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Excess Molar Enthalpies of Diethyl Malonate + (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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Excess molar enthalpies for four binary systems of diethyl malonate + (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 and two local-composition models (NRTL and UNIQUAC). The densities of the diethyl malonate at different temperature were measured by using a vibrating-tube densimeter.

Introduction

Diethyl malonate is a raw material in fine chemical production. Because of its special property, it is widely used in synthesis of medicines, farm chemicals, spices, dyes,[1] chemical reagents,[2−4] and gas chromatography stationary phase and so on.

Until now, no data of excess molar enthalpies of systems containing diethyl malonate could be found in the literature. In this paper, the excess molar enthalpies for four binary systems of diethyl malonate + (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 and two local composition models: the NRTL model and the UNIQUAC model.

Experimental Section

Materials. Diethyl malonate (guaranteed grade, better than w = 0.999) was purchased from Shanghai Jiachen Chemical. Methanol (HPLC grade, better than w = 0.998) was provided by Tianjin Siyou 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. 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 this work. The flow-mixing system was composed of a sample cell and a reference cell (model CSC 4442), two syringe pumps (model 260D, ISCO), and a back pressure regulator (model CSC 4448). The uncertainties of composition on 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 %. The experiment procedure and the reliability of the apparatus have been described in detail elsewhere.[5]

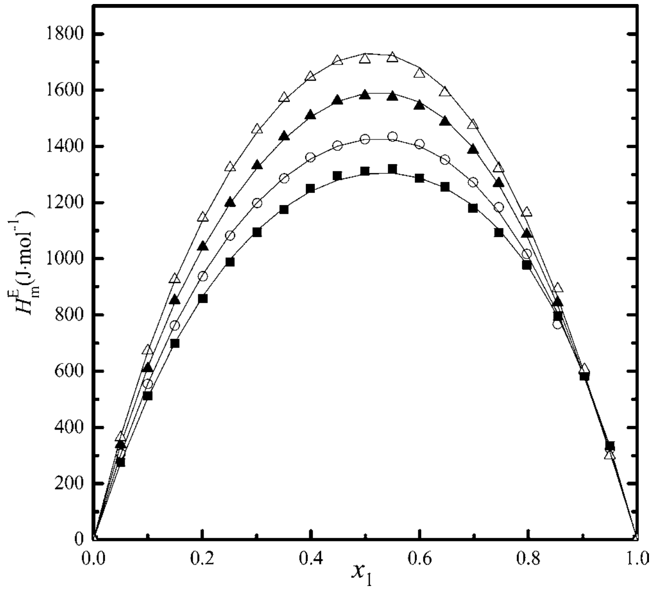

Figure 1. Excess molar enthalpies of the system diethyl malonate (1) + methanol (2) as a function of mole fraction at p = 101.3 kPa, x_1: ■, 288.2 K; ○, 298.2 K; ▲, 313.2 K; △, 328.2 K. The curves were calculated by the Redlich−Kister equation (parameters taken from Table 5).

The densities of diethyl malonate at different temperature (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 diethyl malonate + (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 diethyl malonate (1) + methanol (2) in Table 1 and diethyl malonate (1) + alcohols (2) at 288.2 K and p = 101.3 kPa are plotted in Figures 1 and 2, respectively.

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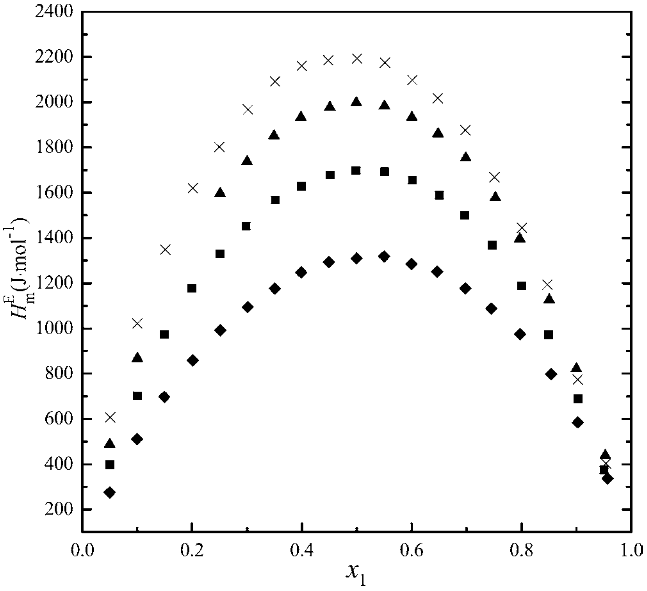

