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EXCESS THERMODYNAMIC PROPERTIES OF BINARY MIXTURES OF n-ALKANES WITH CYCLOALKANONES

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ABSTRACT

Molar excess enthalpies of the systems cyclopentanone/n-alkanes and cyclohexanone/n-alkanes at 298.15 K were determined by direct calorimetric measurements. Molar excess volumes of cyclopentanone and cyclohexanone/n-alkanes were determined at 298.15 and 308.15 K and of cycloheptanone/n-alkanes at 298.15 K by dilatometric measurements of volumes of mixing. The excess thermodynamic properties for a particular cycloalkanone increase with the chain length of the n-alkane, while for a given n-alkane, excess properties decrease as the size of the cycloalkanone increases.

INTRODUCTION

There have been many studies on the thermodynamic properties of binary liquid mixtures of alkanones/n-alkanes [1–4]. However, most of the studies are concerned with the mixtures having aliphatic or aromatic ketones as one of the components. Mixtures of cycloalkanones [5] have not been studied extensively. The object of this work was to study the effect of the chain length of n-alkanes on excess enthalpies, H^E, and excess volumes, V^E, of cycloalkanones/n-alkanes. With this purpose in mind, H^E for cyclopentanone and cyclohexanone/n-alkanes were measured at 298.15 K and V^E values for the same systems were measured at 298.15 and 308.15 K. Excess volumes for cycloheptanone/n-alkanes have been obtained at 298.15 K.

EXPERIMENTAL

Cyclopentanone (Merck, $\geqslant 99$ mol%), cyclohexanone (Baker Analyzed Reagent, 100 mol%), and cycloheptanone (Fluka, purum, $\geqslant 97$ mol%) were distilled and only the middle fraction was collected.

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The n-hexane (Fluka, puriss, $\geqslant$ 99.5 mol%), n-heptane (Fluka, puriss, $\geqslant$ 99.5 mol%), n-octane (Merck, $\geqslant$ 98 mol%), n-decane (Fluka, purum, $\geqslant$ 99 mol%) and n-dodecane (Merck, $\geqslant$ 99 mol%) were carefully dried with

TABLE 1

Experimental molar excess enthalpies, H^E, at 298.15 K of cycloalkanones/n-alkanes

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$(1-x)c\text{-}C_5H_8O + xC_6H_{14}$			
0.1460	538.5	0.6240	1182.8
0.2330	775.1	0.7631	998.3
0.3602	1007.3	0.8288	817.1
0.4551	1130.7	0.8731	651.5
0.5395	1184.2	0.9032	522.4
$(1-x)c\text{-}C_5H_8O + xC_7H_{16}$			
0.0992	492.6	0.6378	1258.3
0.1573	691.4	0.7413	1124.6
0.2219	862.9	0.7885	1012.4
0.3496	1100.5	0.8672	746.0
0.4613	1231.0	0.9009	591.2
0.5321	1267.8		
$(1-x)c\text{-}C_5H_8O + xC_8H_{18}$			
0.1095	542.9	0.5942	1369.2
0.1604	732.1	0.6537	1331.1
0.2381	957.8	0.7310	1202.4
0.3843	1230.7	0.8599	796.2
0.4876	1342.3	0.8978	628.5
$(1-x)c\text{-}C_5H_8O + xC_{10}H_{22}$			
0.0979	577.2	0.5567	1475.8
0.1532	815.7	0.6267	1450.9
0.2422	1095.3	0.7881	1163.7
0.3298	1285.1	0.8572	906.3
0.4586	1437.3	0.8907	744.1
$(1-x)c\text{-}C_5H_8O + xC_{12}H_{26}$			
0.0998	692.5	0.5553	1602.7
0.1549	963.2	0.6617	1521.9
0.2681	1327.8	0.7359	1386.3
0.3953	1538.9	0.7908	1228.6
0.4437	1580.1	0.8909	790.6
$(1-x)c\text{-}C_6H_{10}O + xC_6H_{14}$			
0.0985	371.3	0.6007	1042.4
0.1566	538.1	0.7549	879.9
0.1750	582.5	0.8088	762.3
0.2888	809.8	0.8612	606.2
0.3967	957.4	0.9088	432.9
0.5469	1048.2		

