

Topological aspects of molecular interactions in liquid mixtures of non-electrolytes

PREM P. SINGH and SANJEEV MAKEN

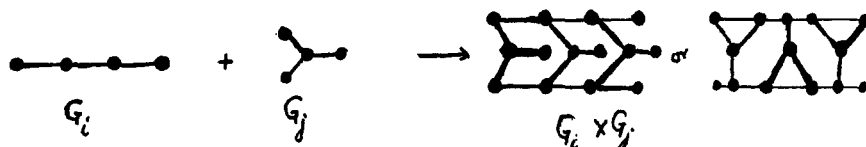
Chemistry Department, Maharshi Dayanand University,
 Rohtak-124001 (INDIA)

Abstract It has been shown that activity coefficients of the components of an (i+j) mixture have a simple topological base and that the same (as well as $G^E(T, x_i)$ and $H^E(T, x_i)$ data) can be well predicted, on the strength of graph-theoretical arguments when only $H^E(T, x_i=0.4$ and $0.5)$ data for the binary mixture, of almost equal sized components, are available. For (i+j) mixtures that are characterized by the presence of 1:1 or 1:1 and 1:2 molecular complexes or have components that differ appreciably in molar volumes the approach has been modified to well reproduce the activity coefficients data when γ_i^∞ datum alone is available for the mixture. The versatility of graph-theoretical arguments have further been made evident by rationalizing volumetric and enthalpic effects in (i or i(S) (i.e. i saturated with a salt (S)) (i+j) mixtures to yield worthwhile insight into i) the molecular state of i and or j (or of the salt S in i and the influence of j on it) and ii) the energetics of molecular interactions that characterize these mixtures.

Solution non-ideality has been attributed (ref.1) to either physical intermolecular forces or to chemical reactions between the components of (i+j) mixtures. Since laws of limited validity (ref. 2) have been employed to describe intermolecular potential functions that characterize interactions between the components of these mixtures, almost all the present theories (ref. 3-9) of solutions of non-electrolytes have limited applicability. Again the process of binary mixture formation may trigger inter or intramolecular changes in either one or both the components and this must be reflected in the molar excess volume V^E and molar excess enthalpy H^E data. In this regard although, a few recent approaches (ref. 10-13) address themselves specifically to this aspect of molecular interactions, yet they require that the molecular states of the pure components be known and that a proper itinerary be maintained of the various entities that exist in these mixtures; this may not be possible always. This calls for an alternative approach.

Topological aspects of the activity coefficients of the components of a (i + j) mixture: conceptual aspects of approach and results

The structural formula of chemists is actually a molecular graph (ref.14) characterized by vertices (atoms) and edges (bonds) $G(e, v)$. If the pure i and j are represented by $G_i(e_i, v_i)$ (or G_i) and $G_j(e_j, v_j)$ (or G_j) respectively, then the (i+j) mixture formation would be characterized by interactions between i and j in the $G_i \times G_j$ molecular graph (ref. 15). As activity coefficient of, say, the i th component



in an (i+j) mixture varies as $\gamma_i \rightarrow 1$ as $x_i \rightarrow 1$, γ_i in fact reflects the influence of the j th component on the i-i interactions of i in the

mixture and is related to the excess partial molar Gibbs free energy of i , \bar{g}_i^E , in this mixture by $RT \ln \gamma_i = \bar{g}_i^E$. If \bar{g}_i^E is assumed to arise due to those interactions of the molecular surfaces of j that influence the i - i interactions of i , \bar{g}_i^E and hence γ_i may be expressed by $RT \ln \gamma_i = X_{ij} S_j$ where S_j is the surface fraction of j and X_{ij} is the molar i - j interaction energy. If V_j/V_i is replaced by B , should be expressible (ref. 16) by

$$RT \ln \gamma_i = X_{ij} (x_j B / (x_i + x_j B)) \quad (1)$$

Activity coefficient of the j th component was then evaluated (ref. 16) via the Gibbs-Duhem equation, in the form

$$RT \ln \gamma_j = B X_{ij} [\ln((x_i + x_j B) / x_j B) - x_i / (x_i + x_j B)] \quad (2)$$

As the molar excess Gibbs free energy G^E , and molar excess enthalpy H^E , of an $(i+j)$ mixture should then be given by

$$G^E = RT \sum x_i \ln \gamma_i \quad (3)$$

and
$$H^E = X_{ij} B x_j \ln((x_i + x_j B) / x_j B) \quad (4)$$

(it being assumed that X_{ij} is practically independent of temperature), G^E and H^E data of $(i+j)$ mixtures should be well described by equations 3-4 provided H^E data at two arbitrary compositions are available. This was indeed found (ref. 16) to be the case in about 44 binary mixtures of non-electrolytes, of almost equal sized components.

