Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 443 (2006) 125–128

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Excess molar enthalpies of methylformate + (1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-pentanol) at $T = 298.15$ K, $p = (5.0, 10.0)$ MPa, and methylformate + 1-propanol at $T = 333.15$ K, $p = 10.0$ MPa

Weidong Yan*, Hong Dong, Rui Zhang, Shengying Li

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

Received 20 October 2005; received in revised form 18 November 2005; accepted 22 November 2005
Available online 18 January 2006

Abstract

A high pressure flow-mixing isothermal calorimeter is used to determine the excess molar enthalpies of methylformate + (1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-pentanol) at $T = 298.15$ K and $p = (5.0, 10.0)$ MPa, and methylformate + 1-propanol at $T = 333.15$ K and $p = 10.0$ MPa. The Redlich–Kister equation is fit to the experimental results.

Keywords: Methylformate; 1-Propanol; 2-Propanol; 1-Butanol; 2-Butanol; 1-Pentanol; Excess molar enthalpy

1. Introduction

For proper design of chemical processes and to test theories of solution, there is a constant need for thermodynamic excess enthalpy data. To determine the influence of temperature and pressure on the excess molar enthalpy, and to overcome the lack of the data on mixtures of ester and alcohols at high pressure, excess molar enthalpies of five binary systems for methylformate and (1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-pentanol) were determined at $T = (298.15, 333.15)$ K and $p = (5.0, 10.0)$ MPa. The excess molar enthalpy of methylformate and 1-propanol at $T = 298.15$ K and $p = 0.1$ MPa was reported in literature [1]. But the published H_m^E data were determined at ambient pressure.

2. Experimental

2.1. Chemicals

In all experiments, methylformate (A.R. grade) and alcohols (A.R. grade) were dried with the help of molecular sieves (3 Å) and filtered by Millipore filter (0.45 μm).

2.2. Apparatus

A commercial isothermal calorimeter (model IMC 4400, Calorimetry Sciences Corporation, USA) was used in these measurements. The flow-mixing system consists of a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO Inc., USA) with a resolution of 0.1 μL min^{-1}, and a back pressure regulator (model CSC 4448). To confirm the reliability of this calorimeter, excess molar enthalpies of three binary systems, ethanol + water at $T = 298.15$ K and $p = (0.2, 0.4)$ MPa [2], methanol + water and acetone + water at $T = 298.15$ K and $p = 0.2$ MPa were measured [2]. The uncertainty of H_m^E values measured in triplicate at the same mole fraction is less than 0.4 J mol^{-1} for the above three systems.

3. Results

Excess molar enthalpies of methylformate and (1-propanol, 2-propanol, 1-butanol, 2-butanol and 1-pentanol) at $T = (298.15, 333.15)$ K and $p = (5.0, 10.0)$ MPa are listed in Tables 1–5. Experimental results were fitted to a Redlich–Kister polynomial:

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

---

[*] Corresponding author. Tel.: +86 571 87951430; fax: +86 571 87951895.
E-mail addresses: yanwd@hzcnc.com (W.D. Yan), donghong1686@hotmail.com (H. Dong).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.11.041

Table 1
Excess molar enthalpies of methylformate (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					
0.0399	328.2	0.3414	1680.5	0.6990	1475.4
0.0788	621.1	0.3893	1746.7	0.7562	1281.4
0.1201	888.2	0.4381	1777.4	0.8146	1059.8
0.1621	1116.1	0.4878	1788.2	0.8743	773.5
0.2066	1311.2	0.5386	1764.2	0.9376	406.4
0.2501	1468.8	0.5903	1706.2		
0.2944	1590.1	0.6452	1605.3		
T = 298.15 K, p = 10.00 MPa					
0.0398	342.4	0.3407	1729.8	0.6983	1491.6
0.0786	646.3	0.3885	1792.3	0.7556	1303.3
0.1197	922.2	0.4373	1824.2	0.8141	1070.4
0.1616	1153.1	0.4870	1823.4	0.8739	773.0
0.2061	1357.6	0.5377	1790.8	0.9374	403.2
0.2495	1515.1	0.5895	1726.2		
0.2937	1637.4	0.6444	1621.4		
T = 333.15 K, p = 10.00 MPa					
0.0403	336.3	0.3404	1972.8	0.7005	1754.3
0.0788	670.4	0.3868	2057.7	0.7572	1528.7
0.1205	986.8	0.4370	2110.2	0.8151	1267.2
0.1629	1264.2	0.4853	2128.3	0.8743	935.7
0.2061	1496.8	0.5374	2097.7	0.9347	516.7
0.2500	1689.7	0.5907	2035.2		
0.2948	1850.9	0.6450	1920.0		

Table 6 contains the parameters of Redlich–Kister equation and standard deviations (S.D.). The experimental data from Tables 1–5 are plotted in Figs. 1–3.

