Survismetric Evaluation of Excess Properties of Binary Mixtures of Diethyl Ether And Hexane At Varying Temperatures

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Abstract: This study was designed to use survismeter to exploit the mixing behavior of a weak polar solvent (diethyl ether) and non-polar solvent (hexane) in varying compositions of diethyl ether and temperature. The densities and viscosities of binary mixed solvents of diethyl ether and hexane were evaluated at temperatures of 303, 313, 323 and 333 K and over varying compositions of diethyl ether using a single capillary pycnometer and Mansingh Survismeter respectively. The excess molar volumes (V^E), excess viscosities (η^E) and excess Gibb's free energy (G^E) of activation for viscous flow of the binary mixtures at the different temperatures were evaluated from the experimental parameters using Redlich Kister equation. The results show negative values of V^E and G^E at all mole fractions and temperatures. The η^E values are positive at 303 and 313 K but negative at 323 and 333 K at all compositions respectively. These observations have been interpreted based on the molecular interactions between the components of the solvent mixtures and structural changes resulting from these interactions.

Keywords: Thermodynamics, Viscosity, Activation energy, Density.

I. Introduction

Solvents are used by scientists and engineers for chemical investigations and a variety of industrial processes. Therefore, good knowledge of the mode of interactions in different media and the effects of combining them in various compositions becomes very important. These solvent interactions depend on the nature or class of solvents studied *i.e.*, whether protic, aprotic, polar or non-polar (Maduelosi and Abia, 2015). They can also be classified according to the acidity or basicity of the liquids or the ability to attract/repel hydrogen ions in solution.

Studies of excess thermodynamic properties of binary mixed solvents are important in the understanding of the nature of intermolecular interactions and flow rate properties associated with solvent mixtures and component liquids (Dikio *et, al*., 2012, Arvinds *et, al.,* 2013, Dikio *et, al*., 2013, Lakshimi et al., 2014, Pandey *et al*., 2014). These excess functions provide the most sensitive numerical measure of solution properties of the pure solvents in original state (Welford- Abbey, *et al* 2009). They are also of theoretical and practical importance such as in Prigogine-Flory-Patterson theory, Nernst distribution equation, Calorimetry, titration, *etc*. (Baskaran *et, al.,* 2010, Elliot and lira, 2012). The knowledge of excess functions is also very useful in dealing with chemical bifurcations, fluid flow and heat transfer processes (Pal and Kumar 2006, Saleh *et al*., 2006) which are applied in testing and designing thermodynamic models used in computing and prognosticating fluid phase equilibria.

Mixing of two solvents has been reported to catalyze specific interactions such as hydrogen bonding, dipole-dipole and ion-solvent interactions (Nallani and Jaana, 2008, Maduelosi *et al*.,2014). Strong and weak interactions between distinct molecular liquid mixtures cause deviations from ideality. This behaviour is usually consociated with large differences in the chemistry and molecular armature of the mixed solvents, the mixing ratios as well as the experimental fettles such as temperature (Salman *et al.,* 2018). Structural changes such as hydrogen bond rupture and loosening of dipole interactions result in positive excess volumes, negative excess viscosities and Gibb's free energies of activation respectively. On the other hand, molecular fitting into interstitial spaces and strong attractive interactions give rise to negative excess molar volumes, positive excess viscosities and Gibb's free energy of activation for viscous flow.

In this research, experimental viscosities and densities of binary mixtures of diethyl ether and hexane are reported at different mole fractions of diethyl ether and temperatures of 303, 313, 323 and 333 K. These values were Fitted into Redlich Kister equation to generate the excess viscosities, excess molar volumes and excess Gibb's free energy of activation for viscous flow.

II. Experimental

Materials/Apparatus

Diethyl ether and hexane were products of JHD chemical reagent Co. Ltd, China and of analytical grade, so were used without further purification. Purities were checked by measuring the densities of the solvents at 25°C and comparing the values with those reported in literature. They were very much comparable as shown in Table 1 (Riddick *et al.,* 2012, Robert *et al*., 2012).

Table 1: Comparison of experimental and literature density values (g/cm^3) of the pure solvents at 25°C temperature

Solvents	Exp.	Lit.
Diethyl ether	0.7130	0.7134
Hexane	0.6700	0.6720

All density measurements were made with a 10ml pyknometer and viscosity values obtained using the Survismeter invented by Man Singh and manufactured by Borosil company, India.

SURVISMETER

Borosil Mansingh Survismeter is an eco-friendly instrument that monitors and tracks molecular activities in solvents and solvent mixtures. This understanding is important in developing and characterizing materials such as drugs, proteins, DNA, dyes, Inks, emulsions, nanoemulsions, colloids, etc. (Man Singh, 2016) With survismeter, interactions associated with cohesive and intermolecular forces in liquids and liquid mixtures as well as the structural changes resulting from structure breaking and making effects are experimentally studied (Man Singh 2007, Chandra *et al.*, 2013, Man Singh, 2016).

