

Excess Molar Enthalpies of Propanone + Heptane, Propanone + Ethanol, Ethanol + Heptane, and 2-Propanol + Water at 283.15, 298.15, 323.15, 343.15, and 363.15 K

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Excess molar enthalpies of the binary systems propanone + heptane, propanone + ethanol, ethanol + heptane, and 2-propanol + water were measured at temperatures of 283.15, 298.15, 323.15, 343.15, and 363.15 K and at a pressure of 0.4 MPa. An LKB flow microcalorimeter was used. The experimental H^E values were correlated with a modified Redlich–Kister equation.

Introduction

As part of a long-term study of the dependence of excess enthalpies on temperature we now report the enthalpies of mixing of four characteristic systems over a large temperature range. We take the two systems propanone + heptane and propanone + ethanol for a symmetric behavior of the isotherms and the system ethanol + heptane for a strong asymmetric one. Also we choose 2-propanol + water for an S-shaped system. All these binary systems were measured at temperatures of 343.15 and 363.15 K, because the majority of H^E measurements have been made within the temperature range 283–323 K (1). We also take H^E data at lower temperatures to get consistent data records and to compare our results with literature data.

Experimental Section

Purity of Materials. Propanone (Roth; analytical grade 99.5%), ethanol (Roth; analytical grade 99.8%), heptane (Roth; analytical grade 99%), and 2-propanol (Roth; analytical grade 99.9%) were used without further purification. Water was double distilled, and all liquids were partially degassed under vacuum before actual measurement.

Calorimetry. Excess molar enthalpies H^E were determined using a flow microcalorimeter LKB TAM 2177 (LKB, Bromma, Sweden) described in ref 2. LKB 2150 HPLC pumps were used to pump the pure liquids into the mixing cell. The system pressure was 0.4 MPa. Temperature was kept constant to within ± 0.001 K. The mixing cell was calibrated electrically with an integral resistance heater before use. The calorimeter was tested in ref 2 by using the reference system ethanol + water at temperatures from 283.15 to 363.15 K. The deviation of the measurements from literature data was less than 2%.

Results

The results for the four binary systems are listed in Tables 3–6. The molar enthalpies H^E were fitted by least squares to the modified Redlich–Kister equation

$$H^E/(\text{J}\cdot\text{mol}^{-1}) = x_1(1 - x_1) \sum_{i=0}^n \frac{a_i(2x_1 - 1)^i}{[1 - k(1 - 2x_1)]} \quad (1)$$

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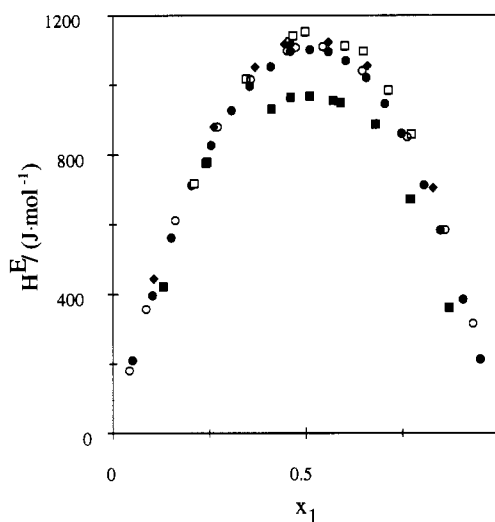


Figure 1. Excess enthalpy H^E of propanone (1) + ethanol (2) at 298.15 K plotted against the mole fraction of propanone: (●) present results, (■) data from ref 3, (□) data from ref 4, (◆) data from ref 5, (○) data from ref 6.

