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Excess molar enthalpies and excess molar volumes of binary mixtures of 1-alkenes with 1-propanol and 2-propanol

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Abstract

Molar excess enthalpies H_m^E and molar excess volumes V_m^E have been determined using a Thermometric flow calorimeter and a Paar DMA 601 density meter, respectively. The measurements were made over the whole composition range for mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K. The results were compared with H_m^E and V_m^E values for binary mixtures of a 1-alkene with methanol and ethanol, and of an *n*-alkane with an alkanol, in order to determine the effect of the double bond in the 1-alkene on the measured properties.

INTRODUCTION

In a previous paper [1] the molar excess enthalpies H_m^E and molar excess volumes V_m^E at 298.15 K for binary mixtures of a 1-alkene with methanol and ethanol were reported and discussed. In this work, the above H_m^E and V_m^E measurements were extended to include the alkanols, 1-propanol and 2-propanol. The results are discussed in terms of specific interactions between the double bond in the 1-alkene and the hydroxyl group in the alkanol and the hydrogen bonds in the alkanol.

EXPERIMENTAL

1-Hexene, 1-heptene and 1-octene were supplied by the Aldrich Chemical Co., and distilled before use. Analysis by GLC showed that total impurities were less than 0.2 mol% for 1-hexene and 1-heptene and less than 0.5 mol.% for 1-octene.

The propanols, supplied by Aldrich Chemical Company, were dried repeatedly using the method of Lund and Bjerrum [2]. The alcohols were analysed for water content before mixing using a Karl-Fischer titration

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TABLE 1

Excess enthalpy H_m^E data in J mol^{-1} for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K

x	H_m^E	Δ'	x	H_m^E	Δ'	x	H_m^E	Δ'
$xC_6H_{12} + (1-x)CH_3CH_2CH_2OH$								
0.0518	75.6	0.2	0.3409	428.8	−1.5	0.7014	655.2	−1.4
0.0836	119.2	−0.3	0.4222	510.7	−1.9	0.7489	640.5	4.2
0.1202	168.5	0.0	0.5052	588.2	3.3	0.8016	585.3	−1.2
0.1895	255.6	−0.9	0.5956	639.8	−1.5	0.8722	461.4	−0.8
0.2518	332.3	1.4	0.6636	658.2	−1.1	0.9334	285.7	0.2
0.2944	380.8	1.3						
$xC_7H_{14} + (1-x)CH_3CH_2CH_2OH$								
0.0559	90.2	1.7	0.4533	598.9	2.9	0.7768	664.8	−1.0
0.0928	144.4	−0.6	0.5317	662.8	1.2	0.7932	647.4	0.3
0.1655	252.4	1.1	0.6157	705.8	−1.4	0.8206	611.5	3.8
0.2072	305.2	−3.7	0.6824	713.5	−2.6	0.9007	420.8	−1.8
0.2807	408.1	3.4	0.7352	699.8	0.9	0.9536	228.2	−0.7
0.3746	511.8	−3.5						
$xC_8H_{16} + (1-x)CH_3CH_2OH_2OH$								
0.0944	169.6	−0.7	0.4798	667.7	0.2	0.7504	730.6	1.6
0.1361	239.9	0.5	0.5387	712.8	0.0	0.8226	640.4	1.0
0.1773	303.8	−0.1	0.6116	749.8	−0.6	0.8612	560.2	1.1
0.2539	414.4	0.3	0.6848	759.0	0.6	0.9033	435.6	−3.7
0.4005	591.0	−0.1	0.7094	750.4	−1.7	0.9568	230.1	1.9
$xC_6H_{12} + (1-x)CH_3CH(OH)CH_3$								
0.0736	151.4	−0.5	0.3294	636.5	0.7	0.6756	863.5	−4.9
0.1446	308.5	3.7	0.3489	660.9	−3.1	0.7044	859.7	0.5
0.1975	412.8	−0.1	0.4357	763.5	0.1	0.7647	811.7	−3.1
0.2556	521.5	0.9	0.5265	838.2	4.1	0.8335	704.6	−2.8
0.2812	560.4	−3.3	0.5734	862.2	5.1	0.9066	502.2	6.8
$xC_7H_{14} + (1-x)CH_3CH(OH)CH_3$								
0.0808	192.4	0.5	0.4455	830.7	3.5	0.7736	833.8	0.1
0.1432	344.8	2.7	0.4677	846.2	1.6	0.8062	786.1	−0.4
0.1814	428.0	−0.7	0.4955	862.0	−1.5	0.8516	690.7	−0.9
0.2526	571.0	−1.6	0.5594	894.7	0.2	0.9055	516.2	−4.5
0.3066	662.7	−1.1	0.6655	904.3	0.0	0.9449	352.6	8.8
0.3304	696.9	−2.0	0.7405	866.7	−0.7			
$xC_8H_{16} + (1-x)CH_3CH(OH)CH_3$								
0.0736	209.4	3.4	0.3133	726.4	1.3	0.6142	952.5	0.1
0.1144	314.8	0.0	0.3970	831.3	−0.4	0.6926	935.5	0.1
0.1425	382.4	−3.3	0.4574	885.7	−1.2	0.7759	858.4	−0.6
0.1622	433.7	0.5	0.5188	926.9	0.9	0.8326	752.7	−2.1
0.2429	605.0	−0.4	0.5333	933.7	0.9	0.9059	528.9	2.7
0.2590	635.2	−0.1						

