Excess Molar Enthalpies of Binary Systems of 2-Octanone or 3-Octanone with Dodecane, Tetradecane, or Hexadecane at 298.15 K

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An isothermal titration calorimeter was used to measure the excess molar enthalpies (H^E) of binary systems of 2-octanone or 3-octanone with dodecane, tetradecane, or hexadecane at 298.15 K under atmospheric pressure. The excess molar enthalpies are all positive and vary nearly symmetrically with the mole fraction of the ketones. The maximum values of the excess enthalpies increase with increasing chain length of *n*-alkanes for the systems containing a given ketone. In addition to a modified Redlich−Kister equation, the Peng−Robinson (PR), the Patel−Teja (PT), and two versions of the Cubic Chain-of-Rotators (CCOR) equations of state were used to correlate the excess molar enthalpies, respectively. The correlated results from the modified Redlich−Kister equation were in good agreement with the experimental values, while the CCOR equation of state with two binary interaction parameters yielded better results than those from other equations of state. The excess molar enthalpy data were also correlated with the NRTL and the Wilson models. It appeared that the NRTL model gave the best representation for those investigated systems.

Introduction

Excess molar enthalpies (H^E) data are useful for the development of thermodynamic models and engineering applications. This property also provides valuable information to reveal the interactions between constituent molecules.[1−6] Benson et al.[7−10] measured the H^E of the mixtures containing ketones and alkanes, while those of the systems containing isomeric octanones with long chains of *n*-alkanes are still unavailable from the literature. In this work, we installed an isothermal titration calorimeter to measure the molar enthalpy of mixing (or H^E) for six binary systems, including 2-octanone or 3-octanone with dodecane, tetradecane, or hexadecane at 298.15 K under atmospheric pressure. The values of H^E of these binary systems were compared to reveal the different molecular interactions between the isomeric octanones and the *n*-alkanes. These experimental H^E data were correlated with a modified Redlich−Kister type equation, the Peng−Robinson (PR),[11] the Patel-Teja (PT),[12] and the Cubic Chain-of-Rotators (CCOR)[13] equations of state, and also the Wilson[14] and the NRTL solution models,[15] respectively.

Experimental Section

Materials. 2-Octanone ($w = 0.99$) and 3-octanone ($w = 0.99$) were supplied by Acros (USA). Dodecane ($w = 0.99$) and tetradecane ($w = 0.99$) were purchased from Aldrich (USA), and hexadecane ($w = 0.99$) was from Fluka (Switzerland). All chemicals were used without further purification. The densities of the chemicals at 298.15 K were measured with an Anton Paar densitometer, DMA 4500, with an uncertainty of $\pm 5 \cdot 10^{-5}$ $g \cdot cm^{-3}$. The results are listed in Table 1, where literature values were also tabulated for comparison purposes. The agreement between the measured and the literature values is satisfactory.

Table 1. Densities of Pure Compounds at 298.15 K

	$\rho/(g \cdot cm^{-3})$	
component	this work	literature
2-octanone	0.81428	0.81484,[16] 0.81556[17]
3-octanone	0.81777	0.82200[18]
dodecane	0.74528	0.74527[19]
tetradecane	0.76020	0.75936[20]
hexadecane	0.77031	0.77003[19]

Apparatus and Procedure. An isothermal titration calorimeter (ITC, model 4400 IMC, Calorimeter Science Corporation, USA) was used to measure excess molar enthalpies H^E. The schematic diagram of this apparatus is presented in Figure 1. Its major parts include a titration cell (**1**), a reference cell (**2**), a highly stable thermostatic water bath (**3**), a refrigerated circulating bath (**4**), a personal computer with data acquisition system (**5**), and a precision syringe pump (**6**, PSD/2 module, Hamilton, USA). The titration cell (with an internal volume of about 60 cm^3)

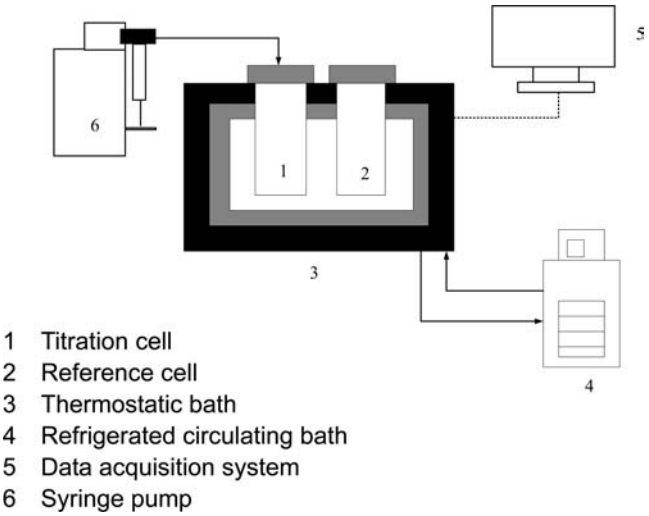

Figure 1. Schematic diagram of the isothermal titration calorimeter.

