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Excess molar enthalpies of *n*-alkanol + *n*-hexane mixtures under high pressure [☆]

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Abstract

Experimentally determined values of the excess molar enthalpy H_m^E are reported for binary mixtures of *n*-decanol, *n*-octanol, *n*-hexanol and *n*-butanol with *n*-hexane, at varying compositions at 298.65 K and 308.65 K and pressures up to 10 MPa. The dependence of H_m^E on the composition, temperature, pressure and the size of the alkanol molecule is discussed. The H_m^E values are positive over the entire mole fraction range, and increase with increasing temperature, but decrease with increasing pressure and increasing chain length of the *n*-alkanol.

Keywords: Alkanol; Binary system; Excess molar enthalpy; Hexane; High pressure

1. Introduction

The thermodynamic properties of substances of various temperatures and pressures, especially under high pressure, are important in the chemical industry, e.g. in the supercritical fluid extraction and liquefaction of coal. Good experimental data obtained under high pressures are necessary for proper process design. From the theoretical point of view, the thermodynamic behavior of alkanol–alkane mixtures under high pressure is of particular interest, as it depends sensitively on the hydrogen-bonding association, the intermolecular interactions (especially the repul-

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sive forces), and the liquid structure. Therefore, reliable experimental data for excess properties under high pressures provide an important test of theoretical models.

In the present study, excess molar enthalpies H_m^E were determined for binary mixtures of *n*-decanol, *n*-octanol, *n*-hexanol and *n*-butanol with *n*-hexane, of various compositions, and under various temperatures and pressures.

2. Experimental

2.1. Materials

n-Decanol, *n*-octanol, *n*-hexanol, *n*-butanol and *n*-hexane (Beijing Chemical Co.) were purified by fractional distillation using a 1.5 m column packed with fine copper rings. All reagents were stored over 4 Å molecular sieves. The measured densities and refractive indices of the reagents agreed well with those reported in the literature [1,2].

2.2. Apparatus

New high-pressure flow calorimetric vessels were designed, made and fitted into the Setaram C80 Calvet calorimeter [3]. The apparatus was checked by measuring the excess molar enthalpy of ethanol–water mixtures at 298.65 K and 0.4 MPa and 10.0 MPa. The results obtained are in agreement with values reported in the literature [4].

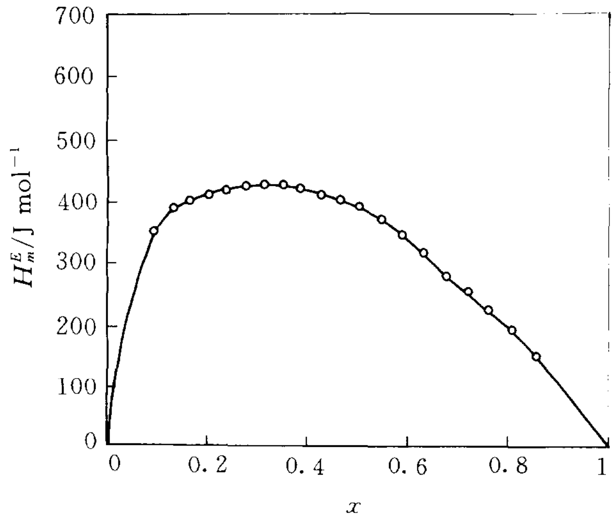

Fig. 1. Excess molar enthalpies of $xn\text{-}C_{10}H_{21}OH + (1-x)n\text{-}C_6H_{14}$: ○, experimental points at 298.65 K, 0.1 MPa; ——, RK equation fitting curve.

Table 1
$H^{E}_{m,exp}$ and $D(H^{E}_{m,exp} - H^{E}_{m,fit})$ for xn-$C_{10}H_{21}OH + (1-x)n$-C_6H_{14} mixtures at 298.65 K and 0.1 MPa

x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})
0.1005	348.5	0.8	0.3575	424.1	0.5	0.6380	311.5	1.6
0.1373	386.3	2.0	0.3933	420.8	−0.1	0.6810	275.1	−5.8
0.1717	397.9	−3.8	0.4340	409.2	−4.3	0.7246	249.3	−1.9
0.2087	408.1	−3.5	0.4724	399.4	−2.4	0.7684	220.7	0.0
0.2453	421.0	3.8	0.5139	385.3	1.1	0.8131	193.6	5.9
0.2814	423.2	2.3	0.5545	366.0	3.3	0.8565	146.9	−3.1
0.3199	423.9	0.5	0.5957	340.7	3.1			

