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Excess Molar Enthalpies of Dimethyl Carbonate with *o*-Xylene, *m*-Xylene, *p*-Xylene, Ethylbenzene, or Ethyl Benzoate at 298.15 K

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Excess molar enthalpies, H^E, for the binary mixtures of dimethyl carbonate with *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, or ethyl benzoate have been measured by using a flow-type isothermal microcalorimeter at 298.15 K under atmospheric pressure. The experimental H^E values are all positive (endothermic) for these binary mixtures over the entire composition range. The maximum H^E values are in the range 386.6 J·mol^{-1} to 674.0 J·mol^{-1} and are exhibited at about $x_i = 0.5$, except for the systems containing ethylbenzene and ethyl benzoate. The experimental results were represented accurately by the Redlich−Kister polynomial equation. These new H^E data were also correlated with the Peng−Robinson and the cubic chain-of-rotators (CCOR) equations of state. With two adjustable interaction parameters, the CCOR equation represents the excess enthalpies of these five binary systems satisfactorily.

Introduction

Although methyl *tert*-butyl ether (MTBE) is widely used as a gasoline additive at present, it is harmful to the environment, creating a demand to find a suitable replacement. Dimethyl carbonate (DMC) is one of the potential candidates because it has about three times the oxygen content as MTBE and can dissolve in a water stream with low toxicity and high biodegradability.[1] DMC has also been applied for synthesis of polycarbonate and isocyanate[2,3] and, as a solvent, for a variety of extractions of industrial importance, among many other applications.[4,5] In the present study, a flow-type isothermal microcalorimeter was used to measure the excess enthalpies of binary mixtures of DMC with *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, or ethyl benzoate at 298.15 K under atmospheric pressure. No literature data are found for these systems at comparable conditions. The experimental results reveal the effects of composition and molecular structure on the heats of mixing.

Experimental Section

Chemicals. Dimethyl carbonate (99 mass %), *o*-xylene (99 mass %), *m*-xylene (99+ mass %), *p*-xylene (99 mass %), and ethylbenzene (99.8 mass %) were purchased from Arcos (USA). Ethyl benzoate (99+ mass %) was supplied by Aldrich (USA). All chemicals were used without further purification. The density of the chemicals at 298.15 K was measured with an Anton Paar densimeter, DMA 4500, with an accuracy of ±5 × 10^{-5} g·cm^{-3}. The densities[6−9] are compared with literature values in Table 1.

Table 1. Densities of Pure Components at 298.15 K, Calibration Constants, and the Data Sources of H^E Used for Determination of Calibration Constants

component	ρ/g·cm^{-3} this work	ρ/g·cm^{-3} lit.	calibration constants a_{0i}/a_{1i}	i	data sources of H^E
dimethyl carbonate	1.0631	1.064 30[6]	2.9913 0.5466	1	ref 10[a]
o-xylene	0.8750	0.875 96[7]	3.0941 0.6996	2	ref 11[b]
m-xylene	0.8600	0.859 90[7]	3.1421 0.4348	2	ref 11[c]
p-xylene	0.8567	0.856 68[7]	3.1832 0.5284	2	ref 12[d]
ethylbenzene	0.8625	0.862 6[8]	3.0606 0.6291	2	ref 13[e]
ethyl benzoate	1.0413	1.041 4[9]	3.4119 0.0010	2	ref 14[f]

[a] Dimethyl carbonate + hexane and dimethyl carbonate + benzene. [b] Benzene + *o*-xylene. [c] Benzene + *p*-xylene. [d] Benzene + *m*-xylene. [e] Methanol + ethylbenzene. [f] Hexane + ethyl benzoate.

