

Preferential Solvation in Binary Liquid Mixtures with Norbornadiene

Abstract. Norbornadiene has been found useful in organic and polymer synthesis and recently its mixtures have been found useful in solar energy storage. Structure factors $S(0)$ help to identify structure and binding at microscopic level and also play a significant role in understanding and characterizing exchanges in liquid systems. Preferential solvation Parameter δ_{ij} provides information about deviation from ideal behavior for the solvent. In this work structure factors $S(0)$ and preferential solvation Parameter δ_{ij} were evaluated of binary Liquid Mixtures of Norbornadiene with Benzene, Cyclohexane, Decane, and Carbon Tetrachloride using Kirkwood Buff formalism. For the said binary mixtures experimental data pertaining to the calculations were taken from literature. Obtained results indicate that molecules which tend to form dipole interactions or hydrogen bonds form favorable interactions as seen in Norbornadiene + carbon tetrachloride where the small molecule of CCl_4 is not sterically hindered to approach the polar Norbornadiene molecule. Long chain and ring structure of carbon have a negative influence on hetero interactions. Studying these parameters will develop predictive techniques to determine the right composition for optimum performance of the liquid mixture.

1. Introduction

The devices that can capture and convert sunlight into stored chemical energy are attractive candidates for future energy technologies. Norbornadiene and its mixtures have recently been found useful in solar energy storage. The Norbornadiene -quadricyclane couple is of particular interest for solar energy storage whenever strain energy stored in quadricyclane is released in a controlled manner to form norbornadiene [1-2]. Despite the usefulness of the compound not many studies [3-4] have been undertaken to estimate the properties of the liquid mixtures containing Norbornadiene. Also the quest continues to look for the right ratio and combination for optimum performance of the liquid mixture. In this context some very useful information about internal structure, molecular order and interactions in the solutions under study can be obtained from studying Kirkwood Buff integrals in solutions [5-6]. Kirkwood Buff theory of solutions [6-7] provides a direct link between the solution structure and the thermodynamic properties of the solution. Kirkwood Buff integrals can be considered to be the average of pair correlation functions in the entire range of intermolecular distances inside the solution.

In this study, we utilize the experimentally obtained [1] density and enthalpy measurements in binary organic solution of Norbornadiene with Benzene, Cyclohexane, Decane, and Carbon Tetrachloride to evaluate Structure factors $S(0)$ and preferential solvation Parameter $\delta_{ii,j}$ [8] using Kirkwood Buff

formalism. In the following investigation we extend an earlier method proposed by us [9-10] to evaluate the Kirkwood-Buff Integrals.

2. Theoretical

In this study the parameters, structure factor $S(0)$ and preferential solvation Parameter $\delta_{ii,j}$ [8] were calculated in solution to analyze the structure of the binary liquid mixture and measurement of non-randomness in the mixture. It is very rare that all necessary data is available to evaluate these parameters. It is, therefore, very important to derive equations which interrelate different thermodynamic functions. Knowledge of some of these properties permits the evaluation of the others. The calculations leading to the following have been explained below,

2.1 Preferential Solvation Parameter $\delta_{ii,j}$

The Kirkwood Buff theory employs KB Integrals which can be defined for a pair of molecules of species i and j as,

$$G_{ij} = \int_0^\infty [g_{ij}(R) - 1] 4\pi R^2 dR \quad (1)$$

g_{ij} is the angle averaged pair correlation function and the integration includes the entire range of intermolecular distances between i and j components. Using the integrals, preferential solvation Parameter δ_{ij} is obtained which provides important information such deviation from ideal behavior for the solvent by the following equations [11];

$$\delta_{ij} = x_i x_j [G_{ij} - G_{jj}] \text{ and } \delta_{ii} = x_i x_j [G_{ii} - G_{ij}] \quad (2)$$

where G_{ij} etc [7] are calculated by :

$$G_{ii} = RT\beta_T + \frac{(1-x_i)\bar{V}_i^2}{x_i V D} - \frac{V}{x_i} \quad (3)$$

$$G_{ij} = RT\beta_T - \frac{\bar{V}_i \bar{V}_j}{V D} \quad (4)$$

$$G_{jj} = RT\beta_T + \frac{\bar{V}_j^2(1-x_j)}{x_j V D} - \frac{V}{x_j} \quad (5)$$

$\bar{V}_i$ is the partial molar volumes of the i th species whose mole fraction is x_i , V is molar volume, K is Boltzmann constant and T is absolute temperature. Calculations show β_T which is isothermal compressibility of the mixture, has a negligible contribution on the KB integrals[11], so it was calculated from the pure values as follows

$$\beta_T = \beta_{T,1}^0 \phi_1 + \beta_{T,2}^0 \phi_2 \quad (6)$$

Here $\beta_{T,1}^0$ and $\beta_{T,2}^0$ are pure components isothermal compressibility y and ϕ_1 and ϕ_2 are volume fraction of the components respectively.

