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TOPOLOGICAL ASPECTS OF THE EFFECT OF TEMPERATURE AND PRESSURE ON THE THERMODYNAMICS OF BINARY MIXTURES OF NON-ELECTROLYTES

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ABSTRACT

An approach, employing the concept of molecular connectivity index of the third degree of graph theory, has been developed to evaluate molar excess enthalpy, $H^E(T_1, x)$, and molar excess volume $V^E(T_1, x)$ of any kind of binary mixture (liquid as well as gaseous) of non-electrolytes, and the calculated $H^E(T_1, x)$ or $V^E(T_1, x)$ values agree well with their corresponding experimental values. This approach has also been extended to study the effect of temperature and pressure on $H^E(T_1, x)$ and $V^E(T_1, x)$ data of any kind of binary mixture of non-electrolytes, and the calculated $H^E(T_2, x, P = 1$ atm), $H^E(T_2, x, P_2 \neq 1$ atm), $V^E(T_2, x, P_2 = 1$ atm) and $V^E(T_2, x, P_2 \neq 1$ atm) values, obtained from $H^E(T_1, x, P = 1$ atm) or $V^E(T_1, x, P = 1$ atm) data, compare well with their corresponding experimental values. The approach has further been utilized to evaluate specific volumes $v(T_1$, x, $P_2 \gg 1$ atm) of pure compounds as well as their mixtures when $v(T_1, P = 1$ atm) or $v(T_1, x, P = 1$ atm) data are available; the calculated $v(T_1, x)$ and $v(T_1, x, P_2)$ values again compare well (within 5% at the worst) with their corresponding experimental values.

INTRODUCTION

Although the thermodynamics of binary mixtures of non-electrolytes have attracted the attention of physical chemists for a considerable time [1–18], no satisfactory approach (theoretical or empirical) is available until now to evaluate reasonably well such thermodynamic properties as the molar excess enthalpy, $H^E(T_1, x, P = 1$ atm), or the molar excess volume, $V^E(T_1, x, P = 1$ atm), or to study the effect of temperature and pressure on $H^E(T_1, x, P = 1$ atm) or $V^E(T_1, x, P = 1$ atm) data of all kinds (liquid, associated or otherwise, or gaseous) of binary mixtures of non-electrolytes.

The situation is all the more acute for those binary mixtures where either one or both the components are associated or when their components undergo specific interactions between themselves; and while all the earlier attempts [11–19] for the latter class of binary mixtures have been concerned with evaluating equilibrium constants of the molecular complexation reaction and the enthalpy of formation of various postulated molecular species

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in the complexation reaction, no approach is available to (a) analyze $H^E(T_1, x, P = 1$ atm) and $V^E(T_1, x, P = 1$ atm) data, and (b) study the effect of temperature or/and pressure on $H^E(T_1, x, P = 1$ atm) and $V^E(T_1, x, P = 1$ atm) data for the former class of binary mixtures. Singh et al. [20,21] have recently utilized the concept of molecular connectivity index of the third degree of graph theory to evaluate $H^E(T_1, x, P = 1$ atm) and $V^E(T_1, x, P = 1$ atm) data of those binary mixtures of non-electrolytes that are not characterized by specific interactions between their components. However, this approach would fail to differentiate H^E or V^E data at T_1 of, for example, [(1 − x) benzene + x n-pentane] from [(1 − x) cyclohexane + x n-pentane], or [(1 − x) benzene + x n-pentane] from [(1 − x) benzene + x pent-1-ene] mixtures. Further, this approach (henceforth called molecular connectivity approach) would not be conducive to evaluate H^E and/or V^E data of binary mixtures that contain hetero atoms in their molecular graph. Again no approach is available to evaluate specific volumes under high pressures, $v(T_1, x, P \gg 1$ atm), of binary mixtures of non-electrolytes when $v(T_1, x, P = 1$ atm) data are available. The present work is concerned with (i) the evaluation of $H^E(T_1, x, P = 1$ atm) and $V^E(T_1, x, P = 1$ atm) data, (ii) the study of the effect of T and P on $H^E(T_1, x, P = 1$ atm) and $V^E(T_1, x, P = 1$ atm) data, and (iii) the evaluation of $\nu(T_1, x, P \gg 1$ atm) of all kinds of binary mixtures of non-electrolytes.

CONCEPTUAL ASPECT OF THE APPROACH AND THE RESULTS

According to the mathematical discipline of graph theory [22–24] the molecular graph of, for example, n-pentane, symbolizing its C–C skeleton, would be

in which while the vertices at positions 2, 3 and 4 are of the degree two (reflecting the number of adjacent carbon atoms in its molecular graph), those at positions 1 and 5 are of the degree one. In order to further quantify the information contained in the molecular graph of a molecule, Kier et al. [25–29] suggested the use of molecular connectivity index, ξ, of the first, second and third degree of the molecule, defined by

$$^1\xi = \sum_{l<m} (\delta_l \delta_m)^{-0.5} \tag{1}$$

$$^2\xi = \sum_{l<m} \sum_{m<n} (\delta_l \delta_m \delta_n)^{-0.5} \tag{2}$$

$$^3\xi = \sum_{l<m} \sum_{m<n} \sum_{n<o} (\delta_l \delta_m \delta_n \delta_o)^{-0.5} \tag{3}$$

where δ_l, δ_m and δ_n etc., denote the degrees of the lth, mth and nth etc., vertices of its molecular graph. Thus the $^1\xi$, $^2\xi$, $^3\xi$ connectivity indices of *n*-pentane would be

$$^{1}\xi = 2.414 \tag{4}$$

$$^{2}\xi = 1.354 \tag{5}$$

$$^{3}\xi = 0.707 \tag{6}$$

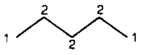
Such a scheme of evaluating the molecular connectivity index, ξ, of a molecule utilizing only the degrees of the various vertices of the C–C skeleton of a molecule would fail to differentiate *n*-pentane from pent-1-ene or benzene from cyclohexane. Moreover, it would also be not conducive to quantify the information contained in the molecular graph of such molecules as alkanols, ethers, esters, pyridine, etc. In order to overcome this problem, Kier [30] advocated the use of δ^v values reflecting explicitly the valency of the atoms forming the bonds (δ^v = valence δ) to evaluate $^{1}\xi$, etc., indices of the molecular graph of a molecule. According to Kier [30], δ^ν of carbon in any C–H linkage should be evaluated from

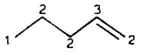
$$\delta^v(\mathrm{C}) = Z - h \tag{7}$$

where Z is the maximum valency of C(i.e. 4), and h is the number of hydrogen atoms linked to the carbon atom. Thus δ^v of C in $-CH_2$, $-CH_3$ or $-CH$ would be

$$\begin{aligned}\delta^v(\mathrm{C}) \quad \text{in } -\mathrm{CH_2} &= 4-2=2\\ \text{in } -\mathrm{CH_3} &= 4-3=1\\ \text{in } -\mathrm{CH} &= 4-1=3\end{aligned}$$

and so the $^{1}\xi$, $^{2}\xi$ and $^{3}\xi$ indices of *n*-pentane and pent-1-ene would be



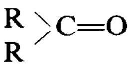


n-pentane	pent-1 ene
$^{1}\xi = 2.414$	$^{1}\xi = 2.024$
$^{2}\xi = 1.354$	$^{2}\xi = 1.077$
$^{3}\xi = 0.707$	$^{3}\xi = 0.493$

which now clearly differentiate them. For molecules containing heteroatoms like N and O, Kier [31] further suggested that δ^v of N or O should also be evaluated from eqn. (7) where Z now denotes the maximum valency of N or O and h is the number of hydrogen atoms linked to N or O. Accordingly, δ^v (N) in the –NH fragment of a molecule would be 5 − 1 = 4. Similarly

$$\delta^v(\mathrm{O}) \text{ in R–OH} = 6 - 1 = 5$$

and



$$\delta^v(\mathrm{O}) \text{ in } \begin{matrix}\mathrm{R}\\ \mathrm{R}\end{matrix}\!\!>\!\mathrm{C{=}O} = 6 - 0 = 6$$

It would thus be possible to quantify the information contained in the molecular graph of any kind of molecule.

Further, since the $^1\xi$ index of a molecule depends on the degrees of the closest vertices of its molecular graph taken two at a time, it has been taken [20] to represent a measure of the oscillations of its bond length. On the other hand, while the $^1\xi$ index of a molecule provides no information [32] about the effect of branching in a molecule, the $^2\xi$ index of a molecule encodes some information [32] about the effect of branching in a molecule. According to Kier [33], more information about the effect of branching in a molecule is obtainable by computing its $^3\xi$ index and it has actually been shown [20] that while an increase in branching in an isomeric compound increases its molar volume, its $^3\xi$ index decreases. In other words, the molar volumes of isomeric compounds vary inversely as their $^3\xi$. Again, $^{1/3}\xi$ of most of the molecules is less than unity, and as branching in an isomeric compound would allow only a part of this surface area to interact effectively with the corresponding surface areas of other molecules, $^{1/3}\xi$ of a molecule has been taken [20] to represent a measure of the probability that its surface area interacts effectively with the surface areas of other molecules. If now the molar excess enthalpy, H^E, of a (x A + (1 − x) B) mixture at T_1 is due essentially to the replacement of like contacts in pure A and B by unlike contacts in the mixture, then it has been shown [21] that the molar excess enthalpy at T_1, $H^E(T_1, x)$, of an [x A + (1 − x) B] mixture is given by

$$H^E(T_1, x) = \frac{x(1-x)\chi_{AB}k_{AB}(^3\xi_A/^3\xi_B)}{x + (1-x)k_{AB}(^3\xi_A/^3\xi_B)} \qquad (8)$$

where all the symbols have their usual meaning [20,21]. Equation (8) has been shown to describe very well H^E data of a very large number of binary mixtures of non-electrolytes that are not characterized by the presence of any specific interactions between their components, if H^E data for the mixture at two compositions close to $x = 0.5$ are known. This earlier approach [20,21], however, suggests that H^E for [(x) cyclohexane + (1 − x) n-pentane] and [x cyclohexane + (1 − x) pent-1-ene] would be the same. However, this is not true. Moreover, this approach is also not conducive to evaluate H^E for binary mixtures in which either one or both the components contain hetero atoms in their molecular graph since their $^3\xi$ index cannot be evaluated. If the $^3\xi$ indices of molecules are evaluated by employing the δ^v values, it appears that eqn. (8) should be able to describe H^E data of any class of binary mixtures of non-electrolytes if H^E data for the mixture at two compositions close to $x = 0.5$ are available. Such H^E values for a number of binary mixtures at $x = 0.3$ and 0.7 are recorded in Table 1 and are also compared with their corresponding experimental values [34–84].

Examination of Table 1 clearly shows that the H^E values calculated from eqn. (8) compare very well their corresponding experimental values even for those mixtures which are known to be characterized by specific interactions between their components or when one of the components is associated. This would then mean that H^E of an $[x\ \mathrm{A} + (1-x)\ \mathrm{B}]$ mixture is due essentially to the interaction energy per contact, χ_{AB}. Consequently, as the temperature is raised from T_1 to T_2, the molecules A and B in this mixture at T_2 would be able to interact less effectively compared to the case at T_1. This would then suggest that as the temperature is raised χ_{AB} decreases or H^E for a binary mixture should decrease with the rise in temperature, and so if $H^E(T_1, x)$ and $H^E(T_2, x)$ denote the H^E of a binary mixture at T_1 and T_2 K, respectively, then

$$\frac{H^E(T_2,x)}{H^E(T_1,x)} = \frac{T_1}{T_2} \tag{9}$$

or

$$H^E(T_2,x) = \frac{T_1}{T_2} H^E(T_1,x) \tag{10}$$

Thus if $H^E(T_1, x)$ data of a binary mixture at T_1 are known or could be evaluated from eqn. (8) in the manner described earlier, it should be possible to evaluate $H^E(T_2, x)$ for any class of binary mixture at T_2. Such $H^E(T_2, x = 0.3, 0.7)$ data for some the various binary mixtures listed in Table 1 are recorded in Table 2 and are also compared with their corresponding experimental values [34,35,37,38,58,59,62,64,65,68,75–77,79,83–85].

Examination of Table 2 again reveals that the $H^E(T_2, x)$ data for the various binary mixtures evaluated from eqn (10) utilizing $H^E(T_1, x = 0.3, 0.7)$ data evaluated from eqn. (8), compare very well with their corresponding experimental values even for those mixtures where one of the components is associated or where the components are known to undergo specific interactions. Table 2 also shows that expression (10) well describes the $H^E(T_2, x = 0.3, 0.7, P = 101.3$ k Pa$)$ data [83–85] of even gaseous mixtures.

