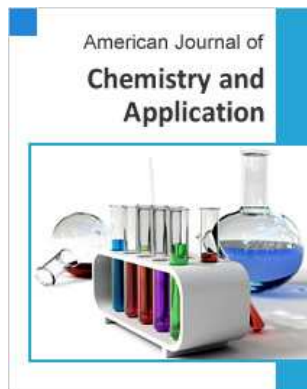




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Solvent Properties of Binary Mixtures of Tetrahydrofuran and Propylene Carbonate Solvents

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Abstract

Varying proportions of binary mixed solvents of tetrahydrofuran (THF) and propylene carbonate (PC) were prepared and some of their solvent properties investigated. These properties include, excess viscosity, excess volume and Grunberg and Nissan 'd' interaction parameter. Investigations were carried out at 25°C. Positive excess volume was observed in the system. Excess viscosities were positive in some fractions and negative in some. The results of the 'd' parameter reveals the non-ideality of the mixture formed. Excess Gibbs free energy (G^E) of activation is positive in all the fractions investigated.

1. Introduction

Solvents are used by scientists to carry out chemical investigations. Volumetric properties of mixtures are of interest to scientists and industrialists. Because of this, proper understanding of solvent interaction properties and the effects of co-solvents on properties of solvent mixtures are very important. The interaction properties are sometimes dependent on the class of solvents studied, whether they are polar, non-polar, aprotic, protic or polar aprotic. They also depend on solute-solvent, solute-solute, solvent-solvent interactions and on the interstitial accommodations of unlike molecules arising from differences in molar volume and free volume of the solution components [1].

Propylene carbonate ($C_4H_6O_3$) is a colorless and odorless liquid and is useful as a polar/aprotic solvent. Due to its high dielectric constant of 64, it is frequently used as a high-permittivity component of electrolytes in batteries, usually together with a low-viscosity solvent [2]. Tetrahydrofuran (CH_2)₄O is a colorless, water-miscible organic liquid with low viscosity at standard temperature and pressure. Several researchers have studied the solvent properties of binary mixtures of some organic solvents. The ultrasonic velocity, viscosity and density of dimethylsulphoxide (DMSO), 1-butanol, 1-hexanol and 1-octanol and also of their binary mixtures, with DMSO as the common solvent at 303.15K have been studied [3]. They reported negative excess velocity and Gibbs free energy of activation for viscous flow throughout the entire range of solvent composition which they attributed to be the indicative of the dominance of structure breaking effects over interaction effects between the component molecules. Studies on the density and viscosity of the binary mixture of Triethylene Glycol Monobutyl Ether (TEGMBE) plus Water from (293.15 to 333.15K) at atmospheric pressure have been carried out [4]. They reported that the excess molar volumes were negative over the entire range of composition with a minimum around $x_1 = 0.26$ of TEGMBE at all temperatures. The negative V^E were

attributed to volume contraction on mixing due to the accommodation of the smaller molecules into the larger ones. Some researchers studied the effect of solvent properties on equivalent conductivity of electrolyte and reported that the conductivities of the solvent mixtures decreased with increasing percentage of the co-solvent [5]. A study on the intermolecular interactions of mixed solvents of tetrahydrofuran and propylene carbonate for magnesium ion battery was conducted by [6]. They found out that a net increase in some solvent properties is achieved when solvents are mixed.

The aim of this research is to determine the influence of mixing on the solvent properties of binary mixtures of tetrahydrofuran and propylene carbonate solvents.

2. Materials

Pycnometer, Ubbelohde viscometer, thermostated water bath etc, were used for this study. The solvents used were; Propylene Carbonate (PC) (99.5%) and tetrahydrofuran (THF) (99.5%)(BDH chemicals Ltd, Poole, England).

3. Methodology

The methods employed in this research are the same as that described by earlier researcher [7]. The solvent mixtures were prepared in varying proportions of 100%, 85%, 75%, 50%, 25%, 15% and 0% tetrahydrofuran. The molar excess volumes, V^E , at 298k were calculated from the densities of the two binary mixtures using the following relationship:

$$V^E = X_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + X_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \quad (1)$$

The excess viscosities η^E , were calculated using the following relationship

$$\eta^E = \eta - (X_1 \eta_1 + X_2 \eta_2) \quad (2)$$

The molar excess Gibbs's free energies of activation for viscous flow, G^{*E} , were calculated using the following relationship:

$$G^{*E} = RT [\ln VM - (X_1 \ln V_1 M_1 + X_2 \ln V_2 M_2)] \quad (3)$$

The Grunberg and Nissan's d parameter was calculated from absolute viscosities, (η), for the two binary systems using the relationship:

$$D = \frac{\ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2)}{x_1 x_2} \quad (4)$$

4. Results

The experimental results are presented in the figures below:

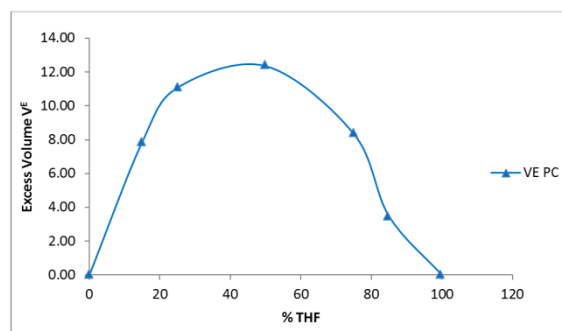


Fig. 1. Excess Volume, V^E , of various mixtures of THF/PC at 25°C.

