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Excess molar enthalpies of *n*-octanol–*n*-alkane and isopentanol–*n*-dodecane mixtures under high pressure [α]

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Abstract

New high pressure flow calorimetric vessels were designed and made. They were fitted into the Setaram C-80 Calvet microcalorimeter. With the vessels, heats of mixing can be measured from ambient temperature and pressure to 573 K and 20 MPa. The excess molar enthalpies of ethanol–water mixtures at 298.65 K and 0.1, 5 and 10 MPa are in good agreement with those in the literature. Excess molar enthalpies of *n*-octanol–*n*-hexane, *n*-octanol–*n*-decane, *n*-octanol–*n*-dodecane and isopentanol–*n*-dodecane mixtures were determined at 298.65 K and 0.1 and 10 MPa. They are positive over the entire mole fraction range for the four binary systems.

INTRODUCTION

Thermodynamic properties under high pressure are very important in the chemical industry, for example, in supercritical extraction and liquefication of coal. Recently, Lentz [1], Heintz [2,3], Christensen et al. [4], Siddiqi and Lucas [5] and Oswald et al. [6] studied the excess enthalpies at high pressure and developed various types of apparatus.

Alkanols can be used as solvent for various kinds of substances owing to their characteristic molecular structure, which consists of a polar hydroxyl group and a non-polar alkyl group. In order to understand the relationship between the thermodynamic properties of such mixtures and the molecular structures of their components under high pressure, investigations on the excess enthalpies of mixtures of alkanols with *n*-alkanes under various pressures are useful.

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EXPERIMENTAL

Materials

Analytical reagents, *n*-hexane, *n*-decane and *n*-dodecane (Beijing Chemical Co.), were purified carefully by fractional distillation using a 1.5 m long column packed with fine copper rings, and *n*-octanol, isopentanol, and ethanol (Beijing Chemical Co., purities in excess of 99%) were used directly. All the reagents were stored over 4 Å molecular sieves. The Karl Fischer method gave the water content of the alcohols as 0.1% or less. The densities and refractive indices of the reagents agreed well with those reported in the literature [7].

Apparatus

New high pressure flow calorimetric vessels were designed and made. They were fitted into the Setaram C-80 Calvet type calorimeter. The vessels are shown in Fig. 1.

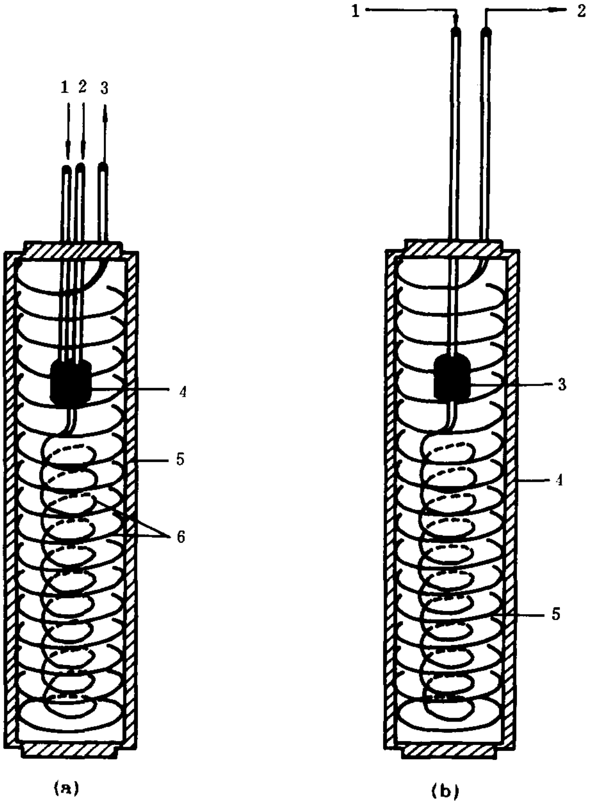

Fig. 1. High pressure flow calorimetric vessel. (a) Measuring vessel: 1, component 1; 2, component 2; 3, mixture; 4, mixing cell; 5, brass cylinder; 6, stainless steel mixing tube. (b) Reference vessel: 1, 2, mixture; 3, valve; 4, brass cylinder; 5, stainless steel tube.

