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Excess molar enthalpies of cyclohexane + *n*-alcohols at 283.15, 298.15, 323.15, 343.15 and 363.15 K and at a pressure of 0.4 MPa

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Abstract

Excess molar enthalpies h^E of the binary systems cyclohexane + ethanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol 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.

Keywords: Alcohol; Cyclohexane; Excess enthalpy

1. Introduction

As part of a long-term study of the dependence of excess enthalpies on temperature [1, 2, 3], we can now report the enthalpies of mixing of five binary systems with cyclohexane and alcohols over a large temperature range. All these binary systems were measured at temperatures of 343.15 and 363.15 K, since the majority of the reported h^E measurements were made within the temperature range 283–323 K [4]. We also took h^E data at lower temperatures in order to obtain consistent data records and to compare our results with other literature data.

1.1. Purity of materials

Ethanol (Roth; analytical grade 99.8%), 1-propanol (Merck; analytical grade 99.9%), 2-propanol (Roth; analytical grade 99.7%), 1-butanol (Merck; analytical grade

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99.5%) 1-pentanol (Roth; analytical grade 98%), cyclohexane (Roth; analytical grade 99.9%) were used without further purification. All liquids were partially degassed under vacuum before actual measurement.

1.2. Calorimetry

Excess molar enthalpies h^E were determined using a flow microcalorimeter LKB TAM 2277 (LKB, Bromma, Sweden) described in Ref. [1]. ProMinent piston pumps (Mikro gamma 5) were used to pump the pure liquids into the mixing cell. The system pressure was 0.4 MPa. The temperature was kept constant to within ± 0.001 K. The mixing cell was calibrated electrically with an integrated resistance heater before use. The calorimeter was tested (described in Ref. [4]) by using the reference system ethanol + water at temperatures from 283.15 K to 363.15 K. The deviation of the measurements from literature data was less than 2%.

2. Results

The results for the five binary systems are listed in Table 1. The molar enthalpies h^E were fitted by least-squares to the modified Redlich–Kister equation

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

Table 1
Experimental excess molar enthalpies h^E ($\mathrm{J\,mol^{-1}}$) at five temperatures as a function of mole fraction x_1 at $p = 0.4$ MPa

x_1	283.15 K	298.15 K	323.15 K	343.15 K	363.15 K
			Ethanol (1) + cyclohexane (2)		
0.060	216.5	328.3	537.4	732.9	909.3
0.128	316.8	469.6	719.8	998.5	1335.3
0.186	374.9	519.8	795.0	1110.0	1510.4
0.237	420.9	560.8	854.1	1188.1	1615.8
0.294	452.3	589.0	901.1	1225.9	1670.0
0.347	468.0	601.7	917.9	1231.5	1689.3
0.399	481.8	607.8	917.0	1222.9	1680.1
0.451	488.0	600.2	903.2	1196.5	1650.0
0.503	486.3	587.1	871.9	1161.4	1589.8
0.548	479.0	570.4	822.2	1102.3	1530.8
0.600	462.8	548.1	781.9	1027.3	1436.3
0.646	442.3	526.4	730.9	959.5	1335.0
0.689					1224.1
0.704	404.2	485.6	645.4	853.0	1173.5
0.732					1093.1
0.749	365.9	444.9	573.6	762.1	1034.8
0.793	319.6	391.0	492.7	658.1	872.2
0.834	270.1	332.3	409.5	549.2	722.0

Table 1 (*Continued*)

