Excess Enthalpies of 2,4-Pentanedione + (Methanol, + Ethanol, + 1-Propanol, and + 2-Propanol) at T = (298.15, 313.15, and 328.15) K and p = (0.1 and 10.0) MPa

Shengying Li, Weidong Yan,* and Hong Dong

Department of Chemistry, Zhejiang University, Hangzhou 310027, China

Molar excess enthalpies of four binary systems for 2,4-pentanedione + (methanol, + ethanol, + 1-propanol, and + 2-propanol) at T = (298.15, 313.15, and 328.15) K and p = (0.1 and 10.0) MPa were determined by a high-pressure flow-mixing isothermal microcalorimeter. The molar excess enthalpies increased with an increase in the temperature and the molecular size of alcohols and decreased slightly with an increase in pressure. The experimental data were correlated by the Redlich–Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

Introduction

2,4-Pentanedione (acetylacetone) is an important industrial chemical, which is widely used as a solvent for acetyl cellulose, additives of gasoline and antifriction, and a desiccant of paint and varnish. 2,4-Pentanedione has also been used as an important medical intermediate to synthesize sulfadimidine, antiviral agents, and diabetic medicine. 2,4-Pentanedione can form coordination complexes with almost all metals in the periodic table, which are extensively used as catalysts for important organic reactions[1,2] and selective extractants.[3] The possible structures of 2,4-pentanedione in the liquid state have been studied with the help of experiments[4,5] and theoretical analyses[6,7] because of its strong intramolecular O−H···O hydrogen bond. The thermodynamic properties of a pure component and its mixtures with other solvents are helpful to better understand and explain molecular interactions as well as to test and develop new models and theories that are able to describe the thermodynamic behavior of liquids.

Until now, very few data of molar excess enthalpies of mixtures containing 2,4-pentanedione have been reported. De Torre[8] has determined the excess molar enthalpies of 2,4-pentanedione + alkanes at T = 303.15 K. In this work, the excess molar enthalpies of four binary systems for 2,4-pentanedione + (methanol, + ethanol, + 1-propanol, and + 2-propanol) were determined using a high-pressure flow-mixing isothermal microcalorimeter at T = (298.15, 313.15, and 328.15) K and p = (0.1 and 10.0) MPa. The experimental data were fitted by the Redlich−Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC).

Experimental Section

Materials. 2,4-Pentanedione (guaranteed grade, w = 0.995) was purchased from Huzhou Haipu Pharmaceutical & Chemical Co., Ltd. Methanol, ethanol, 1-propanol, and 2-propanol (HPLC, w = 0.997) were provided by Tianjin Saifu Technologies Co., Ltd. and dried with molecular sieves (3 to 4) Å. The mass fraction purities of these compounds were determined by gas chromatography to be greater than w = 0.995 for 2,4-pentanedione and greater than w = 0.997 for methanol, ethanol, 1-propanol, and 2-propanol. 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 consisted 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 the 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 experimental procedure and the reliability of the apparatus have been described in detail elsewhere.[9]

Results and Discussion

In this work, the molar excess enthalpies of four binary systems for 2,4-pentanedione + (methanol, + ethanol, + 1-propanol, and + 2-propanol) have been measured at T = (298.15, 313.15, and 328.15) K and p = (0.1 and 10.0) MPa. The experimental data are listed in Tables 1 to 4. As examples, molar excess enthalpies of 2,4-pentanedione (1) + methanol (2) in Table 1 and 2,4-pentanedione (1) + alcohols (2) at 298.15 K and 0.1 MPa are plotted in Figures 1 and 2, respectively.

The experimental data of excess molar enthalpies are correlated by the Redlich–Kister equation and three local composition models (Wilson, NRTL, and UNIQUAC). The expressions of H_m^E can be derived from the G^E model through the Gibbs–Helmholtz equation

$$\left[\frac{\partial(G_m^E/T)}{\partial T}\right]_{P,x} = -\frac{H_m^E}{T^2} \quad (1)$$

Redlich–Kister Equation. The measured H_m^E data were correlated with eq 2, the Redlich–Kister equation[10]

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

where x_1 is the mole fraction of 2,4-pentanedione; A_i is the adjustable parameter; and n is the number of fitted parameters.

* Corresponding author. Tel.: 0086 571 87951430. Fax: 0086 571 87951895. E-mail: yanweidong@zju.edu.cn.

