

Topological investigation of molecular interactions in ternary mixtures of non-electrolytes: excess Gibbs free energy of mixing

Prem P Singh*, S Maken & M Bhatia

Department of Chemistry, Maharshi Dayanand University, Rohtak 124 001

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An approach is presented for evaluating excess Gibbs free energy of mixing for a ternary ($i+j+k$) mixture when the corresponding G^E data for the constituent binary mixtures are available. While the approach describes very well the reported G^E data for water+ethylene glycol+ethanol and acetone+ethanol+water mixtures, it succeeds only moderately well for ethanol+trichloromethane+1,4-dioxane mixtures. The results have been further utilized to understand the nature of molecular interactions in these ternary mixtures.

The molecular connectivity parameters¹ of the constituents of binary as well as ternary mixtures of non-electrolytes have recently been found²⁻⁵ to be of great use not only in evaluating their molar excess volumes, V^E , and molar excess enthalpies, H^E , but also in understanding the nature of molecular interactions between the components of binary mixtures. The approach² has recently been extended⁶ to successfully explain^{6,7} molar excess Gibbs free energy of mixing, G^E , and the activity coefficient, γ_i and γ_j , of a number of binary ($i+j$) mixtures when the corresponding H^E (T , $x_A=0.4$ and 0.5) data alone are available. This approach⁶ makes a complete departure from the conventional approaches⁸⁻¹⁵ of evaluating partition function for the purpose, and makes the following assumptions. (a) The activity coefficient of constituent i in an ($i+j$) mixture is a measure of $i-j$ interactions whose magnitude depends (i) directly on the magnitude of the interaction energy and the effective surface fraction of j that comes into contact with i , and (ii) inversely on the thermal energy. (b) The activity coefficient of j (γ_j), has to be determined from the Gibbs-Duhem equation. Since a ternary ($i+j+k$) mixtures can be regarded as a binary mixture of $i+1$ ($1=j+k$), it appears that this approach⁶ could be extended to evaluate G^E data for ternary mixtures of non-electrolytes.

Theoretical

In a binary solution of i and j , the interaction of i with j would depend directly not only on the surface fraction of j that comes into effective $i-j$ contacts but also on the magnitude of the interaction energy per mole of ($i-j$) contacts, χ_{ij} . Further, the thermal energy would also influence the mag-

nitude of $i-j$ interaction energy; higher the working temperature, smaller would be the effective ($i-j$) interaction energy. Based on these arguments, Singh *et al.*⁶ have expressed the activity coefficient of i (γ_i), in an ($i+j$) mixture by the equation,

$$\ln \gamma_i = \frac{x_j B Y}{x_i + B x_j} \quad \dots (1)$$

where

$$B_{ij} = K_{ij} ({}^3\xi_i / {}^3\xi_j) \quad \dots (2)$$

$$Y = X_{ij} / RT \quad \dots (3)$$

and

${}^3\xi_i$, etc., are the connectivity parameters of the third degree of component i and K_{ij} is a constant characteristic of the ($i+j$) mixture. Further, the connectivity parameter ${}^3\xi_i$ of i is defined² by,

$${}^3\xi_i = \sum_{m < n < o < p} (\delta_m^v \cdot \delta_n^v \cdot \delta_o^v \cdot \delta_p^v)^{-0.5} \quad \dots (4)$$

where δ_m^v reflects^{1(a)} explicitly the valency of the m th vertex in the molecular graph of i and is related^{1(b)} to the maximum valency z_m of the m th vertex and the number of hydrogen atoms h_m attached to it by the relation $\delta_m^v = z_m - h_m$. The activity coefficient of the j th component in the ($i+j$) mixture can be then expressed⁶ via Gibbs-Duhem equation by

$$\ln(\gamma_j) = Y B_{ij} \left[\ln \left(\frac{x_i + x_j B_{ij}}{x_i B_{ij}} \right) - \frac{x_i}{x_i + x_j B_{ij}} \right] \quad \dots (5)$$

