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Excess molar enthalpies of acetone + water, cyclohexane, methanol, 1-propanol, 2-propanol, 1-butanol and 1-pentanol at 283.15, 298.15, 323.15, 343.15 and 363.15 K

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Abstract

Excess molar enthalpies h^E of the binary systems acetone + water, cyclohexane, methanol, 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: Acetone; Alcohol; Excess enthalpies; Water

1. Introduction

As part of a long-term study on the dependence of excess enthalpies on temperature, we now report the enthalpies of mixing of some binary systems with acetone over a large temperature range. In particular, we have found an interesting temperature dependence of the system acetone–ethanol [1] which is not apparent from the literature data, because the majority of h^E measurements were made within the temperature range 283–323 K [2]. We also measured h^E data at lower temperatures in order to obtain consistent data and to compare our results with literature data. We also compare the measured excess enthalpies of the system acetone + 1-butanol with data calculated using the modified UNIFAC model of Gmehling [3].

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2. Experimental

2.1. Purity of materials

Acetone (Roth; analytical grade 99.9%), methanol (Roth; analytical grade 99.9%), 1-propanol (Merck; analytical grade 99.9%), 2-propanol (Roth; analytical grade 99.7%), 1-butanol (Merck; analytical grade 99.5%), 1-pentanol (Roth; analytical grade 98%), and cyclohexane (Roth; analytical grade 99.9%) were used without further purification. Water was double-distilled and all liquids were partially degassed under vacuum before the actual measurements.

2.2. Calorimetry

Excess molar enthalpies h^E were determined using an LKB TAM 2177 flow microcalorimeter (LKB, Bromma, Sweden) as described in Ref. [4]. ProMinent pumps (Mikro gamma 5) were used to pump the pure liquids into the mixing cell as shown in Fig. 1. 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, see Ref. [4], 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%.

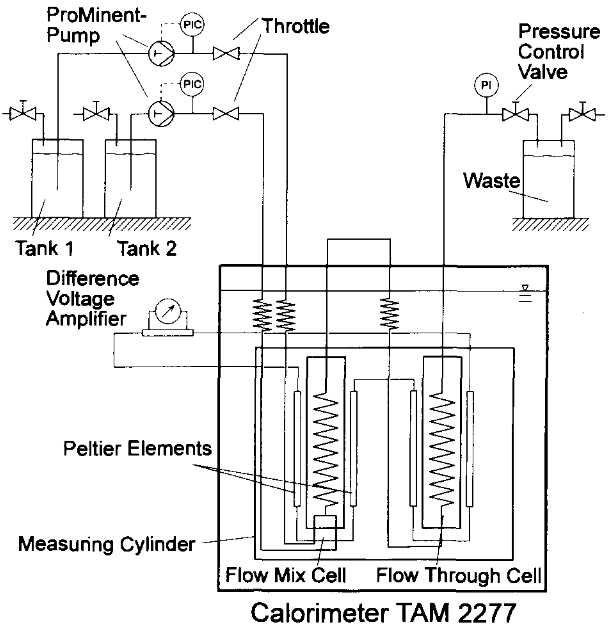

Fig. 1. TAM microcalorimeter with a flow-mixing cell.

Table 1
Experimental excess molar enthalpies h^E at five temperatures as a function of mole fraction x_1 at $p = 0.4$ Mpa

