Chemical Methodologies 4(2020) 123-129

Chemical Methodologies

Journal homepage: http://chemmethod.com

Original Research article

Study of Molecular Interactions in Binary Mixtures of Ethylmethylketone and 2-alkanol by Excess Number of *i* and *j* Molecules Around a Central Molecule *j* (Δn_{ij})

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ARTICLE INFORMATION

Received: 22 March 2019
Received in revised: 13 April 2019
Accepted: 04 July 2019
Available online: 23 October 2019

DOI: 10.33945/SAMI/CHEMM.2020.2.2

KEYWORDS

Kirkwood-buff integrals
Methyl-ethyl-ketone
2-Alkanol
Molecular interactions

ABSTRACT

In order to study the nature, type, and magnitude of interactions in the binary mixtures of methyl-ethyl-ketone and a series of 2-alkanol from 2-propanol up to 2-heptanol, excess (or deficit) numbers of *i* and *j* molecules around a central molecule *j* (Δn_{ij}), by being linked to the KB integrals, have been used and reported at T=298.15 K. Negative values of Δn_{ij} and Δn_{ji} and positive values of Δn_{ii} and Δn_{jj} indicate the fact that in the mixtures the tendency of the similar molecular components to form the new interactions and stay together is much higher than the dissimilar molecular components. Investigating the changes in the calculated quantities for different mixtures shows that with the increase in the length of the alcoholic chain, the tendency of the heterogeneous molecules to interact with each other decreases.

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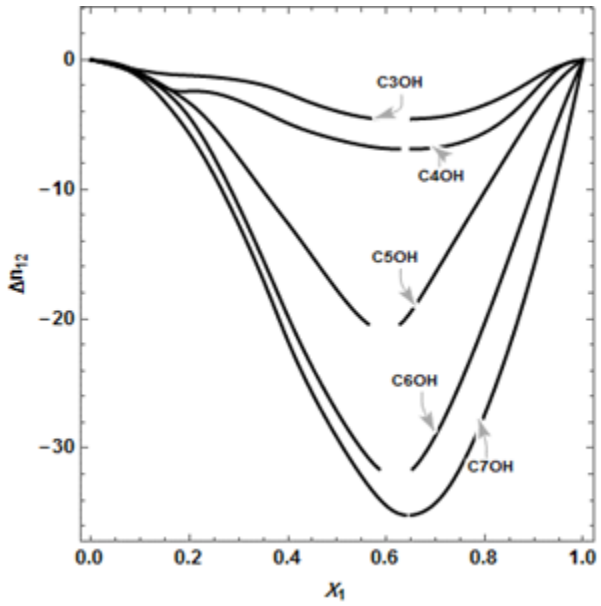
Graphical Abstract



Introduction

Commonly, the extent of correlation between *the* X_i positions of *i* and *j* molecules is measured by the pair correlation function $g_{ij}(X_i, X_j)$ as this function that is used in the KB statistical theory [1-3] can be obtained from the experimental sources and connect the molecular interactions to the macroscopic structure of liquids. The KB integrals determine the extent of mutual affinity between the components of mixtures and find important usage in the preferential solvation and relative stability of molecules in solution. In KB formalism, the G_{ij} is the main quantity that is calculated for solutions. Other parameters such as excess (or deficit) molecules around a central molecule are determined from the G_{ij} integrals. In the current study, excess (or deficit) molecules around a central molecule for MEK+2-alkanol binary systems were reported. The considered alcohols are 2-pentanol, 2-butanol, 2-pentanol, 2-hexanol and 2-heptanol.