Figure 2. Excess molar enthalpies for the system diethyl malonate (1) + alcohols (2) as a function of mole fraction, x_1, at $T = 288.2$ K and $p = 101.3$ kPa: ◆, diethyl malonate (1) + methanol (2); ■, diethyl malonate (1) + ethanol (2); ▲, diethyl malonate (1) + 1-propanol (2); ×, diethyl malonate (1) + 2-propanol (2).

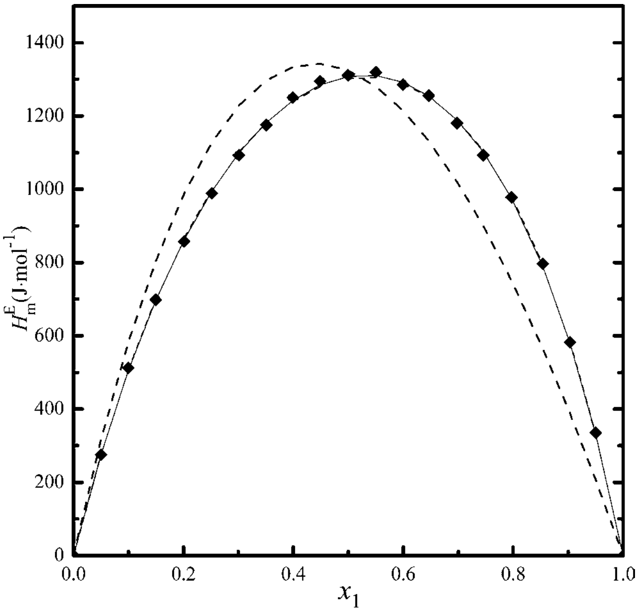

Figure 3. Correlation of excess molar enthalpies of the system diethyl malonate (1) + methanol (2) as a function of mole fraction, x_1: ◆, experiment data at $T = 288.2$ K and $p = 101.3$ kPa; ----, calculated by the Redlich−Kister equation (parameters taken from Table 5); —, calculated by the NRTL equation (parameters taken from Table 6); - -, calculated by the UNIQUAC equation (parameters taken from Table 7).

The experimental data of excess molar enthalpies are correlated by using the Redlich−Kister equation and two local composition models (NRTL and UNIQUAC). The expressions of H^E_m derived from the G^E_m model were developed through the Gibbs−Helmholtz equation

$$\left[\frac{\partial(G^E_m/T)}{\partial T}\right]_{P,x} = -\frac{H^E_m}{T^2} \tag{1}$$

Redlich−Kister Equation. The Redlich−Kister equation[6] is commonly used to correlate H^E_m data because of its simplicity

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

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

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

$$\sigma = \sqrt{\frac{1}{N}\sum_{i}^{N}(H^E_{\mathrm{calcd}(i)} - H^E_{\mathrm{exptl}(i)})^2} \tag{3}$$

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

NRTL Model. The expression of H^E_m derived from the NRTL G^E_m model[7] is given in eq 4

$$H^E_m = x_1x_2\left[\frac{G_{21}(g_{21} - g_{11})(x_1 + x_2G_{21} - x_1\tau_{21}\alpha_{21})}{(x_1 + x_2G_{21})^2} + \frac{G_{12}(g_{12} - g_{22})(x_2 + x_1G_{12} - x_2\tau_{12}\alpha_{12})}{(x_2 + x_1G_{12})^2}\right] \tag{4}$$

