



ELSEVIER

Thermochimica Acta 247 (1994) 283–292

thermochimica
acta

Excess molar enthalpies of cycloalkanol + *n*-alkane mixtures under high pressure

Ge Li *, Yun Liu, Xianda Sun, Fangyu Xue

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Received 29 November 1993; accepted 20 April 1994

Abstract

Excess molar enthalpies of cyclopentanol and cyclohexanol in mixtures with *n*-hexane, *n*-dodecane or *n*-hexadecane have been determined at 298.65 and 308.65 K, and at pressures up to 10 MPa. The H_m^E values are positive over the entire mole fraction range, and increase with increasing temperature and chain length of the *n*-alkane, but decrease with increasing pressure. The dependence of H_m^E on the size and shape of the component molecules is discussed.

Keywords: Alkane; Alkanol; Binary system; Excess molar enthalpy

1. Introduction

Thermodynamic properties at various temperatures and pressures, especially under high pressure, are important in the chemical industry, for example, in the supercritical fluid extraction and liquefaction of coal. Moreover, good experimental high-pressure data are required for proper process design. From the theoretical point of view, the thermodynamic behaviour under high pressure of alkanol–alkane mixtures is of particular interest, as it depends sensitively on hydrogen-bonding association, intermolecular interactions, especially the repulsive forces, and the liquid structure. Therefore, reliable experimental data of excess properties under high pressures provide an important test of theoretical models.

* Corresponding author.

The excess molar enthalpies H_m^E for cycloalkanol + alkane mixtures were previously measured at ambient and various temperatures [1–4]. These results indicate that in addition to the intermolecular energy and H-bond association, the size and shape of the component molecules might play an important role in determining thermodynamic properties of their mixtures.

In this paper, cycloalkanol systems are studied in order to investigate the steric hindrance of the cycloalkyl group on the self-association of the adjacent hydroxyl groups under high pressure.

2. Experimental

2.1. Materials

The analytical reagents, *n*-dodecane and *n*-hexadecane (Beijing Chemical Co.) were purified by fractional distillation using a 1.5 m long column packed with fine copper rings. Cyclopentanol, cyclohexanol and *n*-hexane (Beijing Chemical Co., purities in excess of 99%) were used directly. All the reagents were stored over 4 Å molecular sieves. The densities and refractive indices of the reagents agreed well with those reported in the literature [5,6].

2.2. Apparatus

New high-pressure flow calorimetric vessels were designed and made. They were fitted into the Setaram C-80 Calvet calorimeter. With these vessels, heats of mixing can be measured from ambient temperature and pressure up to 573 K and 15 MPa.

The proper working of the apparatus was checked using the mixture *n*-ethanol + (1 - *x*)H₂O at 298.65 K and at 0.1, 5 and 10 MPa [7]. The results are in agreement with values cited in the literature [8].

3. Results

The excess molar enthalpies were measured for the mixtures: cyclopentanol + *n*-hexane, cyclopentanol + *n*-dodecane, cyclohexanol + *n*-hexane, cyclohexanol + *n*-dodecane, and cyclohexanol + *n*-hexadecane, at 298.65 and 308.65 K, and at 0.1 and 10 MPa. The inaccuracy is estimated to be $\pm(1-2) \times 10^{-3}$ for the mole fraction *x* and about $\pm 2\%$ for H_m^E .

The experimental results are summarized in Table 1. In all cases it is possible to represent the dependence of H_m^E on the molar fraction *x* with the Redlich–Kister equation (RK-fit)

$$H_m^E/(\text{J mol}^{-1}) = x(1-x) \sum_{j=0}^k A_j(2x-1)^j \quad (1)$$

Table 1

Experimental excess molar enthalpies for cycloalkanol + *n*-alkane mixtures $H_{m,\text{exp}}^E$ and D ($H_{m,\text{exp}}^E - H_{m,\text{fit}}^E$), in J mol⁻¹