TABLE 1

The parameters and standard deviations for $C_2H_5OH-H_2O$ mixtures at 298.65 K and pressures of 0.1, 5 and 10 MPa

P (MPa)	k	a_0	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9	a_{10}	s (J mol^{-1})
0.1	0.58	−1658.9	−1121.8	−1530.1	2311.4	−4040.4	−12761.3	16609.6	24541.5	−37319.2	−15478.3	26849.8	1.52
5	0.55	−1685.2	−1185.7	−2569.0	2875.2	3529.3	−12910.0	−7015.1	14769.5				2.02
10	0.39	−1739.4	−1308.7	−2589.8	101.1	4486.1	−6315.3	−18029.5	19051.8				2.01

The proper working of the apparatus was checked by using the mixtures x ethanol plus $(1-x)$ water at 298.65 K and under pressures of 0.1, 5 and 10 MPa. The results were fitted to eqns. (1) and (2):

$$H_{\mathrm{m}}^{\mathrm{E}}(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{j=0}^{n} a_j(1-2x)^j / \left[1-k(1-2x)^j\right] \qquad (1)$$

$$s = \left[\sum_{j=1}^{m}\left(H_{\mathrm{m,exp}}^{\mathrm{E}} - H_{\mathrm{m,calc}}^{\mathrm{E}}\right)^2 / (m-n+1)\right]^{1/2} \qquad (2)$$

The parameters k, a_j ($j = 0, 1, 2, \ldots, n$) and the standard deviations s are given in Table 1. The results are in agreement with data cited in the literature [8].

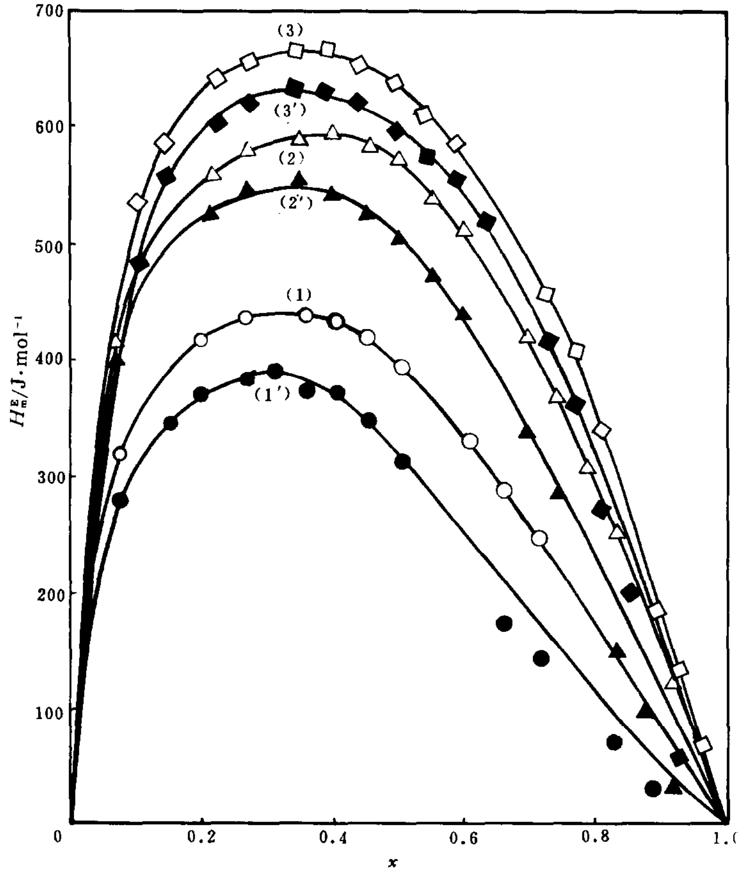

Fig. 2. Excess molar enthalpies of x n-$C_8H_{17}OH$ plus $(1-x)$ n-C_kH_{2k+2} at 298.65 K: ——, calculated from eqn. (3); curves 1 (1′), $k = 6$; curves 2 (2′), $k = 10$; curves 3 (3′), $k = 12$; ●, ▲, ◆, 0.1 MPa; ○, △, ◇, 10 MPa.

