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TOPOLOGICAL ASPECTS OF THE THERMODYNAMICS OF BINARY MIXTURES OF NON-ELECTROLYTES

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ABSTRACT

An approach based on the "graph" theory has been evolved to predict molar excess enthalpies, H^E, and molar excess volumes, V^E, for a number of binary mixtures of non-electrolytes. The calculated H^E and V^E values compare reasonably well with their corresponding experimental values. The limitations of this approach have also been discussed.

INTRODUCTION

According to the mathematical discipline of graph theory, if atoms in the structural formula of a molecule are represented by letters and the bonds joining them by lines, the resulting "graph", which describes the topology of the molecules, gives the totality of information contained in that molecule [1—4]. The elegance and versatility of graph theoretical methods have been utilized to (i) enumerate [5] isomers for alkanes, (ii) determine the relationship [6] between the structure of a molecule and its chemical properties, and (iii) study [7] multi-stage synthesis where optimization of yields is a prerequisite, etc. In the present investigation an approach (based on graph theory) has been evolved to predict H^E and V^E values of binary mixtures of non-electrolytes.

THEORETICAL ASPECTS OF THE APPROACH AND THE RESULTS

According to graph theory, if δ_i, δ_j, δ_k, etc. denote the degrees of i, j, k, etc. vertices of the graph of a molecule, then the connectivity parameters ξ, of the first, second, third etc. degrees are defined by

$$^1\xi = \sum_{i<j} (\delta_i\delta_j)^{-1/2} \tag{1}$$

$$^2\xi = \sum_{i<j}\sum_{j<k} (\delta_i\delta_j\delta_k)^{-1/2} \tag{2}$$

$$^3\xi = \sum_{i<j}\sum_{j<k}\sum_{k<l} (\delta_i\delta_j\delta_k\delta_l)^{-1/2} \tag{3}$$

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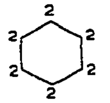
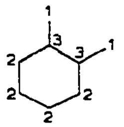
Accordingly the ${}^1\xi$, ${}^2\xi$, ${}^3\xi$ connectivity parameters of benzene, *o*-xylene and 2,3-dimethyl pentane (to name a few) would be



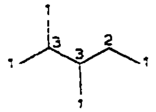
Degrees of various vertices of the C—C skeleton of benzene

$$\left\{\begin{aligned}
{}^1\xi &= 6(1/\sqrt{2\times 2}) = 3.0 \quad \text{(since each vertex is of the second degree)}\\
{}^2\xi &= 6(1/\sqrt{2\times 2\times 2}) = 2.12\\
{}^3\xi &= 6(1/\sqrt{2\times 2\times 2\times 2}) = 1.5
\end{aligned}\right.$$



Degrees of various vertices of the C—C skeleton of *o*-xylene

$$\left\{\begin{aligned}
{}^1\xi &= 1/\sqrt{1\times 3} + 1/\sqrt{3\times 3} + 1/\sqrt{3\times 1} + 1/\sqrt{3\times 2}\\
&\quad + 1/\sqrt{2\times 2} + 1/\sqrt{2\times 2} + 1/\sqrt{2\times 2} + 1/\sqrt{2\times 2}\\
&\quad + 1/\sqrt{2\times 3} = 3.81\\
{}^2\xi &= 1/\sqrt{1\times 3\times 3} + 1/\sqrt{3\times 3\times 1} + 1/\sqrt{3\times 3\times 2}\\
&\quad + 1/\sqrt{1\times 3\times 2} + 1/\sqrt{3\times 2\times 2} + 1/\sqrt{2\times 2\times 2}\\
&\quad + 1/\sqrt{2\times 2\times 2} + 1/\sqrt{2\times 3\times 1} + 1/\sqrt{2\times 3\times 3}\\
&\quad = 2.95\\
{}^3\xi &= 1/\sqrt{1\times 3\times 3\times 2} + 1/\sqrt{1\times 3\times 3\times 1}\\
&\quad + 1/\sqrt{3\times 3\times 2\times 2} + 1/\sqrt{1\times 3\times 2\times 2}\\
&\quad + 1/\sqrt{3\times 2\times 2\times 2} + 1/\sqrt{2\times 2\times 2\times 2}\\
&\quad + 1/\sqrt{2\times 2\times 2\times 3} + 1/\sqrt{2\times 2\times 3\times 1}\\
&\quad + 1/\sqrt{2\times 2\times 3\times 3} + 1/\sqrt{2\times 3\times 3\times 1}\\
&\quad + 1/\sqrt{1\times 3\times 3\times 2} = 2.593
\end{aligned}\right.$$



