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Excess Molar Enthalpies of Tetrahydrofuran or Diisopropyl Ether + 1-Alkanols at 298.15 K, Using a Newly Designed Flow Mixing Cell for an Isothermal Microcalorimeter

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Excess molar enthalpies for the binary mixtures {tetrahydrofuran (THF) + 1-propanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, and + 1-decanol} and {diisopropyl ether (DIPE) + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, and + 1-decanol} at 298.15 K are reported. These measurements were made using a newly designed flow-mixing cell for an isothermal microcalorimeter (Calorimetry Sciences Corporation, UT). The performance of this cell was evaluated through the measurement of the excess molar enthalpies of {cyclohexane + hexane} and {water + acetone or methanol} at 298.15 K. The comparison between these results and reliable literature data shows that the newly designed flow-mixing cell is trustworthy and produces good quality data.

Introduction

The thermodynamic behavior of mixtures composed by an ether and an alcohol has attracted much attention.[1−9] The excess thermodynamic properties for these mixtures have three main contributions, namely (i) the dissociation of the alcohol multimers upon mixing, (ii) the formation of an alcohol−ether complex through H-bonding between the oxygen atom in the ether and the acid proton in the alcohol, and (iii) the so-called physical contributions. Therefore, alcohol + ether are good candidates for testing the performance of several association models.[10−14] From the industrial point of view, tertiary ethers (such as diisopropyl ether, used in this work) are very important because they are blending agents for gasoline due to their nontoxic, nonpolluting, and high octane number characteristics. In addition, ether + alcohol mixtures are also industrially relevant because alkanols are basic components in the synthesis of ethers and therefore are always contained as an impurity. In an effort to contribute to the accumulation of high quality thermodynamic data for ether + alcohol binary mixtures, in this work we report the excess molar enthalpies H^E for the following mixtures: {tetrahydrofuran (THF) + 1-propanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, and + 1-decanol} and {diisopropyl ether (DIPE) + methanol, + ethanol, + 1-propanol, + 1-butanol, + 1-pentanol, + 1-hexanol, + 1-heptanol, + 1-octanol, + 1-nonanol, and + 1-decanol} at 298.15 K. These measurements were done using a newly designed flow-mixing cell for an isothermal microcalorimeter from Calorimetry Sciences Corporation (CSC, UT). Given this situation, it was first necessary to test the performance of this new cell. This test consisted in the measurement of the excess molar enthalpies for {cyclohexane + hexane} and {water + acetone and + methanol} at 298.15 K. These mixtures were selected because reliable literature data are available for comparison, and they allow us to test the new cell with exothermic, endothermic, and S-shaped excess molar enthapies.

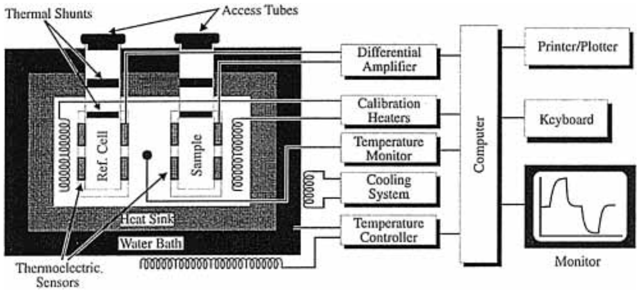

Figure 1. General setup of the 4400 isothermal microcalorimeter (Calorimetry Sciences Corporation, UT).

Experimental Section

Materials. The substances were obtained from Sigma-Aldrich and J. T. Baker (DIPE and acetone). The purity was at least 99% (except for 1-heptanol, 1-nonanol, and 1-decanol, whose purity was 98%). All substances were used without further purification, but they were dried with molecular sieves (Merck 0.4 nm) and degassed by means of an ultrasonic bath. Water was doubly distilled and deionized. The densities at 298.15 K of the pure components used in this work were (in $g\cdot cm^{-3}$) 0.997 05 for water, 0.773 89 for cyclohexane, 0.654 84 for *n*-hexane, 0.784 40 for acetone, 0.718 54 for diisopropyl ether, 0.786 37 for