298.65 K 0.1 MPa			308.65 K 0.1 MPa			298.65 K 10 MPa			308.65 K 10 MPa		
<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>
$x\text{C}_5\text{H}_9\text{OH} + (1-x)\text{C}_6\text{H}_{14}$											
0.0597	203.7	10.8	0.0600	378.0	8.9	0.0592	175.3	3.0	0.0594	362.6	7.0
0.1084	326.1	-10.1	0.1089	552.0	0.2	0.1075	308.2	-3.5	0.1078	532.0	0.7
0.1667	485.4	3.9	0.1675	678.1	-12.2	0.1654	460.8	3.4	0.1659	657.1	-8.3
0.2089	559.0	-7.2	0.2099	756.1	-2.0	0.2073	536.7	-5.7	0.2080	725.3	-6.4
0.2657	652.2	0.3	0.2688	823.7	0.8	0.2638	631.6	4.0	0.2646	800.3	4.4
0.3042	699.0	6.8	0.3054	865.5	10.8	0.3022	670.2	3.2	0.3030	835.6	8.2
0.3605	730.1	2.6	0.3618	890.8	4.5	0.3582	694.8	-5.7	0.3592	864.8	6.2
0.4069	736.8	-0.9	0.4082	897.0	-2.1	0.4046	708.8	-1.2	0.4055	866.1	-4.9
0.4482	732.5	-2.0	0.4496	899.1	-0.9	0.4458	708.0	1.2	0.4468	868.9	-2.5
0.4828	726.6	2.4	0.4842	892.9	0.0	0.4804	701.9	5.0	0.4814	862.3	-1.7
0.5279	703.0	1.2	0.5293	865.2	-7.6	0.5255	679.4	3.8	0.5265	842.7	-1.0
0.5713	660.5	-11.4	0.5727	833.3	-8.9	0.5690	642.2	-5.0	0.5700	808.0	-5.3
0.5983	643.6	-6.2	0.5996	814.7	-3.3	0.5960	618.0	-8.1	0.5969	786.4	-3.2
0.6478	612.9	10.2	0.6490	773.4	9.5	0.6455	585.6	4.6	0.6465	744.8	7.6
0.6838	562.0	-1.6	0.6850	731.3	13.8	0.6817	541.0	-1.8	0.6825	692.3	-0.4
0.7184	530.1	8.0	0.7196	667.5	-0.2	0.7165	505.5	3.4	0.7173	653.1	7.9
0.7539	480.0	4.7	0.7550	608.4	-3.5	0.7522	457.8	1.6	0.7529	595.5	3.6
0.7868	427.8	-0.2	0.7878	559.7	4.0	0.7852	411.4	1.5	0.7859	536.1	-2.1
0.8201	371.5	-4.3	0.8209	493.6	-0.4	0.8187	359.3	0.3	0.8193	478.5	-0.5
0.8533	314.5	-4.6	0.8540	411.1	-15.2	0.8521	304.7	0.5	0.8526	400.6	-13.3
0.8807	260.5	-7.9	0.8813	359.0	-5.9	0.8797	249.4	-6.2	0.8801	349.8	-4.7
0.9148	204.1	4.1	0.9152	285.0	5.4	0.9140	188.4	2.2	0.9143	278.3	6.7
