	4.13	1.120	15.1
0.28	0.279	4.28	1.073	14.8
0.45	0.448	4.73	1.028	14.9
0.66	0.657	4.85	0.973	14.6
0.87	0.865	5.16	0.921	14.5
1.08	1.071	5.74	0.871	14.6
1.33	1.316	5.64	0.815	14.1
1.58	1.559	6.22	0.762	14.2
1.85	1.791	6.74	0.707	14.2
2.05	1.989	6.65	0.668	13.8
2.26	2.186	7.11	0.630	14.0
2.42	2.342	6.66	0.602	13.3
2.62	2.536	7.18	0.568	13.5
2.87	2.767	6.92	0.529	13.0
3.07	2.957	7.77	0.499	12.6
3.27	3.146	7.00	0.470	12.5
3.59	3.337	8.50	0.427	13.7
3.74	3.486	7.29	0.407	12.3
3.90	3.634	7.49	0.388	12.4
4.10	3.818	6.89	0.366	11.6
4.30	4.000	7.24	0.344	11.7
4.49	4.181	7.49	0.324	11.8
4.73	4.396	6.80	0.302	10.9
4.96	4.609	6.96	0.281	10.9
2.15	0.157	7.01	0.649	14.0
2.37	0.373	7.89	0.611	14.6
2.54	0.543	8.04	0.582	14.5
2.70	0.713	8.64	0.555	14.9
2.87	0.882	7.99	0.528	14.0
3.33	1.091	8.15	0.461	13.6
3.58	1.585	8.33	0.428	13.5
3.89	1.830	7.71	0.390	12.6
4.05	1.991	8.50	0.371	13.2
4.22	2.152	8.61	0.353	13.2
4.42	2.350	8.43	0.332	12.8
4.62	2.546	8.01	0.312	12.2
4.83	2.742	8.46	0.293	12.5
5.07	2.974	7.89	0.272	11.8
5.31	3.204	8.11	0.253	11.8
5.72	3.419	8.06	0.225	11.6
5.88	3.569	7.86	0.215	11.3
6.03	3.719	8.05	0.205	11.4
6.23	3.905	7.82	0.194	11.1
6.42	4.089	7.38	0.184	10.5
6.62	4.271	7.77	0.175	10.8
6.85	4.489	7.35	0.165	10.4
7.08	4.704	7.21	0.157	10.1
5.09	0.096	10.20	0.271	14.1
5.25	0.267	9.90	0.257	13.7
5.41	0.437	10.12	0.245	13.8
5.61	0.647	9.62	0.230	13.2
5.82	0.856	9.66	0.216	13.1
6.02	1.063	9.47	0.204	12.8
6.26	1.310	9.22	0.190	12.4
6.49	1.553	9.09	0.179	12.2
6.84	1.793	8.64	0.166	11.6
7.00	1.952	8.92	0.161	11.9
7.16	2.111	8.78	0.153	11.7
7.35	2.308	8.62	0.148	11.5
7.55	2.503	8.56	0.144	11.4
7.74	2.696	8.43	0.140	11.2
7.97	2.926	8.16	0.136	10.9
8.20	3.154	8.29	0.133	11.0
8.70	3.373	8.75	0.128	11.4
8.86	3.523	8.41	0.127	11.1
9.01	3.671	8.09	0.127	10.8
9.19	3.855	8.24	0.126	10.9
9.38	4.038	8.21	0.126	10.9
9.57	4.219	7.89	0.126	10.6
9.79	4.435	7.75	0.127	10.4
10.01	4.648	7.31	0.128	10.0
10.09	0.102	10.17	0.129	12.9
10.24	0.268	9.45	0.130	12.2
10.39	0.434	8.88	0.131	11.6
10.58	0.640	9.00	0.133	11.7
10.77	0.843	8.70	0.135	11.4
10.95	1.045	8.69	0.137	11.5
11.17	1.286	8.14	0.140	10.9
11.39	1.524	8.06	0.144	10.9
11.81	1.759	8.03	0.151	10.9
11.95	1.915	8.00	0.153	10.9
12.10	2.070	7.78	0.156	10.7
12.28	2.262	7.39	0.159	10.4
12.46	2.453	7.21	0.163	10.2
12.63	2.642	6.85	0.167	9.9
12.85	2.867	7.01	0.171	10.1
13.06	3.090	6.92	0.176	10.0
13.69	3.293	6.61	0.190	9.8
13.83	3.439	6.86	0.193	10.1
13.97	3.584	7.04	0.196	10.3
14.11	3.728	6.52	0.199	9.8
14.25	3.872	6.56	0.202	9.9
14.42	4.050	6.45	0.206	9.8
14.63	4.262	6.03	0.211	9.4
14.80	4.437	6.47	0.214	9.9
14.93	4.576	6.29	0.217	9.7