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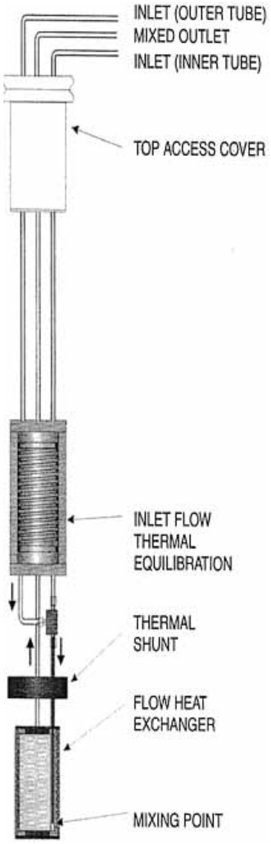

Figure 2. Newly designed 4442 flow-mixing cell (Calorimetry Sciences Corporation, UT).

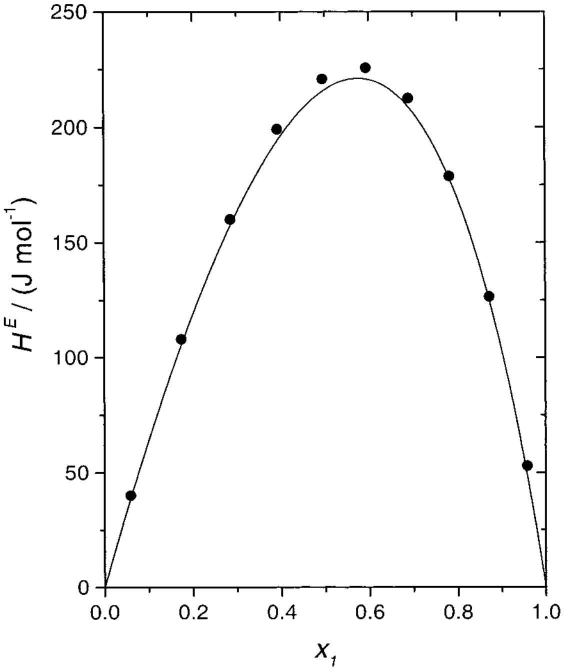

Figure 3. Experimental molar excess enthalpy H^E at 298.15 K for cyclohexane (1) + hexane (2) determined at a total flow rate of 0.20 cm^3·min^{-1}. The curve is the result from ref 16.

methanol, 0.784 93 for ethanol, 0.799 60 for 1-propanol, 0.805 78 for 1-butanol, 0.810 96 for 1-pentanol (all from ref 15), 0.881 93 for tetrahydrofuran, 0.815 20 for 1-hexanol, 0.818 75 for 1-heptanol, 0.821 58 for 1-octanol, 0.824 23 for 1-nonanol, and 0.826 44 for 1-decanol, measured with an Anton Paar densimeter (model DMA) operated in the static mode and capable of a precision of better than 10^{-5} g·cm^{-3}.

Table 1. Experimental Excess Molar Enthalpies H^E at 298.15 K and Their Relative Error for Three Test Systems

x_1	H^E / J·mol^{-1}	% error[a]	x_1	H^E / J·mol^{-1}	% error[a]
Cyclohexane (1) + Hexane (2)					
Total Flow Rate = 0.20 cm^3·min^{-1}					
0.059	40.0	1.07	0.594	225.6	0.35
0.174	107.9	0.62	0.690	212.4	0.32
0.285	160.0	0.50	0.782	178.8	0.29
0.392	199.1	0.38	0.872	126.5	0.49
0.495	220.7	0.38	0.958	52.9	2.06
Water (1) + Acetone (2)					
Total Flow Rate = 0.20 cm^3·min^{-1}					
0.176	314.1	0.31	0.730	−572.7	0.37
0.311	194.8	0.42	0.802	−637.4	0.29
0.417	17.0	3.18	0.859	−628.3	1.37
0.504	−159.1	0.70	0.904	−557.5	0.36
0.575	−304.3	0.37	0.942	−410.7	0.85
0.635	−421.5	0.36	0.973	−225.3	0.76
Total Flow Rate = 0.40 cm^3·min^{-1}					
0.094	243.5	0.34	0.635	−419.0	0.33
0.176	303.5	0.33	0.709	−533.6	0.32
0.248	265.6	0.32	0.768	−602.0	0.29
0.311	207.3	0.43	0.883	−594.8	0.30
0.367	119.0	0.59	0.924	−482.0	0.42
0.417	21.8	1.80	0.966	−270.8	0.32
0.463	−70.0	0.48	0.987	−112.8	0.74
0.503	−143.1	0.49	0.994	−49.4	0.43
0.574	−289.0	0.39			
Water (1) + Methanol (2)					
Total Flow Rate = 0.20 cm^3·min^{-1}					
0.105	−283.8	0.41	0.732	−879.5	0.29
0.283	−581.5	0.32	0.806	−811.8	0.28
0.427	−737.7	0.32	0.899	−572.8	0.28
0.546	−828.5	0.29	0.977	−161.8	0.46
0.646	−882.8	0.29			
Total Flow Rate = 0.40 cm^3·min^{-1}					
0.054	−152.1	0.31	0.770	−849.6	0.31
0.199	−461.0	0.29	0.855	−711.0	0.33
0.358	−670.0	0.29	0.927	−442.9	0.49
0.458	−770.2	0.28	0.989	−75.6	1.62
0.598	−860.6	0.29			

