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Determination and Correlation of Excess Molar Enthalpies of Eight Binary Systems Containing Acetophenone at Different Temperatures

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Excess molar enthalpies of six binary systems for acetophenone + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + *n*-heptane, + cyclohexane, and + water) at $T = (298.2, 313.2, 328.2, 338.2, \text{and } 348.2)$ K and $p = 101.3$ kPa and two binary systems for acetophenone + (*n*-hexane, and + ethyl acetate) at $T = (298.2, 313.2, \text{and } 328.2)$ K and $p = 101.3$ kPa were determined by a flow-mixing isothermal microcalorimeter. The excess molar enthalpies increase with an increase in the temperature. The experimental data were correlated by the Redlich−Kister equation and two local composition models (NRTL and UNIQUAC).

Introduction

Different types of phase equilibria and excess properties are widely used for simultaneous fitting and validating of the interaction parameters of the prediction models.[1] Excess enthalpy data are particularly important to develop the thermodynamic models and to understand the feature of molecular interactions in liquid mixtures. In continuation of our studies,[2,3] the excess molar enthalpies of six binary systems for acetophenone + (1-butanol, + 2-methyl-1-propanol, + 1-pentanol, + *n*-heptane, + cyclohexane, and + water) at $T = (298.2, 313.2, 328.2, 338.2, \text{and } 348.2)$ K and $p = 101.3$ kPa and two binary systems for acetophenone + (*n*-hexane, and + ethyl acetate) at $T = (298.2, 313.2, \text{and } 328.2)$ K and $p = 101.3$ kPa were determined using a flow-mixing isothermal microcalorimeter. The experimental data were fitted by the Redlich−Kister equation and two local composition models (NRTL and UNIQUAC).

Experimental Section

Materials. Acetophenone (guaranteed grade, $w = 0.995$) was provided by Huzhou Haipu Pharmaceutical & Chemical Co., Ltd. 1-Butanol, 2-methyl-1-propanol, 1-pentanol, and *n*-hexane (HPLC grade, $w = 0.997$) were purchased from Tianjin Saifu Technologies Co., Ltd. *n*-Heptane, cyclohexane, and ethyl acetate (analytical grade, $w = 0.995$) were provided by Sinopharm Chemical Reagent Co., Ltd. All chemicals above were dried with molecular sieves (3 to 4) Å and filtrated through a Millipore filter (0.45 μm). The mass fraction purities of these compounds were determined by gas chromatography and were found to be between $w = 0.995$ and 0.999. Deionized water was distilled by a quartz sub-boiling purifier. Before use, all chemicals were degassed by evacuation.

Apparatus and Procedure. A commercial isothermal microcalorimeter (model IMC 4400, Calorimetry Sciences Corporation, USA) with a refrigerating/heating circulator (model 9000, PolyScience Inc., USA) was used in this work. The flow-mixing system was composed of a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO Inc., USA), and a back pressure regulator (model CSC 4448). The uncertainty of composition on a mole fraction basis was 0.0005. The uncertainties of temperature and pressure were 0.1 K and 0.1 kPa, respectively. The uncertainty of the H_m^E value was less than 1.0 %. The experiment procedure and the reliability of the apparatus have been described in detail elsewhere.[4]

Table 1. Excess Molar Enthalpies of the System Acetophenone (1) + 1-Butanol (2) at $p = 101.3$ kPa