RESULTS AND DISCUSSION

The excess enthalpies were measured for the binary mixtures *n*-octanol–*n*-hexane, *n*-octanol–*n*-decane, *n*-octanol–*n*-dodecane and isopentanol–*n*-dodecane at 298.65 K and 0.1 and 10 MPa. The experimental results are summarized in Table 2. They were fitted to the Redlich–Kister equation:

$$H_m^E(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{5} a_i(2x-1)^i \tag{3}$$

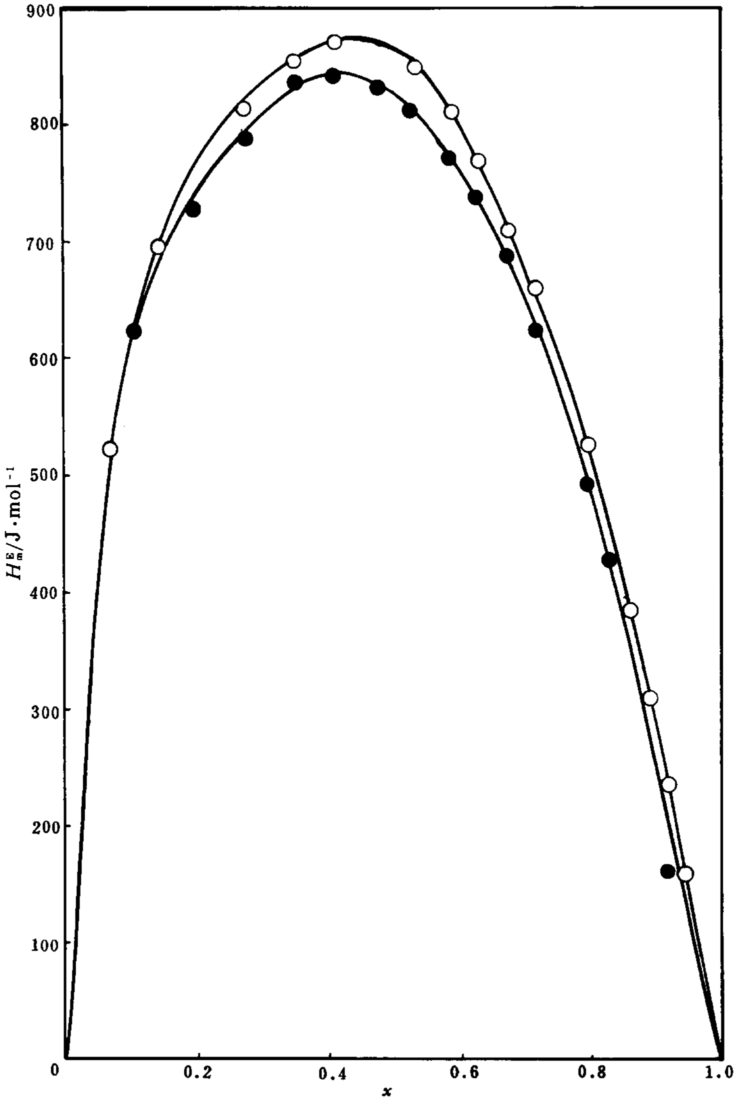

Fig. 3. Excess molar enthalpies of x i-$C_5H_{11}OH$ plus $(1-x)$ n-$C_{12}H_{26}$ at 298.65 K: ——— calculated from eqn. (3); ●, 0.1 MPa; ○, 10 MPa.

TABLE 2

Experimental excess molar enthalpies for alkanol–*n*-alkane mixtures at 298.65 K and 0.1 and 10 MPa