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Table 1. Molar Excess Enthalpies of the System 2,4-Pentanedione (1) + Methanol (2)

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
$T = 298.15$ K, $p = 0.1$ MPa					
0.0502	206.8	0.3995	951.3	0.7507	854.3
0.0995	374.8	0.4492	989.9	0.8006	749.7
0.1494	521.7	0.4990	1012.3	0.8500	615.6
0.1998	645.4	0.5509	1019.8	0.8983	455.1
0.2496	746.5	0.5989	1008.4	0.9500	238.4
0.3006	832.1	0.6509	975.9		
0.3504	897.7	0.7006	926.0		
$T = 298.15$ K, $p = 10.0$ MPa					
0.0501	200.6	0.3993	943.2	0.7505	853.0
0.0994	367.9	0.4490	981.3	0.8004	747.8
0.1493	513.3	0.4988	1005.6	0.8498	614.3
0.1997	635.4	0.5507	1013.3	0.8982	452.5
0.2494	736.3	0.5987	1005.9	0.9499	237.9
0.3004	822.0	0.6507	973.4		
0.3502	890.7	0.7005	923.3		
$T = 313.15$ K, $p = 0.1$ MPa					
0.0502	243.8	0.3995	1162.6	0.7507	1037.4
0.0995	448.7	0.4492	1209.7	0.8006	916.7
0.1494	628.0	0.4990	1232.5	0.8500	764.6
0.1998	780.6	0.5509	1239.8	0.8983	569.0
0.2496	909.4	0.5989	1224.5	0.9500	310.2
0.3006	1018.7	0.6509	1189.2		
0.3504	1102.2	0.7006	1124.3		
$T = 313.15$ K, $p = 10.0$ MPa					
0.0501	242.5	0.3993	1157.6	0.7505	1035.7
0.0994	448.5	0.4490	1209.4	0.8004	916.2
0.1493	628.1	0.4988	1230.5	0.8498	761.3
0.1997	780.4	0.5507	1237.4	0.8982	566.0
0.2494	908.3	0.5987	1221.0	0.9499	303.2
0.3004	1016.1	0.6507	1184.7		
0.3502	1100.9	0.7005	1123.7		
$T = 328.15$ K, $p = 0.1$ MPa					
0.0502	275.1	0.3995	1360.6	0.7507	1195.7
0.0995	510.5	0.4492	1414.5	0.8006	1044.2
0.1494	721.6	0.4990	1445.8	0.8500	856.5
0.1998	897.6	0.5509	1455.1	0.8983	635.8
0.2496	1050.9	0.5989	1432.6	0.9500	346.5
0.3006	1181.2	0.6509	1380.4		
0.3504	1283.9	0.7006	1303.9		
$T = 328.15$ K, $p = 10.0$ MPa					
0.0501	273.8	0.3993	1352.0	0.7505	1178.6
0.0994	508.3	0.4490	1403.5	0.8004	1030.8
0.1493	717.3	0.4988	1436.1	0.8498	849.5
0.1997	896.7	0.5507	1441.4	0.8982	632.0
0.2494	1045.7	0.5987	1422.0	0.9499	342.6
0.3004	1172.8	0.6507	1372.2		
0.3502	1273.4	0.7005	1288.8		

Table 2. Molar Excess Enthalpies of the System 2,4-Pentanedione (1) + Ethanol (2)