x_1	h^E/J mol^{-1}				
	$T = 283.15$ K	$T = 298.15$ K	$T = 323.15$ K	$T = 343.15$ K	$T = 363.15$ K
Acetone (1) + water (2)					
0.010					−40.5
0.025		−212.0			−79.3
0.046	−416.4	−352.5	−289.6	−173.1	−100.9
0.075		−482.6			
0.099	−661.0	−563.1	−391.8	−216.7	−68.2
0.151	−756.0	−643.0	−412.7	−207.9	−2.2
0.195	−772.9	−648.9	−395.9	−169.8	68.7
0.248	−743.9	−618.5	−342.5	−103.9	165.6
0.305	−672.6	−546.7	−262.1	−13.3	276.8
0.349	−590.5	−471.6			
0.350	−601.4		−181.9	65.1	365.3
0.404	−501.9	−369.7	−80.8	163.4	469.3
0.448	−416.6	−279.6	3.5	247.3	551.0
0.497	−317.0	−177.4	97.9	333.7	631.3
0.548	−211.9	−68.9	191.7	413.5	697.9
0.602	−103.5	41.1	281.8	491.6	754.5
0.650	−12.3	124.2	352.5	542.2	781.8
0.699	72.4	197.5	407.4	577.5	786.3
0.752	147.1	257.3	441.6	586.6	758.9
0.801	199.5	290.7	444.1	560.9	696.0
0.853	228.8	284.9	407.4	502.0	597.0
0.901	203.5	239.1	327.2	383.4	441.7
0.948	144.2	154.1	201.9	227.5	259.6
Acetone (1) + cyclohexane (2)					
0.048	376.4	417.8	415.1	379.8	385.1
0.105	728.0	759.1	782.1	740.8	743.5
0.153	966.2	973.7	1022.8	976.5	989.4
0.199	1145.8	1138.6	1201.3	1162.7	1184.5
0.249	1293.0	1289.2	1345.7	1312.0	1345.9
0.297	1416.2	1378.4	1460.6	1432.4	1463.8
0.345	1494.4	1448.0	1550.4	1518.1	1551.2
0.395	1536.9	1502.0	1603.9	1573.3	1608.7
0.446	1553.2	1532.3	1627.5	1601.2	1640.7
0.491	1546.4	1531.2	1633.9	1608.4	1648.5
0.544	1525.4	1509.9	1597.9	1582.6	1627.0
0.592	1475.7	1462.6	1538.8	1531.7	1575.3
0.655	1383.0	1364.6	1422.8	1426.6	1467.2
0.703	1278.9	1259.6	1306.1	1312.5	1349.3
0.753	1148.8	1125.6	1157.8	1169.1	1202.2
0.799	995.1	973.3	993.7	1005.3	1034.6
0.853	784.0	766.8	775.9	785.8	808.8
0.901	566.7	550.8	553.5	560.1	577.2
0.948	318.3	307.1	305.9	310.0	319.2

Table 1 *(continued)*

x_1	h^E/J mol^{-1}				
	T = 283.15 K	T = 298.15 K	T = 323.15 K	T = 343.15 K	T = 363.15 K
Acetone (1) + methanol (2)					
0.054	105.3	116.1	133.8	148.3	159.3
0.101	189.4	210.8	242.1	265.7	286.7
0.157	282.1	312.7	363.5	395.2	425.3
0.205	355.0	392.5	455.0	493.5	529.6
0.258	429.7	470.4	541.6	588.2	631.6
0.308	485.9	533.9	612.0	662.1	711.9
0.359	535.2	583.5	671.3	725.7	780.0
0.406	569.7	622.2	711.1	769.8	825.1
0.456	598.0	653.2	745.6	799.7	853.7
0.510	616.7	672.0	766.7	816.6	871.4
0.560	621.0	676.3	769.0	815.0	866.4
0.606	613.7	669.3	757.6	799.6	848.9
0.653	596.9	649.4	730.5	769.7	813.9
0.700	567.2	615.3	689.1	723.5	759.9
0.757	511.1	556.6	615.6	640.4	672.9
0.800	455.9	492.7	542.3	565.8	588.0
0.848	378.1	408.8	441.6	457.7	476.0
0.903	262.6	289.2	304.9	314.7	326.2
0.955	132.3	150.4	152.9	158.7	162.8
Acetone (1) + 1-propanol (2)					
0.058	290.4	316.3	325.6	309.3	283.4
0.110	508.8	561.8	581.0	559.1	517.0
0.152	658.4	731.2	766.4	738.6	692.0
0.202	819.7	898.0	952.0	927.6	884.0
0.256	964.4	1052.3	1115.2	1100.3	1050.7
0.305	1065.2	1166.0	1234.3	1225.1	1178.0
0.352	1143.7	1240.9	1315.4	1312.5	1268.7
0.405	1203.1	1303.5	1376.0	1383.2	1338.4
0.460	1243.7	1342.6	1413.8	1419.9	1384.4
0.508	1251.1	1352.8	1412.3	1425.6	1396.3
0.560	1228.2	1336.4	1383.4	1398.9	1377.4
0.608	1197.3	1301.4	1334.6	1349.3	1331.2
0.663	1131.7	1232.4	1243.0	1261.3	1242.9
0.707	1060.1	1153.5	1144.3	1166.4	1150.2
0.752	965.6	1050.9	1028.6	1046.7	1030.4
0.799	844.6	920.0	878.6	901.7	884.5
0.852	676.7	736.7	677.1	706.9	689.5
0.896	508.8	553.3	491.2	520.5	502.2
0.945	289.3	313.1	271.3	286.7	274.0
Acetone (1) + 2-propanol (2)					
0.060	360.6	383.8	383.1	324.6	303.8
0.096	550.6	587.3	590.0	501.4	469.2
0.156	824.0	862.6	872.7	761.8	719.8
0.206	1013.6	1062.1	1077.9	947.2	898.5

