J. Chem. Eng. Data **2005,** *50,* 1907−1910 **1907**

Excess Molar Enthalpies of Methyl Acetate and (1-Propanol, 2-Propanol, 1-Butanol, 2-Butanol, and 1-Pentanol) at T = (298.15 and 308.15) K and P = (5.0 and 10.0) MPa

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A high-pressure flow-mixing isothermal calorimeter is used to determinate the excess molar enthalpies of five binary systems for methyl acetate and (1-propanol, 2-propanol, 1-butanol, 2-butanol, and 1-pentanol) at T = (298.15 and 308.15) K and p = (5.0 and10.0) MPa. The smooth values calculated by Redlich−Kister equation of H_m^{E} are also compared with the experimental results.

Introduction

Excess enthalpy is an important thermodynamic property of solution.[1] It can provide information to improve the understanding of the molecular interactions and macroscopic behavior of fluid mixtures.[2] The sign, magnitude, and symmetry of this quality is a direct result of bond breaking and rearranging during the mixing process, and any effect arising from energetic interactions between both like and unlike molecules will be directly reflected in the values of excess enthalpy. [3] For the design of the chemical engineering process and the test of solution theories, there is a constant need for the data of excess enthalpy.[4] For example, to calculate or predict fluid phase equilibrium and to test the thermodynamic consistency of the isobaric VLE data, data of excess enthalpy are required.

Excess molar enthalpies for binary mixtures of methyl acetate and (1-propanol, 2-propanol, 1-butanol, and 2-butanol) have been determined at T = (298.15, 308.15, and 318.15) K and p = 0.1 MPa in the literatures,[5] but the most H_m^{E} data published have determined at ambient pressure. To test the influence of temperature and pressure on the excess molar enthalpy and to overcome the absence of the data of mixtures (ester and alcohols) at high pressure, the excess molar enthalpies of five binary systems for methyl acetate and (1-propanol, 2-propanol, 1-butanol, 2-butanol, and 1-pentanol) have been measured using a high-pressure flow-mixing isothermal calorimeter at T = (298.15, 308.15) K and p = (5.0, 10.0) MPa in this work. The Redlich−Kister correlation of H_m^{E} is also compared with the experimental results.

Experimental Section

Materials. Methyl acetate (99.9+ %, HPLC reagent), and alcohols (99.85+ %, HPLC reagent), they were dried with molecular sieves (3 to 4 Å) and filtrated by Millipore filter (0.45μm). The purity of solvents was checked by gas chromatography. The purity was greater than 99.80 % for all solvents. These solvents were used without further purification.

Table 1. Excess Molar Enthalpies of Methyl Acetate (1) and 1-Propanol (2)

x_1	H^{E}/J·mol^{-1}	x_1	H^{E}/J·mol^{-1}	x_1	H^{E}/J·mol^{-1}
T = 298.15 K, p = 5.00 MPa					
0.051	312.9	0.400	1482.4	0.749	1142.5
0.099	597.4	0.451	1518.1	0.800	987.4
0.149	840.6	0.501	1522.8	0.850	797.4
0.199	1036.7	0.551	1498	0.900	570.9
0.251	1199.9	0.600	1453.8	0.951	297.6
0.300	1321.9	0.650	1382.6		
0.349	1414.3	0.701	1275.8		
T = 298.15 K, p = 10.00 MPa					
0.051	340.1	0.399	1474.9	0.749	1148.0
0.099	608.4	0.450	1512.5	0.799	989.8
0.149	844.4	0.500	1515.8	0.849	790.5
0.199	1038.3	0.550	1495.5	0.899	565.4
0.250	1201.8	0.600	1449.6	0.951	285.6
0.300	1320.8	0.649	1378.7		
0.349	1410.6	0.700	1275.1		
T = 333.15 K, p = 10.00 MPa					
0.051	402.2	0.399	1706.6	0.751	1325.0
0.099	703.7	0.448	1748.8	0.801	1132.2
0.150	972.3	0.500	1766.4	0.850	898.1
0.200	1201.0	0.548	1751.4	0.900	627.0
0.250	1376.7	0.599	1695.3	0.949	314.3
0.300	1519.1	0.650	1605.2		
0.350	1625.8	0.700	1484.9		

Apparatus. A commercial isothermal calorimeter (model IMC 4400, Calorimeter Science Corporation, USA) with a refrigerating/heating circulator (model: 9000, PolyScience Inc., USA) was used. The flow-mixing system comprises a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO Inc., USA) with the resolution of 0.1 μL·min^{-1} and a back pressure regular (model CSC 4448). It can be used to measure the mixing enthalpy at high pressure up to 15 MPa and temperature range from (−20 to 200) °C. It can detect changes in heat flow as small as 0.1 μW and heat effects as small as 40 μJ. The IMC-Acquire software for acquiring experimental data was provided by Calorimeter Science Corporation. To confirm the reliability of this isothermal microcalorimeter, excess molar enthalpies of three binary systems ethanol + water at T = 298.15 K and p = (0.2, 0.4) MPa, methanol + water and acetone +

