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Excess Volumes For 4-Methylpentan-2-Ol With n-Alkanes

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Abstract: ***Excess molar volumes were measured at 308.15K as a function of composition by a direct dilatometer method for binary liquid mixtures of 4-methylpentan-2-ol + n-hexane, + n-heptane, + n-octane, + n-decane and + n-dodecane. All the mixtures exhibit positive excess volumes over the whole mole fraction range.*** V^E ***results of 4-Methylpentan-2-ol with n-alkanes were compared with*** V^E ***of Hexanol-1 + n-alkanes. The variation of*** V^E ***with the change in the position of either alkyl group or –OH group is discussed.***

I. INTRODUCTION

The molar excess volumes of binary liquid mixtures particularly alkanol – alkanes mixtures have been determined by many workers (Kaur et al.,1989, 1991and Mahajan et al.,2013) and the results have been utilized to check the validity of theories of binary solutions, to examine the type of interactions in pure components and solutions and to study the effect of chain length of the molecules on excess volumes of these mixtures.

In the present investigation, molar excess volumes (V^E) of 4-methylpentan-2-ol with n- alkanes have been determined at 308.5K to study the effect of chain length of alkane as well as alkanol molecules and the effect of position of $-CH_3$ and -OH group resulting in steric hindrance on the V^E.

II. EXPERIMENTAL DETAILS

4-methylpantan-2-ol was distilled and the middle fraction was collected. At 298.5K, the density of the alcohol was 0.080329 g/cm^3 which is in good as agreement with the literature value 0.80330 g/cm^3. The n-alkanes were purified and distilled as reported earlier (Kaur et al, 1989, 1991). The excess volumes were measured as a function of composition using the direct dilatometric technique as described previously (Mahl et al,1971, Singh and Mahl,1985) at 309.15k with the temperature controlled to ±0.01K. The components were degassed before loading into the dilatometer.

III. RESULTS AND DISCUSSION

The experimental values of V^E at 308.15K for 4-methylpentan-2-ol + n-alkane mixtures are given in Table 1 and the graphical representation is given in Fig 1.

X	V^E	X	V^E
(x) 4-Methylpentan-2-ol +(1-x) n-Hexane			
0.0805	0.12	0.5604	0.277
0.1319	0.19	0.6502	0.26
0.2486	0.26	0.7694	0.186
0.3502	0.281	0.8355	0.166
0.439	0.292	0.9213	0.09
(x) 4-Methylpentan-2-ol + (1-x) nHeptane			
0.097	0.249	0.5198	0.438
0.1571	0.327	0.6212	0.386
0.2103	0.348	0.7787	0.282
0.2698	0.4	0.854	0.204
0.4133	0.431	0.8897	0.162
(x) 4-Methylpentan-2-ol +(1-x) n-Octane			
0.1091	0.31	0.5466	0.549
0.1752	0.404	0.6328	0.503
0.2257	0.439	0.8102	0.354
0.2924	0.492	0.8671	0.273
0.3949	0.537	0.9002	0.2
(x) 4-mthylpentan-2-ol + (1-x) n-Decane			

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0.1118	0.322	0.6742	0.59
0.266	0.52	0.7407	0.518
0.3942	0.612	0.8663	0.337
0.4805	0.632	0.9142	0.232
0.5854	0.63	0.9397	0.165
(x) 4 Methylpentan-2-ol + (1-x) n-Dodecane			
0.1243	0.368	0.5847	0.672
0.1828	0.469	0.6678	0.661
0.2152	0.51	0.7509	0.554
0.3221	0.609	0.8644	0.408
0.4672	0.679	0.9418	0.242

Table 1: Molar excess volumes, V^E, for (x) 4-Methylpentan-2-ol + (1-x) n-alkane at 308.15K