4. Discussion

All the binary systems showed endothermic and symmetrical behavior over the whole mole fraction range. The explanation of the above behavior is thought to be steric interactions. The most important molecular associations in the pure liquids are through hydrogen bonds in the alcohols and dipole–dipole inter-

Table 2
Excess molar enthalpies of methylformate (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					
0.0399	354.6	0.3471	1871.2	0.7055	1670.1
0.0822	700.2	0.3951	1949.4	0.7606	1488.3
0.1235	985.6	0.4440	1989.8	0.8191	1227.4
0.1656	1232.9	0.4938	1998.5	0.8766	933.2
0.2102	1443.9	0.5447	1977.5	0.9376	507.8
0.2556	1622.4	0.5965	1922.9		
0.3000	1763.0	0.6494	1823.0		
T = 298.15 K, p = 10.00 MPa					
0.0398	358.7	0.3463	1858.9	0.7048	1658.2
0.0820	700.7	0.3943	1934.5	0.7600	1468.6
0.1232	985.5	0.4432	1976.3	0.8186	1213.6
0.1651	1228.5	0.4930	1985.5	0.8762	905.3
0.2096	1441.9	0.5439	1967.9	0.9374	493.8
0.2549	1615.7	0.5957	1906.0		
0.2993	1751.2	0.6487	1809.0		

Table 3
Excess molar enthalpies of methylformate (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					
0.0501	442.1	0.4004	1920.6	0.7494	1431.5
0.1000	831.3	0.4503	1950.0	0.8004	1212.1
0.1496	1145.1	0.5003	1947.3	0.8509	971.0
0.2000	1400.6	0.5505	1910.4	0.9006	677.6
0.2496	1597.3	0.6006	1840.7	0.9495	345.4
0.2999	1747.5	0.6505	1730.4		
0.3508	1851.7	0.7002	1592.9		
T = 298.15 K, p = 10.00 MPa					
0.0500	441.1	0.3996	1909.5	0.7511	1410.0
0.0997	828.1	0.4495	1941.2	0.7999	1205.2
0.1506	1149.2	0.4995	1935.5	0.8505	955.4
0.1994	1396.4	0.5497	1895.9	0.9003	666.2
0.2505	1597.4	0.5998	1822.0	0.9493	331.6
0.2992	1741.8	0.6498	1717.1		
0.3500	1847.6	0.6995	1586.1		

Table 4
Excess molar enthalpies of methylformate (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					
0.0501	454.1	0.4004	2061.0	0.7494	1592.5
0.1000	860.6	0.4503	2103.8	0.8004	1373.6
0.1496	1192.8	0.5003	2108.5	0.8509	1090.4
0.2000	1471.6	0.5505	2074.5	0.9006	768.2
0.2496	1690.1	0.6006	2005.2	0.9495	415.4
0.2999	1859.9	0.6505	1913.0		
0.3508	1985.4	0.7002	1763.3		
T = 298.15 K, p = 10.00 MPa					
0.0996	896.9	0.3993	2090.7	0.7003	1771.3
0.1500	1215.0	0.4504	2131.8	0.7491	1591.6
0.1994	1488.0	0.4992	2133.5	0.7997	1353.7
0.2493	1709.3	0.5501	2097.2	0.8494	1081.2
0.2997	1884.0	0.6006	2030.0	0.9008	729.1
0.3504	2007.0	0.6508	1919.2		

Table 5
Excess molar enthalpies of methylformate (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					
0.0507	550.3	0.4005	2182.7	0.7492	1614.5
0.0997	989.3	0.4488	2208.2	0.7983	1380.5
0.1503	1351.9	0.4998	2198.3	0.8497	1099.4
0.2004	1628.7	0.5506	2134.3	0.8992	757.3
0.2494	1839.0	0.6009	2062.9	0.9509	356.7
0.2991	2000.4	0.6503	1942.7		
0.3496	2113.9	0.6986	1802.7		
T = 298.15 K, p = 10.00 MPa					
0.0505	538.6	0.3997	2172.5	0.7486	1611.1
0.0994	977.3	0.4509	2197.8	0.8020	1370.7
0.1499	1337.0	0.4990	2187.1	0.8493	1100.8
0.1998	1614.9	0.5498	2140.6	0.8988	762.0
0.2510	1832.5	0.6001	2067.3	0.9507	344.8
0.3009	1991.5	0.6496	1950.0		
0.3488	2105.5	0.7017	1787.9		