0.9408	142.7	-0.8	0.9411	215.3	9.5	0.9402	137.4	0.2	0.9404	206.8	7.0
0.9697	82.4	6.2	0.9689	122.9	9.8	0.9694	78.5	5.4	0.9695	119.5	10.2
0.9832	52.5	9.6	0.9833	54.0	-10.7	0.9831	46.1	4.9	0.9831	48.7	-13.8
$x\text{C}_6\text{H}_9\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$											
0.0494	271.2	-2.3	0.0495	357.4	-5.4	0.0493	235.5	-2.5	0.0494	335.2	-4.8
0.0993	490.7	-2.2	0.0994	605.3	5.0	0.0990	444.6	-5.4	0.0991	570.3	5.1
0.1743	722.4	3.8	0.1746	822.4	-0.5	0.1739	698.3	15.1	0.1741	778.8	1.7
0.1873	755.6	8.8	0.1876	855.0	4.2	0.1869	713.4	0.5	0.1870	800.5	-2.9
0.2579	843.3	-13.4	0.2582	950.4	-14.1	0.2573	818.6	-9.3	0.2575	904.8	-6.4
0.3145	905.9	-0.9	0.3148	1028.6	10.7	0.3139	872.4	-5.8	0.3141	974.9	11.8
0.3859	940.1	-1.2	0.3863	1049.1	3.3	0.3852	909.3	-1.5	0.3855	988.5	-5.7
0.4316	960.0	7.7	0.4320	1042.9	-1.5	0.4309	927.4	6.2	0.4312	995.1	-2.9
0.4570	964.5	9.3	0.4574	1033.8	-4.6	0.4563	929.9	5.5	0.4565	996.6	1.0
0.4946	952.4	-2.9	0.4949	1024.2	0.0	0.4938	927.2	1.5	0.4941	986.0	-1.3
0.5272	946.5	-4.3	0.5276	1007.2	-0.6	0.5265	922.1	-1.1	0.5268	975.0	-1.2
0.5437	942.0	-4.8	0.5441	996.2	-2.1	0.5430	916.7	-3.6	0.5432	970.3	0.9
0.5852	927.7	-2.8	0.5855	976.4	4.4	0.5845	907.5	0.0	0.5847	955.3	6.4
0.6601	877.4	1.2	0.6604	916.7	2.5	0.6595	855.3	-3.8	0.6597	900.3	2.3
0.7212	810.5	5.5	0.7215	850.6	-0.3	0.7206	791.9	1.7	0.7208	829.9	-6.3
0.7897	690.6	-3.5	0.7900	739.6	-4.8	0.7892	675.8	-2.5	0.7894	722.8	-5.7
0.8159	646.4	4.2	0.8161	685.1	-3.7	0.8155	630.1	4.9	0.8156	674.4	2.1
0.8651	521.1	-6.8	0.8652	558.3	3.4	0.8647	508.2	-1.1	0.8648	544.7	5.7
0.9099	400.3	2.2	0.9100	408.8	12.3	0.9097	379.3	-0.4	0.9098	390.3	7.0
0.9491	257.6	3.2	0.9492	220.2	-11.7	0.9489	244.2	3.6	0.9490	213.9	-10.1
0.9823	96.6	-3.0	0.9823	79.4	-1.7	0.9823	83.8	-9.3	0.9823	76.3	-1.8

