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Excess Molar Enthalpies of Five Binary Systems Containing Ethyl Acetoacetate at Different Temperatures

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Excess molar enthalpies of five binary systems for ethyl acetoacetate + (1-butanol, + 2-butanol, + 1-pentanol, + water, and + ethyl acetate) at $T = (298.15, 313.15, 328.15, 338.15, \text{and } 348.15)$ K and $p = 0.1$ MPa 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.

Introduction

Excess molar enthalpy is a very important thermodynamic property of solution. This property of solution can provide information about the molecular interaction and macroscopic behavior of fluid mixture. Different types of phase equilibria and excess properties are particularly important for developing the thermodynamic parameters of the prediction models.[1] In a continuation of our studies,[2−4] the excess molar enthalpies of five binary systems for ethyl acetoacetate + (1-butanol, + 2-butanol, + 1-pentanol, + water, and + ethyl acetate) at $T = (298.15, 313.15, 328.15, 338.15, \text{and } 348.15)$ K and $p = 0.1$ MPa were determined by a flow-mixing isothermal microcalorimeter. The experimental data were fitted by the Redlich−Kister equation.

Experimental Section

Materials. Ethyl acetoacetate (guaranteed grade, $w = 0.995$) was purchased from Shanghai Jiachen Chemical. 1-Butanol, 2-butanol, and 1-pentanol (HPLC grade, $w = 0.997$) were provided by Tianjin Saifu, China. Ethyl acetate (analytical grade, $w = 0.995$) was purchased from Sinopharm Chemical Reagent. All chemicals above were dried with molecular sieves of (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) with a refrigerating/heating circulator (model 9000, PolyScience) 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). It can be used to measure the mixing heat at high pressure up to 15 MPa and over the 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 data acquisition software was provided by Calorimeter Science Corporation. 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 experiment procedure and the reliability of the apparatus have been described in detail elsewhere.[5]

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

x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$	x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$	x_1	$\frac{H_m^E}{\text{J·mol}^{-1}}$
$T = 298.15$ K					
0.1003	913	0.4500	1920	0.7000	1688
0.2002	1408	0.5005	1935	0.8005	1345
0.3000	1707	0.5501	1920	0.9007	767
0.3502	1811	0.5999	1877		
0.3999	1877	0.6499	1802		
$T = 313.15$ K					
0.1003	1001	0.4500	2221	0.7000	1863
0.2002	1564	0.5005	2224	0.8005	1415
0.3000	1938	0.5501	2192	0.9007	799
0.3502	2066	0.5999	2122		
0.3999	2154	0.6499	2017		
$T = 328.15$ K					
0.1003	1117	0.4500	2512	0.7000	2065
0.2002	1812	0.5005	2507	0.8005	1551
0.3000	2254	0.5501	2466	0.9007	841
0.3502	2384	0.5999	2374		
0.3999	2471	0.6499	2245		
$T = 338.15$ K					
0.1003	1135	0.4500	2575	0.7000	2078
0.2002	1861	0.5005	2563	0.8005	1555
0.3000	2313	0.5501	2509	0.9007	842
0.3502	2452	0.5999	2415		
0.3999	2533	0.6499	2271		
$T = 348.15$ K					
0.1003	1160	0.4500	2607	0.7000	2082
0.2002	1901	0.5005	2591	0.8005	1558
0.3000	2352	0.5501	2531	0.9007	847
0.3502	2492	0.5999	2418		
0.3999	2575	0.6499	2272		

Results and Discussion

In this work, the excess molar enthalpies of five binary systems for ethyl acetoacetate + (1-butanol, + 2-butanol, +

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Table 2. Excess Molar Enthalpies of the System Ethyl Acetoacetate (1) + 2-Butanol (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 = 298.15 K					
0.1002	980	0.4512	2061	0.6507	1925
0.2008	1519	0.5017	2075	0.7007	1801
0.3009	1837	0.5512	2059	0.8005	1415
0.4011	2019	0.6009	2008	0.8999	805
T = 313.15 K					
0.1002	1126	0.4500	2438	0.6493	2207
0.1997	1760	0.5004	2439	0.7007	2034
0.2998	2164	0.5499	2408	0.8005	1548
0.3999	2380	0.5995	2324	0.8999	872
T = 328.15 K					
0.1002	1200	0.4500	2641	0.6493	2329
0.1997	1938	0.5004	2632	0.7007	2120
0.2998	2375	0.5499	2579	0.8005	1590
0.3999	2608	0.5995	2475	0.8999	882
T = 338.15 K					
0.1002	1225	0.4500	2702	0.6493	2335
0.1997	1974	0.5004	2681	0.7007	2124
0.2998	2440	0.5499	2610	0.8005	1594
0.3999	2666	0.5995	2500	0.8999	885
T = 348.15 K					
0.1002	1229	0.4500	2709	0.6493	2342
0.1997	1983	0.5004	2693	0.7007	2125
0.2998	2442	0.5499	2618	0.8005	1601
0.3999	2673	0.5995	2512	0.8999	889