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

Table 1. Excess Molar Enthalpies of the System Diethyl Malonate (1) + Methanol (2)

x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}	x_1	H^E_m/J·mol^{-1}
$T = 288.2$ K, $p = 101.3$ kPa					
0.0500	276	0.3988	1250	0.7453	1093
0.0996	513	0.4486	1295	0.7969	978
0.1496	698	0.4993	1311	0.8536	796
0.2011	858	0.5500	1319	0.9030	582
0.2515	989	0.5995	1285	0.9500	335
0.3009	1093	0.6464	1256		
0.3506	1175	0.6980	1180		
$T = 298.2$ K, $p = 101.3$ kPa					
0.0500	307	0.3988	1361	0.7453	1184
0.0996	555	0.4486	1402	0.7969	1016
0.1496	763	0.4993	1426	0.8536	768
0.2011	937	0.5500	1435	0.9030	586
0.2515	1083	0.5995	1408	0.9500	323
0.3009	1198	0.6464	1352		
0.3506	1286	0.6980	1272		
$T = 313.2$ K, $p = 101.3$ kPa					
0.0500	339	0.3988	1509	0.7453	1268
0.0996	610	0.4486	1563	0.7969	1086
0.1496	851	0.4993	1580	0.8536	844
0.2011	1042	0.5500	1575	0.9030	602
0.2515	1198	0.5995	1543	0.9500	301
0.3009	1330	0.6464	1486		
0.3506	1434	0.6980	1387		
$T = 328.2$ K, $p = 101.3$ kPa					
0.0500	365	0.3988	1647	0.7453	1321
0.0996	673	0.4486	1703	0.7969	1163
0.1496	926	0.4993	1709	0.8536	893
0.2011	1146	0.5500	1713	0.9030	607
0.2515	1324	0.5995	1657	0.9500	298
0.3009	1459	0.6464	1591		
0.3506	1572	0.6980	1475		

Table 2. Excess Molar Enthalpies of the System Diethyl Malonate (1) + Ethanol (2)

x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}
T = 288.2 K, p = 101.3 kPa					
0.0501	397	0.3990	1630	0.7465	1371
0.1004	702	0.4509	1676	0.8002	1188
0.1491	974	0.4985	1700	0.8497	972
0.1995	1178	0.5503	1692	0.9027	688
0.2507	1329	0.6013	1653	0.9498	375
0.2985	1454	0.6504	1588		
0.3517	1564	0.6967	1503		
T = 298.2 K, p = 101.3 kPa					
0.0501	423	0.3990	1778	0.7465	1473
0.1004	775	0.4509	1821	0.8002	1265
0.1491	1033	0.4985	1848	0.8497	1014
0.1995	1261	0.5503	1828	0.9027	721
0.2507	1446	0.6013	1789	0.9498	396
0.2985	1586	0.6504	1716		
0.3517	1701	0.6967	1613		
T = 313.2 K, p = 101.3 kPa					
0.0501	476	0.3990	1981	0.7465	1590
0.1004	859	0.4509	2032	0.8002	1347
0.1491	1168	0.4985	2045	0.8497	1084
0.1995	1410	0.5503	2031	0.9027	747
0.2507	1620	0.6013	1962	0.9498	441
0.2985	1780	0.6504	1875		
0.3517	1898	0.6967	1764		
T = 328.2 K, p = 101.3 kPa					
0.0501	497	0.3990	2134	0.7465	1658
0.1004	929	0.4509	2184	0.8002	1392
0.1491	1271	0.4985	2203	0.8497	1125
0.1995	1531	0.5503	2165	0.9027	777
0.2507	1757	0.6013	2087	0.9498	424
0.2985	1926	0.6504	1994		
0.3517	2053	0.6967	1850		