On the other hand if i and j components differ appreciably in their molar volumes then γ_i would be determined not only by the i - j interactions but also by the work, G_w^E done in accomodating the j th component into the matrix of i . But G_w^E has been shown (ref. 17) to be given by $G_w^E = C x_i x_j V_i V_j (1 - V_j/V_i) / (\sum x_i V_i)$ where C is a constant. γ_i in that case has been expressed (ref. 17) (in view of $\ln \gamma_i = (\ln \gamma_i)_{i-j, V_i=V_j} + (\ln \gamma_i)_{w, V_i \neq V_j}$) by

$$RT \ln \gamma_i = X_{ij} x_j V_j / \sum x_i V_i + V_i V_j x_j^2 (1 - V_j/V_i) / (\sum x_i V_i) \quad (5)$$

The activity coefficient of the j th component should then have been evaluated via Gibbs-Duhem equation but the resulting expressions became so involved that it was hoped that expressing γ_j (in view of $\ln \gamma_j = (\ln \gamma_j)_{i-j, V_i=V_j} + (\ln \gamma_j)_{w, V_i \neq V_j}$) by

$$RT \ln \gamma_j = (X_{ij} V_j / V_i) [\ln(\sum x_i V_i / x_j V_j) - x_i V_i / \sum x_i V_i] + C x_i^2 V_i^2 V_j (1 - V_j/V_i) / \sum x_i V_i \quad (6)$$

would not have introduced significant errors in the values of γ_j . This was indeed found to be true (ref. 17) in some 30 binary mixtures of non-electrolytes (some of which even were characterized by the presence of 1:1 or 1:1 and 1:2 molecular complexes) when their $(\gamma_i, \gamma_j; x_i = 0.5)$ datum was used to evaluate their X_{ij} and C parameters and subsequently employed to well predict their $(\gamma_i, \gamma_j, x_i)$ data. This suggested that not much error is introduced by expressing γ_j for the j the component of an $(i+j)$ mixture by equation 6. Again as $x_i \rightarrow 0$, the activity coefficient of i at infinite dilution would be given (ref. 17) (in view of equation 5) by

$$RT \ln \gamma_i^\infty = X_{ij} + C V_i (1 - V_j/V_i) \quad (7)$$

so that the activity coefficients of the components of an (i+j) mixture can be expressed in terms of $\ln \gamma_i^\infty$ by

$$\ln \gamma_i = (X_{ij} x_j V_j / RT \sum x_i V_i) [1 - x_j V_j / \sum x_i V_i] + (\ln \gamma_i^\infty) x_j^2 V_j^2 / (\sum x_i V_i)^2 \quad (8)$$

and

$$\ln \gamma_j = (X_{ij} V_j / RT V_i) [\ln(\sum x_i V_i / x_j V_j) - x_i V_i / \sum x_i V_i - x_i^2 V_i^2 / (\sum x_i V_i)^2] + (\ln \gamma_i^\infty) x_i^2 V_i V_j / (\sum x_i V_i)^2 \quad (9)$$

Since the standard state of i has been taken to be that of pure i, equations 8,9 should reproduce the experimental $(\gamma_i, \gamma_j; x_i)$ data of an (i+j) mixture when γ_i^∞ datum for it alone is available or can be determined experimentally by gas-liquid chromatography. It was, however, found (ref. 17) that $(\gamma_i, \gamma_j; x_i)$ data evaluated in this manner compared well with the corresponding experimental data for those (i+j) mixtures that were not characterized by specific interactions between their components; for those (i+j) mixtures that contained 1:1 or 1:1 and 1:2 molecular species, barring the two extreme ends of the composition scale the calculated $(\gamma_i, \gamma_j; x_i)$ data well reproduced the corresponding experimental data.