Results and discussion

The KB formalism provides information about the structure of liquid mixtures at the microscopic level by the parameter of Δn_{ij}, namely the excess (or deficit) numbers of *i* and *j* molecules around a central molecule *j* [4]. Calculation of Δn_{ij} is based on the relation.

$$\Delta n_{ij} = C_i \Delta G_{ij} \quad (1)$$

Δn_{ij}, can be calculated from the corresponding KBIs;

$$\Delta n_{12} = C_1 \Delta G_{12} = \frac{-c_1 V_1 V_2}{V_m} \left(\frac{1-D}{D}\right) \quad (2)$$

$$\Delta n_{21} = C_2 \Delta G_{21} = \frac{-c_2 V_1 V_2}{V_m} \left(\frac{1-D}{D}\right) \quad (3)$$

$$\Delta n_{ii} = C_{ii} \Delta G_{ii} = \frac{-c_i x_j V_j^{\,2}}{x_i V_m} \left(\frac{1-D}{D}\right) \quad i \neq j \quad (4)$$

The obtained results for Δn_{ij}, Δn_{ji}, Δn_{ii} and Δn_{jj} as a function of mole fraction for methyl-ethyl-ketone (MEK)+2-alkanol binary mixtures are listed in Table 1. It is noteworthy that four local compositions in a binary mixture composed of spices 1 and 2 should be considered: x_{11} and x_{21} are the local mole fractions of components 1 and 2 near a central molecule 1, and x_{12} and x_{22} are the local mole fractions of components 1 and 2 near a central molecule 2 [5] .

Calculation of excess or deficit methyl-ethyl-ketone molecules around the central methyl-ethyl-ketone molecule Δn_{ii} shows that this quantity is positive for all binary systems. Data illustrate that there are similar molecules around the central methyl-ethyl-ketone molecule in the mixtures. Comparison of the peaks of Δn_{11} for binary mixtures displays this relation.

Δn_{11} MEK+2-heptanol > Δn_{11} MEK+2-hexanol > Δn_{11} MEK+2-pentanol > Δn_{11} MEK+2-butanol > Δn_{11} MEK+2-propanol

This relation shows that the deficit of MEK molecules around the central molecule of MEK is minimum for the system containing MEK+2-propanol and maximum for MEK+2-heptanol. In the binary mixtures, MEK molecules are most commonly rounded by 2-propanol molecules and less commonly with 2-heptanol molecules. Values of Δn_{21} (number of excess or deficit molecules of alcohols around the central MEK) are negative for all binary systems and suggest that the central MEK molecule is less surrounded with alcohol molecules in the mixture as compared to similar MEK molecules. Comparison of Δn_{21} peak for binary mixtures indicates the following relation:

Δn_{21} MEK+2-propanol > Δn_{21} MEK+2-butanol > Δn_{21} MEK+2-pentanol > Δn_{21} MEK+2-hexanol > Δn_{21} MEK+2-heptanol

This relation implies that there are more 2-propanol molecules around a central MEK molecule as compared to other alcohols and the number of 2-heptanol molecules is the least. By increasing the length of the alcohol chain, the number of alcohol molecules around the MEK decreases as interactions between unlike molecules reduced. This behaviour for MEK (1)+2-alkanol (2) mixtures is presented in Figure 1.

Table 1. The excess (or deficit) number of molecules Δn_{ij} as a function of the mole fraction x_1 of MEK at T=298.15 K