Degrees of various vertices of the C—C skeleton of 2,3-dimethyl pentane

$$\left\{\begin{aligned}
{}^1\xi &= 1/\sqrt{1\times 3} + 1/\sqrt{3\times 1} + 1/\sqrt{3\times 3} + 1/\sqrt{3\times 1}\\
&\quad + 1/\sqrt{3\times 2} + 1/\sqrt{2\times 1} = 3.18\\
{}^2\xi &= 1/\sqrt{1\times 3\times 1} + 2/\sqrt{1\times 3\times 3} + 1/\sqrt{3\times 3\times 1}\\
&\quad + 1/\sqrt{3\times 3\times 2} + 1/\sqrt{1\times 3\times 2}\\
&\quad + 1/\sqrt{3\times 2\times 1} = 2.96\\
{}^3\xi &= 1/\sqrt{1\times 3\times 3\times 1} + 1/\sqrt{1\times 3\times 3\times 2}\\
&\quad + 1/\sqrt{1\times 3\times 3\times 1} + 1/\sqrt{1\times 3\times 3\times 2}\\
&\quad + 1/\sqrt{3\times 3\times 2\times 1} + 1/\sqrt{1\times 3\times 2\times 1} = 2.49
\end{aligned}\right.$$

The connectivity parameters of the first degree of a molecule may be assumed to represent a measure of the oscillations of its bond lengths (since it depends on the degree of its closest vertices taken two at a time), and as the bond length remains practically constant with concentration and temperature, ${}^1\xi$ would be independent of temperature and concentration in a binary mixture. In order to understand the physical significance of $^2\xi$, $^3\xi$ and $^4\xi$ etc., we evaluated these parameters for *n*-heptane, 3-methyl hexane, 2,3-dimethyl pentane, *n*-octane, 2,5-dimethyl hexane, 2,2,4-trimethyl pentane, *n*-nonane, 2,3,5-trimethyl hexane, 3,3-dimethyl pentane, benzene, toluene and *o*-, *m*- and *p*-xylenes. It was observed that while $^2\xi$ and $^4\xi$ obscured the effects of branching in isomeric alkanes, it was clearly brought out by $^3\xi$. Thus the $^3\xi$ values for the various isomeric compounds vary in the order *n*-pentane < isopentane; 2-methyl pentane < *n*-hexane < 3-methyl pentane < 2,3-dimethyl butane; *n*-heptane < 3-methyl hexane < 2,3-dimethyl pentane; 2,2,4-trimethyl pentane < 2,5-dimethyl hexane < *n*-octane; *n*-nonane < 2,3,5-trimethyl hexane < 3,3-dimethyl pentane; and *m*-xylene < *p*-xylene < *o*-xylene.

Further, the molar volumes at 293.15 K of these compounds vary in the order isopentane < *n*-pentane; 3-methyl pentane < *n*-hexane < 2,3-dimethylbutane < 2-methyl pentane; 3-methyl < hexane < *n*-heptane < 2-methyl hexane < 2,3-dimethyl pentane; *n*-octane < 2,5-dimethyl hexane < 2,2,4-trimethyl pentane; 3,3-dimethyl pentane < 2,3,5-trimethyl hexane < *n*-nonane; and *o*-xylene < *m*-xylene < *p*-xylene.

The necessary density data were taken from the literature [8—16].

It is thus apparent that within the same isomeric species the molar volume of a molecule varies inversely as its $^3\xi$. Again $1/^3\xi$ for most of the molecules is less than unity, and as branching in a molecule of the same isomeric species would allow only a part of its surface area to interact effectively with the corresponding surface areas of other molecules, $1/^3\xi$ would also represent a measure of the probability that its surface area interacts effectively with the corresponding surface areas of other molecules.

Now in a binary (A + B) mixture, the A—A and B—B contacts in the pure components would be replaced by A—B contacts, so that the change in energy when A and B are mixed is due to the change in the interaction energies of the close neighbouring molecules. The A—B contacts in turn depend on the surface areas of A and B that can come into effective contact, and since $1/^3\xi$ of a molecule is a measure of the probability that its surface area interacts effectively, $1/^3\xi$ is a quantity of considerable interest in the thermodynamics of binary mixtures. Following Huggins [17,18], we assume that if χ_{AB} is the interaction energy per (A—B) contact and if mixing is regarded as perfectly random, H^E can be expressed by [17,18]

$$H^E = x_A \chi_{AB} S_B \quad (4)$$

where x_A is the mole fraction of component A in the mixture and S_B is the effective contacting surface fractions of B defined by

$$S_B = (1 - x_A) V_B/(x_A V_A + (1 - x_A) V_B) \quad (5)$$

Since $1/^3\xi$ of a molecule has been identified with a measure of the probability that its surface area interacts effectively, and as V_B varies inversely with $^3\xi_B$, V_B/V_A in eqn. (5) should be replaced by

$$V_B/V_A = {}^3\xi_A/{}^3\xi_B \quad (6)$$

TABLE 1

Comparison of H^E values as calculated from eqns. (8) and (9) with their corresponding experimental values at two mole fractions of component 1 for various mixtures