Table 1 *(continued)*

x_1	h^E/J mol^{-1}				
	$T = 283.15$ K	$T = 298.15$ K	$T = 323.15$ K	$T = 343.15$ K	$T = 363.15$ K
0.261	1180.3	1233.7	1262.1	1119.5	1090.0
0.310	1303.8	1358.3	1399.9	1249.7	1216.4
0.358	1393.7	1454.4	1490.6	1348.1	1307.8
0.410	1458.1	1512.3	1560.4	1421.5	1380.1
0.466	1494.6	1548.7	1597.1	1467.3	1425.6
0.514	1496.8	1549.8	1591.7	1465.7	1426.3
0.566	1464.8	1527.9	1555.7	1441.2	1391.2
0.614	1415.7	1476.5	1494.8	1392.2	1337.8
0.668	1324.7	1389.5	1395.9	1301.3	1248.1
0.712	1227.1	1296.0	1301.1	1206.6	1154.2
0.756	1104.1	1177.7	1171.0	1084.1	1033.6
0.802	954.2	1027.7	1010.9	934.1	887.0
0.855	753.7	820.8	798.0	732.8	693.2
0.898	558.9	614.4	588.1	538.1	505.1
0.946	317.3	347.1	326.6	299.0	275.2
Acetone (1) + 1-butanol (2)					
0.048	278.7	313.9	283.2	275.0	259.5
0.089		562.8			
0.099	535.0	600.2	552.7	540.4	507.0
0.151	711.1	840.0	793.3	775.6	726.3
0.198	950.4	1025.0	990.3	964.0	906.8
0.252	1120.7	1197.5	1189.4	1144.4	1077.5
0.311	1265.5	1342.8	1365.4	1301.1	1227.5
0.356	1352.6	1422.3	1457.4	1391.3	1315.7
0.400	1409.4	1480.6	1531.1	1460.0	1380.0
0.454	1459.2	1522.2	1583.7	1508.4	1430.6
0.510	1467.5	1533.2	1605.6	1521.6	1443.2
0.559	1458.3	1518.3	1583.7	1501.8	1425.2
0.609	1409.6	1474.8	1533.2	1451.4	1375.5
0.658	1335.9	1403.8	1452.7	1372.3	1293.2
0.706	1236.6	1306.5	1338.0	1265.9	1191.3
0.758	1108.3	1168.5	1185.4	1121.7	1052.7
0.803	965.8	1024.9	1024.2	967.5	904.6
0.852	762.5	829.8	816.9	769.6	720.1
0.900	559.1	604.7	581.8	547.7	511.1
0.955	269.6	301.0	280.2	263.2	246.0
Acetone (1) + 1-pentanol (2)					
0.057	321.8	378.8	324.5	308.6	260.0
0.107	566.8	664.2	587.0	558.4	475.1
0.152	766.5	883.0	798.1	775.8	664.4
0.203	960.0	1092.6	1006.9	979.1	844.6
0.250	1112.1	1263.3	1173.2	1141.8	996.8
0.302	1252.6	1407.8	1327.4	1294.6	1142.3
0.360	1375.5	1524.2	1460.7	1425.7	1254.6
0.409	1447.0	1597.6	1543.3	1506.6	1345.6
0.459	1492.5	1634.3	1598.7	1559.6	1400.2