[a] Calculated as if xylose were not present. [b] Calculated from smoothing equation. [c] Enthalpies of transfer from the solid state ($\bar{H}_x - \bar{H}_{x,s}$) may be calculated by adding the enthalpy of solution of anhydrous xylose (15.2 kJ/mol) to these values.

compensate most of the thermal effect. Even with this technique, the data scattered about 0.3 kJ/mol with occasional scatter of as much as 0.5 kJ/mol when the secondary process was very slow.

Results and Discussion

The enthalpy of solution of anhydrous D-xylose in water at 45 °C is given in Table I. Any concentration dependence of the enthalpy of solution was below the sensitivity of these measurements. The enthalpy of dilution of 50% aqueous xylose to final concentrations between 0.2 and 1% in pure water was measured as −1620 J/mol with a standard deviation of 20 J/mol.

The results of this work are given in Table II, with compositions given as the average weight fraction of water for addition of an increment of solution (calculated as though the sugar were not present) and the average weight fraction of xylose. The actual average weight fraction of water in the solution may be calculated as $W_w(1 - W_x)$. The third column lists differential enthalpies of mixing of small amounts of 50% aqueous xylose solution with larger amounts of xylose, ethanol, and water. Smoothed values of the partial molar excess enthalpy of water in ethanol + water mixtures (*1*) are listed in the fourth column. These values were multiplied by the molar ratio of water to xylose in the 50% solution (8.3335) and subtracted from the differential enthalpy of mixing and the enthalpy of dilution in pure water to obtain values for the enthalpy of transfer of xylose from infinite dilution in water to the solution of xylose, ethanol, and water ($\bar{H}_x - \bar{H}_{x,w}$). These values may be added to the standard enthalpy of solution of anhydrous xylose (15.2 kJ/mol) to obtain the differential enthalpy of solution of xylose in the specified solution ($\bar{H}_x - \bar{H}_{x,s}$).

Uncertainties in calculated values of $\bar{H}_x - \bar{H}_{x,w}$ range from about 0.4 kJ/mol for solutions with less than 3% water to 0.1 kJ/mol for solutions with more than 10% water.

As was observed for glucose, the differential enthalpy of solution of xylose in ethanol is decreased by addition of either water or sugar. Standard enthalpies of solution of the sugars at infinite dilution in ethanol + water mixtures were obtained by

Table III. Standard Enthalpies of Solution of Glucose and Xylose in Ethanol + Water Mixtures at 45 °C

% water	ΔH°, kJ/mol glucose	ΔH°, kJ/mol xylose
0	30.2 ± 0.2	30.4 ± 0.4
2		29.9 ± 0.4
5	29.1 ± 0.2	29.4 ± 0.3
10	27.9 ± 0.2	28.0 ± 0.3

linear extrapolations of the data for sugar concentrations below 1% and are listed in Table III. There is remarkable agreement between the values for the two sugars in ethanol-rich mixtures, within experimental uncertainty, though the values for xylose are consistently about 0.2 kJ/mol greater than those for glucose. The effect of added water on the differential enthalpy of solution of these sugars is essentially the same, while the effect of added sugar is significantly greater for glucose than for xylose.

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Vapor–Liquid Equilibrium of Ethanol/Water/*N*,*N*-Dimethylformamide

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The low-pressure isothermal vapor–liquid equilibrium of ethanol/water/*N*,*N*-dimethylformamide (DMF) at 85 and 90 °C has been measured. The main finding is that the addition of DMF breaks the ethanol/water azeotrope. In ethanol-rich mixtures containing 30–70 mol % DMF, the lowest relative volatility of ethanol to water is 1.3 and this occurs at infinite dilution of water in ethanol. This suggests that ethanol and water can easily be separated by extractive distillation using DMF. A comparison with our ternary data is made of the predictions of the UNIFAC and a recently proposed solute aggregation activity coefficient model using parameters obtained from binary data.