D is a function [11] which can be obtained by activity coefficients by the following equation

$$D = 1 + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_i} \right)_{T,P} \quad (7)$$

In the above equation γ_i is obtained by first approximating the solution to be regular [12] and then using the following

$$\ln \gamma_i = \frac{(1-x_i)^2 w}{kT} \quad (8)$$

Here the parameter w can be obtained by using the following equations.

$$G^E = x_i x_j N w \text{ and } G^E = H^E - T S^E \quad (9)$$

here experimental results for the enthalpy have been utilized and as w is small and independent of temperature, we can neglect the role of S^E [16]. Molar volumes of binary mixtures are evaluated by use of excess volumes calculated from the experimental density data. V^E data is fitted to form of Redlich-Kister equation from which the partial molar volumes are calculated using [13]

$$V_{2,m} - V_{2,m}^0 = +(\partial V^E / \partial x_2), \text{ and } V_{1,m} - V_{1,m}^0 = +(\partial V^E / \partial x_1) \quad (10)$$

2.2 Structure factor for binary mixture in the Long Wavelength Limit.

Structure factors $S(0)$ [11] help to identify structure and interactions at microscopic level and also play a significant role in understanding and characterizing exchanges in liquid systems. For the long wavelength it is evaluated as follows

$$S(0) = S_{NN}(0) - \frac{S_{NC}(0)^2}{S_{CC}(0)^2} \quad (11)$$

Here the deviation from the ideality is given by Concentration Concentration fluctuation $S_{CC}(0)$ given by the following relation

$$S_{CC}(0) = \frac{x_1 x_2}{D} \quad (12)$$

The other two important parameters, $S_{NN}(0)$ is the number number partial structure factor in the long wavelength limit and $S_{NC}(0)$ is the number mole fraction partial structure factor also in the long wavelength limit, they are calculated from dilation factor [11] using the following equations.

$$\varepsilon = -\frac{1}{V} \left(\frac{\partial V}{\partial x} \right)_{T,P} \quad (13)$$

$$S_{NN}(0) = \frac{RTK_T}{V} - S_{CC}(0)\varepsilon^2 \quad (14)$$

$$S_{NC}(0) = -S_{CC}(0)\varepsilon \quad (15)$$

3. Results and Discussions

The variation of δ_{ij} with the variation of Norbornadiene concentration denoting interaction between the liquid mixtures have been graphically represented in the Figs 1 to 4.

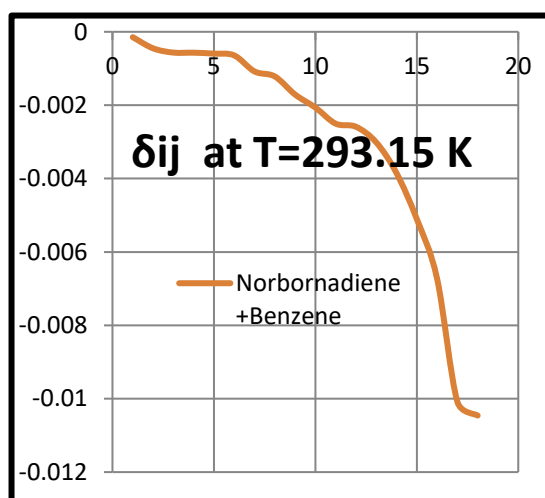


Figure 1 Variation of δ_{ij} with mole fraction of Norbornadiene+Benzene at T=293.15 K

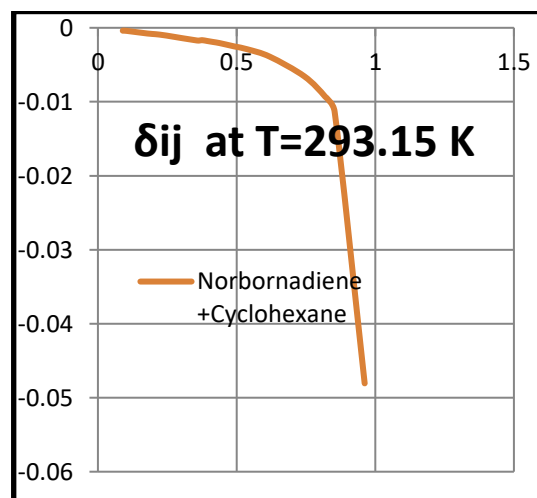


Figure 2 Variation of δ_{ij} with mole fraction of Norbornadiene+Cyclohexane at T=293.15 K