x_1	$\frac{H_\mathrm{m}^\mathrm{E}}{\mathrm{J\cdot mol^{-1}}}$	x_1	$\frac{H_\mathrm{m}^\mathrm{E}}{\mathrm{J\cdot mol^{-1}}}$	x_1	$\frac{H_\mathrm{m}^\mathrm{E}}{\mathrm{J\cdot mol^{-1}}}$
		$T = 298.2$ K			
0.0996	624.2	0.4504	1422.1	0.7001	1291.1
0.2005	1009.0	0.5005	1438.7	0.8000	1055.7
0.3001	1246.0	0.5506	1435.3	0.9001	645.7
0.3501	1326.9	0.6006	1410.1		
0.4002	1384.9	0.6504	1363.8		
		$T = 313.2$ K			
0.0996	718.0	0.4504	1699.4	0.7001	1499.1
0.2005	1183.9	0.5005	1716.2	0.8000	1193.7
0.3001	1492.2	0.5506	1704.9	0.9001	709.4
0.3501	1587.0	0.6006	1667.4		
0.4002	1656.9	0.6504	1597.0		
		$T = 328.2$ K			
0.0996	783.6	0.4504	1891.9	0.7001	1636.5
0.2005	1315.5	0.5005	1907.5	0.8000	1277.6
0.3001	1650.0	0.5506	1889.8	0.9001	738.4
0.3501	1764.2	0.6006	1842.5		
0.4002	1844.4	0.6504	1754.8		
		$T = 338.2$ K			
0.0996	808.7	0.4504	1969.4	0.7001	1674.9
0.2005	1364.5	0.5005	1981.0	0.8000	1300.3
0.3001	1725.3	0.5506	1960.6	0.9001	751.5
0.3501	1841.0	0.6006	1902.5		
0.4002	1923.6	0.6504	1807.4		
		$T = 348.2$ K			
0.0996	824.1	0.4504	2020.9	0.7001	1703.7
0.2005	1400.3	0.5005	2030.2	0.8000	1324.1
0.3001	1769.4	0.5506	2004.3	0.9001	771.3
0.3501	1892.2	0.6006	1937.6		
0.4002	1974.3	0.6504	1840.5		

Results and Discussion

In this work, excess molar enthalpies of six binary systems for acetophenone + (1-butanol, + 2-methyl-1-propanol, +

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Table 2. Excess Molar Enthalpies of the System Acetophenone (1) + 2-Methyl-1-propanol (2) at $p = 101.3$ kPa

x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}
$T = 298.2$ K					
0.1005	695.8	0.4516	1550.2	0.7008	1400.5
0.2010	1102.1	0.5017	1567.3	0.8016	1134.6
0.3010	1366.1	0.5518	1561.4	0.9010	684.2
0.3512	1448.9	0.6016	1532.8		
0.4014	1510.9	0.6513	1479.5		
$T = 313.2$ K					
0.1005	803.9	0.4516	1851.7	0.7008	1626.0
0.2010	1304.6	0.5017	1866.3	0.8016	1276.6
0.3010	1630.0	0.5518	1852.1	0.9010	741.4
0.3512	1732.0	0.6016	1808.4		
0.4014	1806.8	0.6513	1735.4		
$T = 328.2$ K					
0.1005	917.6	0.4516	2106.8	0.7008	1770.8
0.2010	1490.9	0.5017	2113.6	0.8016	1356.4
0.3010	1879.8	0.5518	2083.2	0.9010	764.6
0.3512	1990.1	0.6016	2016.2		
0.4014	2068.5	0.6513	1906.9		
$T = 338.2$ K					
0.1005	933.5	0.4516	2160.1	0.7008	1783.8
0.2010	1537.3	0.5017	2160.6	0.8016	1361.7
0.3010	1925.8	0.5518	2124.7	0.9010	775.9
0.3512	2041.7	0.6016	2047.8		
0.4014	2121.9	0.6513	1937.0		
$T = 348.2$ K					
0.1005	939.9	0.4516	2173.1	0.7008	1789.9
0.2010	1544.2	0.5017	2176.1	0.8016	1378.1
0.3010	1934.1	0.5518	2133.2	0.9010	783.7
0.3512	2055.4	0.6016	2058.4		
0.4014	2131.0	0.6513	1953.1		