Introduction

Recent work at the University of Delaware and the Technical University of Berlin has indicated that *N*,*N*-dimethylformamide (DMF) can be used to affect the relative volatility of polar organic mixtures (*1*). DMF is a Lewis base, and previous studies have shown that the phase behavior of solutions containing DMF are influenced by its chemically basic behavior (*2*). Since water is a stronger Lewis acid than are alcohols, we anticipated that DMF would selectively lower the vapor pressure of water in solutions with alcohols. Thus, if water is the less volatile component, the addition of DMF should increase the relative volatility of the alcohol with respect to water and, therefore, make the separation by distillation easier. In this work we have studied the vapor–liquid equilibrium of the ethanol/water/DMF mixture, because of the widespread use of ethanol as a fuel and solvent.

Experiments

DMF is embryotoxic to laboratory animals and should not be inhaled or allowed to contact skin. Since DMF is such a good solvent, care must be exercised in the choice of materials which contact it.

Table I. VLE Data at 85.00 and 90.00 °C for Ethanol (1)/Water (2)/DMF (3)

T, °C	x_{DMF}[a]	x_1[b]	y_1[b]	y_{DMF}	y_1x_2/y_2x_1	P, kPa
			$x_{DMF} \cong 0.50$			
85	0.4954	0.0306	0.1029	0.1382	3.67	37.15
85	0.5049	0.1202	0.2634	0.1116	2.62	41.90
85	0.5191	0.2511	0.4337	0.0948	2.28	46.40
85	0.4947	0.4121	0.5874	0.0639	2.03	54.45
85	0.5108	0.5600	0.6991	0.0448	1.83	56.74
85	0.5024	0.5608	0.7021	0.0520	1.85	56.88
85	0.5169	0.6165	0.7423	0.0522	1.79	58.86
85	0.5136	0.6781	0.7885	0.0502	1.77	64.45
85	0.4784	0.7871	0.8564	0.0408	1.61	*c*
90	0.545	0.748	0.830	0.0749	1.64	70.24
90	0.526	0.779	0.850	0.0672	1.61	66.30
90	0.520	0.827	0.880	0.0702	1.53	73.26
90	0.515	0.910	0.935	0.0665	1.42	74.68
90	0.505	0.945	0.961	0.0663	1.43	75.11
			Ethanol/Water ≅ 4/1			
90	0.3169	0.8001	0.8390	0.0054	1.30	105.2
90	0.4164	0.7898	0.8457	0.0307	1.46	88.60
90	0.5650	0.7872	0.8514	0.0946	1.55	65.58
90	0.7114	0.7862	0.8526	0.2037	1.57	45.05
			Ethanol/Water ≅ 9/1			
90	0.3146	0.8909	0.9196	0.0044	1.40	106.89
90	0.5202	0.8987	0.9238	0.0672	1.37	74.17
90	0.6171	0.8994	0.9224	0.1174	1.33	60.09
90	0.7361	0.8892	0.9141	0.2186	1.33	43.36
			Ethanol/Water ≅ 18/1			
90	0.328	0.943	0.953	0.0087	1.23	106.2
90	0.408	0.947	0.957	0.0290	1.25	91.97
90	0.526	0.943	0.957	0.0705	1.35	74.12
90	0.628	0.940	0.957	0.1279	1.42	58.92
90	0.633	0.942	0.957	0.1243	1.37	59.52

[a] Ternary. [b] DMF-free basis. [c] Pressure inadvertently not recorded for this point.

The experimental procedures, equipment, and analytical methods used have been discussed in an earlier paper (*1*). High-purity Aldrich gold-label DMF was used and required no further purification, but as it is very hygroscopic it was not contacted with air. The water used was filtered, distilled, and deionized, and gave vapor pressures that agreed to within ±0.05 kPa with literature values (*3*). Punctilious ethanol from National Distillers required no further purification. The gas chromatograph was calibrated for ternary mixtures by using previously described techniques (*1*), and measured phase compositions are accurate and reproducible to within ±0.003 mole fraction. To ensure approximately constant mole fractions of DMF in the liquid phase, all experimental data were measured from separate gravimetrically prepared solutions. Thus, the still

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