x_1	283.15 K	298.15 K	323.15 K	343.15 K	363.15 K
0.879	206.4	257.6	310.1	416.7	539.5
0.919	144.2	181.0	214.0	289.0	370.7
0.958	78.2	98.8	114.8	156.0	197.8
		Cyclohexane (1) + 1-propanol (2)			
0.027		41.7			
0.053	59.0	80.2	109.9	178.5	232.5
0.078		115.8			
0.101	109.8				
0.109		159.5	221.8	354.3	463.5
0.144	153.8	207.8	291.7	458.2	599.4
0.204	209.6	284.8	402.1	621.5	816.0
0.251	251.7	343.0	488.8	743.0	983.1
0.300	295.4	391.0	563.7	866.6	1137.1
0.350	330.5	436.9	653.3	971.0	1274.7
0.396	358.3	474.2	719.4	1050.1	1388.0
0.445	382.6	508.3	775.4	1118.6	1488.8
0.493	400.6	540.0	829.6	1176.9	1576.3
0.548	417.6	571.9	872.7	1231.3	1645.0
0.596	428.2	590.4	904.4	1262.8	1685.1
0.648	432.0	594.8	907.9	1279.2	1703.1
0.698	421.7	590.9	900.9	1275.0	1696.6
0.745	411.2	578.2	879.2	1247.4	1658.0
0.802	382.7	543.1	838.0	1179.7	1566.4
0.854	341.4	490.1	769.4	1081.2	1423.9
0.898	294.5	429.0	680.3	950.4	1238.1
0.946	220.1	329.6	499.2	701.7	876.5
0.054	95.7	121.2	164.1	238.9	293.5
0.103	173.8	226.3	305.0	437.3	544.2
0.147	240.0	311.1	431.9	607.5	756.9
0.207	325.5	422.1	588.6	813.9	1017.7
0.255	386.1	501.8	711.3	957.3	1210.8
0.305	440.4	570.6	816.0	1090.1	1383.6
0.342	476.0				
0.355		634.6	923.4	1204.0	1530.2
0.402	522.6	685.5	996.7	1323.5	1644.0
0.451	550.7	731.5	1060.3	1398.7	1756.3
0.499	565.9	766.0	1108.0	1455.8	1840.2
0.554	579.0	790.4	1138.7	1495.7	1890.1
0.602	586.5	798.8	1146.3	1507.2	1907.1
0.654	585.1	790.8	1142.9	1497.6	1889.6
0.703	573.6	771.0	1121.5	1464.9	1853.9
0.750	547.6	733.0	1075.8	1410.6	1789.8
0.805	495.8	672.7	993.7	1306.0	1656.9
0.857	428.7	585.3	888.5	1177.8	1484.6
0.900	356.9	499.9	770.9	1024.0	1266.0
0.947	255.1	378.2	582.1	742.7	858.3

Table 1 (*Continued*)

x_1	283.15 K	298.15 K	323.15 K	343.15 K	363.15 K
		Cyclohexane (1) + 1-butanol (2)			
0.049	47.5	71.4	93.6	142.2	155.4
0.107	104.0	153.6	204.9	305.8	345.2
0.147	141.0	207.4	282.2	409.3	471.7
0.201	192.3	276.9	385.9	551.5	644.3
0.249	234.1	337.6	473.3	671.0	808.1
0.301	273.4	397.0	566.0	797.1	965.6
0.355	315.6	457.8	646.6	912.3	1115.7
0.413	347.5	513.5	737.7	1021.5	1266.6
0.454	374.2	545.5	788.9	1081.5	1354.1
0.503	399.1	578.8	844.7	1145.4	1445.8
0.556	415.5	602.5	884.0	1204.5	1514.3
0.602	436.1	616.7	905.2	1232.7	1550.7
0.651	440.0	617.2	915.2	1243.6	1569.5
0.702	433.9	608.6	916.8	1229.3	1563.8
0.755	420.4	587.2	887.3	1194.8	1521.6
0.811	393.6	540.5	855.0	1128.9	1444.7
0.852	354.9	494.7	780.0	1051.9	1341.7
0.896	305.9	428.6	692.4	933.7	1179.2
0.956	203.3	307.6	496.6	633.7	867.0
		Cyclohexane (1) + 1-pentanol (2)			
0.058	45.5	85.0	106.0	141.5	165.5
0.109	92.6	159.7	201.9	275.1	315.7
0.155	136.9	226.2	283.7	387.5	451.0
0.203	182.0	299.7	373.7	509.3	590.9
0.258	234.7	371.4	467.7	638.3	749.1
0.304	271.3	431.0	547.4	740.0	880.0
0.354	317.1	492.3	626.4	832.6	1007.1
0.411	361.5	551.8	707.9	943.3	1128.9
0.445			748.2		
0.454	393.5	593.6		1012.7	1206.5
0.504	424.1	631.0	814.4	1091.4	1285.9
0.553	448.4	660.2	843.3	1140.0	1353.6
0.604	461.2	674.4	867.9	1166.2	1387.0
0.659	465.7	668.4	875.3	1176.0	1408.9
0.705	455.6	651.5	868.1	1170.5	1403.3
0.758	437.5	619.9	843.6	1144.7	1370.9
0.810	398.9	570.5	799.6	1092.5	1299.8
0.859	344.7	508.9	734.9	999.6	1184.1
0.911	281.9	409.1	630.8	856.2	992.6
0.962	188.1	248.6	445.3	559.9	589.2

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.