Table 1 (continued)

298.65 K 0.1 MPa			308.65 K 0.1 MPa			298.65 K 10 MPa			308.65 K 10 MPa		
<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>
$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_6\text{H}_{14}$											
0.0518	190.4	22.9	0.0521	409.3	8.2	0.0512	167.4	15.8	0.0515	277.4	26.3
0.0947	275.7	-12.6	0.0953	579.8	4.6	0.0937	263.2	-3.9	0.0941	401.9	-15.6
0.1469	403.7	-12.7	0.1478	680.9	-9.0	0.1454	377.8	-14.7	0.1461	556.8	-18.2
0.1852	497.2	-0.7	0.1863	726.6	-15.0	0.1835	472.2	-1.2	0.1843	668.1	5.5
0.2375	596.3	4.1	0.2378	804.8	10.8	0.2354	568.3	1.6	0.2364	754.6	4.5
0.2734	656.9	11.2	0.2748	827.2	2.8	0.2711	631.7	12.1	0.2722	806.4	-14.1
0.3266	706.4	-1.4	0.3282	870.1	8.1	0.3241	681.4	0.3	0.3253	829.0	-4.1
0.3712	747.8	3.4	0.3728	888.2	3.8	0.3686	719.6	2.0	0.3698	852.9	1.9
0.4114	766.1	0.6	0.4131	891.8	-3.2	0.4086	740.0	0.7	0.4099	852.1	-4.3
0.4456	769.2	-5.8	0.4472	888.8	-6.8	0.4427	745.9	-3.8	0.4440	854.2	0.1
0.4904	767.5	-8.7	0.4921	883.1	-0.9	0.4875	745.0	-7.9	0.4889	832.4	-9.6
0.5343	764.8	-0.8	0.5360	857.9	-1.5	0.5314	739.3	-5.6	0.5328	820.6	-0.2
0.5618	756.5	3.0	0.5635	824.9	-13.1	0.5589	737.2	2.8	0.5603	799.5	-3.4
0.6128	720.2	0.3	0.6144	798.1	10.2	0.6101	708.5	4.6	0.6114	769.4	9.6
0.6504	685.3	-1.0	0.6520	748.0	-4.4	0.6478	672.1	0.1	0.6490	729.4	9.7
0.6871	652.0	5.7	0.6886	704.5	9.0	0.6847	639.5	6.0	0.6858	668.0	-5.6
0.7251	608.5	11.2	0.7264	640.9	0.2	0.7228	592.8	7.4	0.7238	625.6	6.9
0.7606	539.3	-5.0	0.7618	576.4	-7.8	0.7585	528.3	-4.3	0.7595	547.7	-12.8
0.7969	480.5	-2.0	0.7980	520.8	0.9	0.7950	467.7	-3.0	0.7959	500.5	6.0
0.8335	402.5	-9.8	0.8344	447.6	0.5	0.8319	389.1	-10.9	0.8326	413.0	-8.4
0.8640	345.3	-2.3	0.8648	369.6	-9.2	0.8626	334.9	-0.4	0.8633	354.0	-1.2
0.9023	263.0	4.4	0.9029	287.0	4.3	0.9013	252.1	5.4	0.9018	269.0	3.3
0.9318	187.2	2.7	0.9322	200.1	-1.1	0.9311	181.9	7.6	0.9314	201.8	-10.0
0.9649	96.4	-0.3	0.9652	108.9	5.2	0.9646	83.5	-6.4	0.9647	94.1	-8.5
0.9806	59.6	5.8	0.9807	61.9	4.8	0.9803	52.2	2.3	0.9804	59.1	1.0
$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$											
0.0428	368.8	12.6	0.0430	461.0	1.5	0.0426	337.0	13.7	0.0427	450.8	6.4
0.0867	593.9	-6.7	0.0869	730.7	-2.5	0.0863	552.2	-6.6	0.0865	711.9	7.0
0.1538	833.6	-1.2	0.1541	945.2	-3.2	0.1532	768.6	-23.8	0.1535	913.6	-3.1
0.1656	864.2	-0.4	0.1659	982.2	7.1	0.1649	841.5	19.5	0.1652	925.0	-17.0
0.2302	978.2	-10.7	0.2307	1099.4	-2.8	0.2294	942.2	-1.3	0.2298	1053.0	-1.0
0.2831	1057.0	4.5	0.2836	1180.0	-3.6	0.2821	1006.7	2.8	0.2826	1139.4	16.2
0.3204	1075.4	6.8	0.3517	1248.4	9.6	0.3500	1055.8	10.3	0.3505	1192.4	9.3
0.3510	1108.8	15.1	0.3959	1240.7	0.4	0.3941	1053.8	-0.9	0.3947	1199.8	-0.4
0.3953	1090.8	-7.6	0.4209	1213.8	-17.3	0.4189	1051.6	-2.9	0.4196	1187.7	-13.7
0.4201	1097.2	3.1	0.4580	1225.4	17.2	0.4560	1037.9	-9.4	0.4567	1195.5	3.3
0.4571	1069.5	-10.0	0.4906	1180.6	-1.9	0.4886	1035.6	1.0	0.4893	1171.8	-2.4
0.4898	1048.6	-11.0	0.5070	1158.9	-9.7	0.5051	1018.6	-7.5	0.5057	1154.8	-7.2
0.5483	1014.9	3.0	0.5490	1139.5	8.1	0.5472	1004.7	6.2	0.5478	1122.2	-1.3
0.6257	946.6	11.7	0.6263	1049.9	-4.8	0.6246	935.6	6.8	0.6251	1040.6	4.9
0.6901	862.5	-1.9	0.6906	972.3	1.6	0.6890	856.6	0.5	0.6896	966.3	12.0
0.7637	782.8	12.0	0.7642	849.3	6.2	0.7629	759.7	3.1	0.7633	844.2	-1.1
0.7923	708.6	-17.5	0.7928	777.3	-7.9	0.7915	701.8	-9.8	0.7919	788.0	-4.4
0.8466	615.3	-2.1	0.8469	661.2	1.9	0.8460	607.7	-0.9	0.8463	647.7	-14.2
0.8968	480.6	4.9	0.8971	504.9	1.1	0.8964	484.7	5.0	0.8966	502.7	9.3
0.9413	306.1	1.6	0.9415	308.1	-1.5	0.9411	321.0	1.6	0.9412	306.9	6.8
0.9795	117.1	0.1	0.9796	104.6	0.8	0.9794	125.5	-3.9	0.9795	101.8	-5.6