[a] Calculated as $100(s(P)/P + A)$, where P is the mean value of the calorimeter signal when it is stable (in μW) and $s(P)$ is its standard deviation. The value for $A = 0.0027$ was calculated from the pump calibrations.

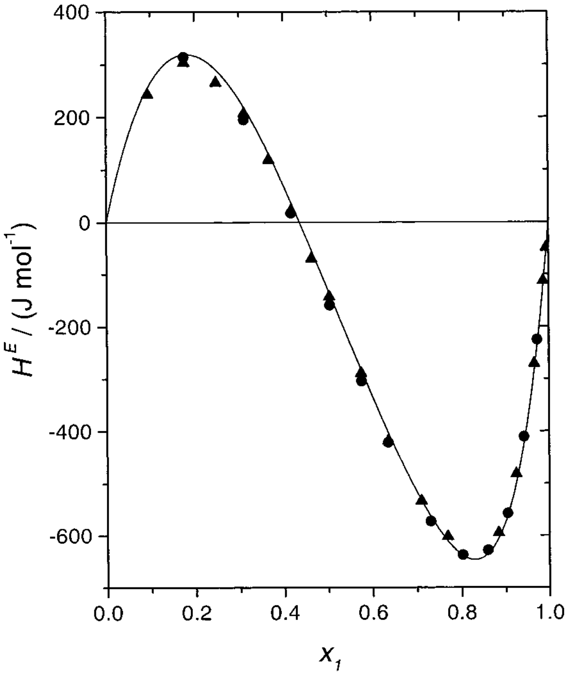

Figure 4. Experimental molar excess enthalpy H^E at 298.15 K for water (1) + acetone (2) determined at two total flow rates: 0.20 cm^3·min^{-1} (●) and 0.40 cm^3·min^{-1} (▲). The curve is the result from ref 17.

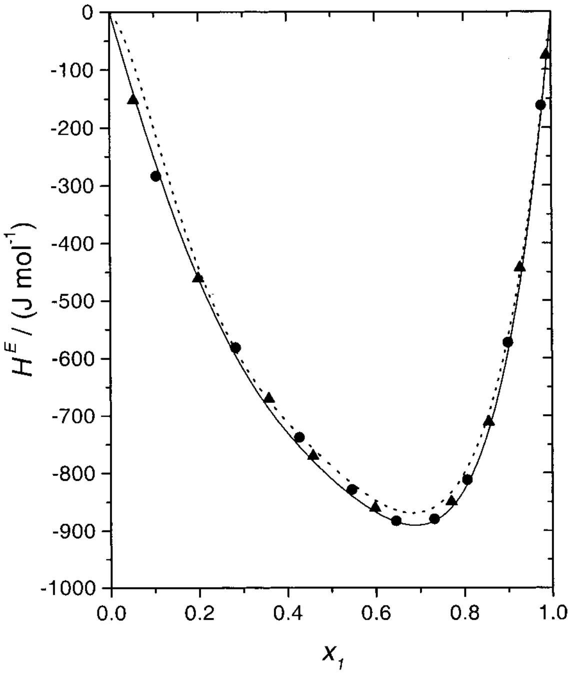

Figure 5. Experimental molar excess enthalpy H^E at 298.15 K for water (1) + methanol (2) determined at two total flow rates: 0.20 $cm^3 \cdot min^{-1}$ (●) and 0.40 $cm^3 \cdot min^{-1}$ (▲). Full and dotted curves are the results from refs 18 and 19, respectively.

