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Registry No. CO_2, 124-38-9; C_2H_6, 74-84-0; anisole, 100-66-3; benzaldehyde, 100-52-7; 1-methylnaphthalene, 90-12-0; tetralin, 119-64-2.

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Excess Molar Enthalpies for Binary Liquid Mixtures of Furfural with Some Aliphatic Alcohols

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Excess molar enthalpies, H_m^E, for the binary liquid mixtures of furfural with some alphatic alcohols, viz., methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, have been determined at 308.15 K. The H_m^E values for all the binary mixtures studied are positive over the entire range of composition. At equimolar concentration, the H_m^E follows the order methanol < ethanol < 1-propanol < 2-propanol < 1-butanol < 2-butanol. Partial molar excess enthalpies have also been computed from the H_m^E data, and the results are discussed in the light of molecular interactions.

Introduction

The thermodynamic properties of binary liquid mixtures containing a self-associated component exhibit significant deviation from ideality arising not only from differences in molecular size but also from the changes related to the nature and extent of hydrogen bonding and molecular interactions between the like and unlike molecules. The ability of component molecules to form hydrogen bonding and interactions of dipolar origin have a marked effect on the enthalpies of mixing (*1*, *2*). In continuation of earlier investigations on thermodynamic properties of binary liquid mixtures containing a self-associated component (*3*–*5*), excess molar enthalpies for the binary mixtures of furfural with six aliphatic alcohols, namely, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol, have been determined at 308.15 K over the entire composition range, and the results are reported in this paper. These studies are aimed at providing information on the binary mixtures with a view to understanding the nature of intermolecular interactions present.

Experimental Section

Laboratory reagent grade 1-propanol and 2-propanol supplied by BDH (India) and analytical reagent grade 1-butanol and 2-butanol supplied by E. Merck were purified as described below (*6*). The alcohols were refluxed over freshly ignited calcium oxide for about 8 h. The material was decanted and refluxed over magnesium turnings for about 4 h and then distilled by use of a 1-m-long column. Spectroscopic grade samples of methanol and ethanol supplied by Fluka were used as such without any further purification treatment. The sample of furfural was essentially the one used in earlier studies (*7*). The liquids were stored in brown glass bottles and fractionally distilled by use of a column of 15 theoretical plates immediately before use. The densities and refractive indexes of the purified liquids (Table I) agreed closely with accepted literature values (*6*, *8*–*10*).

Table I. Densities and Refractive Indexes of Liquids at 298.15 K

	density/g cm^{-3}		refract. index	
liquid	this work	lit.	this work	lit.
furfural	1.154 93	1.154 5 (8)	1.5239	1.5234 (*8*)
methanol	0.786 69	0.786 63 (*9*)	1.3261	1.3265 (*10*)
ethanol	0.785 18	0.785 17 (*9*)	1.3586	1.3594 (*10*)
1-propanol	0.799 62	0.799 87 (*9*)	1.3843	1.3837 (*10*)
2-propanol	0.781 19	0.781 26 (*6*)	1.3746	1.3752 (*10*)
1-butanol	0.806 26	0.806 03 (*9*)	1.3981	1.3973 (*10*)
2-butanol	0.802 72	0.802 60 (*6*)	1.3963	1.3950 (*10*)

Molar excess enthalpies were determined by use of an LKB microcalorimeter (Model 2107). Details of the calorimeter and the experimental method have been described elsewhere (*11*). The temperature of the calorimeter was kept constant to within ±0.005 K by circulating water from a thermostat maintained at 308.15 ± 0.002 K by using a Tronac precision temperature controller. The data points reported in this paper were obtained within ±0.005 K of the reported temperature, which was measured with a precalibrated platinum resistance thermometer coupled with a Leeds and Northrup Miller bridge. The technique and calibration were periodically checked by determining the excess molar enthalpies for the binary mixtures of *n*-hexane and cyclohexane. Our results were always within ±5 J mol^{-1} of the results reported by Ewing and Marsh (*12*).