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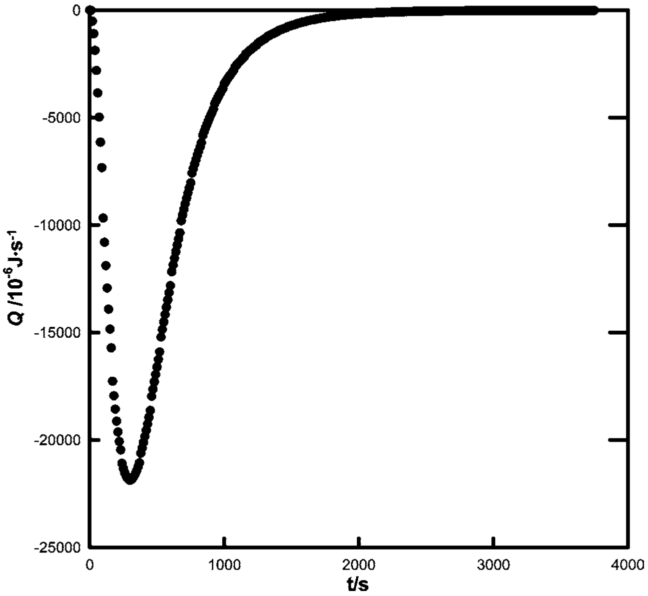

Figure 2. Illustrative example of titration heat flow signal from the isothermal titration calorimeter.

and the reference cell were inserted in the test wells of the highly stable thermostatic water bath, while the refrigerated circulator was used as an auxiliary cooling bath. Throughout the experimental process, the temperature of the water bath was maintained at 298.15 K with a stability of ± 0.0005 K. The precision syringe pump was equipped with a glass syringe (model: 1725 TLL, 250 μL) and a ceramic three-port valve (model: HVC 3-5 SST). The syringe pump was driven by a DC stepper motor to accurately deliver a titrant (one of constituent compounds) into the titration cell. The whole apparatus was housed in a constant temperature booth, also maintained at very near 298.15 K.

At the first step of the measurement, about 15 cm^3 of pure component or liquid mixture that was prepared gravimetrically with an uncertainty of ± 0.0001 in mole fraction filled in the titration cell. The cell was placed into the thermostatic water bath, and the stirrer of the titration cell was turned on. The stirring speed was fixed during any single experiment to maintain a constant baseline. After several hours, the measuring system reached thermal equilibrium, and the titration process was started. A given volume of a constituent compound, about (0.375 ± 0.001) cm^3, was injected into the titration cell via the precision syringe pump. The mass of the injected fluid was calculated from the injected volume with the known density, where the density value was measured with a vibrating-tube densitometer (DMA 4500, Anton Paar, Austria) to an uncertainty of $\pm\ 5.0 \cdot 10^{-5}$ g·cm^{-3}. During the titration process, the thermoelectric sensors, located between the measured sample and the aluminum block in the calorimeter, generated a voltage that is proportional to the temperature gradient across the sensors, and the temperature gradient was directly dependent on the heat flux. The calorimeter measured the heat flow with an uncertainty of ± 0.2 %. Figure 2 is an illustrative thermogram of an endothermic mixing process. Integration of the heat flow signal curve obtained the total amount of heat effect (Q) during the mixing. Provided that the titrant is component 1, the total amount of the heat absorbed ($-Q$) is given by

$$-Q = (n_1^{\mathrm{o}} + n_2^{\mathrm{o}} + \Delta n_1)H(x_1) - (n_1^{\mathrm{o}} + n_2^{\mathrm{o}})H(x_1^{\mathrm{o}}) - \Delta n_1 H_1^* \qquad (1)$$

where n_1^{o} and n_2^{o} are the numbers of moles of components 1 and 2, repectively, in the initial loaded solution; Δn_1 is the molar increment of the component 1 injected by the syringe pump; $H(x_1^{\mathrm{o}})$, $H(x_1)$, and H_1^* are the molar enthalpies of the initial loaded solution, the liquid mixture after titration, and the pure fluid of component 1, respectively. The variables x_1^{o} and x_1 in eq 1 are the mole fractions of component 1 in the initial loaded solution and in the liquid mixture after titration, respectively.