MEK+2-propanol				
x_1	Δn_{12}	Δn_{21}	Δn_{11}	Δn_{22}
0.0819	-0.6	-2.2	5.2	0.4
0.1607	-1.1	-4.4	10.7	1.9
0.24	-1.3	-5.7	14.9	3.1
0.349	-1.9	-6.4	18.4	5.3
0.4405	-3.2	-6.1	18.6	7.1
0.5593	-4.4	-5.2	15	8.6
0.6511	-4.5	-4.4	10.5	8.4
0.7392	-4.2	-3.4	7.4	7.1
0.8496	-2.6	-1.7	0.8	3.3
0.937	-0.7	-0.9	0.9	0.9
MEK+2-butanol				
0.0833	-0.7	-4	9.4	1.2
0.161	-2.3	-6.7	16.9	3
0.2402	-2.5	-9.2	22.7	5
0.3498	-4	-10.7	26.9	8.3
0.441	-5.5	-10.5	26.9	12
0.5609	-6.6	-8.6	22.1	17.6
0.6498	-6.8	-6.7	16	17.4
0.7398	-6.5	-5	9.7	12.9
0.8501	-4.3	-3	3.3	6.6
0.9405	-0.9	-0.2	0.5	2.8
MEK+2-pentanol				
0.0852	0.8	-5.8	7.6	1.5
0.1643	-2.4	-12.6	15.8	3.1
0.2456	-5	-17.7	23.9	6.2
0.3511	-10.2	-19.8	31.9	10.7
0.4422	-14.8	-19.7	33.1	15.3
0.5632	-20.4	-16.2	26	21.2
0.6508	-19.4	-12.1	17.4	21.7
0.7416	-13.8	-6.7	9.2	16.8
0.8512	-7	-2.3	2.6	8.8
0.941	-2	-0.1	0.3	4
MEK+2-hexanol				
0.0874	-0.9	-7.4	11	0.6
0.1661	-2.9	-15.8	20	2.8
0.2482	-7.3	-23.3	28	7.2
0.355	-15.9	-29.4	35	16.4
0.4463	-23.5	-29.2	37.2	24.9
0.5671	-30.9	-23.9	34	31.7
0.6534	-31.6	-16.4	28.7	30.8
0.7422	-25.6	-9	20	25
0.8547	-14.6	-2.5	9.5	14.3
0.942	-5.3	-0.3	2.9	5.2
MEK+2-heptanol				
0.0834	-0.9	-11	11	1.1
0.1619	-3.8	-19.8	22.3	4.4
0.2426	-8.4	-26.6	33.7	9.8
0.3491	-16.9	-31.6	46.8	19.8
0.4375	-24.8	-31.5	51.5	29.1
0.5661	-33	-26	45.8	38.6
0.6502	-35.1	-18.8	37.1	41.2
0.7371	-32.3	-11.4	26.4	37.9
0.8498	-22.1	-3.9	13.5	25.9
0.9401	-10	-0.6	4.9	11.7

Values of Δn_{22} (excess number of alcohols molecules around the central molecule of alcohol) are positive and increase with an increase in carbon chain length of 2-alkanol.

This behaviour shows that there are similar molecules around the central alcohol molecule.

Δn_{22} MEK+2-heptanol > Δn_{22} MEK+2-hexanol > Δn_{22} MEK+2-pentanol > Δn_{22} MEK+2-butanol > Δn_{22} MEK+2-propanol

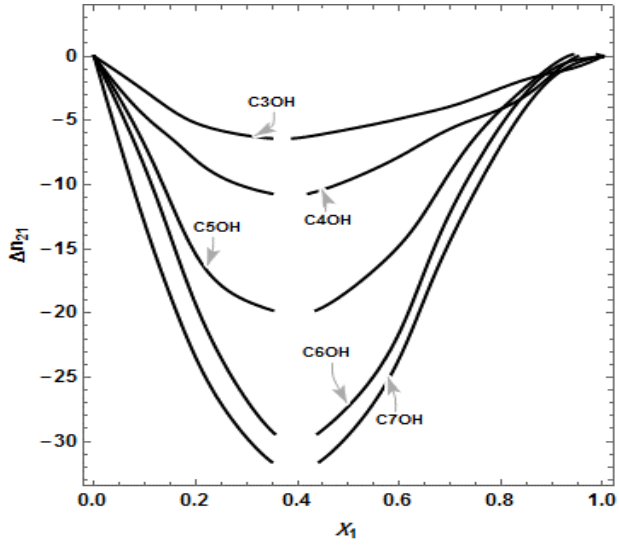


Figure 1. Δn_{21} for methyl-ethyl-ketone (1) +2-alkanol (2) mixtures in the vicinity of methyl-ethyl-ketone molecules at T = 298.15 K

The changing style of these data shows that the minimum number of the similar molecule is around the 2-propanol central molecule, and more closely surrounded by unlike molecules of MEK.