Again if the boiling temperatures of i and j in an (i+j) mixture do not differ significantly and if X_{ij} and C parameters of equations 5 and 6 are taken to be independent of temperature (the effect of pressure on liquid phase properties is usually small except at higher pressures and at conditions near the critical temperature), then it should be possible to predict $(\gamma_i, \gamma_j; x_i)$ data for the mixture when $(\gamma_i, \gamma_j; x_i=0.5)$ data or γ_i^∞ datum at moderate pressures and molar volume data at ordinary temperatures are available. This was found to be reasonably true (ref. 17) of the (n-propanol (i) + water (j)) system at 101.3 bar.

At this stage it may be pertinent to investigate if the topological approach can yield any information about i) the molecular state of the pure components and ii) molecular entities in binary mixtures of non-electrolytes.

Topological aspects of the state of aggregation of the components of an (i + j) mixture

Since molar excess volume V^E , of an (i+j) mixture reflects interactional effects on the packing of molecules and as $(z_i^*)^{-1}$ of i determines (ref. 18) the effectiveness with which the molecular surface of i interacts with that of another i molecule, the interactional part of the molar volume of pure i has been taken (ref. 18) to be proportional to its $(z_i^*)^{-1}$. The ideal interactional molar volume of an (i+j) mixture would then be proportional to $\sum (x_i / z_i^*)$ where x_i and z_i^* denote mole fraction and connectivity parameter of the third degree respectively of i. Further z_i^* is defined (ref. 19) by

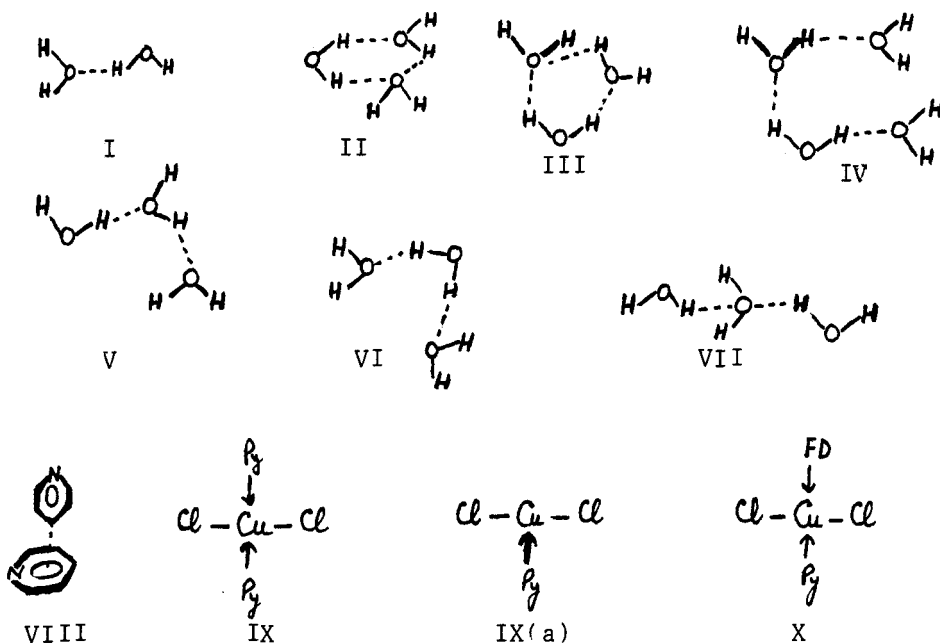
$$z_i^* = \sum_{m < n < o < p} (\delta_m^V \delta_n^V \delta_o^V \delta_p^V)^{-0.5} \quad (10)$$

where δ^V reflects (ref. 20) explicitly the valency of the m th etc. vertex in the molecular graph of i in forming bonds. The interactional part of the molar volume of the mixture should also be proportional to $(z_m^*)^{-1}$ of the mixture. If z_m^* of the real mixture in the $G_i \times G_j$ molecular graph is expressed by $\sum x_i z_i^*$ (where z_i^* denotes z_i^* of i in the mixture) and if the proportionality constant is assumed to be the