TABLE 1 (continued)

x	H^E (J mol^{-1})	x	H^E (J mol^{-1})
$(1-x)c\text{-}C_6H_{10}O + xC_7H_{16}$			
0.1088	448.2	0.5755	1176.6
0.1809	633.4	0.5982	1173.6
0.3294	926.7	0.7245	1057.7
0.3711	989.2	0.7665	969.4
0.4308	1070.6	0.8366	758.3
0.4827	1125.9	0.9050	484.9
$(1-x)c\text{-}C_6H_{10}O + xC_8H_{18}$			
0.0885	385.7	0.4974	1283.3
0.1770	701.1	0.5346	1291.3
0.2218	832.6	0.6623	1216.1
0.3350	1097.1	0.7621	1026.3
0.3994	1202.4	0.8696	674.4
$(1-x)c\text{-}C_6H_{10}O + xC_{10}H_{22}$			
0.1014	542.8	0.4640	1369.3
0.1738	815.2	0.5979	1348.8
0.2450	1026.8	0.7080	1203.5
0.2898	1133.7	0.7904	1009.2
0.3653	1270.1	0.8715	730.1
$(1-x)c\text{-}C_6H_{10}O + xC_{12}H_{26}$			
0.1194	691.4	0.5898	1466.5
0.1878	971.2	0.7122	1290.7
0.2585	1194.1	0.7804	1106.3
0.3592	1390.9	0.8538	833.9
0.4812	1495.2	0.9079	577.7

a molecular sieve (Fluka) and used directly after distillation. Densities of the purified compounds were in good agreement with the values reported in the literature [6].

The excess volumes were measured at 298.15 and 308.15 K by using the direct dilatometric technique in a dilatometer described previously [7,8]. The components were degassed just before they were loaded into the dilatometer. Excess enthalpies were measured in a calorimeter, the details of which are described elsewhere [9,10]. The temperature of the bath in which the H^E and V^E measurements were made was controlled to within ± 0.005 K.

RESULTS

The experimental values of H^E and V^E are listed in Tables 1 and 2, respectively. The results for each mixture were fitted to the equation:

$$X^E = x(1-x)\sum_{i=1}^{n} A_i(1-2x)^{i-1} \quad (1)$$

TABLE 2

Experimental excess volumes, V^E, of cycloalkanones/n-alkanes

Temp. (K)	x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$(1-x)c\text{-}C_5H_8O + xC_6H_{14}$				
298.15	0.0826	−0.091	0.5824	−0.135
	0.1470	−0.140	0.7212	−0.059
	0.2464	−0.187	0.8384	0.001
	0.3726	−0.205	0.8911	0.029
	0.4173	−0.194	0.9291	0.030
308.15	0.0805	−0.095	0.4457	−0.212
	0.1477	−0.158	0.5758	−0.162
	0.2459	−0.211	0.5761	−0.161
	0.3551	−0.232	0.7169	−0.076
	0.3648	−0.231	0.8311	0.000
	0.4382	−0.224	0.8491	0.011
			0.9448	0.029
$(1-x)c\text{-}C_5H_8O + xC_7H_{16}$				
298.15	0.0709	−0.008	0.5495	0.101
	0.1338	−0.009	0.5527	0.103
	0.2482	−0.006	0.6975	0.148
	0.3059	0.015	0.8127	0.153
	0.3523	0.033	0.8411	0.151
	0.3910	0.046	0.9124	0.112
	0.3983	0.048	0.9201	0.102
			0.9281	0.090
308.15	0.0273	−0.007	0.4112	0.049
	0.0696	−0.014	0.4142	0.052
	0.1330	−0.016	0.5542	0.110
	0.2284	−0.010	0.6948	0.170
	0.3388	0.018	0.8217	0.169
			0.9025	0.138
$(1-x)c\text{-}C_5H_8O + xC_8H_{18}$				
298.15	0.0678	0.041	0.5243	0.261
	0.1369	0.079	0.6878	0.278
	0.2112	0.123	0.6888	0.280
	0.3287	0.187	0.7967	0.253
	0.3633	0.208	0.8481	0.221
	0.5192	0.256	0.8994	0.174
308.15	0.0616	0.040	0.5254	0.277
	0.1234	0.076	0.6655	0.309
	0.2101	0.130	0.7602	0.299
	0.3160	0.184	0.8070	0.272
	0.3886	0.215	0.9129	0.177
			0.9431	0.122