Table 1 (continued)

298.65 K 0.1 MPa			308.65 K 0.1 MPa			298.65 K 10 MPa			308.65 K 10 MPa		
<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>	<i>x</i>	H_m^E	<i>D</i>
$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{16}\text{H}_{34}$											
0.0544	641.7	7.8	0.0506	646.5	9.8	0.0543	575.4	5.7	0.0504	395.8	-5.4
0.0716	741.4	-2.2	0.0718	817.6	18.1	0.0714	687.2	11.3	0.0715	562.3	-2.4
0.1088	903.3	4.6	0.1090	976.4	-17.8	0.1085	823.8	-14.8	0.1086	817.7	-4.1
0.1895	1046.4	-18.3	0.1475	1107.8	-11.9	0.1890	1037.6	-0.9	0.1470	1048.0	13.2
0.2033	1083.1	-2.5	0.1898	1220.4	9.0	0.2028	1053.7	-10.2	0.1892	1202.3	-0.6
0.2778	1206.0	14.0	0.2036	1222.4	-13.5	0.2772	1198.2	17.8	0.2030	1250.0	6.0
0.3368	1260.0	-0.4	0.2782	1353.4	10.4	0.3361	1250.7	7.8	0.2774	1362.3	-9.8
0.3581	1286.0	8.2	0.3373	1414.9	7.7	0.3573	1257.5	0.8	0.3364	1391.3	-9.1
0.4103	1309.1	10.6	0.3585	1439.4	14.7	0.4095	1256.3	-12.1	0.3576	1397.6	-4.9
0.4568	1272.8	-15.5	0.4108	1448.2	-3.4	0.4559	1246.4	-6.6	0.4098	1406.7	7.0
0.4825	1262.7	-9.4	0.4572	1436.7	-16.8	0.4816	1232.1	-3.5	0.4562	1404.5	11.8
0.5201	1233.5	-4.2	0.4830	1435.7	-9.8	0.5193	1193.2	-8.6	0.4820	1393.3	5.8
0.5688	1181.3	0.2	0.5206	1419.4	-3.5	0.5680	1164.7	15.0	0.5196	1374.3	-2.8
0.6096	1135.5	5.3	0.5693	1383.2	5.7	0.6088	1111.3	7.2	0.5683	1358.9	4.2
0.6423	1096.2	5.6	0.6101	1334.3	5.2	0.6415	1072.1	3.8	0.6091	1305.8	-18.0
0.7194	1009.7	6.6	0.6427	1286.3	0.6	0.7187	975.2	-7.2	0.6418	1286.1	-2.4
0.7796	922.3	-1.1	0.6830	1227.8	0.3	0.7790	882.3	-9.9	0.6821	1231.1	0.6
0.8061	872.4	-3.3	0.7197	1176.5	6.8	0.8056	837.8	1.2	0.7189	1166.1	2.8
0.8549	741.9	-9.1	0.7416	1140.7	8.6	0.8545	701.5	5.8	0.7408	1125.2	8.2
0.8976	589.8	1.0	0.7799	1056.0	-1.7	0.8973	528.1	4.6	0.7792	1028.0	2.5
0.9538	298.5	7.3	0.8064	990.9	-5.9	0.9536	233.7	-3.9	0.8304	873.8	-10.0
0.9840	106.7	4.6	0.8310	922.2	-8.2	0.9839	74.5	-2.8	0.8763	734.8	1.5
			0.8767	766.8	-5.9				0.8974	664.4	11.7
			0.8978	677.2	-3.3				0.9178	557.2	-7.1
			0.9181	582.3	4.4				0.9537	365.9	-5.0
			0.9539	368.2	8.9				0.9682	273.9	0.8
			0.9683	260.1	3.4				0.9840	151.2	2.2
			0.9840	139.0	4.1						

About six coefficients are necessary to give a good description of H_m^E , such as shown in Figs. 1–5. The RK-fitting parameters A_j together with the standard deviations S are listed in Table 2

$$S/(\text{J mol}^{-1}) = \left[\sum_{i=1}^n (H_{i,\text{exp}}^E - H_{i,\text{fit}}^E)^2 / (n - k + 1) \right]^{1/2} \quad (2)$$

where n is the number of experimental points.