System	Temp. (K)	${}^3\xi_1$	${}^3\xi_2$	x_1	H^E (J mole^{-1})			
					Calc. [from eqn. (8)]	Exp.	Calc. [from eqn. (9)]	Ref.
Benzene(1) + chlorobenzene(2)	298.15	1.500	1.500	0.3	−1.8	−2.2	−1.7	19
				0.7	−1.8	−2.5	−1.8	
Benzene(1) + bromobenzene(2)	298.15	1.500	1.500	0.3	29.1	26.3	27.5	19
				0.7	29.1	29.3	29.4	
Benzene(1) + cyclohexane(2)	308.15	1.500	1.500	0.3	669.5	644.0	631.0	20
				0.7	669.5	660.0	683.0	
Benzene(1) + carbon tetrachloride(2)	298.15	1.500	1.000	0.3	88.7	96.3		21
				0.7	104.1	99.2		
Benzene(1) + methylene chloride(2)	298.15	1.500	1.000	0.3	−76.6	−57.0	−75.1	22
				0.7	−65.1	−75.2	−66.0	
Benzene(1) + 1,2-dichloroethane(2)	298.15	1.500	1.000	0.3	50.5	79.0	55.9	23
				0.7	59.3	41.7	53.4	
Benzene(1) + nitromethane(2)	318.15	1.500	1.000	0.3	600.0	752.0		24
				0.7	700.0	642.0		
Benzene(1) + 2-methylpentane	298.15	1.500	0.866	0.3	687.3	742.0	705.9	25
				0.7	852.5	801.3	825.5	
Benzene(1) + 3-methylpentane	298.15	1.500	1.394	0.3	745.1	739.8	708.9	26
				0.7	787.2	802.8	823.4	
Benzene(1) + *n*-hexane	298.15	1.500	0.957	0.3	689.2	706.2	700.9	27
				0.7	822.8	806.0	817.3	
Benzene(1) + 2,2-dimethylbutane(2)	298.15	1.500	0.817	0.3	682.3	733.4	706.3	28
				0.7	864.7	802.6	827.9	
Benzene(1) + 2,3-dimethylbutane(2)	298.15	1.500	1.333	0.3	748.8	743.2	712.6	29
				0.7	785.0	804.2	829.1	

Benzene(1) + *n*-heptane	298.15	1.500	1.207	0.3	751.2	726.2	713.8	30
				0.7	819.2	853.7	868.8	
Benzene(1) + 1-octane	298.15	1.500	1.457	0.3	534.7	481.1		31
				0.7	541.1	617.2		
Benzene(1) + *n*-hexadecane	298.15	1.500	3.457	0.3	1231.2	865.0	849.9	32
				0.7	895.3	1234.0	1311.1	
Toluene(1) + chlorobenzene(2)	298.15	1.894	1.500	0.3	−71.5	−77.4	−76.2	19
				0.7	−71.5	−66.9	−80.2	
Toluene(1) + bromobenzene(2)	298.15	1.894	1.500	0.3	−57.1	−54.4	−60.0	19
				0.7	−62.6	−62.8	−60.3	
Toluene(1) + methylene chloride(2)	298.15	1.894	1.000	0.3	−156.4	−151.7	−194.9	22
				0.7	−200.5	−206.4	−160.0	
Toluene(1) + nitromethane(2)	303.15	1.894	1.000	0.3	990.9	1133.0	1165.3	33
				0.7	1155.9	1114.0	894.4	
Toluene(1) + *n*-heptane	298.15	1.894	1.207	0.3	425.9	438.4	436.1	34
				0.7	508.9	497.1	495.4	
Toluene(1) + *n*-hexadecane(2)	298.15	1.894	3.457	0.3	693.0	538.4	515.5	35
				0.7	548.1	747.3	752.2	
Toluene(1) + hexafluorobenzene(2)	318.15	1.894	1.500	0.3	311.0	288.0		36
				0.7	398.9	400.0		
o-Xylene(1) + chlorobenzene(2)	298.15	2.590	1.500	0.3	−53.9	−55.4	−61.6	37
				0.7	−66.8	−58.0	−57.7	
o-Xylene(1) + bromobenzene(2)	298.15	2.590	1.500	0.3	−56.4	−57.5	−65.6	37
				0.7	−70.0	−58.5	−62.1	
o-Xylene(1) + methylene chloride(2)	298.15	2.590	1.000	0.3	−170.2	−165.7	−228.1	22
				0.7	−243.5	−238.1	−178.6	
o-Xylene(1) + nitromethane(2)	303.15	2.590	1.000	0.3	999.0	1396.0	1389.1	33
				0.7	1429.0	1194.0	1019.6	
m-Xylene(1) + chlorobenzene(2)	298.15	2.197	1.500	0.3	−79.0	−72.5	−96.0	37
				0.7	−92.0	−71.8	−80.0	
m-Xylene(1) + bromobenzene(2)	298.15	2.197	1.500	0.3	−123.4	−138.0	−137.0	37
				0.7	−143.6	−116.0	−128.7	

