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Excess Molar Enthalpies of Methyl Acetoacetate + (Methanol, + Ethanol, + 1-Propanol, and + 2-Propanol) at T = (288.2, 298.2, 313.2, and 328.2) K and p = 101.3 kPa

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S Supporting Information

ABSTRACT: Excess molar enthalpies for four binary systems of methyl acetoacetate + (methanol, + ethanol, + 1-propanol, and + 2-propanol) at T = (288.2, 298.2, 313.2, and 328.2) K and p = 101.3 kPa were determined by using a flow-mixing isothermal microcalorimeter. The excess molar enthalpies increase with temperature and the molecular size of the alcohols. The experimental data were correlated by using the Redlich−Kister equation. The densities of the methyl acetoacetate at different temperatures were measured by using a vibrating-tube densimeter.

INTRODUCTION

Methyl acetoacetate is considered as a model β-diketone. It is widely used in the syntheses of a number of hetercycles, antipyrenes, farm chemicals, colorants, lacquers, and perfumes.[1−3] Moreover, methyl acetoacetate has a special physical property that is the tautomeric equilibrium between a ketone and its enol at room temperature.[4] Thermodynamic properties of methyl acetoacetate + alcohol mixtures are of particular interest because methyl acetoacetate provides both hydroxy (—OH) and carbonyl (C═O) groups for interactions with alcohols. To understand the nature of interactions in methyl acetoacetate + alcohol mixtures, densities, viscosities, refractive indices, and speeds of sound for methyl acetoacetate + aliphatic alcohols have been measured.[5] In a continuation of our studies on the thermodynamic properties of mixtures with β-diketones and solvents,[6−8] the excess molar enthalpies for four binary systems of methyl acetoacetate + (methanol, + ethanol, + 1-propanol, and + 2-propanol) were determined using a flow-mixing isothermal microcalorimeter at T = (288.2, 298.2, 313.2, and 328.2) K and p = 101.3 kPa. The experimental data were correlated using the Redlich−Kister equation.

EXPERIMENTAL SECTION

Materials. Methyl acetoacetate (guaranteed grade, better than w = 0.994) was purchased from Shanghai Zhuorui Chemicals. Methanol (high-performance liquid chromatography (HPLC) grade, better than w = 0.998) was provided by Tianjin Shield Fine Chemical. Ethanol (analytical grade, better than w = 0.997) was provided by Sinopharm Chemical Reagent. 1-Propanol and 2-propanol (HPLC grade, better than w = 0.995) were purchased from Tianjin Saifu, China. All chemicals above were dried with molecular sieves of (3 to 4) Å and filtrated through a Millipore filter (0.45 μm). Before use, all chemicals were degassed by evacuation.

Table 1. Excess Molar Enthapies of the System Methyl Acetoacetate (1) + Methanol (2) at p = 101.3 kPa

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/K = 288.2			
0.1004	533	0.4497	1248	0.7004	1076
0.2001	875	0.5001	1261	0.7993	847
0.3000	1097	0.5510	1247	0.8988	494
0.3506	1173	0.5993	1210		
0.4003	1224	0.6492	1161		
		T/K = 298.2			
0.1004	567	0.4497	1318	0.7004	1140
0.2001	930	0.5001	1336	0.7993	878
0.3000	1169	0.5510	1315	0.8988	490
0.3506	1246	0.5993	1286		
0.4003	1293	0.6492	1215		
		T/K = 313.2			
0.1004	619	0.4497	1452	0.7004	1221
0.2001	1028	0.5001	1458	0.7993	929
0.3000	1281	0.5510	1445	0.8988	521
0.3506	1373	0.5993	1400		
0.4003	1421	0.6492	1322		
		T/K = 328.2			
0.1004	664	0.4497	1549	0.7004	1280
0.2001	1091	0.5001	1550	0.7993	973
0.3000	1378	0.5510	1532	0.8988	539
0.3506	1466	0.5993	1477		
0.4003	1524	0.6492	1390		

Apparatus and Procedure. A commercial isothermal microcalorimeter (model IMC 4400, Calorimetry Sciences Corporation) with a refrigerating/heating circulator (model 9000, PolyScience)

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Table 2. Excess Molar Enthapies of the System Methyl Acetoacetate (1) + Ethanol (2) at p = 101.3 kPa

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/K = 288.2			
0.1003	733	0.4495	1608	0.7011	1408
0.2002	1163	0.5008	1620	0.7996	1125
0.2995	1423	0.5497	1608	0.9006	647
0.3494	1512	0.5995	1571		
0.3995	1568	0.6500	1505		
		T/K = 298.2			
0.1003	786	0.4495	1782	0.7011	1533
0.2002	1268	0.5008	1791	0.7996	1204
0.2995	1578	0.5497	1773	0.9006	686
0.3494	1668	0.5995	1731		
0.3995	1742	0.6500	1651		
		T/K = 313.2			
0.1003	878	0.4495	2007	0.7011	1695
0.2002	1437	0.5008	2014	0.7996	1308
0.2995	1774	0.5497	1992	0.9006	725
0.3494	1894	0.5995	1930		
0.3995	1968	0.6500	1839		
		T/K = 328.2			
0.1003	952	0.4495	2130	0.7011	1754
0.2002	1550	0.5008	2132	0.7996	1333
0.2995	1888	0.5497	2101	0.9006	728
0.3494	2003	0.5995	2022		
0.3995	2095	0.6500	1912		

was used in these measurements. The flow-mixing system was composed of a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO) with a displacement resolution of 0.02 μL, and a back pressure regulator (model CSC 4448). The IMC data acquisition software was provided by Calorimeter Science Corporation. The uncertainties of composition on a mole fraction basis, temperature, and pressure were 0.0005, 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.[9]