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
$T = 298.15$ K, $p = 0.1$ MPa					
0.0496	247.9	0.3988	1211.7	0.7494	1105.1
0.0992	456.3	0.4484	1260.4	0.7980	987.0
0.1496	652.5	0.4988	1291.5	0.8490	818.6
0.1992	809.0	0.5476	1304.0	0.8992	609.2
0.2491	943.0	0.5991	1291.7	0.9485	344.6
0.2988	1048.8	0.6484	1254.0	0.9688	216.7
0.3482	1140.7	0.6976	1198.7		
$T = 298.15$ K, $p = 10.0$ MPa					
0.0496	240.6	0.3988	1202.0	0.7494	1097.5
0.0992	454.3	0.4484	1252.1	0.7980	978.4
0.1496	641.5	0.4988	1282.6	0.8490	816.4
0.1992	800.5	0.5476	1291.5	0.8992	599.3
0.2491	932.5	0.5991	1279.4	0.9485	340.1
0.2988	1043.0	0.6484	1246.1	0.9688	214.9
0.3482	1131.1	0.6976	1186.9		
$T = 313.15$ K, $p = 0.1$ MPa					
0.0496	279.7	0.3988	1370.1	0.7494	1212.6
0.0992	519.9	0.4484	1422.5	0.7980	1069.7
0.1496	730.9	0.4988	1454.2	0.8490	884.5
0.1992	914.7	0.5476	1460.0	0.8992	643.8
0.2491	1065.8	0.5991	1442.9	0.9485	354.9
0.2988	1186.0	0.6484	1397.1	0.9688	221.3
0.3482	1294.5	0.6976	1321.5		
$T = 313.15$ K, $p = 10.00$ MPa					
0.0496	275.1	0.3988	1360.5	0.7494	1210.4
0.0992	517.5	0.4484	1413.5	0.7980	1071.0
0.1496	728.3	0.4988	1443.9	0.8490	881.9
0.1992	903.2	0.5476	1450.8	0.8992	638.4
0.2491	1056.6	0.5991	1431.6	0.9485	351.4
0.2988	1181.4	0.6484	1389.7	0.9688	219.1
0.3482	1279.8	0.6976	1317.3		
$T = 328.15$ K, $p = 0.1$ MPa					
0.0496	314.8	0.3988	1558.7	0.7494	1355.8
0.0992	592.2	0.4484	1619.9	0.7980	1190.2
0.1496	837.4	0.4988	1652.3	0.8490	976.9
0.1992	1044.3	0.5476	1657.2	0.8992	706.4
0.2491	1213.7	0.5991	1632.3	0.9485	390.8
0.2988	1356.1	0.6484	1578.0	0.9688	244.6
0.3482	1475.5	0.6976	1487.4		
$T = 328.15$ K, $p = 10.0$ MPa					
0.0496	313.5	0.3988	1542.5	0.7494	1328.0
0.0992	582.2	0.4484	1599.7	0.7980	1156.6
0.1496	827.9	0.4988	1635.6	0.8490	936.5
0.1992	1027.9	0.5476	1635.2	0.8992	682.2
0.2491	1202.6	0.5991	1607.8	0.9485	381.3
0.2988	1344.2	0.6484	1553.3	0.9688	237.6
0.3482	1456.2	0.6976	1467.7		

The Redlich–Kister parameters together with max relative deviation (RD) and average relative deviation (ARD) are given in Table 5. The RD and ARD are defined as:

$$\mathrm{RD} = \frac{|H^E_{\mathrm{exptl}(i)} - H^E_{\mathrm{calcd}(i)}|}{H^E_{\mathrm{exptl}(i)}} \tag{3}$$

$$\mathrm{ARD} = \frac{1}{N}\sum_{i}^{N} \frac{|H^E_{\mathrm{exptl}(i)} - H^E_{\mathrm{calcd}(i)}|}{H^E_{\mathrm{exptl}(i)}} \tag{4}$$

where $H^E_{\mathrm{calcd}(i)}$ and $H^E_{\mathrm{exptl}(i)}$ are the calculated values and experimental values of molar excess enthalpies and N is the number of data for each data set.

Wilson Model. The expression of H_m^E can be derived from the Wilson G^E model[11] as follows

$$H_m^E = x_1\left(\frac{\Lambda_{21}x_2}{x_1 + \Lambda_{21}x_2}\right)(\lambda_{21} - \lambda_{22}) + x_2\left(\frac{\Lambda_{12}x_1}{x_2 + \Lambda_{12}x_1}\right)(\lambda_{12} - \lambda_{11}) \tag{5}$$

with

$$\Lambda_{12} = \frac{V_{m1}}{V_{m2}}\exp[-(\lambda_{12} - \lambda_{11})/RT],$$

$$\Lambda_{21} = \frac{V_{m2}}{V_{m1}}\exp[-(\lambda_{21} - \lambda_{22})/RT]$$

where $V_{m,i}$ is the molar volume of pure component i (see Table S2 in the Supporting Information). λ_{ij} and λ_{ii} are the interaction energy parameters. The parameters $(\lambda_{ij} - \lambda_{ii})$ of the Wilson equation are obtained by a nonlinear least-squares fit and listed in Table 6 together with RD and ARD.