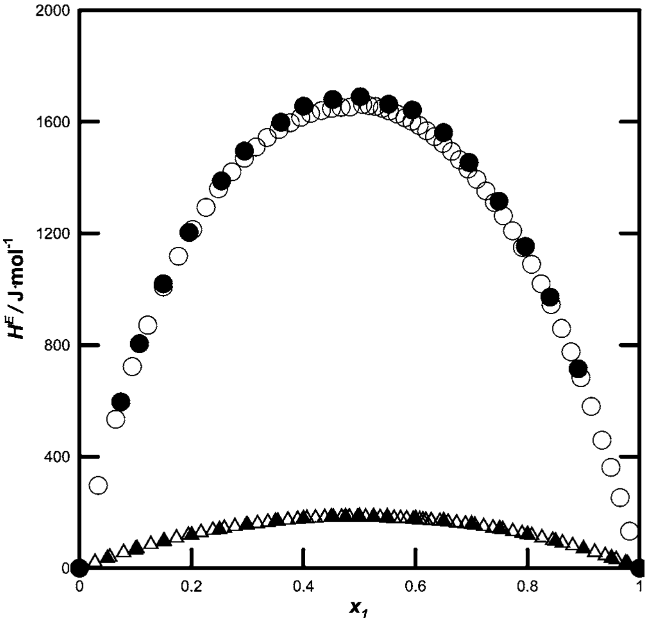

Figure 3. Excess molar enthalpies, H^{E}, for the test systems of butyric anhydride (1) + dodecane (2): ○, experimental values; ●, literature values;[21] dibutyl ether (1) + decane (2): △, experimental values; ▲, literature values[22] at 298.15 K.

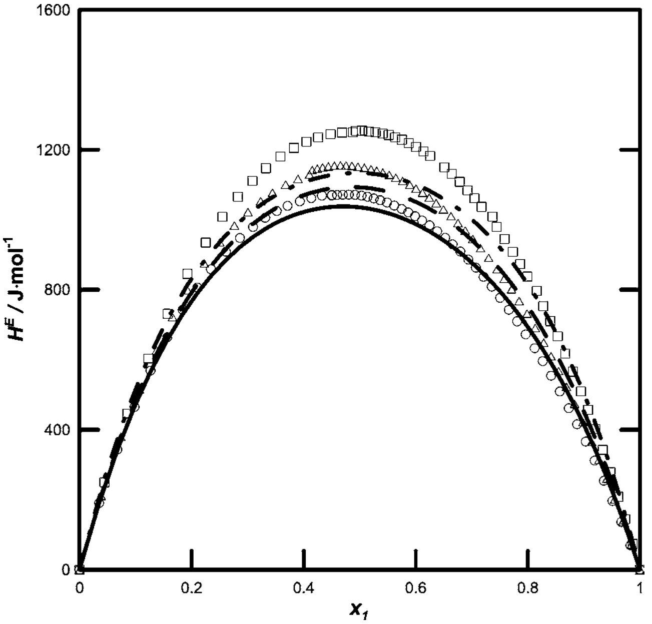

Figure 4. Excess molar enthalpies, H^{E}, for the mixtures ○, −, 2-octanone (1) + dodecane (2); △, ---, 2-octanone (1) + tetradecane (2); and □, − - −, 2-octanone (1) + hexadecane (2) at 298.15 K, where symbols are experimental values and lines are calculated from the NRTL equation.

$$x_1^{\mathrm{o}} = n_1^{\mathrm{o}}/(n_1^{\mathrm{o}} + n_2^{\mathrm{o}}) \qquad (2)$$

$$x_1 = (n_1^{\mathrm{o}} + \Delta n_1)/(n_1^{\mathrm{o}} + n_2^{\mathrm{o}} + \Delta n_1) \qquad (3)$$

By definition, the molar enthalpies of the mixtures before and after the titration can be expressed, respectively, in terms of corresponding excess molar enthalpies by

$$H(x_1) = x_1 H_1^* + (1 - x_1) H_2^* + H^E(x_1) \qquad (4)$$

$$H(x_1^o) = x_1^o H_1^* + (1 - x_1^o) H_2^* + H^E(x_1^o) \qquad (5)$$

Introducing eqs 2 to 5 into eq 1 yields

$$-Q = (n_1^o + n_1^o + \Delta n_1) H^E(x_1) - (n_1^o + n_2^o) H^E(x_1^o) \qquad (6)$$