The densities of methyl acetoacetate at different temperatures (see Table S1 in the Supporting Information) were measured by a vibrating-tube densimeter (model DMA 5000 M). The uncertainty of density and temperature was 0.000005 g·cm^{-3} and 0.01 K, respectively.

RESULTS AND DISCUSSION

In this work, the excess molar enthalpies of four binary systems for methyl acetoacetate + (methanol, + ethanol, + 1-propanol, and + 2-propanol) have been measured at T = (288.2, 298.2, 313.2, and 328.2) K and p = 101.3 kPa. The experimental data are listed in Tables 1, 2, 3, and 4. As examples, excess molar enthalpies of methyl acetoacetate + methanol in Table 1 and methyl acetoacetate + alcohols at 298.2 K and p = 101.3 kPa are plotted in Figures 1 and 2, respectively.

Table 3. Excess Molar Enthapies of the System Methyl Acetoacetate (1) + 1-Propanol (2) at p = 101.3 kPa

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/K = 288.2			
0.0994	824	0.4500	1806	0.7000	1620
0.1995	1303	0.5008	1821	0.8001	1312
0.2993	1591	0.5498	1815	0.9003	778
0.3492	1685	0.6007	1779		
0.3995	1757	0.6495	1716		
		T/K = 298.2			
0.0994	918	0.4500	2035	0.7000	1788
0.1995	1470	0.5008	2053	0.8001	1408
0.2993	1799	0.5498	2039	0.9003	803
0.3492	1916	0.6007	1990		
0.3995	1997	0.6495	1910		
		T/K = 313.2			
0.0994	1022	0.4500	2341	0.7000	1972
0.1995	1672	0.5008	2348	0.8001	1511
0.2993	2071	0.5498	2315	0.9003	849
0.3492	2206	0.6007	2234		
0.3995	2298	0.6495	2123		
		T/K = 328.2			
0.0994	1098	0.4500	2508	0.7000	2041
0.1995	1811	0.5008	2515	0.8001	1549
0.2993	2250	0.5498	2454	0.9003	861
0.3492	2375	0.6007	2361		
0.3995	2468	0.6495	2228		

The experimental data of excess molar enthalpies are correlated by using the Redlich−Kister equation.

Redlich−Kister Equation. The Redlich−Kister equation[10] is widely used to correlate the H_m^E data because of its simplicity

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

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

The Redlich−Kister parameters were obtained by the least-squares fit method and are listed in Table 5 together with the root-mean-square deviations (σ). The σ is defined as

$$\sigma = \sqrt{\frac{1}{N}\sum_{i}^{N}(H_{calcd(i)}^E - H_{(i)}^E)^2} \tag{2}$$

where $H_{calcd(i)}^E$ and $H_{(i)}^E$ are the calculated values and experimental values of excess molar enthalpies. N is the number of experimental data points of each data set.

From Tables 1 to 4, the positive values of H_m^E indicate that the mixing processes for all binary systems in this work show endothermic values and the methyl acetoacetate may not easily interact with alcohols to form crossed associations through the intermolecular hydrogen bond. Figure 1 indicates that H_m^E values increase with temperature. There may be at least two reasons for this. The first is that the association of the H-bonds of the

Table 4. Excess Molar Enthapies of the System Methyl Acetoacetate (1) + 2-Propanol (2) at p = 101.3 kPa

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/K = 288.2					
0.1002	956	0.4493	1981	0.6991	1748
0.2005	1460	0.4998	1993	0.7997	1405
0.2998	1766	0.5504	1979	0.9002	810
0.3500	1873	0.6008	1935		
0.4004	1929	0.6492	1859		
T/K = 298.2					
0.1002	1049	0.4493	2242	0.6991	1927
0.2005	1648	0.4998	2243	0.7997	1509
0.2998	2010	0.5504	2221	0.9002	860
0.3500	2109	0.6008	2167		
0.4004	2196	0.6492	2068		
T/K = 313.2					
0.1002	1139	0.4493	2513	0.6991	2063
0.2005	1854	0.4998	2504	0.7997	1566
0.2998	2266	0.5504	2463	0.9002	859
0.3500	2382	0.6008	2366		
0.4004	2467	0.6492	2243		
T/K = 328.2					
0.1002	1194	0.4493	2673	0.6991	2133
0.2005	1963	0.4998	2651	0.7997	1597
0.2998	2412	0.5504	2592	0.9002	881
0.3500	2532	0.6008	2480		
0.4004	2650	0.6492	2336		