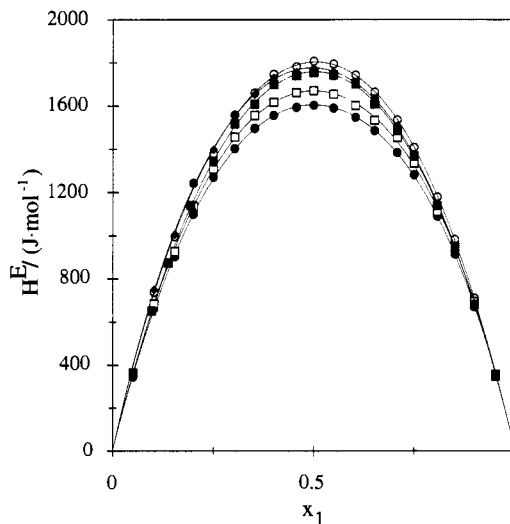


Figure 2. Excess enthalpy H^E of propanone (1) + heptane (2) plotted against the mole fraction of propanone: (●) 283.15 K, (□) 298.15 K, (◆) 323.15 K, (○) 343.15 K, (■) 363.15 K.

where the a_i and k are the fitted coefficients and x_1 is the mole fraction of the component with the lower boiling point.

Table 1. Coefficients a_i and Standard Deviations $\sigma(H^E)$ for the Representation of Excess Enthalpies H^E by Eq 1

T/K	a_0	a_1	a_2	a_3	a_4	k	$\sigma(H^E)/(J/mol)$	T/K	a_0	a_1	a_2	a_3	a_4	k	$\sigma(H^E)/(J/mol)$
Propanone (1) + Heptane (2)															
283.15	6420	-43	1421	364			4.3	343.15	7215	97	1105	-276			11.3
298.15	6682	-15	1348	327			9.9	363.15	7036	47	758	33			6.3
323.15	7108	-106	1202	-344			9.5								
Propanone (1) + Ethanol (2)															
283.15	4185	306	320	23			2.6	343.15	5228	-102	-63	-302			4.8
298.15	4422	263	80	-306			4.5	363.15	4887	-674	60	24			2.4
323.15	5086	98	179	-302			4.2								
Ethanol (1) + Heptane (2)															
283.15	1792	1463	746	1113	463	0.97	3.7	343.15	5535	2991	318	576	619	0.92	7.6
298.15	2401	1875	757	704	-25	0.98	3.9	363.15	7109	4065	-7	1202	209	0.98	9.3
323.15	3854	2246	322	943	607	0.96	5.1								
2-Propanol (1) + Water (2)															
283.15	-763	2694	504	1482	-2658	0.66	3.7	343.15	1732	2934	740	29	-530	0.85	4.2
298.15	-67	2777	710	871	-1680	0.72	5.8	363.15	2315	3239	579	-355	-328	0.95	1.6
323.15	1006	3258	1045	-250	-115	0.93	3.6								

Table 2. Average Deviations σ_a between Data from This Work and Literature Data

system	ref	temp/K	$\sigma_a/(J/mol)$	system	ref	temp/K	$\sigma_a/(J/mol)$
propanone + heptane	7	298.15	47.8	ethanol + heptane	11	283.15	14.0
propanone + heptane	8	298.15	17.5	ethanol + heptane	12	298.15	17.7
propanone + heptane	9	323.15	26.9	ethanol + heptane	13	323.15	17.9
propanone + ethanol	3	298.15	114.0	2-propanol + water	14	298.15	25.8
propanone + ethanol	4	298.15	41.3	2-propanol + water	15	298.15	44.7
propanone + ethanol	5	298.15	36.6	2-propanol + water	16	298.15	10.3
propanone + ethanol	6	298.15	16.8	2-propanol + water	17	298.15	71.3
propanone + ethanol	6	323.15	20.8	2-propanol + water	15	323.15	40.1
ethanol + heptane	10	283.15	12.7				

