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Excess Molar Enthalpies of Dimethyl Carbonate and (Methanol, Ethanol, 1-Propanol, and 2-Propanol) at T = (298.15, 313.15, and 328.15) K and p = (0.1, 1.0, and 10.0) MPa

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A high-pressure flow-mixing isothermal microcalorimeter is used to determine the excess molar enthalpies of four binary systems for dimethyl carbonate and (methanol, ethanol, 1-propanol, and 2-propanol) at T = (298.15, 313.15, and 328.15) K and p = (0.1, 1.0, and 10.0) MPa. The smooth values of H_m^E calculated by the Redlich−Kister equation are also compared with the experimental results.

1. Introduction

In the last few years, papers and patents involving dimethyl carbonate have increased because this fluid is benign with respect to the environment. Dimethyl carbonate is an additive for gasoline and is a component of hydraulic fluids. It has also been shown to be very useful in lithium battery technology. Furthermore, dimethyl carbonate is a versatile solvent used in the synthesis of many chemicals (e.g., polycarbonates, pharmaceuticals, agrochemicals, and isocyanates) and is used as a replacement for hazardous chemicals. (For example, dimethyl carbonate has been used as an effective carbonylation agent to substitute for the phosgene in manufacturing plastics polycarbonate and as a useful methylation agent to replace dimethyl sulfate.[1]) Dimethyl carbonate has been successfully manufactured by using carbon dioxide and methanol as raw materials according to a zero-discharge process coproducing propylene glycol.[2]

Excess enthalpy is a very important solution thermodynamic property. This solution property can provide information about the molecular interactions and macroscopic behavior of fluid mixtures. The determination and research of excess enthalpy not only aids in clarifying the structure of solutions and testing and improving solution theories but also can provide significant thermodynamic basic data for the development and design of chemical engineering process (e.g., predicting vapor−liquid equilibrium data and testing the thermodynamic consistency of the isobaric VLE data).

The excess molar enthalpies of dimethyl carbonate + (methanol, ethanol, and 1-propanol) at T = 313.15 K and at atmospheric pressure were reported in the literature.[3] However, data for these binary systems at other temperatures and pressures are very limited in the literature. To study the influence of temperature and pressure on the excess molar enthalpies and to enlarge the existing database on the excess molar enthalpies of dimethyl carbonate, a high-pressure flow-mixing isothermal microcalorimeter was used to determine the excess molar enthalpies of four binary systems of dimethyl carbonate + (methanol, ethanol, 1-propanol, and 2-propanol) at T = (298.15, 313.15, and 328.15) K and p = (0.1, 1.0, and 10.0) MPa in this work.

Table 1. Excess Molar Enthalpies for the System Dimethyl Carbonate (1) + Methanol (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 = 1.00 MPa					
0.2500	1141.8	0.4500	1323.2	0.6500	1144.1
0.3000	1227.0	0.5000	1309.7	0.7000	1049.2
0.3500	1286.5	0.5500	1269.4	0.7500	932.7
0.4000	1318.0	0.6000	1213.6	0.8000	807.7
T = 313.15 K, p = 0.10 MPa					
0.0480	312.8	0.3503	1426.9	0.6489	1285.9
0.1000	644.0	0.4001	1467.1	0.6987	1187.8
0.1492	886.4	0.4510	1479.2	0.7499	1062.6
0.2014	1096.6	0.4985	1452.6	0.7992	904.6
0.2506	1245.2	0.5501	1426.5	0.8510	710.7
0.3020	1355.0	0.6014	1361.8	0.9500	234.7
T = 313.15 K, p = 1.00 MPa					
0.0477	355.8	0.3487	1423.9	0.6504	1277.2
0.0994	661.2	0.3985	1472.2	0.7001	1177.8
0.1484	901.6	0.4493	1483.5	0.7512	1049.6
0.2003	1103.2	0.5006	1462.9	0.8005	899.2
0.2493	1242.4	0.5485	1424.4	0.8501	707.4
0.3006	1351.1	0.5998	1358.5	0.9497	223.4
T = 313.15 K, p = 10.00 MPa					
0.0477	368.9	0.3487	1429.3	0.6504	1292.1
0.0994	678.3	0.3985	1469.3	0.7001	1189.2
0.1484	915.6	0.4493	1479.7	0.7512	1050.4
0.2003	1112.7	0.5006	1468.3	0.8005	902.8
0.2493	1250.7	0.5485	1432.3	0.8501	724.9
0.3006	1360.5	0.5998	1374.6	0.9497	234.9
T = 328.15 K, p = 1.00 MPa					
0.0500	383.7	0.3500	1569.0	0.6500	1427.6
0.1000	724.9	0.4000	1624.6	0.7000	1313.4
0.1500	982.8	0.4500	1646.1	0.7500	1167.5
0.2000	1199.5	0.5000	1629.1	0.8000	997.2
0.2500	1365.5	0.5500	1588.2	0.8509	789.1
0.3000	1487.5	0.6000	1522.0	0.9500	261.7