x	H_m^E (J mol^{-1})	H_m^E (calc) (J mol^{-1})	ΔH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	H_m^E (calc) (J mol^{-1})	ΔH_m^E (J mol^{-1})
x n-$C_8H_{17}OH + (1-x)$ n-C_6H_{14} at 0.1 MPa							
0.0759	319.4	318.3	1.1	0.5034	393.8	396.4	−2.6
0.1989	416.8	420.4	−3.6	0.6069	330.9	327.6	3.3
0.2672	437.0	433.3	3.7	0.6601	287.7	288.1	−0.4
0.3610	439.5	439.5	0.0	0.7135	247.2	247.9	−0.7
0.4047	434.5	434.3	0.2	0.8245	155.1	156.0	−0.9
0.4535	419.5	420.0	−0.5	0.8819	98.8	98.0	0.8
x n-$C_8H_{17}OH + (1-x)$ n-C_6H_{14} at 10 MPa							
0.0760	279.9	278.0	1.9	0.4535	349.3	346.8	2.5
0.1542	344.9	351.2	−6.3	0.5032	313.2	310.6	2.6
0.1989	371.6	366.9	4.7	0.6600	172.8	177.2	−4.4
0.2673	384.3	382.5	1.7	0.7132	142.5	139.8	2.7
0.3091	391.0	387.4	3.6	0.8247	70.5	70.0	0.5
0.3608	374.9	384.6	−9.7	0.8820	29.1	29.7	−0.6
0.4047	373.0	372.1	0.9				
x n-$C_8H_{17}OH + (1-x)$ n-$C_{10}H_{22}$ at 0.1 MPa							
0.0672	413.7	411.7	2.0	0.5528	541.7	545.7	−4.0
0.2135	557.3	564.0	−6.7	0.6015	513.8	509.1	4.7
0.2700	579.1	573.8	5.3	0.6968	420.9	418.4	2.5
0.3519	592.1	589.5	2.6	0.7429	368.9	367.6	1.3
0.3998	596.3	594.2	2.1	0.7877	309.0	313.4	−4.4
0.4568	583.2	588.9	−5.7	0.8318	253.3	253.9	−0.6
0.5030	573.7	573.5	0.2	0.9175	121.1	119.2	1.9
x n-$C_8H_{17}OH + (1-x)$ n-$C_{10}H_{22}$ at 10 MPa							
0.0672	400.6	397.6	3.0	0.5527	471.8	474.5	−2.7
0.2135	523.5	532.9	−9.4	0.6015	439.5	433.8	5.7
0.2698	544.2	538.6	5.6	0.6968	339.5	337.7	1.8
0.3510	555.1	545.8	9.3	0.7429	286.3	283.4	2.9
0.3999	541.1	543.8	−2.7	0.8317	149.4	159.6	−10.2
0.4568	525.5	529.9	−4.4	0.8750	95.4	91.6	3.8
0.5029	504.3	508.0	−3.7	0.9175	31.8	29.0	2.8
x n-$C_8H_{17}OH + (1-x)$ n-$C_{12}H_{26}$ at 0.1 MPa							
0.1046	534.9	528.9	6.0	0.5415	612.4	617.5	−5.1
0.1451	585.3	592.7	−7.4	0.5905	588.2	584.9	3.3
0.2222	641.9	642.3	−0.4	0.7282	459.7	454.9	4.8
0.2715	656.7	655.2	1.5	0.7713	399.5	401.7	−2.2
0.3421	666.3	664.5	1.8	0.8122	342.4	344.0	−1.6
0.3879	667.9	665.0	2.9	0.8908	208.4	210.0	−1.6
0.4375	655.7	658.7	−3.0	0.9285	135.5	136.3	−0.8
0.4952	640.7	640.7	0.0	0.9648	68.7	64.1	4.6

TABLE 2 (continued)