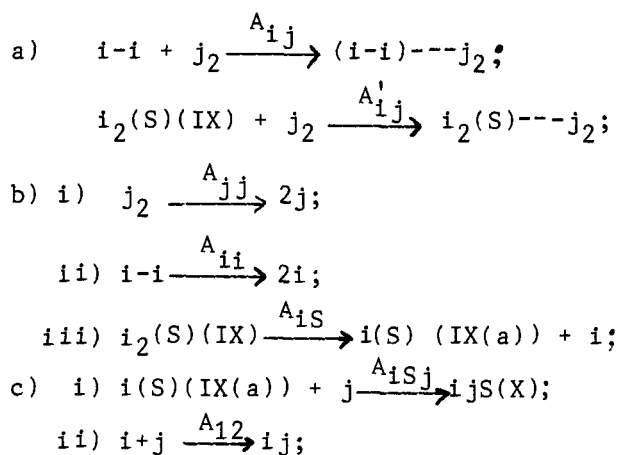
same for both the mixture and its pure components then V^E may be expressed (ref. 18) by

$$V^E = \alpha \left[\sum (x_i \cdot 3z_i^*)^{-1} - \sum x_i / 3z_i \right] \quad (11)$$

where α is a constant characteristic of the (i+j) mixture. As V^E reflects changes in the packing of i and j in the (i+j) mixture, useful information about the state of aggregation of pure i and j and of the molecular species in these binary mixtures should be obtainable (ref. 21-28) from their V^E data if $3z_i^*$ and $3z_i$ parameters of i etc. are regarded as adjustable parameters and are evaluated (ref. 21-28) by fitting equation 11 to the experimental V^E data; only those $3z_i$ and $3z_i^*$ etc. values should be retained for which the variance of fit was minimum. A series of structures are then assumed for the pure i and j and of i and j in the mixture and their $3z_i^*$ parameters evaluated from equation 10. Any structure or a combination of structures that yield $3z_i^*$ values which best reproduce the corresponding $3z_i$ values obtained from V^E data via equation 10, is taken (ref. 21-28) to be the best representative molecular state of the pure components and of the components in the mixture. In this respect analysis (ref. 27) of V^E data at 308.15 K of water (i) + formamide(j) mixture in terms of equation 11 has suggested (ref. 27) that while water in the pure state exists as an equilibrium mixture of I-IV (CNDO/2 studies (ref. 29) have inferred that water exists mainly as open chain trimers V-VII (VII to be the most stable structure); Hoyland et al (ref. 30) however regard V to be more stable one), formamide should exist (ref. 27) as an equilibrium mixture of monomers and dimers (this is consistent with Davies views (ref. 31) about the state of aggregation in lower amides). This approach has also been employed to investigate the state of anhydrous cupric chloride in pyridine and of the influence of formamide (FD) (or N,N-dimethylformamide (DMF)) or aniline (An) (or o-toluidine (OT)) on it, by analysing (ref. 24) V^E data of pyridine (i) (saturated with anhydrous CuCl_2 (S)) (i(S) + j (j= FD or DMF or An or OT) mixtures. This analysis has revealed (ref. 22,24) that while i(S) in i(S)+FD(j) mixtures is an equilibrium mixture of pure i (VIII) and IX, FD in the pure state exists as an equilibrium mixture of FD and $(\text{FD})_2$, the mixture should contain the molecular entity X; infra-red and molecular weight studies (ref. 24) (Rast method) on the solid that is left behind



when this mixture is allowed to evaporate slowly in vacuum substantiated the existence of X in this mixture. Further if $i(S)+FD(j)$ mixture formation is visualized (ref. 26) to involve a) the establishment of unlike $(i-i)---j_2$ and $i_2(S)(IX)---j_2$ contact formation b) these unlike contacts then cause rupture of i) self association in j to yield monomers ii) intramolecular interactions in pure i to yield monomers of i and iii) intermolecular displacement in $i(S)(IX)$ to yield $i(S)(IX(a))$ and i and c) the monomers of j then interact with i) $i(S)(IX)(a)$ to yield ijS and ii) with i to yield ij entities. If the various molar interaction energies, A, are as



then H^E for this mixture should be expressed (ref. 25) by

$$H^E = (x_i x_j B / (x_i + x_j B)) [A_{ij} + A'_{ij} + Kx_i A_{jj} + Kx_i A_{ii} + Kx_i A_{iS} + K'x_j A_{iSj} + K'x_j A_{12}] \quad (12)$$

where $B = (z_j^3 / z_i^3)$. Further if $A_{ij} = K'A_{iSj} = A_0$;

$$K'A_{iS} = KA_{jj} = KA_{ii} = KA_{12} = A_1, \text{ and } A_{ij} = 0$$

then equation 12 reduces to

$$H^E = (x_i x_j B / (x_i + x_j B)) [(1+x_j)A_0 + (1+2x_i)A_1] \quad (13)$$

Equation 13 contains only two unknowns (A_0 and A_1) and if H^E data at two compositions are available then it should be possible to predict H^E data of this mixture over the entire composition range. This was indeed found (ref. 25) to be the case. The present analysis thus has also revealed (ref. 25) that exchange process also plays an important role in the mixing process in $i(S)+FD$ (or DMF or An or OT) mixtures.