and the excess molar enthalpy can thus be calculated from the following equation

Table 2. Experimental Results of the Excess Molar Enthalpies

x_1	H^E / $(J \cdot mol^{-1})$	x_1	H^E / $(J \cdot mol^{-1})$	x_1	H^E / $(J \cdot mol^{-1})$	x_1	H^E / $(J \cdot mol^{-1})$	x_1	H^E / $(J \cdot mol^{-1})$	x_1	H^E / $(J \cdot mol^{-1})$
2-Octanone (1) + Dodecane (2)											
0.0350	190.6	0.4698	1071.3	0.7210	836.4	0.3096	979.1	0.5866	1020.9	0.8730	461.9
0.0677	343.6	0.4804	1071.4	0.7355	808.5	0.3314	1005.3	0.5986	1009.8	0.8877	415.8
0.0982	465.6	0.4915	1071.0	0.7505	776.5	0.3519	1024.8	0.6113	997.6	0.9032	366.4
0.1267	569.4	0.5031	1068.8	0.7661	742.6	0.3712	1039.5	0.6244	983.8	0.9191	311.9
0.1564	664.4	0.5138	1065.6	0.7808	709.9	0.3931	1052.5	0.6381	966.9	0.9356	254.3
0.1841	742.2	0.5250	1060.6	0.7961	672.9	0.4135	1061.7	0.6525	948.3	0.9509	196.7
0.2101	805.9	0.5366	1055.5	0.8120	633.4	0.4325	1068.6	0.6658	929.4	0.9667	136.5
0.2345	858.1	0.5488	1049.1	0.8265	596.2	0.4499	1068.1	0.6795	908.9	0.9831	69.9
0.2613	908.2	0.5615	1040.4	0.8414	554.8	0.4504	1070.5	0.6938	885.8		
0.2862	947.6	0.5749	1030.7	0.8570	509.7	0.4596	1070.5	0.7072	862.7		
2-Octanone (1) + Tetradecane (2)											
0.0383	211.6	0.3678	1100.2	0.5082	1148.8	0.3443	1077.4	0.4968	1151.8	0.6364	1047.5
0.0737	379.9	0.3898	1116.9	0.5200	1144.6	0.6494	1029.7	0.7844	767.6	0.9138	365.4
0.1066	516.2	0.4102	1128.9	0.5304	1140.0	0.6629	1010.4	0.7985	731.6	0.9271	314.6
0.1373	627.2	0.4151	1142.0	0.5412	1134.6	0.6753	990.8	0.8131	691.7	0.9409	260.2
0.1659	722.0	0.4243	1146.1	0.5525	1128.2	0.6882	969.2	0.8282	649.7	0.9550	201.7
0.1927	798.6	0.4339	1149.6	0.5643	1120.1	0.7016	945.1	0.8413	610.6	0.9695	138.7
0.2226	874.5	0.4440	1152.5	0.5765	1110.7	0.7155	918.4	0.8549	568.4	0.9845	71.1
0.2504	934.9	0.4546	1154.4	0.5893	1099.7	0.7300	890.7	0.8689	523.2		
0.2763	983.5	0.4657	1155.6	0.6004	1089.1	0.7451	858.5	0.8834	474.7		
0.3005	1022.2	0.4756	1155.2	0.6120	1076.9	0.7709	800.7	0.8983	422.1		
0.3231	1053.0	0.4860	1154.1	0.6240	1063.1						
2-Octanone (1) + Hexadecane (2)											
0.0446	250.1	0.5751	1229.1	0.9075	457.0	0.4050	1223.3	0.7443	978.9		
0.0854	446.8	0.5874	1219.4	0.9204	401.9	0.4258	1235.9	0.7583	944.9		
0.1228	604.4	0.6003	1208.7	0.9337	342.7	0.4480	1245.2	0.7732	907.9		
0.1573	731.1	0.6138	1195.8	0.9473	278.9	0.4685	1249.3	0.7861	873.2		
0.1926	844.8	0.6257	1182.5	0.9614	208.9	0.4876	1250.0	0.7993	836.9		
0.2251	934.1	0.6508	1150.2	0.9739	144.8	0.4933	1254.4	0.8131	796.2		
0.2550	1008.1	0.6642	1130.8	0.9868	74.2	0.5044	1254.6	0.8273	752.8		
0.2827	1065.2	0.6781	1108.5			0.5161	1252.8	0.8400	710.8		
