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Excess Molar Enthalpies of Binary Systems of *n*-Valeric Anhydride or *n*-Hexanoic Anhydride with *n*-Dodecane, *n*-Tetradecane, or *n*-Hexadecane at 298.15 K

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ABSTRACT: Excess molar enthalpies, H^E, of binary mixtures of *n*-valeric anhydride or *n*-hexanoic anhydride with *n*-dodecane, *n*-tetradecane, or *n*-hexadecane were measured by an isothermal titration calorimeter at 298.15 K under atmospheric pressure. The experimental H^E values are positive for all binary systems over the entire composition range. In these six investigated systems, the maximum values of H^E exhibit at the composition ranging from 0.47 to 0.49 and 0.44 to 0.47 in the mole fraction of anhydrides for the mixtures containing *n*-valeric anhydride and *n*-hexanoic anhydride, respectively. The maximum values increase with increasing chain length of the alkanes for the mixtures containing a given anhydride. A Redlich−Kister equation correlated the experimental H^E data to within the experimental uncertainty. The new enthalpy data were also correlated, respectively, with the Peng−Robinson (PR), the Patel−Teja (PT), and two versions of the cubic chain-of-rotators (CCOR) equations of state and the NRTL model as well. The CCOR equation of state with two binary interaction parameters yielded the best representation for the investigated systems.

INTRODUCTION

Excess molar enthalpies (H^E) are essentially needed for many engineering applications, such as heat exchanger design and process design. This thermodynamic property is also fundamentally important for understanding the interactions between the constituent molecules. Ott and Sipowska[1] extensively reviewed the enthalpy data measurements with several different types of calorimeters and provided fundamentally important knowledge on H^E for a variety of mixtures. While a flow-type calorimeter was widely used for enthalpy measurements, much effort should be made for accurately calibrating the calorimeter because the calibration coefficients may be changed with different flow rates and the routes of streams even for the same chemical system.[2−6] For each new binary system, four calibration coefficients must be determined by fitting the results of calibration runs to literature H^E data of the related binary systems.[2] Alternatively, the calibration is much simpler and more straightforward for an isothermal titration calorimeter (ITC). To avoid the difficulties of calibration by using a flow calorimeter as mentioned above, an ITC was employed in the present study to measure the H^E data for mixtures containing anhydrides and long-chain paraffins at ambient conditions. Although there is a plenty of enthalpy data for *n*-alkane-containing mixtures, those are very scarce for the systems containing anhydrides. Among these quite limited data sources, Garcia et al.[7,8] reported the H^E data of the systems containing *n*-alkanes with *n*-butyric anhydride or *n*-heptanoic anhydride. In this work, we conducted the H^E measurements for the binary systems composed of *n*-valeric anhydride or *n*-hexanoic anhydride with *n*-dodecane, *n*-tetradecane, or *n*-hexadecane. The new results can provide an additional data basis for developing thermodynamic models, such as for determining the group interaction parameters of group-contribution models for the mixtures containing anhydride group. The newly obtained H^E data were correlated, respectively, with a Redlich−Kister type equation, the Peng−Robinson (PR),[9] the Patel−Teja (PT),[10] and the cubic chain-of-rotators (CCOR)[11] equations of state and the solution model of the NRTL[12] as well.

Table 1. Densities of Pure Compounds at 298.15 K

	ρ	
	$g\cdot cm^{-3}$	
component	this work	literature
n-valeric anhydride	0.93915	
n-hexanoic anhydride	0.92396	0.92390[13]
n-dodecane	0.74528	0.74527[14]
n-tetradecane	0.76020	0.76003[15]
n-hexadecane	0.77031	0.77003[14]

EXPERIMENTAL SECTION

Materials. *n*-Hexanoic anhydride ($w = 0.99$) was supplied by Alfa Aesar (U.S.). *n*-Dodecane ($w = 0.99$) and *n*-tetradecane ($w = 0.99$) were purchased from Aldrich (U.S.), while *n*-hexadecane ($w = 0.99$) and *n*-valeric anhydride ($w = 0.99$) were from Fluka (Switzerland). The densities of the chemicals at 298.15 K were measured by an Anton Paar densitometer, DMA 4500, with an accuracy of $\pm\ 5\cdot10^{-5}$ $g\cdot cm^{-3}$. The measured densities are compared with the literature values in Table 1, indicating that the