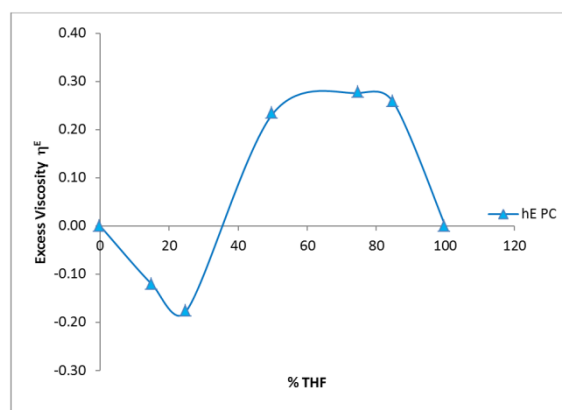


Fig. 2. Excess viscosity, η^E , of various mixtures of THF/PC at 25°C.

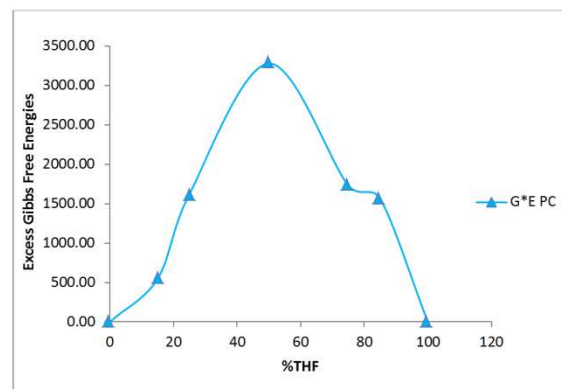


Fig. 3. Excess Gibbs free energies of activation for viscous flow for various mixtures of THF/PC system at 25°C.

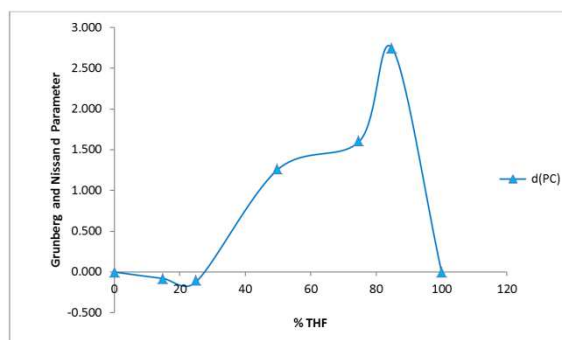


Fig. 4. Grunberg and Nissan's d Parameter for various mixtures of THF/PC system at 25°C.

5. Discussions

Excess Volume (V^E): The results of the excess volume in figure 1 show that positive excess volume was observed in the system. This is attributed to physical interactions involving dispersions and increase in chain length between the different components of the molecules. Similar observations have been made [8].

Excess Viscosities, η^E : The results of excess viscosities of the binary system shown in figure 2 were positive. This is attributed to the dominance of structure making effect in the regions, while the negative excess viscosities suggest dominance of dispersion forces due to difference in molecular sizes. Some researchers, [9] recorded similar result in their work.

The Grunberg and Nissan 'd' Parameter: The results of the d parameters for the binary system shown in figure 3 show that it is highest at 85% THF. The positive d values indicate that the resultant mixture deviates negatively from Rault's law while negative values suggest dominance of dispersion forces at these points. Earlier researchers, [10] made such reports. Generally, d parameter is a characteristic of each system and represents the intermolecular interactions between solvent molecules.

Excess Gibbs free energy (G^{*E}): The results of the calculated excess Gibbs free energy (G^{*E}) of activation for the two binary systems in figure 4 show that G^{*E} is positive in all the fractions. The magnitude of G^{*E} represents the strength of interaction between unlike molecules and is influenced by the concentrations and size of the solute. Positive G^{*E} shows that specific interactions are dominant in the system. [10] [11] made similar reports.

6. Conclusion

The strength of solvent-solvent interactions has been revealed in this work. Volume contraction/expansion influence other properties of the solution. Solvents that interact strongly form mixtures that deviate strongly from ideality. Thermodynamic properties are good analytical tools for understanding intermolecular interactions.

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