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STUDY OF HETEROMOLECULAR INTERACTION OF NONAQUEOUS BINARY SOLUTIONS

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Ушбу ишда диметилформамид-этанол ва циклогексан-этанол аралашмаларининг молекулалараро таъсирларини ўрганиш учун рефрактометрия методи қўлланилди. Диметилформамид ва циклогексан ((0–1.0 мол улушли) турли концентрацияларидаги аралашмаларининг синдириш кўрсатгичлари 25°C ҳароратда ўлчанди. Бинар аралашмалардаги кучли водород боғланишлар ҳисобига вужудга келадиган гетеромолекуляр комплекслар ~0.5 мол улушли концентрациясида ҳосил бўлиши кўрсатилди. Нисбатан заиф молекулалараро таъсирлар диметилформамиднинг ~0.2 ва ~0.9 ва циклогексаннинг ~0.2 ва ~0.8 мол улушли концентрацияларида аниқланди.

В данной работе метод рефрактометрии использован для изучения молекулярных взаимодействий и структурных характеристик бинарных смесей диметилформамид-этанола и циклогексан-этанола. Показатели преломления смесей измерены в широком диапазоне концентраций диметилформамида и циклогексана ((0–1.0 мольные доли) при 25°C. Показано, что гетеромолекулярные комплексы в бинарных растворах образуются при концентрации ~0.5 мольной доли благодаря сильным Н-связям. Относительно слабые взаимодействия определяются при концентрации ~0.2 и ~0.9 мольной доли диметилформамида и ~0.2 и ~0.8 мольной доли циклогексана.

In this work, the refractometry method was used to study of the molecular interactions and structural characteristics of dimethylformamide-ethanol and cyclohexane-ethanol binary mixtures. The refractive indices of mixtures were measured over a wide range of dimethylformamide and cyclohexane concentrations (0–1.0 mole fractions) at 25°C. It has been shown that heteromolecular complexes in binary solutions are formed at the concentration of ~0.5 mole fraction of those compounds due to strong H-bonds. Relatively weak interactions are determined at a concentration of ~0.2 and ~0.9 mole fraction of dimethylformamide and ~0.2 and ~0.8 mole fraction of cyclohexane.

I. INTRODUCTION

The experimental data on macroscopic properties such as excess refractive indices often provide valuable information for the understanding of the nature homo- and hetero-molecular interactions. Futhermore, alcohol-amide solutions are practical importance [1]. Dimethylformamide (DMF) and ethanol solution is used for the electro-hydrogenation of coal [2]. Ethanol and cyclohexane one is intensively used in various technological processes. One of them is the usage of ethanol-cyclohexane mixture in the creation of conductive films based on polypyrrole films [3]. Ethanol is an interesting non-aqueous solvent, in particular because it is strongly self-associated through hydrogen bonding despite its low dipole moment. Dimethylformamide on the other hand is highly polar, but

is practically unassociated, and behaves as a good solvent for many properties of compounds [4]. Cyclohexane is a non-polar, hydrophobic hydrocarbon used as oil extractant, paint and varnish remover. It is used in laboratories in analysis and as a standard because of its unique chemical and conformational properties. Ethanol is associated through hydrogen bonding, forms azeotropic mixture with cyclohexane at 337.8 K. Moreover ternary mixtures with alcohols as one component are used in industries to avoid the formation of azeotropes [5-6].

Refractometry method is sensitive to determine the structural states of solutions [7-8]. The advantages of this method are high accuracy and simple and quick determinations of parameters of a substance. In the present paper, we report excess refractive indices of dimethylformamide-ethanol and cyclohexane-ethanol mixtures covering whole miscibility range. Deviation in refractive indices has been noted to be an essential parameter for characterization and understanding the thermodynamic properties of solutions.

II. EXPERIMENTAL

Materials: Dimethylformamide, cyclohexane, ethanol (99.9%, Sigma-Aldrich, USA).

Preparation of solutions. Ethanol solutions of dimethylformamide and cyclohexane were prepared by gravimetric method described in a paper [9].

Study of refractive indices of solutions. The data obtained by using the RX-7000-alpha digital refractometer with the temperature recording function (Atago, Japan). The measurement error n is less than 0.0001. The measurement of both n and temperature of solutions are taken not more than 20 seconds. For the refractive indicesx measurements, dimethylformamide-ethanol and cyclohexane-ethanol solutions were prepared in a concentration range of 0–1.0 mole fraction. For each solution, several values (at least three) were measured at a fixed temperature of 298 ± 0.05 K. The end result is obtained by averaging over the entire series of measurements. Excess refractive indices n^E are calculated by the formula [10]:

$$n^E = n_{solution} - (xn_1 + (1-x)n_2). \quad (1)$$

The measured values of refractive indices n and calculated excess refractive indices n^E have been given at Table.