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Table 2. Experimental Results of the Excess Molar Enthalpies

	H^E		H^E		H^E		H^E		H^E		H^E
x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}	x_1	J·mol^{-1}
n-Valeric Anhydride (1) + *n*-Dodecane (2)											
0.0248	196	0.3935	1367	0.6545	1229	0.2518	1154	0.5100	1384	0.8298	774
0.0484	362	0.4025	1373	0.6699	1202	0.2699	1192	0.5229	1377	0.8474	709
0.0709	495	0.4118	1378	0.6861	1170	0.2827	1224	0.5342	1370	0.8657	640
0.0923	611	0.4217	1383	0.7003	1140	0.3038	1251	0.5461	1363	0.8849	563
0.1128	709	0.4320	1386	0.7151	1107	0.3195	1274	0.5585	1353	0.9022	491
0.1324	791	0.4428	1389	0.7305	1069	0.3411	1317	0.5715	1340	0.9202	408
0.1511	866	0.4542	1392	0.7467	1028	0.3488	1326	0.5851	1327	0.9389	321
0.1691	927	0.4644	1392	0.7635	982	0.3569	1335	0.5993	1311	0.9584	221
0.1914	998	0.4750	1392	0.7811	931	0.3654	1344	0.6122	1294	0.9788	117
0.2126	1059	0.4861	1390	0.7967	884	0.3743	1352	0.6257	1275		
0.2327	1110	0.4978	1388	0.8129	831	0.3837	1360	0.6398	1254		
n-Valeric Anhydride (1) + *n*-Tetradecane (2)											
0.0319	253	0.3186	1373	0.4638	1521	0.2997	1340	0.4524	1520	0.6049	1440
0.0618	461	0.3364	1400	0.4757	1522	0.6178	1423	0.7495	1147	0.8978	585
0.0899	622	0.3569	1432	0.4883	1522	0.6313	1402	0.7655	1099	0.9133	507
0.1164	761	0.3714	1466	0.5015	1519	0.6454	1380	0.7822	1047	0.9294	422
0.1414	872	0.3810	1475	0.5127	1517	0.6601	1354	0.7997	988	0.9461	330
0.1650	969	0.3911	1485	0.5245	1511	0.6754	1326	0.8145	936	0.9634	230
0.1873	1051	0.4020	1494	0.5369	1504	0.6916	1290	0.8299	878	0.9814	120
0.2126	1133	0.4130	1501	0.5498	1495	0.7052	1259	0.8459	815		
0.2363	1201	0.4294	1508	0.5633	1484	0.7194	1226	0.8625	746		
0.2587	1254	0.4312	1513	0.5776	1470	0.7341	1188	0.8798	669		
0.2798	1301	0.4416	1517	0.5926	1454						
n-Valeric Anhydride (1) + *n*-Hexadecane (2)											
0.0353	290	0.5424	1588	0.8739	765	0.3399	1505	0.6970	1373		
0.0683	525	0.5564	1577	0.8892	687	0.3619	1537	0.7103	1342		
0.0990	706	0.5695	1566	0.9050	605	0.3825	1558	0.7242	1309		
0.1278	859	0.5819	1554	0.9214	515	0.4019	1576	0.7386	1270		
0.1567	989	0.5935	1540	0.9361	429	0.4200	1590	0.7536	1226		
0.1837	1100	0.6046	1527	0.9513	334	0.4371	1600	0.7692	1180		
0.2090	1188	0.6168	1518	0.9670	231	0.4532	1605	0.7832	1134		
0.2329	1265	0.6292	1500	0.9832	118	0.4705	1606	0.7977	1084		
0.2553	1326	0.6421	1479			0.4866	1606	0.8128	1028		
0.2770	1383	0.6556	1458			0.5018	1604	0.8285	966		
0.2993	1433	0.6696	1430			0.5161	1599	0.8448	898		
0.3202	1474	0.6842	1401			0.5296	1594	0.8591	833		
n-Hexanoic Anhydride (1) + *n*-Dodecane (2)											
0.0213	153	0.3301	1114	0.5850	1101	0.2374	961	0.4442	1175	0.7854	736
0.0417	279	0.3392	1122	0.5987	1086	0.2533	990	0.4560	1175	0.8039	696
0.0612	386	0.3471	1129	0.6130	1068	0.2625	1021	0.4672	1174	0.8233	634
0.0800	476	0.3555	1136	0.6280	1049	0.2688	1032	0.4789	1172	0.8436	573
0.098	558	0.3642	1143	0.6438	1025	0.2754	1043	0.4913	1168	0.8649	507
0.1154	627	0.3733	1150	0.6604	1001	0.2824	1054	0.5043	1162	0.8874	432
0.1349	697	0.3830	1156	0.6778	970	0.2897	1064	0.5162	1156	0.9079	360
0.1536	756	0.3931	1162	0.6941	939	0.2974	1075	0.5286	1149	0.9293	283
0.1714	810	0.4023	1166	0.7112	908	0.3056	1086	0.5417	1140	0.9517	197
0.1886	855	0.4120	1169	0.7291	869	0.3134	1095	0.5554	1130	0.9753	103
0.2050	895	0.4222	1172	0.7480	829	0.3215	1105	0.5698	1116		
0.2208	929	0.4329	1174	0.7678	782						