Table 3. Experimental Excess Molar Enthalpies H^E of Propanone (1) + Heptane (2) Mixtures as a Function of Mole Fraction x_1 at $p = 0.4$ MPa

x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$
$T = 283.15$ K											
0.050	344.2	0.250	1270.3	0.399	1555.6	0.549	1590.3	0.708	1383.5	0.852	915.2
0.102	662.5	0.303	1402.4	0.457	1593.0	0.604	1546.3	0.750	1281.2	0.900	670.8
0.154	902.3	0.352	1495.8	0.499	1602.8	0.652	1485.0	0.808	1088.9	0.952	348.1
0.200	1100.3										
$T = 298.15$ K											
0.050	362.2	0.250	1306.6	0.399	1617.3	0.549	1654.3	0.708	1452.6	0.852	948.8
0.102	685.2	0.303	1455.7	0.457	1661.7	0.604	1602.4	0.750	1335.6	0.900	693.5
0.154	926.3	0.352	1556.2	0.499	1671.3	0.652	1532.8	0.808	1110.7	0.952	357.2
0.200	1134.9										
$T = 323.15$ K											
0.102	749.9	0.250	1397.4	0.399	1729.9	0.549	1759.3	0.708	1507.5	0.852	949.4
0.154	1005.4	0.303	1561.4	0.457	1756.5	0.604	1703.1	0.750	1368.6	0.900	687.2
0.200	1244.6	0.352	1653.0	0.499	1774.8	0.652	1636.2	0.808	1145.3		
$T = 343.15$ K											
0.102	737.4	0.250	1378.5	0.399	1746.6	0.549	1794.1	0.708	1534.9	0.852	981.3
0.154	996.1	0.303	1557.5	0.457	1782.1	0.604	1743.1	0.750	1407.4	0.900	711.3
0.200	1242.7	0.352	1660.3	0.499	1806.9	0.653	1664.2	0.808	1178.0		
$T = 363.15$ K											
0.051	361.6	0.250	1342.9	0.399	1700.0	0.549	1743.0	0.708	1486.7	0.852	945.8
0.096	650.3	0.303	1517.3	0.457	1739.9	0.604	1702.1	0.750	1368.1	0.900	680.8
0.138	873.9	0.352	1608.7	0.499	1755.8	0.652	1608.9	0.808	1137.2	0.952	348.2
0.193	1138.4										

The coefficients a_i and k and the standard deviations

$$\sigma(H^E) = \left(\frac{\sum_{i=1}^N (H_{\text{meas}(i)}^E - H_{\text{calc}(i)}^E)^2}{N - n} \right)^{1/2} \quad (2)$$

are reported in Table 1. N is the number of experimental points and n the number of coefficients in eq 1.

Discussion

The average deviations

$$\sigma_a = \sum_{i=1}^N |H_{\text{lit}(i)}^E - H_{\text{calc}(i)}^E| / N \quad (3)$$

between literature data and the calculated excess enthal-

pies H_{calc}^E of this work are listed in Table 2. For every system and every temperature there is at least one data record in the literature with an average deviation σ_a below 20 J/mol. All these data agree well with the present work. Figure 1 shows all literature data and our results of propanone + ethanol at 298.15 K. The results of Paz-Andrade et al. (3) are much lower than ours, the results of Coomber and Wormald (4) and Hirobe (5) are somewhat higher, whereas the average deviation σ_a between our results and data from Nicolaides and Eckert (6) is less than 17 J/mol.

The measured data and the Redlich-Kister polynomials at the five temperatures are plotted in Figures 2-5 for the four binary systems.