2. Experiments

2.1. Materials. Dimethyl carbonate (99.9 + mass %, guarantee grade) and alcohols (99.0 + mass %, HPLC grade) were dried with molecular sieves (3 to 4 Å). The purity was checked by gas chromatography and was found to be greater than 99.9 mass % for dimethyl carbonate.

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Table 2. Excess Molar Enthalpies for the System Dimethyl Carbonate (1) + Ethanol (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 = 1.00 MPa					
0.0500	423.5	0.3500	1640.6	0.6500	1497.7
0.1000	786.8	0.4000	1683.0	0.7000	1385.4
0.1500	1056.7	0.4500	1701.5	0.7500	1239.8
0.2000	1275.3	0.5000	1693.3	0.8000	1063.7
0.2500	1445.8	0.5500	1654.8	0.8500	846.9
0.3000	1559.7	0.6000	1579.8		
T = 313.15 K, p = 0.10 MPa					
0.0521	411.7	0.4008	1854.0	0.7513	1361.0
0.0980	775.8	0.4516	1870.2	0.7987	1186.4
0.1514	1118.0	0.5007	1868.1	0.8497	957.0
0.1988	1345.6	0.5515	1832.0	0.9012	657.9
0.2488	1541.8	0.6003	1756.0	0.9504	338.0
0.3012	1687.2	0.6506	1660.7		
0.3519	1788.0	0.6990	1541.0		
T = 313.15 K, p = 1.00 MPa					
0.0520	434.5	0.4006	1855.8	0.7511	1363.5
0.0979	794.1	0.4515	1881.2	0.7986	1181.5
0.1513	1128.6	0.5006	1872.0	0.8496	955.8
0.1986	1361.3	0.5513	1829.7	0.9011	649.2
0.2487	1557.0	0.6002	1761.7	0.9504	326.7
0.3011	1701.2	0.6504	1661.6		
0.3517	1797.5	0.6988	1538.6		
T = 313.15 K, p = 10.00 MPa					
0.0517	406.7	0.3992	1832.03	0.7500	1362.71
0.1019	796.6	0.4500	1857.94	0.8004	1167.47
0.1505	1098.7	0.4991	1850.65	0.8489	946.19
0.2019	1352.1	0.5498	1812.15	0.9006	655.44
0.2517	1539.0	0.5987	1746.22	0.9501	321.45
0.2998	1675.3	0.6491	1648.37		
0.3503	1772.2	0.7005	1516.72		
T = 328.15 K, p = 1.00 MPa					
0.9500	366.5	0.6000	1966.6	0.2500	1711.8
0.9000	728.9	0.5500	2031.0	0.2000	1491.6
0.8500	1049.4	0.5000	2067.8	0.1500	1221.1
0.8000	1312.3	0.4500	2070.6	0.1000	898.3
0.7500	1528.3	0.4000	2043.0	0.0500	482.5
0.7000	1721.1	0.3500	1971.3		
0.6500	1869.0	0.3000	1860.7		

These solvents were filtered with Millipore filters (0.45 μm) and used without further purification.