Table 3. Excess Molar Enthalpies of the System Diethyl Malonate (1) + 1-Propanol (2)

x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}
T = 288.2 K, p = 101.3 kPa					
0.0499	487	0.4510	1976	0.7525	1575
0.1004	866	0.4990	1998	0.7970	1399
0.2513	1595	0.5503	1982	0.8506	1126
0.3000	1738	0.6002	1932	0.9003	821
0.3491	1853	0.6479	1862	0.9527	438
0.3982	1935	0.6986	1755		
T = 298.2 K, p = 101.3 kPa					
0.0499	534	0.3982	2110	0.7525	1669
0.1004	941	0.4510	2156	0.7970	1473
0.1588	1315	0.4990	2175	0.8506	1173
0.2090	1575	0.5503	2142	0.9003	826
0.2513	1751	0.6002	2080	0.9527	435
0.3000	1908	0.6479	1992		
0.3491	2029	0.6986	1872		
T = 313.2 K, p = 101.3 kPa					
0.0499	578	0.3982	2320	0.7525	1747
0.1004	1045	0.4510	2363	0.7970	1511
0.1588	1444	0.4990	2371	0.8506	1188
0.2090	1738	0.5503	2338	0.9003	856
0.2513	1915	0.6002	2256	0.9527	432
0.3000	2094	0.6479	2140		
0.3491	2231	0.6986	1967		
T = 328.2 K, p = 101.3 kPa					
0.0499	597	0.3982	2482	0.7525	1817
0.1004	1112	0.4510	2525	0.7970	1569
0.1588	1554	0.4990	2517	0.8506	1230
0.2090	1872	0.5503	2477	0.9003	854
0.2513	2054	0.6002	2374	0.9527	418
0.3000	2244	0.6479	2255		
0.3491	2387	0.6986	2064		

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

x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}	x_1	$H_{\rm m}^{\rm E}$/J·mol^{-1}
T = 288.2 K, p = 101.3 kPa					
0.0511	607	0.3998	2161	0.7508	1667
0.1001	1022	0.4484	2188	0.8007	1444
0.1511	1347	0.5003	2193	0.8468	1196
0.2012	1619	0.5513	2173	0.9023	773
0.2494	1803	0.6007	2097	0.9537	403
0.3015	1965	0.6478	2019		
0.3507	2091	0.6977	1880		
T = 298.2 K, p = 101.3 kPa					
0.0511	632	0.3998	2344	0.7508	1804
0.1001	1102	0.4484	2380	0.8007	1584
0.1511	1465	0.5003	2369	0.8468	1292
0.2012	1753	0.5513	2342	0.9023	918
0.2494	1955	0.6007	2257	0.9537	465
0.3015	2134	0.6478	2175		
0.3507	2266	0.6977	2015		
T = 313.2 K, p = 101.3 kPa					
0.0511	659	0.3998	2534	0.7508	1888
0.1001	1160	0.4484	2578	0.8007	1636
0.1511	1581	0.5003	2556	0.8468	1339
0.2012	1877	0.5513	2510	0.9023	892
0.2494	2134	0.6007	2433	0.9537	436
0.3015	2329	0.6478	2321		
0.3507	2451	0.6977	2137		
T = 328.2 K, p = 101.3 kPa					
0.0511	681	0.3998	2636	0.7508	1901
0.1001	1220	0.4484	2674	0.8007	1618
0.1511	1631	0.5003	2664	0.8468	1264
0.2012	1977	0.5513	2595	0.9023	845
0.2494	2223	0.6007	2496	0.9537	391
0.3015	2412	0.6478	2348		
0.3507	2555	0.6977	2161		

obtained by a nonlinear least-squares fit. The parameters of the NRTL equation and σ are listed in Table 6.