EFFECT OF PRESSURE ALONE ON THE $H^E(T_2, x, P = 1$ ATM$)$ DATA OF GASEOUS MIXTURES

When a binary gaseous mixture $[x\ \mathrm{A} + (1-x)\ \mathrm{B}]$ at T_2 and P_2 is subjected to an increase of pressure from P_2 to P_2^1, the increased pressure would cause the gaseous components to interact more effectively at T_2 and P_2^1 as compared to that at T_2 and P_2. This would then mean that as pressure on a mixture at a given T_2 is increased, the interaction energy per unlike contact, χ_{AB}, increases and so should its $H^E(T_2, x, P_2^1)$. Accordingly, if $H^E(T_2, x, P_2^1)$ and $H^E(T_2, x, P_2)$ denote the molar excess enthalphy of a binary mixture at P_2^1 and P_2 and at a given temperature T_2, then

$$H^E(T_2, x, P_2^1) \propto P_2^1 \tag{11}$$

TABLE 1

Comparison of H^E (T_1, x) values as calculated from eqn. (8) with their corresponding experimental values at $x = 0.3$, 0.7 for various mixtures

Mixture	T_1	$^3\xi_A$	$^3\xi_B$	χ_{AB} (J mole^{-1})	k_{AB}	x	H^E (J mole^{-1})		Ref.
							Calcd.	Exptl.	
(a) Liquid mixtures									
1. x Methylene chloride +	273.15	1.0	1.0	−3312.9	1.2711	0.3	−743.3	−760.2	34
$(1-x)$ 2-propanone						0.7	−817.8	−820.5	
2. x Methylene chloride	303.15	1.0	0.287	−2980.9	0.3311	0.3	−652.0	−627.0	35
$(1-x)$ methyl ethanoate						0.7	−690.3	−675.2	
3. x Methylene chloride +	303.15	1.0	1.076	−5123.1	1.2711	0.3	−1026	−1050	36
$(1-x)$ oxane						0.7	−967	−898	
4. x Methylene chloride +	303.15	1.0	0.744	−3360.0	1.309	0.3	−810.6	−795.0	37
$(1-x)$ 1,4-dioxane						0.7	−1011.1	−965.0	
5. x Chloroform + $(1-x)$	303.15	1.0	0.744	−5520.2	1.929	0.3	−1421.1	−1423.2	38
1,4-dioxane						0.7	−2033.8	−1990.5	
6. x Chloroform + $(1-x)$	298.15	1.0	0.408	−10422.9	0.444	0.3	−2243.4	−2108.0	39
diethylether						0.7	−2321.0	−2129.0	
7. x Chloroform + $(1-x)$	308.15	1.0	0.566	−5958.2	1.036	0.3	−1448	−1444	40
pyridine						0.7	−1833	−1859	
8. x Chloroform + $(1-x)$	308.15	1.0	0.814	−9165.5	1.342	0.3	−2182	−2180	40
α-picoline						0.7	−2657	−2540	
9. x Chloroform + $(1-x)$	308.15	1.0	0.847	−8102.3	1.384	0.3	−1926	−1796	40
γ-picoline						0.7	−2336	−2180	
10. x Chloroform + $(1-x)$	298.15	1.0	0.612	−5756.7	0.666	0.3	−1239	−1250	41
di-*tert*-butyl ether						0.7	−1282	−1254	
11. x Chloroform + $(1-x)$	298.15	1.0	1.158	−5384.3	1.306	0.3	−1171	−1130	42
di-isopentyl ether						0.7	−1229	−1240	
12. x Carbon tetrachloride +	298.15	1.0	0.408	−2013.9	0.408	0.3	−422.9	−396.0	43
$(1-x)$ diethyl ether						0.7	−422.9	−400.6	

13.	x Carbontetrachloride	303.15	1.0	1.076	−3286.5	0.856	0.3	−640.7	−645.1	44
	$+(1-x)$ oxane						0.7	−584.8	−564.2	
14.	x Carbon tetrachloride	298.15	1.0	1.158	−530.6	1.172	0.3	−111.8	−118.0	41
	$+(1-x)$di-isopentyl ether						0.7	−112.4	−120.0	
15.	x Carbon tetrachloride	298.15	1.0	0.612	199.8	0.902	0.3	46.4	46.0	41
	$+(1-x)$ di.*tert*.butyl						0.7	54.1	56.0	
	ether									
16.	x Carbon tetrachloride	298.15	1.0	0.827	−2670	1.195	0.3	−617.9	−618.9	45
	$+(1-x)$ tetrahydrofuran						0.7	−714.8	−707.2	
17.	x Carbon tetrachloride	298.15	1.0	0.539	−848.2	0.2846	0.3	140.4	143.7	45
	$+(1-x)$ 1,3-dioxolane						0.7	109.6	111.1	
18.	x Carbon tetrachloride	298.15	1.0	1.076	−2658.9	1.1014	0.3	−627.0	−633.6	45
	$+(1-x)$ oxane						0.7	−585.9	−588.5	
19.	x Carbon tetrachloride	298.15	1.0	0.889	−248.7	22.464	0.3	−145.9	−135.3	45
	$+(1-x)$ 1,3-dioxane						0.7	−73.0	−64.5	
20.	x Ethane $+(1-x)$ethanol	298.15	1.0	1.0	−793.2	0.655	0.3	−143.8	−132.4	46
	$(P = 6900$ kPa)						0.7	−121.7	−192.8	
21.	x Ethane $+(1-x)$ propan-1-ol	298.15	1.0	1.0	−938.4	1.140	0.3	−204.6	−204.0	46
	$(P = 6900$ kPa)						0.7	−215.6	−192.8	
22.	x Ethane $+(1-x)+$ butan-1-ol	298.15	1.0	0.512	−972.2	0.809	0.3	−229.4	−227.6	46
	$(P = 6900$ kPa)						0.7	−274.8	−260.8	
23.	x Ethane $+(1-x)$ pentan-1-ol	298.15	1.0	0.762	−982.8	1.602	0.3	−244.9	−244.3	46
	$(P = 6900$ kPa)						0.7	−326.0	−326.8	
24.	x Ethane $+(1-x)$ hexane-1-ol	298.15	1.0	1.012	−942.3	2.842	0.3	−245.3	−250.0	46
	$(P = 6900$ kPa)						0.7	−360.2	−376.4	
25.	x Ethane $+(1-x)$ octane-1-ol	298.15	1.0	1.512	−740.3	21.29	0.3	−215.5	−217.6	46
	$(P = 6900$ kPa)						0.7	−444.6	−433.8	
26.	x Ethane $+(1-x)$ decan-1-ol	298.15	1.0	2.012	−531.2	−13.312	0.3	−170.5	−165.7	46
	$(P = 6900$ kPa)						0.7	−574.4	−454.5	
27.	x Trimethylene oxide $+(1-x)$	298.15	0.577	0.667	−1471.4	1.426	0.3	−327.6	−316.0	47
	benzene						0.7	−356.2	−350.0	
28.	x Methyl ethanoate $+(1-x)$	298.15	0.287	1.0	3356.1	5.258	0.3	784.2	790.2	48
	methanol						0.7	922.7	950.0	

TABLE 1 (continued)

Mixture	T_1	$^3\xi_A$	$^3\xi_B$	χ_{AB} (J mole^{-1})	k_{AB}	x	H^E (J mole^{-1})		Ref.
							Calcd.	Exptl.	
29. x Methyl ethanoate + $(1-x)$ ethanol	298.15	0.287	1.0	4560.9	4.729	0.3	1034.4	1057.4	49
						0.7	1171.1	1233.5	
30. x Ethyl ethanoate + $(1-x)$ methanol	298.15	0.348	1.0	2880.3	5.129	0.3	663.6	706.0	50
						0.7	832.2	891.0	
31. x Ethyl ethanoate + $(1-x)$ ethanol	298.15	0.348	1.0	4444.8	3.903	0.3	1014.0	1021.0	51
						0.7	1145.0	1160.0	
32. x Ethyl ethanoate + $(1-x)$ propan-1-ol	298.15	0.348	1.0	5423.0	3.608	0.3	1213.0	1227.0	52
						0.7	1328.0	1365.0	
33. x Ethyl ethanoate + $(1-x)$ butan-1-ol	298.15	0.348	0.512	6104.6	1.749	0.3	1346.0	1361.0	53
						0.7	1443.0	1485.0	
34. x Ethyl ethanoate + $(1-x)$ *n*-hexane	298.15	0.348	0.957	5684.9	2.254	0.3	1120.0	1160.0	54
						0.7	1035.0	1080.0	
35. x Ethyl ethanoate + $(1-x)$ cyclohexane	298.15	0.348	1.50	6495.8	2.862	0.3	1184.0	1191.0	55
						0.7	1007.0	1048.0	
36. x Butan-1-ol + $(1-x)$ methanol	298.15	0.512	1.0	973.2	0.808	0.3	143.4	142.8	56
						0.7	102.6	105.0	
37. x Tetrahydrofuran + $(1-x)$ benzene	298.15	0.827	0.667	−122.64	1.1781	0.1621	−175.6	−185.2	45
						0.3	−284.5	−296.1	
						0.7	−330.5	−316.5	
38. x 1,3-Dioxane + $(1-x)$ benzene	298.15	0.889	0.667	574.2	0.781	0.3	−122.0	−117.0	57
						0.7	−124.0	−117.0	
39. x 1,4-Dioxane + $(1-x)$ benzene	298.15	0.744	0.667	−253.9	−0.180	0.3	−67.1	−48.3	58
						0.7	−16.7	−5.1	
40. x 1,4-Dioxane + $(1-x)$ cyclohexane	298.15	0.744	1.5	6992.0	1.692	0.3	1388	1398	59
						0.7	1295	1320	
41. x Oxane + $(1-x)$benzene	298.15	1.076	0.667	−937.71	0.8837	0.3	−216.3	−205.9	60
						0.7	−248.9	−217.1	

42.	x Butan-1-ol + (1 − x) ethanol	298.15	0.512	1.0	270.0	1.082	0.3	45.7	45.1	61
							0.7	36.3	36.4	
43.	x Butan-1-ol + (1 − x) propan-1-ol	298.15	0.512	1.0	15.2	4.888	0.3	3.9	4.8	61
							0.7	5.5	4.3	
44.	x Pyridine + (1 − x) benzene	298.15	0.566	0.667	92.12	0.2541	0.3	9.3	8.0	62
							0.7	5.5	5.4	
45.	x Pyridine + (1 − x) *N*-methyl piperidine	298.15	0.566	1.580	3029.5	2.030	0.3	571.7	551.0	63
							0.5041	633.0	634.0	
							0.7	503.6	501.0	
46.	x Piperidine + (1 − x) benzene	298.15	1.132	0.667	2001.4	0.6504	0.3	432.5	434.0	64
							0.4996	525.0	524.0	
							0.7	449.8	417.0	
47.	x Piperidine + (1 − x) toluene	298.15	1.132	0.940	2161.6	0.742	0.3	438.2	400.0	65
							0.5038	509.7	516.0	
							0.7	418.9	439.0	
48.	x Piperidine + (1 − x) cyclohexane	298.15	1.132	1.500	4298.8	0.828	0.3	765.1	777.0	66
							0.496	822.0	824.0	
							0.7	636.0	689.0	
49.	x Piperidine + (1 − x) methyl cyclohexane	298.15	1.132	1.894	4415.2	1.044	0.3	785.4	765.0	67
							0.4935	850.9	853.0	
							0.7	652.4	665.0	
50.	x Aniline + (1 − x) benzene	293.15	0.799	0.667	4890.8	0.472	0.3	834.6	807.7	68
							0.7	541.6	596.0	
51.	x Aniline + (1 − x) toluene	293.15	0.799	0.940	5126.9	0.7915	0.3	939.6	941.5	67
							0.7	803.2	813.7	
52.	x Aniline + (1 − x) *o*-xylene	293.15	0.799	1.426	6234.0	1.084	0.3	1096.2	1085.3	68
							0.7	900.9	872.9	
53.	x Aniline + (1 − x) *m*-xylene	293.15	0.799	1.174	6245.1	1.081	0.3	1183.6	1200.7	68
							0.7	1047.3	1102.1	
54.	x 1-Hexanol + (1 − x) methanol	298.15	1.012	1.0	2133.3	0.281	0.3	255.3	256.0	69
							0.7	162.2	170.0	
55.	x 1-Hexanol + (1 − x) ethanol	298.15	1.012	1.0	760.4	0.492	0.3	122.6	124.0	70
							0.7	93.6	96.1	

TABLE 1 (continued)

Mixture	T_1	${}^3\xi_A$	${}^3\xi_B$	χ_{AB} (J mole^{-1})	k_{AB}	x	H^E (J mole^{-1}) Calcd.	H^E (J mole^{-1}) Exptl.	Ref.
56. x 1-Hexanol + (1 − x) propan-1-ol	298.15	1.012	1.0	287.0	0.741	0.3	54.8	56.8	71
						0.7	48.2	52.0	
57. x 1-Hexanol + (1 − x) butan-1-ol	298.15	1.012	0.512	135.4	0.3356	0.3	24.7	24.2	61
						0.7	21.0	21.5	
58. x Methyl benzoate + (1 − x) n-hexane	298.15	1.136	0.957	6466.7	0.6124	0.3	1220.5	7230.1	72
						0.7	1075.2	1080.3	
59. x Octane-1-ol + (1 − x) methanol	298.15	1.512	1.0	3691.8	0.148	0.3	378.0	375.2	73
						0.7	226.2	224.3	
60. x Octan-1-ol + (1 − x) ethanol	298.15	1.512	1.0	1512.46	0.267	0.3	220.1	220.0	61
						0.7	156.2	156.0	
61. x 2-Methyl pyridine + (1 − x) hexafluorobenzene	318.15	0.814	0.667	−5048.2	0.219	0.3	−581.6	−556.9	74
						0.7	−363.1	−340.8	
62. x N-Methyl piperidine + (1 − x) benzene	298.15	1.580	0.667	1114.0	0.2225	0.3	184.3	180.0	75
						0.5012	192.1	193.0	
						0.7	143.7	129.0	
63. x N-Methyl piperidine + (1 − x) cyclohexane	298.15	1.580	1.500	689.6	0.766	0.3	135.1	121.0	76
						0.7	124.1	117.0	
64. x N-Methyl piperidine + (1 − x) toluene	298.15	1.580	0.940	205.0	0.5666	0.3	42.4	36.0	77
						0.7	41.6	35.0	
65. x 3,5-Dimethylpyridine + (1 − x) hexafluorobenzene	318.15	0.788	0.667	−4460.4	0.2477	0.3	−543.0	−525.0	78
						0.7	−347.9	−289.4	
66. x Di-n-Butylether + (1 − x) benzene	298.15	0.931	0.667	2260.3	0.2824	0.3	324.9	326.2	79
						0.7	228.7	226.7	
67. x Ethyl benzoate + (1 − x) n-hexane	298.15	1.213	0.957	5781.6	0.486	0.3	1023	1035	80
						0.7	846	862	
68. x Ethyl benzoate + (1 − x) benzene	298.15	1.217	0.667	408.7	0.057	0.3	23.9	27.4	81
						0.7	12.2	6.0	
69. x Octan-1-ol + (1 − x) methanol	298.15	1.512	1.0	3691.8	0.148	0.3	378.0	375.2	81
						0.7	226.2	224.3	