TABLE 1 (*continued*)

System	Temp. (K)	${}^3\xi_1$	${}^3\xi_2$	x_1	H^E (J mole^{-1})			
					Calc. [from eqn. (8)]	Exp.	Calc. [from eqn. (9)]	Ref.
m-Xylene(1) + methylene chloride(2)	298.15	2.197	1.000	0.3	−152.8	−131.5	−200.8	22
				0.7	−206.7	−214.7	−156.2	
m-Xylene(1) + nitromethane(2)	303.15	2.197	1.000	0.3	1013.2	1278.0	1384.2	33
				0.7	1370.4	1228.0	1009.5	
p-Xylene(1) + chlorobenzene(2)	298.15	2.305	1.500	0.3	−56.5	−60.2	63.8	37
				0.7	−67.0	−56.5	59.1	
p-Xylene(1) + bromobenzene(2)	298.15	2.305	1.500	0.3	−66.9	−79.4	−79.8	37
				0.7	−84.5	−71.4	−74.8	
p-Xylene(1) + methylene chloride(2)	298.15	2.305	1.000	0.3	−182.1	−165.9	−241.1	22
				0.7	−250.4	−251.9	−187.3	
p-Xylene(1) + nitromethane(2)	303.15	2.305	1.000	0.3	1015.3	1358.0	1395.3	33
				0.7	1396.6	1149.0	1016.4	
Ethylbenzene(1) + pentafluorobenzene(2)	308.15	2.348	1.500	0.3	−110.3	−150.0		38
				0.7	−131.9	−160.0		
n-Propylbenzene(1) + pentafluorobenzene(2)	328.15	2.337	1.500	0.3	−12.9	4.7		38
				0.7	−10.8	−26.0		
Cyclohexane(1) + 2-methylpentane(2)	298.15	1.500	0.866	0.3	152.4	150.8	162.7	39
				0.7	189.1	192.0	176.2	
Cyclohexane(1) + 3-methylpentane(2)	298.15	1.500	1.105	0.3	144.1	143.7	147.5	40
				0.7	162.7	167.2	158.6	
Cyclohexane(1) + *n*-hexane(2)	288.15	1.500	0.957	0.3	176.0	175.0	184.5	41
				0.7	210.1	220.1	199.0	
Cyclohexane(1) + 2,2-dimethylbutane(2)	298.15	1.500	1.062	0.3	119.5	116.3	122.9	42
				0.7	137.1	118.0	133.4	
				0.3	100.6	110.0	97.0	43
				0.7	110.0	100.7	111.8	

Cyclohexane(1) + 2,3-dimethylbutane(2)	298.15	1.500	1.403	0.3	128.1	133.9	131.6	44
				0.7	134.2	134.2	141.8	
Cyclohexane(1) + *n*-heptane(2)	298.15	1.500	1.207	0.3	211.3	183.4	198.7	45
				0.7	193.8	230.1	224.2	
Cyclohexane(1) + *n*-octane(2)	298.15	1.500	1.457	0.3	219.6	195.2		46
				0.7	217.0	250.3		
Cyclohexane(1) + 2,2,4-trimethylpentane(2)	298.15	1.500	1.021	0.3	144.7	150.4	143.8	47
				0.7	169.8	164.7	170.0	
Cyclohexane(1) + 1-octene(2)	298.15	1.500	1.457	0.3	188.1	185.6		48
				0.7	190.3	240.4		
Cyclohexane(1) + *m*-dodecane(2)	298.15	1.500	2.457	0.3	334.6	258.2		49
				0.7	347.5	362.0		
Cyclohexane(1) + *n*-hexadecane(2)	298.15	1.500	3.457	0.3	500.8	376.0	350.2	50
				0.7	362.2	497.4	508.1	
Cyclohexane(1) + hexafluorobenzene(2)	318.15	1.500	1.500	0.3	1411.2	1360.0		51
				0.7	1411.2	1501.0		
Methylcyclohexane(1) + *n*-heptane(2)	298.15	1.894	1.207	0.3	31.4	26.3	27.8	52
				0.7	37.9	30.9	29.3	
Cyclopentane(1) + 2,3-dimethylbutane(2)	298.15	1.250	1.403	0.3	−1.53	−2.8	−1.42	53
				0.7	−1.49	−0.1	−1.62	
Cyclopentane(1) + tetrachloroethane(2)	298.15	1.250	1.000	0.3	169.2	199.0	179.3	54
				0.7	147.5	194.0	185.4	
Cycloheptane(1) + 2,3-dimethylbutane(2)	298.15	1.250	1.403	0.3	129.9	131.1		55
				0.7	144.7	140.5		
n-Heptane(1) + *n*-hexadecane(2)	298.15	1.207	3.457	0.3	43.4	35.8	30.9	56
				0.7	29.4	32.7	40.4	
Cyclo-octane(1) + 2,3-dimethylbutane(2)	298.15	2.000	1.333	0.3	136.9	158.1		57
				0.7	160.7	151.4		
Cyclo-octane(1) + cyclopentane(2)	308.32	2.000	1.250	0.3	−39.2	−48.0		58
				0.7	−47.2	−36.2		
	298.15			0.3	−31.1	−40.6	−40.6	59
				0.7	−37.3	−37.3	−25.3	