4. Conclusions

Several conclusions can be drawn from the above experimental H_m^E data and the H_m^E vs. x fitting curves for cycloalkanol–alkane mixtures.

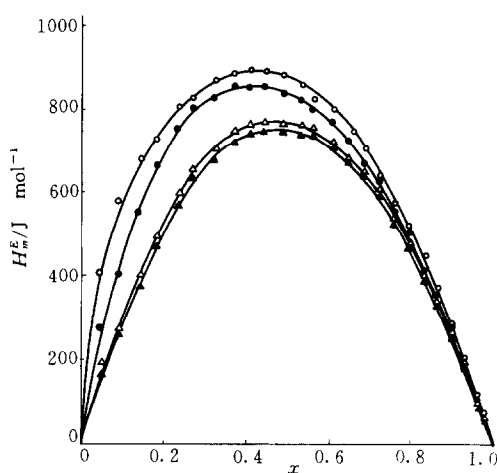


Fig. 1. Excess molar enthalpies ($H_{m,\text{exp}}^E$) of $x\text{C}_5\text{H}_9\text{OH} + (1-x)\text{C}_6\text{H}_{14}$ and R-K equation fitting curves: \triangle , 298.65 K, 0.1 MPa; \blacktriangle , 298.65 K, 10.0 MPa; \circ , 308.65 K, 0.1 MPa; \bullet , 308.65 K, 10.0 MPa.

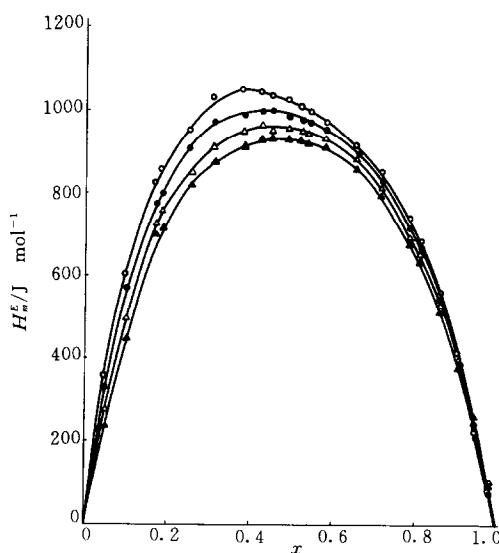


Fig. 2. Excess molar enthalpies ($H_{m,\text{exp}}^E$) of $x\text{C}_5\text{H}_9\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$ and R-K equation fitting curves. See Fig. 1 for key.

(1) The excess molar enthalpies in all cases are positive over the whole mole fraction range. When an alkanol is mixed with an alkane, the excess enthalpy is in general determined by a positive contribution from the rupture of hydrogen bonds [9].

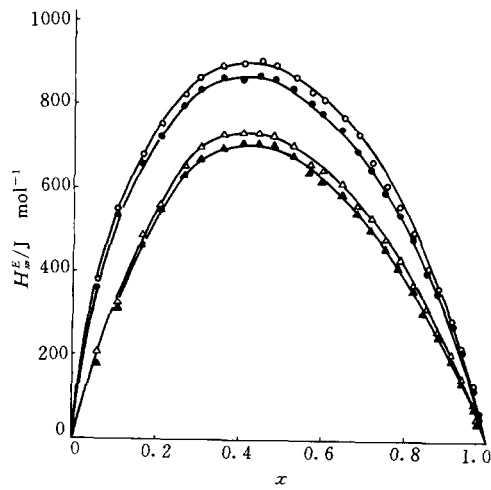


Fig. 3. Excess molar enthalpies ($H_{m,\text{exp}}^E$) of $x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_6\text{H}_{14}$ and R-K equation fitting curves. See Fig. 1 for key.