70. x Octan-1-ol + $(1-x)$ ethanol	318.15	1.512	1.0	1512.5	0.267	0.3	220.1	220.0	61
						0.7	156.2	156.0	
71. x Octan-1-ol + $(1-x)$ propan-1-	298.15	1.512	1.0	776.4	0.4324	0.3	140.7	141.2	61
-ol						0.7	119.0	125.6	
72. x Octan-1-ol + $(1-x)$ butan-1-ol	298.15	1.512	0.512	482.9	0.2553	0.3	92.4	92.8	61
						0.7	85.5	84.7	
73. x Octan-1-ol + $(1-x)$ hexanol	318.15	1.512	1.012	92.4	2.862	0.3	20.8	22.1	61
						0.7	23.0	21.2	
74. x Decan-1-ol + $(1-x)$ methanol	318.15	2.012	1.0	4153.8	0.1176	0.3	443.3	452.0	70
						0.7	267.7	254.2	
75. x Decan-1-ol + $(1-x)$ ethanol	318.15	2.012	1.0	1507.9	0.2015	0.3	219.9	217.0	70
						0.7	156.3	156.0	
76. x Decan-1-ol + $(1-x)$ propan-1-	298.15	2.012	1.0	1284.8	0.321	0.3	231.7	233.8	70
-ol						0.7	195.0	192.2	
77. x Decan-1-ol + $(1-x)$ butan-1-ol	298.15	2.012	0.512	910.2	0.2012	0.3	177.1	180.2	61
						0.7	161.3	166.0	
78. x Decan-1-ol + $(1-x)$ hexan-1-ol	318.15	2.012	1.012	415.8	0.4283	0.3	83.1	85.2	71
						0.7	77.8	78.4	
79. x Decan-1-ol + $(1-x)$ octan-1-ol	318.15	2.012	1.512	89.54	0.7728	0.3	19.5	19.2	61
						0.7	19.0	18.2	
80. x Tri-*n*-butylamine +	303.15	2.168	0.667	5418.4	0.1233	0.3	785.5	800.9	82
$(1-x)$ benzene						0.7	555.9	590.1	
(b) Gaseous mixtures									
81. x Water(g) + $(1-x)$ nitrogen(g)	373.15	1.0	1.0	179.5	1.507	0.5	54.0	53.5	83
						0.610	53.7	50.7	
82. x Water(g) + $(1-x)$	373.15	1.0	1.207	649.5	1.2936	0.5	168.1	169.6	83
n-heptane (v)						0.587	164.0	169.9	
$P = 101.325$ kPa									
83. x 2-Propanone(g) + $(1-x)$	323.3	1.0	1.0	−2013.5	0.1315	0.392	−133.7	−123.8	84
chloroform (v)						0.570	−103.6	−107.0	
$P = 44$ kPa						0.625	−92.0	−113.6	
$P = 101.3$ kPa	353.2	1.0	1.0	−399.9	1.3246	0.350	−99.5	−103.0	84
						0.474	−112.8	−112.6	
						0.675	−105.1	−97.9	

TABLE 2

Comparison of H^E (T_2, x) values [evaluated from H^E (T_1, x) values by means of eqn. (10)] with their corresponding experimental values for various mixtures

Mixture	T_1 (K)	T_2 (K)	x	$H^E(T_2, x)$ (J mole^{-1})		Ref.
				Calcd.	Exptl.	
(a) Liquid mixtures						
1. x Methylene chloride + $(1-x)$ 2-propanone	273.15	288.15	0.3	−704.6	−727.2	34
			0.7	−775.2	−783.2	
		303.15	0.3	−669.7	−735.5	34
			0.7	−736.9	−740.4	
		318.15	0.3	−638.2	−700.3	34
			0.7	−702.1	−747.2	
2. x Methylene chloride + $(1-x)$ methyl ethanoate	303.15	318.15	0.3	−621.3	−624.6	35
			0.7	−657.8	−647.5	
3. x Methylene chloride + $(1-x)$ 1,4-dioxane	303.15	318.15	0.3	−772.4	−760.5	37
			0.7	−963.4	−945.3	
4. x Chloroform + $(1-x)$ 1,4-dioxane	303.15	318.15	0.3	−1354.1	−1360.2	38
			0.7	−1937.9	−1863.3	
5. x 1,4-Dioxane + $(1-x)$ benzene	298.15	288.15	0.3	−69.4	−57.5	58
			0.7	−17.3	−6.9	
6. x 1,4-Dioxane + $(1-x)$ cyclohexane	298.15	288.15	0.3	1436.6	1360	59
			0.7	1339.0	1345	
		318.15	0.3	1301.0	1280	59
			0.7	1213.0	1260	
		333.15	0.3	1243.0	1220	59
			0.7	1159.0	1220	
7. x Aniline + $(1-x)$ benzene	293.15	298.15	0.3	820.5	743.4	68
			0.7	532.5	573.7	
		303.15	0.3	807.1	701.7	68
			0.7	523.7	551.2	
		308.15	0.3	794.0	678.0	68
			0.7	515.2	499.5	
8. x Aniline + $(1-x)$ toluene	293.15	298.15	0.3	923.8	935.3	68
			0.7	789.7	781.4	
		303.15	0.3	908.6	866.1	68
			0.7	776.7	726.8	
		308.15	0.3	893.9	820.0	68
			0.7	764.1	675.4	
9. x Aniline + $(1-x)$ o-xylene	293.15	298.15	0.3	1077.8	1034.2	68
			0.7	885.8	838.6	
		303.15	0.3	1060.0	942.2	68
			0.7	871.2	759.6	
		308.15	0.3	1042.8	859.5	68
			0.7	857.0	720.0	

TABLE 2 (continued)

Mixture	T_1 (K)	T_2 (K)	x	$H^E(T_2, x)$ (J mole^{-1})		Ref.
				Calcd.	Exptl.	
10. x Aniline + $(1-x)$ *m*-xylene	293.15	298.15	0.3	1163.8	1149.3	68
			0.7	1029.7	967.4	
		303.15	0.3	1144.6	1081.4	68
			0.7	1012.8	956.7	
		308.15	0.3	1126.0	1008.2	68
			0.7	996.0	840.3	
11. x Pyridine + $(1-x)$ benzene	298.15	313.15	0.3	8.9	25.5	62
			0.7	5.2	17.0	
		333.15	0.3	8.3	47.3	62
			0.7	4.9	32.0	
12. x Piperidine + $(1-x)$ benzene	298.15	283.15	0.4996	552.8	608.0	64
13. x Piperidine + $(1-x)$ toluene	298.15	283.15	0.5038	536.8	590.0	65
14. x *N*-Methyl piperidine + $(1-x)$ cyclohexane	298.15	283.15	0.5215	161.0	161.0	76
15. x *N*-Methyl piperidine + $(1-x)$ benzene	298.15	283.15	0.5012	202.2	205.0	75
16. x *N*-Methyl piperidine + $(1-x)$ toluene	298.15	283.15	0.5038	536.8	590.0	77
17. x Di-*n*-butylether + $(1-x)$ benzene	298.15	308.15	0.3	314.4	309.8	79
			0.7	221.3	217.8	
(b) Gaseous mixtures						
18. x Water + $(1-x)$ nitrogen $P = 101.325$ kPa	373.15	380.15	0.5	53.0	48.4	83
		390.15	0.5	51.6	42.9	
		400.15	0.5	50.4	38.0	
		410.15	0.5	49.1	34.9	
		423.15	0.5	47.6	30.6	
19. x Water + $(1-x)$ *n*-heptane $P = 101.325$ kPa	373.15	398.15	0.5	157.5	132.6	83
		423.15	0.5	148.2	105.6	
20. x 2-Propanone + $(1-x)$ chloroform $P = 101.325$ kPa	353.3	363.2	0.35	−96.5	−81.2	84
			0.675	−101.9	−81.4	
		373.2	0.35	−93.9	−64.3	84
			0.675	−99.2	−62.5	
	343.2, $P = 101.3$ kPa	343.2, $P = 35.0$ kPa	0.474	−40.1	−47.2	84
		343.2, $P = 46.1$ kPa	0.474	−52.8	−64.5	
		343.2, $P = 67.2$ kPa	0.474	−77.0	−95.1	

TABLE 2 (continued)

Mixture	T_1 (K)	T_2 (K)	x	$H^E(T_2, x)$ (J mole^{-1})		Ref.
				Calcd.	Exptl.	
		343.2, $P = 88.5$ kPa	0.474	−101.4	−126.7	
		343.2, $P = 104.5$ kPa	0.474	−119.8	−150.4	
	338.2, $P = 101.3$ kPa	323.3, $P = 43.1$ kPa	0.474	−54.7	−120.2	84
		327.8, $P = 60.8$ kPa	0.474	−75.1	−90.6	
		338.2, $P = 87.8$ kPa	0.474	−102.1	−139.4	

and

$$H^E(T_2, x, P_2) \propto P_2 \tag{12}$$

or

$$H^E(T_2, x, P_2^1) = \frac{P_2^1}{P_2} H^E(T_2, x, P_2) \tag{13}$$

Thus, if the $H^E(T_2, x, P_2)$ data of a gaseous mixture are known or can be evaluated from eqn. (10) utilizing the $H^E(T_1, x, P_2)$ data computed from eqn. (8) in the manner described above, it should be possible to evaluate $H^E(T_2, x, P_2^1)$ data for the gaseous mixture at any pressure P_2^1.

Doyle et al. [84] have recently made measurements on the molar excess enthalpy of a gaseous [x acetone + $(1 - x)$ chloroform] mixture as a function of temperature and pressure, and it would be interesting to see how eqn. (13) describes the H^E (T_2, x, P_2^1) data of this gaseous mixture. For this purpose, H^E $(T_1 = 353.2$ K, $x = 0.474$, $P_2 = 101.3$ kPa) data for this mixture were first evaluated from eqn. (8) utilizing $H^E(T_1 = 353.2$, $P_2 = 101.3$ kPa) data at two compositions. Such H^E $(T_1 = 353.2$ K, $x = 0.474$, $P_2 = 101.3$ kPa) data were next utilized to estimate $H^E(T_2 = 343.2$ and 338.2 K, $x = 0.474$, $P_2 = 101.3$ kPa) values by means of eqn. (10) which was then employed to evaluate H^E $(T_2 = 343.2$ and 338.2 K, $x = 0.474$, $P_2^1 = 35.0$, 46.1, 67.2, 88.5, and 104.5 kPa) for this mixture. Such H^E (T_2, x, P_2^1) values for this mixture are recorded in Table 2 and are also compared with their corresponding experimental values [84]; the calculated $H^E(T_2, x = 0.474, P_2^1)$ data compare reasonably well with their corresponding experimental values [84].

EFFECT OF TEMPERATURE AND PRESSURE ON THE H^E DATA OF A GASEOUS MIXTURE

If $H^E(T_1, x, P_2)$ data for a gaseous mixture are known, then from eqns. (10) and (13), $H^E(T_2, x, P_2^1)$ data for the mixture can be readily evaluated from

$$H^E(T_2, x, P_2^1) = \frac{P_2^1}{P_2} \cdot \frac{T_1}{T_2} H^E(T_1, x, P_2) \tag{14}$$

In order to check eqn. (14), $H^E(T_1 = 353.2\ \text{K}, x = 0.474, P_2 = 101.3\ \text{kPa})$ data for a gaseous [x acetone + $(1 - x)$ chloroform] mixture evaluated from eqn. (8) were employed to evaluate $H^E(T_2 = 327.8\ \text{K}, x = 0.474, P_2^1 = 60.8\ \text{kPa})$ and $H^E(T_2 = 323.3\ \text{K}, x = 0.474, P_2^1 = 43.1\ \text{kPa})$. Such $H^E(T_2, x, P_2^1)$ values for an [x acetone + $(1 - x)$ chloroform] mixture are recorded in Table 2 and are also compared with their corresponding experimental values [84]; and bearing in mind the overall simplicity of this approach these compare well with each other.