The coefficients a_i and k as well as the standard deviations

$$\sigma(h^E)=\left(\sum_{i=1}^{N}(h^E_{\mathrm{mes(i)}}-h^E_{\mathrm{calc(i)}})^2/N-n\right)^{1/2} \quad (2)$$

are reported in Table 2. N is the number of experimental points and n the number of coefficients in Eq. (1).

Table 2
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	k	$\sigma(h^E)$ (J mol^{-1})
			Ethanol(1)+cyclohexane (2)			
283.15	1954	1552	283		0.90	2.2
298.15	2366	1538	700		0.83	9.5
323.15	3502	2060	−164		0.95	6.5
343.15	4632	2349	180		0.90	8.6
363.15	6402	3018	−81		0.88	12.6
			Cyclohexane(1)+1-propanol (2)			
283.15	1625	−823	−245		−0.94	1.2
298.15	2197	−987	−260		−0.93	5.9
323.15	3329	−1301	−651		−0.93	10.1
343.15	4760	−2149	−271		−0.91	6.4
363.15	6333	−2595	−431		−0.88	4.5
			Cyclohexane(1)+2-propanol (2)			
283.15	2289	−1332	−141		−0.90	7.3
298.15	3070	−1872	−497		−0.97	3.9
323.15	4421	−2569	−728		−0.97	6.7
343.15	5803	−3373	−389		−0.93	6.3
363.15	7314	−3776	−305		−0.88	10.4
			Cyclohexane(1)+1-butanol (2)			
283.15	1598	−600	−354		−0.92	4.4
298.15	2306	−1098	−629		−0.98	1.2
323.15	3343	−1276	−892		−0.96	8.5
343.15	4572	−1915	−854		−0.94	6.7
363.15	5733	−2228	−1708		−0.97	9.6
			Cyclohexane(1)+1-pentanol (2)			
283.15	1690	−614	−813		−0.99	2.2
298.15	2504	−1090	−776		−0.95	5.0
323.15	3205	−1287	−868		−0.97	6.9
343.15	4294	−1583	−923		−0.94	7.2
363.15	5112	−1600	−1033		−0.90	9.4

3. Discussion

The average deviations

$$\sigma_a = \sum_{i=1}^{N} |h^E_{\mathrm{lit(i)}} - h^E_{\mathrm{calc(i)}}|/N \tag{3}$$

between literature data and the calculated excess enthalpies h^E_{calc} of this work are listed in Table 3. In the literature, there is usually only one data record at 298.15 K for each system with a reported average deviation σ_a below 25 J/mol. All these data agree well with the present work. Fig. 1 shows a comparison between data of the system

Table 3
Average deviations σ_a/(J/mol^{-1}) of h^E between this work and literature data

System	283.15 K σ_a/(J mol^{-1}) [Ref.]	298.15 K σ_a/(J mol^{-1}) [Ref.]	323.15 K σ_a/(J mol^{-1}) [Ref.]
Ethanol + cyclohexane	44.5 [5]	20.9 [6]; 24.4 [5]; 31.1 [7]; 42.1 [8]	
Cyclohexane + 1-propanol		11.5 [6]; 23.5 [9]; 26.7 [7]; 38.2 [10]; 64.5 [11]	48.6 [9]
Cyclohexane + 2-propanol		13.6 [12]; 23.2 [13]; 27.2 [11]; 29.2 [9]	48.0 [9]; 59.4 [12]
Cyclohexane + 1-butanol		10.1 [14]; 12.2 [6]; 13.1 [15]; 14.2 [11]; 17.4 [10]	39.6 [15]
Cyclohexane + 1-pentanol		23.0 [16]	