Apparatus and Procedure. A flow-type isothermal microcalorimeter (model 4400 IMC, Calorimeter Science Corporation, USA) was employed in this study to measure the enthalpy changes of mixing. Its schematic diagram and the procedure of the operations have been detailed elsewhere.[15] The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition system, and two liquid pumps (model PU-1580, JASCO, Japan) with an on-line degasser. The temperature of the bath was controlled to within ±0.05 K. The enthalpy of mixing can be measured to within a sensitivity of ±0.1 μW.

The molar ratio of the two mixing-streams was calculated from the molecular weights, densities, and volumetric flow rates of components 1 and 2. The uncertainty of flow rate is within ±0.1%. In general, the total flow rates were kept at about 0.4 cm^3 min^{-1}, which is a preferable condition as a result of test runs. However, the total flow rates may vary to as high as 0.8 cm^3 min^{-1} in the region of dilute DMC.

The excess molar enthalpy was obtained from the following equation:

$$H^E = \frac{\epsilon_m (V_m - V_m^\circ)}{\dfrac{f_1 \rho_1}{MW_1} + \dfrac{f_2 \rho_2}{MW_2}} \qquad (1)$$

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Table 2. Excess Molar Enthalpies H^E of Binary Mixtures Containing Dimethyl Carbonate at 298.15 K

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
Dimethyl Carbonate (1) + *o*-Xylene (2)			
0.0511	111.2	0.5519	642.0
0.1006	231.3	0.6007	624.0
0.1503	332.6	0.6502	594.6
0.2016	389.8	0.7002	551.6
0.2513	444.6	0.7504	500.8
0.3024	521.0	0.8008	434.0
0.3519	574.5	0.8513	351.7
0.3998	614.9	0.8998	253.3
0.4514	638.8	0.9501	134.9
0.5013	650.3		
Dimethyl Carbonate (1) + *m*-Xylene (2)			
0.0502	125.1	0.5515	668.3
0.1006	242.3	0.6004	652.9
0.1510	344.8	0.6522	624.7
0.2014	425.7	0.7018	584.7
0.2517	498.5	0.7517	529.9
0.3004	554.7	0.8017	457.6
0.3503	602.7	0.8517	367.4
0.4014	638.7	0.9015	263.6
0.4506	660.7	0.9509	141.1
0.5007	670.7		
Dimethyl Carbonate (1) + *p*-Xylene (2)			
0.0504	123.3	0.5524	670.2
0.1010	227.1	0.6013	651.7
0.1515	350.2	0.6507	622.7
0.2020	428.4	0.7004	581.2
0.2529	499.1	0.7503	523.1
0.3012	555.2	0.8003	455.8
0.3512	606.6	0.8502	367.9
0.4022	641.9	0.9018	259.8
0.4515	663.3	0.9511	138.1
0.5016	674.0		
Dimethyl Carbonate (1) + Ethylbenzene (2)			
0.0501	89.9	0.5507	641.6
0.1003	204.8	0.6020	629.7
0.1490	267.4	0.6513	605.4
0.2010	354.8	0.7011	565.1
0.2512	434.4	0.7512	513.1
0.2998	499.3	0.8012	445.5
0.3525	557.0	0.8513	362.0
0.4005	599.7	0.9012	260.7
0.4524	628.9	0.9509	140.3
0.5025	641.8		
Dimethyl Carbonate (1) + Ethyl Benzoate (2)			
0.0500	57.9	0.5495	386.6
0.0999	118.8	0.5990	381.2
0.1497	172.8	0.6506	364.8
0.1991	226.2	0.6993	347.5
0.2482	268.4	0.7495	313.8
0.2984	305.5	0.8007	274.1
0.3495	336.5	0.8507	222.9
0.4012	360.2	0.8993	161.9
0.4503	376.7	0.9498	86.4
0.4998	384.6		