If now a ternary solution containing n_i moles of i , n_j moles of j and n_k moles of k be regarded as a binary solution of n_i moles of i and $n' = (n_j + n_k)$ moles of a hypothetical liquid, l , then while pure i is characterized by $(i-i)$ interactions, the hypothetical liquid, l , is characterized by $j-j$, $k-k$ and $j-k$ interactions. If the component j , in l , has no preference for any particular site on the surface of k , then the whole of the surface of k would be available to j for establishing $j-k$ contacts. In a similar manner, the whole of the surface of j would be available to k for establishing $j-k$ contacts so that the total contact volume available to j and k in l would be given by $n_j V_j + n_k V_k + (n_j V_k + n_k V_j)$ where V_k , etc. denote the molar volume of k , etc. The total contact volume, v , in the $(i+l)$ mixture may then be approximated by

$$v = n_i V_i + n_j V_j + n_k V_k + n_j V_k + n_k V_j = n_i V_i + (n_j + n_k)(V_j + V_k) \quad \dots (6)$$

or

$$V = x_i V_i + (x_j + x_k)(V_j + V_k) \quad \dots (7)$$

where

$$V = v/(n_i + n_j + n_k)$$

Since activity coefficients are a measure of unlike interactions, the activity coefficient of, say, i in the $i+l$ ($l=j+k$) mixture would involve contributions from $i-l$, i.e. $i-j$ and $i-k$ interactions. If $i-j$ and $i-k$ interactions are assumed to make independent contributions to the activity coefficient of i , then $\ln(\gamma_i)$ should be expressible by,

$$\ln(\gamma_i) = (\ln \gamma_i)_{i-j} + (\ln \gamma_i)_{i-k} \quad \dots (8)$$

Now $(\ln \gamma_i)_{i-j}$ in the $(i+j+k)$ mixture would depend directly on (i) the ratio of the molar volume of i in this mixture to the total contact volume, (ii) the effectiveness of the $i-j$ contact in an $(i+j+k)$ mixture, (iii) the interaction energy, x_{ij} , per mole of $i-j$ contact, and inversely on (iv) the thermal energy. Following our earlier work⁶, we express $(\ln \gamma_i)_{i-j}$ by

$$\ln(\gamma_i)_{i-j} = \frac{x_i V_i (x_j / RT) f_{ij}}{x_i V_i + (x_j + x_k)(V_j + V_k)} \quad \dots (9)$$

where f_{ij} measures the effectiveness of the $i-j$ contacts. In a similar manner $(\ln \gamma_i)_{i-k}$ may be expressed by

$$\ln(\gamma_i)_{i-k} = \frac{x_i V_i (x_k / RT) f_{ik}}{x_i V_i + (x_j + x_k)(V_j + V_k)} \quad \dots (10)$$

so that $\ln(\gamma_i)$ would be given (in view of Eq. 8) by

$$\ln(\gamma_i) = \frac{x_i V_i (X_{ij} / RT) f_{ij} + x_k V_k (X_{ik} / RT) f_{ik}}{P} \quad \dots (11)$$

where

$$P = x_i V_i + (x_j + x_k)(V_j + V_k) \quad \dots (12)$$

If the basic arguments used in deriving Eq. 11 are valid, then as (say) $x_k \rightarrow 0$, Eq. 11 should express the activity coefficient, γ_i , of i in an $(i+j)$ mixture. Evidently, Eq. 11 satisfies this requirement and further ensures that the activity coefficient of j is given by Eq. 5, as required by Gibbs-Duhem equation. Further, it follows from Eq. 11 that the activity coefficients of j and k in the $(i+j+k)$ mixture may also be expressed by

$$\ln(\gamma_j) = \frac{x_i V_i (X_{ij} / RT) f_{ij} + x_k V_k (X_{jk} / RT) f_{jk}}{P} \quad \dots (13)$$

and

$$\ln(\gamma_k) = \frac{x_i V_i (X_{ik} / RT) f_{ki} + x_j V_j (X_{jk} / RT) f_{kj}}{P} \quad \dots (14)$$