Table 4. Experimental Excess Molar Enthalpies H^E of Propanone (1) + Ethanol (2) Mixtures as a Function of Mole Fraction x_1 at $p = 0.4$ MPa

x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$
$T = 283.15$ K											
0.050	198.1	0.254	782.5	0.408	999.0	0.557	1040.7	0.705	910.4	0.848	586.6
0.102	376.3	0.306	872.7	0.459	1038.7	0.603	1019.6	0.747	835.4	0.905	401.2
0.150	525.4	0.353	938.2	0.510	1043.7	0.656	975.7	0.805	702.2	0.950	225.3
0.203	667.0										
$T = 298.15$ K											
0.050	210.3	0.254	826.9	0.408	1052.2	0.557	1095.5	0.705	945.3	0.848	582.9
0.102	396.4	0.306	926.0	0.459	1096.8	0.603	1069.5	0.747	860.2	0.905	385.0
0.150	561.1	0.353	995.7	0.510	1101.3	0.656	1020.3	0.805	712.7	0.950	213.2
0.203	712.0										
$T = 323.15$ K											
0.102	479.1	0.254	976.6	0.408	1223.4	0.557	1256.0	0.705	1069.7	0.848	662.6
0.150	666.4	0.306	1076.7	0.459	1269.2	0.603	1219.0	0.747	972.7	0.905	439.2
0.203	834.5	0.353	1160.3	0.510	1269.1	0.656	1161.2	0.805	806.0		
$T = 343.15$ K											
0.102	496.4	0.254	1010.5	0.408	1262.5	0.557	1283.6	0.705	1073.9	0.848	653.2
0.150	686.1	0.306	1114.1	0.459	1309.3	0.603	1242.6	0.747	964.1	0.905	426.2
0.203	862.0	0.353	1199.5	0.510	1309.4	0.656	1172.7	0.805	791.2		
$T = 363.15$ K											
0.046	241.2	0.249	978.2	0.402	1209.0	0.548	1193.1	0.700	973.1	0.850	568.9
0.100	491.3	0.302	1089.7	0.451	1226.2	0.595	1144.8	0.757	841.6	0.909	364.4
0.151	693.4	0.350	1160.9	0.495	1222.3	0.652	1063.5	0.799	724.1	0.930	280.1
0.205	859.9										

Table 5. Experimental Excess Molar Enthalpies H^E of Ethanol (1) + Heptane (2) Mixtures as a Function of Mole Fraction x_1 at $p = 0.4$ MPa

x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$	x_1	$H^E/(J/mol)$
$T = 283.15$ K											
0.053	225.5	0.247	412.2	0.396	451.2	0.556	434.3	0.701	386.0	0.852	275.9
0.102	289.6	0.295	433.5	0.444	453.4	0.613	420.6	0.753	364.8	0.900	212.9
0.152	351.8	0.353	446.8	0.501	456.2	0.653	410.3	0.807	321.9	0.950	122.4
0.193	381.6										
$T = 298.15$ K											
0.053	333.4	0.247	573.3	0.396	612.5	0.556	579.0	0.701	508.1	0.852	323.7
0.102	422.7	0.295	598.6	0.444	608.4	0.613	555.9	0.753	447.5	0.900	239.4
0.152	498.4	0.353	610.8	0.501	597.9	0.653	536.3	0.807	387.5	0.950	130.3
$T = 323.15$ K											
0.102	803.7	0.247	993.6	0.396	1017.7	0.556	914.6	0.701	734.7	0.852	455.1
0.152	884.4	0.295	1005.9	0.444	1001.5	0.613	855.8	0.753	665.2	0.900	327.3
0.193	933.8	0.353	1021.4	0.501	959.0	0.653	799.7	0.807	560.2		
$T = 343.15$ K											
0.048	822.7	0.247	1423.9	0.396	1453.3	0.556	1314.3	0.701	1050.4	0.852	624.6
0.102	1141.4	0.295	1443.7	0.444	1436.3	0.613	1224.4	0.753	923.5	0.900	448.8
0.152	1262.1	0.353	1471.2	0.501	1373.4	0.653	1148.1	0.807	771.2	0.948	247.0
0.193	1335.5										
$T = 363.15$ K											
0.102	1373.7	0.247	1818.6	0.396	1882.0	0.556	1680.6	0.701	1323.2	0.852	779.7
0.152	1572.8	0.295	1852.0	0.444	1843.2	0.613	1565.3	0.753	1174.3	0.900	551.7
0.193	1676.7	0.353	1883.9	0.501	1773.4	0.653	1459.8	0.807	971.0		