Results and Discussion

The H_m^E values for the binary mixtures studied are summarized in Table II and are shown graphically as a function of the mole fraction of furfural, *x*, in Figure 1. Each set of experimental values were fitted to a smoothing equation of the type

$$H_m^E = x(1 - x)[A_0 + A_1(1 - 2x) + A_2(1 - 2x)^2 + A_3(1 - 2x)^3] \qquad (1)$$

where A_i's are adjustable parameters. Values of these parameters were determined by the least-squares methods and are presented in Table III, along with the standard deviation $\sigma(H_m^E)$. Since $\sigma(H_m^E)$ values for all the systems studied are less

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Table II. Excess Molar Enthalpies, H_m^E, for the Binary Mixtures at 308.15 K

x	H_m^E/J mol^{-1}	x	H_m^E/J mol^{-1}
	(x)Furfural + (1 − x)Methanol		
0.1352	324	0.6204	878
0.2012	475	0.7175	783
0.2903	647	0.7822	669
0.3884	789	0.8610	476
0.5148	893	0.9061	334
	(x)Furfural + (1 − x)Ethanol		
0.1648	691	0.6313	1197
0.2063	832	0.7348	1019
0.3002	1076	0.8013	835
0.4348	1247	0.8554	643
0.5260	1266	0.8862	513
	(x)Furfural + (1 − x)1-Propanol		
0.1487	745	0.5242	1552
0.2172	1021	0.6813	1326
0.3348	1376	0.7620	1088
0.4147	1518	0.8286	818
0.4865	1559	0.9079	463
	(x)Furfural + (1 − x)1-Butanol		
0.1401	809	0.5453	1709
0.2216	1182	0.6670	1528
0.2803	1398	0.8003	1083
0.3742	1609	0.8676	763
0.4741	1723	0.9214	484
	(x)-Furfural + (1 − x)2-Propanol		
0.1625	844	0.5947	1583
0.1778	906	0.6562	1472
0.2261	1087	0.7503	1211
0.3417	1459	0.8487	796
0.4973	1662	0.9134	502
	(x)Furfural + (1 − x)2-Butanol		
0.1452	825	0.5754	1731
0.2361	1239	0.6884	1513
0.2984	1457	0.7662	1232
0.3648	1643	0.8203	1008
0.4663	1763	0.8912	635

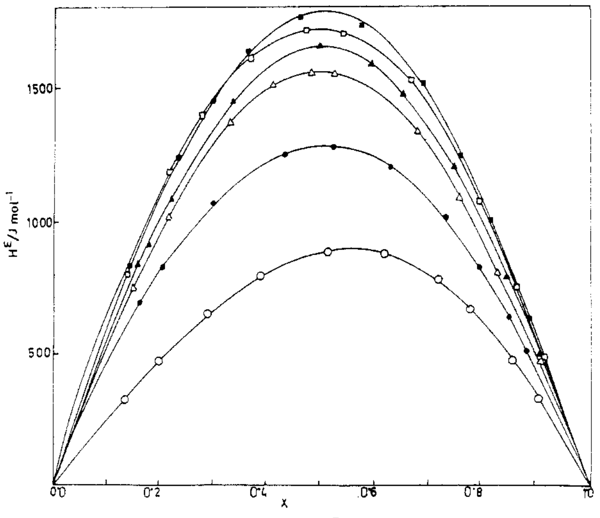

Figure 1. Molar excess enthalpies, H_m^E, for binary mixtures of furfural with aliphatic alcohols at 308.15 K: ○, methanol; ●, ethanol; △, 1-propanol; ▲, 2-propanol; □, 1-butanol; ■, 2-butanol.

than the estimated experimental uncertainty, the constants of eq 1 can be taken to represent the experimental results.

The partial molar excess enthalpies of the alcohols ($\bar{H}_1^E$) and that of the furfural ($\bar{H}_2^E$) for the binary mixtures were computed by using the parameters A_i from the expressions

$$\bar{H}_1^E = H_m^E - x(\partial H^E/\partial x)_{P,T,n_i} \quad (2)$$

$$\bar{H}_2^E = H_m^E - (1 - x)(\partial H^E/\partial x)_{P,T,n_i} \quad (3)$$

Table III. Parameters A_i (J mol^{-1}) and Standard Deviation $\sigma(H_m^E)$ for the Least-Square Representations of H_m^E for the Binary Mixtures at 308.15 K by Eq 1

mixture	A_0	A_1	A_2	A_3	σ
furfural + methanol	3550	899	−339	−196	6
furfural + ethanol	5109	188	27	−240	11
furfural + 1-propanol	6250	−41	−906	−150	7
furfural + 2-propanol	6588	−7	−755	346	13
furfural + 1-butanol	6918	−113	−379	176	9
furfural + 2-butanol	7131	−75	−905	−111	10