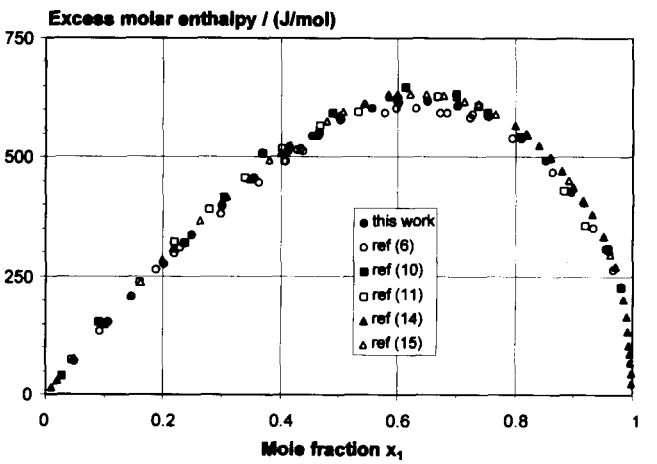

Fig. 1. Comparison of literature data with data of this work: excess enthalpy h^E of cyclohexane (1) + 1-butanol (2) plotted against mole fraction of cyclohexane at a pressure of 0.4 MPa and a temperature of 298.15 K.

cyclohexane + 1-butanol at 298.15 K from five authors claiming the smallest average deviation σ_a as well as our results. The results of Vesely and Pick [6] are lower than ours; the results of Belousov et al. [10], Zhu Ziqiang [11] and Vesely et al. [15] are somewhat higher, whereas the average deviation σ_a between our results and data from Nagata et al. [13] are less than 11 J/mol.

Our measured data and the Redlich–Kister polynomials are plotted in Figs. 2–6 showing five isotherms for all the five systems measured.

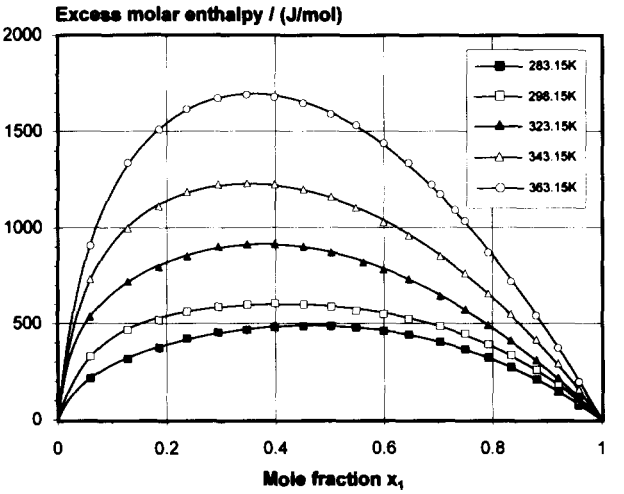

Fig. 2. Excess enthalpy h^E of ethanol (1) + cyclohexane (2) plotted against mole fraction of ethanol at a pressure of 0.4 MPa.

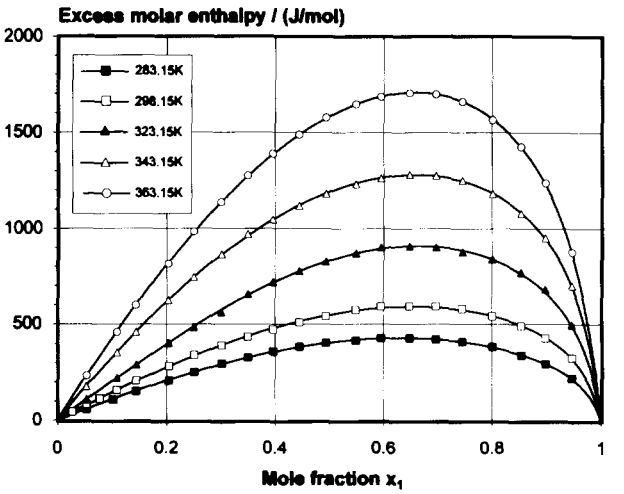

Fig. 3. Excess enthalpy h^E of cyclohexane (1) + 1-propanol (2) plotted against mole fraction of cyclohexane at a pressure of 0.4 MPa.