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10.1021/je050175u CCC: $30.25

Table 2. Excess Molar Enthalpies of Methyl Acetate (1) and 2-Propanol (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
$T = 298.15$ K, $p = 5.00$ MPa					
0.100	557.9	0.401	1486.0	0.700	1383.8
0.151	794.2	0.450	1537.0	0.750	1254.8
0.199	982.6	0.499	1565.3	0.799	1096.5
0.249	1152.8	0.551	1563.3	0.851	882.7
0.299	1290.1	0.599	1534.0	0.900	643.5
0.349	1399.0	0.649	1471.8	0.949	357.6
$T = 298.15$ K, $p = 10.00$ MPa					
0.100	552.4	0.401	1480.1	0.699	1367.5
0.151	794.0	0.450	1530.6	0.749	1239.5
0.201	995.2	0.501	1556.0	0.799	1081.3
0.252	1161.2	0.550	1552.2	0.851	868.1
0.301	1296.8	0.601	1519.1	0.900	626.9
0.351	1402.9	0.651	1456.3	0.949	339.0
$T = 308.15$ K, $p = 10.00$ MPa					
0.049	311.9	0.342	1494.8	0.643	1574.6
0.097	592.9	0.392	1587.1	0.693	1481.3
0.145	831.0	0.441	1642.9	0.743	1355.9
0.195	1049.6	0.490	1672.1	0.793	1185.1
0.243	1224.1	0.541	1673.5	0.897	708.2
0.293	1375.6	0.592	1639.7	0.949	379.9

Table 3. Excess Molar Enthalpies of Methyl Acetate (1) and 1-Butanol (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
$T = 298.15$ K, $p = 5.00$ MPa					
0.050	324.6	0.399	1502.6	0.751	1188.9
0.101	606.8	0.450	1548.2	0.801	1021.4
0.149	840.1	0.501	1558.0	0.851	812.7
0.199	1037.6	0.550	1540.7	0.899	589.0
0.249	1202.8	0.600	1501.6	0.951	303.9
0.300	1337.7	0.651	1427.0		
0.349	1435.4	0.699	1322.6		
$T = 298.15$ K, $p = 10.00$ MPa					
0.050	322.2	0.401	1504.4	0.751	1187.9
0.100	603.6	0.449	1543.8	0.800	1020.1
0.149	835.0	0.500	1556.3	0.851	818.2
0.201	1041.1	0.550	1540.9	0.899	590.8
0.251	1206.6	0.599	1498.8	0.951	303.7
0.300	1331.0	0.650	1424.6		
0.351	1434.0	0.701	1315.8		
$T = 308.15$ K, $p = 10.00$ MPa					
0.047	306.4	0.343	1519.2	0.641	1542.4
0.098	615.5	0.390	1596.4	0.692	1439.3
0.146	871.8	0.441	1651.0	0.744	1294.9
0.193	1077.1	0.492	1666.7	0.794	1117.7
0.243	1258.7	0.541	1655.8	0.896	659.6
0.291	1400.8	0.591	1610.3	0.947	353.4

Table 4. Excess Molar Enthalpies of Methyl Acetate (1) and 2-Butanol (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
$T = 298.15$ K, $p = 5.00$ MPa					
0.303	1427.8	0.553	1683.5	0.801	1132.4
0.352	1541.0	0.603	1640.5	0.851	914.7
0.402	1622.8	0.654	1565.3	0.902	646.3
0.453	1677.4	0.702	1453.9	0.951	346.2
0.504	1695.0	0.751	1319.2		
$T = 298.15$ K, $p = 10.00$ MPa					
0.049	314.1	0.401	1622.2	0.752	1308.8
0.099	611.0	0.449	1673.7	0.799	1139.9
0.150	870.1	0.500	1692.1	0.849	913.0
0.199	1083.9	0.550	1681.1	0.901	642.4
0.249	1268.8	0.600	1641.4	0.950	338.7
0.300	1417.9	0.651	1564.3		
0.349	1532.8	0.699	1459.8		
$T = 308.15$ K, $p = 10.00$ MPa					
0.047	298.6	0.390	1690.4	0.744	1403.0
0.098	620.5	0.492	1780.5	0.794	1216.3
0.146	890.0	0.492	1770.9	0.896	702.5
0.193	1111.5	0.541	1774.4	0.947	381.4
0.243	1313.3	0.591	1737.7		
0.291	1470.8	0.641	1665.1		
0.343	1602.6	0.692	1553.9		