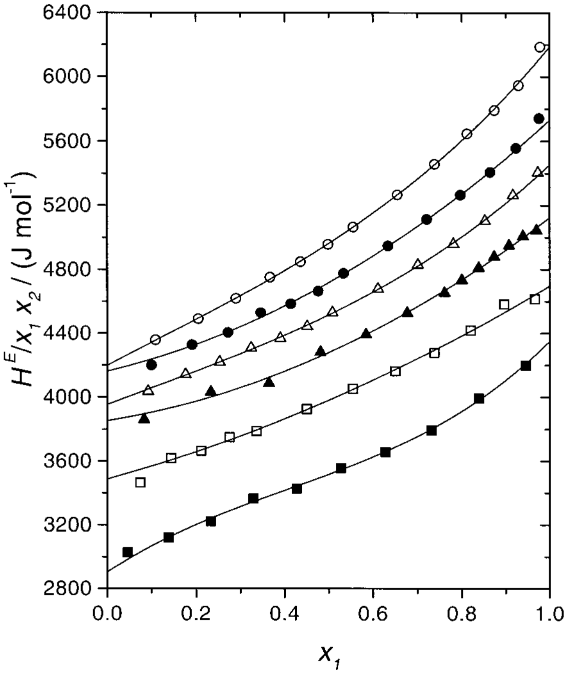

Figure 6. Experimental H^E/x_1x_2 at 298.15 K for THF (1) + 1-propanol (■), 1-hexanol (□), 1-heptanol (▲), 1-octanol (Δ), 1-nonanol (●), or 1-decanol (○).

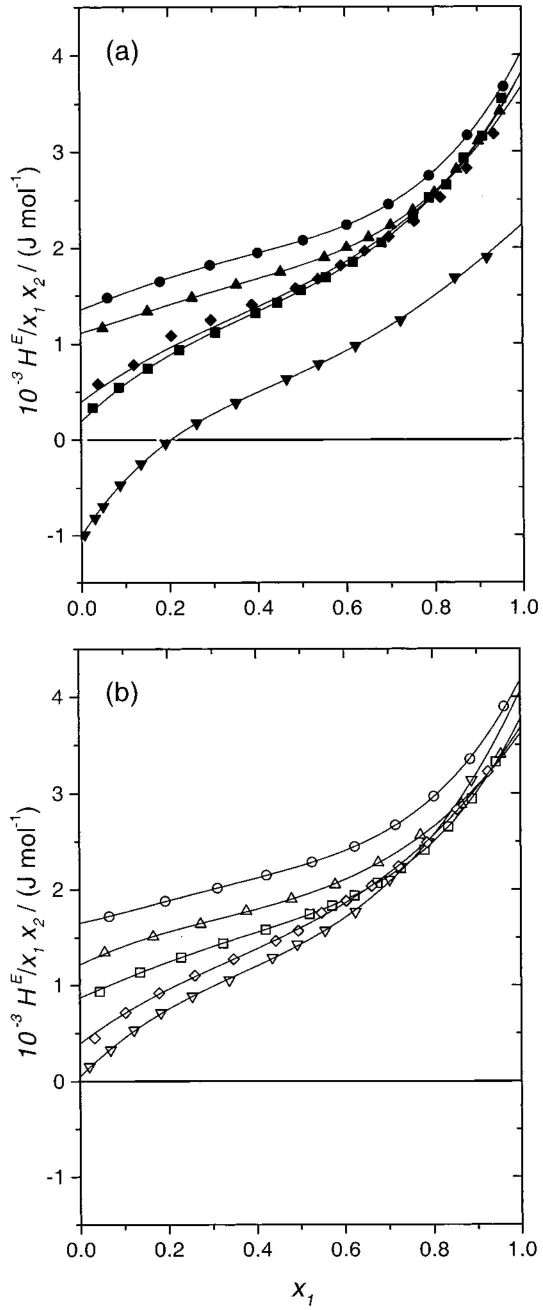

Figure 7. Experimental H^E/x_1x_2 at 298.15 K for (a) DIPE (1) + methanol (▼), + 1-propanol (■), + 1-pentanol (◆), + 1-heptanol (▲) and + 1-nonanol (●) and for (b) DIPE (1) + ethanol (∇), + 1-butanol (◇), + 1-hexanol (□), + 1-octanol (Δ), and + 1-decanol (○).