UNIQUAC Model. From the UNIQUAC $G_{\rm m}^{\rm E}$ model,[8] $H_{\rm m}^{\rm E}$ can be derived as follows

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

	Redlich−Kister Equation				
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}
Diethyl Malonate (1) + Methanol (2)					
288.2	5207	478	1471	241	8
298.2	5699	480	1077	−370	11
313.2	6355	581	618	−1121	9
328.2	6922	389	320	−1293	15
Diethyl Malonate (1) + Ethanol (2)					
288.2	6783	319	1644	−650	5
298.2	7363	219	1522	−687	5
313.2	8138	−194	1595	−438	12
328.2	8779	−517	1158	−513	7
Diethyl Malonate (1) + 1-Propanol (2)					
288.2	7935	33	2376	−469	9
298.2	8641	−98	2041	−975	9
313.2	9422	−610	1691	−1030	11
328.2	10085	−953	1160	−1122	7
Diethyl Malonate (1) + 2-Propanol (2)					
288.2	8754	−150	2338	−2120	15
298.2	9442	−543	2820	−1019	14
313.2	10286	−812	1887	−1475	11
328.2	10677	−1176	1184	−2050	12

$$H_m^E = q_1 x_1 \left(\frac{\theta_2}{\theta_1 + \theta_2 \tau_{21}} \right) \tau_{21} \Delta u_{21} + q_2 x_2 \left(\frac{\theta_1}{\theta_2 + \theta_1 \tau_{12}} \right) \tau_{12} \Delta u_{12} \tag{5}$$

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 Δu_{12} and Δu_{21} are the interaction energy parameters, which are obtained by a nonlinear least-squares fit. They are given in Table 7 together with σ. q_i is the structural parameter of the pure component (see Table S3 in the Supporting Information).

From Tables 1, 2, 3 and 4, the positive value of H_m^E indicates that the mixing processes of all the binary systems are endothermic and the diethyl malonate 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. These may due to the reduction of H-bonds probably between methanol and diethyl malonate as temperature increases. From Figure 2, it can be seen that the H_m^E value increases with the increasing of branch and carbon number of alcohols. It may be due to the increasing difficulty to form crossed associations between different molecules with increasing steric hindrance and aliphatic chain of alcohol. Compared with the binary mixtures of diethyl malonate + *n*-alkanols, the H_m^E value of the binary mixtures of diethyl carbonate + *n*-alkanols at 298.2 K and $p = 101.3$ kPa from the literature[9] is smaller. So it also indicates that the steric hindrance is the main influence factor of the increasing H_m^E value.

Table 6. Parameters of the NRTL Equation with the Root-Mean-Square Deviation (σ) at $p = 101.3$ kPa

NRTL			
$(g_{12} - g_{22})$ / J·mol^{-1}	$(g_{21} - g_{11})$ / J·mol^{-1}	α_{12}	σ / J·mol^{-1}
Diethyl Malonate (1) + Methanol (2)			
1509	1782	−0.91	6
Diethyl Malonate (1) + Ethanol (2)			
2132	2177	−0.68	10
Diethyl Malonate (1) + 1-Propanol (2)			
2512	2471	−0.62	9
Diethyl Malonate (1) + 2-Propanol (2)			
3002	2560	−0.53	23

Table 7. Parameters of the UNIQUAC Equation with the Root-Mean-Square Deviation (σ) at $p = 101.3$ kPa

UNIQUAC		
Δu_{21}/J·mol^{-1}	Δu_{12}/J·mol^{-1}	σ/J·mol^{-1}
Diethyl Malonate (1) + Methanol (2)		
1975	−1479	127
Diethyl Malonate (1) + Ethanol (2)		
2079	−1599	60
Diethyl Malonate (1) + 1-Propanol (2)		
1812	v583	62
Diethyl Malonate (1) + 2-Propanol (2)		
1595	161	64

From Tables 5, 6, and 7, it can be seen that the Redlich−Kister equation and the NRTL model give a good correlation of the excess molar enthalpies for the systems in this work, while the UNIQUAC model has obvious deviations. This may be due to the less fitting parameters of UNIQUAC model. As a typical example, the correlation curves for excess molar enthalpies of diethyl malonate (1) + methanol (2) at 288.2 K and $p = 101.3$ kPa are plotted in Figure 3.

Supporting Information Available:

Tables S1, S2, and S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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