Table 3. Excess Molar Enthalpies of the System Ethyl Acetoacetate (1) + 1-Pentanol (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 = 298.15 K					
0.0998	913	0.4504	1926	0.7002	1744
0.1996	1384	0.5003	1945	0.7995	1431
0.3006	1711	0.5498	1939	0.9004	851
0.3505	1809	0.6000	1904		
0.4001	1879	0.6497	1842		
T = 313.15 K					
0.0998	1050	0.4504	2318	0.7002	2020
0.1996	1669	0.5003	2332	0.7995	1593
0.3006	2052	0.5498	2307	0.9004	898
0.3505	2181	0.6000	2258		
0.4001	2265	0.6497	2164		
T = 328.15 K					
0.0998	1125	0.4504	2598	0.7002	2181
0.1996	1854	0.5003	2603	0.7995	1666
0.3006	2301	0.5498	2560	0.9004	928
0.3505	2456	0.6000	2492		
0.4001	2545	0.6497	2355		
T = 338.15 K					
0.0998	1181	0.4504	2682	0.7002	2201
0.1996	1924	0.5003	2683	0.7995	1669
0.3006	2390	0.5498	2634	0.9004	930
0.3505	2535	0.6000	2541		
0.4001	2632	0.6497	2396		
T = 348.15 K					
0.0998	1184	0.4504	2695	0.7002	2206
0.1996	1928	0.5003	2694	0.7995	1670
0.3006	2393	0.5498	2644	0.9004	933
0.3505	2537	0.6000	2551		
0.4001	2644	0.6497	2404		

1-pentanol, + water, and + ethyl acetate) have been measured at T = (298.15, 313.15, 328.15, 338.15, and 348.15) K and p = 101.3 kPa. The experimental data are listed in Tables 1, 2, 3, 4, and 5. As typical examples, excess molar enthalpies of ethyl acetoacetate (1) + 1-butanol (2) in Table 1 and ethyl acetoacetate (1) + solvents (2) at 298.15 K and 0.1 MPa are plotted in Figures 1 and 2, respectively.

Table 4. Excess Molar Enthalpies of the System Ethyl Acetoacetate (1) + Water (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 = 298.15 K					
0.1502	175	0.6014	923	0.8474	870
0.2994	428	0.7001	1078	0.9034	600
0.4491	684	0.7514	1128	0.9496	320
T = 313.15 K					
0.1502	276	0.6014	1232	0.8474	998
0.2994	597	0.7001	1401	0.9034	696
0.4491	920	0.7514	1320	0.9496	385
T = 328.15 K					
0.1502	386	0.6014	1570	0.8474	1074
0.2994	783	0.7001	1584	0.9034	736
0.4491	1185	0.7514	1466	0.9496	390
T = 338.15 K					
0.1502	472	0.6014	1823	0.7514	1564
0.2994	929	0.6499	1787	0.7970	1383
0.4491	1398	0.7001	1698	0.9034	778
T = 348.15 K					
0.1502	558	0.6014	1932	0.7514	1615
0.2994	1087	0.6499	1892	0.7970	1412
0.4491	1616	0.7001	1786	0.9034	786

Table 5. Excess Molar Enthalpies of the System Ethyl Acetoacetate (1) + Ethyl Acetate (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 = 298.15 K					
0.1005	25	0.4496	57	0.7001	46
0.1995	41	0.4998	56	0.7994	35
0.2996	52	0.5500	55	0.9004	19
0.3495	54	0.6001	52		
0.3995	56	0.6502	49		
T = 313.15 K					
0.1005	25	0.4496	61	0.7001	52
0.1995	42	0.4998	61	0.7994	42
0.2996	53	0.5500	60	0.9004	28
0.3495	57	0.6001	58		
0.3995	59	0.6502	56		
T = 328.15 K					
0.1005	21	0.4496	49	0.7001	37
0.1995	35	0.4998	48	0.7994	27
0.2996	44	0.5500	47	0.9004	18
0.3495	47	0.6001	44		
0.3995	48	0.6502	41		
T = 338.15 K					
0.1005	19	0.4496	47	0.7001	37
0.1995	33	0.4998	46	0.7994	29
0.2996	41	0.5500	45	0.9004	17
0.3495	44	0.6001	43		
0.3995	46	0.6502	41		
T = 348.15 K					
0.1005	17	0.4496	42	0.7001	35
0.1995	29	0.4998	42	0.7994	27
0.2996	36	0.5500	41	0.9004	17
0.3495	39	0.6001	39		
0.3995	41	0.6502	38		

The experimental data of excess molar enthalpies are correlated by the Redlich–Kister equation[6]