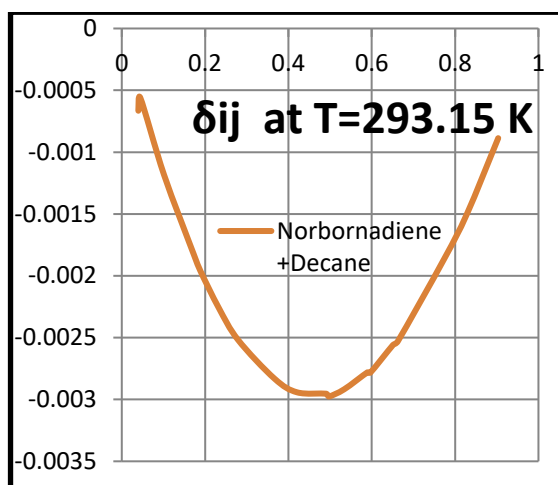


Figure 3 Variation of δ_{ij} with mole fraction of Norbornadiene+Decane at $T=293.15\text{ K}$

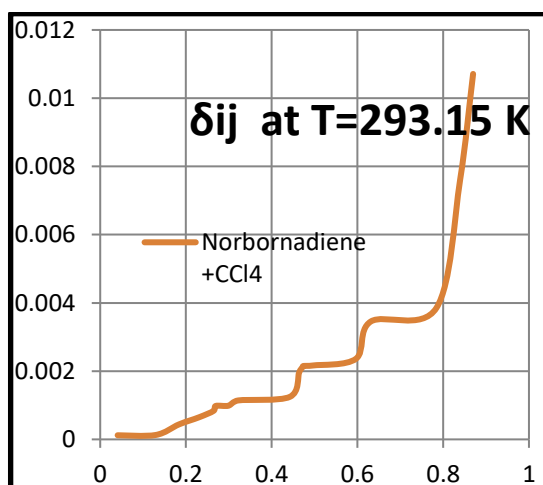


Figure 4 Variation of δ_{ij} with mole fraction of Norbornadiene+CCl₄ at $T=293.15\text{ K}$

It can be seen that for Benzene(x₂) and cyclohexane(x₂) systems, the values show a decreasing, more negative trend whereas for decane it shows a U-shaped variation and for CCl₄, an increasing trend is observed with increase in the concentration of Norbornadiene. Another interesting point to be taken into account is that except for the Norbornadiene + CCl₄ system, all other systems exhibit negative values of δ_{ij} over the entire range of concentration. The highest negative values for the Norbornadiene + Benzene(x₂) system indicate that the interactions between both the constituent components are minimized due to steric hindrances. It is further accentuated by the higher stability of benzene due to delocalization. Similar trends exhibited by the Norbornadiene + Cyclohexane(x₂) system is on expected lines. A somewhat similar trend is observed in the structure factor $S(0)$ values for the 4 binary systems under investigation depicted in Fig. 5-8.

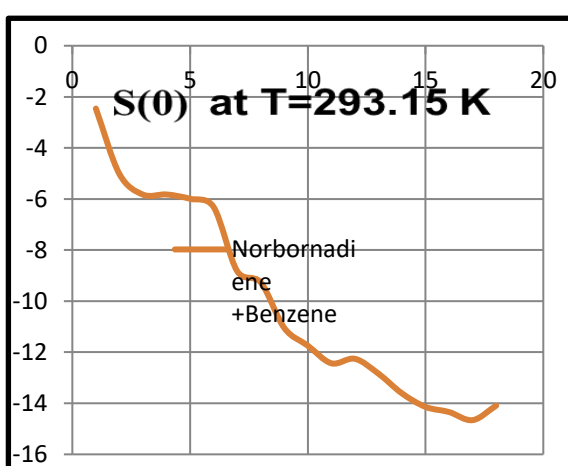


Figure 5 Variation of $S(0)$ with mole fraction of Norbornadiene+Benzene at $T=293.15\text{ K}$