Table 3. Excess Molar Enthalpies of the System Acetophenone (1) + 1-Pentanol (2) at $p = 101.3$ kPa

x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}
$T = 298.2$ K					
0.1003	631.2	0.4496	1416.0	0.7003	1286.2
0.1998	1005.5	0.4994	1433.3	0.8004	1053.2
0.2998	1246.3	0.5497	1430.5	0.8995	652.8
0.3497	1322.4	0.6004	1405.3		
0.4001	1380.9	0.6501	1358.7		
$T = 313.2$ K					
0.1003	729.4	0.4496	1702.5	0.7003	1519.8
0.1998	1185.3	0.4994	1721.3	0.8004	1217.3
0.2998	1487.7	0.5497	1715.1	0.8995	729.7
0.3497	1582.9	0.6004	1680.8		
0.4001	1657.0	0.6501	1614.8		
$T = 328.2$ K					
0.1003	777.9	0.4496	1894.2	0.7003	1645.3
0.1998	1300.6	0.4994	1911.6	0.8004	1282.3
0.2998	1650.0	0.5497	1896.9	0.8995	740.2
0.3497	1760.0	0.6004	1848.0		
0.4001	1844.8	0.6501	1767.0		
$T = 338.2$ K					
0.1003	796.9	0.4496	1978.1	0.7003	1706.0
0.1998	1356.9	0.4994	1995.0	0.8004	1319.7
0.2998	1723.1	0.5497	1977.1	0.8995	760.2
0.3497	1839.4	0.6004	1920.1		
0.4001	1928.0	0.6501	1833.7		
$T = 348.2$ K					
0.1003	801.7	0.4496	2009.5	0.7003	1717.3
0.1998	1370.6	0.4994	2024.6	0.8004	1330.3
0.2998	1744.4	0.5497	2000.9	0.8995	769.9
0.3497	1870.9	0.6004	1940.6		
0.4001	1959.3	0.6501	1843.9		

Table 4. Excess Molar Enthalpies of the System Acetophenone (1) + *n*-Heptane (2) at $p = 101.3$ kPa

x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}
$T = 298.2$ K					
0.0999	723.2	0.4504	1366.9	0.6998	1103.1
0.2002	1132.7	0.5003	1347.9	0.8001	869.3
0.3005	1308.9	0.5504	1311.2	0.8999	505.6
0.3498	1349.8	0.6006	1257.9		
0.4007	1365.7	0.6496	1190.7		
$T = 313.2$ K					
0.0999	742.2	0.4504	1515.2	0.6998	1218.5
0.2002	1194.2	0.5003	1497.9	0.8001	938.6
0.3005	1426.2	0.5504	1457.9	0.8999	523.9
0.3498	1480.7	0.6006	1398.9		
0.4007	1515.5	0.6496	1321.2		
$T = 328.2$ K					
0.0999	764.6	0.4504	1635.8	0.6998	1318.0
0.2002	1247.1	0.5003	1621.0	0.8001	1009.8
0.3005	1510.8	0.5504	1580.3	0.8999	565.6
0.3498	1580.8	0.6006	1516.6		
0.4007	1621.8	0.6496	1431.8		
$T = 338.2$ K					
0.0999	767.9	0.4504	1681.7	0.6998	1350.3
0.2002	1259.0	0.5003	1671.0	0.8001	1025.3
0.3005	1542.9	0.5504	1629.7	0.8999	570.5
0.3498	1624.2	0.6006	1562.1		
0.4007	1666.7	0.6496	1470.9		
$T = 348.2$ K					
0.0999	770.2	0.4504	1688.5	0.6998	1361.9
0.2002	1262.6	0.5003	1676.1	0.8001	1030.8
0.3005	1544.4	0.5504	1633.2	0.8999	579.0
0.3498	1628.3	0.6006	1566.1		
0.4007	1673.8	0.6496	1480.1		