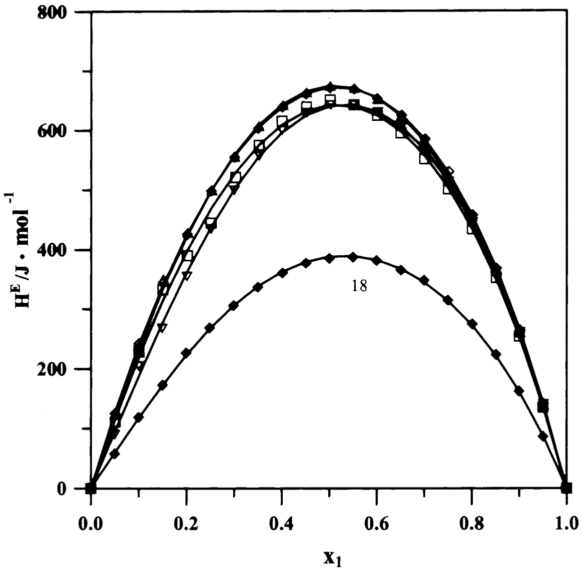

Figure 1. Excess molar enthalpies, H^E, for dimethyl carbonate + *o*-xylene (□), + *m*-xylene (◇), + *p*-xylene (△), + ethylbenzene (▽), and + ethyl benzoate (◆) at 298.15 K; calculated from the Redlich−Kister equation (—).

Table 3. Correlated Results from the Redlich−Kister Equation

component 2	h_0 J·mol^{-1}	h_1 J·mol^{-1}	h_2 J·mol^{-1}	h_3 J·mol^{-1}	$\sigma(H^E)^a$ J·mol^{-1}
o-xylene	2566.8	165.3	81.0	102.6	9.85
m-xylene	2687.0	161.5	194.1	52.8	1.99
p-xylene	2696.7	110.9	100.4	150.6	4.67
ethylbenzene	2558.2	356.8	−87.4	266.0	5.63
ethyl benzoate	1551.0	199.4	−10.7	156.4	2.31

[a] Defined as in eq 6.

where f_i, ρ_i, and MW$_i$ are the volumetric flow rate, density, and molecular weight of component *i*, respectively. The voltage generated from the mixing process, V_m, is one of the measurable variables from the data acquisition system. The voltage of the baseline, V_m°, was calculated from

$$V_m^\circ = \frac{f_1V_1^\circ + f_2V_2^\circ}{f_1 + f_2} \tag{2}$$

where V_i° is the baseline voltage for component *i*. The baseline voltages were determined by charging with a pure compound at several different flow rates. In general, the value of V_m° is much smaller (<0.1%) than that of V_m. The variable ϵ_m in eq 1 is the calibration coefficient for mixing runs. Its value was estimated from the following equation:

$$\epsilon_m = \Phi_1\epsilon_1 + \Phi_2\epsilon_2 = \left(\frac{f_1}{f_1 + f_2}\right)\epsilon_1 + \left(\frac{f_2}{f_1 + f_2}\right)\epsilon_2 \tag{3}$$

where Φ_i and ϵ_i are the volumetric fraction and calibration coefficient for constituent *i*, respectively. It should be noted that the values of the calibration coefficients, ϵ_i, vary with several factors, including temperature, volumetric flow rate, and the path of streams. At a given operating temperature, the relationship between ϵ_i and the flow rate f_i for a specific stream was found to be linear over the entire experimental conditions of this study. Equation 3 can thus be expressed as

$$\epsilon_m = \left(\frac{f_1}{f_1 + f_2}\right)(a_{01} + a_{11}f_1) + \left(\frac{f_2}{f_1 + f_2}\right)(a_{02} + a_{12}f_2) \tag{4}$$

where (a_{01}, a_{11}) and (a_{02}, a_{12}) are the calibration constants for streams 1 and 2, respectively. The calibration constants for each constituent compound need to be determined by fitting the voltages to eq 1 with reference to reliable literature H^E data of the related mixtures, prior to measuring a new system. The calibration constants and the sources of the literature data[10−14] used for determination of the calibration constants are listed in Table 1. The accuracy of the reported H^E in this study is estimated to be better than ±2%.