TABLE 2 (continued)

Temp. (K)	x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$(1-x)c\text{-}C_5H_8O + xC_{10}H_{22}$				
298.15	0.0602	0.110	0.4826	0.482
	0.0998	0.165	0.6195	0.479
	0.1804	0.267	0.6992	0.455
	0.2908	0.382	0.7665	0.417
	0.3286	0.409	0.8260	0.339
	0.4756	0.477	0.8802	0.273
308.15	0.0563	0.107	0.3448	0.450
	0.1069	0.184	0.4835	0.507
	0.1100	0.191	0.5720	0.521
	0.1798	0.293	0.6313	0.516
	0.1837	0.292	0.7939	0.415
	0.2833	0.399	0.8992	0.253
$(1-x)c\text{-}C_5H_8O + xC_{12}H_{26}$				
298.15	0.0548	0.153	0.4421	0.627
	0.0891	0.226	0.4466	0.629
	0.1633	0.364	0.6388	0.604
	0.2645	0.504	0.7297	0.539
	0.2966	0.541	0.8014	0.473
			0.8984	0.289
308.15	0.0974	0.259	0.5993	0.654
	0.1663	0.394	0.7460	0.552
	0.2581	0.525	0.7989	0.480
	0.3102	0.584	0.8546	0.394
	0.4446	0.664	0.9384	0.200
$(1-x)c\text{-}C_6H_{10}O + xC_6H_{14}$				
298.15	0.0711	−0.091	0.6169	−0.272
	0.1040	−0.115	0.7203	−0.206
	0.1739	−0.201	0.7286	−0.198
	0.2783	−0.274	0.7893	−0.151
	0.3954	−0.323	0.8560	−0.093
	0.4232	−0.332	0.8585	−0.083
	0.4897	−0.323	0.8967	−0.057
308.15	0.0900	−0.131	0.4805	−0.370
	0.1703	−0.223	0.6066	−0.333
	0.1721	−0.224	0.6091	−0.324
	0.2760	−0.320	0.6167	−0.322
	0.2767	−0.317	0.7418	−0.235
	0.4055	−0.370	0.8444	−0.122
	0.4468	−0.371	0.8636	−0.124

TABLE 2 (continued)

Temp. (K)	x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$(1-x)c\text{-}C_6H_{10}O + xC_7H_{16}$				
298.15	0.0533	−0.009	0.3883	−0.044
	0.1689	−0.032	0.4523	−0.029
	0.2490	−0.041	0.4541	−0.033
	0.2624	−0.042	0.5881	−0.004
	0.2966	−0.044	0.7200	0.044
	0.3744	−0.046	0.8201	0.065
			0.8988	0.060
308.15	0.0874	−0.028	0.5802	−0.022
	0.1531	−0.049	0.5969	−0.006
	0.2554	−0.063	0.7180	0.027
	0.3692	−0.071	0.8350	0.054
	0.4290	−0.057	0.8815	0.057
	0.4472	−0.056	0.9178	0.048
$(1-x)c\text{-}C_6H_{10}O + xC_8H_{18}$				
298.15	0.0671	0.037	0.3548	0.141
	0.0719	0.042	0.4498	0.162
	0.1439	0.074	0.5529	0.187
	0.1461	0.071	0.5570	0.185
	0.2448	0.105	0.6923	0.195
	0.3408	0.137	0.8299	0.172
			0.8762	0.146
308.15	0.0816	0.040	0.5649	0.182
	0.1398	0.063	0.7184	0.192
	0.2398	0.096	0.8292	0.171
	0.3443	0.125	0.8957	0.132
	0.4159	0.151	0.9358	0.082
$(1-x)c\text{-}C_6H_{10}O + xC_{10}H_{22}$				
298.15	0.0433	0.075	0.3933	0.419
	0.0675	0.117	0.5141	0.444
	0.1283	0.201	0.5176	0.443
	0.2097	0.290	0.6639	0.420
	0.3016	0.367	0.7895	0.338
	0.3205	0.372	0.8789	0.235
			0.9470	0.118
308.15	0.0677	0.123	0.5090	0.447
	0.1311	0.208	0.6595	0.430
	0.2096	0.293	0.7504	0.388
	0.3150	0.377	0.8038	0.342
	0.3811	0.414	0.9134	0.192