Table 1 *(continued)*

x_1	h^E/J mol^{-1}				
	$T=283.15$ K	$T=298.15$ K	$T=323.15$ K	$T=343.15$ K	$T=363.15$ K
0.507	1512.0	1655.8	1621.8	1581.3	1422.5
0.552	1505.3	1643.3	1612.9	1579.3	1421.8
0.600	1470.8	1605.2	1581.6	1540.6	1387.3
0.653	1407.2	1529.8	1505.8	1454.4	1315.7
0.703	1319.3	1425.7	1400.5	1343.0	1213.2
0.759	1175.1	1270.3	1240.3	1179.7	1076.5
0.812	999.1	1082.1	1049.1	987.7	908.6
0.852	838.4	903.2	869.9	816.5	750.1
0.903	592.1	643.0	607.1	564.9	516.5
0.949	331.6	365.4	335.3	312.4	281.6

3. Results

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

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

where 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 and the standard deviations

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

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

4. 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 excess enthalpies h^E_{calc} of this work are listed in Table 3. In the literature, there is usually one data record for each system and each temperature, with a reported average deviation σ_a below 30 J mol^{-1}. All these data agree well with the present work. Fig. 2 shows a comparison between the data for the system acetone + water reported by the five authors claiming the smallest average deviation σ_a

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}
Acetone (1) + water (2)						
283.15	−1244	3376	1215	2044	0.54	4.1
298.15	−744	3759	1925	1153	0.62	1.3
323.15	406	4180	2986	835	0.84	2.6
343.15	1346	4579	2889	671	0.84	4.2
363.15	2514	5352	2753	399	0.92	2.6
Acetone (1) + cyclohexane (2)						
283.15	6219	161	1244		0.12	7.9
298.15	6119	3582	759		0.68	4.9
323.15	6497	3791	223		0.71	5.0
343.15	6423	2979	487		0.56	4.1
363.15	6591	2865	510		0.53	5.9
Acetone (1) + methanol (2)						
283.15	2459	−426	−69		−0.39	1.1
298.15	2688	−1134	−128		−0.59	0.5
323.15	3055	1074	162		0.17	1.3
343.15	3264	−87	−44		−0.15	0.6
363.15	3483	1329	44		0.28	0.6
Acetone (1) + 1-propanol (2)						
283.15	4989	125	512			6.0
298.15	5410	−51	675			1.3
323.15	5669	−369	−25			7.3
343.15	5709	−133	−99			5.7
363.15	5594	37	−367			7.0
Acetone (1) + 2-propanol (2)						
283.15	5985	−153	376			1.9
298.15	6208	−226	798			4.2
323.15	6376	−200	336			10.1
343.15	5873	57	−69			3.4
363.15	5701	3	−364			16.1
Acetone (1) + 1-butanol (2)						
283.15	5886	−444	348		−0.09	5.7
298.15	6137	335	884		0.08	1.0
323.15	6415	3055	−62		0.45	2.8
343.15	6088	−5229	−72		−0.87	0.3
363.15	5768	−776	−159		−0.14	1.3
Acetone (1) + 1-pentanol (2)						
283.15	6042	−1301	365		−0.29	2.0
298.15	6613	−576	812		−0.11	3.1
323.15	6479	790	142		0.04	0.8
343.15	6327	−995	−303		−0.22	4.6
363.15	5677	1462	−238		0.16	7.2

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

System	298.15 K σ_a/J mol^{-1} [Ref.]	323.15 K σ_a/J mol^{-1} [Ref.]
Acetone + water	12.5 [6]; 20.6 [7]; 23.5 [8]; 25.5 [5]; 30.6 [9]; 46.2 [10]; 49.8 [11]; 57.5 [12]	18.3 [13]; 32.2 [14]; 34.6 [5]; 46.5 [11]
Acetone + cyclohexane	26.5 [15]; 41.6 [16]	
Acetone + methanol	7.4 [17]; 7.8 [18]; 17.4 [12]; 31.7 [19]; 39.1 [20]	10.6 [21]
Acetone + 1-propanol	39.6 [12]; 100.3 [19]	
Acetone + 2-propanol	22.7 [22]	
Acetone + 1-butanol	49.9 [12]; 111.7 [23]; 122.7 [19]; 153.8 [11]	97.4 [11]
Acetone + 1-pentanol	46.4 [12]; 65.5 [24]	