Apparatus and Procedures. Excess molar enthalpies were determined using a 4400 isothermal microcalorimeter (CSC, UT) with a newly designed 4442 flow-mixing assembly kit (CSC, UT). A diagram of the general setup of the calorimeter is shown in Figure 1. The measuring unit is a large aluminum heat sink incorporating a test well. The heat produced or absorbed by any process occurring in the test well is exchanged with the heat sink that is kept at a constant temperature. A heat change occurring in a sample creates a temperature difference between the sample and the heat sink. The thermoelectric sensors, located between the sample and the aluminum block, generate a voltage that is proportional to the temperature gradient across the sensors. This temperature gradient is directly dependent on the heat flux. A reference cell is used to correct for electronic noise and any heat flux due to temperature fluctuations in the heat sink. The differential signal from the twin calorimeter test wells, sample and reference, corresponds to the rate of heat production from the sample itself. The newly designed flow-mixing cell is shown in Figure 2. Mixing is achieved at the mixing point using a concentric tube consisting of an inner tube inlet and an outer tube inlet. During an experiment, the denser of the two fluid components must be introduced through the inner tube inlet to ensure proper mixing. For optimal performance, a total flow rate between (0.1 and 0.5)

Table 2. Experimental Excess Molar Enthalpies H^E at 298.15 K and Their Relative Error for THF (1) and DIPE (1) + 1-Alkanol (2) Mixtures[a]