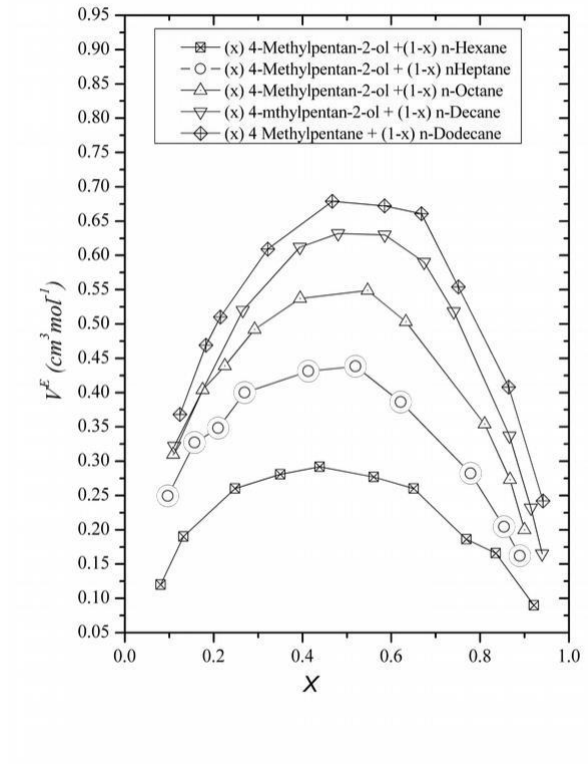

Figure 1: Molar excess volumes, V^E, for (x) 4-Methylpentan-2-ol + (1-x) n-alkane at 308.15K

The results were fitted by the method of least square to one of the following two expressions.

$$V^E\ (cm^3\ mol^{-1}) = x(1-x)\sum_{i=1}^{n} A_i\, x^{(i-1)/2} \qquad (1)$$

$$V^E\ (cm^3\ mol^{-1}) = x(1-x)\sum_{i=1}^{n} A_i\, (1-2x)^{(i-1)} \qquad (2)$$

where x is the mole fraction of the first component that is alcohol. The values of the coefficient A and the standard deviation $\sigma(V^E)$ are given in Table 2 and were calculated from the equation giving the best fit to the data.

Mixture	A_1	A_2	A_3	A_4	$\sigma\ (V^E)$ (cm^{3}mol^{-1})	Equation used
(x) 4-Methylpentan-2-ol +(1-x) n-Hexane	1.2436	3.7692	10.03	6.3583	0.008	1
(x) 4-Methylpentan-2-ol + (1-x) nHeptane	5.818	-13.7065	15.2422	-5.7265	0.009	1
(x) 4-Methylpentan-2-ol +(1-x) n-Octane	6.6093	-15.3266	17.1743	-6.1135	0.008	1
(x) 4-mthylpentan-2-ol + (1-x) n-Decane	5.9239	12.3555	-4.4896		0.004	1
(x) 4 Methylpentane + (1-x) n-Dodecane	2.7588	0.05556	0.1336	0.3658	0.007	2

Table 2: Coefficients Ai and standard deviations σ (V^E) for the representation of molar excess volumes at 308.15 K

As indicated in Table 1 and plotted in Fig 1, V^E values of 4-methyl pentan-2-ol + n-alkanes are positive over the whole mole fraction range as compared to V^E value of Hexan-1-ol +n-alkanes (H. Kaur,1985) which give sigmoid shape with (n-hexane, n-heptane and n-decane), i.e. show both negative and positive values at low and high mole fraction range. This can be explained as consequence of two opposing effects, the disruption of H-bonded alcohol aggregates by alkane molecules contribute negative V^E whereas change in free volume and interstitial accommodation of smaller alkane molecules into the alkanol structure give negative contribution. The latter effect gets stoically hindered in 4-methylpentan-2-ol due to positive contribution due and is dominated by the positive contribute due to disruption of H-bonds. Self association due to H-bonds also become weaker due to steric hindrance to H-bond formation in 4-methylpentan-2-ol as compared to Hexan-1-ol which cause more positive V^E values for 4-methylpentan-2-ol. The shape of the molecule is another factor which contributes more positive value of V^E to 4-methylpentan-2-ol. The Hexan-1-ol molecule is planer and elongated in same fashion as those of n-alkanes. The alignment of these molecules on mixing is ordered due to Vander Waal's forces. The 4- methylpentan-2-ol molecules are bulky and spherical in shape. The alignment on mixing is likely to be random. These molecules may also destroy the ordered alignment of n-alkane molecules.

The excess volumes of 4-methylpentan-2-ol + n-alkanes have also been interpreted to see the effect of chain length of alkanol and n-alkane on V^E. With the increase in chain length of alkanes, there is decrease in V^E when mixed with the same n-alkanes. On the other hand, V^E increases with the increase in chain length of n-alkanes, medicating that the interstitial accommodation becomes more effective as the length of alkanol is increased or n-alkane is decreased.

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