Table 2. Continued

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 / $J \cdot mol^{-1}$
n-Hexanoic Anhydride (1) + *n*-Tetradecane (2)											
0.0274	201	0.2431	1058	0.3204	1197	0.4299	1293	0.5979	1215	0.8214	733
0.0533	361	0.2493	1072	0.3284	1208	0.4404	1295	0.6126	1197	0.8397	671
0.0779	492	0.2559	1086	0.3368	1217	0.4514	1297	0.6261	1177	0.8589	606
0.1012	602	0.2628	1099	0.3456	1228	0.4630	1298	0.6401	1157	0.8790	531
0.1234	694	0.2691	1111	0.3548	1238	0.4734	1297	0.6548	1133	0.9001	451
0.1445	773	0.2757	1124	0.3630	1246	0.4843	1296	0.6702	1107	0.9185	374
0.1681	851	0.2826	1137	0.3715	1254	0.4958	1292	0.6863	1078	0.9376	293
0.1904	916	0.2899	1150	0.3805	1261	0.5077	1288	0.7032	1043	0.9575	204
0.2115	972	0.2975	1163	0.3899	1268	0.5203	1283	0.7185	1011	0.9783	107
0.2316	1032	0.3056	1176	0.3998	1275	0.5335	1275	0.7345	973		
0.2372	1046	0.3129	1186	0.4012	1280	0.5453	1266	0.7512	933		
0.4103	1285	0.5703	1244	0.7869	837	0.5575	1257	0.7686	889		
0.4199	1289	0.5838	1231	0.8038	786						
n-Hexanoic Anhydride (1) + *n*-Hexadecane (2)											
0.0307	232	0.3646	1344	0.6020	1331	0.2889	1226	0.4907	1405	0.7742	975
0.0596	416	0.3747	1355	0.6153	1315	0.2962	1240	0.5034	1402	0.7907	925
0.0868	563	0.3853	1365	0.6292	1296	0.3038	1254	0.5144	1398	0.8078	871
0.1125	684	0.3954	1375	0.6437	1274	0.3118	1269	0.5258	1393	0.8233	818
0.1368	790	0.4059	1383	0.6589	1250	0.3202	1283	0.5377	1386	0.8393	758
0.1597	876	0.4170	1392	0.6721	1224	0.3291	1297	0.5502	1380	0.8560	696
0.1815	950	0.4262	1395	0.6857	1197	0.3373	1309	0.5633	1370	0.8733	627
n-Hexanoic Anhydride (1) + *n*-Hexadecane (2)											
0.2022	1013	0.4357	1399	0.6999	1166	0.3460	1321	0.5771	1359	0.8914	552
0.2219	1067	0.4457	1402	0.7147	1132	0.3550	1333	0.5893	1347	0.9102	468
0.2406	1113	0.4562	1405	0.7287	1098	0.9269	390	0.9411	304	0.9620	206
0.2627	1161	0.4671	1406	0.7433	1061	0.9807	111				
0.2820	1211	0.4787	1406	0.7584	1020						

agreement is satisfactory. The purity levels of the substances were also confirmed with gas chromatographic analysis. The impurity peaks of these tested samples are less than 0.01 in area fraction. All chemicals were used without further purification.