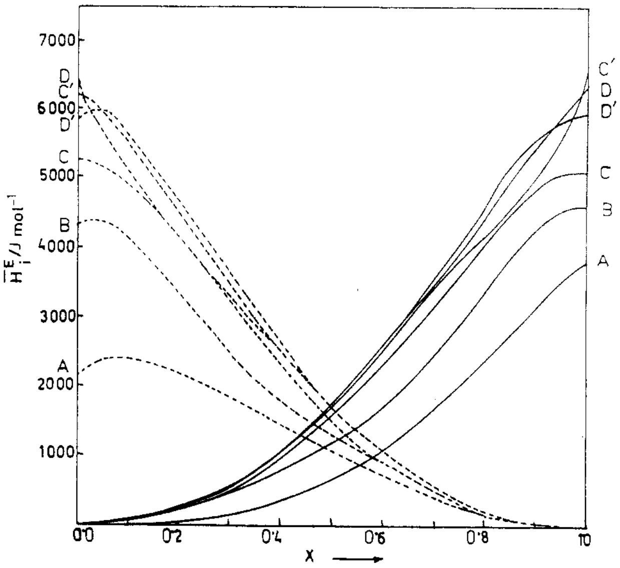

Figure 2. Partial molar excess enthalpies of furfural ($\bar{H}_2^E$) and aliphatic alcohols ($\bar{H}_1^E$) in binary mixtures at 308.15 K (alcohols, solid lines; furfural, dashed lines). A, methanol; B, ethanol; C, 1-propanol; C′, 2-propanol; D, 1-butanol; D′, 2-butanol.

The variations of $\bar{H}_1^E$ and $\bar{H}_2^E$ with composition are shown in Figure 2.

It is observed from Figure 1 that the mixing process for all the binary mixtures under investigation are endothermic and the plots of H_m^E versus x are nearly symmetrical to the composition axis, the maxima being in the composition range x = 0.45–0.55. The excess molar enthalpies at equimolar concentration, $H_m^E{}_{0.5}$, for the binary mixtures follow the order methanol < ethanol < 1-propanol < 2-propanol < 1-butanol < 2-butanol. There is no available data in the literature for the excess enthalpies of the binary mixtures under investigation to compare with our results.

The heat effects in the binary systems under consideration are composed of (i) a positive component arising from the breaking up of self-associated alcohol aggregates, (ii) a positive component arising from the rupture of dipole–dipole interactions in furfural, and (iii) a negative component arising from the intermolecular interactions between alcohols and furfural. The high positive H_m^E values for the binary mixtures reveal that the enthalpy changes accompanying the structure breaking of polymer aggregates of alcohol and furfural are predominant in determining the excess enthalpies in these systems.

It is observed, from Figure 1, that there is a marked difference in $H_m^E{}_{0.5}$ values in going from methanol ($H_m^E{}_{0.5}$ = 900 J mol^{-1}) to ethanol ($H_m^E{}_{0.5}$ = 1300 J mol^{-1}) to higher alcohols ($H_m^E{}_{0.5}$ = 1700 J mol^{-1}). It is also observed, from Figure 2, that the values of $\bar{H}_2^E$ at the alcohol-rich end and $\bar{H}_1^E$ at the furfural-rich end are smaller for methanol solutions than for those containing other alcohols. These results are indicative of a relatively lower degree of deassociation of methanol aggregates and a strong intermolecular interaction between methanol and the proton-accepting carbonyl group of furfural resulting in the formation of a hydrogen bond of the type $-O—H\cdots O{=}C<$. The hydrogen-bonding interactions would be relatively weak in the systems containing higher and branched chain alcohols for steric reasons (*13*–*15*). Also, the degree of deassociation of alcohol aggregates in these systems would be higher. In view of this, the positive contributions to the excess enthalpies associated with structure breaking of alcohols and furfural aggregates, which occurs as a consequence of their mixing, outweigh the negligibly small negative contribution arising from the interaction between alkanol and furfural molecules. A similar conclusion was drawn from the studies on the volumetric behavior of these binary mixtures (*16*).