Table. Experimental mole fraction x, refractive indices n, and excess refractive indices n^E for cyclohexane and DMF.

x, cyclohexane	n	n^E	x, DMF	n	n^E
0.0000	1.3604	0.0000	0.0000	1.3610	0.0000
0.0600	1.3648	0.0006	0.0819	1.3680	0.0015
0.1258	1.3704	0.0020	0.1672	1.3753	0.0032
0.1978	1.3756	0.0064	0.2561	1.3822	0.0100
0.2773	1.3805	0.0025	0.3487	1.3878	0.0036
0.3653	1.3864	0.0029	0.4454	1.3957	0.0050
0.4633	1.3922	0.0113	0.5464	1.3983	0.0134
0.5731	1.3980	0.0113	0.6521	1.4075	0.0031
0.6971	1.4075	0.0030	0.7626	1.4122	0.0004
0.8382	1.4164	0.0029	0.8784	1.4221	0.0026
1.0000	1.4237	0.0000	1.0000	1.4276	0.0000

III. RESULTS AND DISCUSSION

Figure 1 represent experimental data of excess refractive index from different concentration binary mixtures of DMF-ethanol. The first peak at a concentration of ~0.2 mole fraction is corresponded to strong interaction between ethanol molecules. Maximum value of refractive index was detected at a concentration of ~0.5 mole fraction. The second peak at the ~0.5 mole fraction characterizes the hetero-molecular structure formation between DMF and ethanol molecules.The third peak at the ~0.9 mole fraction describes weak interactions between dimethylformamide and ethanol

This interaction between constituent molecules such as hetero-molecular association through the formation of H bond, often termed as strong specific interaction. DMF results from the replacement of aminic hydrogens of formamide by two $–CH_3$ groups. Therefore, no self-association of DMF through H-bonding is possible because of the absence of aminic hydrogen. The attachment of two $–CH_3$ groups to the nitrogen atom increases electron density on the nitrogen atom and carbonyl oxygen of the amide. The possibility of H-bond formation with alcohol molecules appears by one or two of the following ways: (i) $>C{=}O...HO$, (ii) $\cdot(CH_3)_2N...HO$. At the same time the presence of two $–CH_3$ groups on the nitrogen atom of DMF creates a steric hindrance that prevents alcohol molecules to come sufficiently close to it. On the other hand, alcohol molecules undergo self- and cross-association because of the presence of hydrogen bonds [11-12]. Mixing of DMF with an alcohol will induce changes in hydrogen bonding (in the alcohol) and dipolar interactions (in the DMF). On addition of DMF in the pure alcohol the self-association will be disrupted partly or fully, and new H-bonds between alcohol and DMF will be formed. At the same time, segmental inclusion of DMF into the vacant spaces in the structural network of alcohol may also occur.

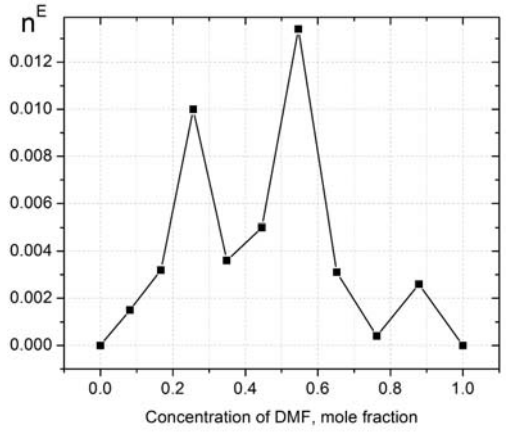


Fig. 1. Changes of excess refractive indices n^E of freshly prepared DMF-ethanol at different initial concentrations of components.

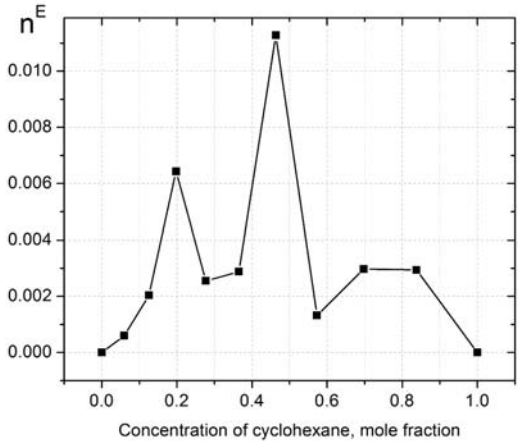


Fig. 2. Changes of excess refractive indices n^E of freshly prepared cyclohexane-ethanol at different initial concentrations of components.

Figure 2 shows experimental data of excess refractive indices for different concentration binary mixtures of ethanol-cyclohexane. The first peak at a concentration of ~0.2 mole fraction is corresponded to dispersive weak interaction between cyclohexane molecules [13]. The second peak at the ~0.5 mole fraction characterizes the

hetero-molecular structure formation between cyclohexane and ethanol molecules. The third peak at the ~0.8 mole fraction describes the hydrogen bonds between ethanol molecules. Ethanol is a good solvent that can dissolve both the polar and nonpolar components. The hydrophilic –OH group of ethanol can dissolve the polar component whereas the short hydrophobic hydrocarbon group can dissolve the nonpolar component. In the ethanol mixture, the cyclohexane is completely dissolved and only the interaction with the cyclohexane ring and the active groups of ethanol are presented, which are mostly dispersive in nature. The increase in mole fraction of cyclohexane increases the net dispersive interactions. As the mole fraction of cyclohexane increase, the hydrogen bond is ruptured and that lead to additional dipole type interactions. The strong dipolar interactions are restricted more and more whereas the weak dispersive interactions are predominating with maximum around ~0.8 mole fraction.

IV. CONCLUSION

It was shown that with a change in the concentration of DMF and cyclohexane in ethanol solutions, a restructuring of the solution occurs, accompanied by a local reorganization of the formed complexes and associates. The experimental data on the excess refractive indices gave information about heteromolecular structures due to strong H-bonds which occur at the concentration ~0.5 mole fraction of both mixtures. Also, the graphics showed that there are weaker complexes at the concentration ~0.2, ~0.9 and ~0.2, ~0.8 mole fractions of DMF and cyclohexane, respectively.

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