Table 6
The parameters of Redlich–Kister equation and standard deviations

	A_0	A_1	A_2	A_3	A_4	A_5	S.D.[a] (J mol^{-1})
Methylformate + 1-propanol							
298.15 K, 5 MPa	7121.3	649.21	1392.0	899.11	−719.70	−740.05	3.77
298.15 K, 10 MPa	7252.4	903.69	1593.3	572.30	−957.71	−292.95	3.23
333.15 K, 10 MPa	8495.30	472.78	1436.0	1407.5	−1354.8	−2184.7	7.38
Methylformate + 2-propanol							
298.15 K, 5 MPa	7980.1	377.33	1717.1	287.83	−510.96	−502.15	5.50
298.15 K, 10 MPa	7931.6	386.00	1607.3	539.65	−456.79	−485.17	3.20
Methylformate + 1-butanol							
298.15 K, 5 MPa	7753.4	883.79	1726.5	−7.3452	−1303.6	417.33	6.28
298.15 K, 10 MPa	7692.0	976.52	1906.7	−290.83	−1661.8	888.99	6.50
Methylformate + 2-butanol							
298.15 K, 5 MPa	8418.0	563.40	1623.5	−42.272	−955.48		3.78
298.15 K, 10 MPa	8500.3	445.67	1854.3	1409.2	−1980.8	−1280.2	13.64
Methylformate + 1-pentanol							
298.15 K, 5 MPa	8731.3	1328.9	2522.6	−984.74	−1788.5	2407.1	7.34
298.15 K, 10 MPa	8695.7	1291.1	2786.9	−1320.5	−2377.8	2914.3	10.73

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

actions between molecules of ester. The main interactions in the hydrogen bonds are those between the oxygen atoms of the ester group and hydrogen atoms of the alcohol hydroxyl group [3]. The reduction of hydrogen bonds in alcohols aggregates upon mixing provides a positive contribution to H^E; the formation of cross-associates between methyl formate and alcohols provides a negative contribution. The values of H^E will depend on the balance between these two opposite contributions. The positive values of H^E indicate a preponderance of the endothermic perhaps associated to the reduction of self-associated interactions (hydrogen bonds in alcohols and dipole–dipole interac-

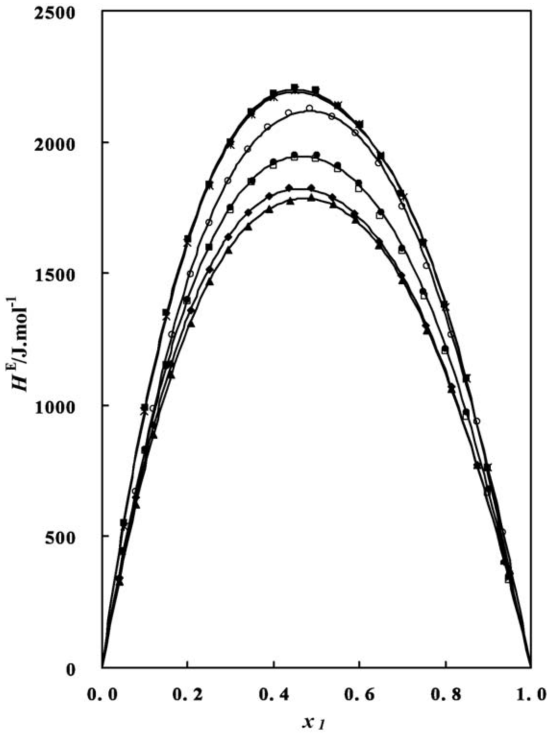

Fig. 1. Excess molar enthalpies for methylformate (1) and alcohols (2) as a function of x_1. The curves were calculated using the parameters of Table 6 from the Redlich–Kister equation as described in the text. 1-Propanol: (▲) 298.15 K, 5 MPa; (◆) 298.15 K, 10 MPa; (◯) 333.15 K, 10 MPa. 1-Butanol: (●) 298.15 K, 5 MPa; (□) 298.15 K, 10 MPa. 1-Pentanol: (■) 298.15 K, 5 MPa; (*) 298.15 K, 10 MPa.