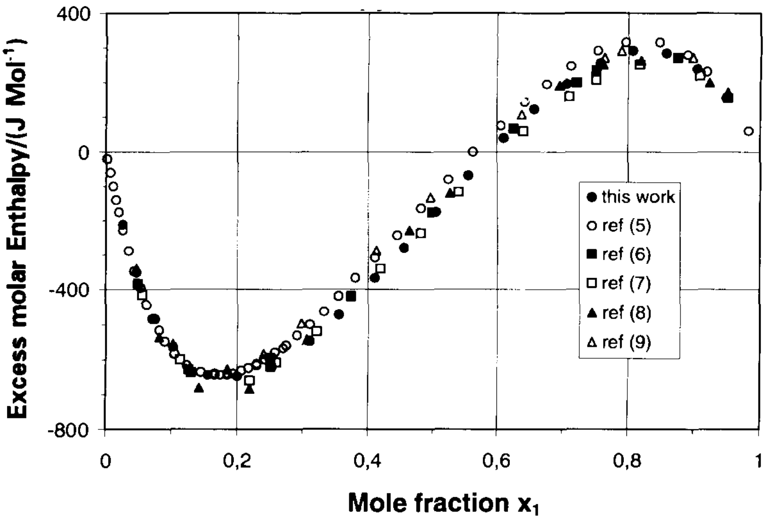

Fig. 2. Comparison of literature data with the data of the present work. Excess enthalpy h^E of acetone (1) + water (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

and our results at 298.15 K. At low mole fractions, x_{Acetone} there is no significant difference between our results and any of the literature data. However, there are authors who report higher excess enthalpies (French [5] and Ferino et al. [9]) and others who report lower data (Hanson and van Winkle [6], Khurma and Fendy [7] and Rhim and Kim [8]) than were obtained in our measurements. Nevertheless, the average deviations σ_a between our results and those of the five authors mentioned are less than 30 J mol^{-1}.

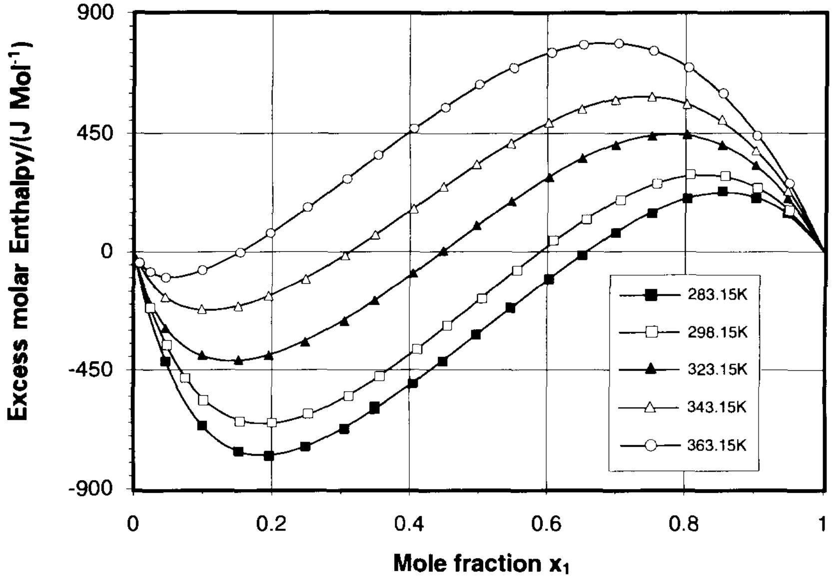

Fig. 3. Excess enthalpy h^E of acetone (1) + water (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

