Thermochimica Acta, 52 (1982) 87–102
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

TOPOLOGICAL ASPECT OF THE EXCESS ENTHALPIES OF BINARY MIXTURES OF NON-ELECTROLYTES

PREM P. SINGH *, RAM K. NIGAM, VINOD K SHARMA, SATYA P SHARMA and KRISHAN C SINGH

Department of Chemistry, Maharshi Dayanand University, Rohtak-124 001, Haryana (India)

(Received 4 June 1981)

ABSTRACT

An approach based on the graph theory has been evolved to predict molar excess enthalpies H^E of binary mixtures of non-electrolytes The calculated H^E values compare reasonably well with the corresponding experimental values The approach has also been successful in predicting H^E data for binary mixtures at other temperatures from H^E data at two mole fractions at one temperature only

INTRODUCTION

Excess enthalpies, H^E, of binary mixtures of non-electrolytes are due essentially to the replacement of the i–i or j–j contacts in the pure i and j components by the i–j contacts in the mixture. The number of these i–j interactions depends on the surface areas of the i and j components that come into effective i–j interaction so that branching in a molecule would allow only a part of its surface area to come into effective i–j interaction. Thus, H^E would be influenced by the topology of the molecules that undergo these interactions. Since the mathematical discipline of graph theory deals with the topology of molecules, it should be able to predict excess enthalpies of binary mixtures of non-electrolytes. The present paper is concerned with an approach, based on the graph theory, to predict H^E for binary mixtures as a function of temperature and composition from their H^E data at two mole fractions at any one temperature alone.

THEORETICAL ASPECTS OF THE APPROACH AND THE RESULTS

According to graph theory, if atoms in the structural formula of a compound are represented by letters and the bonds joining them by lines, the resulting graph gives the totality of information contained in that molecule [1–4]. Thus the graph

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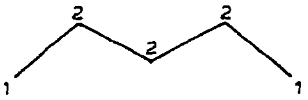
* To whom correspondence should be addressed

theoretical description of (say) *n*-pentane would be



in which 2, 3 and 4 vertices would be of the second degree (since in each case each vertex is directly linked to two nearest vertices) while those at positions 1 and 5 would be of the first degree. Consequently, 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 of the first, $^1\xi$, second $^2\xi$, and third degrees, $^3\xi$, are expressed by

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

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

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

The connectivity parameter of the first degree of a molecule depends on the degrees of its closest vertices and so it may be identified with a measure of the oscillations of its bond length. Since the bond length remains practically constant with temperature and composition, $^1\xi$ may be assumed to be independent of both. In order to understand the relationship between $^2\xi$, $^3\xi$ etc. parameters, on the one hand, and the effect of branching on the molar volumes of components, on the other, we evaluated these parameters for a number of non-electrolytes and it was observed that while $^2\xi$ and $^4\xi$ etc. obscured the effect of branching on the molar volumes of isomeric compounds, the same was clearly brought out by $^3\xi$ values. Thus while the $^4\xi$ values of 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

their molar volumes at 293.15 K vary in the order

isopentane < *n*-pentane;
3-methyl pentane < *n*-hexane < 2,3-dimethyl butane < 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 [5–13]). It is apparent that within the same isomeric species, the molar volumes of most of the compounds vary inversely as its $^3\xi$. $^3\xi$ of a molecule may, therefore, be assumed to measure its tendency to fold itself. Again the $1/^3\xi$ value for most of the compounds containing four or more skeletal carbon atoms was found to be 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 in the i–j interaction, $1/{}^3\xi$ may also be identified to measure the probability that the surface area of a molecule interacts effectively with the surface area of another molecule. For compounds belonging to different isomeric species, the molar volume should also depend on ${}^1\xi$. Actually, Kier and Hall [14] express the molar volumes of alkanes by

$$V=\frac{\alpha}{{}^3\xi}+\beta{}^1\xi+\gamma \tag{4}$$

where α, β and γ are constants. Since the number of i–j contacts is determined primarily by that part of the molar volumes of i and j that determines their tendency to fold themselves, the $1/{}^3\xi$ value of a compound is a quantity of considerable importance in the thermodynamics of binary mixtures.

