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EXCESS ENTHALPIES AND VOLUMES OF BINARY MIXTURES OF 1-ALKENES WITH METHANOL AND WITH ETHANOL

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ABSTRACT

Molar excess enthalpies H_m^E have been determined using an LKB flow calorimeter, and molar excess volumes V_m^E using a Paar DMA 601 densitometer over the whole composition range, for all the binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K. The results were compared with H_m^E and V_m^E values for mixtures of an *n*-alkane with methanol and with ethanol in order to determine the effect of the double bond in the 1-alkene with alcohol mixtures.

INTRODUCTION

Previous studies have determined molar excess enthalpies H_m^E and molar excess volumes V_m^E at 298.15 K for binary mixtures of an *n*-alkane with methanol and with ethanol [1–8]. In the present work we report H_m^E and V_m^E values for binary mixtures of a 1-alkene (1-hexene, 1-heptene or 1-octene) with methanol and with ethanol. The patterns generated are compared to the patterns of H_m^E and V_m^E results for mixtures of an *n*-alkane with methanol and with ethanol. The results are discussed in terms of specific interactions between the double bonds in the 1-alkene and the hydroxyl group in the alcohol.

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 the 1-hexene and 1-heptene, and less than 0.5 mol% for the 1-octene. The densities of the 1-hexene, 1-heptene and 1-octene were 0.66840, 0.69260 and 0.71070, respectively, which compared well with literature values [9].

The methanol (Merck, Urasol grade) and ethanol (absolute grade from NCP, South Africa) were dried repeatedly using the method of Lund and

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Bjerrum described by Vogel [10]. The method involves refluxing with magnesium metal activated with iodine before distillation. The water impurity in both methanol and ethanol was determined by a Karl Fischer titration to be less than 0.01 mol%. The alcohols were kept in a dry box before use.

The excess volumes were measured using a vibrating tube densitometer (Paar DMA 601) method which has been described elsewhere [11]. The temperature was controlled to within 2 mK, and the densitometer calibrated for each measurement using water, methanol and ethanol. The excess molar

TABLE 1

Excess enthalpy H_m^E data for binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K

x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})	x	H_m^E (J mol^{-1})	δH_m^E (J mol^{-1})
x1-$C_6H_{12}+(1-x)CH_3OH$								
0.0473	123.6	1.0	0.3462	497.4	3.7	0.6632	573.4	−0.1
0.1249	274.6	−0.8	0.4113	529.1	4.9	0.7693	530.9	−1.2
0.1915	363.2	−4.9	0.4845	553.2	3.4	0.8166	480.9	−5.6
0.2732	442.4	−4.0	0.5614	570.1	1.9	0.9221	285.0	1.8
x1-$C_7H_{14}+(1-x)CH_3OH$								
0.0842	234.5	2.2	0.3346	516.3	−3.3	0.6852	590.8	1.4
0.1388	330.7	−4.8	0.4268	560.9	5.5	0.7775	540.1	−5.5
0.1833	399.6	1.1	0.5428	587.7	3.4	0.9065	340.0	1.1
0.2360	453.5	−0.5	0.6548	592.5	−0.7			
x1-$C_8H_{16}+(1-x)CH_3OH$								
0.0630	201.5	1.3	0.4650	596.3	1.8	0.7318	601.0	−3.4
0.1550	385.7	−2.1	0.5394	617.4	4.5	0.8342	501.3	−4.7
0.2161	457.3	−6.6	0.6425	626.1	1.4	0.9050	360.7	2.5
0.3216	546.3	5.3						
x1-$C_6H_{12}+(1-x)C_2H_5OH$								
0.1120	167.1	0.7	0.5421	575.6	2.0	0.7798	585.9	−4.9
0.2417	332.3	−3.0	0.6556	616.1	0.9	0.8273	550.2	6.6
0.3196	414.7	−1.1	0.7132	613.1	−4.1	0.8655	480.1	−1.6
0.4466	521.3	4.3						
x1-$C_7H_{14}+(1-x)C_2H_5OH$								
0.0696	136.8	2.3	0.3751	518.0	4.7	0.7310	648.1	−7.7
0.1289	235.9	−0.6	0.4855	591.9	8.2	0.8105	601.9	−4.3
0.1687	290.2	−6.8	0.6489	655.6	2.1	0.8712	513.0	3.9
0.1879	322.0	−1.8						
x1-$C_8H_{16}+(1-x)C_2H_5OH$								
0.0898	186.5	2.2	0.6120	660.7	7.3	0.8823	548.4	−4.9
0.1638	323.5	−3.2	0.7018	686.0	4.3	0.9102	478.7	4.2
0.2579	458.7	−5.4	0.7891	668.3	−6.9	0.9189	448.8	4.3
0.3385	538.6	−0.3	0.8669	580.4	−6.3	0.9384	365.5	−7.5
0.4576	605.0	5.6						