Table 5. Excess Molar Enthalpies of Methyl Acetate (1) and 1-Pentanol (2)

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
$T = 298.15$ K, $p = 5.00$ MPa					
0.049	343.7	0.401	1648.6	0.801	1105.3
0.100	658.8	0.451	1691.4	0.850	892.2
0.150	922.3	0.500	1703.4	0.901	627.3
0.200	1141.7	0.550	1686.7	0.950	334.7
0.249	1315.4	0.599	1636.8		
0.299	1460.3	0.650	1550.4		
0.349	1570.1	0.749	1296.8		
$T = 298.15$ K, $p = 10.00$ MPa					
0.049	346.1	0.400	1647.7	0.800	1101.2
0.100	661.2	0.450	1691.4	0.850	879.8
0.150	923.5	0.499	1704.5	0.901	612.1
0.199	1141.2	0.550	1685.6	0.950	312.6
0.248	1316.2	0.599	1635.5		
0.299	1463.1	0.649	1550.2		
0.348	1570.3	0.748	1292.2		
$T = 308.15$ K, $p = 10.00$ MPa					
0.051	359.0	0.400	1700.6	0.752	1324.0
0.100	679.1	0.450	1747.5	0.800	1139.8
0.150	932.2	0.499	1753.6	0.850	920.6
0.199	1174.5	0.550	1737.1	0.901	634.1
0.251	1360.3	0.599	1680.2	0.950	327.1
0.299	1512.1	0.649	1596.4		
0.351	1621.7	0.701	1469.7		

water at $T = 298.15$ K and $p = 0.2$ MPa were measured.[6] The uncertainty of H_m^E values measured in triplicate at the same mole fraction is less than 0.4 J·mol^{-1} for above three test systems. The uncertainty of composition on mole fraction base is 0.001. It can be seen that the good quality data can be produced by the high-pressure flow-mixing isothermal microcalorimeter as compared the smooth values of experimental data with literature data. Details of the experimental setup have been described previously.[6]

Result and Discussion

Experimental excess molar enthalpies for five binary mixtures (methyl acetate +1-propanol, 2-propanol, 1-butanol, 2-butanol, and 1-pentanol) at $T = (298.15, 308.15)$ K and $p = (5.0, 10.0)$ MPa are listed in Tables 1 to 5. As a typical example, experimental data from Table 1 are plotted in Figure 1. The experimental data were correlated using the Redlich−Kister equation:

$$H_m^E/\text{J·mol}^{-1} = x_1(1 - x_1)\sum_{i=0}^{N} A_i(1 - 2x_1)^i \qquad (1)$$

where x_1 represents the mole fraction of methyl acetate, and A_i is the parameters of Redlich−Kister equation. The parameters, A_i of Redlich−Kister equation were fitted to the experimental data with the least-squares method. The values of parameters (A_i) and standard deviations (SD) were listed in Table 6.

Figure 1 shows good agreement between experimental and calculated values. It can be seen from the figure that

Table 6. Parameters of Redlich−Kister Equation and Standard Deviations

T/K	p/MPa	A_0	A_1	A_2	A_3	A_4	A_5	SD^a/J·mol^{-1}
				Methyl Acetate + 1-Propanol				
298.15	5.0	6068.8	212.42	976.63	558.60	−603.10	−890.75	4.6
298.15	10.0	6059.1	331.14	862.08	−427.95	−244.75	842.07	2.1
333.15	10.0	7046.5	238.78	871.93	−538.66	−575.23	1844.7	4.7
				Methyl Acetate + 2-Propanol				
298.15	5.0	6257.2	−528.19	677.53	63.572	−19.238	−282.88	1.1
298.15	10.0	6211.5	−408.87	897.25	−110.26	−584.23		2.0
308.15	10.0	6695.9	−382.81	774.93	−270.55			2.3
				Methyl Acetate + 1-Butanol				
298.15	5.0	6234.3	59.469	653.33	64.074	−132.26	128.73	1.7
298.15	10.0	6221.4	72.185	670.66	−75.284	−165.35	273.53	1.3
308.15	10.0	6654.7	0.53011	864.77	378.86	−561.01	−697.18	3.6
				Methyl Acetate + 2-Butanol				
298.15	5.0	6783.2	−253.10	502.47				1.9
298.15	10.0	6759.3	−222.48	746.19	−13.274	−620.48		2.4
308.15	10.0	7108.4	−359.99	854.82	955.33	−955.32	−1444.1	3.7
				Methyl Acetate + 1-Pentanol				
298.15	5.0	6806.3	118.22	758.23	144.14	−301.20	−75.899	2.2
298.15	10.0	6797.4	187.56	934.14	−210.29	−795.17	717.94	3.4
308.15	10.0	6995.8	262.90	1066.0	−579.90	−1024.9	816.60	6.2

[a] SD = $[\Sigma(H^{E}_{\text{calc}} - H^{E}_{\text{exp}})^2/n]^{1/2}$, where n is the number of data for each data set.