Now in a binary mixture of non-electrolytes, the i–i and j–j contacts in the pure i–j components are replaced by i–j contacts in the mixture so that the excess enthalpy is due essentially to a change in the interaction energy of the neighbouring molecules. Following Huggins [15,16], we assume that if χ_{ij} is the interaction energy per i–j contact and if mixing is assumed to be perfectly random, H^E can be expressed by

$$H^E=x_i x_j \chi_{ij} V_j/(x_i V_i+x_j V_j) \tag{5}$$

where x_i is the mole fraction of i in the mixture and V_i and V_j are the molar volumes of pure i and j. Since the number of effective i–j contacts in a (i+j) mixture is determined primarily by that part of the molar volumes of i and j that determine their tendency to fold themselves

$$V_j/V_i \propto \left[\left(\alpha/{}^3\xi_j\right)/\left(\alpha/{}^3\xi_i\right)\right] \text{ (where } \alpha \text{ is a constant)}$$

or

$$V_j/V_i=k\left({}^3\xi_i/{}^3\xi_j\right) \text{ (where } k \text{ is a constant)}$$

Hence eqn. (5) reduces to

$$H^E=x_i x_j \chi_{ij} k\left({}^3\xi_i/{}^3\xi_j\right)/\left[x_i+x_j\left({}^3\xi_i/{}^3\xi_j\right)\right] \tag{6}$$

Evaluation of H^E from eqn. (6) requires in addition to a knowledge of χ_{ij} and k, ${}^3\xi$ parameters of the pure components. Now while the ${}^3\xi$ value for a molecule containing four or more skeletal carbon atoms can be readily determined from eqn. (3) (see Appendix) the same is not possible for small molecules that contain one or two skeletal carbon atoms. Since these small molecules cannot fold themselves, the whole of their surface areas can take part in effective i–j contacts and hence for these molecules we have taken ${}^3\xi=1$. The only unknown parameters, χ_{ij} and k, in eqn. (6) can be evaluated if H^E data for the mixture at two mole fractions are known. In the present investigations, we have evaluated these parameters from H^E data at one temperature and two mole fractions close to $x_i=0.5$. These values of χ_{ij} and k were then utilized to calculate H^E data for the mixture at $x_i=0.1$, 0.3, 0.7 and 0.9. These values are recorded in Table 1 and are also compared with their corre-

TABLE I

Comparison of H^E values (in J mole^{-1}) as calculated from eqn (6) from the H^E data at two mole fractions x_1 of component 1, with their corresponding experimental values at different mole fractions of component 1 for various mixtures

Mixture	Temp (K)	x_1	H^E	x_1				Ref
				0.1	0.3	0.7	0.9	
Cyclopentane (1)+ carbon tetrachloride (2)	288.15	0.4798, 0.4486	Calc	32.7	74.2	70.3	29.3	17
			Expt	32.0	74.1	71.0	29.0	
Cyclopentane (1)+ 2,3-dimethyl butane (2)	288.15	0.4346, 0.409	Calc	−4.4	−6.3	−4.5	−1.6	18
			Expt	−3.6	−6.9	−4.3	−1.2	
Cyclohexane (1)+ carbon tetrachloride (2)	298.15	0.4981, 0.4727	Calc	65.0	148.1	141.4	59.3	19
			Expt	66.0	143.4	139.0	59.0	
Cyclohexane (1)+ 2,3-dimethyl butane (2)	288.15	0.5083, 0.4753	Calc	54.6	129.5	134.2	58.6	20
			Expt	53.8	128.7	133.5	56.8	
Cyclohexane (1)+ 2-methyl pentane	298.15	0.497, 0.426	Calc	60.8	154.5	187.6	101.9	21
			Expt	61.1	150.3	190.8	95.9	
Cyclohexane (1)+ 3-methyl pentane	298.15	0.4797, 0.4420	Calc	59.6	145.7	160.8	72.7	22
			Expt	59.1	143.7	166.7	78.3	
Cyclohexane (1)+ 2,2-dimethyl butane	298.15	0.4952, 0.4500	Calc	55.3	125.4	118.9	49.6	23
			Expt	54.6	130.9	116.3	42.1	
Cyclohexane (1)+ 2,3-dimethyl butane	298.15	0.5112, 0.4410	Calc	58.7	136.7	136.3	58.3	24
			Expt	58.4	135.1	139.6	60.0	
Cyclohexane (1)+ *n*-hexane	298.15	0.4906, 0.4568	Calc	63.3	188.5	205.3	101.1	25
			Expt	61.3	160.9	210.3	102.6	
Cyclohexane (1)+ *n*-heptane	298.15	0.5360, 0.4640	Calc	71.5	183.3	228.4	111.6	26
			Expt	68.0	178.0	228.1	112.0	
Cyclohexane (1)+ 2,2,4-trimethyl pentane (2)	298.15	0.5441, 0.4871	Calc	55.6	139.8	165.6	78.2	27
			Expt	58.0	142.0	160.0	70.0	
Cyclohexane (1)+ *n*-octane	298.15	0.5061, 0.4040	Calc	73.2	191.4	252.0	128.3	28
			Expt.	80.2	195.2	250.3	127.4	