0.3084	1110.9	0.6926	1083.5			0.5282	1250.4	0.8531	666.7		
0.3324	1147.3	0.7048	1061.0			0.5410	1246.1	0.8666	617.8		
0.3585	1180.7	0.7174	1036.8			0.5519	1242.1	0.8805	566.1		
0.3826	1205.3	0.7370	1008.7			0.5633	1236.0	0.8949	509.5		
3-Octanone (1) + Dodecane (2)											
0.0352	170.7	0.4959	1025.0	0.7405	767.0	0.3042	920.2	0.6057	956.6	0.8883	400.7
0.0679	313.5	0.5109	1021.9	0.7557	737.7	0.3248	946.3	0.6194	943.6	0.9036	352.3
0.0985	427.6	0.5250	1017.2	0.7693	709.8	0.3477	969.3	0.6320	930.1	0.9194	300.1
0.1272	526.5	0.5383	1010.8	0.7833	679.9	0.3691	988.3	0.6451	914.8	0.9358	244.8
0.1541	606.6	0.5524	1002.2	0.7980	646.2	0.3892	1000.7	0.6588	897.5	0.9511	189.8
0.1794	676.6	0.5657	993.2	0.8133	609.4	0.4080	1011.2	0.6730	878.8	0.9668	130.8
0.2078	744.9	0.5782	983.7	0.8289	568.8	0.4257	1018.1	0.6855	864.3	0.9831	67.2
0.2344	803.3	0.5798	976.9	0.8453	525.6	0.4450	1022.8	0.6985	841.3		
0.2592	848.6	0.5900	973.7	0.8592	487.0	0.4631	1025.7	0.7120	818.9		
0.2824	888.2	0.5925	967.6	0.8735	445.5	0.4800	1026.1	0.7260	794.3		
3-Octanone (1) + Tetradecane (2)											
0.0384	195.0	0.3687	1053.9	0.5762	1063.0	0.3013	976.5	0.5316	1092.9	0.6906	924.9
0.0740	353.4	0.3907	1074.0	0.5904	1050.5	0.3240	1006.9	0.5458	1085.1	0.7037	903.5
0.1070	486.6	0.4111	1088.1	0.6033	1037.6	0.3452	1033.5	0.5618	1074.3	0.7172	879.3
0.1377	591.3	0.4303	1096.1	0.6131	1024.7	0.7313	852.3	0.8138	662.3	0.8988	404.5
0.1664	681.7	0.4482	1102.3	0.6255	1012.3	0.7459	823.2	0.8288	622.1	0.9142	349.5
0.1933	757.0	0.4650	1104.8	0.6385	998.1	0.7586	796.6	0.8419	585.4	0.9552	191.5
0.2233	828.9	0.4833	1104.6	0.6519	981.4	0.7716	767.0	0.8555	545.4	0.9696	131.0
0.2512	889.8	0.5005	1103.0	0.6660	962.3	0.7852	735.0	0.8694	502.1	0.9846	70.0
0.2771	936.7	0.5166	1098.8	0.6781	944.4	0.7992	700.2	0.8838	455.3		
3-Octanone (1) + Hexadecane (2)											
0.0448	229.3	0.5677	1194.8	0.8482	657.2	0.3599	1142.4	0.7163	992.8	0.9740	138.2
0.0857	412.9	0.5827	1184.0	0.8621	610.2	0.3822	1168.6	0.7302	964.9	0.9868	70.9
0.1233	561.5	0.5995	1168.7	0.8741	568.2	0.4079	1188.0	0.7423	940.4		
0.1578	683.4	0.6150	1153.1	0.8865	521.8	0.4316	1204.4	0.7547	913.7		
0.1899	783.4	0.6293	1136.9	0.8993	473.1	0.4534	1214.5	0.7676	883.7		
0.2195	865.6	0.6426	1119.8	0.9124	419.2	0.4737	1219.8	0.7809	851.9		
0.2522	949.3	0.6550	1102.6	0.9259	362.5	0.4956	1219.8	0.7947	816.7		
0.2824	1016.0	0.6775	1059.2	0.9375	312.1	0.5158	1218.9	0.8090	777.5		
0.3102	1068.3	0.6900	1039.2	0.9494	258.6	0.5345	1212.8	0.8216	740.5		
0.3360	1109.5	0.7029	1017.8	0.9615	199.8	0.5517	1203.8	0.8347	701.4		