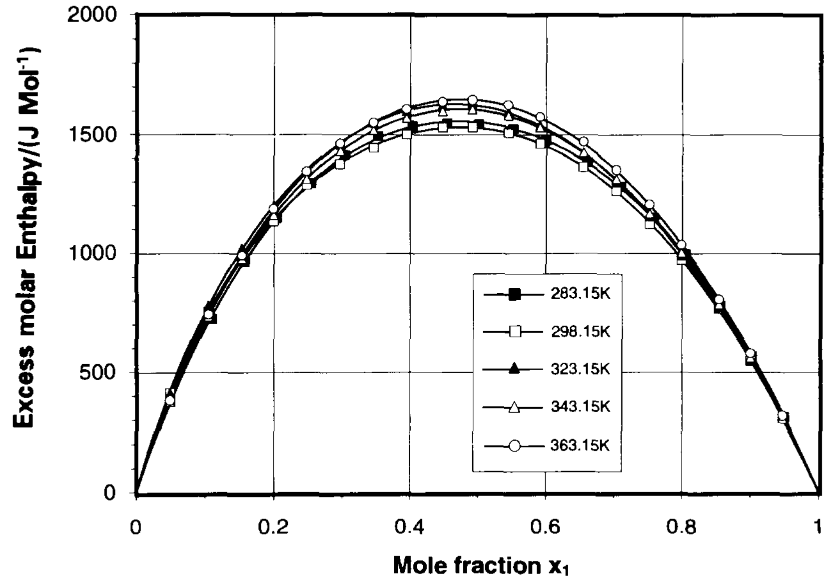

Fig. 4. Excess enthalpy h^E of acetone (1) + cyclohexane (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

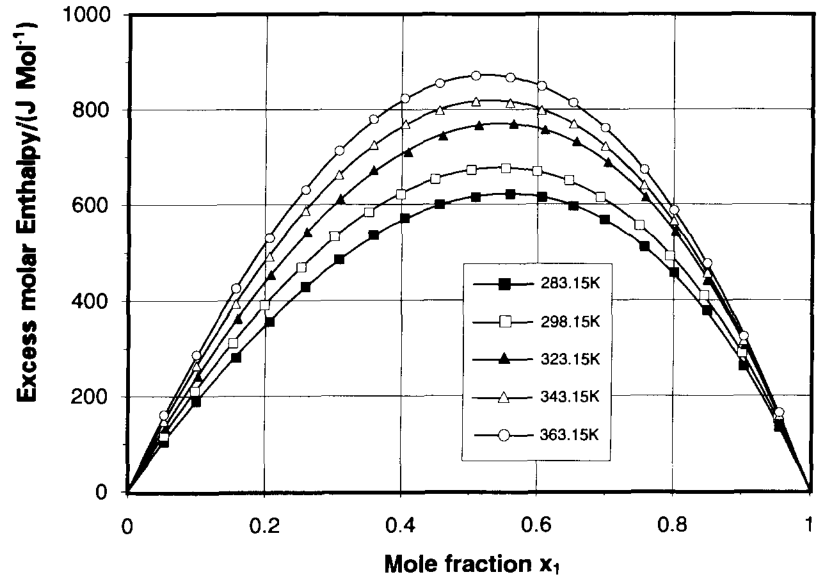

Fig. 5. Excess enthalpy h^E of acetone (1) + methanol (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

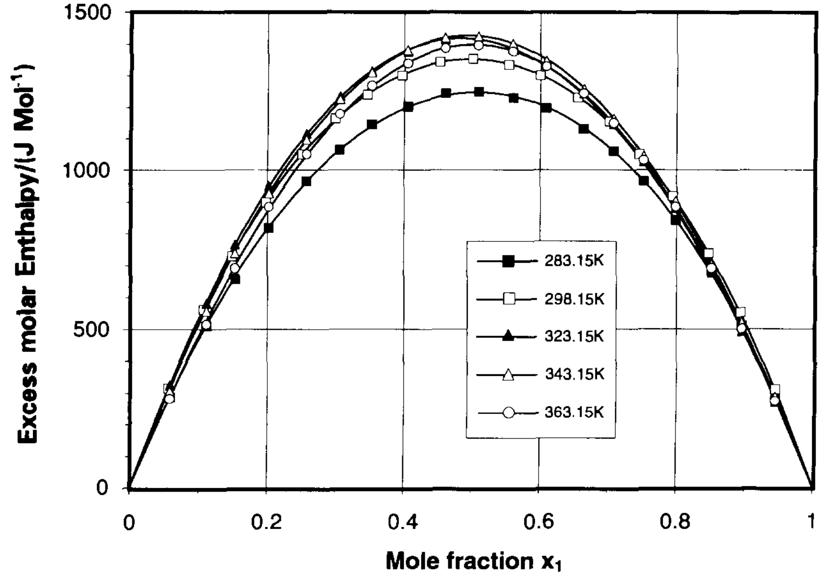

Fig. 6. Excess enthalpy h^E of acetone (1) + 1-propanol (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