Further, in view of the use of δ^v to evaluate the $^3\xi$ molecular connectivity index of a molecule, it appears that it should also be possible to evaluate V^E data for any kind of binary mixtures of non-electrolytes. It has already been shown [20] that the molar volume, V, for a wide range of non-electrolytes is well described by

$$V = \alpha/{}^3\xi + \beta({}^1\xi) + \gamma \tag{15}$$

where α, β and γ are constants. Consequently, for a binary [x A + $(1 - x)$ B] mixture while

$$V_A = \alpha_A/{}^3\xi_A + \beta_A{}^1\xi_A + \gamma_A \tag{16}$$

$$V_B = \alpha_B/{}^3\xi_B + \beta_B{}^1\xi_B + \gamma_B \tag{17}$$

the ideal molar volume for the mixture would be given by

$$V_m(\text{id}) = xV_A + (1 - x)V_B \tag{18}$$

$$= x\left[\alpha_A/{}^3\xi_A + \beta_A({}^1\xi_A) + \gamma_A\right] + (1 - \text{x})\left[\alpha_B/({}^3\xi_B) + \beta_B({}^1\xi_B) + \gamma_B\right] \tag{19}$$

The molar volume, V_m, of the mixture should also be expressible by an expression analogous to eqn. (15) so that

$$V_m = \alpha_m/{}^3\xi_m + \beta_m({}^1\xi_m) + \gamma_m \tag{20}$$

If it is assumed that

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

$$\beta_m({}^1\xi_m) = x\beta_A({}^1\xi_A) + (1 - x)\beta_B({}^1\zeta_B) \tag{22}$$

$$\gamma_m = x\gamma_A + (1 - x)\gamma_B \tag{23}$$

TABLE 3

Comparison of V^E (T_1, x) values calculated from eqn. (24) with their corresponding experimental values at $x_A = 0.3$ and 0.7 for the various mixtures

Mixture	T_1 (K)	$^3\xi_A$	$^3\xi_B$	α_{AB}	x_A	V^E (cm^3 mole^{-1})		Ref.
						Calcd.	Exptl.	
1. Water (A)+propanioc acid (B)	298.15	1.0	0.303	1.852	0.3	−1.2177	−0.9358	85
					0.7	−0.7884	−1.0067	
2. Water (A)+butanoic acid(B)	298.15	1.0	0.474	4.793	0.3	−0.9299	−0.764	85
					0.7	−0.6980	−0.820	
3. Methylene chloride(A)+ methyl ethanoate(B)	298.15	1.0	0.287	−0.446	0.3	0.331	0.250	35
					0.7	0.211	0.263	
4. Methylene chloride(A)+ aniline (B)	298.15	1.0	0.799	9.108	0.3	−0.113	−0.090	86
					0.7	−0.103	−0.120	
5. Methylene chloride (A)+ *o*-toluidine (B)	298.15	1.0	1.188	12.65	0.3	−0.070	−0.056	86
					0.7	−0.075	−0.092	
6. Ethylenediamine(A)+ isopropanol(B)	303.15	0.167	1.0	0.4308	0.3	−0.501	−0.812	87
					0.7	−0.902	−0.528	
7. Ethylenediamine(A)+ isobutanol(B)	303.15	0.167	0.365	1.684	0.3	−0.744	−1.036	87
					0.7	−1.005	−0.673	
8. Ethylenediamine(A)+ isopentanol(B)	303.15	0.167	0.707	0.478	0.3	−0.455	−0.772	87
					0.7	−0.754	−0.413	
9. Ethylenediamine(A)+ benzene(B)	303.15	0.167	0.667	−0.2787	0.3	0.254	0.361	88
					0.7	0.414	0.271	
10. Ethylenediamine(A)+ toluene(B)	303.15	0.167	0.940	−0.240	0.3	0.271	0.441	88
					0.7	0.481	0.287	
11. Ethylenediamine(A)+ *o*-xylene(B)	303.15	0.167	1.426	−0.313	0.3	0.417	0.616	88
					0.7	0.803	0.486	
12. Ethylenediamine(A)+ *m*-xylene	303.15	0.167	1.174	−0.347	0.3	0.433	0.486	88
					0.7	0.804	0.639	

TABLE 3 (continued)

Mixture	T_1 (K)	$^3\xi_A$	$^3\xi_B$	α_{AB}	x_A	V^E (cm^3 mole^{-1})		Ref.
						Calcd.	Exptl.	
13. Ethylenediamine(A)+ *p*-xylene(B)	303.15	0.167	1.217	−0.2944	0.3	0.372	0.537	88
					0.7	0.696	0.416	
14. Chloroform(A)+Diethylether(B)	303.15	1.0	0.408	4.377	0.3	−1.348	−1.160	39
					0.7	−0.959	−1.021	
15. Bromoform(A)+benzene(B)	303.15	1.0	0.667	0.3008	0.3	−0.014	−0.009	89
					0.7	−0.012	−0.014	
16. Chloroform(A)+pyridine (B)	303.15	1.0	0.566	1.2423	0.3	−0.125	−0.115	89
					0.7	−0.099	−0.148	
17. Chloroform(A)+di.*tert.* butylether(B)	298.15	1.0	0.612	15.715	0.3	−1.115	−1.071	42
					0.7	−0.919	−0.995	
18. Carbon tetrachloride(A)+ diethylether (B)	298.15	1.0	0.408	2.3374	0.3	−0.720	−0.637	43
					0.7	−0.513	−0.559	
19. Carbon tetrachloride(A)+ di.*tert* butylether(B)	298.15	1.0	0.612	1.0459	0.3	−0.0742	−0.0693	42
					0.7	−0.0611	−0.0663	
20. Carbon tetrachloride(A)+ di.*n*-butylether(B)	298.15	1.0	0.931	124.31	0.3	−0.1363	−0.1354	79
					0.7	−0.1403	−0.1370	
21. Carbon tetrachloride(A)+ di-isopentylether(B)	298.15	1.0	1.158	8.088	0.3	−0.033	−0.137	42
					0.7	−0.028	−0.039	
22. Trimethylene oxide(A)+ benzene (B)	298.15	0.577	0.667	37.77	0.3	−0.260	−0.255	90
					0.7	−0.279	−0.277	
23. 1,4-Dioxane(A)+benzene (B)	298.15	0.744	0.667	16.33	0.3	−0.058	−0.075	91
					0.7	−0.042	−0.037	
24. 1,4-Dioxane(A)+cyclohexane(B)	298.15	0.744	1.500	−8.3265	0.3	0.703	0.703	92
					0.7	0.923	0.756	
25. 1,3-Dioxane(A)+benzene(B)	298.15	0.889	0.667	7.2112	0.3	−0.172	−0.168	93
					0.7	−0.153	−0.150	

TABLE 3 (continued)

Mixture	T_1 (K)	$^3\xi_A$	$^3\xi_B$	α_{AB}	x_A	V^E (cm^3 mole^{-1})		Ref.
						Calcd.	Exptl.	
26. *n*-Butylamine(A)+ *n*-propanol(B)	303.15	0.558	1.0	8.695	0.3	−0.737	−0.820	94
					0.7	−0.926	−0.809	
27. *n*-Butylamine(A)+ *n*-butanol(B)	303.15	0.558	0.512	274.36	0.3	−0.815	−0.816	94
					0.7	−0.787	−0.761	
28. *n*-Butylamine(A)+ *n*-pentanol(B)	303.15	0.558	0.762	24.788	0.3	−0.727	−0.773	94
					0.7	−0.823	−0.747	
29. *n*-Butylamine(A)+ *n*-hexanol(B)	303.15	0.558	1.012	7.897	0.3	−0.691	−0.753	94
					0.7	−0.872	−0.753	
30. Butanol(A)+methanol(B)	298.15	0.512	1.0	−0.4813	0.3	0.055	0.079	95
					0.7	0.071	0.051	
31. Butanol(A)+ethanol(B)	298.15	0.512	1.0	−0.078	0.3	0.009	0.013	96
					0.7	0.012	0.008	
32. Butanol(A)+propan-1-ol (B)	298.15	0.512	1.0	0.0124	0.3	−0.0014	−0.0014	96
					0.7	−0.0018	−0.0012	
33. Oxane(A)+benzene(B)	298.15	1.076	0.667	2.409	0.3	−0.149	−0.133	97
					0.7	−0.124	−0.141	
34. Hexanol(A)+methanol(B)	298.15	1.012	1.0	−3252.2	0.3	0.097	0.141	98
					0.7	0.093	0.066	
35. Hexanol(A)+ethanol(B)	298.15	1.012	1.0	−1018.07	0.3	0.030	0.043	71
					0.7	0.030	0.022	
36. Hexanol(A)+propan-1-ol (B)	298.15	1.012	1.0	−528.83	0.3	0.016	0.018	70
					0.7	0.016	0.013	
37. Hexanol(A)+butan-1-ol(B)	298.15	1.012	0.512	−0.073	0.3	0.0112	0.0111	99
					0.7	0.0085	0.0090	
38. Pyridine(A)+benzene(B)	303.15	0.566	0.667	18.2526	0.3	−0.163	−0.162	89
					0.7	−0.174	−0.180	
39. Aniline(A)+benzene(B)	293.15	0.799	0.667	20.895	0.3	−0.203	−0.195	68
					0.7	−0.189	−0.176	

40. Aniline(A)+toluene(B)	293.15	0.799	0.940	−14.716	0.3	−0.091	−0.081	68
					0.7	−0.092	−0.094	
41. Aniline(A)+*o*-xylene(B)	293.15	0.799	1.426	−2.309	0.3	0.134	0.184	68
					0.7	0.169	0.124	
42. Aniline(A)+*m*-xylene(B)	293.15	0.799	1.174	−1.632	0.3	0.048	0.088	68
					0.7	0.056	0.027	
43. Cyclohexylamine(A)+ Butan-1-ol(B)	303.15	1.496	0.512	3.933	0.3	−1.293	−1.046	100
					0.7	−0.870	−0.987	
44. Cyclohexylamine(A)+ butan-2-ol(B)	303.15	1.496	0.498	2.249	0.3	−0.792	−0.661	100
					0.7	−0.528	−0.599	
45. Cyclohexylamine(A)+ pentan-1-ol(B)	303.15	1.496	0.762	10.673	0.3	−1.079	−0.958	100
					0.7	−0.830	−0.864	
46. Cyclohexylamine(A)+ hexan-1-ol(B)	303.15	1.496	1.012	31.12	0.3	−0.874	−0.821	100
					0.7	−0.749	−0.736	
47. Cyclohexylamine(A)+ heptan-1-ol(B)	303.15	1.496	1.085	44.145	0.3	−0.799	−0.790	100
					0.7	−0.703	−0.736	
48. Octan-1-ol(A)+methanol(B)	298.15	1.512	1.0	−4.494	0.3	0.142	0.196	101
					0.7	0.120	0.110	
49. Octan-1-ol(A)+ethanol(B)	298.15	1.512	1.0	−1.739	0.3	0.055	0.070	96
					0.7	0.0045	0.040	
50. Octan-1-ol(A)+propan-1-ol (B)	298.15	1.512	1.0	−1.487	0.3	0.0469	0.0492	61
					0.7	0.0400	0.0382	
51. Octan-1-ol(A)+butan-1-ol(B)	298.15	1.512	0.512	−0.1294	0.3	0.0432	0.0372	61
					0.7	0.0291	0.0328	
52. Octan-1-ol(A)+hexan-1-ol(B)	298.15	1.512	1.012	−0.303	0.3	0.0089	0.0090	61
					0.7	0.0076	0.0076	
53. Di-*n*-butylether(A)+ benzene(B)	298.15	0.931	0.667	−3.696	0.3	0.1167	0.0874	79
					0.7	0.1024	0.1400	
54. Decan-1-ol(A)+methanol(B)	298.15	0.937	1.00	−1.361	0.3	0.112	0.142	102
					0.7	0.085	0.070	
55. Decan-1-ol(A)+ethanol(B)	298.15	2.012	1.0	−1.0533	0.3	0.086	0.102	71
					0.7	0.066	0.060	
56. Decan-1-ol(A)+propan-1-ol (B)	298.15	2.012	1.0	−1.052	0.3	0.0863	0.0842	71
					0.7	0.0658	0.0692	

TABLE 3 (continued)

Mixture	T_1 (K)	$^3\xi_A$	$^3\xi_B$	α_{AB}	x_A	V^E (cm^3 mole^{-1}) Calcd.	V^E (cm^3 mole^{-1}) Exptl.	Ref.
57. Decan-1-ol(A)+butan-1-ol (B)	298.15	2.012	0.512	−0.180	0.3	0.0858	0.0712	96
					0.7	0.0529	0.0630	
58. Decan-1-ol(A)+ *n*-pentane(B)	298.15	2.012	0.707	4.561	0.00076	−0.0058	−0.0016	103
					0.00139	−0.0107	−0.0029	
					0.3	−1.044	−0.946	
					0.7	−0.708	−0.746	
					0.97573	−0.0653	−0.0768	
59. Decan-1-ol(A)+ *n*-hexane(B)	298.15	2.012	0.957	5.938	0.00178	−0.0064	0.0018	103
					0.00547	−0.0194	0.0037	
					0.3	−0.5662	−0.5216	
					0.7	−0.4251	−0.4568	
					0.98453	−0.0261	−0.0329	
60. Decan-1-ol(A)+hexan-1-ol(B)	298.15	2.012	1.012	−0.462	0.3	0.0363	0.0324	96
					0.7	0.0278	0.0322	
61. Decan-1-ol(A)+octan-1-ol(B)	298.15	2.012	1.512	−0.652	0.3	0.0068	0.0066	96
					0.7	0.0060	0.0065	
62. Decan-1-ol(A)+ *n*-octane (B)	298.15	2.012	1.457	12.4800	0.00083	−0.0007	0.0034	103
					0.0052	−0.0046	0.0182	
					0.3	−0.1696	−0.1283	
					0.7	−0.1492	−0.1828	
					0.99688	−0.0020	−0.0028	
					0.99768	−0.0020	−0.0021	
63. Decan-1-ol(A)+ *n*-hexadecane(B)	298.15	2.012	3.457	−11.1494	0.00145	0.0014	0.0087	103
					0.00787	0.0076	0.0422	
					0.03356	0.1541	0.1202	
					0.3	0.2325	0.2862	
					0.7	0.2874	0.2432	
					0.97209	0.0442	0.0320	
					0.99314	0.0103	0.0083	

then the molar excess volume for this mixture is given by

$$V^{\mathrm{E}} = \alpha_{\mathrm{AB}}\left[\frac{1}{x_{\mathrm{A}}({}^{3}\xi_{\mathrm{A}}) + (1-x)({}^{3}\xi_{\mathrm{B}})} - \frac{x}{{}^{3}\xi_{\mathrm{A}}} - \frac{(1-x)}{{}^{3}\xi_{\mathrm{B}}}\right] \tag{24}$$

$$\alpha_{\mathrm{AB}} = \alpha_{\mathrm{m}} = \alpha_{\mathrm{A}} = \alpha_{\mathrm{B}}$$

Evaluation of V^{E} from eqn. (24) requires a knowledge of α_{AB} for the mixture and this was evaluated by fitting $V^{\mathrm{E}}(T_1, x = 0.5)$ data to eqn. (24). This value of α_{AB} was next employed to evaluate $V^{\mathrm{E}}(T_1, x = 0.3, 0.7)$ data for the mixture. Such V^{E} (T_1, x) data for various binary mixtures are recorded in Table 3 and are also compared with their corresponding experimental values [35,39,42,43,61,68,70,71,79,85–103].