Table 2
H^{E}_{m} and $D(H^{E}_{m,exp} - H^{E}_{m,fit})$ for xn-$C_8H_{17}OH + (1-x)n$-C_6H_{14} mixtures under various temperature and pressure conditions

x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{E}_{m,exp}$/ (J mol^{-1})	D/ (J mol^{-1})
298.65 K, 0.1 MPa								
0.0949	355.1	3.9	0.3967	438.1	−0.3	0.7045	275.0	6.0
0.1495	397.8	−6.5	0.4485	427.6	0.1	0.7483	230.5	−2.4
0.2033	425.0	1.2	0.5034	407.1	1.1	0.8007	185.5	−0.6
0.2485	435.2	3.1	0.5522	378.5	−0.8	0.8479	135.7	−3.6
0.2994	437.5	−0.8	0.5696	346.9	−3.6	0.8963	90.3	3.1
0.3508	440.9	−0.1	0.6518	311.1	1.0			
298.65 K, 10.0 MPa								
0.0949	305.0	4.8	0.4025	389.6	−1.1	0.7054	241.3	2.2
0.1531	352.7	−5.6	0.4475	380.4	0.2	0.7496	205.6	−1.4
0.1956	375.1	−2.8	0.4951	360.5	−2.8	0.8006	164.7	−1.9
0.2556	394.9	3.3	0.5397	340.0	−2.6	0.8513	120.4	−2.2
0.3027	399.0	2.8	0.5983	311.8	2.0	0.9027	77.5	2.9
0.3468	397.2	0.7	0.6522	278.1	2.5			
308.65 K, 0.1 MPa								
0.0712	315.3	−8.6	0.3487	487.3	1.2	0.6521	340.7	3.3
0.0951	392.7	15.0	0.4023	475.1	−2.8	0.6984	295.4	−7.4
0.1514	431.8	−11.0	0.4501	462.5	0.0	0.7533	255.5	−3.2
0.1957	469.0	3.4	0.4963	438.0	−2.7	0.8019	219.1	5.1
0.2556	480.2	−0.6	0.5544	405.2	−0.6	0.8483	164.9	1.0
0.3071	489.5	3.1	0.6078	375.3	6.0	0.8907	110.0	−1.9
308.65 K, 10.0 MPa								
0.0674	319.5	3.2	0.3522	468.2	−2.9	0.6507	330.1	10.7
0.0951	375.6	3.1	0.3910	465.7	−2.1	0.6933	281.0	−6.9
0.1517	417.9	−9.6	0.4509	449.7	−1.0	0.7534	240.7	−2.1
0.2007	444.1	−3.0	0.4986	425.8	−1.2	0.8009	200.4	−2.8
0.2513	469.0	9.7	0.5517	390.3	−2.3	0.8493	161.0	5.5
0.3071	471.5	3.0	0.5913	365.5	1.7	0.8906	106.3	−1.8

Table 3

H^E_m and $D(H^E_{m,exp} - H^E_{m,fit})$ for $xn\text{-}C_6H_{13}OH + (1-x)n\text{-}C_6H_{14}$ mixtures under various temperature and pressure conditions