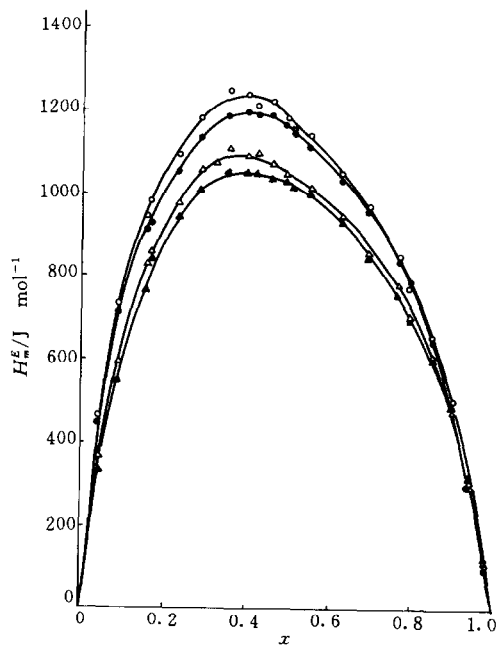


Fig. 4. Excess molar enthalpies ($H_{m,\text{exp}}^E$) of $x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$ and R-K equation fitting curves. See Fig. 1 for key.

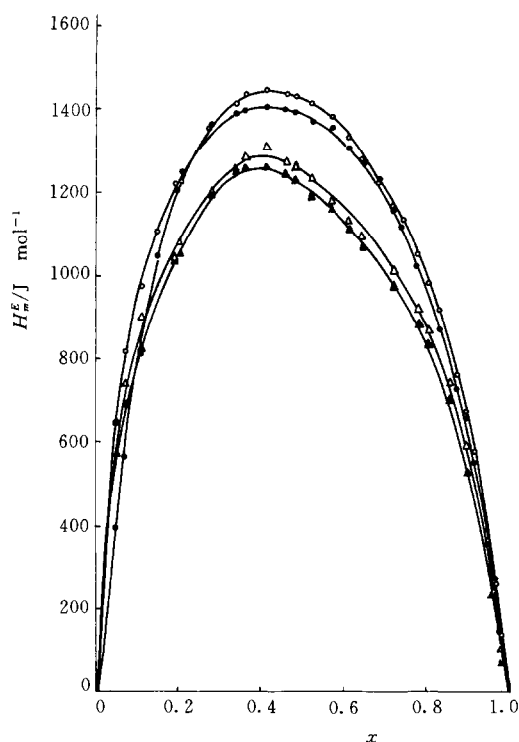


Fig. 5. Excess molar enthalpies ($H_{m,\text{exp}}^E$) of $x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{16}\text{H}_{34}$ and R-K equation fitting curves. See Fig. 1 for key.

(2) The excess molar enthalpies increase with an increase in the chain length of the *n*-alkane molecules, and increase with an increase in the ring size of the cycloalkanol molecules. The H_m^E values increase in the sequence: cyclopentanol + *n*-hexane < cyclohexanol + *n*-hexane < cyclopentanol + *n*-dodecane < cyclohexanol + *n*-dodecane < cyclohexanol + *n*-hexadecane.

The dependence of H_m^E on the size and shape of the component molecules can be explained by the existence of some kind of molecular order arrangement. The longer the chain-like molecule, the more pronounced the CMO (correlation of molecular order) [10]. Upon mixing the compact molecules (cycloalkanol), the CMO in *n*-alkane is destroyed, and the associated energy leads to an endothermic contribution to H_m^E , which increases with increasing CMO.

(3) Figs. 1–5 show the marked effect of temperature on H_m^E . The H_m^E apparently increases with increasing temperature in all cases. With increasing temperature and increased molecular thermal motion, the number of disrupted H-bonds greatly increases, making a positive contribution to H_m^E .

(4) Excess molar enthalpies decrease significantly with an increase in pressure for all the investigated systems, and Figs. 1–5 also show that the H_m^E maxima skew slightly to alkane-rich regions with increasing pressure.

Table 2
Values of parameters of the Redlich–Kister equation and the standard deviation S ($k = 0.5$)