NRTL Model. The expression of H_m^E derived from the NRTL G^E model[12] is given in eq 6

Table 3. Excess Molar Enthalpies of the System 2,4-Pentanedione (1) + 1-Propanol (2)

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
		T = 298.15 K, p = 0.1 MPa			
0.0502	301.8	0.4502	1416.2	0.6994	1293.5
0.1502	770.2	0.5006	1439.5	0.8006	1036.8
0.2502	1084.2	0.5501	1439.6	0.8504	845.0
0.3504	1301.1	0.5997	1417.5	0.9493	332.4
0.4001	1368.6	0.6495	1367.8		
		T = 298.15 K, p = 10.0 MPa			
0.0502	297.8	0.4505	1412.4	0.6997	1290.6
0.1504	758.7	0.5010	1438.9	0.8009	1029.9
0.2504	1080.7	0.5505	1435.6	0.8506	842.0
0.3507	1293.3	0.6001	1416.9	0.9494	330.8
0.4004	1363.7	0.6499	1365.4		
		T = 313.15 K, p = 0.1 MPa			
0.0502	329.5	0.4502	1565.9	0.6994	1393.5
0.1502	855.8	0.5006	1591.5	0.8006	1092.1
0.2502	1209.0	0.5501	1583.5	0.8504	884.6
0.3504	1451.3	0.5997	1551.1	0.9493	349.5
0.4001	1524.8	0.6495	1487.4		
		T = 313.15 K, p = 10.0 MPa			
0.0502	324.1	0.4505	1552.8	0.6997	1376.2
0.1504	839.2	0.5010	1570.5	0.8009	1076.5
0.2504	1194.2	0.5505	1567.5	0.8506	867.1
0.3507	1436.3	0.6001	1536.8	0.9494	337.3
0.4004	1509.3	0.6499	1471.9		
		T = 328.15 K, p = 0.1 MPa			
0.0502	363.6	0.4502	1739.8	0.6994	1530.8
0.1502	936.4	0.5006	1759.6	0.8006	1195.7
0.2502	1344.8	0.5501	1752.1	0.8504	974.2
0.3504	1609.9	0.5997	1714.2	0.9493	382.1
0.4001	1688.5	0.6495	1638.2		
		T = 328.15 K, p = 10.0 MPa			
0.0502	362.3	0.4505	1726.3	0.6997	1507.8
0.1504	929.9	0.5010	1746.9	0.8009	1180.1
0.2504	1327.5	0.5505	1735.8	0.8506	952.6
0.3507	1584.7	0.6001	1693.6	0.9494	373.9
0.4004	1670.2	0.6499	1617.6		

Table 4. Molar Excess Enthalpies of the System 2,4-Pentanedione (1) + 2-Propanol (2)

x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}	x_1	H_m^E / J·mol^{-1}
		T = 298.15 K, p = 0.1 MPa			
0.0503	412.0	0.4498	1677.0	0.7000	1489.5
0.1501	984.5	0.5001	1692.9	0.7999	1192.6
0.2502	1344.9	0.5507	1685.8	0.8503	979.6
0.3499	1562.9	0.6000	1651.8	0.9504	382.5
0.3997	1632.9	0.6493	1588.9		
		T = 298.15 K, p = 10.0 MPa			
0.0502	388.2	0.4490	1653.6	0.6994	1480.6
0.1497	938.3	0.4993	1673.9	0.7993	1189.7
0.2496	1304.0	0.5498	1667.5	0.8499	977.8
0.3492	1534.9	0.5992	1634.3	0.9503	379.7
0.3989	1607.6	0.6486	1574.3		
		T = 313.15 K, p = 0.1 MPa			
0.0503	423.0	0.4498	1806.5	0.7000	1571.1
0.1501	1033.2	0.5001	1822.6	0.7999	1238.0
0.2502	1440.7	0.5507	1806.0	0.8503	997.2
0.3499	1686.3	0.6000	1759.1	0.9504	390.8
0.3997	1762.7	0.6493	1682.0		
		T = 313.15 K, p = 10.0 MPa			
0.0502	412.4	0.4490	1802.9	0.6994	1565.2
0.1497	1024.5	0.4993	1818.4	0.7993	1230.0
0.2496	1428.0	0.5498	1805.0	0.8499	995.7
0.3492	1680.6	0.5992	1756.4	0.9503	385.8
0.3989	1756.3	0.6486	1679.3		
		T = 328.15 K, p = 0.1 MPa			
0.0503	430.8	0.4498	1921.6	0.7000	1642.7
0.1501	1095.1	0.5001	1931.6	0.7999	1276.7
0.2502	1525.6	0.5507	1911.7	0.8503	1028.1
0.3499	1797.7	0.6000	1857.9	0.9504	392.9
0.3997	1873.8	0.6493	1767.3		
		T = 328.15 K, p = 10.0 MPa			
0.0502	430.8	0.4490	1908.8	0.6994	1640.0
0.1497	1079.9	0.4993	1923.5	0.7993	1271.4
0.2496	1513.6	0.5498	1904.3	0.8499	1020.1
0.3492	1782.1	0.5992	1852.9	0.9503	386.5
0.3989	1863.3	0.6486	1766.2		