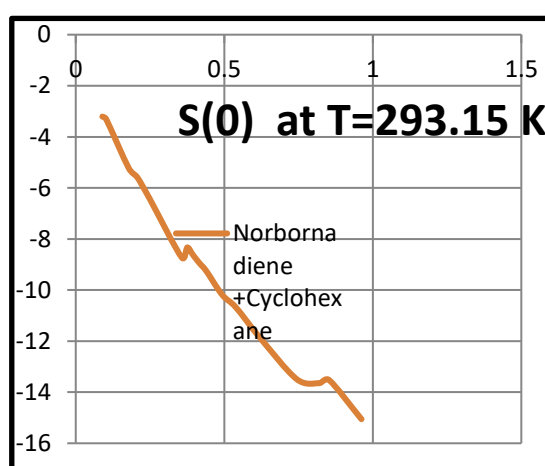


Figure 6 Variation of $S(0)$ with mole fraction of Norbornadiene+Cyclohexane at $T=293.15\text{ K}$

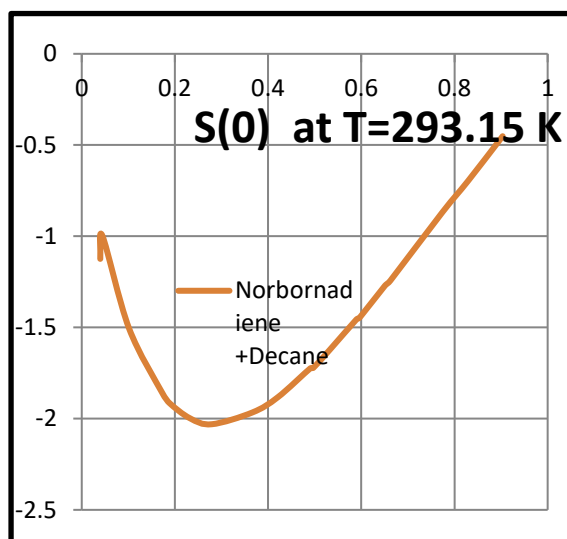


Figure 7 Variation of $S(0)$ with mole fraction of Norbornadiene+Decane at $T=293.15$ K

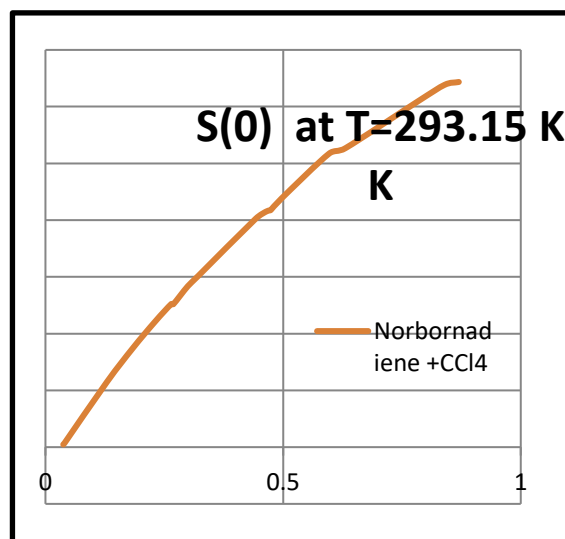


Figure 8 Variation of $S(0)$ with mole fraction of Norbornadiene+ CCl_4 at $T=293.15$ K

Here also all the systems other than Norbornadiene + CCl_4 exhibit negative values over the entire range of concentration. This may be arising due to the interstitial accommodation of the smaller CCl_4 molecule in the larger Norbornadiene molecule leading to volume contractions as evidenced by the negative excess volume values [1] as given in Table 1. Negative excess enthalpy values point towards exothermic process accompanied by evolution of heat, thereby providing the system with higher stability on mixing as compared to that of constituent components.

Table 1 Variation of G_{ij} , G_{ii} and Excess Volume with mole fraction of first component Norbornadiene at $T=293.15$ K							
Norbornadiene +Benzene				Norbornadiene +Cyclohexane			
x_1	G_{ij}	G_{ii}	V_E	x_1	G_{ij}	G_{ii}	V_E
0.03559	-0.00419	0.09681	0.026	0.08958	-0.00449	0.04734	0.102
0.10524	-0.0043	0.03113	0.059	0.10251	-0.00414	0.03748	0.114
0.13754	-0.00413	0.02196	0.075	0.17848	-0.00448	0.02134	0.176
0.14223	-0.00401	0.02051	0.077	0.20753	-0.00431	0.01698	0.199
0.14818	-0.00402	0.01957	0.08	0.24716	-0.00442	0.01388	0.224
0.15924	-0.00404	0.01807	0.082	0.3572	-0.00502	0.0093	0.257
0.24303	-0.00439	0.01156	0.108	0.37508	-0.00466	0.00798	0.263