x	H^{E}_{m} (J mol^{-1})	H^{E}_{m} (calc) (J mol^{-1})	ΔH^{E}_{m} (J mol^{-1})	x	H^{E}_{m} (J mol^{-1})	H^{E}_{m} (calc) (J mol^{-1})	ΔH^{E}_{m} (J mol^{-1})
x n-$C_8H_{17}OH + (1-x)$ n-$C_{12}H_{26}$ at 10 MPa							
0.1046	485.2	486.5	−1.3	0.5417	575.5	582.0	−6.5
0.1450	557.7	553.0	4.7	0.5906	556.6	553.3	3.3
0.2222	604.5	609.9	−5.4	0.6377	520.5	517.4	3.1
0.2714	621.7	623.9	−2.2	0.7285	417.3	418.4	−1.1
0.3419	634.0	630.4	3.6	0.7713	363.4	354.4	9.0
0.3877	633.0	628.1	4.9	0.8123	273.7	281.9	−8.2
0.4374	621.7	620.0	1.7	0.8523	199.7	202.6	−2.9
0.4953	597.0	602.6	−5.6	0.9285	56.4	52.4	4.0
x i-$C_5H_{11}OH + (1-x)$ n-$C_{12}H_{26}$ at 0.1 MPa							
0.0706	523.7	518.8	4.9	0.6760	709.7	712.6	−2.9
0.1446	696.9	703.4	−6.5	0.7181	660.5	654.2	6.3
0.2762	813.4	810.0	3.3	0.7950	525.5	527.7	−2.2
0.3502	854.8	852.3	2.5	0.8622	387.1	388.3	−1.2
0.4114	872.2	874.3	−2.1	0.8930	308.5	312.6	−4.1
0.5293	850.6	854.3	−3.7	0.9219	235.7	234.6	1.1
0.5868	812.6	811.9	0.7	0.9494	159.4	154.6	4.8
0.6308	769.3	767.3	2.0				
x i-$C_5H_{11}OH + (1-x)$ n-$C_{12}H_{26}$ at 10 MPa							
0.1084	625.6	623.0	2.6	0.5867	771.1	770.0	1.1
0.1970	726.2	732.6	−6.4	0.6308	735.5	730.5	5.0
0.2762	792.3	788.7	3.6	0.6760	686.0	683.0	3.0
0.3501	836.6	829.7	6.9	0.7182	624.3	630.1	−5.8
0.4114	839.3	845.1	−5.8	0.7950	492.8	499.6	−6.8
0.4782	831.9	835.8	−3.9	0.8299	428.3	420.3	8.0
0.5293	811.4	811.3	0.1	0.9219	157.4	158.8	−1.4

TABLE 3

Values of parameters of the Redlich–Kister equation and the standard deviations s

P (MPa)	a_0	a_1	a_2	a_3	a_4	a_5	s (J mol^{-1})
n-$C_8H_{17}OH$ + n-C_6H_{14}							
0.1	1593.21	−1087.17	85.80	615.81	1911.38	−3065.73	2.1
10	1252.77	−1602.45	−117.86	1771.58	1586.86	−3861.34	4.2
n-$C_8H_{17}OH$ + n-$C_{10}H_{22}$							
0.1	2299.28	−860.87	−80.66	−198.83	3195.57	−3416.27	3.8
10	2038.53	−1124.55	−66.51	−8.03	2255.48	−4341.01	5.8
n-$C_8H_{17}OH$ + n-$C_{12}H_{26}$							
0.1	2554.70	−870.95	725.50	−642.53	2274.10	−2400.25	3.7
10	2403.10	−781.03	1023.69	−1169.90	415.64	−2562.54	4.9
i-$C_5H_{11}OH$ + n-$C_{12}H_{26}$							
0.1	3471.68	−735.44	96.08	−250.30	3744.37	−3295.45	3.8
10	3308.05	−924.21	685.28	1177.16	2086.35	−6021.57	5.1

The least-squares parameters and the standard deviations are listed in Table 3. The observed values and the smoothed ones (shown as curves) are presented in Figs. 2 and 3.

CONCLUSIONS

Several conclusions can be drawn, as follows:

(1) The excess molar enthalpies for *n*-octanol–*n*-alkane and for isopentanol–*n*-dodecane mixtures are positive over the entire mole fraction range, under both ambient and high pressures. This is because the excess enthalpies of the *n*-alkanol–*n*-alkane systems are determined in general by a positive contribution from the rupture of the hydrogen bonds when the alkanol is mixed with *n*-alkane.

(2) The excess molar enthalpies increase with increase in chain length of the *n*-alkane molecules. The H_m^E values increase in the sequence of *n*-octanol–*n*-hexane < *n*-octanol–*n*-decane < *n*-octanol–*n*-dodecane.

(3) Excess molar enthalpies decrease with an increase in pressure for all the systems studied.

(4) Figure 2 also shows that H_m^E maxima for *n*-octanol–*n*-alkane systems skew slightly to the *n*-alkane-rich region with an increase in pressure.

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