Density Measurement.

Binary mixtures of the solvents at varying mole fractions ranging from 0.1 to 1.0 were prepared by mass. Densities of the pure solvents and binary mixtures at the different compositions and temperatures were measured in triplicate and the average values recorded. Distilled water was used to calibrate the pyknometer at the working temperatures.

Viscosity Measurement

Viscosity measurements were carried out using the Man Singh Survismeter. This was done by filling the reservoir bulb of the Survismeter with 25ml of the experimental liquid via the inlet limb. The meniscus of the liquid was ensured to be on the upper calibrated part of the instrument. The flow rates observed were used to compute the viscosity values.

The experimental density and viscosity data of the pure solvents and the binary mixtures obtained were used to calculate V^E, η^E and G^E values (equations 1 – 6) and correlated with Redlich-Kister polynomial equation

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

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

ρ_1 and ρ_2 are densities, η_1 and η_2, dynamic viscosities, X_1 and X_2, the compositions, M_1 and M_2, molar masses of diethyl ether and hexane respectively while ρ_{mix} and η, the respective densities and dynamic viscosities of the mixtures. The kinematic viscosity (υ) values were obtained from equation 3

$$\upsilon = kt \qquad (3)$$

where k is Man Singh viscometer constant and t, the flow time through the Survismeter capillary. The dynamic viscosities were computed from the experimental kinematic viscosity and density values using equation 4

$$\eta = \upsilon\rho \qquad (4)$$

The excess Gibb's free energy of activation for viscous flow was obtained from equation 5.

$$G^E = RT ln V_m - [X_1 ln V_1 M_1 - X_2 ln V_2 M_2] \qquad (5)$$

R is the universal gas constant and T, the absolute temperature. V_m, V_1 and V_2 are molar volumes of mixture, diethyl ether and hexane respectively. V_m was obtained from equation 6

$$V_m = \left(\frac{X_1 M_1 + X_2 M_2}{\rho_{mix}}\right) \qquad (6)$$

$$Y^E = X_1 X_2 \sum_{i=1}^{n} A_i \left(2X_i - 1\right)^{i-1} \qquad (7)$$

III. Results and Discusion

The excess molar volumes of the binary mixtures of diethyl ether and hexane at the different compositions of diethyl ether and temperatures were calculated from the experimental density (g/cm^3) data and tabulated below.

Table 2: Density and Excess Molar Volume (cm^3/mol) values of the binary mixtures of diethyl ether and hexane at different compositions of diethyl ether and temperatures (K).

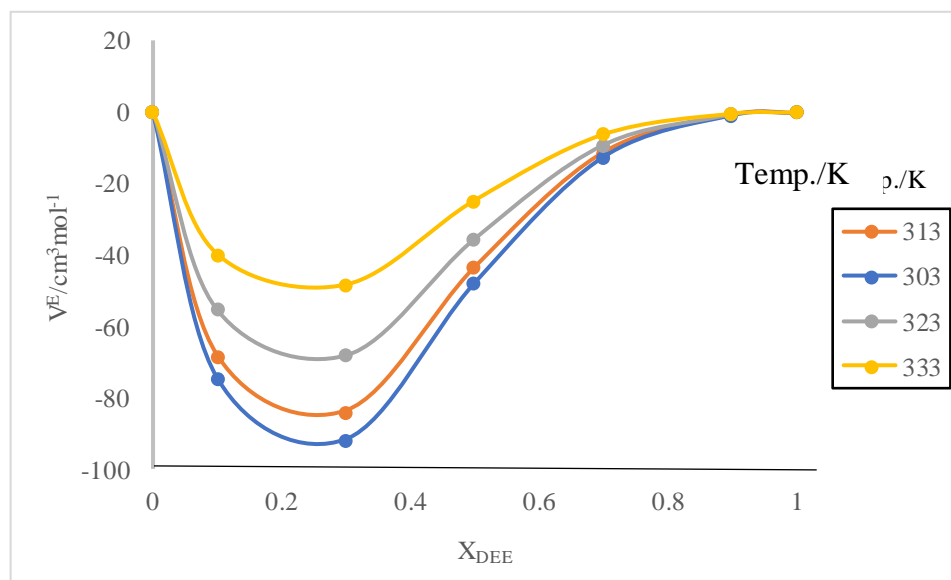| X	ρ	V^E (cm^3/mol) 303	313	323	333 K
0.0	0.7134	0.0000	0.0000	0.0000	0.0000
0.1	0.7923	-2.9300	-2.6032	-2.6032	-2.6032
0.3	0.7710	-4.9228	-4.9878	-4.6619	-4.8740
0.5	0.7492	-9.0718	-8.3689	-6.7714	-5.4314
0.7	0.7117	-10.3544	-116863	-8.3302	-7.7015
0.9	0.6705	-11.2400	-9.9036	-10.6856	-8.5291
1.0	0.6720	0.0000	0.0000	0.0000	0.0000

Figure 1: Plots of Excess Molar Volumes (V^E) of binary mixed solvents of diethyl ether and hexane versus mole fractions of diethyl ether (X$_{DEE}$) at different temperatures.