procedure. The water content was always found to be <0.02 mol.%. The densities of the 1-hexene, 1-heptene, 1-octene, 1-propanol and 2-propanol were found to be 0.6684, 0.6926, 0.7107, 0.7998 and 0.7815 g cm^{-3}, respectively.

RESULTS

Results for H_m^E and V_m^E are given in Tables 1 and 2, respectively, together with the corresponding deviations Δ' and Δ''. The deviations were

TABLE 2

Excess volume V_m^E data in $cm^3\,mol^{-1}$ for binary mixtures of 1-hexene, 1-heptene and 1-octene with 1-propanol and 2-propanol at 298.15 K

x	V_m^E	$\Delta'' \times 10^4$	x	V_m^E	$\Delta'' \times 10^4$	x	V_m^E	$\Delta'' \times 10^4$
$xC_6H_{12} + (1-x)CH_3CH_2CH_2OH$								
0.0394	−0.032	1	0.3773	−0.038	−5	0.8027	0.116	6
0.1273	−0.071	10	0.4837	0.012	28	0.8362	0.112	−2
0.1995	−0.081	−15	0.5917	0.056	−35	0.9100	0.084	−7
0.2673	−0.071	4	0.7237	0.108	15			
$xC_7H_{14} + (1-x)CH_3CH_2CH_2OH$								
0.0276	−0.001	−7	0.4013	0.123	−6	0.8314	0.180	4
0.0779	0.001	−32	0.4706	0.154	−9	0.8736	0.151	−5
0.1747	0.031	37	0.5563	0.189	10	0.9276	0.100	−3
0.3181	0.084	−9	0.6964	0.214	2			
$xC_8H_{16} + (1-x)CH_3CH_2CH_2OH$								
0.0492	0.023	−21	0.3195	0.179	−30	0.6133	0.270	−6
0.0900	0.053	31	0.4401	0.230	25	0.7134	0.278	−3
0.1673	0.100	9	0.5232	0.253	20	0.8703	0.225	17
0.2333	0.137	−15						
$xC_6H_{12} + (1-x)CH_3CH(OH)CH_3$								
0.0557	0.021	1	0.3694	0.276	−28	0.7268	0.397	23
0.1294	0.061	−27	0.4987	0.382	−22	0.8254	0.296	−37
0.1950	0.115	8	0.6039	0.427	18	0.8910	0.205	16
0.2680	0.185	44						
$xC_7H_{14} + (1-x)CH_3CH(OH)CH_3$								
0.0566	0.069	−33	0.3505	0.393	−2	0.7241	0.492	22
0.1031	0.131	19	0.4667	0.480	−9	0.8704	0.312	2
0.1886	0.227	−13	0.6027	0.525	−14	0.9409	0.160	−20
0.2516	0.299	23						
$xC_8H_{16} + (1-x)CH_3CH(OH)CH_3$								
0.0419	0.074	−1	0.3305	0.434	15	0.7012	0.529	−14
0.0916	0.153	−1	0.4383	0.511	−7	0.8534	0.363	36
0.1633	0.253	3	0.5435	0.555	2	0.9401	0.170	−38
0.2304	0.332	−10						

TABLE 3

Values at 298.15 K of coefficients A_r in J mol^{-1} for eqn. (1)

Mixture	A_r			
	A_0	A_1	A_2	A_3
x1-C_6H_{12} + (1 − x)$CH_3CH_2CH_2OH$	2323	−1575	993	−242
x1-C_7H_{14} + (1 − x)$CH_3CH_2CH_2OH$	2549	−1636	1057	−362
x1-C_8H_{16} + (1 − x)$CH_3CH_2CH_2OH$	2737	−1603	1191	−428
x1-C_6H_{12} + (1 − x)$CH_3CH(OH)CH_3$	3268	−1403	1221	−1178
x1-C_7H_{14} + (1 − x)$CH_3CH(OH)CH_3$	3465	−1200	1360	−1411
x1-C_8H_{16} + (1 − x)$CH_3CH(OH)CH_3$	3663	−1169	1451	−1129

calculated from the smoothing equation

$$\Delta = X_m^E - x(1-x)\sum_{r=0}^{r=3} X_r(1-2x)^r \quad (1)$$

where Δ may be either Δ' or Δ'', X_m^E may be either H_m^E or V_m^E and X_r may be either A_r or B_r, respectively. The coefficients A_r and B_r are given in Tables 3 and 4.