Results and Discussion

The experimental results are listed in Table 2 for the binary systems of DMC with *o*-xylene, *m*-xylene, *p*-xylene,

Table 4. Calculated Results of H^E from the Equations of State

	PR		CCOR$_1$		CCOR$_2$		
component (2)	k_{aij}	H^E AAD[a] (%)	k_{aij}	H^E AAD[a] (%)	k_{aij}	k_{cij}	H^E AAD[a] (%)
o-xylene	0.0247	5.3	0.0165	8.2	−0.1100	−0.1457	2.3
m-xylene	0.0226	6.5	0.0226	9.0	−0.1200	−0.1561	8.6
p-xylene	0.0220	6.8	0.0145	9.3	−0.1195	−0.1543	2.1
ethylbenzene	0.0210	2.6	0.0145	4.5	−0.0232	−0.0430	3.3
ethyl benzoate	−0.0176	13.7	−0.0444	36.2	−0.1136	−0.0702	5.7

[a] H^E AAD (%) $= 100/N\sum_{i=1}^{N}|H^E_{i,\text{calc}} - H^E_{i,\text{expt}}|/H^E_{i,\text{expt}}$.

ethylbenzene, or ethyl benzoate at 298.15 K. Figure 1 illustrates the excess molar enthalpies varying with the mole fraction of DMC. As shown from the results, the excess molar enthalpies are all positive (endothermic) over the entire composition range for each binary system. The maximum H^E values are located at about $x_1 = 0.5$, except for the systems containing ethylbenzene and ethyl benzoate, for which the maximum values exhibit at $x_1 = 0.5507$ and 0.5495, respectively. The maximum values of H^E are 674.0, 670.7, 650.3, 641.8, and 386.6 J·mol^{-1} for the systems containing *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene, and ethyl benzoate, respectively. The results also show that stronger chemical effects between DMC and ethyl benzoate molecules lead to lower heats of mixing. In comparison with the results of the corresponding binary systems of diethyl carbonate,[16] the excess molar enthalpies of the DMC systems are much higher.

Data Correlation. The new H^E data were fitted to the Redlich−Kister (R−K) equation:

$$H^E = x_1(1 - x_1)\sum_{i=0}^{m} h_i(1 - 2x_1)^i \qquad (5)$$

The values of the coefficients h_i were determined by a least-squares regression for each binary system. The results are reported in Table 3, in which $\sigma(H^E)$ is the standard deviation, defined as

$$\sigma(H^E) = \left[\frac{\sum_{j=1}^{N}(H^E_{\text{calc},j} - H^E_{\text{expt},j})^2}{N - n}\right]^{0.5} \qquad (6)$$

where N and n are the number of experimental data points and the number of coefficients h_i, respectively. As indicated in Table 3 and Figure 1, the Redlich−Kister equation correlates these new H^E data accurately.

The experimental H^E data were also correlated with the Peng−Robinson (PR)[17] and the cubic chain-of-rotators (CCOR)[18] equations of state. In the calculation, a single binary interaction constant, k_{aij}, was introduced into the combining rule of a_{ij} for the PR equation. Two different treatments were made for the CCOR equation. The first one is similar to that for the PR equation, containing a single binary interaction constant, k_{aij}, denoted as CCOR$_1$. The second treatment, denoted as CCOR$_2$, adds another binary interaction parameter k_{cij} into the combining rule of c_{ij}. Table 4 presents the correlated results by both the PR and the CCOR equations of state. Figures 2 and 3 compare the calculated results with the experimental excess molar enthalpies for DMC + *o*-xylene and DMC + ethyl benzoate, respectively. Comparable results were obtained from the PR and the CCOR$_1$ equations for a majority of the investigated binary systems, except for the system containing ethyl benzoate. By using an additional interaction parameter k_{cij}, the CCOR$_2$ improves the accuracy of enthalpy calculation for the ethyl benzoate system, which may involve stronger chemical interactions between the dissimilar constituents.