Cyclohexane (1)+ *n*-dodecane (2)	298.15	0.488, 0.385	Calc	94.1	254.2	371.9	207.4	29
			Expt	100.2	258.2	361.9	189.2	
Cyclohexane (1)+ *n*-hexadecane (2)	298.15	0.5237, 0.4380	Calc	136.5	361.1	493.2	258.7	30
			Expt	147.7	360.2	507.6	274.0	
		0.514, 0.6134	Calc	142.0	371.8	493.2	251.7	31
			Expt	140.0	360.0	475.0	260.0	
Cyclohexane (1)+ 1,2,4-trimethyl benzene (2)	298.15	0.4762, 0.3937	Calc	193.6	484.3	566.2	265.0	32
			Expt	186.6	474.7	593.7	288.6	
Cyclohexane (1)+ 1,3,5-trimethyl benzene (2)	298.15	0.5000, 0.4373	Calc	290.9	583.9	456.3	176.3	33
			Expt	187.8	461.6	586.2	294.5	
Methyl cyclohexane (1)+ *n*-heptane (2)	298.15	0.486, 0.415	Calc	10.2	26.3	33.2	16.4	34
			Expt	9.8	26.0	29.9	14.0	
n-Heptane (1)+ *n*-hexadecane (2)	323.15	0.487, 0.420	Calc	14.2	34.3	37.1	16.6	35
			Expt	17.0	37.1	32.0	18.3	
n-Octane (1)+ 2,2,4-trimethyl pentane (2)	298.15	0.434, 0.367	Calc	9.0	21.4	22.1	9.7	36
			Expt	10.1	24.3	20.0	8.0	
1-Octane (1)+ cyclohexane (2)	298.15	0.4589, 0.5307	Calc	71.0	184.7	239.5	120.5	37
			Expt	100.0	235.0	188.0	75.0	
1-Octane (1)+ *n*-heptane (2)	298.15	0.4200, 0.3500	Calc	17.0	36.1	30.7	12.2	38
			Expt	15.0	35.0	32.1	15.0	
1-Octane (1)+ *n*-hexadecane (2)	298.15	0.5212, 0.4201	Calc	49.9	125.5	148.5	70.1	39
			Expt	50.0	130.0	140.0	67.2	
Cycloheptane (1)+ 2,3-dimethyl pentane (2)	298.15	0.488, 0.517	Calc	56.7	136.5	145.8	64.7	40
			Expt	56.9	136.2	146.9	66.1	
Cyclooctane (1)+ cyclopentane (2)	298.15	0.4912, 0.4686	Calc	−20.4	−39.8	−30.0	−11.5	41
			Expt	−19.2	−40.7	−24.8	−5.6	
Cyclooctane (1)+ 2,3-dimethyl butane (2)	288.15	0.493, 0.462	Calc	74.2	163.4	147.0	60.0	42
			Expt	71.0	160.1	151.4	63.5	
n-Hexane (1)+ *n*-hexadecane (2)	298.15	0.5000, 0.4916	Calc	33.9	86.6	106.6	51.6	43
			Expt	47.3	94.8	95.1	34.7	

TABLE I (continued)

Mixture	Temp (K)	x_1	H^E	x_1 0.1	0.3	0.7	0.9	Ref
2-Methyl pentane (1) +	298.15	0.4950, 0.4460	Calc	62.0	149.6	160.6	71.5	44
n-hexadecane (2)			Expt	66.2	154.5	154.5	66.2	
3-Methyl pentane (1) +	298.15	0.5000, 0.4650	Calc	46.7	137.7	149.9	67.2	45
n-hexadecane (2)			Expt	60.3	142.0	145.1	62.8	
2,2-Dimethyl butane (1) +	298.15	0.5096, 0.4940	Calc	113.0	225.1	174.1	67.1	46
n-hexadecane (2)			Expt	81.3	190.3	207.1	95.2	
2,3-Dimethyl butane (1) +	298.15	0.4918, 0.4500	Calc	81.2	170.4	141.8	56.1	47
n-hexadecane (2)			Expt	64.9	154.2	159.9	69.8	
Tetrachloroethane (1) +	298.15	0.5000, 0.4645	Calc	83.9	197.0	199.3	95.8	48
cyclopentane (2)			Expt	80.3	193.5	198.5	94.0	
Carbon tetrachloride (1) +	298.15	0.5066, 0.4712	Calc	108.2	270.9	317.4	148.8	49
n-heptane (2)			Expt	115.9	176.1	318.7	152.4	
Carbon tetrachloride (1) +	298.15	0.5000, 0.4816	Calc	125.5	312.5	361.3	168.0	50
n-nonane (2)			Expt	134.1	313.7	377.0	188.4	
Carbon tetrachloride (1) +	298.15	0.5023, 0.4613	Calc	138.9	351.7	424.1	202.6	51
n-dodecane (2)			Expt	159.2	365.8	431.8	216.2	
Benzene (1) +	298.15	0.4932, 0.4635	Calc	40.5	95.8	98.4	42.8	52
carbon tetrachloride (2)			Expt	39.2	96.6	99.1	39.1	
Benzene (1) +	298.15	0.4752, 0.4129	Calc	−23.6	−62.0	−82.1	−41.9	53
methylene chloride (2)			Expt	−15.6	−57.1	−75.1	−31.1	
Benzene (1) +	298.15	0.500, 0.486	Calc	365.1	650.0	745.0	300.0	54
n-hexane (2)			Expt	288.8	713.6	794.0	357.0	
Benzene (1) +	298.15	0.4999, 0.4778	Calc	277.3	695.7	840.0	402.2	55
2-methylpentane (2)			Expt	310.8	733.4	812.6	378.7	
Benzene (1) +	298.15	0.5212, 0.4700	Calc	280.6	828.2	802.4	390.1	56
3-methylpentane (2)			Expt	316.0	803.0	743.0	370.5	