TABLE 1 (*continued*)

System	Temp. (K)	$^{3}\xi_1$	$^{3}\xi_2$	x_1	H^E (J mole^{-1})			
					Calc. [from eqn. (8)]	Exp.	Calc. [from eqn. (9)]	Ref.
n-Octane(1) + 2,2,4-trimethylpentane	298.15	1.457	1.021	0.3	20.0	21.4	21.4	60
				0.7	23.0	21.4	21.4	
1-Octane(1) + *n*-hexadecane(2)	298.15	1.457	3.457	0.3	131.8	139.7		61
				0.7	139.7	136.3		
n-Hexadecane(1) + 2,2,4-trimethylpentane(2)	298.15	3.457	1.021	0.3	160.4	202.4	220.1	62
				0.7	249.7	190.4	175.9	
Carbon tetrachloride(1) + nitromethane(2)	318.15	1.000	1.000	0.3	1142	1160.0		63
				0.7	1142	1240.0		

Hence

$$S_B = (1 - x_A)(^3\xi_A/^3\xi_B)/[x_A + (1 - x_A)(^3\xi_A/^3\xi_B)] \tag{7}$$

and

$$H^E = x_A(1 - x_A)\,\chi_{AB}(^3\xi_A/^3\xi_B)/[x_A + (1 - x_A)(^3\xi_A/^3\xi_B)] \tag{8}$$

Evaluation of H^E from eqn. (8) requires, in addition to a knowledge of χ_{AB}, $^3\xi$ parameters of the A and B components of the binary mixture. The $^3\xi$ of components containing four or more carbon atoms can be readily determined from eqn. (3), but the same cannot be said of small molecules that contain two or less than two skeletal carbon atoms. Since these small molecules cannot fold themselves, the whole of their surface areas can come into effective (A—B) contact and hence for these small molecules we have assumed $^3\xi = 1$. The only unknown parameter χ_{AB} in eqn. (8), which cannot be determined by independent methods, can be evaluated from the H^E values at any composition (preferably between 0.2 and 0.8). In the present investigation we have evaluated it from the H^E data for an equimolar mixture. This χ_{AB} value was then used to calculate H^E values for the mixture at $x_A = 0.3$ and 0.7. The H^E values calculated in this manner for various mixtures are recorded in Table 1 and are also compared with the corresponding literature values [19—63]. Reasonably good agreement between the calculated and experimental H^E values lends credence to our basic assumption that $1/^3\xi$ of a molecule is a measure of the probability of its surface area that can come into effective A···B interaction and that for small molecules $^3\xi = 1$.

In order to further check as to how far the H^E values as calculated from eqn. (8) compare with those evaluated from

$$H^E = x_A\,(1 - x_A)(V_B/V_A)/[x_A + (1 - x_A)(V_B/V_A)] \tag{9}$$

we computed H^E values from both of these equations and compared them with their corresponding literature values [19—63] (see Table 1). An examination of Table 1 reveals that the H^E values calculated in both ways compare reasonably well with the literature values for most of the binary mixtures; eqn. (8) being better in some cases. One important limitation of eqn. (9), however, is that it cannot be employed if the relevant density data of the components of the binary mixtures are not available (e.g. cyclo-octane, 1-octene etc.). No such limitations are inherent in eqn. (8); it requires H^E datum at one composition (preferably $0.3 < x_1 < 0.7$) only. One apparent weakness of eqn. (8) is that it requires H^E to be either positive or negative. This approach would thus fail for those mixtures where H^E changes sign with composition.