Table 5. Excess Molar Enthalpies of the System Acetophenone (1) + Cyclohexane (2) at $p = 101.3$ kPa

x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}	x_1	$H^{\mathrm{E}}_{\mathrm{m}}$ / J·mol^{-1}
$T = 298.2$ K					
0.1004	752.0	0.4497	1352.9	0.7004	1090.9
0.1999	1106.4	0.4996	1338.3	0.8005	836.8
0.2999	1277.8	0.5498	1303.8	0.8995	475.1
0.3499	1327.2	0.6005	1252.4		
0.4002	1349.5	0.6503	1181.5		
$T = 313.2$ K					
0.1004	796.6	0.4497	1493.5	0.7004	1172.3
0.1999	1194.3	0.4996	1474.2	0.8005	873.2
0.2999	1406.2	0.5498	1433.1	0.8995	489.6
0.3499	1463.7	0.6005	1368.1		
0.4002	1490.6	0.6503	1283.2		
$T = 328.2$ K					
0.1004	807.1	0.4497	1570.1	0.7004	1209.1
0.1999	1236.0	0.4996	1547.9	0.8005	889.2
0.2999	1475.3	0.5498	1501.0	0.8995	493.2
0.3499	1540.0	0.6005	1427.4		
0.4002	1566.4	0.6503	1334.0		
$T = 338.2$ K					
0.1004	816.6	0.4497	1613.3	0.7004	1238.5
0.1999	1265.2	0.4996	1581.2	0.8005	911.4
0.2999	1515.6	0.5498	1537.1	0.8995	506.2
0.3499	1576.4	0.6005	1462.3		
0.4002	1609.8	0.6503	1363.7		
$T = 348.2$ K					
0.1004	819.4	0.4497	1618.5	0.7004	1251.3
0.1999	1270.3	0.4996	1599.7	0.8005	926.7
0.2999	1521.1	0.5498	1553.4	0.8995	511.0
0.3499	1587.3	0.6005	1477.7		
0.4002	1622.3	0.6503	1377.5		

1-pentanol, + *n*-heptane, + cyclohexane, and + water) at $T = (298.2, 313.2, 328.2, 338.2$, and $348.2)$ K and $p = 101.3$ kPa and two binary systems for acetophenone + (*n*-hexane, and + ethyl acetate) at $T = (298.2, 313.2$, and $328.2)$ K and $p = 101.3$

Table 6. Excess Molar Enthalpies of the System Acetophenone (1) + Water (2) at p = 101.3 kPa

x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$
T = 298.2 K					
0.1002	70.7	0.5003	341.3	0.8515	575.7
0.1997	137.9	0.5991	407.8	0.8967	588.2
0.3001	205.9	0.6986	474.7	0.9534	300.6
0.3991	273.0	0.7987	541.4		
T = 313.2 K					
0.1002	90.6	0.5003	443.2	0.8515	732.3
0.1997	177.5	0.5991	530.6	0.8967	669.8
0.3001	266.1	0.6986	618.9	0.9534	331.7
0.3991	353.8	0.7987	704.7		
T = 328.2 K					
0.1002	130.8	0.5003	606.5	0.8515	1003.4
0.1997	247.8	0.5991	724.3	0.8967	788.7
0.3001	366.4	0.6986	841.9	0.9534	387.4
0.3991	485.4	0.7987	959.9		
T = 338.2 K					
0.1002	143.0	0.5003	654.2	0.8515	1024.1
0.1997	254.4	0.5991	787.8	0.8967	802.3
0.3001	397.6	0.6986	923.7	0.9534	392.0
0.3991	517.8	0.7987	1060.1		
T = 348.2 K					
0.1002	167.1	0.5003	804.7	0.8515	1145.9
0.1997	323.0	0.5991	963.0	0.8967	855.1
0.3001	483.2	0.6986	1124.6	0.9534	418.6
0.3991	639.2	0.7987	1286.8		