Figure 1 and Table 2 show the variation of excess molar volumes of binary mixtures of diethyl ether and hexane at varying mole fractions of diethyl ether and temperatures. The excess molar volumes are negative over the entire range of solvent compositions and the magnitude increased with increasing composition of diethyl ether upto a maximum of 0.3, above which the V^E values gradually decreased in magnitude. The excess molar volumes of binary mixed solvents are reflection of different structural changes pure solvents under go as they interact with each other (Cookey and Kemeakegha, 2020) . Molar volume of diethyl ether is 103.9 cm^{3}mol^{-1} and hexane is 130.7 cm^{3}mol^{-1}. Thus, increasing negative values of V^E with mole fraction of diethyl ether may be attributed to structural differences in size and shape of the component molecules of the mixture. Interstitial fitting of smaller volume of diethyl ether into larger volume of hexane is suspected at lower compositions. It is expected that the mixing of a polar solvent; diethyl ether

and a non-polar solvent; hexane would result in repulsive interactions between the molecules. The excess molar volume of such effect will be positive as the volume of the mixture will be larger than that of the sum of the molar volumes of the component solvents. Therefore, negative values of V^E may indicate that structural effect dominated over intermolecular interactions. It is also possible that other specific interactions such as ion-ion or induced dipole-dipole interactions played significant role in mixing the two solvents together.

The excess viscosities of the binary mixtures of diethyl ether and hexane at different composition of diethyl ether were calculated from experimental density values using equation 2.

Table 3: Density (g/cm^3) and excess viscosity (Pa.s) values of the binary mixtures of diethyl ether and hexane at different compositions of diethyl ether and temperatures (K).

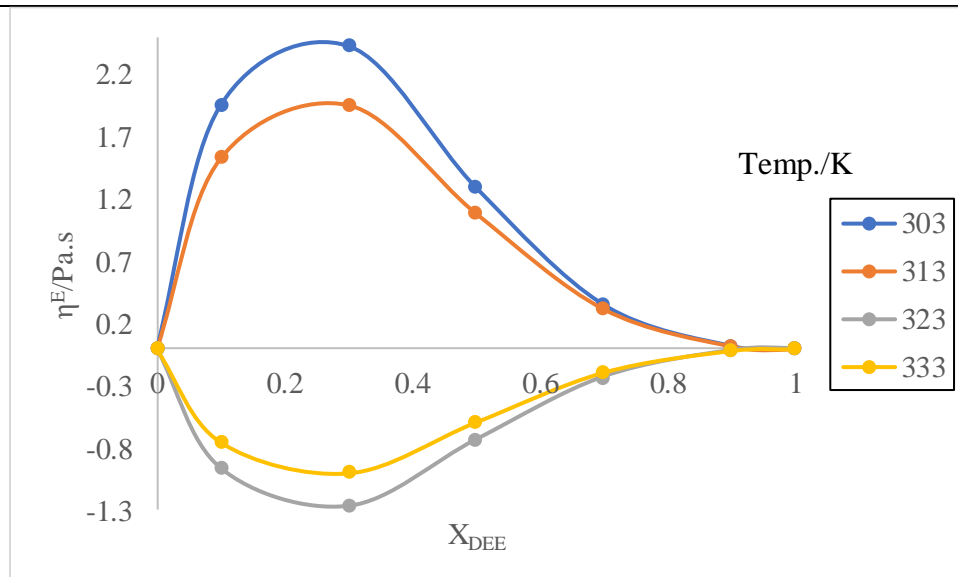| X	ρ	η^E			
		303	313	323	333
0.0	0.7134	0.0000	0.0000	0.0000	0.0000
0.1	0.7813	0.1325	0.1230	-0.1170	-0.1236
0.3	0.7708	0.0937	0.0958	-0.0958	-0.1038
0.5	0.7443	0.0625	0.0648	-0.0712	-0.0823
0.7	0.7121	0.3800	0.4070	-0.0450	-0.0730
0.9	0.6887	0.0227	0.0222	-0.0240	-0.0466
1.0	0.6720	0.0000	0.0000	0.0000	0.0000

Figure 2. Plots of excess viscosity (η^E) against mole fraction for diethyl ether and hexane mixtures at different temperatures.