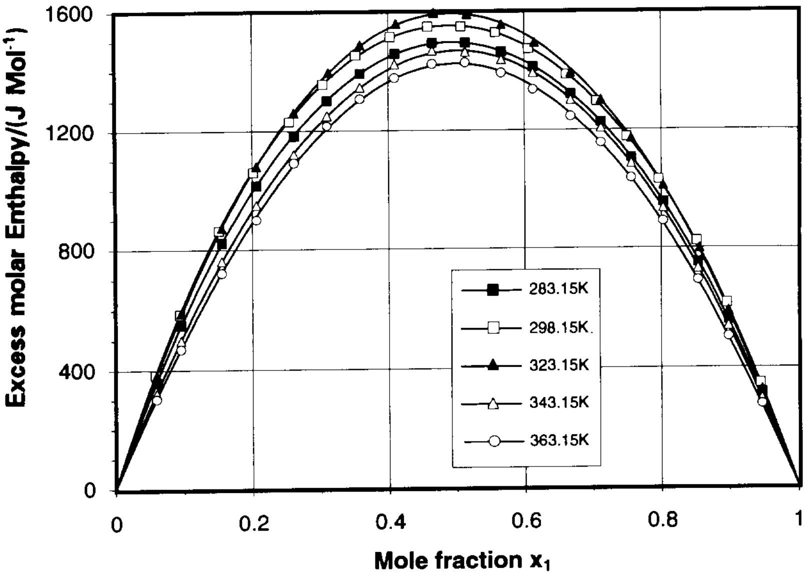

Fig. 7. Excess enthalpy h^E of acetone (1) + 2-propanol (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

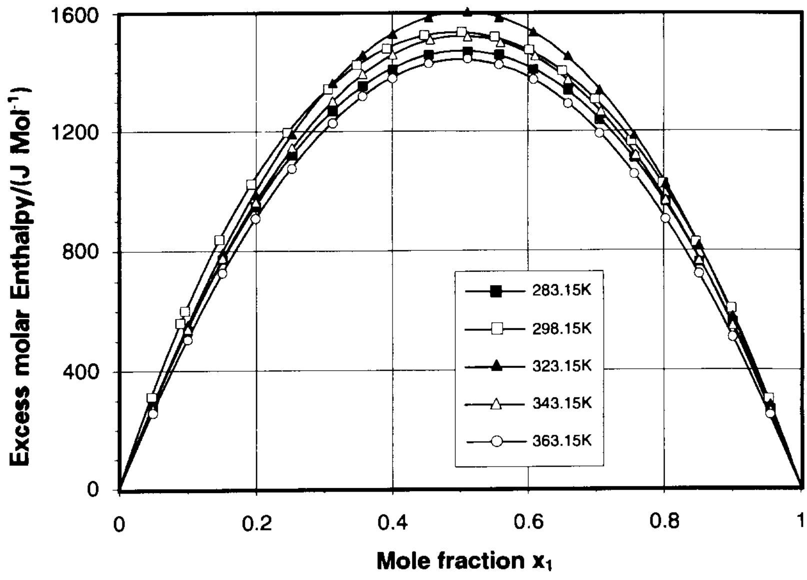

Fig. 8. Excess enthalpy h^E of acetone (1) + 1-butanol (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

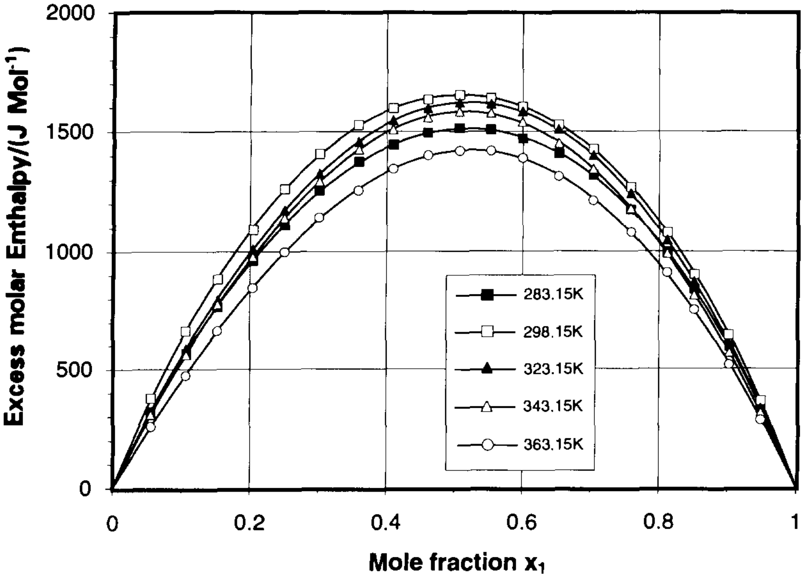

Fig. 9. Excess enthalpy h^E of acetone (1) + 1-pentanol (2) plotted against mole fraction of acetone at a pressure of 0.4 Mpa.