0.28194	-0.00423	0.0091	0.119	0.39458	-0.00474	0.00747	0.269
0.36385	-0.00456	0.0067	0.133	0.41697	-0.00485	0.00695	0.272
0.42668	-0.00465	0.00524	0.136	0.43874	-0.00494	0.00648	0.278
0.48798	-0.00488	0.00428	0.139	0.49269	-0.00538	0.00568	0.283
0.50947	-0.00482	0.00387	0.139	0.53932	-0.00568	0.00496	0.269
0.55158	-0.00515	0.00349	0.136	0.62006	-0.00665	0.00417	0.26
0.61898	-0.0058	0.00297	0.122	0.74449	-0.00934	0.00327	0.214
0.69411	-0.00678	0.00247	0.109	0.81946	-0.01205	0.0027	0.172
0.75994	-0.00807	0.0021	0.092	0.85347	-0.01408	0.00245	0.146
0.8326	-0.0109	0.0018	0.067	0.96188	-0.0531	0.00213	0.042
0.84473	-0.01113	0.00167	0.065				
Norbornadiene +Decane				Norbornadiene +CCl4			
x1	Gij	Gii	VE	x1	Gij	Gii	VE
0.03973	-0.01655	0.2471	0.047	0.03751	0.00311	-0.07841	-0.034
0.0445	-0.01248	0.16558	0.052	0.04061	0.00306	-0.071	-0.03
0.10135	-0.01133	0.0662	0.123	0.12945	0.00328	-0.02171	-0.097
0.17298	-0.01016	0.03495	0.199	0.18381	0.00339	-0.01484	-0.126
0.18831	-0.01	0.03162	0.211	0.23058	0.00349	-0.01148	-0.145
0.23231	-0.00939	0.02414	0.253	0.26452	0.00356	-0.00976	-0.155
0.27909	-0.00884	0.01896	0.29	0.26931	0.00352	-0.00943	-0.164
0.36639	-0.00792	0.013	0.337	0.29946	0.00365	-0.00844	-0.169
0.4208	-0.00747	0.01073	0.354	0.32179	0.00371	-0.00774	-0.174
0.49025	-0.00692	0.00857	0.361	0.4423	0.00426	-0.00532	-0.194

0.49702	-0.00693	0.00848	0.358	0.46422	0.00434	-0.00497	-0.194
0.53383	-0.00664	0.00759	0.351	0.47156	0.00436	-0.00484	-0.198
0.58932	-0.00627	0.00652	0.335	0.47407	0.00436	-0.0048	-0.194
0.59683	-0.00627	0.00645	0.333	0.49646	0.00454	-0.00458	-0.2
0.65089	-0.00591	0.0056	0.297	0.59663	0.00552	-0.00371	-0.188
0.66255	-0.00589	0.00549	0.291	0.63118	0.00581	-0.00338	-0.182
0.77387	-0.00522	0.00421	0.202	0.78424	0.00922	-0.00254	-0.123
0.82895	-0.00503	0.00383	0.153	0.83948	0.01212	-0.00232	-0.101
0.9034	-0.0047	0.00332	0.081	0.86967	0.01454	-0.00219	-0.086

4. Conclusion

To obtain information about the overall structure of binary mixtures with Norbornadiene as the primary component, values of δ_{ij} and $S(0)$ were calculated using Kirkwood-Buff integrals. For Mixtures with Benzene, Cyclohexane and Decane both the parameters were found to be negative which indicates that ordering in binary mixtures is less than random orientations while for carbon tetrachloride positive values were obtained which denote the opposite and show ordering is the governing factor in this case. As expected, results for cyclohexane as a mixing partner are similar to benzene because of the ring structures of benzene and of cyclohexane. Decane is linear and has a large surface area by which they interact with other molecules and even if their δ_{ij} values are also negative there is a turning point in the graph at a particular mole fraction of Decane which indicates after this concentration the interactions becomes stronger. The significance of the above study lies in the information about interactions between the pairs of molecules found in binary mixtures. The composition at which δ_{ij} is a maximum can lead to a potentially stable liquid mixture while being used as an energy storage device.

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