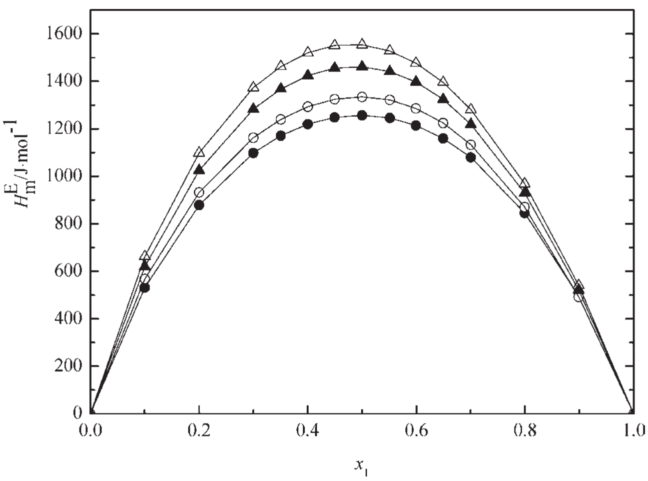

Figure 1. Excess molar enthalpies of the system methyl acetoacetate (1) + methanol (2) as a function of mole fraction at p = 101.3 kPa. ●, 288.2 K; ○, 298.2 K; ▲, 313.2 K; △, 328.2 K. The curves were calculated by the Redlich–Kister equation (parameters taken from Table 5).

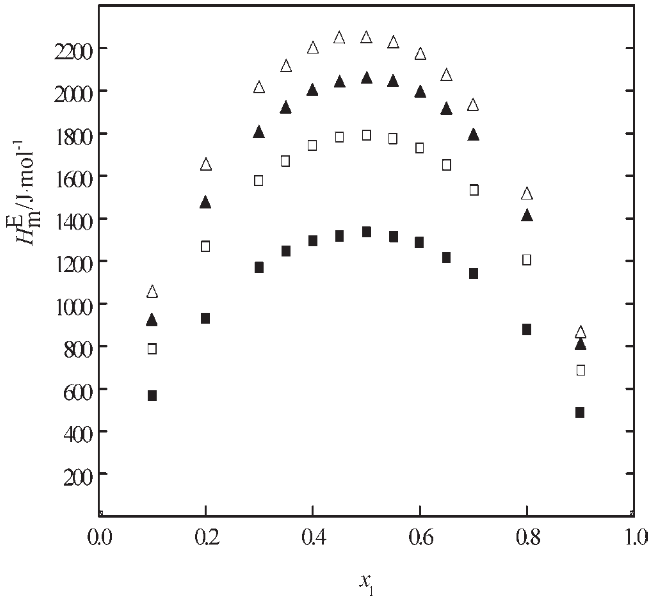

Figure 2. Excess molar enthalpies of the system methyl acetoacetate (1) + alcohols (2) as a function of mole fraction at T = 298.2 K and p = 101.3 kPa: ■, methanol; □, ethanol; ▲, 1-propanol; △, 2-propanol.

Table 5. Parameters, A_i, of the Redlich–Kister Equation with the Root-Mean-Square Deviation (σ) at p = 101.3 kPa

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}
Methyl Acetoacetate (1) + Methanol (2)					
288.2	5030	−473	982	−378	2
298.2	5340	−48	796	−783	4
313.2	5847	−261	702	−694	2
328.2	6216	−435	658	−690	3
Methyl Acetoacetate (1) + Ethanol (2)					
288.2	6466	98	1881	−1012	3
298.2	7163	−58	1582	−921	3
313.2	8069	−291	1336	−1132	2
328.2	8512	−593	1299.3	−1442	5
Methyl Acetoacetate (1) + 1-Propanol (2)					
288.2	7261	352	2586	−1045	5
298.2	8212	135	2168	−1451	4
313.2	9378	−461	1640	−1173	4
328.2	10007	−1056	1420	−953	4
Methyl Acetoacetate (1) + 2-Propanol (2)					
288.2	7941	222.3	2876	−1833	5
298.2	8972	−169	2517	−1717	4
313.2	10022	−959	1711	−1500	4
328.2	10603	−1525	1426	−982	4

alcohols will be weakened as the temperature increases, where the association positively contributes to H_m^E. The second is that the increase of the molecular heat motion leads with difficulty to form crossed associations between methyl acetoacetate and alcohols, where the crossed association negatively contributes to H_m^E. From Figure 2, it can be seen that the H_m^E value increases with the increasing number of branches and carbon number of alcohols. This may be due to the increasing difficulty in forming crossed associations between methyl acetoacetate and alcohols

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with an increase in the steric hindrance and aliphatic chain length of alcohols. Therefore, mixtures of methyl acetoacetate with higher alcohols give larger H_m^E as compared to lower alcohols.

■ ASSOCIATED CONTENT

Supporting Information. Table S1: Densities of methyl acetoacetate at different temperatures with the standard deviation. This material is available free of charge via the Internet at http://pubs.acs.org.

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