x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]
THF + 1-Propanol											
0.046	132.9	0.57	0.329	742.9	0.32	0.628	854.5	0.30	0.838	542.1	0.30
0.138	371.4	0.29	0.427	838.9	0.61	0.732	744.4	0.30	0.945	218.2	0.42
0.233	576.0	0.52	0.527	886.8	0.35						
THF + 1-Hexanol											
0.074	237.5	1.48	0.275	747.7	0.62	0.554	1001.6	0.31	0.820	652.3	0.40
0.144	446.0	0.84	0.336	845.6	0.49	0.650	947.2	0.40	0.896	427.1	0.51
0.211	610.2	0.64	0.450	971.9	0.31	0.738	827.1	0.37	0.966	151.6	0.41
THF + 1-Heptanol											
0.083	293.8	0.39	0.584	1067.2	0.30	0.800	757.4	0.30	0.907	417.6	0.30
0.233	720.5	0.36	0.677	990.1	0.33	0.838	653.0	0.28	0.939	286.9	0.43
0.364	946.1	0.58	0.761	846.4	0.33	0.873	541.1	0.33	0.970	146.8	0.42
0.481	1069.0	0.31									
THF + 1-Octanol											
0.092	337.2	0.67	0.390	1039.3	0.29	0.611	1112.1	0.30	0.852	643.5	0.29
0.176	600.5	0.36	0.451	1100.2	0.29	0.701	1012.3	0.32	0.916	405.0	0.31
0.253	797.5	0.41	0.508	1132.3	0.31	0.781	848.2	0.30	0.973	142.0	0.64
0.324	943.4	0.36									
THF + 1-Nonanol											
0.100	377.9	0.31	0.414	1112.2	0.30	0.634	1147.9	0.32	0.864	635.3	0.31
0.191	668.6	0.32	0.476	1163.4	0.29	0.721	1028.5	0.27	0.923	394.9	0.37
0.272	872.1	0.38	0.533	1188.7	0.33	0.797	851.8	0.30	0.976	134.5	0.73
0.346	1024.6	0.40									
THF + 1-Decanol											
0.109	423.2	0.68	0.436	1192.2	0.33	0.655	1190.0	0.33	0.874	637.8	0.28
0.205	731.8	0.39	0.498	1239.3	0.28	0.739	1052.6	0.30	0.929	392.2	0.38
0.290	950.8	0.40	0.555	1250.8	0.32	0.812	862.0	0.29	0.978	133.1	0.55
0.367	1103.8	0.37									
DIPE + Methanol											
0.007	−6.9*	1.37	0.135	−29.1	0.40	0.465	157.4	0.32	0.723	249.0	0.45
0.031	−24.6	0.57	0.191	−6.0	2.27	0.537	196.0	0.47	0.846	219.5	0.64
0.049	−32.4	0.31	0.261	33.0	0.36	0.621	230.2	0.38	0.919	141.2*	0.43
0.088	−37.7	0.28	0.350	87.1	0.37						
DIPE + Ethanol											
0.021	3.2	3.59	0.254	167.4	0.35	0.556	388.0	0.32	0.790	413.4	0.42
0.069	21.1	1.56	0.338	235.5	0.28	0.625	413.9	0.38	0.837	372.1*	0.37
0.122	57.0	0.31	0.436	317.0	0.37	0.703	438.5	0.41	0.888	311.7	0.29
0.137	71.2*	0.46	0.493	356.8	0.37	0.790	413.0*	0.30	0.942	194.1*	0.47
0.183	106.2	0.31									
DIPE + 1-Propanol											
0.027	8.8	0.54	0.395	315.6	0.36	0.616	438.1	0.35	0.828	378.0	0.37
0.086	43.1	0.39	0.445	352.6	0.50	0.681	446.7	0.39	0.868	335.7*	0.31
0.151	95.5	0.52	0.498	389.6	0.30	0.752	430.3	0.36	0.910	258.9	0.41
0.223	162.5	0.62	0.555	417.8	0.40	0.789	420.1*	0.29	0.954	156.0*	0.65
0.304	237.2	0.51									
DIPE + 1-Butanol											
0.033	14.4	0.65	0.348	289.5	0.36	0.604	449.8	0.32	0.787	417.3	0.35
0.103	66.0	0.64	0.444	361.4	0.41	0.662	455.1	0.35	0.855	351.0	0.47
0.179	134.7	0.31	0.495	392.6	0.35	0.723	448.4	0.38	0.925	223.6	0.84
0.260	211.7	0.41	0.548	434.9	0.38						
DIPE + 1-Pentanol											
0.039	21.8	2.12	0.387	333.4	0.35	0.643	452.0	0.31	0.814	382.4	0.40
0.120	82.7	1.01	0.486	393.3	0.31	0.698	446.5	0.35	0.874	311.0	0.57
0.205	176.8	0.42	0.537	416.3	0.30	0.755	421.3	0.29	0.936	190.5	1.00
0.294	259.1	0.49	0.589	439.0	0.33						
DIPE + 1-Hexanol											
0.045	40.2	1.80	0.421	385.8	0.40	0.675	453.3	0.41	0.835	365.6	0.46
0.136	133.6	0.84	0.521	435.9	0.32	0.728	439.5	0.38	0.889	290.5	0.55
0.229	228.5	0.52	0.572	448.4	0.41	0.781	412.5	0.42	0.944	175.8	0.32
0.324	315.7	0.47	0.623	454.9	0.36						
DIPE + 1-Heptanol											
0.050	55.4	2.23	0.452	432.6	0.45	0.702	468.1	0.37	0.851	356.8	0.46
0.151	171.5	0.73	0.552	469.5	0.39	0.752	446.1	0.35	0.901	277.3	0.57
0.252	278.6	0.67	0.602	480.5	0.37	0.801	410.5	0.49	0.950	162.4	0.90
0.352	367.6	0.44	0.652	478.8	0.36						

Table 2 (Continued)

x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]	x_1	H^E J·mol^{-1}	% error[b]
					DIPE + 1-Octanol						
0.056	71.1	1.72	0.377	417.2	0.34	0.677	497.9	0.33	0.865	336.7	0.32
0.166	209.2	0.78	0.480	474.3	0.39	0.772	451.4	0.29	0.955	146.1	1.01
0.273	326.1	0.59	0.579	499.6	0.39						
					DIPE + 1-Nonanol						
0.061	84.6	1.79	0.401	467.7	0.51	0.698	517.1	0.36	0.876	344.0	0.46
0.180	242.9	0.89	0.504	519.8	0.40	0.789	457.8	0.39	0.959	144.4	0.85
0.293	376.7	0.51	0.603	536.4	0.36						
					DIPE + 1-Decanol						
0.067	107.6	1.56	0.423	524.1	0.43	0.716	543.0	0.37	0.885	341.2	0.30
0.194	293.7	0.73	0.527	569.3	0.38	0.803	469.6	0.30	0.963	138.9	0.83
0.312	432.1	0.50	0.624	573.6	0.39						