It would now be interesting to see if this approach can also be used to predict V^E for binary mixtures of non-electrolytes. We have already pointed out that the molar volumes of an isomeric molecule varies inversely as its $^3\xi$. Further, for *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane benzene, toluene and xylenes, etc., both the $^3\xi$ and molar volumes of the molecules vary in the order:

n-nonane > *n*-octane > *n*-heptane > *n*-hexane > *n*-pentane; and xylene > toluene > benzene.

This suggests that the molar volume of compound in addition to its dependence on $1/{}^3\xi$ should also depend directly on the length of its C—C chain, i.e. on its ${}^1\xi$ value. Consequently, the molar volume of a compound should vary inversely as its ${}^3\xi$ and directly as its ${}^1\xi$ values.

Kier and Hall [64] represented the molar volumes of alkanes in terms of their ${}^3\xi$ and ${}^1\xi$ connectivity parameters by

$$V = \alpha/{}^3\xi + \beta{}^1\xi + \gamma \tag{10}$$

where α, β and γ are constants. It was observed that the molar volumes at 293.15 K of benzene, toluene, *o*-, *m*- and *p*-xylenes could be represented by

$$V\,(\text{cm}^3\ \text{mole}^{-1}) = -9.555/{}^3\xi + 40.8\ {}^1\xi - 27.3 \tag{11}$$

The parameters α, β and γ of eqn. 10 were evaluated from the molar volumes at 293.15 K of benzene, toluene and *p*-xylene. These were then used to calculate molar volumes of *m*-xylene and *o*-xylene. The calculated and experimental V values of *m*-xylene and *o*-xylene are 122.9 (122.7) and 124.2 (123.1) cm^3 mole^{-1}, respectively; the quantities in parentheses are their experimental molar volumes.

Again, while the molar volumes at 293.15 K of monobromoalkanes containing five or more skeletal carbon atoms are reasonably well represented by

$$V\,(\text{cm}^3\ \text{mole}^{-1}) = -9.555/{}^3\xi + 49.0\ {}^1\xi - 2.72 \tag{12}$$

(monobromoalkanes)

those of monochloro- and monofluoroalkanes can be well described by

$$V\,(\text{cm}^3\ \text{mole}^{-1}) = -9.555/{}^3\xi + 70.0\ {}^1\xi - 2.72 \tag{13}$$

(monochloroalkanes)

and

$$V\,(\text{cm}^3\ \text{mole}^{-1}) = -9.555/{}^3\xi + 45.0\ {}^1\xi - 2.72 \tag{14}$$

(monofluoroalkanes)

The calculated and experimental V values for some of the compounds at 293.15 K are: *n*-heptyl bromides 156.6 (157.0); isoamyl bromide 122.1 (125.5); *n*-octyl bromide 180.5 (176.4); *sec.* butyl chloride 107 (106); *tert.* butyl chloride 109.0 (109.9); *n*-hexylfluoride 118.5 (117.5); *n*-heptyl fluoride 145.0 (147.0); and *n*-oxtyl fluoride 165.1 (164.0) cm^3 mole^{-1}, respectively. The quantities in parentheses are their experimental molar volumes at 293.15 K; the necessary data were taken from the literature [65—69]. On the other hand, the molar volumes of alkanes could also be well represented by

$$V\,(\text{cm}^3\ \text{mole}^{-1}) = -9.555/{}^3\xi + 56\ {}^1\xi - 2.72 \tag{15}$$

(alkanes)

The calculated and experimental V values for some of the alkanes are: 2,2-dimethyl butane 131.6 (132.5); *n*-pentane 119 (115); 3-methyl pentane 133 (129.5); 2,2-dimethyl pentane 155.9 (149.7); and 2-methyl pentane

138.4 (141.6) $\mathrm{cm^3\ mole^{-1}}$, respectively. For small molecules for which it is not possible to evaluate ${}^3\xi$ and ${}^1\xi$ by eqns. (1) and (3) it was observed that their molar volumes at 293.15 K can also be expressed by

$$\begin{aligned} V\,(\mathrm{cm^3\ mole^{-1}}) &= -9.555/{}^3\xi + \text{const.} + \text{const.} \\ &= -9.555 + \beta'\,{}^1\xi + \gamma' \end{aligned} \tag{16}$$

Consequently, we assumed that the molar volumes of components A and B of the (A + B) mixture can be represented at any temperature by

$$V_A = \alpha/{}^3\xi_A + \beta_A\,{}^1\xi_A + \gamma_A \tag{17}$$

$$V_B = \alpha/{}^3\xi_B + \beta_B\,{}^1\xi_B + \gamma_B \tag{18}$$

The ideal molar volume of the mixture x_AA + (1 $-$ x_A) B would then be

$$\begin{aligned} V_{\text{ideal}} = \Sigma\, x_A V_A = x_A\alpha/{}^3\xi_A + x_A\beta_A\,{}^1\xi_A + x_A\gamma_A + \alpha x_B/{}^3\xi_B \\ + x_B\beta_B\,{}^1\xi_B + x_B\gamma_B \end{aligned} \tag{19}$$