$$H_m^E = x_1 x_2 \left[\frac{G_{21}(g_{21}-g_{11})(x_1 + x_2 G_{21} - x_1 \tau_{21} \alpha_{21})}{(x_1 + x_2 G_{21})^2} + \frac{G_{12}(g_{12}-g_{22})(x_2 + x_1 G_{12} - x_2 \tau_{12} \alpha_{12})}{(x_2 + x_1 G_{12})^2} \right] \quad (6)$$

with

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

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 a nonlinear least-squares fit. The parameters of the NRTL equation, RD and ARD, are listed in Table 7.

UNIQUAC Model. From the UNIQUAC G^E model,[13] H_m^E can be derived as follows

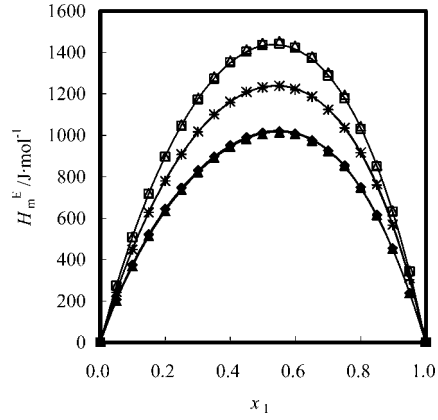

Figure 1. Molar excess enthalpies of the system 2,4-pentanedione (1) + methanol (2) as a function of mole fraction x_1: ♦, 298.15 K, 0.1 MPa; ▲, 298.15 K, 10.0 MPa; × , 313.15 K, 0.1 MPa; +, 313.15 K, 10.0 MPa; Δ, 328.15 K, 0.1 MPa; □, 328.15 K, 10.0 MPa. The curves were calculated by the Redlich–Kister equation (parameters taken from Table 5).

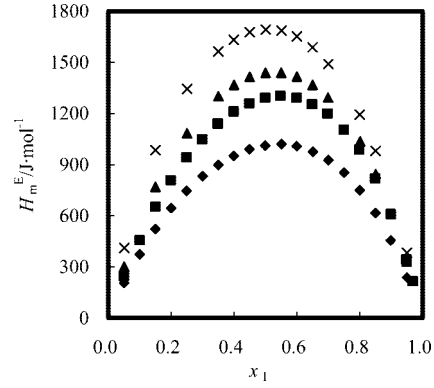

Figure 2. Molar excess enthalpies for the system 2,4-pentanedione (1) + alcohols (2) as a function of mole fraction x_1 at 298.15 K and 0.1 MPa: ♦, 2,4-pentanedione (1) + methanol (2); ■, 2,4-pentanedione (1) + ethanol (2); ▲, 2,4-pentanedione (1) + 1-propanol (2); × , 2,4-pentanedione (1) + 2-propanol (2).

Table 5. Parameters A_i of the Redlich–Kister Equation with Max Relative Deviation (RD) and Average Relative Deviation (ARD)