x	$H^E_{m,exp}/$ (J mol^{-1})	$D/$ (J mol^{-1})	x	$H^E_{m,exp}/$ (J mol^{-1})	$D/$ (J mol^{-1})	x	$H^E_{m,exp}/$ (J mol^{-1})	$D/$ (J mol^{-1})
298.65 K, 0.1 MPa								
0.0697	320.4	−2.5	0.3517	507.8	2.8	0.6487	349.2	2.1
0.0993	394.9	8.1	0.3989	499.9	−1.6	0.6915	303.3	−4.1
0.1497	440.5	−5.8	0.4533	484.9	−1.6	0.7513	255.1	3.8
0.2036	472.1	−4.1	0.4991	460.5	−3.9	0.7984	204.0	−2.1
0.2493	492.5	2.0	0.5514	428.8	−0.8	0.8484	153.1	−3.0
0.2998	504.5	3.8	0.6037	392.0	4.8	0.9033	100.3	2.8
298.65 K, 10.0 MPa								
0.0785	295.1	−2.5	0.3516	467.0	3.7	0.6507	300.6	2.5
0.1034	355.6	8.4	0.4011	450.5	−3.0	0.6901	259.6	−4.4
0.1496	400.2	−6.6	0.4533	430.1	−4.6	0.7509	215.3	4.4
0.2036	440.5	−3.0	0.4991	412.7	1.4	0.8004	167.5	−0.9
0.2501	460.3	1.3	0.5513	377.1	−0.3	0.8484	123.2	−4.6
0.2998	469.1	3.8	0.6034	339.4	1.7	0.9031	85.1	3.3
308.65 K, 0.1 MPa								
0.0703	345.5	2.4	0.3736	557.0	−2.7	0.6513	361.0	−6.7
0.1240	449.7	−4.1	0.4132	547.6	−3.7	0.6909	319.9	−7.6
0.1677	500.5	0.3	0.4511	534.9	−1.0	0.7301	290.7	2.3
0.2078	525.8	−0.2	0.4929	512.5	1.2	0.7692	249.3	−0.8
0.2504	547.5	3.4	0.5317	485.7	3.9	0.8078	218.6	6.3
0.2917	557.5	2.1	0.5727	446.2	0.7	0.8464	173.9	0.4
0.3316	560.1	−0.7	0.6121	414.8	7.6	0.8849	129.4	−3.2
308.65 K, 10.0 MPa								
0.0909	369.4	0.5	0.3734	541.4	−1.3	0.6119	410.9	8.2
0.1676	469.7	−3.7	0.4133	536.0	0.6	0.6512	360.5	−5.2
0.2078	505.0	3.5	0.4510	522.6	1.0	0.7301	288.9	0.9
0.2501	524.3	2.3	0.4930	500.1	1.4	0.8077	215.0	2.2
0.2916	534.1	−1.4	0.5315	471.9	0.2	0.8904	120.7	−1.0
0.3315	540.5	−1.9	0.5726	433.3	−4.7			

3. Results

The experimental results obtained for the n-alkanol + n-alkane mixtures are smmarized in Tables 1–4, and shown in Figs. 1–4. In all cases, it is possible to represent the dependence of H^E_m on the mole fraction (x) by using the Redlich–Kister equation (RK fit)

$$H^E_m/(\text{J mol}^{-1}) = x(1-x)\sum_{j=0}^{k} A_j(2x-1)^j \tag{1}$$

Table 4
$H^{\mathrm{E}}_{\mathrm{m}}$ and $D(H^{\mathrm{E}}_{\mathrm{m,exp}} - H^{\mathrm{E}}_{\mathrm{m,fit}})$ for xn-$\mathrm{C_4H_9OH} + (1-x)n$-$\mathrm{C_6H_{14}}$ mixtures under various temperature and pressure conditions

x	$H^{\mathrm{E}}_{\mathrm{m,exp}}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{\mathrm{m}}_{\mathrm{m,exp}}$/ (J mol^{-1})	D/ (J mol^{-1})	x	$H^{\mathrm{m}}_{\mathrm{m,exp}}$/ (J mol^{-1})	D/ (J mol^{-1})
298.65 K, 0.1 MPa								
0.0792	356.9	3.0	0.4478	530.7	−0.4	0.7174	298.6	2.8
0.1196	425.5	−5.4	0.4893	513.0	6.0	0.7523	263.8	1.2
0.1616	479.3	1.3	0.5276	475.8	−2.4	0.7863	229.3	−1.4
0.2152	515.9	1.5	0.5963	440.7	−0.6	0.8193	198.3	−0.9
0.2632	539.4	3.8	0.6068	409.1	4.0	0.8511	169.9	2.4
0.3125	546.2	−2.9	0.6456	360.4	−6.0	0.8824	133.9	−0.6
0.3591	550.1	−3.0	0.6820	329.3	−0.9	0.9127	99.6	−0.8
0.4029	546.9	−0.4						
298.65 K, 10.0 MPa								
0.0993	375.4	−0.5	0.4476	519.0	5.2	0.7174	289.3	1.5
0.1615	461.9	1.4	0.4892	490.9	−2.5	0.7520	260.1	5.9
0.2150	495.6	−1.8	0.5275	465.7	−2.3	0.7863	219.7	−2.9
0.2631	519.0	2.0	0.5690	435.1	0.8	0.8191	189.9	−4.0
0.3126	527.1	−1.3	0.6066	403.9	4.4	0.8511	169.0	2.3
0.3589	530.4	−1.1	0.6455	354.7	−6.0	0.9052	119.3	0.2
0.4027	526.3	−0.7	0.6820	322.8	−0.7			
308.65 K, 0.1 MPa								
0.1099	450.1	−2.8	0.4476	621.7	5.7	0.7174	350.2	3.8
0.1617	529.9	1.9	0.4891	595.6	4.1	0.7523	307.0	1.1
0.2153	576.7	1.4	0.5275	565.3	4.9	0.7862	274.1	6.7
0.2629	609.3	5.0	0.5691	518.9	−0.5	0.8192	225.8	−4.5
0.3122	621.4	−3.1	0.6067	471.9	−5.7	0.8509	194.8	0.7
0.3589	625.0	−8.4	0.6455	430.8	−1.2	0.8986	135.7	−1.2
0.4027	628.5	−2.3	0.6819	382.4	−6.1			
308.65 K, 10.0 MPa								
0.0861	390.5	−1.7	0.4025	605.7	−1.8	0.6456	419.7	7.6
0.1617	510.4	2.0	0.4478	598.8	6.8	0.6821	365.5	−6.3
0.2150	551.9	0.4	0.4893	570.1	3.2	0.7175	330.9	−2.7
0.2631	580.7	0.7	0.5276	530.3	−5.3	0.7523	298.3	1.6
0.3121	600.3	−0.6	0.5692	499.0	3.8	0.7864	265.9	5.3
0.3591	604.9	−5.1	0.6068	448.9	−6.1	0.8511	186.1	−2.7