Examination of Table 3 reveals that the $V^{\mathrm{E}}(T_1, x = 0.3, 0.7)$ data so obtained for the various mixtures compare well with their experimental values even for mixtures where either one or both the components are associated, or where the components are known to undergo specific interaction between themselves, the quantitative agreement between the theoretical and experimental V^{E} (T_1, x) values for binary mixtures containing ethylenediamine, cyclohexylamine and water is not good. For x ethylenediamine + $(1-x)$ isopronanol, $+(1-x)$ isobutanol and $+(1-x)$ isopentanol mixtures while $\{V^{\mathrm{E}}_{\text{calcd.}}(T_1, x = 0.3) - V^{\mathrm{E}}_{\text{exptl.}}(T_1, x = 0.3)\} = 0.3$ cm^3 mole^{-1}, $\{V^{\mathrm{E}}_{\text{calcd.}}(T_1, x = 0.7) - V^{\mathrm{E}}_{\text{exptl.}}(T_1, x = 0.7)\} = -0.35$ cm^3 mole^{-1}. This is understandable since both ethylenediamine and alkanols are associated in the pure state through hydrogen bonding [87 and refs. cited therein] so that their V^{E} data are due essentially to (i) mutual breaking up of O–H $\cdots$ O and N–H $\cdots$ N bonds represented by

$$(\mathrm{R{-}O{-}H})_n \rightleftharpoons n(\mathrm{ROH})$$

$$[(\mathrm{H_2N})_2(\mathrm{CH_2})_2]_n \rightleftharpoons n(\mathrm{NH_2{-}CH_2{-}CH_2NH_2})$$

in the self-associated alkanols as well as ethylenediamine; and (ii) the formation of an O–H $\cdots$ N bond between unlike molecules.

Consequently, for these mixtures when $x = 0.3$, while all these alkanols remain practically as $(\mathrm{ROH})_n$, the ethylenediamine undergoes almost complete depolymerization and its monomers undergo N $\cdots$ H–O bond formation with alkanols. Since ethylenediamine is a strong bidentate ligand, effects due to (ii) outweigh those due to effect (i) so that the $V^{\mathrm{E}}_{\text{calcd.}}(T_1, x)$ values [calculated on the basis that there are no effects like (i) and (ii) as in the present case] would be more positive than the $V^{\mathrm{E}}_{\text{exptl.}}(T_1, x)$ values, and $\{V^{\mathrm{E}}_{\text{calcd.}}(T_1, x = 0.3) - V^{\mathrm{E}}_{\text{exptl.}}(T_1, x = 0.3)\}$ would have the same value for all these mixtures. An opposite effect will characterize these mixtures for $x = 0.7$.

For x ethylenediamine + $(1-x)$ benzene, $+(1-x)$ toluene, $+(1-x)$ *o*-xylene, $+(1-x)$ *p*-xylene and $+(1-x)$ *m*-xylene mixtures at $x = 0.3$, while ethylenediamine undergoes almost complete depolymerization, the ability of the aromatics to interact with these ethylenediamine monomers through N–H $\cdots \pi$ interaction would be governed by the ability of the aromatic hydrocarbons to donate their π-electrons. Now while this ability to donate π-electrons increases in the order *o*-xylene $\geqslant$ *m*-yxlene $>$ *p*-xylene $>$ toluene $>$ benzene, the steric repulsion increases in the same order so that if the effects due to steric repulsion between ethylenediamine monomers and the aromatic hydrocarbons do not outweigh those due to specific N–H $\cdots\cdots \pi$ interactions between them, the $\{V^{\mathrm{E}}_{\mathrm{calcd.}}(T_1, x = 0.3)$ [as calculated on the basis that there are no effects like (i) and (ii) in the present case] $- V^{\mathrm{E}}_{\mathrm{exptl.}}(T_1, x = 0.3)\}$ value would be negative and would vary with the nature of the aromatic hydrocarbon as has indeed been observed; it varies in the order *m*-xylene $>$ benzene $>$ toluene $\approx$ *p*-xylene $>$ *o*-xylene. An opposite effect would characterize these mixtures for $x = 0.7$. x Cyclohexylamine $+ (1 - x)$ butan-1-ol, $+(1 - x)$ butan-2-ol, $+(1 - x)$ pentan-1-ol, $+(1 - x)$ hexan-1-ol and $+(1 - x)$ heptan-1-ol mixtures may also be characterized by similar effects if it is assumed that while cyclohexylamine undergoes depolymerization [100], the alkanol remains as $(\mathrm{ROH})_n$. A similar situation may also characterize binary mixtures containing water.

The very fact that the present approach describes very well $V^{\mathrm{E}}\ (T_1, x)$ data for (x alkanol $+ (1 - x)$ Alkanol) mixtures suggests that the depolymerization of alkanol is governed primarily by the other component in the mixture and that for the present case they behave as normal molecules and do not undergo depolymerization.

EFFECT OF TEMPERATURE ON $V^{\mathrm{E}}\ (T_1, x)$ DATA OF A BINARY MIXTURE

Since the molar volume, V, of a fluid varies almost directly as its T, it follows that

$$V_{\mathrm{A}}(T_1) \propto T_1 \tag{25}$$

and

$$V_{\mathrm{A}}(T_2) \propto T_2 \tag{26}$$

or

$$V_{\mathrm{A}}(T_2) = \frac{T_2}{T_1} V_{\mathrm{A}}(T_1) = \frac{T_2}{T_1}\left[\alpha_{\mathrm{A}}/{}^3\xi_{\mathrm{A}} + \beta_{\mathrm{A}}({}^1\xi_{\mathrm{A}}) + \gamma_{\mathrm{A}}\right] \tag{27}$$

so that $V^{\mathrm{E}}\ (T_2, x)$ for an $[x\ \mathrm{A} + (1 - x)\ \mathrm{B}]$ mixture would be given by

$$V^{\mathrm{E}}(T_2, x) = \frac{T_2}{T_1} V^{\mathrm{E}}(T_1, x) \tag{28}$$

Thus, if $V^{\mathrm{E}}(T_1, x)$ data for a binary mixture are known or can be evaluated from eqn. (27) from the $V^{\mathrm{E}}\ (T_1, x = 0.5)$ data, it should be possible to evaluate $V^{\mathrm{E}}(T_2, x)$ data for the mixture. Such $V^{\mathrm{E}}(T_2, x)$ data for some

TABLE 4

Comparison of V^E (T_2, x) values evaluated from V^E (T_1, x) values by means of eqn. (28) utilizing V^E $(T_1, x, = 0.5)$ data alone with their corresponding experimental values for various mixtures

Mixture	T_1	T_2	x	V^E (T_2, x) (cm^3 mole^{-1})		Ref.
				Calcd.	Exptl.	
1. x Methylene chloride +	298.15	308.15	0.3	0.337	0.261	35
$(1-x)$ methyl ethanoate			0.7	0.215	0.271	
2. x Methylene chloride +	298.15	308.15	0.3	−0.117	−0.113	86
$(1-x)$ aniline			0.7	−0.107	−0.186	
3. x Methylene chloride +	298.15	308.15	0.3	−0.072	−0.083	86
$(1-x)$ *o*-toluidine			0.7	−0.078	−0.130	
4. x Chloroform +	303.15	308.15	0.3	−0.127	−0.114	89
$(1-x)$ pyridine			0.7	−0.102	−0.150	
5. x Bromoform +	303.15	308.15	0.3	−0.013	−0.018	89
$(1-x)$ benzene			0.7	−0.012	−0.019	
6. x Carbon tetrachloride +	298.15	308.15	0.3	−0.1409	−0.1317	79
$(1-x)$ di-*n*-butylether			0.7	−0.1450	−0.1319	
7. x 1,4-Dioxane +	298.15	288.15	0.3	−0.056	−0.066	91
$(1-x)$ benzene			0.7	−0.041	−0.025	
		308.15	0.3	−0.062	−0.087	91
			0.7	−0.044	−0.054	
8. x 1,4-Dioxane +	298.15	288.7	0.3	0.679	0.845	92
$(1-x)$ cyclohexane			0.7	0.892	0.723	
		318.15	0.3	0.750	0.944	92
			0.7	0.985	0.799	
9. x *n*-Butylamine +	303.15	313.15	0.3	−0.761	−0.890	94
$(1-x)$ propan-1-ol			0.7	−0.957	−0.919	
10. x *n*-Butylamine +	303.15	313.15	0.3	−0.842	−0.888	94
$(1-x)$ butan-1-ol			0.7	−0.813	−0.819	
11. x *n*-Butylamine +	303.15	313.15	0.3	−0.751	−0.843	94
$(1-x)$ pentan-1-ol			0.7	−0.850	−0.834	
12. x *n*-Butylamine +	303.15	313.15	0.3	−0.714	−0.921	94
$(1-x)$ hexan-1-ol			0.7	−0.901	−0.829	
13. x Pyridine +	303.15	308.15	0.3	−0.165	−0.168	89
$(1-x)$ benzene			0.7	−0.177	−0.160	
14. x Aniline + $(1-x)$ benzene	293.15	298.15	0.3	−0.204	−0.208	68
			0.7	−0.192	−0.179	
		303.15	0.3	−0.210	−0.224	68
			0.7	−0.195	−0.192	
		308.15	0.3	−0.213	−0.239	68
			0.7	−0.199	−0.205	
15. x Aniline + $(1-x)$ toluene	293.15	298.15	0.3	−0.093	−0.090	68
			0.7	−0.094	−0.095	
		303.15	0.3	−0.094	−0.096	68
			0.7	−0.095	−0.098	
		308.15	0.3	−0.096	−0.099	68
			0.7	−0.097	−0.112	

TABLE 4 (continued)

Mixture	T_1	T_2	x	$V^E(T_2, x)$ (cm^3 mole^{-1}) Calcd.	$V^E(T_2, x)$ (cm^3 mole^{-1}) Exptl.	Ref.
16. x Aniline + $(1-x)$ *o*-xylene	293.15	298.15	0.3	0.136	0.188	68
			0.7	0.172	0.131	
		303.15	0.3	0.139	0.199	68
			0.7	0.175	0.142	
		308.15	0.3	0.141	0.207	68
			0.7	0.178	0.146	
17. x Aniline + $(1-x)$ *m*-xylene	293.15	298.15	0.3	0.049	0.096	68
			0.7	0.057	0.036	
		303.15	0.3	0.050	0.098	68
			0.7	0.058	0.042	
		308.15	0.3	0.051	0.101	68
			0.7	0.059	0.050	
18. x Di-*n*-butylether + $(1-x)$ benzene	298.15	308.15	0.3	0.1206	0.0882	79
			0.7	0.1057	0.1375	

binary mixtures (listed in Table 3) are recorded in Table 4 and are also compared with their corresponding experimental values [35,68,79,86,89, 91,92,94].

Examination of Table 4 reveals that $V^E(T_2, x = 0.3, 0.7)$ values so calculated compare reasonably well with the corresponding experimental values even for those mixtures which are known to be characterized by specific interaction between their components or when one of the compounds is even associated.