Benzene (1)+ 2,2-dimethylbutane (2)	298.15	0.510, 0.477	Calc Expt	320.5 318.5	773.8 799.7	756.3 743.4	335.5 366.7	57
Benzene (1)+ 2,3-dimethylbutane (2)	298.15	0.4863, 0.470	Calc Expt	296.9 314.7	817.1 804.2	729.8 743.2	374.1 373.6	58
Benzene (1)+ cyclohexane (2)	298.15	0.4916, 0.458	Calc Expt	302.6 283.3	687.7 654.2	653.9 670.2	273.5 319.4	59
Benzene (1)+ toluene (2)	298.15	0.5000, 0.4593	Calc Expt	23.0 25.6	55.3 54.4	58.9 58.8	26.1 21.8	60
Benzene (1)+ *n*-heptane (2)	298.15	0.5034, 0.4031	Calc Expt	385.0 300.2	660.0 700.0	702.8 840.0	436.0 400.0	61
Benzene (1)+ chlorobenzene (2)	303.15	0.5086, 0.4000	Calc. Expt	−1.0 −0.8	−2.4 −2.5	−2.5 −2.5	−1.1 −1.0	62
Benzene (1)+ bromobenzene (2)	303.15	0.4843, 0.3322	Calc Expt	−10.2 −12.6	−26.0 −29.3	−31.5 −25.1	−15.1 −12.6	62
Benzene (1)+ *p*-xylene (2)	298.15	0.498, 0.4152	Calc Expt	55.4 53.8	135.7 133.4	151.0 152.4	68.6 69.9	63
Benzene (1)+ 2,2,4-trimethyl pentane	298.15	0.5207, 0.4406	Calc Expt	309.8 290.0	774.7 755.0	904.5 900.0	423.1 460.0	64
Benzene (1)+ 1,2,4-trimethyl benzene (2)	298.15	0.5000, 0.4413	Calc Expt	121.1 126.7	298.3 302.3	335.8 336.5	153.5 156.0	65
Benzene (1)+ 1,3,5-trimethyl benzene (2)	298.15	0.5000, 0.4456	Calc Expt	139.9 142.8	346.4 345.9	395.1 402.8	182.1 191.5	66
Benzene (1)+ decalin (2)	298.15	0.5000, 0.4413	Calc Expt	239.2 240.0	603.7 610.0	721.9 735.8	342.9 340.0	67
Benzene (1)+ *n*-hexadecane	298.15	0.6693, 0.697	Calc Expt	322.6 340.6	872.0 900.0	1278.0 1270.0	713.3 689.0	68
Toluene (1)+ methylene chloride (2)	298.15	0.4318, 0.3000	Calc Expt	−48.4 −49.6	−137.3 −151.6	−219.5 −206.5	−131.1 −96.6	53
Toluene (1)+ cyclohexane (2)	298.15	0.5044, 0.4208	Calc Expt	252.9 230.5	557.2 560.1	501.2 520.2	204.5 195.4	69

TABLE I (continued'