[a] Measured at total flow rate = 0.2 cm^3·min^{-1} except when indicated (*), where the total flow rate 0.40 cm^3·min^{-1} was used. [b] See footnote in Table 1.

cm^3·min^{-1} is recommended. The calorimeter was calibrated electrically at 298.15 K by the addition, through built-in calibration heaters, of a constant rate of electrical energy. The detectors in the measuring unit give a voltage output proportional to the amount of energy flowing through them. Then, a heat rate per volt can be calculated. The calibration constant $K = (dq_e/dt)/(S_h - S_{bl})$ was calculated from the rate of electrical energy input dq_e/dt and the difference between the output signal with the calibration heater on (h) and off, that is the stable baseline (bl) signal, $(S_h - S_{bl})$. For any given mixing experiment, when the signal (S_m) (at times beyond the transient period) is significantly different from the stable baseline signal, the heat rate is given by $dq_m/dt = K(S_m - S_{bl})$. For all the measurements, as well as for the calibration, the temperature of the room was kept constant at (298 ± 1) K. The pure liquids were pumped into the calorimeter using two Series II digital HPLC pumps from SSI (Scientific Systems Inc.). Each pump was carefully calibrated using water for flow rates between (0.01 and 0.40) cm^3·min^{-1}. Considering the variation of room temperature (±1 K) during the calibration period, the error of the determination of the mass of pumped water (Mettler AT-250 with a 2×10^{-4} g precision), and the error in the measurement of the time elapsed for that amount of water to be pumped (±1 s), we have calculated that using these two pumps the error in the mole fraction is less than 0.5%. Using the densities for the pure components, the signals from the calorimeter, in microwatts, were transformed into the usual joule per mole units.

Table 3. Parameters A_j and Standard Deviations σ (Both in J·mol^{-1}) for Representation of Excess Molar Enthalpies H^E by Eq 1 for the Test Mixtures Cyclohexane (1) + Hexane (2) and Water (1) + Acetone (2) and + Methanol (2), and for THF (1) and DIPE (1) + 1-Alkanol (2) Mixtures at 298.15 K

	p[a]	A_1	A_2	A_3	A_4	A_5	σ
cyclohexane +							
hexane	10	883	261	96			1.96
water +							
acetone	29	−586	−4022	−608	−2486	−1824	6.73
methanol	18	−3195	−1562	−2243	−769		4.26
THF +							
1-propanol	10	3518	518	110	205		3.20
1-hexanol	12	3982	605	110			3.20
1-heptanol	13	4280	635	209			3.20
1-octanol	13	4516	676	188	74		4.02
1-nonanol	13	4719	785	227			1.49
1-decanol	13	4964	897	228	98		2.87
DIPE +							
methanol	14	703	1054	221	568	−301	1.83
ethanol	17	1429	1224	618	753		3.19
1-propanol	17	1552	1151	452	665		2.84
1-butanol	14	1603	1161	435	481		3.95
1-pentanol	14	1617	978	395	604		4.02
1-hexanol	14	1707	807	353	644	261	0.71
1-heptanol	14	1819	768	381	587	269	1.13
1-octanol	10	1928	743	489	458		2.28
1-nonanol	10	2075	693	368	646	249	1.10
1-decanol	10	2245	686	379	575	290	0.79

[a] Number of experimental points.

Results

Testing Systems. The molar excess enthalpies H^E for {cyclohexane + hexane}, {water + acetone}, and {water + methanol} at 298.15 K are given in Table 1 for one or two different total flow rates. As seen in Figures 4 and 5, the results are independent of flow rate, provided room temperature is kept constant and close to the measurement temperature. Table 1 also reports the relative error for each measurement. The main contributions to these relative errors are the standard deviation of the calorimetric signal and the error of the mole fraction determination. The H^E values for these three test systems are displayed in Figures 3–5, together with reliable results from the literature.[16–19] The comparisons shown in Figures 3–5 and the relative error in Table 1 indicate that the newly designed flow-mixing cell is trustworthy and produces good quality data.