The molar volume of the mixture would also be expressed by an expression analogous to (9), i.e.

$$V_m = \alpha/{}^3\xi_m + \beta_m\,{}^1\xi_m + \gamma_m \tag{20}$$

We now assume that

$${}^3\xi_m = x_A\,{}^3\xi_A + (1 - x_A)\,{}^3\xi_B \tag{21}$$

$$\beta_m\,{}^1\xi_m \approx x_A\beta_A\,{}^1\xi_A + (1 - x_A)\,\beta_B\,{}^1\xi_B \tag{22}$$

and

$$\gamma_m = x_A\gamma_A + x_B\gamma_B \tag{23}$$

Therefore, molar excess volume

$$\begin{aligned} V^E &= V_m - \Sigma\, x_A V_B \\ &= \frac{\alpha}{x_A\,{}^3\xi_A + (1 - x_A)\,{}^3\xi_B} - \frac{x_A\alpha}{{}^3\xi_A} - \frac{(1 - x_A)\,\alpha}{{}^3\xi_B} \end{aligned} \tag{24}$$

The only unknown parameter, α, in this expression can be evaluated from the V^E values at any composition. However, in the present investigations it was evaluated from the V^E data for an equimolar mixture. V^E values calculated in this manner for the various mixtures at $x_1 = 0.3$ and 0.7 are recorded in Table 2 and are also compared with the corresponding literature values [19,37,44,53—57,70—79].

Examination of Table 2 reveals that this approach predicts accurately the V^E data for most of the various binary mixtures. An apparent weakness of this approach is that for mixtures for which ${}^3\xi_A = {}^3\xi_B$, V^E according to expression (24) should be zero. However, this is not the case, as is clearly brought about the V^E data for benzene + cyclohexane mixtures. This approach, however, predicts that V^E for benzene + chlorobenzene and

TABLE 2

Comparison of V^E values as calculated from eqn. (23) with the corresponding experimental values for two mole fractions of component 1 for various binding mixtures

System	Temp. (K)	$^3\xi_1$	$^3\xi_2$	x_1	V^E (cm^3 mole^{-1}) Calc.	Exp.	Ref.
Benzene(1) + *n*-pentane(2)	293.15	1.500	0.707	0.3	0.093	0.100	70
				0.7	0.123	0.116	
Benzene(1) + methylene chloride(2)	298.15	1.500	1.000	0.3	0.237	0.222	71
				0.7	0.206	0.226	
Benzene(1) + toluene(2)	298.15	1.500	1.894	0.3	0.064	0.073	19
				0.7	0.079	0.070	
Benzene(1) + chlorobenzene(2)	298.15	1.500	1.500	0.3	0.000	0.015	19
				0.7	0.000	0.016	
	313.15			0.3	0.000	0.000	72
				0.7	0.000	0.000	
Benzene(1) + bromobenzene(2)	298.15	1.500	1.500	0.3	0.000	−0.003	19
				0.7	0.000	−0.003	
Benzene(1) + cyclohexane(2)	298.15	1.500	1.500	0.3	0.000	0.553	19
				0.7	0.000	0.570	
Benzene(1) + 1,2-dichloroethane(2)	298.15	1.500	1.000	0.3	0.200	0.152	73
				0.7	0.175	0.191	
Benzene(1) + nitromethane(2)	303.15	1.500	1.000	0.3	0.188	0.199	74
				0.7	0.165	0.138	
Benzene(1) + carbon tetrachloride(2)	298.15	1.500	1.000	0.3	0.153	0.142	75
				0.7	0.130	0.140	
Toluene(1) + methylene chloride(2)	298.15	1.894	1.000	0.3	0.154	0.161	71
				0.7	0.130	0.109	
Toluene(1) + chlorobenzene(2)	298.15	1.894	1.000	0.3	−0.097	−0.088	19
				0.7	−0.091	−0.083	
Toluene(1) + bromobenzene(2)	298.15	1.894	1.000	0.3	−0.105	−0.100	19
				0.7	-0.097	−0.097	