TABLE 2 (continued)

Temp. (K)	x	V^E (cm^3 mol^{-1})	x	V^E (cm^3 mol^{-1})
$(1-x)c\text{-}C_6H_{10}O + xC_{12}H_{26}$				
298.15	0.0782	0.202	0.3435	0.579
	0.1096	0.273	0.4723	0.617
	0.1892	0.408	0.6246	0.593
	0.2769	0.521	0.6301	0.584
	0.3003	0.537	0.7828	0.450
	0.3430	0.567	0.9531	0.129
308.15	0.0524	0.157	0.4727	0.634
	0.1067	0.281	0.6278	0.605
	0.1875	0.430	0.7670	0.492
	0.2885	0.550	0.8412	0.372
	0.3448	0.590	0.9109	0.256
$(1-x)c\text{-}C_7H_{12}O + xC_6H_{14}$				
298.15	0.1012	−0.186	0.4956	−0.533
	0.1804	−0.306	0.5598	−0.516
	0.2412	−0.387	0.6318	−0.487
	0.3155	−0.464	0.7829	−0.346
	0.3921	−0.518	0.8828	−0.208
$(1-x)c\text{-}C_7H_{12}O + xC_7H_{16}$				
298.15	0.0869	−0.064	0.5494	−0.209
	0.1664	−0.128	0.6051	−0.196
	0.2844	−0.199	0.6832	−0.169
	0.3878	−0.228	0.7615	−0.130
	0.4736	−0.221	0.8872	−0.054
$(1-x)c\text{-}C_7H_{12}O + xC_8H_{18}$				
298.15	0.0866	−0.006	0.4856	−0.011
	0.1447	−0.012	0.5940	0.005
	0.2302	−0.018	0.7477	0.036
	0.2798	−0.019	0.8454	0.044
	0.3889	−0.019	0.8827	0.043
$(1-x)c\text{-}C_7H_{12}O + xC_{10}H_{22}$				
298.15	0.0643	0.079	0.5001	0.284
	0.1282	0.136	0.5692	0.285
	0.2385	0.203	0.6454	0.272
	0.3292	0.238	0.7208	0.256
	0.4145	0.268	0.8565	0.185
$(1-x)c\text{-}C_7H_{12}O + xC_{12}H_{26}$				
298.15	0.0572	0.111	0.4883	0.484
	0.1132	0.215	0.5764	0.472
	0.2173	0.339	0.6756	0.429
	0.3045	0.422	0.7689	0.365
	0.3655	0.459	0.8538	0.271

TABLE 3

Coefficients, A_i, and standard deviations, $\sigma(H^E)$, for the representations of molar excess enthalpies at 298.15 K by eqn. (1)

Mixture	A_1	A_2	A_3	A_4	A_5	A_6	A_7	$\sigma(H^E)$ (J mol^{-1})
$(1-x)$c-$C_5H_8O + xC_6H_{14}$	4661.0	−1361.8	935.2	1153.6	502.0	−1136.7	−1426.0	2.54
$(1-x)$c-$C_5H_8O + xC_7H_{16}$	5023.5	−1141.5	1547.5	688.9	128.7			1.83
$(1-x)$c-$C_5H_8O + xC_8H_{18}$	5410.9	−1296.7	1174.8	1952.2	139.0	−1837.6		2.1
$(1-x)$c-$C_5H_8O + xC_{10}H_{22}$	5858.3	−841.4	1972.7	162.8				1.75
$(1-x)$c-$C_5H_8O + xC_{12}H_{26}$	6418.2	−393.4	2411.2	139.1				1.51
$(1-x)$c-$C_6H_{10}O + xC_6H_{14}$	4138.9	−880.4	859.3	386.1				1.09
$(1-x)$c-$C_6H_{10}O + xC_7H_{16}$	4555.5	−1559.8	904.7	1481.2				2.73
$(1-x)$c-$C_6H_{10}O + xC_8H_{18}$	5138.8	−780.7	418.9					1.55
$(1-x)$c-$C_6H_{10}O + xC_{10}H_{22}$	5525.4	−343.3	592.5	−213.7	1070.9			2.34
$(1-x)$c-$C_6H_{10}O + xC_{12}H_{26}$	6001.9	−143.5	1181.5					2.79