$$H^{E}(x_1) = [-Q + (n_1^{o} + n_2^{o})H^{E}(x_1^{o})]/(n_1^{o} + n_2^{o} + \Delta n_1) \qquad (7)$$

In the case of the mixing process starting from titration of pure fluid 1 into pure fluid 2, i.e., $n_1^{o} = 0$ and $H^{E}(x_1^{o} = 0) = 0$, the excess molar enthalpy of this data point can be determined by

$$H^{E}(x_1) = -Q/(n_2^{o} + \Delta n_1) \qquad (8)$$

The measurement can be continued by injecting additional titrant after the heat rate curve of the previous run returning to the baseline. As usual, about six successive titration runs were made for each new loaded solution. The titration runs were also started alternatively from the injection of pure fluid 2 into the loaded pure fluid 1 by using a similar procedure and data treatment. The uncertainty of the H^{E} data determined in the present study is estimated to be ± 0.5 %.

Results and Discussion

To verify the reliability of measurements, two reference systems, butyric anhydride + dodecane and dibutyl ether + decane, were measured. Figure 3 graphically compares our experimental results with literature values,[21,22] indicating that the agreement is about within the experimental uncertainty. The experimental H^{E} data are reported in Table 2 for the binary systems of 2-octanone + dodecane, + tetradecane, + hexadecane and 3-octanone + dodecane, + tetradecane, + hexadecane. The variations of H^{E} with the mole fraction of the ketones (x_1) are illustrated in Figures 4 and 5. The H^{E} values of these six investigated binary systems are all positive; that is, all the mixing processes are endothermic, and the physical interactions between dissimilar molecules are the dominant contribution. The H^{E} values are nearly symmetric with the composition as also shown in Figures 4 and 5. The maximum values of H^{E} for the 2-octanone-containing systems follow the order of hexadecane (1254.6 J·mol^{-1}) > tetradecane (1140.1 J·mol^{-1}) > dodecane (1071.1 J·mol^{-1}), and the 3-octanone-containing systems exhibit the same order of hexadecane (1219 J·mol^{-1}) > tetradecane (1104.8 J·mol^{-1}) > dodecane (1026.1 J·mol^{-1}). It reveals that the physical forces between 2-octanone and the *n*-alkanes are substantially greater that those between 3-octanone and the *n*-alkanes due to the higher asymmetric structure of 2-octanone.[8] The experimental results also exhibit that the H^{E} values increase with increasing chain length of the *n*-alkanes for the systems containing a given ketone. This finding is consistent with the spectroscopic results[23,24] which show the presence of orientational order among long-chain *n*-alkanes, and the degrees of order also increase with an increase of the chain length of *n*-alkanes.

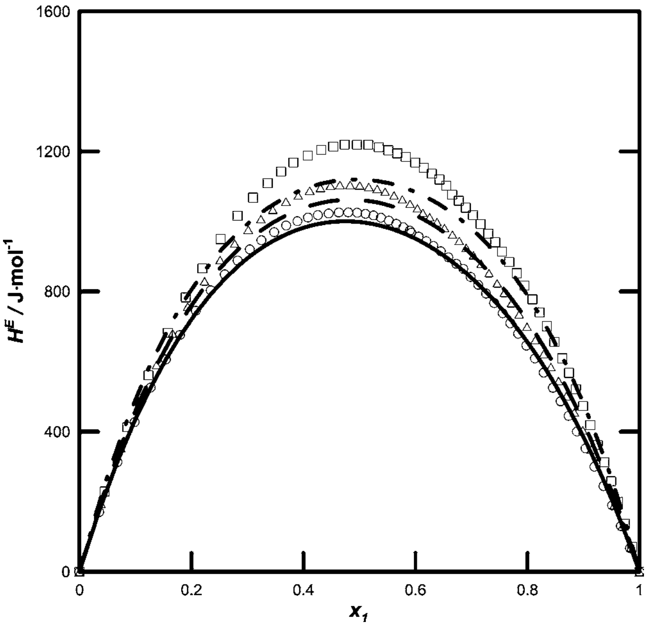

Figure 5. Excess molar enthalpies, H^{E}, for the mixtures ○, −, 3-octanone (1) + dodecane (2); △, ---, 3-octanone (1) + tetradecane (2); □, − - −, 3-octanone (1) + hexadecane (2) at 298.15 K, where symbols are experimental values and lines are calculated from the NRTL equation.

The H^{E} data were fitted to a modified Redlich−Kister equation[1]

$$H^{E}/\mathrm{J\cdot mol^{-1}} = x_1(1 - x_1)\sum_{i=0}^{n} a_i(1 - 2x_1)^{i}/[1 - k(1 - 2x_1)] \qquad (9)$$

where the coefficients a_i and the skewing factor k ($-1 < k < 1$) were determined by minimization of the following objective function

$$\mathrm{ARD}\ H^{E} = \frac{1}{N}\sum_{i=1}^{N} |H^{E}_{\mathrm{calc},i} - H^{E}_{\mathrm{expt},i}|/|H^{E}_{\mathrm{expt},i}| \qquad (10)$$

where ARD is average absolute relative deviation and N is the number of data points. The calculated results are reported in Table 3, in which the standard deviation $\sigma(H^{E})$ is defined as

$$\sigma(H^{E}) = [\sum_{j=1}^{N} (H^{E}_{\mathrm{calc},j} - H^{E}_{\mathrm{expt},j})^2/(N - m)]^{0.5} \qquad (11)$$

where m is the number of coefficients a_i. As depicted in Table 3, the modified Redlich−Kister equation correlates the H^{E} data to an ARD no greater than 0.3 % for each binary system.