Table 7. Excess Molar Enthalpies of the System Acetophenone (1) + *n*-Hexane (2) at p = 101.3 kPa

x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$
T = 298.2 K					
0.0997	706.4	0.4503	1342.1	0.7005	1075.9
0.2000	1102.1	0.4995	1323.4	0.8000	836.8
0.2994	1279.4	0.5494	1287.5	0.8995	474.1
0.3503	1324.3	0.5999	1234.0		
0.4006	1343.4	0.6499	1164.0		
T = 313.2 K					
0.0997	722.5	0.4503	1465.4	0.7005	1110.2
0.2000	1158.3	0.4995	1446.6	0.8000	847.6
0.2994	1375.9	0.5494	1404.8	0.8995	483.1
0.3503	1435.6	0.5999	1333.4		
0.4006	1460.8	0.6499	1226.2		
T = 328.2 K					
0.0997	732.6	0.4503	1534.4	0.7005	1160.3
0.2000	1190.4	0.4995	1518.8	0.8000	867.6
0.2994	1430.2	0.5494	1476.9	0.8995	491.2
0.3503	1492.5	0.5999	1409.9		
0.4006	1527.0	0.6499	1307.7		

kPa have been measured. The experimental data are listed in Tables 1 to 8. As typical examples, excess molar enthalpies of acetophenone (1) + 1-butanol (2) in Table 1 and acetophenone (1) + solvents (2) at 298.2 K and 101.3 kPa are plotted in Figures 1 and 2, respectively.

The experimental data of excess molar enthalpies are correlated by the Redlich−Kister equation and two local composition models (NRTL and UNIQUAC).

Redlich−Kister Equation. The Redlich−Kister equation[5] is widely used to correlate the H_m^E data

$$H_m^E = x_1(1 - x_1)\sum_{i=0}^{n} A_i(2x_1 - 1)^i \tag{1}$$

where x_1 is the mole fraction of acetophenone; A_i is the adjustable parameter; and n is the number of fitted parameters.

Table 8. Excess Molar Enthalpies of the System Acetophenone (1) + Ethyl Acetate (2) at p = 101.3 kPa

x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$	x_1	$\frac{H_m^E}{J \cdot mol^{-1}}$
T = 298.2 K					
0.1000	−12.2	0.4002	−30.9	0.7005	−26.3
0.2004	−21.3	0.4503	−31.6	0.8004	−20.2
0.2999	−27.6	0.5002	−31.6	0.9003	−10.3
0.3501	−29.6	0.5997	−30.0		
T = 313.2 K					
0.1000	−11.9	0.4002	−29.4	0.7005	−24.0
0.2004	−20.7	0.4503	−29.9	0.8004	−18.0
0.2999	−26.6	0.5002	−29.7	0.9003	−9.8
0.3501	−28.4	0.5997	−27.9		
T = 328.2 K					
0.1000	−11.7	0.4002	−29.0	0.7005	−22.6
0.2004	−20.5	0.4503	−29.2	0.8004	−16.4
0.2999	−26.2	0.5002	−28.8	0.9003	−8.2
0.3501	−28.2	0.5997	−26.7		

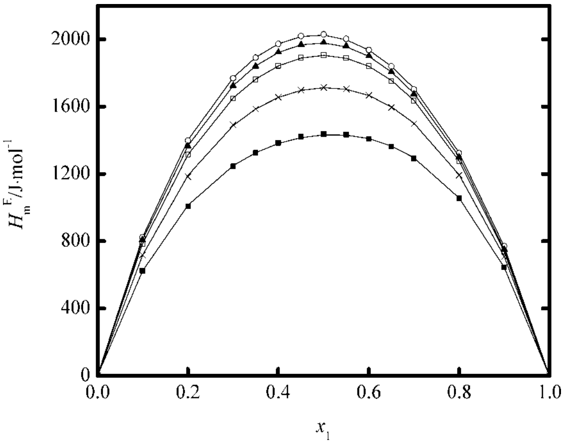

Figure 1. Excess molar enthalpies of the system acetophenone (1) + 1-butanol (2) as a function of mole fraction x_1. ■, 298.2 K; ×, 313.2 K; □, 328.2 K; ▲, 338.2 K; ○, 348.2 K. The curves were calculated by the Redlich−Kister equation (parameters taken from Table 9).