Apparatus and Procedure. An ITC (model 4400 IMC, Calorimeter Science Corporation, U.S.) was used in the present study to measure the molar enthalpies of mixing or excess molar enthalpies H^E. The schematic diagram and the experimental procedure have been described elsewhere.[16] The apparatus consists of a titration cell, a reference cell, a highly stable thermostatic water bath, a refrigerated circulating bath, a personal computer with data acquisition system. and a precision syringe pump (PSD/2 module, Hamilton, U.S.). 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 and also maintained at very near 298.15 K. 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 %. The uncertainty of the H^E data determined in the present study is estimated to be ± 0.5 %, and that of the reported composition is about ± 0.0001 in mole fraction.

RESULTS AND DISCUSSION

The H^E data for the binary systems of *n*-valeric anhydride + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane and *n*-hexanoic anhydride + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane are listed in Table 2. Figures 1 and 2 illustrate the variation of H^E data with the mole fraction of anhydrides for systems of *n*-valeric anhydride- and *n*-hexanoic anhydride-containing binaries, respectively. The H^E data of these six binaries are all positive (endothermic) over the entire composition range, indicating that a net decrease of order was resulting from the mixing process in each binary system. The maximum H^E values are located in the ranges of 0.45 to 0.49 and 0.44 to 0.48 in the mole fraction of anhydride for the systems containing *n*-valeric anhydride and *n*-hexanoic anhydride, respectively. These maximum values are 1606 $J \cdot mol^{-1}$, 1524 $J \cdot mol^{-1}$, and 1392 $J \cdot mol^{-1}$ for the binaries of *n*-valeric anhydride with *n*-hexadecane, *n*-tetradecane, and *n*-dodecane, respectively. Similarly, the maximum H^E values for the *n*-hexanoic anhydride binaries decrease in the order of 1406 $J \cdot mol^{-1}$ (with *n*-hexadecane) > 1298 $J \cdot mol^{-1}$ (with *n*-tetradecane)

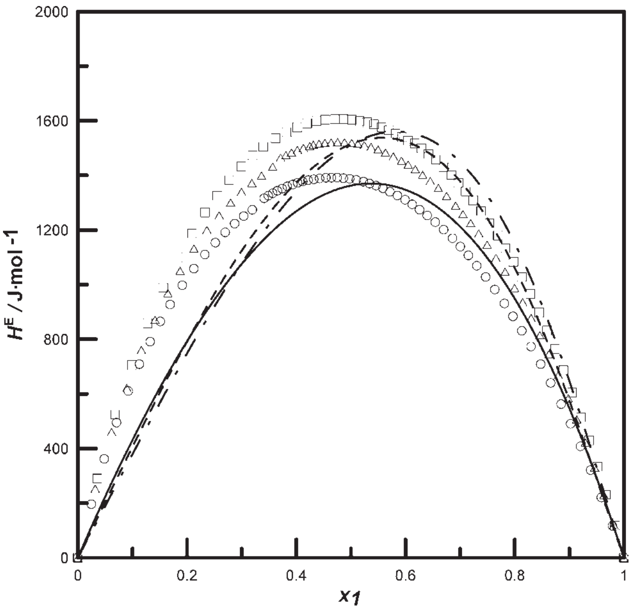

Figure 1. Excess molar enthalpies, H^E, for: ○, solid line, *n*-valeric anhydride (1) + *n*-dodecane (2); Δ, dashed line, *n*-valeric anhydride (1) + *n*-tetradecane (2); □, dash−dot−dashed line, *n*-valeric anhydride (1) + *n*-hexadecane (2); at 298.15 K, where symbols are experimental values and curves are calculated results from the CCOR2.