By increasing the length of alcohols, the numbers of similar molecules increase over the central alcohol and the similar interactions increase. This effect for MEK (1) +2-alkanol (2) mixtures is shown graphically in Figure 2. Values of Δn_{12} (excess or deficit number of MEK around to the central molecule of alcohol) are negative for all binary systems. Thus, the central alcohol molecule in the mixtures is most surrounded by alcohol molecules, and similar interactions are more favourable. Comparison of Δn_{12} peak in different mixtures shows the following relation:

Δn_{12} MEK+2-propanol > Δn_{12} MEK+2-butanol > Δn_{12} MEK+2-pentanol > Δn_{12} MEK+2-hexanol > Δn_{12} MEK+2-heptanol

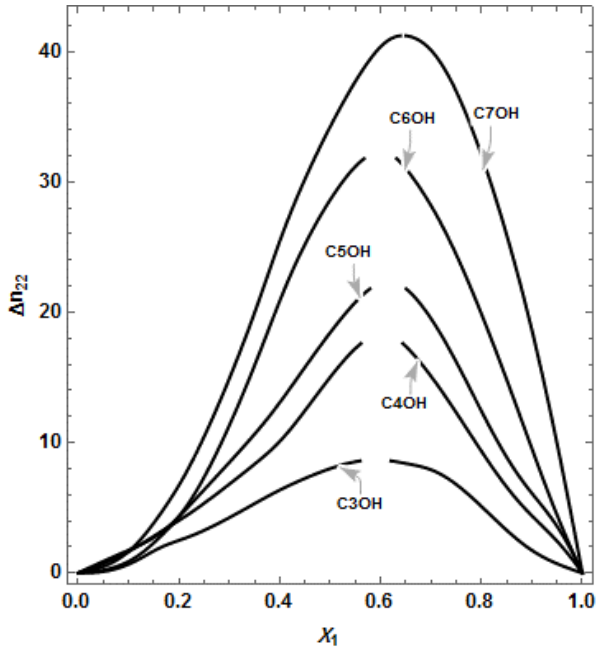


Figure 2. Δn_{22} for methylethylketone (1) + 2-alkanol (2) mixtures in the vicinity of alcohol molecules at T = 298.15 K

The above relation indicates that the highest numbers of MEK molecules are around the 2-propanol central molecule and the increase in the length of 2-alkanol causes the reduction of the number of MEK around the alcohol molecule. Results suggest that increase of alkyl chain of 2-alkanol plays the role of a weakening agent in interactions.

Conclusions

With the aim of gaining new insights into the nature and type of molecular interactions that occur in the binary mixtures methyl-ethyl-ketone+2-alkanol, excess (or deficit) numbers of i and j molecules around a central molecule j, Δn_{ij} were calculated. Application of this parameter to the binary mixtures shows that the structure of binary mixtures is determined by weak unlike interactions, especially in MEK+2-heptanol mixture. For solutions with a given MEK, Δn_{12} is negative and decrease with an increase in the methyl groups of alcohols chain in the following sequences:

Δn_{12} MEK+2-propanol > Δn_{12} MEK+2-butanol > Δn_{12} MEK+2-pentanol > Δn_{12} MEK+2-hexanol > Δn_{12} MEK+2-heptanol

Conflict of Interest

We have no conflicts of interest to disclose.

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How to cite this manuscript: Elham Shahbazi, Mohammad Almasi*, Study of Molecular Interactions in Binary Mixtures of Ethylmethylketone and 2-Alkanol by Excess Number of *i* and *j* Molecules Around a Central Molecule *j* (Δn_{ij}). Chemical Methodologies 4(2), 2020, 123-129. DOI:10.33945/SAMI/CHEMM.2020.2.2.