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

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

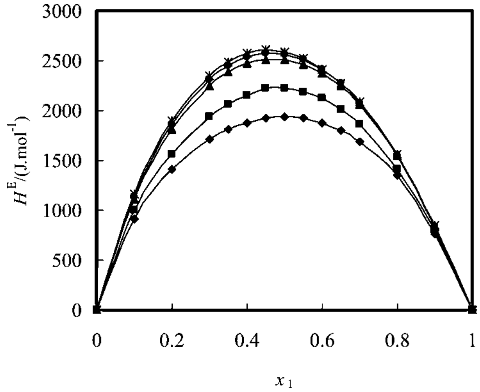

Figure 1. Excess molar enthalpies of the system ethyl acetoacetate (1) + 1-butanol (2) as a function of mole fraction, x_1: ◆, 298.15 K; ■, 313.15 K; ▲, 328.15 K; ●, 338.15 K; *, 348.15 K. The curves were calculated by the Redlich−Kister equation (parameters taken from Table 6).

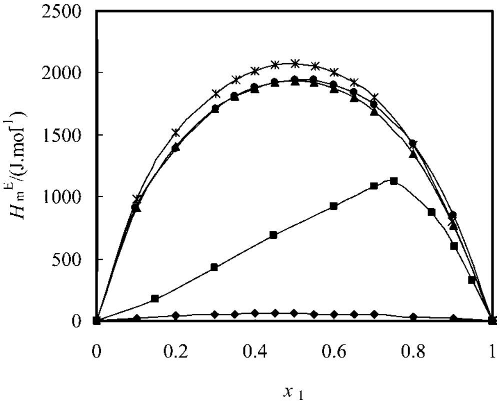

Figure 2. Excess molar enthalpies of the system ethyl acetoacetate (1) + solvents (2) as a function of mole fraction, x_1, at 298.15 K and 101.3 kPa: ▲, 1-butanol; *, 2-butanol; ●, 1-pentanol; ◆, ethyl acetate; ■, water.

The Redlich−Kister parameters were obtained by the least-squares fit method and are listed in Table 6 together with the root-mean-square deviations (σ). The σ is defined as

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

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.

From Tables 1, 2, 3, 4, and 5, it can be seen that the mixing processes for all binary systems in this work show endothermic behavior. The positive value of H^{E}_{m} indicates that ethyl acetoacetate cannot easily interact with alcohols to form crossed associations through the intermolecular hydrogen bond. For three binary systems ethyl acetoacetate + alcohols, the experimental data of excess molar enthalpies increase with an increase in the temperature, carbon number, and branch of alcohols. It may be due to the increasing difficulty of forming crossed associations between ethyl acetoacetate and alcohols with increasing steric hindrance and aliphatic chain of alkanol. For the system ethyl acetoacetate + ethyl acetate, the positive values of the excess molar enthalpies are small, showing nearly ideal mixing because of their similar structure. For the immiscible system ethyl acetoacetate + water, the values of excess molar enthalpies were linearly increased with an increase in molar fraction of water and then linearly decreased.

Table 6 Parameters, A_i, of the Redlich−Kister Equation with Root-Mean-Square Deviations (σ)

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}
Ethyl Acetoacetate (1) + 1-Butanol (2)					
298.15	7715.1	203.9	2519.7	−1781.2	7.4
313.15	8829.4	−158.4	1714	−1840.5	13.9
328.15	10 047	−844.2	1322.2	−1569.5	4.5
338.15	10 265	−1179	1147.7	−1228.1	3.0
348.15	10 358	−1458.8	1263.2	−1004.3	4.1
Ethyl Acetoacetate (1) + 2-Butanol (2)					
298.15	8281.8	157.8	2511.2	−2103.9	6.0
313.15	9711.3	−411.66	2053.7	−2073.8	10.8
328.15	10 505	−1291.3	1587.4	−1411	6.1
338.15	10 678	−1668.4	1531.7	−1033	9.2
348.15	10 709	−1668.5	1555.3	−1039	11
Ethyl Acetoacetate (1) + 1-Pentanol (2)					
298.15	7742.2	517.99	3167.5	−1384.9	13
313.15	9323.9	123.72	2384.6	−1788.5	6.2
328.15	10 418	−543.9	1594.8	−1281	4.1
338.15	10 699	−892.11	1594.8	−1317.7	5.3
348.15	10 736	−885.7	1569.7	−1327.8	7.7
Ethyl Acetoacetate (1) + Water (2)					
298.15	3254.2	4833.7	1520.4	−2587.2	47
313.15	4337.3	5280.6	1312.9	−2807.5	34
328.15	5467.9	5417.8	458.63	−3409.8	16
338.15	6324.2	5097.1	−155.66	−2892.2	29
348.15	7025.2	4406.5	−776.96	−2241.1	22
Ethyl Acetoacetate (1) + Ethyl Acetate (2)					
298.15	224.4	−36.7	34.8	1.8	0.3
313.15	240.0	−16.7	74.8	57.8	0.7
328.15	202.6	−37.145	31.4	10.2	0.3
338.15	183.9	−32.7	24.3	37.6	0.2
348.15	165.73	−13.932	27.426	24.982	0.2

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