		Redlich–Kister Equation					
T	p	A_0 / J·mol^{-1}	A_1 / J·mol^{-1}	A_2 / J·mol^{-1}	A_3 / J·mol^{-1}	100 max RD	100 ARD
		2,4-Pentanedione (1) + Methanol (2)					
298.15 K	0.1 MPa	4058.7	651.2	800.6	−300.9	1.17	0.37
	10.0 MPa	4037.8	679.5	748.9	−273.8	1.11	0.41
313.15 K	0.1 MPa	4931.2	640.7	1087.6	189.7	0.38	0.16
	10.0 MPa	4931.7	663.5	1025.0	88.9	0.81	0.27
328.15 K	0.1 MPa	5776.2	712.4	892.7	142.4	0.67	0.24
	10.0 MPa	5730.0	664.1	890.8	166.7	0.53	0.24
		2,4-Pentanedione (1) + Ethanol (2)					
298.15 K	0.1 MPa	5164.7	794.1	1202.8	271.1	1.07	0.22
	10.0 MPa	5131.0	777.4	1132.3	316.6	0.54	0.14
313.15 K	0.1 MPa	5828.1	794.5	962.4	−48.1	0.93	0.31
	10.0 MPa	5797.9	835.4	928.0	−102.5	1.16	0.43
328.15 K	0.1 MPa	6624.3	723.7	911.5	13.2	0.55	0.18
	10.0 Mpa	6535.8	624.1	813.9	18.0	0.95	0.28
		2,4-Pentanedione (1) + 1-Propanol (2)					
298.15 K	0.1 Mpa	5767.6	587.7	1092.6	−319.4	0.76	0.33
	10.0 Mpa	5754.7	611.9	1026.3	−299.3	0.61	0.24
313.15 K	0.1 MPa	6367.6	275.3	905.1	−113.5	0.71	0.19
	10.0 MPa	6309.8	319.5	756.4	−241.1	0.45	0.21
328.15 K	0.1 MPa	7047.2	241.8	912.4	−77.7	0.26	0.11
	10.0 MPa	6969.2	248.1	874.1	−177.5	0.29	0.16
		2,4-Pentanedione (1) + 2-Propanol (2)					
298.15 K	0.1 MPa	6753.2	256	1969.7	−645.5	0.57	0.28
	10.0 MPa	6679.5	393	1726.2	−528.6	0.86	0.35
313.15 K	0.1 MPa	7264.4	−3.3	1559.6	−377.6	0.82	0.32
	10.0 MPa	7258.5	−8.3	1396.4	−326.9	0.39	0.18
328.15 K	0.1 MPa	7729.2	−219.1	1179.4	−207.4	0.59	0.13
	10.0 MPa	7693.2	−116.6	1124.5	−449.3	0.16	0.05

Table 6. Parameters of the Wilson Equation with Max Relative Deviation (RD) and Average Relative Deviation (ARD)

	Wilson			
p	$(\lambda_{12} - \lambda_{11})$ / J·mol^{-1}	$(\lambda_{21} - \lambda_{22})$ / J·mol^{-1}	100 max RD	100 ARD
	2,4-Pentanedione (1) + Methanol (2)			
0.1 MPa	4330.34	3147.52	37.2	26.3
10.0 MPa	4329.85	3147.34	36.8	21.7
	2,4-Pentanedione (1) + Ethanol (2)			
0.1 MPa	4006.79	3270.22	50.6	41.5
10.0 MPa	4003.38	3269.18	50.1	41.0
	2,4-Pentanedione (1) + 1-Propanol (2)			
0.1 MPa	3768.21	3313.66	55.9	50.6
10.0 MPa	3766.68	3311.51	55.5	50.1
	2,4-Pentanedione (1) + 2-Propanol (2)			
0.1 MPa	3728.58	3339.07	60.2	57.3
10.0 MPa	3729.48	3337.37	59.9	56.9

Table 7. Parameters of the NRTL Equation with Max Relative Deviation (RD) and Average Relative Deviation (ARD)

	NRTL				
p	$(g_{12} - g_{22})$ / J·mol^{-1}	$(g_{21} - g_{11})$ / J·mol^{-1}	α_{12}	100 max RD	100 ARD
	2,4-Pentanedione (1) + Methanol (2)				
0.1 MPa	6821.17	5315.93	0.276	31.3	10.6
10.0 MPa	6751.36	5263.55	0.278	43.6	11.6
	2,4-Pentanedione (1) + Ethanol (2)				
0.1 MPa	7235.84	5543.29	0.233	21.7	7.2
10.0 MPa	7040.90	5405.38	0.236	23.5	6.9
	2,4-Pentanedione (1) + 1-Propanol (2)				
0.1 MPa	7047.09	6463.49	0.216	18.5	5.2
10.0 MPa	6830.44	6243.02	0.218	17.6	5.1
	2,4-Pentanedione (1) + 2-Propanol (2)				
0.1 MPa	7103.48	7398.13	0.188	6.9	2.0
10.0 MPa	7094.14	7249.02	0.190	8.7	2.5