enthalpies were measured using an LKB 2107 calorimeter. The method has been described elsewhere [12].

RESULTS

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

TABLE 2

Excess volume V_m^E data for binary mixtures of 1-hexene, 1-heptene and 1-octene with methanol and with ethanol at 298.15 K

x	V_m^E (cm^3 mol^{-1})	$10^4\,\delta V_m^E$ (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$10^4\,\delta V_m^E$ (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	$10^4\,\delta V_m^E$ (cm^3 mol^{-1})
x1-$C_6H_{12}+(1-x)CH_3OH$								
0.0979	0.1211	25	0.3934	0.2751	36	0.7934	0.2290	−55
0.1434	0.1601	−18	0.5430	0.2807	75	0.8602	0.1916	−60
0.2499	0.2246	−81	0.7162	0.2616	56	0.9414	0.1121	20
x1-$C_7H_{14}+(1-x)CH_3OH$								
0.0843	0.1886	6	0.4709	0.3641	−8	0.7964	0.2761	−47
0.2066	0.3150	−31	0.5063	0.3680	46	0.8565	0.2315	33
0.3553	0.3644	19	0.6531	0.3437	−7	0.8968	0.1800	−4
0.3586	0.3620	−7						
x(1-$C_8H_{16}+(1-x)CH_3OH$								
0.0501	0.1482	13	0.4170	0.3952	−1	0.7753	0.3138	3
0.0994	0.2484	−6	0.5372	0.3833	48	0.8738	0.2177	−123
0.1588	0.3255	−34	0.5704	0.3791	57	0.9544	0.1070	30
0.2510	0.3845	−34	0.6809	0.3561	48			
x1-$C_6H_{12}+(1-x)C_2H_5OH$								
0.1005	0.0340	20	0.3978	0.1587	12	0.7546	0.2306	22
0.1582	0.0524	−25	0.4622	0.1862	37	0.8030	0.2092	−49
0.2414	0.0895	−10	0.5488	0.2138	27	0.8534	0.1817	−39
0.2807	0.1037	−39	0.6884	0.2366	22	0.9405	0.0994	14
x1-$C_7H_{14}+(1-x)C_2H_5OH$								
0.0854	0.0967	14	0.5024	0.2929	85	0.7871	0.2688	−52
0.2307	0.2013	−47	0.6620	0.3056	59	0.8997	0.1894	44
0.2629	0.2175	−52	0.7693	0.2781	−89	0.9603	0.0888	−4
0.3586	0.2635	42						
x1-$C_8H_{16}+(1-x)C_2H_5OH$								
0.0478	0.0841	24	0.5375	0.3527	87	0.8596	0.2450	−106
0.1042	0.1555	−47	0.5488	0.3540	99	0.8955	0.2067	−73
0.2457	0.2750	−83	0.6943	0.3381	20	0.9421	0.1448	63
0.3947	0.3342	14						

TABLE 3

Values at 298.15 K of coefficients A_r for eqn. (1)

Mixture	A_r (J mol^{-1})			
	A_0	A_1	A_2	A_3
x1-$C_6H_{12}+(1-x)CH_3OH$	2216.7	−548.8	1506.5	−314.9
x1-$C_7H_{14}+(1-x)CH_3OH$	2300.8	−467.2	1793.4	−244.3
x1-$C_8H_{16}+(1-x)CH_3OH$	2415.0	−502.4	1955.0	−116.7
x1-$C_6H_{12}+(1-x)C_2H_5OH$	2202.2	−1169.6	1346.3	−926.1
x1-$C_7H_{14}+(1-x)C_2H_5OH$	2366.8	−1079.2	1732.2	−1011.2
x1-$C_8H_{16}+(1-x)C_2H_5OH$	2457.1	−680.1	2336.6	−2204.9