DISCUSSION

The H_m^E values for 1-alkene + 1-propanol or 2-propanol are all positive with a maximum at a composition between 0.6 and 0.7 mole fraction of 1-alkene. This is most likely a reflection of the breaking of the hydrogen bonds between the alkanol molecules as a result of the mixing process.

TABLE 4

Values at 298.15 K of coefficients B_r in cm^3 mol^{-1} for eqn. (1)

Mixture	B_r			
	B_0	B_1	B_2	B_3
x1-C_6H_{12} + (1 − x)$CH_3CH_2CH_2OH$	0.068	−1.015	0.126	–
x1-C_7H_{14} + (1 − x)$CH_3CH_2CH_2OH$	0.670	−0.827	0.142	–
x1-C_8H_{16} + (1 − x)$CH_3CH_2CH_2OH$	0.980	−0.538	0.624	−0.633
x1-C_6H_{12} + (1 − x)$CH_3CH(OH)$	1.540	−1.239	−0.383	0.378
x1-C_7H_{14} + (1 − x)$CH_3CH(OH)CH_3$	1.994	−0.922	0.182	–
x1-C_8H_{16} + (1 − x)$CH_3CH(OH)CH_3$	2.165	−0.736	0.389	–

Comparing these results with those published previously [1] on related mixtures of 1-alkene with methanol or ethanol, it can be seen that H^E_m(maximum) increases slightly with increasing alcohol carbon number. For example H^E_m(maximum) for mixtures of 1-hexene with methanol, ethanol and 1-propanol are 570, 620 and 660 J mol^{-1}, respectively.

For each 1-alkene, H^E_m(maximum) for mixtures containing 2-propanol are greater than H^E_m(maximum) for mixtures containing 1-propanol. For example, H^E_m(maximum) for 1-heptene with 2-propanol and 1-propanol are 920 and 710 J mol^{-1}, respectively.

For each alkanol, the H^E_m(maximum) value increases slightly with increasing 1-alkene carbon number. For example, H^E_m(maximum) for mixtures containing methanol with 1-hexene, 1-heptene and 1-octene are 570, 590 and 630 J mol^{-1}, respectively.

The double bond in the 1-alkene has only a slight effect on the H^E_m(maximum) value. This can be seen by comparing H^E_m(maximum) for 1-hexene + ethanol (620 J mol^{-1}) with the value for hexane + ethanol (580 J mol^{-1}) from the literature [3].

The magnitude of the partial molar excess enthalpies at infinite dilution gives some clue to the process taking place on mixing. For each mixture ($x_1$1-C_yH_{2y} + $x_2C_zH_{2z+1}OH$), $H^E_2(x_2 = 0) > H^E_1(x_1 = 0)$, indicating a higher endothermic enthalpy for the complete dissociation of the alkanol molecules ($x_2 = 0$) than for the dissociation of 1-alkene molecules and the association of a 1-alkene with an alkanol molecule ($x_1 = 0$). The partial molar excess enthalpies at infinite dilution $H^E_i(x_i = 0)$ were calculated by the method described by Letcher and Jerman [4] and are given in Table 5.

The volume changes on mixing a 1-alkene with an alkanol are largely positive which again reflects the dissociation effect of the alkanol. This is reinforced by the magnitude of the parital molar excess volumes of the alkanols at infinite dilution, $V^E_2(x_2 = 0)$ which are longer than $V^E_1(x_1 = 0)$. These values are given in Table 5.

TABLE 5

Values of the partial molar excess properties $H^E_1(x_1 = 0)$, $H^E_2(x_2 = 0)$, $V^E_1(x_1 = 0)$ and $V^E_2(x_2 = 0)$

Mixture	$H^E_1(x_1 = 0)$/ J mol^{-1}	$H^E_2(x_2 = 0)$/ J mol^{-1}	$V^E_1(x_1 = 0)$/ cm^3 mol^{-1}	$V_2(x_2 = 0)$/ cm^3 mol^{-1}
x1-C_6H_{12} + (1 − x)$CH_3CH_2CH_7OH$	1499	5133	−0.82	1.21
x1-C_7H_{14} + (1 − x)$CH_3CH_2CH_2OH$	1608	5604	−0.02	1.64
x1-C_8H_{16} + (1 − x)$CH_3CH_2CH_2OH$	1897	5959	0.43	2.78
x1-C_6H_{12} + (1 − x)$CH_3CH(OH)CH_3$	1908	7070	−0.30	3.54
x1-C_7H_{14} + (1 − x)$CH_3CH(OH)CH_3$	2214	7436	1.25	3.10
x1-C_8H_{16} + (1 − x)$CH_3CH(OH)CH_3$	2816	7412	1.82	3.29

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