Figure 2 and Table 3 show variation of excess viscosity against mole fraction of diethyl ether. The excess viscosities are positive at temperatures of 303 and 313 K but negative at 323 and 333 K. The positive deviations of the excess viscosity of the binary mixtures at lower temperatures may suggest strong intermolecular interactions of the single mixture components. However, as the temperature increased, molecular agitation increased which perhaps led to weakening of bonds and subsequent structure breaking effect resulting in more viscous flow. These observations suggest that among other contributions, strong dipole-dipole interactions existed between the molecules of diethyl ether and those of hexane. This is in agreement with the negative values obtained for excess molar volumes at all solvent compositions and temperature.

The excess Gibb's free energy of activation for viscous flow of the binary mixtures of diethyl ether and hexane at different compositions of diethyl ether and temperatures were calculated from experimental density values using equation 5 and presentated in Table 4 and Figure 3.

Table 4: Density and Excess Gibb's free energy of activation values of the binary mixtures of diethyl ether and hexane at different compositions of diethyl ether and temperatures.

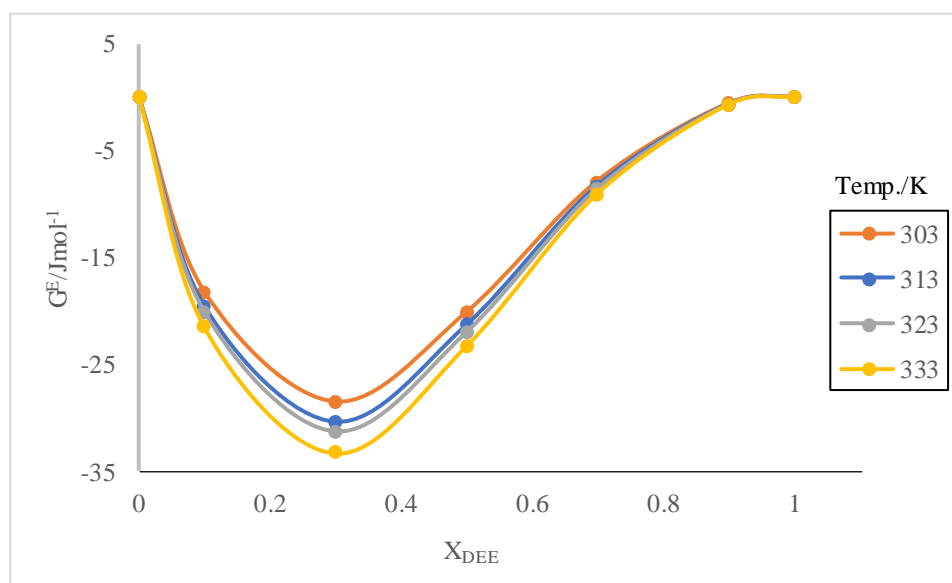| X	$\rho(g/cm^3)$	G^E (Jmol^{-1})			
		303K	313K	323K	333K
0	0.7134	0.0000	0.0000	0.0000	0.0000
0.1	0.7134	11.6643	12.2100	12.4574	12.9078
0.3	0.7558	11.5750	11.9640	12.4031	12.8119
0.5	0.7334	11.5640	11.9700	12.3981	12.8219
0.7	0.7101	11.6501	12.0400	12.4363	12.8216
0.9	0.6646	11.8435	12.2360	12.6254	12.9597
1.0	0.6270	0.0000	0.0000	0.0000	0.0000

Figure 3: Excess Gibb's free energy of activation for viscous flow of binary mixed solvents of diethyl ether/hexane mixtures at different compositions of diethyl ether and temperatures

Excess Gibb's free energy of activation gives information about molecular interaction behaviours of mixed solvents. This understanding helps to improve thermodynamic models for computing and predicting equilibria phase of fluids and fluid mixtures (Dikio *et al.*, 2012).The values of excess Gibb's free energy of activation are negative in the entire mole fraction range with a maximum at 0.3 composition of diethyl ether. Beyond this composition, G^E values gradually decrease at all compositions and temperatures. This observation may be attributed to spontanuity in mixing the two solvents and strong intermolecular interactions between the unlike molecules (Parveen *et al.*, 2010) at lower mole fractions of diethyl ether which gradually weakens at higher compositions and temperatures.

IV. Conclusion

The deviations in excess viscosity, excess molar volume and excess Gibb's free energy of activation for viscous flow for the binary mixed solvents of diethyl ether and hexane at temperatures of 303, 313, 323 and 333K and varying mole fractions of diethyl ether have been reported. The results show spontanuous mixing behaviour between the ester and alkane.The results suggest that among

other contributions strong and specific interactions exist between the molecules of diethyl ether and those of hexane at lower temperatures which weakens at higher temperatures.

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