The Redlich−Kister parameters were obtained by the least-squares fit method and were listed in Table 9 together with the root-mean-square deviations (σ). The σ is defined as

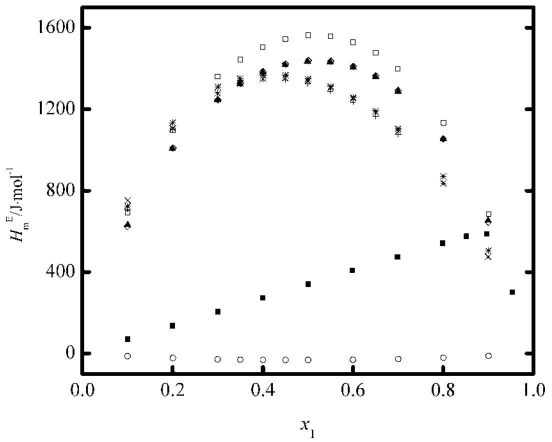

Figure 2. Excess molar enthalpies for the system acetophenone (1) + solvents (2) as a function of mole fraction x_1 at 298.2 K and 101.3 kPa. ◇, 1-butanol; □, 2-methyl-1-propanol; Δ, 1-pentanol; +, *n*-hexane; *, *n*-heptane; ×, cyclohexane; ○, ethyl acetate; ■, water.

$$\sigma = \sqrt{\frac{1}{N}\sum_{i}^{N}(H^{E}_{\mathrm{calcd}(i)} - H^{E}_{(i)})^{2}} \qquad (2)$$

where $H^{E}_{\mathrm{calcd}(i)}$ and $H^{E}_{(i)}$ are the calculated values and experimental values of excess molar enthalpies. N is the number of experimental data.

NRTL Model. From the NRTL G^{E} model,[6] the expression of H^{E}_{m} can be derived as follows

$$H^{E}_{m} = x_1 x_2\left[\frac{G_{21}(g_{21}-g_{11})(x_1 + x_2 G_{21} - x_1\tau_{21}\alpha_{21})}{(x_1 + x_2 G_{21})^{2}} + \frac{G_{12}(g_{12}-g_{22})(x_2 + x_1 G_{12} - x_2\tau_{12}\alpha_{12})}{(x_2 + x_1 G_{12})^{2}}\right] \qquad (3)$$

with

$$\tau_{21} = (g_{21} - g_{11})/RT,\ \tau_{12} = (g_{12} - g_{22})/RT,\quad G_{12} = \exp(-\alpha_{12}\tau_{12}),\ G_{21} = \exp(-\alpha_{21}\tau_{21})$$

where $(g_{21} - g_{11})$ and $(g_{12} - g_{22})$ are the interaction energy parameters and α_{12} is the nonrandomness parameter. They are obtained by nonlinear least-squares fit and listed in Table 10 together with σ.

UNIQUAC Model. The expression of H^{E}_{m} can be derived from the UNIQUAC G^{E} model[7] as follows

$$H^{E}_{m} = q_1 x_1\left(\frac{\theta_2}{\theta_1 + \theta_2\tau_{21}}\right)\tau_{21}\Delta u_{21} + q_2 x_2\left(\frac{\theta_1}{\theta_2 + \theta_1\tau_{12}}\right)\tau_{12}\Delta u_{12} \qquad (4)$$

with

$$\tau_{21} = \exp(-\Delta u_{21}/RT),\ \tau_{12} = \exp(-\Delta u_{12}/RT)\quad \theta_1 = x_1 q_1/(x_1 q_1 + x_2 q_2),\ \theta_2 = x_2 q_2/(x_1 q_1 + x_2 q_2)$$

where q_i is the structural parameter of pure component and Δu_{12} and Δu_{21} are the interaction energy parameters, which are obtained by nonlinear least-squares fit and given in Table 11 together with σ.