The excess molar enthalpy data were also correlated with the PR, the PT, the CCOR equations of state and the solution models of Wilson and the NRTL, respectively. The physical properties of the constituent compounds needed in the data correlations are listed in Table 4. The van der Waals one-fluid mixing rules with a single adjustable binary interaction parameter (k_{aij}) in the combining rule of a_{ij} were adopted in the calculation for the PR and the PT equations of state; i.e.

Table 3. Correlated Results from the Modified Redlich−Kister Equation

mixture[a]	a_0	a_1	a_2	a_3	a_4	k	σ[b] (J·mol^{-1})	10^2 ARD[c]
M1	4275.07	198.86	655.12	208.74	6.42	0.072	1.2	0.2
M2	4601.30	502.29	586.07	154.04	154.84	−0.017	2.2	0.2
M3	5023.42	−13.34	813.03	−0.25	29.27	0.031	2.8	0.2
M4	4090.18	7.14	467.13	−3.34	13.77	0.106	1.5	0.2
M5	4403.94	−239.92	452.59	−58.42	92.84	0.142	1.6	0.1
M6	4882.66	−43.03	361.69	−233.09	275.34	0.040	3.0	0.2

[a] M1, 2-octanone + dodecane; M2, 2-octanone + tetradecane; M3, 2-octanone + hexadecane; M4, 3-octanone + dodecane; M5, 3-octanone + tetradecane; M6, 3-octanone + hexadecane. [b] Defined as in eq 11. [c] Defined as in eq 10.

$$a_{ij} = (1 - k_{aij})(a_i a_j)^{0.5} \tag{12}$$

$$b_{ij} = (b_i + b_j)/2 \tag{13}$$

$$c_{ij} = (c_i + c_j)/2 \tag{14}$$

where c_{ij} is used for the PT equation of state only. Table 5 reports the correlated results from the PR and the PT equations of state, where the optimal value of k_{aij} for each binary system was also determined by minimization of the objective function as defined in eq 10. The values of ARD from these two equations of state are almost identical.

Two types of combining rules were incorporated with the CCOR equation of state in the present study. The first type of the combining rules is the same as those in the PR and the PT equations of state as defined above. Only one binary interaction parameter (k_{aij}) was included in this model and thus denoted as CCOR1. An additional binary interaction parameter (k_{cij}) was introduced in the second type of combining rules and denoted as CCOR2. The combining rule of c_{ij} for CCOR2 is defined as

$$c_{ij} = (1 - k_{cij})(c_i + c_j)/2 \tag{15}$$

Table 6 lists the correlated results from the CCOR equations of state. The calculated results show that using the additional binary interaction parameter k_{cij} (CCOR2) can substantially improve the accuracy of the data correlation. The optimal values of the interaction parameters and the 10^2ARD H^E obtained from the Wilson and the NRTL models are listed in Table 7, where the nonrandomness parameter, α, in the NRTL model was fixed at 0.3 for each system. Among the tested equations of state and the solution models, the NRTL gives the best presentation with a grand ARD as low as 4.2 %. It should also be noted that the Wilson model has an inherent upper limit, about 800 J·mol^{-1}, regardless of the values of the model parameters used. As a consequence, the Wilson model fails to correlate the H^E data for these investigated systems since their maximum values of H^E are far above 800 J·mol^{-1}.

Table 4. Physical Properties of Pure Compounds

compound	MW (g·mol^{-1})	T_c[a] K	P_c[a] MPa	ω[a]	V_L[b] (cm^3·mol^{-1})
2-octanone	128.21	632.70	26.40	0.4549	157.44
3-octanone	128.21	615.49 [c]	27.04 [c]	0.5239 [d]	156.78
dodecane	170.33	658.00	18.20	0.5764	228.54
tetradecane	198.39	693.00	15.70	0.6430	250.04
hexadecane	226.44	723.00	14.00	0.7174	293.96

[a] Taken from the Aspen Plus Databank. [b] Calculated from density values as given in Table 1. [c] Estimated from the Joback group contribution method.[25] [d] Calculated from the following equation[26]

$$\omega = -[\ln(P_c/1.01325) + f^{(0)}(T_{br})]/f^{(1)}(T_{br})$$

with

$$f^{(0)} = (-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^{5})/T_{br}$$

$$f^{(1)} = (-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^{5})/T_{br}$$

$$T_{br} = T_b/T_c$$

and $\tau = 1 - T_{br}$ where P_c is critical pressure, T_c is critical temperature, and T_b is normal boiling point.