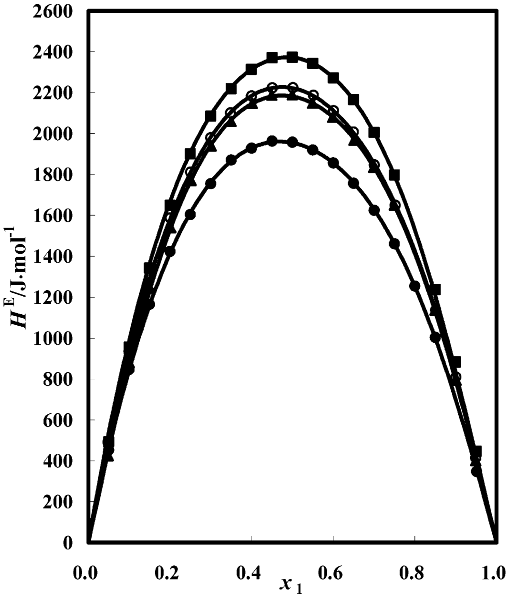

Figure 1. Excess molar enthalpies for the system dimethyl carbonate (1) + propan-1-ol (2) as a function of mole fraction x_1: ●, 298.15 K, 10.0 MPa; ▲, 313.15 K,1.0 MPa; ○, 313.15 K, 10.0 MPa; ■, 328.15 K, 1.0 MPa. The curves were calculated with the Redlich−Kister equation (parameters taken from Table 5).

Table 3. Excess Molar Enthalpies for the System Dimethyl Carbonate (1) + 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 = 1.00 MPa					
0.0500	451.7	0.3500	1870.3	0.6500	1757.1
0.1000	847.1	0.4000	1928.0	0.7000	1624.5
0.1500	1164.1	0.4500	1963.0	0.7500	1461.0
0.2000	1423.0	0.5000	1957.6	0.8000	1253.7
0.2500	1603.6	0.5500	1919.7	0.8500	1002.5
0.3000	1754.6	0.6000	1856.4	0.9515	347.5
T = 313.15 K, p = 1.00 MPa					
0.0485	424.8	0.3497	2059.0	0.6506	1967.2
0.1002	879.1	0.4014	2148.0	0.6988	1834.0
0.1512	1245.0	0.4490	2188.5	0.7495	1650.7
0.2017	1540.4	0.4995	2189.8	0.8491	1135.7
0.2516	1770.7	0.5494	2148.9	0.9010	794.4
0.3009	1938.8	0.5987	2079.8	0.9493	400.4
T = 313.15 K, p = 10.00 MPa					
0.0482	490.2	0.3483	2100.3	0.6493	2007.6
0.0996	934.3	0.3999	2183.3	0.7007	1846.4
0.1504	1297.6	0.4509	2223.6	0.7515	1649.2
0.2007	1587.7	0.5013	2224.4	0.8514	1137.5
0.2505	1810.9	0.5512	2187.5	0.9005	809.0
0.2997	1979.6	0.6005	2111.9	0.9490	413.9
T = 328.15 K, p = 1.00 MPa					
0.0500	493.0	0.3500	2219.2	0.6500	2165.0
0.1000	956.0	0.4000	2313.8	0.7000	2004.7
0.1500	1341.9	0.4500	2370.8	0.7500	1797.5
0.2000	1648.8	0.5000	2372.6	0.8500	1236.8
0.2500	1900.4	0.5500	2341.9	0.9000	882.5
0.3000	2086.0	0.6000	2272.7	0.9500	445.7

2.2. Apparatus. A commercial isothermal microcalorimeter (model IMC 4400, Calorimeter Science Corporation) with a refrigerating/heating circulator (model 9000, PolyScience Inc.) was used. The flow-mixing system comprises a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO Inc.) with a resolution of 0.1 μL·min^{-1}, and a back-pressure regular (model CSC 4448). It can be used to measure the mixing enthalpy at high pressure up to 15 MPa in 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-Acquire software for acquiring experimental data was provided by the Calorimeter Science Corporation. To confirm the reliability of this isothermal microcalorimeter, excess molar enthalpies of three binary systems of ethanol + water at T = 298.15 K and p = (0.2 and 0.4) MPa and methanol + water and acetone + water at T = 298.15 K and p = 0.2 MPa were measured.[4] The uncertainty of H_m^E