Topological approach thus provides an alternative view point of molecular interactions in binary liquid mixtures of non-electrolytes.

REFERENCES

1. J.M.Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, Molecular Thermodynamics of Fluid Phase Equilibria, p. 333, Prentice-Hall, Englewood Cliffs (1986).
2. G.C.Maitland, M.Rigby and W.A. Wakeham, Intermolecular Forces, p.519, Clarendon, Oxford) (1981).

3. I. Prigogine, The Molecular Theory of Solutions, Chap. VII, North-Holland, Amsterdam (1957).
4. P.J. Flory, J. Am. Chem. Soc. **87**, 1833-38 (1965).
5. J.A. Barker, Aust. J. Chem. **6**, 207-13 (1953).
6. R.P. Rastogi and H.L. Girdhar, Proc. Nat. Inst. Sci (INDIA). **28**, 40-45 (1962).
7. C.A. Eckert, H. Renon and J.M. Prausnitz, Ind. Engg. Chem. "Fundamental". **6**, 52-57 (1967).
8. R.L. Lacombe and I.C. Sanchez, J. Phys. Chem. **80**, 2352-62 (1976).
9. D.S.H. Wong and S.I. Sandler, Ind. Engg. Chem. "Fundamental", **23**, 38-44 (1984).
10. M.L. McGlashan and R.P. Rastogi, Trans. Faraday Soc. **54**, 496-501 (1968).
11. L.G. Hepler and D.V. Fenby, J. Chem. Thermodyn. **5**, 471-74 (1973).
12. W.E. Acree, Jr., D.R. McHan and J.H. Rytling, J. Pharm. Sci. **72**, 929-35 (1983).
13. J.W. McCargar and W.E. Acree, Jr., J. Pharm. Sci. **76**, 572-78 (1987).
14. F. Harary, Graph Theory, Addison-Wesley, Reading Mass (1969).
15. Applications of Graph Theory, R. J. Wilson and L.W. Beineke (eds.), p. 36-37, Academic Press, London (1979).
16. P.P. Singh, H.P. Dahiya and S. Dager, Z. Phys. Chim. (Leipzig) **269**, 817-31 (1988).
17. P.P. Singh and S. Maken, Can. J. Chem. **70**, 1631-34 (1992).
18. P.P. Singh, R.K. Nigam, K.C. Singh and V.K. Sharma, Thermochim. Acta, **46**, 175-190 (1981).
19. L.B. Kier and L.H. Hall, Molecular Connectivity in Chemistry and Drug Research, Academic Press, New York 1976.
20. L.B. Kier, Physical Chemical Properties of Drugs, p. 295, Marcel-Dekkar, New York (1980).
21. P.P. Singh, V.K. Sharma and S.P. Sharma, Thermochim. Acta, **106**, 293-307 (1986).
22. P.P. Singh, J. Chem. Soc. Faraday Trans. I. **84**, 1807-16 (1988).
23. P.P. Singh and M. Bhatia, Can. J. Chem. **68**, 74-78 (1990).
24. P.P. Singh and M. Bhatia, J. Chem. Soc. Faraday Trans. I. **85**, 3797-3805 (1989).
25. P.P. Singh and M. Bhatia, J. Chem. Soc. Faraday Trans. I. **85**, 3807-12 (1989).
26. P.P. Singh and M. Bhatia, J. Chem. Soc. Faraday Trans. I. **87**, 2579-81 (1991).
27. P.P. Singh, P.K. Sharma and S. Maken, Ind. J. Chem. **31A**, 619-25 (1992).
28. P.P. Singh and S. Yadav, Ind. J. Chem. **28A**, 745-51 (1989).
29. A. Goel, A.S.N. Murthy and C.N.R. Rao, Ind. J. Chem. **9**, 56-61 (1971).
30. J.R. Hoyland and L.B. Kier, Theor. Chim. Acta. **15**, 61-65 (1969).
31. M. Davies, Hydrogen Bonding, p. 271, Pergamon, New York (1956).