The RK-fitting parameters (A_j) and the standard deviations (δ) are listed in Table 5.

$$\delta/(\mathrm{J\,mol^{-1}}) = \left\{ \left[\sum_{i=0}^{n} (H^{\mathrm{E}}_{i,\mathrm{exp}} - H^{\mathrm{E}}_{i,\mathrm{fit}})^2 \right] \Big/ (n-k+1) \right\}^{1/2} \qquad (2)$$

where n is the number of experimental points.

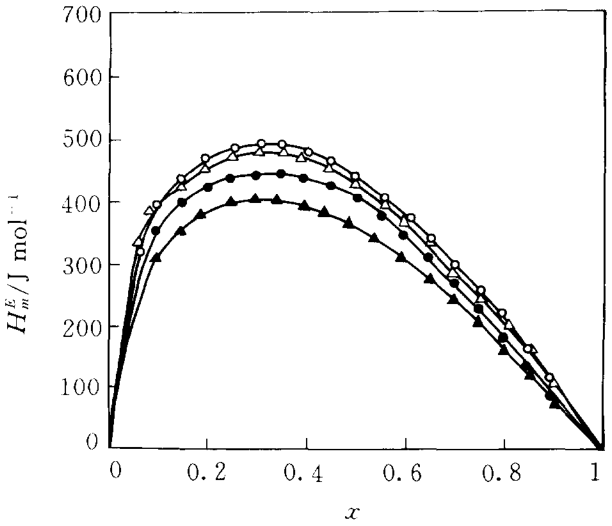

Fig. 2. Excess molar enthalpies of xn-$C_8H_{17}OH + (1-x)n$-C_6H_{14}: ○, 308.65 K, 0.1 MPa; △, 308.65 K, 10.0 MPa; ●, 298.65 K, 0.1 MPa; ▲, 298.65 K, 10.0 MPa; ——, RK equation fitting.

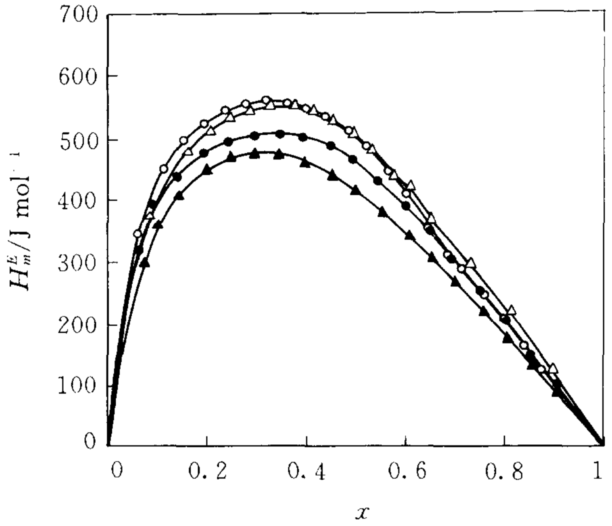

Fig. 3. Excess molar enthalpies of xn-$C_6H_{13}OH + (1-x)n$-C_6H_{14}: ○, 308.65 K, 0.1 MPa; △, 308.65 K, 10.0 MPa; ●, 298.65 K, 0.1 MPa; ▲, 298.65 K, 10.0 MPa; ——, RK equation fitting.

4. Conclusions

Several conclusions can be drawn from the experimental values of H^E_m and the x fitting curves for n-alkanol + n-hexane mixtures.