From Tables 1 to 8, it can be seen that the mixing process for binary systems shows endothermic behavior except the system acetophenone + ethyl acetate. For (acetophenone + alcohol) systems, the experimental data of excess molar en-

Table 9. Parameters A_i of the Redlich−Kister Equation with Root-Mean-Square Deviations (σ)

	Redlich−Kister equation				
T/K	A_0/J·mol^{-1}	A_1/J·mol^{-1}	A_2/J·mol^{-1}	A_3/J·mol^{-1}	σ/J·mol^{-1}
Acetophenone (1) + 1-Butanol (2)					
298.2	5734.8	321.2	2051.6	−273.1	3.8
313.2	6853.4	129.2	1677.0	−300.4	3.3
328.2	7623.0	−2.4	1322.0	−508.7	1.4
338.2	7917.8	−221.3	1177.3	−297.0	2.5
348.2	8101.7	−377.6	1189.0	−9.0	3.4
Acetophenone (1) + 2-Methyl-1-propanol (2)					
298.2	6246.0	344.0	2202.3	−546.3	5.2
313.2	7462.0	149.03	1764.4	−789.4	2.9
328.2	8449.6	−419.0	1394.4	−856.4	5.7
338.2	8629.3	−690.5	1339.4	−509.0	4.0
348.2	8675.1	−672.2	1393.0	−508.3	5.6
Acetophenone (1) + 1-Pentanol (2)					
298.2	5709.4	301.0	2143.2	−234.1	4.7
313.2	6873.0	294.5	1857.1	−455.4	3.4
328.2	7649.6	87.4	1185.3	−551.7	1.7
338.2	7987.3	−46.2	1012.4	−347.6	2.7
348.2	8090.4	−167.4	961.5	−97.9	1.7
Acetophenone (1) + *n*-Heptane (2)					
298.2	5385.9	−1128.3	2285.9	−614.5	3.6
313.2	6011.7	−1126.3	1653.5	−609.8	5.0
328.2	6492.4	−1054.9	1440.8	−516.7	3.2
338.2	6688.2	−1055.2	1189.3	−494.9	2.3
348.2	6708.9	−1038.4	1242.7	−459.5	2.4
Acetophenone (1) + Cyclohexane (2)					
298.2	5318.5	−854.11	2249.3	−1648.2	6.7
313.2	5867.4	−1147.2	1883.4	−1524.4	6.9
328.2	6168.3	−1369.1	1540.8	−1257.9	6.1
338.2	6327.7	−1461.3	1503.4	−1078.9	4.8
348.2	6383.0	−1401.3	1489.7	−1144.3	4.5
Acetophenone (1) + Water (2)					
298.2	1229.6	1231.9	3096.4	2945.5	31.2
313.2	1699.8	2139.7	3309.2	2128.4	31.3
328.2	2438.5	3513.5	3767.6	907.9	54.0
338.2	2682.1	4049.2	3671.1	131.4	54.8
348.2	3389.2	5087.2	3483.6	−1080.4	71.4
Acetophenone (1) + *n*-Hexane (2)					
298.2	5294.9	−1078.1	2002.6	−872.2	3.1
313.2	5747.6	−1484.5	1451.5	−332.8	8.2
328.2	6050.8	−1446.8	1122.6	−443.9	9.7
Acetophenone (1) + Ethyl Acetate (2)					
298.2	−127.8	3.9	1.7	12.4	0.3
313.2	−119.6	14.7	−2.5	−0.9	0.1
328.2	−116.9	20.6	8.1	5.7	0.2

Table 10. Parameters of the NRTL Equation with Root-Mean-Square Deviations (σ)