EFFECT OF PRESSURE ON $V^E(T_1, x)$ DATA OF A BINARY MIXTURE

An increase of pressure on a fluid at a given temperature, T_1 would reduce its molar volume, and the extent to which its molar volume is decreased by an increase of presence would be determined by its isothermal compressibility and the applied pressure. Thus, if V_A (T, P) and V_A^1 (T, P^1) denote the molar volume of A at a given T and pressures P and P^1, respectively, and if $K_T(P)$ is the isothermal compressibility of A at P, then

$$V_A^1(T, P^1) = V_A(T, P)[1 - K_T(P)(P' - P)] \tag{29}$$

Further, according to Wilhelm (see Takagi [104]), K_T of a liquid varies with pressure as

$$(\partial K_T/\partial P)_T = -CK_T^2 \tag{30}$$

where C is a constant with a very small or zero temperature dependence and has a value of approximately 10 for most of the common organic liquids. Integration of eqn. (30) yields

$$1/K_T(P') \approx \frac{1}{K_T(P = 1 \text{ atm})} + CP' \tag{31}$$

where $K_T\,(P^1)$ and $K_T(P = 1$ atm) denote the isothermal compressibility of a liquid at pressure P^1 and atmospheric pressure, respectively. Accordingly

$$V_{\mathrm{A}}^1(T_1, P^1) = V_{\mathrm{A}}(T_1, P = 1 \text{ atm})\left\{1 - \frac{K_T(P = 1 \text{ atm})(P^1 - 1)}{1 + K_T(P = 1 \text{ atm})CP^1}\right\} \tag{32}$$

where

$$K_T(P = 1 \text{ atm}) = \left(1 + T\alpha^2U^2/C_{\mathrm{P}}\right)/\left(U^2\right)_{P=1 \text{ atm}} \tag{33}$$

and α, U and C_{P} represent the expansivity, ultrasonic speed in m s^{-1} and molar heat capacity of A at the thermodynamic temperature T_1 and $P = 1$ atm. Thus, if ultrasonic speed U in a fluid at a given temperature T_1 and $P = 1$ atm are known, eqn. (32) would express the molar volume of A at T and pressure P^1. Takagi [104] has determined the density of benzene, m-xylene, p-xylene, chlorobenzene, aniline and benzene $+m$-xylene, $+p$-xylene, +aniline and chlorobenzene +aniline mixtures from the pressure dependence of ultrasonic speed in the pure components as well the mixtures. Table 5 clearly shows that $V_{\mathrm{A}}^1(T_1$, $P^1 = 100, 200, 300, 400, 500$ atm, etc.) values of benzene, m-xylene, p-xylene chlorobenzene and aniline evaluated from eqn. (32) utilizing the $V_{\mathrm{A}}(T_1$, $P = 1$ atm) values [104] compare very well with the corresponding V_{A}^1 (T_1, P^1) values [104] obtained from the pressure dependence of ultrasonic speeds at T_1 in them.

TABLE 5

Comparison of molar volumes V' $(T_1 = 303.15$, $P^1)$, data of pure compounds evaluated from eqn. (32) employing their $V(T_1 = 303.15$, $P = 1$ atm) data with their corresponding experimental values for various compounds

P^1 (atm)	$V(T_1, P^1)$ (cm^3 mole^{-1})									
	Benzene		m-Xylene		p-Xylene		Chloroform		Aniline	
	Calcd.	Exptl. [104]	Calcd.	Exptl. [104]	Calcd.	Exptl. [104]	Calcd.	Exptl. [105]	Calcd.	Exptl. [105]
100	89.19	88.98	123.04	122.78	123.54	123.30				
200	88.64	88.21	122.32	121.81	122.80	122.30				
400	87.73	86.84	121.11	120.07	121.58	120.40				
500	87.35	86.24	120.61	119.6	121.06	119.76				
552.6	87.17	85.51					99.67	98.74	89.81	89.32
1035.2							98.31	96.52	88.82	87.84
1517.8							97.36	94.54	88.05	86.59

This would then mean that for an $[x\ \mathrm{A} + (1-x)\ \mathrm{B}]$ mixture

$$V_{\mathrm{A}}^{1}(T_1, P^1) = V_{\mathrm{A}}(T_1, P = 1\ \mathrm{atm})\left[1 - \frac{K_{T_{\mathrm{A}}}(P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_{T_{\mathrm{A}}}(P = 1\ \mathrm{atm})CP^1}\right] \tag{34}$$

and

$$V_{\mathrm{B}}^{1}(T_1, P^1) = V_{\mathrm{B}}(T_1, P = 1\ \mathrm{atm})\left[1 - \frac{K_{T_{\mathrm{B}}}(P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_{T_{\mathrm{B}}}(P = 1\ \mathrm{atm})CP^1}\right] \tag{35}$$

so that $V^{\mathrm{E}}(T_1, x, P^1)$ would be given by

$$\begin{aligned} V^{\mathrm{E}}(T_1, x, P^1) = \alpha_{\mathrm{AB}}\Bigg[&\left(1 - \frac{K_{T_m}(P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_{T_m}(P = 1\ \mathrm{atm})CP^1}\right)\left(\frac{1}{x^3\xi_{\mathrm{A}} + (1-x)^3\xi_{\mathrm{B}}}\right) \\ &- \frac{x}{^3\xi_{\mathrm{A}}}\left(1 - \frac{K_{T_{\mathrm{A}}}(P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_{T_{\mathrm{A}}}(P = 1\ \mathrm{atm})CP^1}\right) - \frac{(1-x)}{^3\xi_{\mathrm{B}}} \\ &\times\left(1 - \frac{K_{T_{\mathrm{B}}}(P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_T(P = 1\ \mathrm{atm})CP^1}\right)\Bigg] \end{aligned} \tag{36}$$

We now consider two cases

case (i) when

$$\begin{aligned} K_{T_m}(T_1, P = 1\ \mathrm{atm}) &= xK_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm}) + (1-x)K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm}) \\ &\approx K_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm}) \approx K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm}) \end{aligned}$$

so that eqn. (36) yields

$$V^{\mathrm{E}}(T_1, x, P^1) = V^{\mathrm{E}}(T_1, x, P = 1\ \mathrm{atm})\left[1 - \frac{K_{T_m}(T_1, P = 1\ \mathrm{atm})(P^1 - 1)}{1 + K_{T_m}(T_1, P = 1\ \mathrm{atm})CP^1}\right] \tag{37}$$

case (ii) when

$$\begin{aligned} K_{T_m}(T_1, P = 1\ \mathrm{atm}) &= xK_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm}) + (1-x)K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm}) \\ &\neq K_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm}) \neq K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm}) \end{aligned}$$

so that $V^{\mathrm{E}}(T_1, x, P^1)$ of an $[x\ \mathrm{A} + (1-x)\ \mathrm{B}]$ mixture is given by

$$\begin{aligned} V^{\mathrm{E}}(T_1, x, P^1) &= V^{\mathrm{E}}(T_1, x, P = 1\ \mathrm{atm}) \\ &\quad - \alpha_{\mathrm{AB}}(P^1 - 1)\left\{\frac{K_{T_m}(T_1, P = 1\ \mathrm{atm})}{[1 + K_{T_m}(T_1, P = 1\ \mathrm{atm})][x(^3\xi_{\mathrm{A}}) + (1-x)(^3\xi_{\mathrm{B}})]}\right. \\ &\quad \left. - \frac{xK_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm})}{[1 + K_{T_{\mathrm{A}}}(T_1, P = 1\ \mathrm{atm})(^3\xi_{\mathrm{A}})]} - \frac{(1-x)K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm})}{[1 + K_{T_{\mathrm{B}}}(T_1, P = 1\ \mathrm{atm})(^3\xi_{\mathrm{B}})]}\right\} \end{aligned} \tag{38}$$

Takagi [104] has determined the density of [x benzene + $(1 - x)$ m-xylene] and [x benzene + (1 − x) p-xylene] mixtures at $T_1 = 303.15$ K from the pressure dependence of ultrasonic speeds in these mixtures at normal as well as high pressures. Since K_{T_m} $(T_1, P = 1 \text{ atm}) = x\, K_{T_{\text{benzene}}}$ $(T_1, P = 1 \text{ atm}) + (1 - x)$ $K_{T_{m\ m\text{- or } p\text{-xylene}}}(T_1, P = 1 \text{ atm}) \approx K_{T_{\text{benzene}}}(T_1, P = 1 \text{ atm}) \approx K_{T_{m\ (m\text{- or } p\text{-xylene})}}(T_1, P = 1 \text{ atm})$, $V^{\mathrm{E}}(T_1, x, P^1)$ data at $P' = 100, 200, 300, 400$ atm, etc., for these mixtures should be well described by eqn. (37) when the corresponding $V^{\mathrm{E}}(T_1, x, P = 1 \text{ atm})$ data for these mixtures are known or can be evaluated from eqn. (24) utilizing $V^{\mathrm{E}}(T_1, x = 0.5, P = 1 \text{ atm})$ data alone. Such $V^{\mathrm{E}}(T_1, x, P^1)$ data for these mixtures at $x = 0.2$ 0.4, 0.6 and 0.8 are recorded in Table 6 and are also compared with their corresponding experimental $V^{\mathrm{E}}(T_1, x, P^1)$ data [104] obtained from the pressure of ultrasonic speeds in these mixtures as also in the pure components at T_1. Examination of Table 6 shows that eqn. (37) well describes the V^{E} (T_1, x, P^1) data of these mixtures.

Takagi [105] has also determined the densities of [$(1 - x)$ benzene + x aniline] and [$(1 - x)$ chlorobenzene + x aniline] mixtures at $T_1 = 298.15$ K from the pressure dependence of ultrasonic speeds in them at $P^1 =$ 1, 552.6, 1032.6, 1517.8 and 2069.4 atm. For these mixtures at $T_1 = 298.15$ K, $K_{T_m}(T_1, P = 1 \text{ atm}) \neq K_{T_A}(T_1, P = 1 \text{ atm})$ so that the $V^{\mathrm{E}}(T_1, x, P^1)$ of these mixtures could be evaluated from eqn. (38) if $V^{\mathrm{E}}(T_1, x, P = 1 \text{ atm})$ data for these mixtures are known. Examination of Table 5, however, suggests that eqn. (32) well describes the molar volume data of chlorobenzene and aniline at $P^1 = 552.6$ atm only; at pressures higher than 552.6 atm, the molar volume data of these mixtures differ substantially from their corresponding experimental values. Consequently, only $V^{\mathrm{E}}(T_1 = 298.15$ K, x, $P = 552.6)$ data for these mixtures were evaluated from eqn. (38) and are also recorded in Table 6. These are also compared with their corresponding $V^{\mathrm{E}}(T_1 = 298.15, x, P^1 = 552.6 \text{ atm})$ data [105] in Table 6. It is evident that while the $V^{\mathrm{E}}(T_1 = 298.15 \text{ K}, x, P^1 = 552.6 \text{ atm})$ values calculated from eqn. (38) for these mixtures have the same sign as the corresponding experimental $V^{\mathrm{E}}(T_1, x, P^1)$ values, the quantitative agreement is not good; the calculated $V^{\mathrm{E}}(T_1, x, P^1)$ values are consistently smaller than the corresponding experimental values and while the discrepancy between the experimental and theoretical $V^{\mathrm{E}}(T_1, x, P^1)$ values for [$(1 - x)$ benzene + x aniline] mixtures is more acute for $x > 0.5$, the theoretical $V^{\mathrm{E}}(T_1, x, P^1 = 552.6 \text{ atm})$ values for [$(1 - x)$ chlorobenzene + x aniline] mixtures are consistently smaller than the corresponding experimental values by about 0.06 cm^3 mole^{-1}.

This is understandable since benzene (A) + aniline $\mathrm{B}_n (n = 2,3 \cdots)$ mixtures are assumed [106] to be characterized by the presence of AB, AB_2, $\mathrm{A}_2\mathrm{B}_2$ molecular species in equilibrium with A and B_n according to the reaction.

$$\mathrm{A} + \mathrm{B}_n \rightleftharpoons \mathrm{AB} + \mathrm{AB}_2 + \mathrm{A}_2\mathrm{B}_2 + \mathrm{B}$$

TABLE 6

Comparison of V^E (T_1, x, P^1) values evaluated from eqn. (37) or (38) (see text) employing V^E (T_1, x, $P = 1$ atm) data with their corresponding experimental values at various P^1 for some binary mixtures

Mixture	T_1 (K)	x	V^E (T_1, x, P^1) (cm^3 mole^{-1})			
			$P^1 = 100$ atm		$P^1 = 200$ atm	
			Calcd.	Exptl. [104]	Calcd.	Exptl. [104]
$(1-x)$ Benzene + x *p*-xylene	303.15	0.2	0.1176	0.1560	0.1080	0.1156
		0.4	0.1365	0.1284	0.1255	0.1101
		0.6	0.2231	0.2270	0.2053	0.2139
		0.8	0.0609	0.0651	0.0561	0.0516
$(1-x)$ Benzene + x *m*-xylene	303.15	0.2	0.1521	0.1635	0.1398	0.1599
		0.4	0.2746	0.2867	0.2527	0.2868
		0.6	0.2629	0.2818	0.2422	0.2742
		0.8	0.1819	0.1960	0.1677	0.1934
$(1-x)$ Benzene + x aniline	298.15	0.1537				
		0.3074				
		0.4611				
		0.5916				
		0.7221				
		0.8269				
$(1-x)$ Chlorobenzene + x aniline	298.15	0.2852				
		0.4150				
		0.5467				
		0.6917				
		0.8218				

and as $V^E(T_1, x, P = 1$ atm) for this mixture is negative, an increase of pressure would cause the reaction to proceed more towards the right. $K_{T_m}(T_1, x, P = 1$ atm) values for this mixture should therefore be > $\{(K_{T_A}(T_1, x, P = 1$ atm) $x_A + (1 - x_A)$ $K_{T_B}(\mathrm{T}_1, x, P = 1$ atm)$\}$ since AB, etc., species are less compressible than A or B so that $V^E(T_1, x, P^1)$ values evaluated from eqn (37) on the assumption that there are no molecular species in this solution would be smaller than the $V^E(T_1, x, P^1)$ values, as has indeed been observed. Further, $\{V^E_{\text{calcd.}}(T_1, x, P^1) - V^E_{\text{exptl.}}(T_1, x, P^1)\}$ value for this mixture would vary with x and would be maximum corresponding to x at which maximum amounts of the less compressible species are produced in this mixture. Similar arguments would also apply to chlorobenzene (A) + aniline (B_n, $n = 2,3 \cdots$) mixtures if it is assumed that this mixture is characterized by the reaction $A + B_n \rightleftharpoons AB_n$ so that the $\{V^E_{\text{calcd.}}(T_1, x, P^1) - V^E_{\text{exptl.}}(T_1, x, P^1)\}$ value for this mixture will be almost

$P^1 = 300$ atm		$P^1 = 400$ atm		$P^1 = 500$ atm		$P^1 = 552.6$ atm	
Calcd.	Exptl. [104]	Calcd.	Exptl. [104]	Calcd.	Exptl. [104]	Calcd.	Exptl. [105]
0.985	0.0972	0.0889	0.0900	0.0794	0.0931		
0.1145	0.0980	0.1036	0.0811	0.0926	0.0750		
0.1875	0.1975	0.1697	0.1850	0.1519	0.1783		
0.512	0.0365	0.0464	0.0350	0.0416	0.0330		
0.1275	0.1618	0.1153	0.1589	0.1030	0.1592		
0.2308	0.2833	0.2089	0.1955	0.1870	0.2143		
0.2215	0.2663	0.2008	0.2656	0.1801	0.2625		
0.1536	0.1942	0.1395	0.1857	0.1253	0.1805		
						−0.2811	−0.0028
						−0.2910	−0.0316
						−0.4948	−0.0366
						−0.2387	−0.0921
						−0.1608	−0.1066
						−0.1660	−0.0965
						0.0302	0.0844
						0.0315	0.1126
						0.0670	0.1305
						0.0635	0.1283
						0.0272	0.0851

constant with x, as has been observed. Alternatively, when the isothermal compressibility data at T_1 and $P = 1$ atm for the pure components as well as their mixtures are not available, it may still be possible to study the effect of pressure on the molar or the specific volume of binary mixtures as well as their pure components.