Mixture	Temp (K)	x_i	H^E	x_i				Ref
				0 1	0 3	0 7	0 9	
Toluene (1) + chloiobenzene (2)	303 15	0 5405, 0 463	Calc	−30 7	−76 5	−88 9	−44 1	62
			Expt	−25 1	−73 4	−73 4	−25 1	
Toluene (1)+ bromobenzene (2)	303 15	0 5334, 0 367	Calc	−20 3	−53 0	−70 0	−35 6	62
			Expt	−33 5	−71 1	−58 6	−23 0	
Toluene (1)+ *p*-xylene (2)	298 15	0 4529, 0 3723	Calc	6 5	15 5	16 2	7.1	70
			Expt	6 9	15 6	16 6	7.8	
Toluene (1)+ 1,2,4-trimethyl benzene (2)	298 15	0 4785, 0 3968	Calc	37 6	94 3	110 6	51 9	71
			Expt	35 7	95 3	103 6	42 8	
Toluene (1)+ 1,3,5-trimethyl benzene (2)	298 15	0 4839, 0 4000	Calc	56 4	129 7	126 2	53.4	72
			Expt	60 4	134 5	123 1	50 2	
o-Xylene (1)+ methylene chloride (2)	298 15	0 4435, 0 2951	Calc	−60 1	−167 2	−271 9	−169 5	53
			Expt	−44 7	−165 0	−238 0	−106 7	
o-Xylene (1)+ chlorobenzene (2)	298 05	0 530, 0 398	Calc	−26 3	−60 0	−60 9	−25 5	73
			Expt	−19 7	−57 5	−55 5	−21 2	
o-Xylene (1)+ bromobenzene (2)	298 05	0 5102, 0 3511	Calc	−22 4	−57 1	−70 5	−34 2	73
			Expt	−22 8	−58 1	−56.4	−21.4	
m-Xylene (1)+ methylene chloride (2)	298 15	0 2459, 0 4975	Calc	−64 2	−162 0	−193 6	−91 9	53
			Expt	−78 5	−133 1	−218 8	−105 3	
m-Xylene (1)+ chlorobenzene (2)	298 05	0 4778, 0 3428	Calc	−27 4	−70 2	−100 7	−58 0	73
			Expt	−26 8	−72 5	−72 4	−46.2	
m-Xylene (1)+ bromobenzene (2)	298 05	0 5037, 0 3269	Calc	−60 6	−136 8	−128 1	−53 2	73
			Expt	−55 5	−134 6	−118 1	−47 4	
m-Xylene (1)+ *n*-heptane (2)	298 15	0 514, 0 443	Calc	137 9	329 1	345.0	151.5	74
			Expt	125 0	335 0	352 0	145 0	

m-Xylene (1)+ cyclohexane (2)	298 15	0 438, 0 370	Calc	244.9	520 9	442 5	176 4	75
			Expt	225 0	530 0	460 0	200 0	
p-Xylene (1)+ methylene chloride (2)	298.15	0 4759, 0 3028	Calc	−57 2	−164 2	−283 5	−135 9	53
			Expt	−47 0	−166 7	−251.2	−119 5	
p-Xylene (1)+ chlorobenzene (2)	298 05	0 4778, 0 3500	Calc	−22 5	−57 1	−68 7	−32 8	73
			Expt	−22 6	−57 3	−60 2	−22.5	
p-Xylene (1)+ bromobenzene (2)	298 05	0 4573, 0 3342	Calc	−30 0	−75 0	−87 6	−41 0	73
			Expt.	−32 6	−75 4	−72.6	−31 0	
p-Xylene (1)+ cyclohexane (2)	298.15	0 4673, 0 3852	Calc	247 8	519 4	439 1	174 7	76
			Expt	180 9	523 3	423 2	164.2	
p-Xylene (1)+ 1,2,4-trimethyl benzene (2)	298 15	0 5000, 0 4416	Calc	14 5	33 3	33 4	13 7	77
			Expt	14 1	32 8	32 9	13 7	
p-Xylene (1)+ 1,3,5-trimethyl benzene (2)	298 15	0 5000, 0 4478	Calc.	9 9	23 4	24 4	10 6	78
			Expt	7 0	24 5	26 1	8 3	
1,3,5-Trimethyl benzene (1)+ 1,2,4-trimethyl benzene (2)	298 15	0 504, 0 4208	Calc	1 5	3 7	4.1	1 9	79
			Expt	2 1	4 2	4 1	2 1	
Decalin (1)+ *n*-heptane (2)	298 15	0 547, 0 4232	Calc	23 6	59 6	71 7	34 2	80
			Expt	25 0	70 0	70 0	30 0	
Decalin (1)+ *n*-hexadecane (2)	298 15	0 524, 0 423	Calc	63 0	161 4	201 0	98 2	81
			Expt	0 60	160 0	202 0	95 0	
Tetralin (1)+ cyclohexane (2)	298 15	0.505, 0 385	Calc	210 6	448 9	379 3	150 8	82
			Expt	206 0	475 0	380 0	157 0	
Tetralin (1)+ *n*-heptane (2)	298 15	0 5000, 0 460	Calc	162 5	394 5	429 2	192.4	83
			Expt	175 0	415 0	433 0	185 0	
Tetralin (1)+ *n*-hexadecane (2)	298 15	0 5000, 0 4713	Calc	184 2	483 3	643 2	330 3	84
			Expt	185 0	475 0	635 0	325 0	
n-Hexadecane (1)+ 2,2,4-trimethyl pentane	298 15	0 485, 0 414	Calc	91 0	203 8	188 4	77 8	85
			Expt	80 0	200 0	190 0	73 0	