TABLE 4

Coefficients, A_i, and standard deviations $\sigma(V^E)$ for the representations of molar excess volumes by eqn. (1)

Mixture	T (K)	A_1	A_2	A_3	A_4	A_5	$\sigma(V^E)$ ($cm^3\ mol^{-1}$)
$(1-x)$c-$C_5H_8O+xC_6H_{14}$	298.15	−0.688	−0.679	0.183	−0.392	0.338	0.004
	308.15	−0.794	−0.795	0.253	−0.310	0.363	0.003
$(1-x)$c-$C_5H_8O+xC_7H_{16}$	298.15	0.329	−0.800	0.421	−0.130		0.004
	308.15	0.338	−0.898	0.525	−0.267		0.004
$(1-x)$c-$C_5H_8O+xC_8H_{18}$	298.15	1.007	−0.579	0.434	−0.317		0.003
	308.15	1.063	−0.757	0.549	−0.201		0.003
$(1-x)$c-$C_5H_8O+xC_{10}H_{22}$	298.15	1.928	−0.444	0.478			0.006
	308.15	2.063	−0.437	0.504	−0.127		0.003
$(1-x)$c-$C_5H_8O+xC_{12}H_{26}$	298.15	2.536	−0.221	0.709			0.007
	308.15	2.690	−0.098	0.508	−0.207	0.268	0.002
$(1-x)$c-$C_6H_{10}O+xC_6H_{14}$	298.15	−1.291	−0.436	0.493			0.005
	308.15	−1.474	−0.410	0.350			0.005
$(1-x)$c-$C_6H_{10}O+xC_7H_{16}$	298.15	−0.092	−0.523	0.495			0.003
	308.15	−0.176	−0.580	0.450			0.004
$(1-x)$c-$C_6H_{10}O+xC_8H_{18}$	298.15	0.693	−0.424	0.483	−0.127		0.002
	308.15	0.679	−0.509	0.404			0.004
$(1-x)$c-$C_6H_{10}O+xC_{10}H_{22}$	298.15	1.769	−0.271	0.398			0.003
	308.15	1.776	−0.312	0.563			0.003
$(1-x)$c-$C_6H_{10}O+xC_{12}H_{26}$	298.15	2.489	−0.004	0.476			0.004
	308.15	2.527	−0.014	0.778			0.007
$(1-x)$c-$C_7H_{12}O+xC_6H_{14}$	298.15	−2.131	−0.122	0.176	0.169		0.004
$(1-x)$c-$C_7H_{12}O+xC_7H_{16}$	298.15	−0.881	−0.287	−0.014	0.139	0.530	0.002
$(1-x)$c-$C_7H_{12}O+xC_8H_{18}$	298.15	−0.035	−0.314	0.332			0.002
$(1-x)$c-$C_7H_{12}O+xC_{10}H_{22}$	298.15	1.126	−0.174	0.227	−0.094	0.405	0.003
$(1-x)$c-$C_7H_{12}O+xC_{12}H_{26}$	298.15	1.930	0.062	0.377	−0.275		0.004

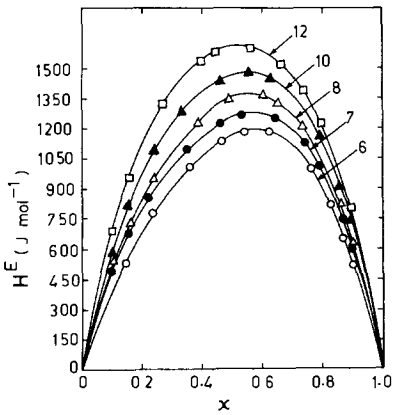

Fig. 1. Excess enthalpies, H^E, for $[(1-x)\text{c-}C_5H_8O + xC_NH_{2N+2}]$ at 298.15 K. (○, ●, △, ▲, □) Our experimental results, (———) calculated from eqn. (1). Labels indicate number, N, of carbon atoms in n-alkane molecules.

where X^E is the excess thermodynamic function and x is the mole fraction of the n-alkane. The values of A_i and the standard deviations, $\sigma(H^E)$ and $\sigma(V^E)$, were determined by the least-squares method with all points weighted equally; the values are given in Tables 3 and 4, respectively. The experimental points and the curves calculated from eqn. (1) are given in Figs. 1–5.