Table 5. Correlated Results from the Peng−Robinson and the Patel−Teja Equations of State

	PR		PT	
mixture [a]	k_{aij}	10^2 ARD H^E	k_{aij}	10^2 ARD H^E
M1	0.0284	12.4	0.0282	12.4
M2	0.0229	14.8	0.0227	14.8
M3	0.0202	14.2	0.0193	14.7
M4	0.0203	12.8	0.0202	12.8
M5	0.0131	15.8	0.0128	15.8
M6	0.0097	15.8	0.0090	15.8
10^2 grand ARD [b]		14.3		14.3

[a] M1, 2-octanone + dodecane; M2, 2-octanone + tetradecane; M3, 2-octanone + hexadecane; M4, 3-octanone + dodecane; M5, 3-octanone + tetradecane; M6, 3-octanone + hexadecane. [b] Grand ARD = $\sum_{i=1}^{6}(\text{ARD}_i \cdot N_i)/\sum_{j=1}^{6} N_j$ where ARD$_i$ is the average of relative deviation of binary system i and N_i is the number of data points of binary system i.

Table 6. Correlated Results from the CCOR Equation of State

	CCOR1		CCOR2		
mixture[a]	k_{aij}	10^2 ARD H^E	k_{aij}	k_{cij}	10^2 ARD H^E
M1	0.0132	14.1	−0.0616	−0.1246	6.6
M2	0.0022	18.9	−0.0857	−0.1392	6.0
M3	−0.0085	21.2	−0.0873	−0.1208	5.7
M4	0.0063	14.3	−0.0935	−0.1636	7.8
M5	−0.0069	19.5	−0.1186	−0.1734	8.8
M6	−0.0190	22.8	−0.1029	−0.1268	8.0
10^2 grand ARD[b]		18.4			7.1

[a] M1, 2-octanone + dodecane; M2, 2-octanone + tetradecane; M3, 2-octanone + hexadecane; M4, 3-octanone + dodecane; M5, 3-octanone + tetradecane; M6, 3-octanone + hexadecane. [b] Grand ARD = $\sum_{i=1}^{6}(\text{ARD}_i \cdot N_i)/\sum_{j=1}^{6} N_j$ where ARD$_i$ is the average of relative deviation of binary system i and N_i is the number of data points of binary system i.

Table 7. Correlated Results from the Wilson and the NRTL Models

	Wilson		
mixture[a]	$[(\lambda_{12} - \lambda_{11})/R]$/K	$[(\lambda_{21} - \lambda_{22})/R]$/K	10^2 ARD H^E
M1	481.12	481.12	28.2
M2	481.12	429.04	32.2
M3	481.12	481.12	36.8
M4	360.84	360.84	25.5
M5	481.12	481.12	29.4
M6	481.12	481.12	33.6
10^2 grand ARD[c]			31.0
	NRTL [b]		
mixture[a]	$[(g_{12} - g_{22})/R]$/K	$[(g_{21} - g_{11})/R]$/K	10^2 ARD H^E
M1	241.40	563.75	4.1
M2	321.26	564.23	4.7
M3	410.51	629.06	6.3
M4	232.98	495.19	2.5
M5	295.64	521.65	3.1
M6	411.59	577.58	4.7
10^2 grand ARD[c]			4.2

[a] M1, 2-octanone + dodecane; M2, 2-octanone + tetradecane; M3, 2-octanone + hexadecane; M4, 3-octanone + dodecane; M5, 3-octanone + tetradecane; M6, 3-octanone + hexadecane. [b] α = 0.3. [c] Grand ARD = $\sum_{i=1}^{6}(\text{ARD}_i \cdot N_i)/\sum_{j=1}^{6} N_j$ where ARD$_i$ is the average of relative deviation of binary system i and N_i is the number of data points of binary system i.

Conclusions

An isothermal titration calorimeter was used to measure the excess molar enthalpies of the binary systems of 2-octanone + dodecane, + tetradecane, + hexadecane and 3-octanone + dodecane, + tetradecane, + hexadecane. All the obtained H^E values are positive, indicating that the mixing processes are endothermic. For a given ketone, the H^E values increase with the chain length of the *n*-alkanes. For a given *n*-alkane, the H^E values of the 2-octanone-containing systems are greater than those of the 3-octanone-containing systems. Moreover, the H^E values vary nearly symmetrically with the mole fraction of ketones. The modified Redlich−Kister equation correlated the H^E data to within the experimental uncertainty. The PR, the PT, and the CCOR equations of state together with the solution models of Wilson and the NRTL were adopted, respectively, to correlate the H^E data. The correlated results from both the

PR and the PT equations of state are almost identical, and the CCOR equation with two binary interaction parameters (CCOR2) yielded better results among these tested equations of state. The NRTL model gave the best representation, while the Wilson model failed the data correlation.

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