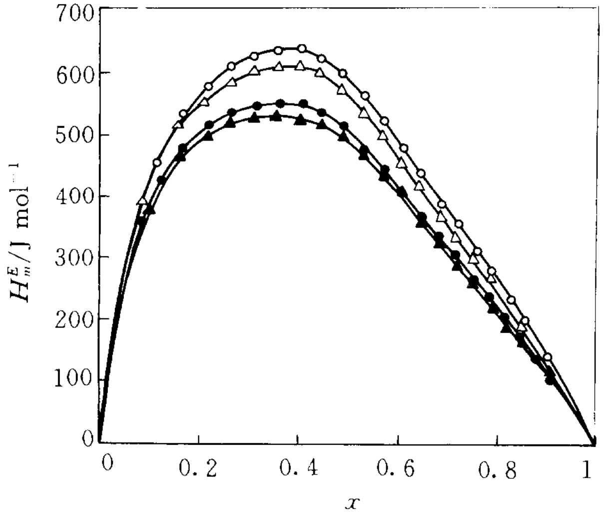

Fig. 4. Excess molar enthalpies of xn-$C_4H_8OH + (1-x)n$-C_6H_{14}: ○, 308.65 K, 0.1 MPa; △, 308.65 K, 10.0 MPa; ●, 298.65 K, 0.1 MPa; ▲, 298.65 K, 10.0 MPa; ——, RK equation fitting.

Table 5
Parameters A_j for Eq. (1) and the standard deviation $\delta(H^E_m)$ for Eq. (2)

Mixture: *n*-hexane+	T/ K	P/ MPa	A_0/ (J mol^{-1})	A_1/ (J mol^{-1})	A_2/ (J mol^{-1})	A_3/ (J mol^{-1})	A_4/ (J mol^{-1})	A_5/ (J mol^{-1})	$\delta(H^E_m)$/ (J mol^{-1})
n-Decanol	298.65	0.1	1562.9	−889.2	164.0	145.5	2134.1	−2065.2	3.74
n-Octanol	298.65	0.1	1630.6	−937.8	89.2	102.7	1873.3	−2542.9	3.86
n-Octanol	298.65	10.0	1444.9	−850.5	276.3	−114.8	1259.5	−1650.1	3.62
n-Octanol	308.65	0.1	1754.7	−1092.7	511.1	423.6	1509.5	−2844.3	7.39
n-Octanol	308.65	10.0	1704.6	−1167.7	197.5	986.3	1992.0	−3490.2	6.42
n-Hexanol	298.65	0.1	1855.5	−1155.4	−33.9	81.9	2156.5	−2170.4	4.77
n-Hexanol	298.65	10.0	1643.1	−1164.0	229.6	−395.8	1403.7	−893.8	4.98
n-Hexanol	308.65	0.1	2025.2	−1424.0	13.8	365.9	2222.1	−2156.8	4.56
n-Hexanol	308.65	10.0	1976.9	−1316.6	106.6	443.7	1752.5	−2170.3	4.06
n-Butanol	298.65	0.1	1998.2	−1442.6	−50.8	694.0	2168.2	−2375.4	3.53
n-Butanol	298.65	10.0	1947.4	−1257.5	−167.1	−222.6	2305.7	−877.1	3.68
n-Butanol	308.65	0.1	2333.7	−1538.0	−284.1	515.4	2449.6	−2096.4	5.20
n-Butanol	308.65	10.0	2235.3	−1555.3	−229.8	1109.8	2365.9	2927.7	5.36

(1) In all cases, the excess molar enthalpy is positive over the entire mole-fraction range. When a *n*-alkanol was mixed with a *n*-hexane, the H^E_m is generally due to a positive contribution arising from the rupture of hydrogen bonds.

(2) The excess molar enthalpy of *n*-alkanol + *n*-hexane mixtures decreases with increasing chain length of the *n*-alkanol molecule. The H^E_m values decrease in the sequence: *n*-decanol + *n*-hexane < *n*-octanol + *n*-hexane < *n*-hexanol + *n*-hexane < *n*-butanol + *n*-hexane.

(3) The excess molar enthalpy apparently increases with increasing temperature. As the temperature is increased, the thermal motion of the molecules speeds up, and thus number of disrupted hydrogen bonds increases greatly, making a positive contribution to H_m^E.

(4) The excess molar enthalpy decreases with increasing pressure. The dependence of H_m^E on pressure can be explained by taking into account the fact that the shift in the thermodynamic equilibrium and the number of disrupted hydrogen bonds decreases with increasing pressure.

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