DISCUSSION

The excess enthalpies for cyclopentanone and cyclohexanone with an n-alkane are large and positive over the entire range of mole fractions. The

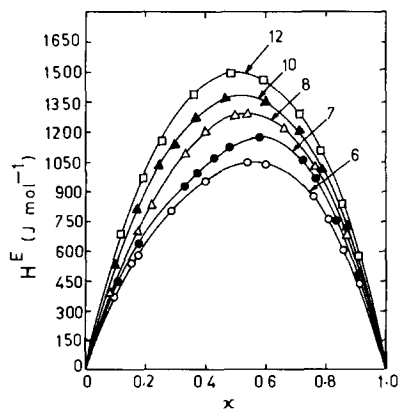

Fig. 2. Excess enthalpies, H^E, for $[(1-x)\text{c-}C_6H_{10}O + xC_NH_{2N+2}]$ at 298.15 K. (○, ●, △, ▲, □) Our experimental results, (———) calculated from eqn. (1). Labels indicate number, N, of carbon atoms in n-alkane molecules.

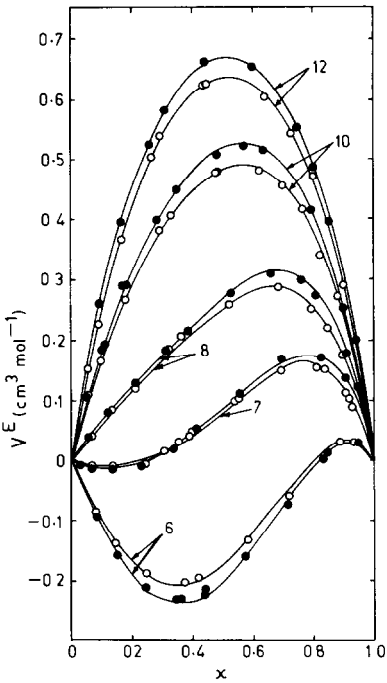

Fig. 3. Excess volumes, V^E, for $[(1-x)$c-$C_5H_8O + xC_NH_{2N+2}]$ at 298.15 K (○) and 308.15 K (●). (○, ●) Our experimental results, (———) calculated from eqn. (1). Labels indicate number, N, of carbon atoms in n-alkane molecules.

excess enthalpy for a given n-alkane decreases as the size of the cycloalkanone increases. The same trend is found in the results of Kiyohara et al. [1] for mixtures of aliphatic ketones with n-alkanes. It was suggested by Kiyohara et al. [1] that the large positive excess enthalpy for aliphatic ketones/n-alkanes arise mainly from the breaking of strong dipole–dipole interactions between ketone molecules. The same explanation can be extended to mixtures of cycloalkanone/n-alkanes. The decreasing trend in H^E of a cycloalkanone with a given n-alkane, as the size of the cycloalkanone increases, is apparently due to a weakening of the interactions between ketoxy groups of higher cyclic ketones.

Figures 1 and 2 show that there is a systematic increase in the excess enthalpies with the increase in chain length of the n-alkane. With the assumption of a quadratic dependence on the number, N, of carbon atoms in the n-alkane and with unit weight assigned to all the experimental points, the expression [1]:

$$H_N^E = x(1-x)\sum_{i=1}^{5}\sum_{j=1}^{3} C_{ij}N^{j-1}(1-2x)^{j-1} \qquad (2)$$

was fitted to the sets of results for a given ketone (cyclopentanone or

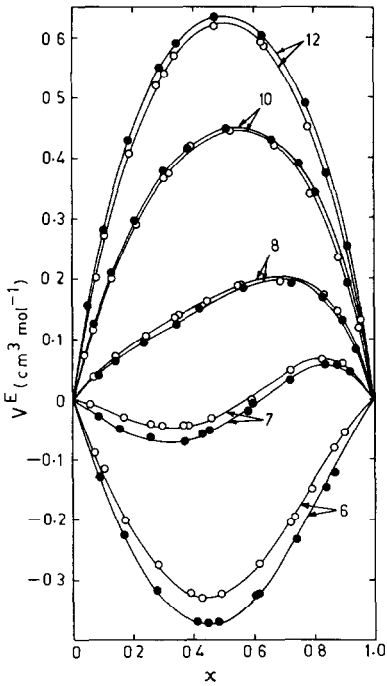

Fig. 4. Excess volumes, V^E, for $[(1-x)\text{c-}C_6H_{10}O + xC_NH_{2N+2}]$ at 298.15 K (○) and 308.15 K (●). (○, ●) Our experimental results, (———) calculated from eqn. (1). Labels indicate number, N, of carbon atoms in n-alkane molecules.