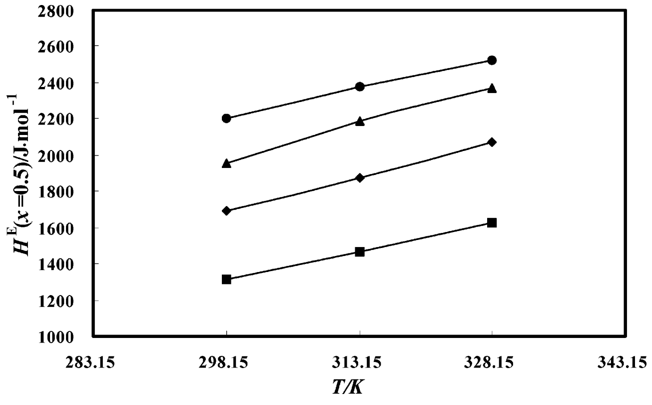

Figure 2. Excess molar enthalpies H_m^E (x = 0.5) for the system dimethyl carbonate (1) + alcohols (2) at p = 1.0 MPa as a function of the test temperature: ■, methanol; ♦, ethanol; ▲, 1-propanol; ●, 2-propanol.

Table 4. Excess Molar Enthalpies for the System Dimethyl Carbonate (1) + 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 = 1.00 MPa					
0.0500	502.7	0.3500	2049.5	0.6500	2010.5
0.1000	928.8	0.4000	2132.5	0.7000	1865.7
0.1500	1267.1	0.4500	2180.6	0.7500	1678.8
0.2000	1545.8	0.5000	2202.6	0.8000	1433.2
0.2500	1761.2	0.5500	2171.9	0.9500	447.0
0.3000	1924.4	0.6000	2112.2		
T = 313.15 K, p = 0.10 MPa					
0.0483	467.2	0.3489	2207.7	0.6498	2194.1
0.0998	931.7	0.4005	2315.9	0.7012	2044.9
0.1507	1316.4	0.4515	2376.0	0.7488	1848.9
0.2011	1623.5	0.4986	2392.5	0.8486	1312.7
0.2509	1871.3	0.5485	2364.4	0.9007	935.2
0.3002	2060.3	0.6011	2302.2	0.9492	483.5
T = 313.15 K, p = 1.00 MPa					
0.0483	463.5	0.3487	2210.5	0.6497	2184.6
0.0998	933.4	0.4003	2315.5	0.7011	2033.3
0.1507	1312.2	0.4513	2360.6	0.7487	1843.1
0.2010	1619.6	0.4984	2375.9	0.8486	1301.0
0.2508	1868.0	0.5516	2352.2	0.9007	924.3
0.3000	2063.3	0.6009	2291.1	0.9491	490.9
T = 313.15 K, p = 10.00 MPa					
0.0517	458.2	0.3989	2262.2	0.7507	1809.6
0.0992	886.9	0.4499	2325.0	0.8011	1560.0
0.1499	1267.9	0.5003	2342.0	0.8509	1277.7
0.2000	1576.5	0.5501	2316.8	0.9001	932.3
0.2497	1822.0	0.5995	2256.2	0.9488	526.7
0.2988	2013.9	0.6515	2147.0		
0.3508	2165.9	0.6998	2008.3		
T = 328.15 K, p = 1.00 MPa					
0.0500	541.2	0.4000	2435.8	0.7500	1957.5
0.1000	978.6	0.4500	2494.5	0.8000	1687.9
0.1500	1372.0	0.5000	2524.6	0.8500	1362.6
0.2000	1695.5	0.5500	2506.9	0.9000	962.1
0.2500	1955.6	0.6000	2448.1	0.9500	486.5
0.3000	2157.3	0.6500	2325.7		
0.3500	2325.1	0.7000	2145.4		

values measured in triplicate at the same mole fraction is less than 0.4 J·mol^{-1} for the above three systems.

3. Results

In this work, the excess molar enthalpies of four binary systems of dimethyl carbonate + (methanol, ethanol, 1-propanol, and 2-propanol) have been measured at T = (298.15, 313.15, nad 328.15) K and p = (0.1, 1.0, and 10.0) MPa. The experimental data are listed in Tables 1 to 4 and fitted to a Redlich−Kister polynomial equation:

$$H_m^E/\text{J·mol}^{-1} = x_1(1 - x_1)\sum_{i=0}^{N} A_i(1 - 2x_1)^i \qquad (1)$$

The A_i parameters of the Redlich−Kister equation and standard deviations SD are listed in Table 5. As a typical example, experimental data from Table 3 are plotted in Figure 1.