TABLE 2

Comparison of H^E values (in J mole^{-1}) as calculated from eqn. (10) at different temperatures from the H^E data at the temperature and mole fractions x_1 of component 1 as specified in Table 1, with their corresponding experimental values for various mixtures

Mixture	Temp (K)	H^E	x_1				Ref.
			0.1	0.3	0.7	0.9	
Cyclopentane (1)+ carbon tetrachloride (2)	298.15	Calc	31.6	71.7	67.9	28.3	17
		Expt	30.5	68.0	66.0	29.5	
	308.15	Calc	30.6	69.4	65.7	27.4	17
		Expt	28.0	62.8	64.0	25.0	
Cyclohexane (1)+ carbon tetrachloride (2)	298.15	Calc	67.3	153.2	146.3	61.4	19
		Expt	60.0	144.0	140.4	63.1	
	318.15	Calc	60.9	138.8	132.5	55.6	19
		Expt	60.0	132.1	130.4	51.1	
Cyclohexane (1)+ 2,2,4-trimethylpentane (2)	323.15	Calc	51.3	128.9	152.8	72.2	27
		Expt	48.0	135.0	155.0	70.0	
Cyclohexane (1)+ 2,3-dimethyl butane (2)	298.15	Calc	52.8	125.2	129.7	56.6	24
		Expt	53.1	127.4	133.4	57.7	
	308.15	Calc	51.1	121.1	125.5	54.8	24
		Expt	52.0	125.3	133.8	58.5	
Cyclohexane (1)+ 1-octene (2)	323.15	Calc	111.2	221.0	170.4	65.5	37
		Expt	72.0	160.0	180.0	70.0	
Cyclohexane (1)+ *n*-heptane (2)	323.15	Calc	66.0	169.1	210.7	102.9	26
		Expt	50.0	139.5	195.7	95.1	
Cyclohexane (1)+ *n*-hexadecane	323.15	Calc	131.0	343.0	454.1	232.2	30
		Expt	110.0	280.0	350.0	160.0	
Cycloheptane (1)+ 2,3-dimethyl butane	298.15	Calc	54.8	131.9	140.9	62.5	40
		Expt	60.0	131.2	134.2	61.5	
Cyclooctane (1)+ cyclopentane (2)	288.25	Calc	−21.1	−41.2	−31.0	−11.9	41
		Expt	−16.0	−32.4	−15.7	−0.6	
	308.32	Calc	−19.7	−38.5	−29.0	−11.1	41
		Expt	−22.5	−48.7	−34.5	−10.3	
Cyclooctane (1)+ 2,3-dimethyl butane	298.15	Calc	71.7	157.9	142.1	58.0	42
		Expt	68.0	152.8	144.1	60.5	
	313.15	Calc	68.3	150.4	135.3	55.2	42
		Expt	62.7	140.4	130.8	54.4	
n-Octane (1)+ 2,2,4-trimethyl pentane (2)	323.15	Calc	8.3	19.7	20.6	8.9	36
		Expt	6.5	15.0	15.5	7.5	
1-Octene (1)+ *n*-heptane (2)	323.15	Calc	15.7	33.3	28.3	11.3	38
		Expt	12.0	30.0	32.1	15.0	
1-Octene (1)+ *n*-hexadecane	323.15	Calc	46.0	115.8	137.0	64.7	39
		Expt.	33.0	80.0	91.0	40.0	

TABLE 2 (continued)