Ether + 1-Alkanol Systems. The molar excess enthalpies H^E at 298.15 K for THF and DIPE mixed with a series of 1-alkanols are reported in Table 2 together with the relative error for each determination. The H^E data were represented by the Redlich–Kister (RK) equation:

$$H^E/\text{J·mol}^{-1} = x_1 x_2 \sum_{j=1} A_j (x_1 - x_2)^{j-1} \qquad (1)$$

where the ethers are component 1. The A_j parameters for all the mixtures studied here (including the three test systems) are given in Table 3, together with the corresponding standard deviations. The H^E/x_1x_2 data and their RK representations are displayed in Figures 6 and 7. For the THF case, H^E data are available in the literature for methanol,[3,6,20–22] ethanol,[3,6] 1-propanol,[3,6,11] 1-butanol,[3] and 1-pentanol.[3] The only common system is THF + 1-propanol, with our smoothed equimolar H^E (879 J·mol^{-1}) lying between those from refs 3 and 6 (946 and 933 J·mol^{-1}, respectively) and that from ref 11 (849 J·mol^{-1}). To our knowledge no other H^E measurements for THF or DIPE + 1-alkanols have been reported.

All the H^E values for THF + 1-alkanols (methanol to 1-decanol) are positive, nearly symmetrical, and consider-

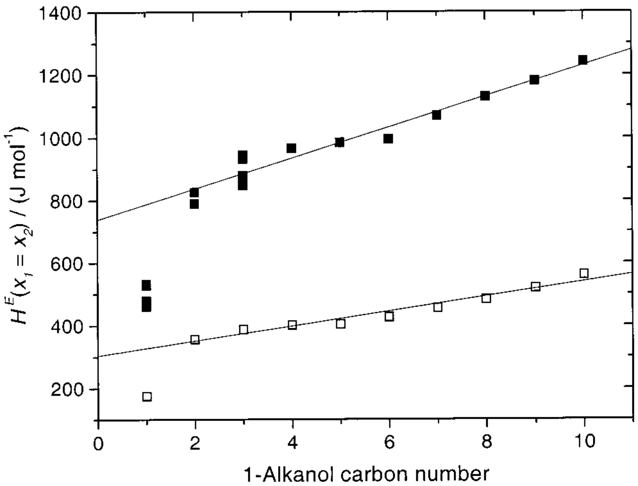

Figure 8. Experimental equimolar molar excess enthalpy H^E ($x_1 = x_2$) against 1-alkanol carbon number for 1-alkanol + THF (■) and + DIPE (□) mixtures. Lines are the linear fits to the data (ethanol to 1-decanol). Data for THF + methanol are from refs 3, 6, and 20−22, those for THF + ethanol are from refs 3 and 6, those for THF + 1-propanol are from refs 3, 6, and 11, and those for THF + 1-butanol and + 1-pentanol are from ref 3.

ably larger than those for the corresponding DIPE mixtures. For DIPE + 1-alkanols the H^E curves are asymmetrical, their maximum being displaced toward high ether concentration. For DIPE + methanol an S-shaped H^E curve was found, the negative H^E region occurring at low DIPE concentration. For both THF and DIPE, the H^E values increase in magnitude as the 1-alkanol chain length increases. At equimolar concentration, in going from ethanol and 1-decanol, this increase is linear with the 1-alkanol carbon number, as seen in Figure 8. The slope for the THF case is double (49.1 ± 3.5) J·mol^{-1} that for the DIPE case (23.7 ± 2.0) J·mol^{-1}. Methanol is, however, outside these linear trends, its experimental H^E values with THF (507 J·mol^{-1}, average of values in refs 3, 6, and 20−22) and with DIPE (176 J·mol^{-1}) being considerable lower than the values given by an extrapolation from the linear correlation (788 J·mol^{-1} for THF and 326 J·mol^{-1} for DIPE). The H^E data reported here possess contributions from the disruption of the self-association of the 1-alkanols in the pure state, from the ether−alkanol complex formation via H-bonding, and from the so-called physical contributions. To model and understand in more detail these contributions, it is necessary to obtain information on other excess thermodynamic properties such as the excess volumes V^E and the excess heat capacities C_p^E, whose measurements are currently underway.

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