4. Discussion

As can be seen from Figure 1, good agreement between experimental and calculated values is achieved for the binary systems. It can also be seen from Figure 1 that the influence of temperature on the excess molar enthalpy is distinct. However, the influence of pressure on the excess molar enthalpy is slight. The influence of pressure on the structure of the solution or the molecular interaction forces may be neglected in the pressure range considered in this study. For a given temperature and pressure, the H_m^E (x = 0.5) values increase as the number of carbon atoms in the alkanol molecule increases (Figure 2). All of the binary systems studied in this work showed endothermic and symmetrical behavior over the whole mole fraction range.

The positive values of H_m^E indicate a preponderance of the endothermic. The hydrogen bonds in alkanols, the strong dipole−dipole interactions in both components, and the hydrogen bond association of alkanols with the carbonate considerably affect the properties of the mixtures with endothermic as well as exothermic contributions.[5] The H_m^E values increase with the molecular size of the alkanol. This phenomenon may be closely connected with the increasing

Table 5. Parameters of the Redlich−Kister Equation and Standard Deviations

	A_0	A_1	A_2	A_3	A_4	A_5	SD/J·mol^{-1}[a]
Dimethyl Carbonate + Methanol							
298.15 K, 1.0 MPa	5232.7	1050.6	1054	161.5	709.7		1.62
313.15 K, 0.1 MPa	5827.1	1065.2	1745.2	−497.0	−1764.5	732.1	5.21
313.15 K, 1.0 MPa	5841.4	1203.7	1428.1	−1378.8	−1003.5	2488.2	4.31
313.15 K, 10.0 MPa	5865.7	1069.5	1410.0	−668.3	−631.0	1761.0	4.55
328.15 K, 1.0 MPa	6505.2	1105.4	1243.3	−632.6	−791.9	1319.1	5.29
Dimethyl Carbonate + Ethanol							
298.15 K, 1.0 MPa	6754.1	1002.4	1668.7	352.3	−357.0	6754.1	3.85
313.15 K, 0.1 MPa	7451.9	886.4	1695.4	301.2	−1201.5	−654.0	7.91
313.15 K, 1.0 MPa	7468.4	991.2	1753.1	−52.2	−1175.9	148.2	6.66
313.15 K, 10.0 MPa	7379.3	934.3	1839.2	−59.6	−1527.1	−89.0	7.32
328.15 K, 1.0 MPa	8276.6	787.4	1751.5	263.3	−1005.5	481.2	4.86
Dimethyl Carbonate + 1-Propanol							
298.15 K, 1.0 MPa	7819.1	775.4	1723.6	2.5	−836.2	546.0	4.94
313.15 K, 1.0 MPa	8725.9	695.0	1963.8	−253.5	−1856.5	30.6	7.70
313.15 K, 10.0 MPa	8889.5	759.1	1633.8	−39.6	−638.1	497.9	5.22
328.15 K, 1.0 MPa	9486.7	396.3	1874.2	675.0	−1356.1	−666.0	5.64
Dimethyl Carbonate + 2-Propanol							
298.15 K, 1.0 MPa	8788.9	140.0	1469.3	1564.6	26.3	−1115.5	2.63
313.15 K, 0.1 MPa	9549.0	146.1	1693.7	−257.8	−768.7	86.0	7.53
313.15 K, 1.0 MPa	9509.2	218.7	1787.6	−289.2	−930.2	−6.7	5.36
313.15 K, 10.0 MPa	9358.0	11.9	1515.4	893.4	−540.4	−2248.4	4.54
328.15 K, 1.0 MPa	1009.2	26	1465.0	−471.0	−552.0	1212.0	8.03

[a] SD = $[\sum(H_{\text{calcd}}^E - H_{\text{exptl}}^E)^2/n\ ]^{1/2}$, where n is the number of data for each data set.

difficulty of producing heteromolecular interactions when the aliphatic chain of the alkanol is increased. These results also suggest weak heteromolecular interactions.[6]

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