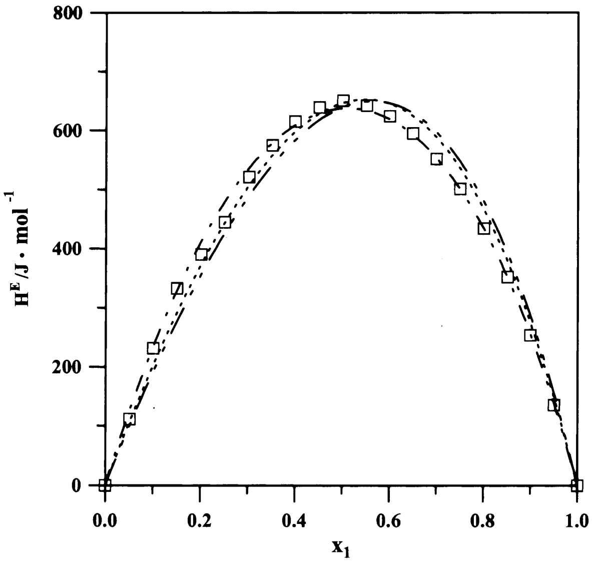

Figure 2. Excess molar enthalpies, H^E, for dimethyl carbonate + *o*-xylene (□); calculated from the PR (- - -); from the CCOR$_1$ (— — - - - — —); and from the CCOR$_2$ (— - —) equations of state

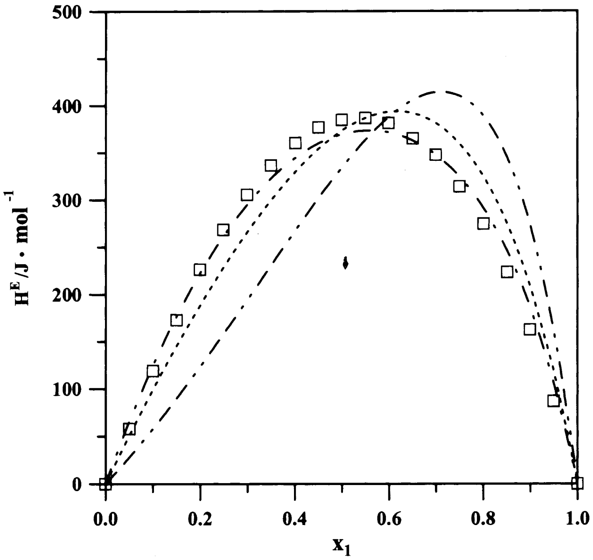

Figure 3. Excess molar enthalpies, H^E, for dimethyl carbonate + ethyl benzoate (□); calculated from the PR (- - -); from the CCOR$_1$ (— - - —); and from the CCOR$_2$ (— - —) equations of state.

Conclusions

The excess enthalpies have been measured for the binary mixtures of dimethyl carbonate + *o*-xylene, + *m*-xylene, + *p*-xylene, + ethylbenzene, and + ethyl benzoate at 298.15 K under atmospheric pressure. It was found that the mixing process is endothermic for each binary system. The maximum H^E of these five binary systems followed the order *p*-xylene > *m*-xylene > *o*-xylene > ethylbenzene > ethyl benzoate. The excess enthalpies of dimethyl carbonate + ethyl benzoate are substantially lower than those of other systems, indicating that strong chemical interactions may exist between the constituent molecules. The experimental H^E data were well represented by the Redlich−Kister equation. By using one adjustable interaction parameter, both the Peng−Robinson and the CCOR equations of state correlated these H^E data to an AAD better than 10%, except for dimethyl carbonate + ethyl benzoate. Substantial improvement has been achieved by using the CCOR equation with two binary interaction constants, k_{aij} and k_{cij}.

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