Toluene(1) + 1,2-dichloroethane(2)	298.15	1.894	1.000	0.3	0.152	0.155	73
				0.7	0.121	0.120	
Toluene(1) + nitromethane(2)	303.15	1.894	1.000	0.3	0.151	0.157	74
				0.7	0.119	0.116	
Toluene(1) + *n*-pentane(2)	293.15	1.894	0.707	0.3	−0.220	−0.274	70
				0.7	−0.226	−0.290	
Toluene(1) + hexafluorobenzene(2)	313.15	1.894	1.500	0.3	0.363	0.288	76
				0.7	0.343	0.400	
o-Xylene(1) + chlorobenzene(2)	298.15	2.590	1.500	0.3	−0.020	−0.021	37
				0.7	−0.016	−0.025	
o-Xylene(1) + bromobenzene(2)	298.15	2.590	1.500	0.3	−0.048	−0.042	37
				0.7	−0.038	−0.043	
o-Xylene(1) + methylene chloride	298.15	2.590	1.000	0.3	0.224	0.210	71
				0.7	0.157	0.162	
o-Xylene(1) + 1,2-dichloroethane	298.15	2.590	1.000	0.3	0.208	0.214	73
				0.7	0.297	0.270	
o-Xylene(1) + nitromethane	303.15	2.590	1.000	0.3	0.267	0.278	74
				0.7	0.174	0.170	
o-Xylene(1) + *n*-pentane(2)	293.15	2.590	0.707	0.3	−0.460	−0.550	70
				0.7	−0.734	−0.584	
m-Xylene(1) + bromobenzene(2)	298.15	2.197	1.500	0.3	−0.072	−0.066	37
				0.7	−0.064	−0.071	
m-Xylene(1) + methylene chloride	298.15	2.197	1.000	0.3	0.335	0.318	71
				0.7	0.249	0.242	
m-Xylene(1) + 1,2-dichloroethane(2)	298.15	2.197	1.000	0.3	0.333	0.328	73
				0.7	0.262	0.256	
m-Xylene(1) + nitromethane(2)	303.15	2.197	1.000	0.3	0.270	0.263	74
				0.7	0.200	0.215	
m-Xylene(1) + *n*-pentane(2)	293.15	2.197	0.707	0.3	−0.356	−0.433	70
				0.7	−0.540	−0.457	
p-Xylene(1) + chlorobenzene(2)	298.15	2.305	1.500	0.3	−0.065	−0.060	37
				0.7	−0.053	−0.068	

TABLE 2 (*continued*)

System	Temp. (K)	$^3\xi_1$	$^3\xi_2$	x_1	V^E (cm^3 mole^{-1}) Calc.	Exp.	Ref.
p-Xylene(1) + bromobenzene(2)	298.15	2.305	1.500	0.3	−0.112	−0.103	37
				0.7	−0.092	−0.103	
p-Xylene(1) + methylene chloride	298.15	2.305	1.000	0.3	0.230	0.227	71
				0.7	0.167	0.161	
p-Xylene(1) + 1,2-dichloroethane(2)	298.15	2.305	1.000	0.3	0.251	0.249	73
				0.7	0.183	0.175	
p-Xylene(1) + nitromethane(2)	303.15	2.305	1.000	0.3	0.223	0.236	74
				0.7	0.164	0.145	
p-Xylene(1) + *n*-pentane(2)	293.15	2.305	0.707	0.3	−0.368	−0.440	70
				0.7	−0.566	−0.497	
p-Xylene + hexafluorobenzene(2)	313.15	2.305	1.500	0.3	0.074	0.040	77
				0.7	0.065	0.140	
Cyclohexane(1) + *n*-pentane(2)	293.15	1.500	0.707	0.3	−0.096	−0.100	70
				0.7	−0.128	−0.140	
Cyclohexane(1) + carbon tetrachloride(2)	303.15	1.500	1.000	0.3	0.150	0.142	78
				0.7	0.134	0.140	
Isopropylbenzene(1) + hexafluorobenzene(2)	313.15	2.305	1.500	0.3	0.491	0.412	79
				0.7	0.391	0.453	
Methylchloride(1) + cyclohexane(2)	298.15	1.000	1.500	0.3	0.739	0.812	71
				0.7	0.853	0.805	
Cyclopentane(1) + 2,3-dimethylpentane	288.15	1.250	1.333	0.3	−0.225	−0.226	53
				0.7	−0.227	−0.226	
Cyclohexane(1) + 2,3-dimethylpentane	288.15	1.500	1.333	0.3	−0.082	−0.083	44
				0.7	−0.085	−0.090	
Cycloheptane(1) + 2,3-dimethylpentane(2)	288.15	1.750	1.333	0.3	−0.349	−0.352	55
				0.7	−0.307	−0.302	
Cyclo-octane(1) + 2,3-dimethylpentane(2)	288.15	2.000	1.333	0.3	−0.569	−0.500	57
				0.7	−0.485	−0.550	

benzene + bromobenzene mixtures should be zero. The experimental V^E values partially support this conclusion.

The present approach thus predicts reasonably well the H^E and V^E data for most of the binary mixtures.

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