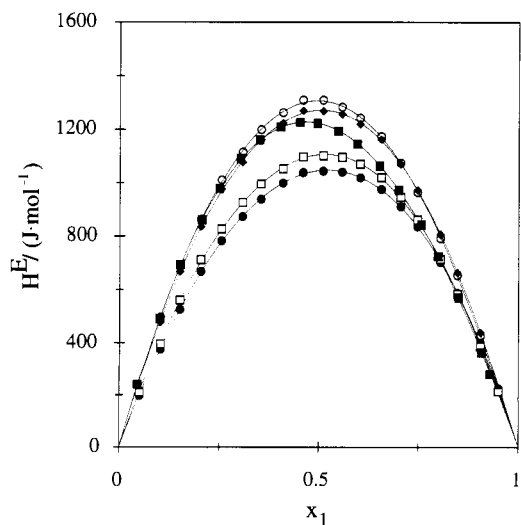
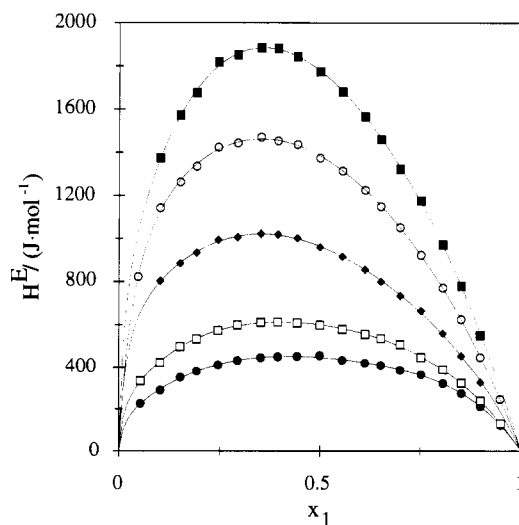
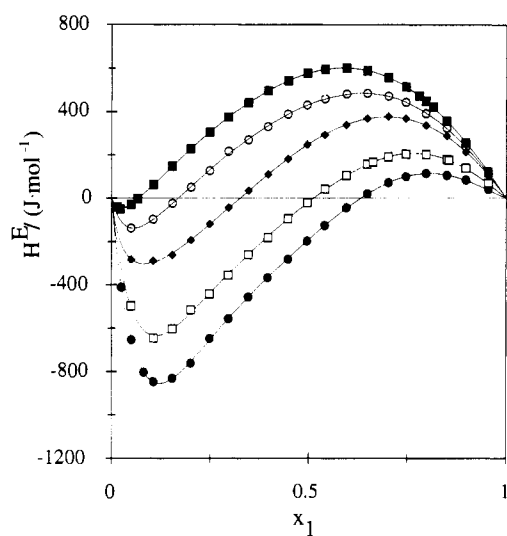
**Figure 3.** Excess enthalpy H^E of propanone (1) + ethanol (2) plotted against the mole fraction of propanone: (●) 283.15 K, (□) 298.15 K, (◆) 323.15 K, (○) 343.15 K, (■) 363.15 K.**Figure 4.** Excess enthalpy H^E of ethanol (1) + heptane (2) plotted against the mole fraction of ethanol: (●) 283.15 K, (□) 298.15 K, (◆) 323.15 K, (○) 343.15 K, (■) 363.15 K.