$$H_m^E = q_1 x_1 \left(\frac{\theta_2}{\theta_1 + \theta_2 \tau_{21}}\right) \tau_{21} \Delta u_{21} + q_2 x_2 \left(\frac{\theta_1}{\theta_2 + \theta_1 \tau_{12}}\right) \tau_{12} \Delta u_{12} \quad (7)$$

with

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

where q_i is the structural parameter of the pure component (see Table S4 in the Supporting Information) and Δu_{12} and Δu_{21} are the interaction energy parameters, which are obtained by a nonlinear least-squares fit and given in Table 8 together with RD and ARD.

The mixing processes for all binary systems in this work show endothermic behavior because they have positive excess molar enthalpies as shown in Tables 1 to 4. From Figure 1, H_m^E values increase with an increase of temperature and slightly decrease with an increase of pressure. The effect of temperature on molar excess enthalpies is more distinct than pressure. From Figure 2, it can be seen that the H_m^E value increases with an increase of branch and carbon number of alcohols. It may be due to the increasing difficulty to form crossed associations between 2,4-pentanedione and alcohols with increasing steric hindrance and aliphatic chain of alkanol.

As can be seen from Tables 5 to 8, the Redlich–Kister equation and the NRTL and UNIQUAC models can give a good correlation of the molar excess enthalpies for the systems in this work, while the Wilson model has an obvious deviation. As a typical example, the correlation curves for molar excess enthalpies of 2,4-pentanedione (1) + methanol (2) at 313.15 K and 0.1 MPa are plotted in Figure 3.

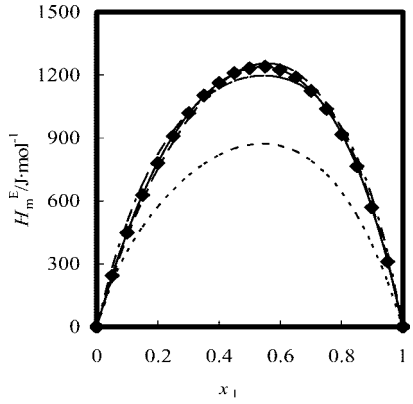

Figure 3. Correlation of molar excess enthalpies of the system 2,4-pentanedione (1) + methanol (2) as a function of mole fraction x_1: ♦, experimental data at 313.15 K and 0.1 MPa; —, calculated by the Redlich–Kister equation (parameters taken from Table 5); -----, calculated by the Wilson equation (parameters taken from Table 6); -•-•-, calculated by the NRTL equation (parameters taken from Table 7); ———, calculated by the UNIQUAC equation (parameters taken from Table 8).

Table 8. Parameters of the UNIQUAC Equation with Max Relative Deviation (RD) and Average Relative Deviation (ARD)

	UNIQUAC			
p	Δu_{21} / J·mol^{-1}	Δu_{12} / J·mol^{-1}	100 max RD	100 ARD
	2,4-Pentanedione (1) + Methanol (2)			
0.1 MPa	608.47	4431.62	32.1	9.8
10.0 MPa	585.95	4377.28	30.9	9.9
	2,4-Pentanedione (1) + Ethanol (2)			
0.1 MPa	740.38	3474.29	11.0	5.7
10.0 MPa	713.84	3401.32	11.6	5.4
	2,4-Pentanedione (1) + 1-Propanol (2)			
0.1 MPa	927.40	2355.89	12.5	5.5
10.0 MPa	908.48	2326.06	13.1	5.3
	2,4-Pentanedione (1) + 2-Propanol (2)			
0.1 MPa	1484.15	2444.38	6.2	2.8
10.0 MPa	1431.69	2460.02	8.1	2.8

It has been reported that the enol form of 2,4-pentanedione is in the majority with a strong intramolecular hydrogen bond in the liquid phase.[4] When 2,4-pentanedione interacts with alcohols, there are two opposite thermodynamic processes. The first one is the reduction of hydrogen bonds in alcohols and 2,4-pentanediones themselves, which is an endothermic process.[14] The second one is the formation of crossed associations between 2,4-pentanedione and alcohols, which is an exothermic process. The positive value of H_m^E indicates that 2,4-pentanedione can not easily interact with alcohols to form crossed associations through the intermolecular hydrogen bond.

Supporting Information Available:

Tables S1 to S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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