TABLE 4

Values at 298.15 K of coefficients B_r for eqn. (1)

Mixture	B_r (cm^3 mol^{-1})			
	B_0	B_1	B_2	B_3
x1-$C_6H_{12}+(1-x)CH_3OH$	1.0991	0.0467	0.7376	−0.5219
x1-$C_7H_{14}+(1-x)CH_3OH$	1.4549	0.1019	1.0999	0.2344
x1-$C_8H_{16}+(1-x)CH_3OH$	1.5362	0.2938	1.4724	0.1275
x1-$C_6H_{12}+(1-x)C_2H_5OH$	0.7833	−0.6741	0.3180	−0.1842
x1-$C_7H_{14}+(1-x)C_2H_5OH$	1.1562	−0.2835	0.7447	−0.3740
x1-$C_8H_{16}+(1-x)C_2H_5OH$	1.3709	−0.0895	1.0080	−0.4342

calculated from the smoothing equation

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

where 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

At 298.15 K, CH_3OH does not mix in all proportions with the *n*-alkanes C_6H_{14}, C_7H_{16} and C_8H_{18}, but does mix with the 1-alkenes 1-C_6H_{12}, 1-C_7H_{14} and 1-C_8H_{16}. This could be considered as evidence for specific interactions between the double bond of the 1-alkene and the hydroxyl group of the alcohol.

The H_m^E results for the 1-C_6H_{12}, 1-C_7H_{14} and 1-C_8H_{16} + C_2H_5OH mixtures show skew curves with single maxima at about 0.7 mole fraction 1-alkene of 620, 660 and 700 J mol^{-1}, respectively. These H_m^E(maximum) values are between 40 and 50 J mol^{-1} more positive than those for C_6H_{14}, C_7H_{16} and C_8H_{18} + C_2H_5OH mixtures [2,7,8].

The self association between 1-alkene molecules is relatively weak, as judged by the small positive values of H_m^E(maximum) for 1-C_6H_{12} + n-C_6H_{14} [13], 1-C_7H_{14} + n-C_7H_{16} [13] and 1-C_8H_{16} + n-C_7H_{16} [14] mixtures, of between 40 and 55 J mol^{-1}. The small positive enthalpy effect resulting from the dissociation of 1-alkene molecules is probably the cause of the H_m^E(maximum) values for 1-alkene + C_2H_5OH mixtures being slightly more positive than those for n-alkane + C_2H_5OH mixtures. The fact that the H_m^E(maximum) results for the 1-alkene + C_2H_5OH mixtures are only slightly more positive than those for the corresponding n-alkene + C_2H_5OH mixtures indicates that the association between 1-alkene and C_2H_5OH molecules is not strong. In both sets of data, the dominant feature is the dissociation of alcohol molecules, resulting in relatively large positive H_m^E(maximum) values.

The H_m^E(maximum) values for 1-C_6H_{12}, 1-C_7H_{14} and 1-C_8H_{16} + C_2H_5OH at 298 K are between 50 and 70 J mol^{-1} more positive than those for 1-C_6H_{12}, 1-C_7H_{14} and 1-C_8H_{16} + CH_3OH.

The V_m^E(maximum) values for 1-C_6H_{12}, 1-C_7H_{14} and 1-C_8H_{16} + C_2H_5OH are 0.23, 0.30 and 0.35 cm^3 mol^{-1}, respectively, and are less positive than those for 1-C_6H_{14}, 1-C_7H_{16} and 1-C_8H_{18} + C_2H_5OH (0.41, 0.47 and 0.52 cm^3 mol^{-1}, respectively [3–6]).

The fact that the V_m^E(maximum) values obtained for the 1-alkene + C_2H_5OH mixtures studied in the present work are less positive than those for the corresponding n-alkane + C_2H_5OH mixtures could be a result of a packing effect induced by specific interaction of the double bond and the hydroxyl group.

The V_m^E(maximum) values for the 1-alkene + C_2H_5OH mixtures are less positive than those for the corresponding 1-alkene + CH_3OH mixtures.

The Flory–Patterson theory of liquid mixtures will be fitted to the V_m^E and H_m^E results presented here once the compressibilities of the 1-alkenes have been determined.

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