Table 6. Experimental Excess Molar Enthalpies H^E of 2-Propanol (1) + Water (2) Mixtures as a Function of Mole Fraction x_1 at $p = 0.4$ MPa

x_1	H^E /(J/mol)	x_1	H^E /(J/mol)	x_1	H^E /(J/mol)	x_1	H^E /(J/mol)	x_1	H^E /(J/mol)	x_1	H^E /(J/mol)
$T = 283.15$ K											
0.026	-410.6	0.154	-831.6	0.347	-456.8	0.541	-125.9	0.702	72.5	0.850	106.3
0.050	-653.5	0.201	-761.0	0.396	-367.0	0.596	-44.8	0.747	99.2	0.898	84.2
0.081	-804.8	0.248	-647.8	0.447	-281.5	0.649	20.8	0.797	114.9	0.955	40.7
0.105	-847.6	0.296	-556.9	0.496	-197.8						
$T = 298.15$ K											
0.050	-496.9	0.248	-441.7	0.447	-95.5	0.649	156.5	0.747	203.9	0.855	175.6
0.105	-645.9	0.296	-356.2	0.496	-21.8	0.663	167.2	0.797	202.0	0.898	138.8
0.154	-603.2	0.347	-260.3	0.541	42.6	0.702	191.0	0.850	180.3	0.955	68.7
0.201	-516.3	0.396	-180.6	0.596	106.4						
$T = 323.15$ K											
0.050	-283.4	0.248	-119.3	0.396	110.8	0.541	293.2	0.702	377.3	0.850	287.5
0.105	-288.6	0.296	-43.3	0.447	182.7	0.596	339.1	0.747	368.5	0.898	214.0
0.154	-260.9	0.347	36.0	0.496	247.6	0.649	367.7	0.797	336.8	0.955	103.0
0.201	-192.7										
$T = 343.15$ K											
0.050	-138.6	0.248	127.7	0.396	331.3	0.541	459.3	0.702	471.4	0.850	323.9
0.105	-97.3	0.296	217.0	0.447	387.7	0.596	481.4	0.747	443.7	0.898	237.2
0.154	-23.7	0.347	270.1	0.496	430.3	0.649	484.9	0.797	391.7	0.955	112.2
0.201	51.6										
$T = 363.15$ K											
0.014	-40.4	0.105	62.9	0.296	374.0	0.496	577.7	0.702	556.6		
0.023	-51.3	0.154	148.4	0.347	441.2	0.541	595.9	0.747	514.3	0.850	356.8
0.050	-29.7	0.201	228.5	0.396	497.3	0.596	601.5	0.780	474.1	0.898	256.2
0.066	-3.1	0.248	303.8	0.447	543.8	0.649	588.7	0.797	450.0	0.995	121.6

**Figure 5.** Excess enthalpy H^E of 2-propanol (1) + water (2) plotted against the mole fraction of 2-propanol: (●) 283.15 K, (□) 298.15 K, (◆) 323.15 K, (○) 343.15 K, (■) 363.15 K.

Figures 2 and 3 show for the mixtures of propanone with heptane and ethanol positive H^E values increasing with the temperature to 343.15 K. With higher temperatures the excess enthalpy decreases. The maximum of the isotherms at 363.15 K of both systems is lower than that at 323.15 K.

The system propanone + heptane shows a symmetric behavior of the isotherms from 283.15 to 363.15 K. Propanone + ethanol becomes more asymmetric at higher temperatures. The maximum of the isotherm at 283.15 K is at mole fraction $x_1 = 0.51$, and the maximum of the isotherm at 363.15 K is at $x_1 = 0.451$.

The system ethanol + heptane is shown in Figure 4. The system shows a high temperature dependence with the maximum of the isotherm at 283.15 K at $H^E = 456.2$ J/mol

and the maximum of the isotherm at 363.15 K at $H^E = 1883.9$ J/mol. The system is strongly asymmetric.

The results of 2-propanol + water are presented in Figure 5. These curves are typical S-shaped curves for a mixture of alcohol with water. At lower temperatures the maxima of the isotherms are located on the 2-propanol-rich side near $x_1 = 0.8$ and shift to lower concentrations at increasing temperatures. At the same time the excess enthalpies become higher positive values.

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