Mixture	Temp. (K)	H^E	x_1				Ref.
			0.1	0.3	0.7	0.9	
n-Heptane (1)+	298.15	Calc	15.7	37.9	41.1	18.4	35
n-hexadecane		Expt	35.0	82.1	71.0	30.0	
Methyl cyclohexane (1)+	323.15	Calc	9.4	24.3	30.6	15.1	34
n-heptane (2)		Expt	5.0	12.0	17.8	8.0	
Decalin (1)+	323.15	Calc	316.4	666.1	557.0	220.7	67
benzene (2)		Expt	285.0	620.0	480.0	205.0	
Decalin (1)+	323.15	Calc	21.8	55.0	66.0	31.6	80
n-heptane (2)		Expt	16.0	42.0	52.0	20.0	
Decalin (1)+	323.15	Calc	58.1	148.9	185.4	90.6	81
n-hexadecane		Expt	40.0	93.0	122.0	51.0	
Tetralin (1)+	323.15	Calc	194.3	414.2	350.0	139.1	83
cyclohexane (2)		Expt	170.0	370.0	340.0	140.0	
Tetralin (1)+	323.15	Calc	149.9	364.0	396.0	177.5	82
n-heptane (2)		Expt	142.0	375.0	390.0	175.0	
Tetralin (1)+	323.15	Calc	169.9	445.9	593.4	304.7	83
n-hexadecane (2)		Expt	130.0	430.0	560.0	270.0	
Benzene (1)+	288.15	Calc	41.9	99.1	101.8	44.3	52
carbon tetrachloride (2)		Expt	37.6	88.1	91.0	42.0	
	318.15	Calc	38.0	89.8	92.2	40.1	52
		Expt	54.0	110.0	114.0	54.0	
Benzene (1)+	323.15	Calc	279.2	634.5	603.3	252.3	59
cyclohexane (2)		Expt	270.0	615.0	605.0	220.0	
Benzene (1)+	323.15	Calc	355.0	610.0	649.0	402.0	61
n-heptane (2)		Expt	240.0	660.0	760.0	320.0	
Benzene (1)+	303.15	Calc	−23.2	−60.9	−80.6	−41.2	53
methylene chloride (2)		Expt	−15.4	−55.3	−76.0	−29.4	
Benzene (1)+	308.15	Calc	−0.9	−2.3	−2.5	−1.1	62
chlorobenzene (2)		Expt	$\sim$0	$\sim$0	$\sim$0	$\sim$0	
Benzene (1)+	308.15	Calc.	−10.0	−25.6	−31.0	−14.8	62
bromobenzene (2)		Expt.	−12.5	−23.0	−31.0	−12.6	
Benzene (1)+	323.15	Calc	285.8	714.8	834.5	390.4	64
2,2,4-trimethyl pentane (2)		Expt	205.0	660.0	840.0	393.0	
Benzene (1)+	288.15	Calc.	65.5	195.0	212.4	104.6	54
n-hexane (2)		Expt	68.0	177.1	220.1	109.1	
	318.15	Calc	59.3	176.7	192.4	94.7	54
		Expt	56.7	140.7	178.8	94.1	
Benzene (1)+	323.15	Calc.	355.0	610.0	649.0	402.0	61
n-heptane (2)		Expt.	240.0	660.0	760.0	320.0	
Benzene (1)+	323.15	Calc	297.6	804.5	1179.1	658.1	68
n-hexadecane (2)		Expt.	297.0	750.0	1100.0	500.0	

TABLE 2 (continued)

Mixture	Temp (K)	H^E	x_1				Ref
			0.1	0.3	0.7	0.9	
Toluene (1)+	303.15	Calc	−47.6	−135.0	−215.9	−128.9	53
methylene chloride (2)		Expt	−48.4	−147.0	−200.5	−93.9	
Toluene (1)+	308.15	Calc	−30.2	−75.3	−87.5	−40.7	62
chlorobenzene (2)		Expt	−12.6	−62.8	−58.6	−16.7	
Toluene (1)+	308.15	Calc	−20.0	−52.2	−68.8	−35.0	62
bromobenzene (2)		Expt	−25.1	−41.8	−55.4	−14.6	
o-Xylene (1)+	303.15	Calc	−59.1	−164.4	−267.4	−166.7	73
methylene chloride (2)		Expt	−44.4	−102.8	−233.7	−104.6	
o-Xylene (1)+	293.05	Calc	−26.8	−62.0	−61.0	−25.9	73
chlorobenzene (2)		Expt.	−24.8	−65.6	−60.3	−24.1	
o-Xylene (1)+	293.05	Calc	−22.8	−58.1	−71.7	−34.8	73
bromobenzene		Expt	−37.1	−89.2	−88.5	−34.0	
m-Xylene (1)+	303.15	Calc	−63.1	−159.3	−190.4	−90.4	53
methylene chloride		Expt	−60.1	−128.7	−210.8	−102.3	
m-Xylene (1)+	293.05	Calc	−27.9	−71.4	−102.4	−59.0	73
chlorobenzene (2)		Expt	−38.3	−91.0	−85.2	−35.0	
m-Xylene (1)+	293.05	Calc	−61.8	−139.2	−130.3	−54.1	73
bromobenzene (2)		Expt	−83.4	−166.2	−159.4	−78.5	
m-Xylene (1)+	323.15	Calc	127.2	303.6	318.3	139.8	74
n-heptane (2)		Expt	100.0	300.0	323.0	140.0	
m-Xylene (1)+	323.15	Calc	225.9	480.6	408.3	162.8	75
cyclohexane (2)		Expt	180.0	446.0	440.0	190.0	
p-Xylene (1)+	303.15	Calc	−56.3	−161.5	−270.5	−132.2	53
methylene chloride (2)		Expt	−45.4	−161.8	−244.9	−117.5	
p-Xylene (1)+	293.05	Calc	−22.9	−58.1	−69.9	−33.3	73
chlorobenzene (2)		Expt	−30.2	−84.5	−89.8	−37.8	
p-Xylene (1)+	293.05	Calc	−30.5	−76.3	−89.1	−41.7	73
bromobenzene (2)		Expt	−48.0	−109.2	−107.1	−43.6	
n-Hexadecane (1)+	323.15	Calc	83.9	188.0	173.8	83.9	85
2,2,4-trimethyl pentane		Expt	50.0	125.0	115.0	50.0	