$\frac{(g_{12} - g_{22})}{\text{J·mol}^{-1}}$	$\frac{(g_{21} - g_{11})}{\text{J·mol}^{-1}}$	α_{12}	$\frac{\sigma}{\text{J·mol}^{-1}}$
Acetophenone (1) + 1-Butanol (2)			
8882.1	9176.0	0.194	91.0
Acetophenone (1) + 2-Methyl-1-propanol (2)			
9183.0	10277.9	0.178	104.5
Acetophenone (1) + 1-Pentanol (2)			
8984.3	9029.2	0.194	93.0
Acetophenone (1) + *n*-Heptane (2)			
5535.3	8301.8	0.220	33.5
Acetophenone (1) + Cyclohexane (2)			
4590.0	8256.3	0.220	23.5
Acetophenone (1) + Water (2)			
13435.8	2567.5	0.249	84.4
Acetophenone (1) + *n*-Hexane (2)			
4371.2	7698.3	0.225	21.1
Acetophenone (1) + Ethyl Acetate (2)			
−400.3	388.6	0.915	0.6

Table 11. Parameters of the UNIQUAC Equation with Root-Mean-Square Deviations (σ)

Δu_{21}/J·mol^{-1}	Δu_{12}/J·mol^{-1}	σ/J·mol^{-1}
Acetophenone (1) + 1-Butanol (2)		
1304.05	1806.97	146.0
Acetophenone (1) + 2-Methyl-1-propanol (2)		
1721.07	1836.98	154.1
Acetophenone (1) + 1-Pentanol (2)		
1359.01	1374.62	151.8
Acetophenone (1) + *n*-Heptane (2)		
2157.9	229.45	70.6
Acetophenone (1) + Cyclohexane (2)		
2107.9	546.6	57.4
Acetophenone (1) + Water (2)		
−113.0	7833.9	124.0
Acetophenone (1) + *n*-Hexane (2)		
2058.64	269.28	48.4
Acetophenone (1) + Ethyl Acetate (2)		
−345.99	357.28	1.0

thalpies increase with an increase in the temperature, carbon number, and branch of alcohols. It may be due to the increasing difficulty to form crossed associations between acetophenone and alcohols with increasing steric hindrance and aliphatic chain of alkanol. For the system acetophenone + ethyl acetate, the negative values of the excess molar enthalpies are small, showing nearly ideal mixing. For the systems acetophenone + alkanes, the experimental data of excess molar enthalpies increase with an increase in the temperature and the size of alkanes. For the immiscible system acetophenone + water, the values of excess molar enthalpies were linearly increased with an increase in molar fraction of water and then linearly decreased.

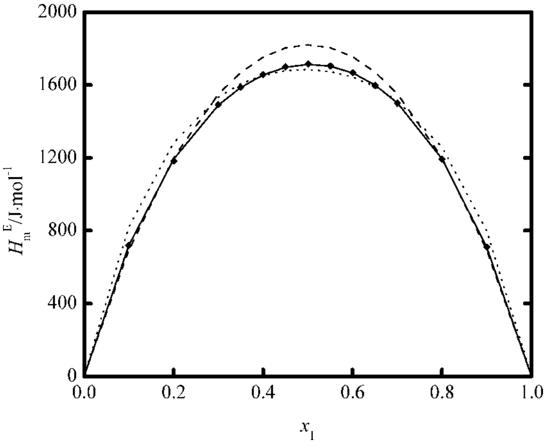

Figure 3. Correlation of excess molar enthalpies of the system acetophenone (1) + 1-butanol (2) at T = 313.2 K and p = 101.3 kPa as a function of mole fraction x_1. ◆, experimental data at 313.2 K and 101.3 kPa; −, calculated by the Redlich−Kister equation (parameters taken from Table 9); - -, calculated by the NRTL equation (parameters taken from Table 10); •••••, calculated by the UNIQUAC equation (parameters taken from Table 11).

From Tables 9 to 11, it can be seen that the Redlich−Kister equation, NRTL, and UNIQUAC are able to present the experimental data of the excess molar enthalpies. However, the Redlich−Kister equation has too many parameters, compared to the NRTL and UNIQUAC. As a typical example, the correlation curves for excess molar enthalpies of acetophenone (1) + 1-butanol (2) at 313.2 K and 101.3 kPa are plotted in Figure 3. It can be seen that the NRTL equation could give a better correlated result for the system than the UNIQUAC equation in this work.

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