Since

$$G^E = RT \sum (x_i \ln(\gamma_i)) \quad \dots (15)$$

and if $f_{ij} = f_{ji}$, $f_{jk} = f_{kj}$ and $f_{ik} = f_{ki}$

then $g_{ijk} = G_{ijk}^E / RT$ would be given by

$$g_{ijk} = \frac{1}{P} [(x_i x_j (X_{ij} / RT) (V_j + V_i) f_{ij} + x_i x_k (X_{ik} / RT) f_{ik} \times (V_i + V_k) + x_j x_k (X_{jk} / RT) (V_j + V_k) f_{jk})] \quad \dots (16)$$

or

$$g_{ijk} = \frac{1}{Q} [(x_i x_j (X_{ij} / RT) (1 + B_{ij}) f_{ik} + x_i x_k (X_{ik} / RT) \times (1 + B_{ik}) f_{ik} + x_j x_k (X_{jk} / RT) (B_{ij} + B_{ik}) f_{jk}] \quad \dots (17)$$

$$Q = x_i + (x_j + x_k)(B_{ij} + B_{ik}) \quad \dots (18)$$

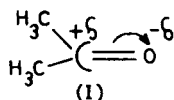
Results and Discussion

Van Ness *et al.*¹⁵⁻¹⁷ have determined g_{ijk} data at 323.15K for water (W) (i) + ethylene glycol (EG) (j) + ethanol (Et) (k); acetone A (i) + ethanol (Et) (J) + water (W) (k); and ethanol (Et) (i) + chloroform (C) (j) + 1,4-dioxane (D) (k) mixtures. It would, therefore, be interesting to see as to how

far Eq. 17 expresses the g_{ijk} data of these $(i+j+k)$ mixtures. For this purpose we utilized the g_{ij} , etc., data of $(i+j)$, etc., mixtures to evaluate B_{ij} , etc., and X_{ij} , etc., parameters from Eqs 1 and 5. These parameters were then coupled with the g_{ijk} data of the $(i+j+k)$ mixtures at three different compositions to evaluate f_{ij} parameters for the $(i+j+k)$ mixture. These B_{ij} , X_{ij} and f_{ij} etc. parameters were next employed to calculate g_{ijk} data for the $(x_i + x_j + x_k)$ mixture. Such g_{ijk} data are recorded in Table 1 and are also compared with the corresponding experimental data; the necessary g_{ij} data at 323.15K were taken from the literature¹⁵⁻¹⁷.

An examination of Table 1 reveals that the g_{ijk} data calculated from Eq. 17 compare very well with the corresponding experimental g_{ijk} data^{15,16} for $W(i) + EG(j) + ET(k)$ and $A(i) + ET(j) + W(k)$ mixtures. For $Et(i) + C(j) + D(k)$ mixtures, although the calculated g_{ijk} values are of the right order of magnitude, the quantitative agreement is not very impressive. It is, however, instructive to note that McGlashan and Rastogi¹⁸ have explained G^E data at 323.15K for chloroform (j) + 1,4-dioxane (k) mixtures in terms of the molecular entities of the type ij and i_2j . Evidently, the present simple approach cannot be expected to express the g_{ijk} data of the $Et(i) + C(i) + D(k)$ mixture accurately but it is satisfying to note that the calculated g_{ijk} data are of the right order of magnitude.

Since B_{ij} , etc., are a measure of the abilities² of the surfaces of i and j to enter into $i-j$ contacts and f_{ij} , etc., are a measure of the effectiveness of these contacts, the values of these parameters for ternary mixture $A(i) + Et(j) + W(k)$ (Table 2) suggest that the effectiveness of the binary contacts in this ternary mixture $(i+j+k)$ varies as: $(j-k) > (i-k) > (i-j)$. This is understandable. The $+I$ inductive effect of the CH_3 -substituents in $A(i)$ would cause the electromeric shift in $C=O$ bond as shown in (I).