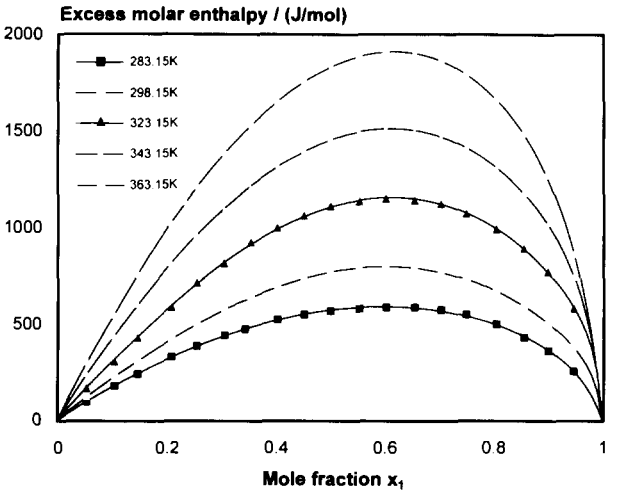

Fig. 4. Excess enthalpy h^E of cyclohexane (1) + 2-propanol (2) plotted against mole fraction of cyclohexane at a pressure of 0.4 MPa.

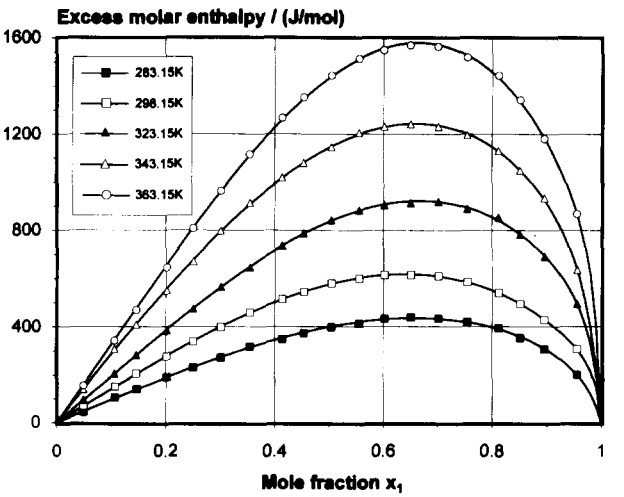

Fig. 5. Excess enthalpy h^E of cyclohexane (1) + 1-butanol (2) plotted against mole fraction of cyclohexane at a pressure of 0.4 MPa.

All the binary systems show strongly asymmetric isotherms in the measured temperature range and exhibit a high temperature dependence, increasing with temperature.

As the hydrocarbonated chain of the alcohols grows, the maximum of the isotherms decreases from $h^E = 1689.3$ J/mol of ethanol at 363.15 K to $h^E = 1408.9$ J/mol of 1-pentanol.

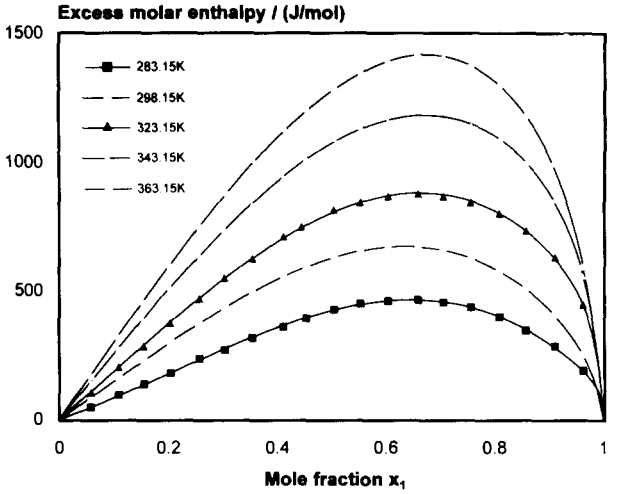

Fig. 6. Excess enthalpy h^E of cyclohexane (1) + 1-pentanol (2) plotted against mole fraction of cyclohexane at a pressure of 0.4 MPa.

These additional h^E data have a high temperature dependence, thereby providing improved parameters of g^E models such as the modified UNIFAC (the original UNIFAC model has no temperature dependence of the parameters).

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