T/K	P/MPa	$A_0/\text{J mol}^{-1}$	$A_1/\text{J mol}^{-1}$	$A_2/\text{J mol}^{-1}$	$A_3/\text{J mol}^{-1}$	$A_4/\text{J mol}^{-1}$	$A_5/\text{J mol}^{-1}$	$A_6/\text{J mol}^{-1}$	$A_7/\text{J mol}^{-1}$	$A_8/\text{J mol}^{-1}$	$S_{\text{Fit}}/\text{J mol}^{-1}$
298.65	0.1	2867.1	-948.5	495.7	$x\text{C}_3\text{H}_9\text{OH} + (1-x)\text{C}_6\text{H}_{14}$ 569.8	-406.7	30.6				7.3
308.65	0.1	3549.1	-810.1	532.5	-585.0	1941.6	-581.7				8.9
298.65	10.0	2754.9	-919.9	556.7	348.9	-696.9	461.3				4.7
308.65	10.0	3428.2	-854.8	512.8	-331.8	1888.7	-788.4				7.8
298.65	0.1	3819.4	-181.7	1787.9	$x\text{C}_3\text{H}_9\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$ -1504.4	428.1	1673.8				6.7
308.65	0.1	4087.5	-936.5	2414.2	1414.0	319.8	-2767.2				7.5
298.65	10.0	3702.1	-83.2	2011.5	-1762.9	-465.4	2214.1				6.7
308.65	10.0	3942.4	-615.3	2305.6	752.2	177.6	-2192.6				6.5
298.65	0.1	3099.4	-336.1	135.5	$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_6\text{H}_{14}$ 348.6	-95.8	-370.2				9.0
308.65	0.1	3522.2	-937.6	153.6	279.1	3086.9	-3205.1				8.3
298.65	10.0	3006.9	-261.0	180.3	157.7	-392.0	-176.8				8.0
308.65	10.0	3350.2	-861.4	956.3	-732.3	72.4	403.8				11.5
298.65	0.1	4209.3	-1483.6	1956.7	$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{12}\text{H}_{26}$ 1677.7	1894.5	-2270.0				10.5
308.65	0.1	4698.4	-1701.5	3866.5	1920.1	-10713.3	-2515.2	26277.6	-2095.9	-15226.0	9.9
298.65	10.0	4115.4	-1064.4	1627.8	125.0	2137.7	-116.0				11.0
308.65	10.0	4665.8	-1513.2	1274.6	2833.6	3444.6	-5487.6				10.5
298.65	0.1	5030.0	-1822.7	1066.5	$x\text{C}_6\text{H}_{11}\text{OH} + (1-x)\text{C}_{16}\text{H}_{34}$ 5598.1	5688.5	-9240.8				9.8
308.65	0.1	5747.0	-1175.1	1396.6	1900.5	5833.3	-4937.4				10.7
298.65	10.0	4880.5	-1799.6	1961.9	5018.7	2906.0	-8475.0				10.5
308.65	10.0	5532.3	-540.8	4044.1	-4678.0	-722.3	6522.2				8.5

To explain the dependence of H_m^E on pressure, three points can be considered: the filling gap effect, the shift in thermodynamic equilibrium, and the CMO effect.

References

- [1] D.E.G. Jones, I.A. Weeks, S.C. Anand, R.W. Wetmore and G.C. Benson, *J. Chem. Eng. Data*, 17 (1972) 501.
- [2] G.C. Benson, C.A. Subhash and O. Kiyohara, *J. Chem. Eng. Data*, 19 (1974) 258.
- [3] S.E.M. Haman, M.K. Kumaran and G.C. Benson, *J. Chem. Thermodyn.*, 16 (1984) 1013.
- [4] H. Kaur, J.R. Khurma and B.S. Mahl, *Fluid Phase Equilibria*, 45 (1989) 121.
- [5] K.R. Hall, *Selected Values of Properties of Chemical Compounds*, Vol. 1, Thermodynamic Research Center, Texas, A & M, University, 1981.
- [6] K.R. Hall and L.B. Beach, *Selected values of Props. of Hydrocarbons and Related Compd.*, Vol. 2, Thermodynamic Research Center, Texas, A & M, University, 1982.
- [7] Yan Jiang, Yun Liu, Xianda Sun and Zhiwu Yu, *Thermochim. Acta*, 183 (1991) 99.
- [8] J.B. Ott, C.E. Stouffer, G.V. Corentt, B.F. Woodfield, R.C. Wirthlin and J.J. Christensen, *J. Chem. Thermodyn.*, 18 (1986) 867; 19 (1987) 337.
- [9] H. Renon and J.M. Prausnitz, *Chem. Eng. Sci.*, 22 (1967) 229.
- [10] H. Wagner and R.N. Lichtenthaler, *Thermochim. Acta*, 67 (1985) 94.