Now in $W(k)$, the difference in electronegativities¹⁹ of oxygen and hydrogen atoms would cause a concentration of electronic charge on the oxygen atom and a depletion of the electronic charge on the hydrogen atom. On the other hand, because of the presence of a CH_3-CH_2 substituent in $Et(j)$, the depletion of electronic charge on the hydrogen atom of the $O-H$ group would be lesser in $Et(j)$ than that in $W(k)$. Consequently, $(i-k)$ contacts in this $(i+j+k)$ mixture would be more effective

Table 1—Comparison of $g_{ijk} = G_{ijk}^E/RT$ values calculated at 323.15K from Eq. 17 with the corresponding experimental values as functions of x_i for the various $(i+j+k)$ mixtures

x_i	x_j	g_{ijk}	
		Calc	Exptl
W(i) + EG(j) + Et(k)			
0.4926	0.0204	0.3076	0.2998
0.4744	0.0510	0.2985	0.2893
0.4498	0.1006	0.2817	0.2724
0.4244	0.1513	0.2647	0.2549
0.3994	0.2014	0.2478	0.2389
0.3745	0.2512	0.2312	0.2228
0.3493	0.3015	0.2145	0.2064
0.3239	0.3523	0.1976	0.1750
0.2991	0.4019	0.1812	0.1747
0.2742	0.4517	0.1650	0.1592
0.2492	0.5016	0.1487	0.1440
0.0304	0.6487	0.1367	0.1587
0.0638	0.6264	0.1450	0.1558
0.1251	0.5853	0.1520	0.1512
0.1835	0.5462	0.1525	0.1474
0.2405	0.5081	0.1491	0.1444
0.2969	0.4704	0.1433	0.1410
0.3527	0.4331	0.1358	0.1327
0.4068	0.3968	0.1274	0.1340
0.4593	0.3618	0.1183	0.1699
0.5106	0.3274	0.1087	0.1242
0.5605	0.2941	0.0989	0.1172
0.0499	0.3137	0.1943	0.1774
0.1002	0.2971	0.2351	0.1844
0.1504	0.2805	0.2578	0.2005
0.2005	0.2640	0.2687	0.2137
0.2507	0.2474	0.2715	0.2270
0.3003	0.2310	0.2681	0.2289
0.3501	0.2146	0.2604	0.2355
0.4003	0.1980	0.2493	0.2402
0.4502	0.1815	0.2356	0.2422
0.4990	0.1654	0.2201	0.2418
0.6627	0.3266	0.0036	-0.0178
0.6517	0.3211	0.0158	-0.008
0.6327	0.3118	0.0363	0.0335
0.5691	0.2804	0.1026	0.1245
0.4950	0.2439	0.1733	0.1698
0.3250	0.6595	0.0041	-0.0182
0.3042	0.6172	0.0471	0.0369
0.2773	0.5627	0.0985	0.0957
0.2488	0.5050	0.1470	0.1427
0.2188	0.4440	0.1907	0.1869
0.1873	0.3800	0.2262	0.1971
Et(i) + C(j) + D(k)			
0.2962	0.0206	0.1818	0.1715
0.2862	0.0500	0.1698	0.1509

Contd

Table 1—Comparison of $g_{ijk} = G_{ijk}^E/RT$ values calculated at 323.15K from Eq. 17 with the corresponding experimental values as functions of x_i for the various (i + j + k) mixtures—*Contd*