As pressure on a liquid is increased, its molar or specific volume should decrease. In other words, the molar or specific volume of a liquid at a given T_1 should vary as some inverse function of the applied pressure so that if $V_A(T_1, P_1)$ and $v_A(T_1, P_1)$ represent the molar and specific volume, respectively, of A at T_1 and P_1, then

$$V_A(T_1, P_1) \propto f(1/P_1) \tag{39}$$

or

$$v_A(T_1, P_1) \propto f(1/P_1) \tag{40}$$

TABLE 7

Comparison of specific volume $\nu(T_1, P_2)$ values evaluated from eqn (46) utilizing $v(T_1, P_l)$ values at various T and P_2 with their corresponding experimental values for some compounds and their mixtures

Compound		T_1 (K)	$v(T_1, P_2)$ (cm^{-3} g^{-1})			
			$P_2 = 99$ atm		$P_2 = 393$ atm	
			Calcd.	Exptl.	Calcd.	Exptl.
Chlorobenzene [108]		298.15	0.85748	0.90175	0.84283	0.88495
		318.15	0.87470	0.91900	0.85976	0.89992
		338.15	0.89280	0.93699	0.87755	0.91528
Bromobenzene [108]		298.15	0.63412	0.66737	0.62329	0.65613
		318.15	0.64587	0.67921	0.63484	0.66654
		338.15	0.65814	0.69150	0.64690	0.67720
Nitrobenzene [108]		298.15	0.78792	0.83051	0.77446	0.81959
		318.15	0.80118	0.84404	0.78749	0.83186
		338.15	0.81490	0.85799	0.80099	0.84436
Aniline [108]		298.15	0.92802	0.97851	0.91218	0.96679
		318.15	0.94413	0.99499	0.92801	0.98148
		338.15	0.96089	1.01206	0.94448	0.99688
Methylcyclopentane [107]		298.2	1.2699	1.330	1.2482	1.292
		323.2	1.31240	1.372	1.29000	1.324
Ethanol [107]		298.2	1.28659	1.179	1.10716	1.146
		323.2	1.15000	1.203	1.13036	1.165
		348.2	1.17171	1.124	1.15171	1.182
n-Heptane [107]		298.2	1.38982	1.454	1.36609	1.409
		323.2	1.43136	1.493	1.40692	1.441
		348.2	1.48518	1.542	1.45982	1.476
$(1-x)$ Ethanol + x methylcyclopentane [107]	298.2	0.0985	1.21798	1.276	1.19718	1.242
		0.1857	1.22836	1.286	1.20739	1.251
		0.4880	1.25291	1.311	1.23152	1.273
		0.5426	1.25480	1.312	1.2337	1.273
		0.6992	1.26330	1.323	1.24173	1.284
		0.8495	1.26802	1.328	1.24637	1.291
	323.2	0.0985	1.25480	1.311	1.23337	1.270
		0.1857	1.26708	1.321	1.24544	1.281
		0.4880	1.29634	1.352	1.27421	1.307
		0.5426	1.29729	1.353	1.27514	1.308
		0.6992	1.30480	1.362	1.28256	1.317
		0.8495	1.31240	1.371	1.28999	1.324
	348.2	0.0985	1.30012	1.350	1.27792	1.302
		0.1857	1.30484	1.363	1.28256	1.313
		0.4880	1.34450	1.398	1.32154	1.340

$P_2 = 687$ atm		$P_2 = 1178$ atm		$P_2 = 1962$ atm	
Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
0.83697	0.87090	0.83189	0.85381	0.82606	0.82784
0.85378	0.88428	0.84859	0.86549	0.84265	0.83745
0.87145	0.89786	0.86615	0.87726	0.86009	0.84704
0.61896	0.64659	0.61520	0.63479	0.61089	0.61661
0.63043	0.65597	0.62659	0.64306	0.62221	0.62349
0.64241	0.66548	0.63850	0.65138	0.63403	0.63033
0.76908	0.81001	0.76440	0.79780	0.75905	0.77831
0.78202	0.82130	0.77726	0.80799	0.77182	0.78700
0.79542	0.83270	0.79058	0.81817	0.78505	0.79559
0.90584	0.95581	0.90031	0.94213	0.89402	0.92009
0.92156	0.96967	0.91595	0.95468	0.90954	0.93085
0.93792	0.98378	0.93221	0.96734	0.92569	0.94158
1.23954	1.263	1.2320	1.2790	1.22338	1.184
1.28102	1.290	1.27322	1.2490	1.26431	1.204
1.09946	1.127				
1.12250	1.145				
1.14370	1.158				
1.35659	1.374	1.34747	1.330	1.33890	1.284
1.39714	1.401	1.38774	1.353	1.37892	1.300
1.44967	1.431	1.43992	1.378	1.43077	1.320
1.18886	1.215	1.18086	1.180	1.17336	1.141
1.19899	1.224	1.19093	1.196	1.18336	1.148
1.22296	1.245	1.21473	1.196	1.20701	1.167
1.22480	1.246	1.21656	1.199	1.20883	1.168
1.23309	1.255	1.22480	1.210	1.21702	1.181
1.23770	1.262	1.22938	1.214	1.22156	1.186
1.22480	1.241	1.21656	1.204	1.20883	1.161
1.23678	1.249	1.22846	1.211	1.22065	1.166
1.26535	1.273	1.25684	1.231	1.24885	1.185
1.26627	1.274	1.25776	1.235	1.24976	1.188
1.27629	1.283	1.26508	1.242	1.25704	1.199
1.28367	1.290	1.27240	1.248	1.26431	1.203
1.26904	1.267	1.26050	1.225	1.25249	1.179
1.27364	1.276	1.26508	1.233	1.25704	1.183
1.31235	1.302	1.30353	1.255	1.29524	1.202

TABLE 7 (continued)

Compound		T_1 (K)	$v\ (T_1, P_2)$ (cm^{-3} g^{-1}) $P_2 = 99$ atm Calcd.	Exptl.	$P_2 = 393$ atm Calcd.	Exptl.
$(1-x)$ *n*-Heptane + x ethanol [107]	298.2	0.3047	1.36433	1.425	1.34103	1.381
		0.5732	1.32467	1.387	1.30205	1.345
		0.8190	1.26896	1.327	1.24730	1.290
	323.2	0.3047	1.40587	1.465	1.38186	1.412
		0.5732	1.36716	1.424	1.34381	1.373
		0.8190	1.31145	1.370	1.28906	1.325
	348.2	0.5732	1.41625	1.470	1.39207	1.407
		0.8190	1.35488	1.411	1.33175	1.356
$(1-x)$ Methyl-cyclopentane + x *n*-heptane [107]	298.2	0.1191	1.28690	1.348	1.26493	1.310
		0.3837	1.32278	1.384	1.30019	1.343
		0.5025	1.33694	1.398	1.31411	1.357
		0.6472	1.35394	1.415	1.33082	1.372
		0.8317	1.37377	1.436	1.35031	1.392
	323.2	0.1191	1.32561	1.385	1.30298	1.426
		0.3837	1.36527	1.426	1.34196	1.375
		0.5025	1.37943	1.439	1.35588	1.389
		0.6472	1.39832	1.457	1.37444	1.405
		0.8317	1.41720	1.478	1.39300	1.425
	348.2	0.5025	1.42853	1.483	1.40414	1.424
		0.6472	1.44741	1.502	1.42270	1.439
		0.8317	1.46724	1.524	1.44219	1.458

	T_1 (K)	x	$P_2 = 1.0$ atm Calcd.	Exptl.	$P_2 = 1032.6$ atm Calcd.	Exptl.
$(1-x)$ Benzene + x aniline [105]	298.15	0.1537	1.16007	1.11380	1.06368	1.04505
		0.3074	1.13500	1.08652	1.04070	1.02453
		0.4611	1.11149	1.06023	1.01914	1.00518
		0.5916	1.09207	1.03933	1.00133	1.98885
		0.7211	1.07404	1.01983	1.98480	1.97375
		0.8269	1.01024	1.00516	1.97215	1.896670
$(1-x)$ Chlorobenzene + x aniline [105]	298.15	0.2852	0.97287	0.92770	0.89204	0.88006
		0.4150	0.97493	0.93693	0.90231	0.89097
		0.5467	0.99590	0.94670	0.91315	0.90245
		0.6917	0.93277	0.95779	0.92552	0.91563
		0.8218	0.94415	0.96811	0.93681	0.94449

$P_2 = 687$ atm		$P_2 = 1178$ atm		$P_2 = 1962$ atm	
Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.
1.33170	1.347	1.32275	1.305	1.31434	1.260
1.29300	1.315	1.28430	1.275	1.27614	
1.23862	1.262	1.23030	1.226	1.22247	1.185
1.37225	1.372	1.36303	1.323	1.35436	1.276
1.33447	1.336	1.32550	1.291	1.31707	
1.28010	1.292	1.27149	1.250	1.26340	1.203
1.38239	1.363	1.37310	1.310	1.36437	
1.32249	1.319	1.31360	1.273	1.30524	1.220
1.25613	1.279	1.24769	1.200	1.23975	1.200
1.29115	1.312	1.28247	1.273	1.27432	1.229
1.30498	1.326	1.29620	1.287	1.28796	1.242
1.32157	1.341	1.31268	1.300	1.30434	1.255
1.34092	1.361	1.33190	1.319	1.32344	1.274
1.29392	1.303	1.28522	1.260	1.27705	
1.33263	1.340	1.32367	1.295	1.31525	
1.34645	1.352	1.33740	1.308	1.32889	
1.36488	1.369	1.35570	1.323	1.34709	
1.38331	1.387	1.37401	1.341	1.36528	
1.39437	1.381	1.38500	1.331	1.37619	1.276
1.41280	1.397	1.40331	1.345	1.39438	1.290
1.43216	1.414	1.42253	1.360	1.41348	1.304

$P_2 = 1517.8$ atm		$P_2 = 2069.4$ atm	
Calcd.	Exptl.	Calcd.	Exptl.
1.03568	1.00503		
1.01423	0.98732	1.01031	0.97035
1.99650	0.97210	0.99266	0.95607
1.98005	0.95814	0.97627	0.94284
1.96746	0.94414	0.46373	0.93091
0.88774	0.86479	0.88431	0.85009
0.89796	0.87593	0.89449	0.86159
0.90875	0.88774	0.90524	0.87409
0.92105	0.90140	0.91750	0.88766
0.93229	0.93091	0.92869	

similarly

$$V_A(T_1, P_2) \propto f(1/P_2) \tag{41}$$

or

$$v_A(T_1, P_2) \propto f(1/P_2) \tag{42}$$

$$\frac{V_A(T_1, P_2)}{V_A(T_1, P_1)} = \frac{v_A(T_1, P_2)}{v_A(T_1, P_1)} = f\left(\frac{P_1}{P_2}\right) \tag{43}$$

or

$$v_A(T_1, P_2) = v_A(T_1, P_1)\, f(P_1/P_2) \tag{44}$$

or

$$V_A(T_1, P_2) = V_A(T_1, P_1)\, f(P_1/P_2) \tag{45}$$

Ozawa et al. [107] and Gibson and Loeffler [108] have determined the specific volume $v_A(T, P)$ of ethanol, methyl, cyclopentane, n-heptane, chlorobenzene, bromobenzene, nitrobenzene and aniline as a function of temperature and pressure. It was found that the specific volumes $v(T_1, P_2)$ of these compounds satisfy the relation (see Table 6)

$$\frac{v(T_1, P_2)}{v(T_1, P_1)} = \left(\frac{P_1}{P_2}\right)^{0.0125} \tag{46}$$

where P_1 and P_2 are expressed in atm, and while $P_1 = 1$ atm, P_2 had the values 99, 393, 687, 1118 and 1962 atm. The $v(T_1, P_2)$ data for chlorobenzene, bromobenzene, nitrobenzene and aniline were computed from the various parameters given by Gibson and Loeffler [108] for these compounds while those of the remaining compounds were taken from the literature [107].

If expression (46) is assumed to hold even for binary mixtures it should be possible to determine the molar or specific volume $V(T_1, x, P_2)$ or $v(T_1, x, P_2)$ of a binary mixture when $V(T_1, x, P = 1$ atm) or $v(T_1, x, P = 1$ atm) data are available.