TABLE 5

Coefficients, C_{ij}, and standard deviations, $\sigma(H_N^E)$, for representations of molar excess enthalpies of $xC_NH_{2N+2} + (1-x)$ketone at 298.15 K by using eqn. (2)

Ketone	Cyclopentanone	Cyclohexanone
C_{11}	2360.8	295.59
C_{12}	437.93	813.99
C_{13}	−8.326	−28.292
C_{21}	−1209.4	−933.39
C_{22}	−73.962	−140.06
C_{23}	11.615	17.768
C_{31}	−2042.0	1506.25
C_{32}	687.75	−199.56
C_{33}	−28.035	12.703
C_{41}	381.48	2836.8
C_{42}	46.762	−435.68
C_{43}	−5.778	15.754
C_{51}	402.0	258.75
C_{52}	−232.25	−90.375
C_{53}	18.773	9.383
$\sigma(H_N^E)$ (J mol^{-1})	15.1	21.0

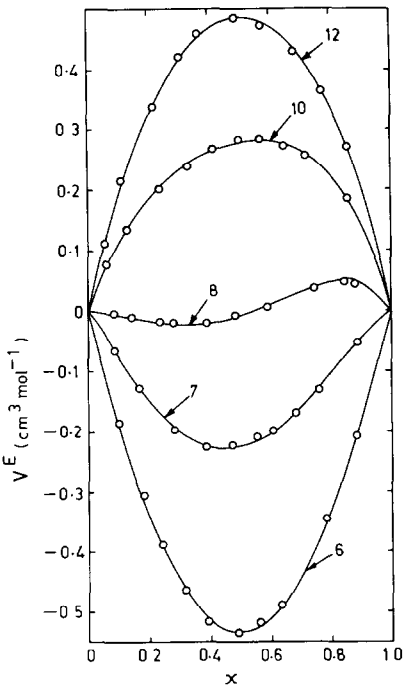

Fig. 5. Excess volumes, V^E, for $[(1-x)\text{c-}C_7H_{12}O + xC_NH_{2N+2}]$ at 298.15 K. (O) Our experimental results, (———) calculated from eqn. (1). Labels indicate number, N, of carbon atoms in n-alkane molecules.

cyclohexanone) mixed with the five n-alkanes. Values of the coefficients, C_{ij}, and the standard deviations of the fit, $\sigma(H_N^E)$, are given in Table 5. A comparison of $\sigma(H^E)$ and $\sigma(H_N^E)$ values indicates that eqn. (2) does not give as good a representation of the results as the representation obtained with eqn. (1) for the individual mixtures. Nevertheless, eqn. (2) can still be used for estimating H^E values for mixtures of the ketones with n-nonane and n-undecane, and could possibly be used for rough estimates of H^E for mixtures with n-alkanes of longer chain length.

As can be seen in Figs. 3–5, the excess volumes of cyclopentanone, cyclohexanone and cycloheptanone mixtures with a given n-alkane decrease as the size of the cycloalkanone increases and, for a given ketone, the increase in V^E with the chain length of the n-alkane follows the same trend as is found with the H^E values of these systems.

The V^E curves at 298.15 K have a positive slope over the whole mole-fraction range for the larger n-alkanes but become sigmoid or negative for shorter n-alkanes. The V^E results observed for these systems are the consequence of physical and structural effects of the pure liquids and of the mixtures. The former, deriving from non-specific physical dipole–dipole interactions between cycloalkanone molecules, give a positive contribution

to V^E, while the latter, which generally cause a contraction of volume, essentially derive from changes in free volumes, interstitial accommodation and conformational changes. The excess volumes of the systems studied in this work are the net result of these effects.

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