Glossary

H_m^E	excess molar enthalpy, J mol^{-1}
x	mole fraction of furfural
A_i	constants in eq 1, J mol^{-1}
$\sigma(H_m^E)$	standard deviation of the least-squares fit, J mol^{-1}
$\bar{H}_i^E$	partial molar excess enthalpies, J mol^{-1}
P	pressure, bar
T	temperature, K
$H_{m\,0.5}^E$	excess molar enthalpy at equimolar concentration, J mol^{-1}

Registry No. Furfural, 98-01-1; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-butanol, 78-92-2.

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Solubility of Ethane in *n*-Hexane at Pressures to 5.4 MPa and Temperatures from 311 to 394 K

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Solubility data are presented for ethane in *n*-hexane at temperatures from 311 to 394 K (100 to 250 °F) at pressures to 5.4 MPa (780 psia). These data are in significant disagreement with the earlier measurements of Zais and Silberberg. The new data can be described with average deviations of less than 0.001 mole fraction by the Soave–Redlich–Kwong or Peng–Robinson equations when two interaction parameters per isotherm are used in the equation.

Introduction

As part of our work on the solubilities of ethane in *n*-paraffin solvents (*1*, *2*), we observed that the literature data on the solubility of ethane in *n*-hexane (*3*) appears to be inconsistent with similar data for ethane in higher and lower carbon number *n*-paraffin solvents. This inconsistency became apparent during our investigations of generalized parameter equation-of-state (EOS) representations (*4*, *5*) of such systems. Oellrich et. al (*6*) have reported similar inconsistencies. As a result, we decided to perform additional measurements on ethane + *n*-hexane.

Experimental Details

The apparatus and procedures were identical with those described previously (*7*). Estimated uncertainties in experimental measurements are 0.1 K in temperature and less than 0.002 in mole fraction. The uncertainty in the measured bubble-point pressure depends on the steepness of the *p*–*x* relation and is on the order of 25 kPa (4 psia) in the present work.

The ethane employed in this work had a stated purity of 99.9+ mol % and was supplied by Matheson. The *n*-hexane was from Aldrich Chemical Company with a quoted purity of 99+ mol %. Both were used without further purification.

Table I. Solubility of Ethane in *n*-Hexane

mole fracn of ethane	pressure		mole fracn of ethane	pressure	
	MPa	psia		MPa	psia
310.9 K (37.8 °C, 100 °F)					
0.095	0.393	57.0	0.403	1.689	245.0
0.136	0.552	80.1	0.503	2.164	313.8
0.163	0.600	95.7	0.522	2.257	327.3
0.206	0.834	121.0	0.552	2.401	348.3
0.259	1.057	153.3	0.602	2.657	385.4
0.288	1.178	170.8	0.610	2.699	391.4
0.347	1.429	207.3	0.652	2.914	422.7
0.373	1.560	226.3			
338.7 K (65.6 °C, 150 °F)					
0.072	0.463	67.1	0.392	2.372	344.0
0.107	0.642	93.1	0.442	2.717	394.0
0.201	1.180	171.1	0.499	3.119	452.4
0.204	1.200	174.0	0.520	3.268	474.0
0.301	1.787	259.2	0.564	3.590	520.7
0.352	2.116	306.9			
366.5 K (93.3 °C, 200 °F)					
0.109	0.958	138.9	0.300	2.428	352.1
0.111	0.964	139.8	0.306	2.471	358.4
0.112	0.982	142.4	0.310	2.507	363.6
0.202	1.659	240.6	0.382	3.121	452.6
0.203	1.643	238.3	0.397	3.254	471.9
0.208	1.690	245.1			
394.3 K (121.1 °C, 250 °F)					
0.076	1.051	152.5	0.309	3.256	472.3
0.108	1.333	193.3	0.358	3.772	547.1
0.162	1.819	263.8	0.401	4.223	612.5
0.199	2.157	312.9	0.407	4.309	625.0
0.251	2.672	387.6	0.504	5.399	783.0
0.307	3.236	469.3			

Results

The experimental results appear in Table I. Comparison with the data of Zais and Silberberg appears in Figure 1. This comparison is shown in terms of deviations of their measured