Ozawa et al. [107] have determined the specific volumes $v(T, x, P)$ of [$(1-x)$ ethanol + x methylcyclopentane], [(1-x) n-heptane + x ethanol] and [(1 − x) methylcyclopentane + x n-heptane mixtures as a function of T and P. If $v(T, x, P = 1$ atm) data for these mixtures are taken from the literature [106], then from eqn. (46)

$$v(T, x, P_2) = v(T, x, P = 1 \text{ atm}) \left[(1/P_2)^{0.0125}\right] \tag{47}$$

Such $v(T, x, P_2)$ values at $T = 298.2$, 323.2 and 348.2 K and $P_2 = 99$, 393, 687, 1178 and 1962 atm are recorded in Table 7 and are also compared with their corresponding experimental values [107,108]. It is quite evident that the calculated $v(T, x, P_2)$ values compare very well with the corresponding experimental values; the maximum difference being 5%.

Takagi [105] has determined the density at 298.15 K of [$(1-x)$ benzene +

x aniline] and [$(1 - x)$ chlorobenzene + x aniline] mixtures from the pressure dependence of ultrasonic speeds in them. It would now be interesting to see how eqn. (46) describes the $v(T = 298.15\ \mathrm{K}, \mathrm{P}_2)$ data of these mixtures when $v(T = 298.15\ \mathrm{K}, P_1 = 552.6\ \mathrm{atm})$ data are known. Such $v(T = 298.15, P_2 = 1,$ $1032.6, 1517.8$ and $2069.4\ \mathrm{atm})$ values are recorded in Table 7 and are also compared with their corresponding experimental values; again the agreement is good [maximum difference between the calculated and the experimental $\nu(T, x, P_2)$ values [105] is about 5%].

The present approach thus provides a convenient means to (i) evaluate $H^{\mathrm{E}}(T_1, x)$ or $V^{\mathrm{E}}(T_1, x)$ data, (ii) study the effect of temperature and pressure on H^{E} (T_1, x) or $V^{\mathrm{E}}(T_1, x)$ for any kind of binary mixture of non-electrolytes when $H^{\mathrm{E}}(T_1, x)$ or $V^{\mathrm{E}}(T_1, x)$ data for the mixture at two compositions at T_1 are available. This approach also enables the evaluation of specific volumes $v(T_1, x, P_2)$ of pure components as well their binary mixtures when $v(T_1, x, P_1)$ data are available.

REFERENCES

1 W. Heitler, Ann. Phys., 80 (1926) 629.
2 E.A. Guggenheim, Mixtures, Oxford University Press, Oxford, 1952.
3 J.H. Hildebrand, R.L. Scott and J.M. Prausnitz, Regular and Related Solutions, Van Nostrand, New York, 1970.
4 I. Prigogine, Molecular Theory of Solutions, North-Holland Publishing Co., Amsterdam, 1957.
5 J.S. Rowlinson, Liquid Mixtures, Butterworths, London, 1959.
6 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
7 C.A. Eckert, H. Renon and J.M. Prausnitz, Ind. Eng. Chem., Fundam., 6 (1967) 52.
8 M.L. McGlashan, K.N. Marsh and C. Warr, Trans Faraday Soc., 66 (1970) 2453.
9 J. Winnick, Ind. Eng. Chem., Fundam., 12 (1973) 203.
10 I.C. Sanchez and R.L. Lacombe, J. Phys. Chem., 80 (1976) 2352.
11 J.A. Barker, I. Brown and F. Smith, Discuss. Faraday Soc., 15 (1953) 188.
12 J.A. Barker, I.D. Watson and A.G. Williamson, Aust. J. Chem., 24 (1971) 2047.
13 L. Sarolea-Mathot, Trans. Faraday Soc., 8 (1953) 49.
14 R.P. Rastogi and H.L. Girdhar, Proc. Natl. Inst. Sci. India, 28 (1962) 40.
15 M.L. McGlashan and R.P. Rastogi, Trans. Faraday Soc., 54 (1958) 496.
16 L.G. Hepler and D.V. Fenby, J. Chem. Thermodyn., 5 (1978) 471.
17 D.V. Fenby and L.G. Hepler, J. Chem. Thermodyn., 6 (1974) 185.
18 R. Phillippe, C. Jambon and P. Clechet, J. Chem. Thermodyn., 5 (1973) 431.
19 P.P. Singh, B.R. Sharma and K.S. Sidhu, Aust. J. Chem., 30 (1977) 1241.
20 P.P. Singh, R.K. Nigam, K.C. Singh and V.K. Sharma, Thermochim. Acta, 46 (1981) 175.
21 P.P. Singh, R.K. Nigam, V.K. Sharma, S.P. Sharma and K.C. Singh, Thermochim. Acta, 52 (1982) 87.
22 D.H. Rouvary, RIC Rev., 4 (1971) 173.
23 C.A. Coulson, Proc. Cambridge Philos. Soc., 46 (1950) 202.
24 A.T. Balaban (Ed.), Chemical Applications of Graph Theory, Academic Press, London, 1974.
25 L.B. Kier, L.H. Hall, W.J. Murray and M. Randic, J. Pharm. Sci., 64 (1975) 1971.

26 L.B. Kier, W.J. Murray, M. Randic and L.H. Hall, J. Pharm, Sci., 65 (1976) 1226.
27 L.B. Kier and L.H. Hall, J. Pharm. Sci., 65 (1976) 1806.
28 L.H. Hall and L.B. Kier, J. Pharm Sci., 67 (1978) 1743.
29 L.B. Kier, in S.H. Yalkowsky, A.A. Sinkula and S.C. Valvani (Eds.), Physical Chemical Properties of Drugs, Medicinal Research Series No. 10, Marcel Dekker, New York and Basel, 1980, p. 227.
30 L.B. Kier, in S.H. Yalkowsky, A.A. Sinkula and S.C. Valvani (Eds.), Physical Chemical Properties of Drugs, Medicinal Research Series No. 10, Marcel Dekker, New York and Basel, 1980, p. 295.
31 L.B. Kier, in S.H. Yalkowsky, A.A. Sinkula and S.C. Valvani (Eds.), Physical Chemical Properties of Drugs, Medicinal Research Series No. 10, Marcel Dekker, New York and Basel, 1980, p. 297.
32 L.B. Kier, in S.H. Yalkowsky, A.A. Sinkula and S.C. Valvani (Eds.), Physical Chemical Properties of Drugs, Medicinal Research Series No. 10, Marcel Dekker, New York and Basel, 1980, p. 289.
33 L.B. Kier, in S.H. Yalkowsky, A.A. Sinkula and S.C. Valvani (Eds.), Physical Chemical Properties of Drugs, Medicinal Research Series No. 10, Marcel Dekker, New York and Basel, 1980, p. 290.
34 H.C. Van ness and M.N. Abbott, Int. Data Ser. A, 2 (1974) 89.
35 H.C. Van ness and M.M. Abbott, Int. Data Ser. A, 2 (1974) 91.
36 H.C. Van ness and M.M. Abbott, Int. Data Ser. A, 2 (1974) 87.
37 J.C. Van ness and M.M. Abbott, Int. Data Ser. A, 2 (1974) 88.
38 H.C. Van ness and M.M. Abbott, Int. Data Ser. A, 2 (1974) 93.
39 A.G. Williamson, Int. Data Ser. A, 1 (1973) 13.
40 R.C. Phutela, P.S. Arora and P.P. Singh, J. Chem. Thermodyn., 6 (1974) 801.
41 L.A. Beath and A.G. Williamson, J. Chem. Thermodyn., 1 (1969) 51.
42 L.A. Beath, S.P. O'Neill and A.G. Williamson, J. Chem. Thermodyn., 1 (1969) 293.
43 A.G. Williamson, Int. Data Ser. A, 1 (1973) 14.
44 H.C. Van ness and M.M. Abbott, Int. Data Ser. A, 2 (1974) 85.
45 A. Inglese, E. Wilhelm, J.P.E. Grolier and H.V. Kehiaian, J. Chem. Theromodyn., 13 (1981) 229.
46 T.A. McFall, M.E. Post, J.J. Christensen and R.M. Izatt, J. Chem. Thermodyn., 13 (1981) 441.
47 K.W. Morcom, Int. Data Ser. A, 1 (1973) 52.
48 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 106.
49 J.P.E. Grolier, Int. Data Ser. A, 1 (1973) 18.
50 J.P.E. Grolier, Int. Data Ser. A, 1 (1973) 17.
51 J.P.E. Grolier, Int. Data Ser. A, 1 (1973) 19.
52 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 113.
53 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 114.
54 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 110.
55 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 111.
56 J.P.E. Grolier, Int. Data Ser. A, 1 (1973) 10.
57 K.W. Morcom, Int. Data Ser. A, 1 (1973) 55.
58 K.W. Morcom, Int. Data Ser. A, 1 (1973) 51.
59 K.W. Morcom, Int. Data Ser. A, 1 (1973) 56.
60 K.W. Morcom, Int. Data Ser. A, 1 (1973) 53.
61 A.E. Pope, H.D. Pflug, B. Dacre and G.C. Benson, Can. J. Chem., 45 (1967) 2665.
62 K.W. Morcom, Int. Data Ser. A, 1 (1973) 58.
63 W. Woycicki, Int. Data Ser. A, 1 (1975) 37.
64 W. Woycicki, Int. Data Ser. A, 1 (1975) 35.
65 W. Woycicki, Int. Data Ser. A, 1 (1975) 36.

66 W. Woycicki, Int. Data Ser. A, 1 (1975) 33.
67 W. Woycicki, Int. Data Ser. A, 1 (1975) 34.
68 K.C. Singh, Ph.D. Thesis, Maharshi Dayanand University, Rohtak, India, 1979.
69 G.C. Benson, Int. Data Ser. A, 2 (1975) 78.
70 G.C. Benson and H.D. Pflug, J. Chem. Eng. Data, 13 (1968) 408.
71 G.C. Benson and H.D. Pflug, J. Chem. Eng. Data, 15 (1970) 382.
72 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 105.
73 G.C. Benson, Int. Data Ser. A, 1 (1973) 8.
74 R. Meyer, Int. Data Ser. A, 2 (1973) 134.
75 W. Woycicki, Int. Data Ser. A, 2 (1973) 127.
76 W. Woycicki, Int. Data Ser. A, 2 (1973) 126.
77 W. Woycicki, Int. Data Ser. A, 2 (1973) 128.
78 R. Meyer, Int. Data Ser. A, 2 (1973) 134.
79 J.B. Ott, K.N. Marsh and A.E. Richards, J. Chem. Thermodyn., 13 (1981) 447.
80 J.P.E. Grolier, Int. Data Ser. A, 2 (1973) 106.
81 J.P.E. Grolier, Ing. Data Ser. A, 2 (1973) 107.
82 A.S. Kertes, J. Phys. Chem., 77 (1973) 3107.
83 P. Richards, C.J. Wormald and T.J. Verlett, J. Chem. Thermodyn., 13 (1981) 623.
84 J.A. Doyle, D.J. Hutchings, J.C. Mayr and C.J. Wormald, J. Chem. Thermodyn., 13 (1981) 261.
85 C. Casanova, E. Wilhelm, J.P.E. Grolier and H.V. Kehiaian, J. Chem. Thermodyn., 13 (1981) 241.
86 J.L. Kapoor and P.P. Singh, J. Chem. Thermodyn., 6 (1974) 407.
87 D.N. Rao, A. Krishnaiah and P.R. Naidu, J. Chem. Thermodyn., 13 (1981) 367.
88 D.N. Rao, A. Krishnaiah and P.R. Naidu, J. Chem. Thermodyn., 13 (1981) 677.
89 B.R. Sharma, Ph.D. Thesis. Panjabi University, Patiala, 1978.
90 K.W. Morcom, Int. Data Ser. A, 1 (1973) 29.
91 K.W. Morcom, Int. Data Ser. A, 1 (1973) 24.
92 K.W. Morcom, Int. Data Ser. A, 1 (1973) 25.
93 K.W. Morcom, Int. Data Ser. A, 1 (1973) 30.
94 A. Krishnaiah and P.R. Naidu, Acta. Chim. Acad. Sci. Hung., Tomus, 104(3) (1980) 295.
95 G.C. Benson, Int. Data Ser. A, 1 (1973) 10.
96 H.D. Pflug and G.C. Benson, Can. J. Chem., 46 (1968) 287.
97 K.W. Morcom, Int. Data Ser. A, 1 (1973) 28.
98 G.C. Benson, Int. Data Ser. A, 2 (1973) 88.
99 G.C. Benson, Int. Data Ser. A, 2 (1974) 109.
100 G. Dharamraju, G. Narayanaswamy and G.K. Raman, J. Chem. Thermodyn., 13 (1981) 249.
101 G.C. Benson, Int. Data Ser. A, 1 (1973) 11.
102 G.C. Benson, Int. Data Ser. A, 1 (1973) 85.
103 A.J. Treszezanowicz, O. Kiyohara and G.C. Benson, J. Chem. Thermodyn., 13 (1981) 253.
104 T. Takagi, J. Chem. Thermodyn., 13 (1981) 291.
105 T. Takagi, J. Chem. Thermodyn., 12 (1980) 277.
106 R.K. Nigam, P.P. Singh and K.C. Singh, Can. J. Chem.
107 S. Ozawa, N. Ooyatsu, M. Yamabe, S. Honmo and Y. Ogino, J. Chem. Thermodyn., 12 (1980) 229.
108 R.E. Gibson and O.H. Loeffler, J. Am. Chem. Soc., 61 (1939) 2515.