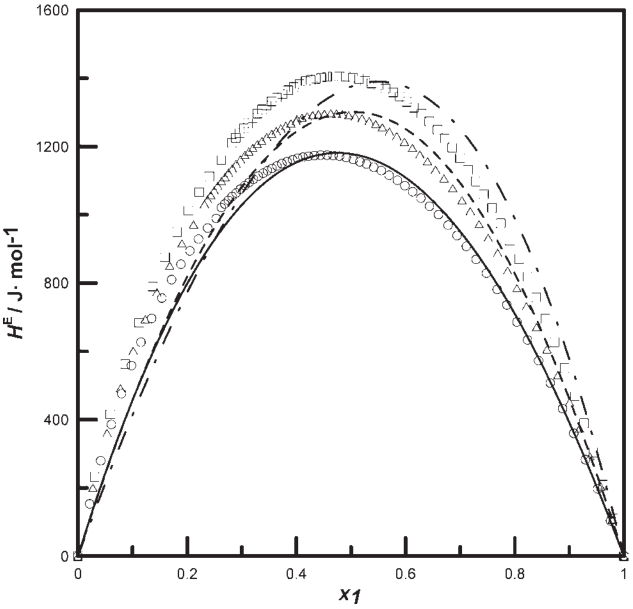

Figure 2. Excess molar enthalpies, H^E, for: ○, solid line, *n*-hexanoic anhydride (1) + *n*-dodecane (2); Δ, dashed line, *n*-hexanoic anhydride (1) + *n*-tetradecane (2); □, dash−dot−dashed line, *n*-hexanoic anhydride(1) + *n*-hexadecane (2); at 298.15 K, where symbols are experimental values and curves are calculated results from the CCOR2.

Table 3. Correlated Results from the Redlich−Kister Equation

						σ^a	
mixture[b]	a_0	a_1	a_2	a_3	a_4	J·mol^{-1}	10^2 ARD $H^{E\,c}$
M1	5548.3	−518.9	809.3	−821.3	742.5	3.6	0.3
M2	6070.5	−339.9	965.0	−607.1	605.1	4.3	0.3
M3	6418.4	381.4	1535.5	−115.7	45.7	3.0	0.2
M4	4662.2	−763.6	660.6	−747.3	518.1	4.5	0.4
M5	5166.6	−569.4	612.0	−712.8	600.6	3.5	0.3
M6	5616.0	−391.3	740.8	−614.9	582.7	3.3	0.3

[a] Defined as in eq 3. [b] M1: *n*-valeric anhydride + *n*-dodecane; M2: *n*-valeric anhydride + *n*-tetradecane; M3: *n*-valeric anhydride + *n*-hexadecane; M4: *n*-hexanoic anhydride + *n*-dodecane; M5: *n*-hexanoic anhydride + *n*-tetradecane; M6: *n*-hexanoic anhydride + *n*-hexadecane. [c] Defined as in eq 2.

Table 4. Physical Properties of Pure Compounds

	MW	$T_c{}^a$	$P_c{}^a$	
compound	g·mol^{-1}	K	MPa	ω^a
n-valeric anhydride	186.25	611.25[b]	24.12[b]	0.8096[c]
n-hexanoic anhydride	214.30	675.95[b]	20.14[b]	0.8919[c]
n-dodecane	170.33	658.00	18.20	0.5764
n-tetradecane	198.39	693.00	15.70	0.6430
n-hexadecane	226.44	723.00	14.00	0.7174

[a] Taken from Aspen Plus Databank. [b] Estimated from the Joback and Reid contribution method.[19] [c] Calculated from the following equation:[20] $\omega = -[\ln(P_c/1.01325) + f^{(0)}(T_{br})]/f^{(1)}(T_{br})$ with $f^{(0)} = (-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5)/T_{br}$; $f^{(1)} = (-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5)/T_{br}$; $T_{br} = T_b/T_c$; $\tau = 1 - T_{br}$; where P_c is critical pressure, T_c is critical temperature, and T_b is normal boiling point.