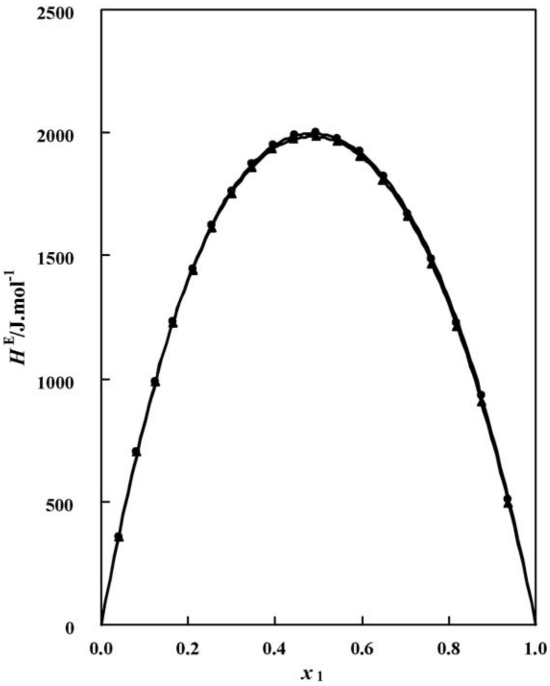

Fig. 2. Excess molar enthalpies for methylformate (1) and 2-propanol (2) as a function of x_1. The curves were calculated using the parameters of Table 6 from the Redlich–Kister equation as described in the text. (●) 298.15 K, 5 MPa; (▲) 298.15 K, 10 MPa.

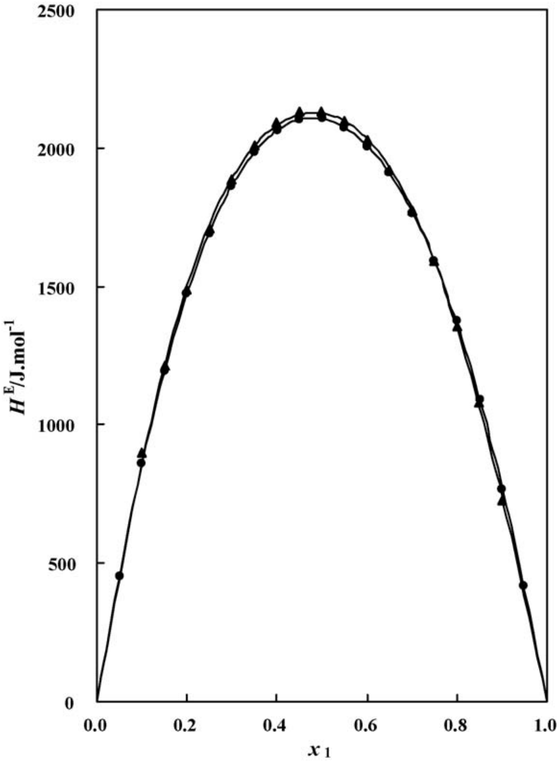

Fig. 3. Excess molar enthalpies for methylformate (1) and 2-butanol (2) as a function of x_1. The curves were calculated using the parameters of Table 6 from the Redlich–Kister equation as described in the text. (●) 298.15 K, 5 MPa; (▲) 298.15 K, 10 MPa.

tions in both components) [4,5]. The increasing of H^E with the side chain of the alcohol was ascribed to the difficulty of cross-interaction between the alcohol and methyl formate in the mixture.

The excess enthalpies of propanol and butanol isomers increase with shielding around the hydroxyl group. This suggests that more bonds in the branches alcohols will break at a given concentration than for the normal alcohol solution [6].

References

[1] F. Sarmiento, M. López, M.I. Paz Andrade, J. Fernández, Excess molar enthalpies at 298.15 K of (an *n*-alkyl formate + an *n*-alkanol) III. $\{x\mathrm{HCO_2CH_3} + (1-x)\mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH}\}$ ($n = 3$ to 10), J. Chem. Thermodyn. 20 (1988) 1315–1319.

[2] R. Zhang, W.D. Yan, X. Wang, R.S. Lin, Molar excess enthalpies of ethyl acetate + alkanols at $T = 298.15$ K, $p = 10$ MPa, Thermochim. Acta 429 (2005) 155–161.

[3] J. Fernandez, M.I. Paz Andrade, F. Sarmiento, R. Bravo, Excess enthalpies of (methyl propanoate or methyl pentanoate + 1-alkanol) at 298.15 K, J. Chem. Thermodyn. 15 (1983) 1145–1149.

[4] E. Romano, J.L. Trenzado, Thermophysical properties of four binary dimethyl carbonate + 1-alcohol systems at 288.15–313.15 K, Fluid Phase Equilibr. 211 (2003) 219–240.

[5] H.Y. Yang, J.P. Zhao, H.P. Li, M. Dai, Excess molar enthalpies of *n*-alkanols or isomeric alkanols + *N*,*N*-dimethlethanolamine at 298.15 K, Thermochim. Acta 253 (1995) 69–75.

[6] R. Garriga, S. Martúnez, P. Pėrez, M. Gracia, Vapour pressure at several temperatures, and excess functions at $T = 298.15$ K of (butanone + 2-butanol), J. Chem. Thermodyn. 31 (1999) 117–127.