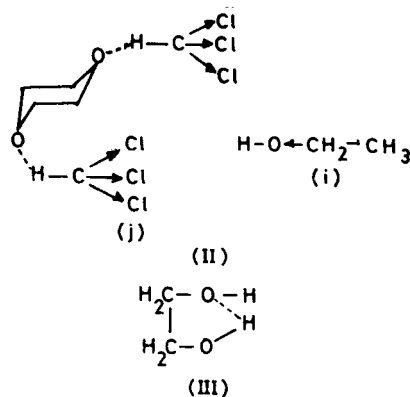
x_i	x_j	g_{ijk}	
		Calc	Exptl
Et(i) + C(j) + D(k)			
0.2720	0.1004	0.1494	0.1193
0.2420	0.1228	0.1105	0.0721
0.2119	0.2993	0.0736	0.0427
0.1816	0.3993	0.0392	0.0284
0.1515	0.4990	0.0084	0.0255
0.6840	0.0232	0.0955	0.1924
0.6259	0.1061	0.0878	0.1642
0.5910	0.1559	0.0832	0.1529
0.5169	0.2617	0.0732	0.1399
0.4525	0.3536	0.0646	0.1371
0.3831	0.4528	0.0552	0.1391
0.1008	0.2688	0.0139	-0.0246
0.1487	0.5957	0.0026	0.0592
0.3991	0.4205	0.0589	0.1357
0.4992	0.3505	0.0574	0.1474
0.1496	0.3497	0.0321	0.0054
0.1646	0.3847	0.0334	0.0167
0.1797	0.4199	0.0346	0.0296
0.1946	0.4547	0.0356	0.0440
A(i) + Et(j) + W(k)			
0.0540	0.6395	0.3699	0.2956
0.2618	0.4990	0.3182	0.3126
0.2154	0.5364	0.3344	0.3079
0.3565	0.4350	0.2818	0.3072
0.4045	0.4026	0.2623	0.3088
0.0544	0.2876	0.4429	0.2901
0.1604	0.2554	0.4820	0.3613
0.5053	0.3344	0.2200	0.2891
0.4126	0.1788	0.3876	0.4063
0.4610	0.1640	0.3600	0.3672
0.6225	0.0574	0.2933	0.3472
0.5258	0.2040	0.2861	0.3502
0.4271	0.3535	0.2754	0.3254
0.3306	0.4996	0.2595	0.2857
0.5008	0.1492	0.3308	0.3833
0.2776	0.0524	0.5022	0.3995
0.3344	0.2010	0.4989	0.5428
0.1461	0.5026	0.3992	0.3256
0.5896	0.2515	0.2010	0.2782
0.3625	0.4513	0.2655	0.2940
0.4158	0.1774	0.3860	0.4060
0.3463	0.1478	0.4443	0.4214
0.5098	0.1492	0.3308	0.3833

than the i-j contacts. This scheme of molecular interaction would further require that in the presence of A(i), the j-k contacts would be energetically more effective than even the i-k contacts, as has indeed been found.

For Et(i) + C(j) + D(k) mixtures, the B_{ij} and f_{ij} data in Table 2 reveal that the effectiveness of the binary contacts in this ternary mixture varies as $(j-k) > (i-k) > (i-j)$. This again is understandable. If D is assumed to exist in the chair configuration (structure II), then the lone pairs of electrons on the oxygen atom of D would be involved in hydrogen bonding with the hydrogen atom of chloroform (C) on one hand and the hydrogen atom of the O-H group of Et on the other. The presence of electron withdrawing chlorine atoms in C(j) and that of electron releasing CH_3-CH_2- substituent in Et(i) would then require that the hydrogen atom of C(j) should form a more effective contact with the oxygen atom/(s) of D(k) than that with the hydrogen atom of the O-H group of Et(i).

This scheme of molecular interactions would require that in the presence of (k), the i-j contacts would be less effective than the j-k contacts, as has indeed been observed.

For W(i) + EG(j) + Et(k) mixture, the B_{ij} and F_{ij} parameters in Table 2, however, reveal that the effectiveness of the various binary contacts varies as $(j-k) > (i-k) > (i-j)$. This is understandable if EG(j) is assumed to have intramolecular hydrogen bonding as shown in (III).



Evidently, i-j contacts would be energetically less favourable than the i-k contacts. Further, since the general environment of EG(j) is the same as that of Et(k), j-k contacts, in the presence of i, would be energetically the most favoured ones.

The present approach, thus, not only explains G^E data of ternary mixtures of non-electrolytes, but also provides a deeper insight into the nature of the molecular interactions.

Table 2— B_{ij} , X_{ij} and f_{ij} , etc. parameters of the ternary mixtures

Parameter	W(i) + EG(j) + Et(k)	Et(i) + C(j) + D(k)	A(i) + Et(j) + W(k)
B_{ij}	0.074	0.0185	0.63
B_{jk}	0.122	0.117	0.0043
B_{ik}	0.061	0.090	0.053
X_{ij}/kT	-1.536×10^{-5}	6.227×10^{-5}	6.734×10^{-5}
X_{jk}/RT	6.968×10^{-5}	-1.239×10^{-4}	4.649×10^{-5}
X_{ik}/RT	1.585×10^{-4}	1.033×10^{-4}	1.596×10^{-4}
f_{ij}	199.7	1141.6	3213.69
f_{jk}	20512.08	9193.3	35296.3
f_{ik}	4492.32	3029.2	5484.0

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