Table 5. Correlated Results from the PR and the PT Equations of State

	PR		PT	
mixture[a]	k_{aij}	10^2 ARD $H^{E\,b}$	k_{aij}	10^2 ARD $H^{E\,b}$
M1	0.0211	12.4	0.0212	12.5
M2	0.0131	13.7	0.0133	13.8
M3	0.0060	15.1	0.0060	15.1
M4	0.0196	10.3	0.0199	10.4
M5	0.0140	11.5	0.0150	11.6
M6	0.0094	12.2	0.0102	12.2
10^2 grand ARD[c]		12.4		12.5

[a] M1: *n*-valeric anhydride + *n*-dodecane; M2: *n*-valeric anhydride + *n*-tetradecane; M3: ^{n}-valeric anhydride + *n*-hexadecane; M4: *n*-hexanoic anhydride + *n*-dodecane; M5: ^{n}-hexanoic anhydride + *n*-tetradecane; M6: *n*-hexanoic anhydride + *n*-hexadecane. [b] Defined as in eq 2. [c] Grand ARD = $\Sigma_{i=1}^{6}(\text{ARD}_i \cdot N_i)/\Sigma_{j=1}^{6} N_j$, 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.

> 1175 J·mol^{-1} (with *n*-dodecane). This trend is consistent with the results of the *n*-butyric anhydride + *n*-alkanes binary systems[7] and also agrees with other previous observations,[17,18] which exhibited orientational order among the long chain *n*-alkanes and the degree of order increase with an increase of the chain length of *n*-alkanes. For a given *n*-alkane at the same condition, the H^E values of *n*-valeric anhydride binaries are greater than those of the corresponding *n*-hexanoic anhydride binaries.

Table 6. Correlated Results from the CCOR Equation of State

	CCOR1		CCOR2		
mixture[a]	k_{aij}	10^2 ARD $H^{E\,b}$	k_{aij}	k_{cij}	10^2 ARD $H^{E\,b}$
M1	0.0085	11.1	0.0087	0.0003	11.1
M2	−0.0029	13.2	−0.0931	−0.1428	11.1
M3	−0.0146	16.0	−0.0478	−0.0516	12.8
M4	0.0108	8.2	0.0294	0.0329	4.9
M5	0.0061	9.9	0.0533	0.0838	6.3
M6	0.0005	11.7	0.0017	0.0026	11.6
10^2 grand ARD[c]		12.0			9.6

[a] M1: *n*-valeric anhydride + *n*-dodecane; M2: *n*-valeric anhydride + *n*-tetradecane; M3: *n*-valeric anhydride + *n*-hexadecane; M4: *n*-hexanoic anhydride + *n*-dodecane; M5: *n*-hexanoic anhydride + *n*-tetradecane; M6: *n*-hexanoic anhydride + *n*-hexadecane. [b] Defined as in eq 2. [c] Grand ARD = $\Sigma_{i=1}^{6}(\mathrm{ARD}_i \cdot N_i)/\Sigma_{j=1}^{6} N_j$, 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.

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

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

where the coefficients a_i were determined by minimization of the following objective function:

$$\mathrm{ARD}\ H^E = \frac{1}{N} \sum_{i=1}^{N} |H^E_{\mathrm{calc},i} - H^E_{\mathrm{expt},i}|/|H^E_{\mathrm{expt},i}| \qquad (2)$$

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:

$$\sigma(H^E) = \left[\sum_{j=1}^{N} (H^E_{\mathrm{calc},j} - H^E_{\mathrm{expt},j})^2/(N - m)\right]^{0.5} \qquad (3)$$

where m is the number of coefficients a_i. As seen from Table 3, the Redlich−Kister equation correlated the H^E data to within experimental uncertainty, with the ARD no greater than 0.4 %, for each binary system.

The PR, the PT, the CCOR equations of state, and the solution model of the NRTL were also applied to correlate H^E data, and the physical properties of the constituent compounds needed in the data correlations are listed in Table 4. For the PR and the PT equations of state, 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. The combination rules were defined as:

$$a_{ij} = (1 - k_{aij})(a_i a_j)^{0.5} \qquad (4)$$

$$b_{ij} = (b_i + b_j)/2 \qquad (5)$$

$$c_{ij} = (c_i + c_j)/2 \qquad (6)$$

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 a specific binary system was also determined by minimization of the objective function as defined in eq 2. The values of ARD obtained from these two equations of state are almost identical.