sponding literature values [17–85]. An examination of Table 1 reveals that the H^E values as calculated by the present approach reproduce the experimental H^E data reasonably well.

It would now be interesting to see if this approach can be employed to predict H^E data for the mixture at a temperature T_1 from its H^E data at a given temperature T and two mole fractions close to $x_1 = 0.5$.

H^E according to eqn. (6) is dependent directly on χ_{ij}, and as the temperature is raised from T to T_1 the i and j components come into less effective i–j contacts so that χ_{ij} at T_1 would be lower than χ_{ij} at T. In other words, H^E should vary inversely with temperature, i.e.

$$H^E(T_1) \propto 1/T_1 \tag{7}$$

and

$$H^E(T) \propto 1/T \tag{8}$$

Therefore

$$H^E(T_1)/H^E(T) = T/T_1 \tag{9}$$

Hence

$$H^E(T_1) = (T/T_1)H^E(T) \tag{10}$$

Now H^E at a given temperature T, $H^E(T)$, can be calculated from eqn. (6) in the manner explained above and hence H^E at any other temperature T_1, $H^E(T_1)$, can be readily determined from eqn. (10). The $H^E(T_1)$ values calculated in this way for a number of binary mixtures are recorded in Table 2 and are also compared with the corresponding literature values. An examination of Table 2 reveals that the H^E values calculated by the present approach again reproduce the experimental H^E data well.

Thus, the present approach provides a convenient method to predict H^E for binary mixtures, as a function of temperature and composition, if H^E data at one temperature and two mole fractions only are known. One apparent weakness of this approach is that it requires H^E to be either positive or negative. This approach would then fail for those mixtures for which H^E changes sign with composition. This approach has also been quite successful [86] to predict V^E data for a number of binary mixtures. The present approach also removes the shortcomings observed with the earlier approach [86] to predict H^E at the two extreme ends of the mole fraction scale with some of the binary mixtures.

ACKNOWLEDGEMENTS

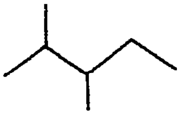
V.K.S. and S.P.S. thank the authorities of C.S.I.R., New Delhi, for the award of Junior Research Fellowship.

APPENDIX

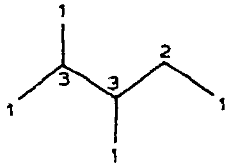
The connectivity parameters of the first, second and third degree of 2,3-dimethyl pentane can be calculated as follows.

2,3-Dimethyl pentane

The carbon–carbon skeleton of this compound would be



Now while the second and third vertices are of the third degree (since each of them is directly linked to three vertices), the first and fifth vertices of the first degree and the fourth vertex is of the second degree. The graph of 2,3-dimethyl pentane with the degree of its various vertices would be



$$^{1}\xi = 1/\sqrt{1\times3} + 1/\sqrt{1\times3} + 1/\sqrt{3\times3} + 1/\sqrt{3\times1} + 1/\sqrt{3\times2} + 1/\sqrt{2\times1} = 3.18$$

$$^{2}\xi = 1/\sqrt{1\times3\times1} + 1/\sqrt{1\times3\times3} + 1/\sqrt{1\times3\times3} + 1/\sqrt{3\times3\times1} + 1/\sqrt{3\times3\times2} + 1/\sqrt{1\times3\times2} + 1/\sqrt{3\times2\times1} = 2.63$$

and

$$^{3}\xi = 1/\sqrt{1\times3\times3\times1} + 1/\sqrt{1\times3\times3\times2} + 1/\sqrt{1\times3\times3\times1} + 1/\sqrt{1\times3\times3\times2} + 1/\sqrt{3\times3\times2\times1} + 1/\sqrt{1\times3\times2\times1} = 2.49$$

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