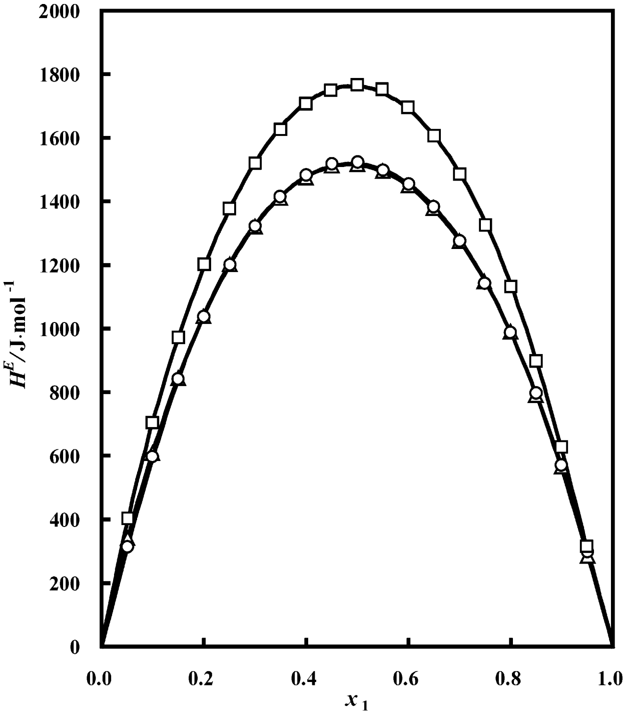

Figure 1. Excess molar enthalpies for methyl acetate (1) and 1-propanol (2) as a function of mole fraction x_1: ○, 298.15 K, 5.0 MPa; △, 298.15 K, 10.0 MPa; □, 333.15 K, 10.0 MPa. The curves were calculated by Redlich−Kister equation (parameters taken from Table 6).

the influence of pressure is slight for the excess molar enthalpy, but the influence of temperature is significant. All the binary systems showed endothermic and symmetrical behavior over the whole mole fraction range. So it is possible that the influence of pressure on the excess molar enthalpy could be ignored at the range of p = 0.1 MPa to p =10.0 MPa. For a given temperature and pressure, the H_m^E values increase with increasing the number of carbon atoms in the alkanol molecule (see Figure 2).

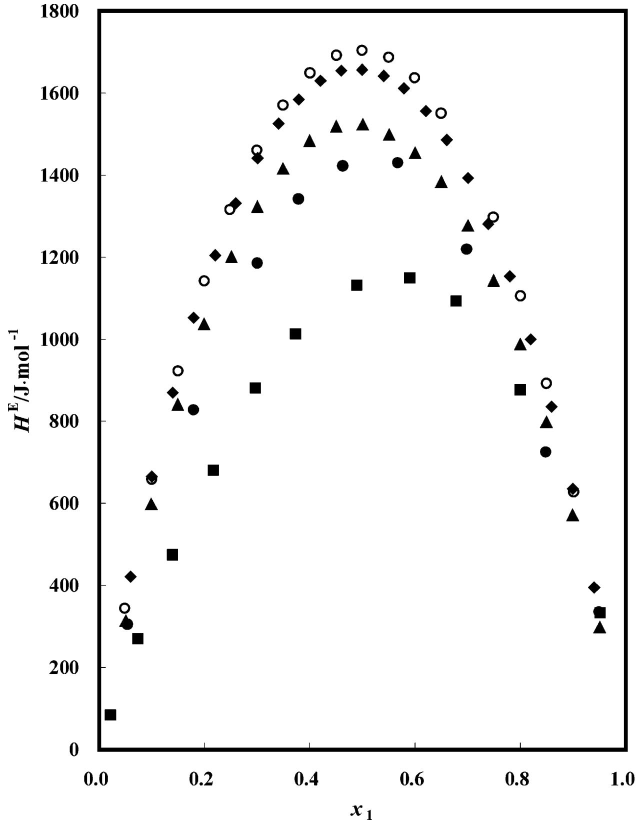

Figure 2. Excess molar enthalpies for methyl acetate (1) and 1-alkanol (2) as a function of mole fraction x_1 (Ortega, J. *Int. Data Ser., Selective Data Mixtures Ser. A* **1995**, *23*, 154). (298 K, 0.1 MPa): ■, methanol; ●, ethanol; this work (298.15 K, 5.0 MPa): ▲, 1-propanol; ◆, 1-butanol; ○, 1-pentanol.

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Received for review May 8, 2005. Accepted August 23, 2005.

JE050175U