Table 7. Correlated Results from the NRTL Model[a]

mixture[b]	$(g_{12}-g_{22})/R$/K	$(g_{21}-g_{11})/R$/K	10^2 ARD H^{Ec}
M1	405.82	726.49	14.4
M2	420.25	774.12	18.7
M3	427.59	830.65	21.6
M4	309.47	666.47	8.3
M5	385.97	684.27	11.0
M6	408.23	720.71	14.5
10^2 grand ARD[d]			14.4

[a] α = 0.3. [b] M1: *n*-valeric anhydride + *n*-dodecane; M2: *n*-valeric anhydride + *n*-tetradecane; M3: *n*-valeric anhydride + *n*-hexadecane; M4: *n*-hexanoic anhydride + *n*-dodecane; M5: *n*-hexanoic anhydride + *n*-tetradecane; M6: *n*-hexanoic anhydride + *n*-hexadecane. [c] Defined as in eq 2. [d] Grand ARD = $\Sigma_{i=1}^{6}(\mathrm{ARD}_i \cdot N_i)/\Sigma_{j=1}^{6} N_j$, 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.

Two types of combining rules were incorporated with the CCOR equation of state in the present study. The first type contains only one binary interaction parameter (k_{aij}) embedded in a_{ij} as defined in eq 4 and denoted as CCOR1. The second type has an additional binary interaction parameter (k_{cij}) in the combining rule of c_{ij} as defined in eq 7 and denoted as CCOR2.

$$c_{ij} = (1 - k_{cij})(c_i + c_j)/2 \qquad (7)$$

Table 6 lists the correlated results fro4m the CCOR equations of state. The tabulated values reveal that using the additional binary interaction parameter k_{cij} (CCOR2) can obviously reduce the deviations of the data correlation. The smoothed curves shown in Figures 1 and 2 are the results from the CCOR2. Since the generalized correlations of the equations of state were developed mainly from the properties of hydrocarbons with short chain lengths, those models may be insufficient for the mixtures containing long-chain molecules and the constituent compounds with an anhydride group. Other works[21−23] also indicated that the lattice fluid theories failed to accurately calculate the excess functions.

In addition to the equations of state, the solution model of the NRTL was also employed to correlate the enthalpy data. Table 7 reports the correlated results. In the calculations, the nonrandomness, α, of the NRTL model was fixed at 0.3, and thus two adjustable parameters, $(g_{12}-g_{22})/R$ and $(g_{21}-g_{11})/R$, were included in the model for each binary system. In comparison with the correlated results from the equations of state, those from the NRTL model are even worse. As mentioned in our previous work,[16] mathematically the Wilson model[24] has an upper limit for excess enthalpy calculation, about 800 $\mathrm{J \cdot mol^{-1}}$. The Wilson model fails to correlate the H^E data for these investigated systems, since the majority of the H^E values is far above 800 $\mathrm{J \cdot mol^{-1}}$. Among the tested models, the CCOR2 gives the best presentation for the investigated systems, with a grand ARD of about 0.096.

■ CONCLUSIONS

The excess molar enthalpies have been measured with an ITC for the binary systems of *n*-valeric anhydride + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane and *n*-hexanoic anhydride + *n*-dodecane, + *n*-tetradecane, and + *n*-hexadecane at 298.15 K and atmospheric pressure. The excess molar enthalpies are all positive, indicating that the mixing processes are endothermic. For a given anhydride, the H^E values increase with an increase of the chain length of *n*-alkanes. For a specific *n*-alkane, the H^E values of *n*-valeric anhydride-containing systems are greater than those of *n*-hexanoic anhydride-containing systems at the same conditions. The measured H^E data were correlated with the Redlich−Kister equation to within the experimental uncertainty. The H^E data were also correlated with various equations of state and solution models. The calculated results showed that the CCOR equation of state with two adjustable binary interaction parameters (CCOR2) yielded the best representation for the investigated systems.

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