Our measured data and the Redlich–Kister-polynomials are plotted in Figs. 3–9 which show five isotherms for all seven systems measured.

The results for acetone + water are presented in Fig. 3 which shows the typical S-shaped h^E curves. At lower temperatures, the maxima of the h^E isotherms are located on the acetone-rich side near to $x_1 = 0.8$, shifting to lower concentrations when the temperature increases. At the same time the maxima become higher positive values and the excess enthalpies shift towards more positive values.

The system acetone + cyclohexane (Fig. 4) shows a symmetric behaviour of the h^E isotherms over the whole temperature range without any great dependence on temperature.

Fig. 5 gives positive h^E values for the mixture acetone + methanol which increase with temperature.

All the mixtures of acetone with the other alcohols (Figs. 6–9) always show positive h^E values. The maximum of the isotherms increases with temperature at low temperatures and start to decrease at higher temperatures. The highest data for h^E for the system acetone + 1-propanol are found for the isotherm of 343.15 K, for the systems acetone + 2-propanol and + 1-butanol for the isotherm of 323.15 K, and for the system acetone + 1-pentanol for the isotherm of 298.15 K. This interesting temperature dependence of the h^E isotherms was also recorded for the system acetone + ethanol in Ref. [1]. Fig. 10 shows the temperature and concentration dependence of h^E for the system acetone + 1-butanol as calculated using the modified UNIFAC-model of Gmehling [3]. The maximum of the h^E surface at $x_1 = 0.5$ is found at a temperature of 293.15 K. We can

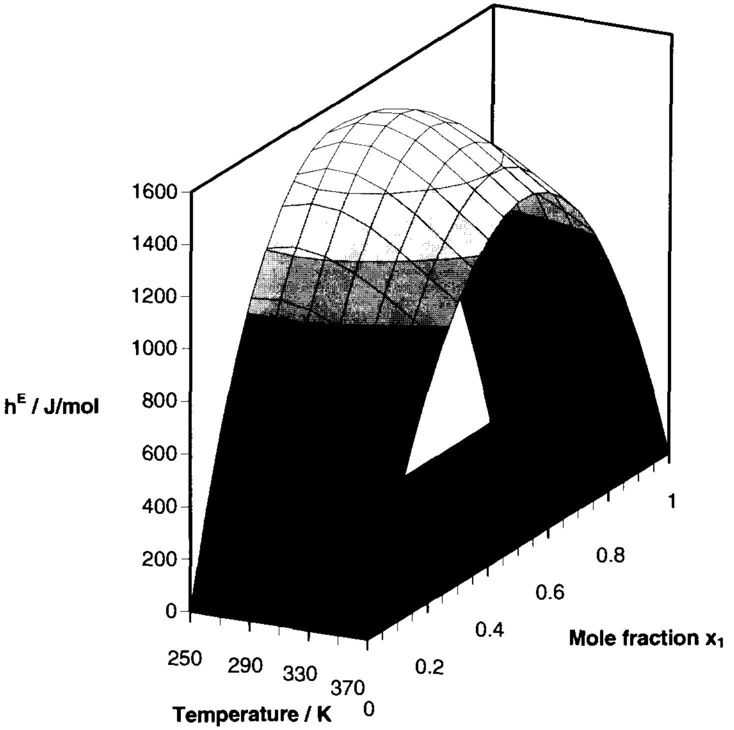

Fig. 10. Excess enthalpy h^E of acetone (1) + 1-butanol (2) plotted against mole fraction of acetone and temperature as calculated by the UNIFAC model.

confirm that the modified UNIFAC-model of Gmehling calculates well the quantitative characteristic temperature dependence of all the acetone + alcohol systems.

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