Study of Molecular Interaction in Binary Mixtures of Poly (Propylene Glycol) Monobutyl Ether(PPGMBE) 1000 with 2-(Methylamino) Ethanol (MAE) and 1-Butanol using Thermodynamic and ^{1}H NMR Spectroscopy

Manisha Gupta,* and Sudir Kumar

***Abstract*---** Polypropylene glycol monobutyl ethers (PPGMBE) were tested extensively as lubricants for automobile engines. The thermodynamic behaviour of poly (propylene glycol) monobutyl ether 1000(PPGMBE) with 2-(methylamino) ethanol (MAE) and 1-butanol have been investigated over the whole composition range at temperature 293.15, 303.15 and 313.15K to probe the interaction in binary mixtures. For the purpose, viscometric excess parameters like deviation in viscosity($\Delta\eta$) and excess Gibb's free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the experimental values. The molecular interactions in binary mixtures have been also investigated through the ^{1}H spectroscopy. The NMR spectral parameters for various protons of PPGMBE, MAE and butanol show the interaction of varying strengths between PPGMBE with MAE and butanol binary mixtures.

***Keywords*---** Chemical Shift, ^{1}H NMR, Molecular Interaction, Viscometry.

I. Introduction

KNOWLEDGE of thermodynamic properties of polymer solutions has been proven to be a very useful tool in evaluating the structural interactions occurring in polymer solutions. Physico-chemical properties of liquid mixtures formed by two or more components associated through hydrogen bonds is important from theoretical and process design aspects [1]-[3]. The formation of hydrogen bond in solutions and its effect on the physical properties of the mixtures have received much attention. Hydrogen bonding and complex formation in liquid mixtures have been extensively studied using thermodynamic technique by many workers [4]–[6]. Earlier studies of our group suggest that various types of interaction prevail in the binary mixtures of polymers and organic solvents [7]-[11].

NMR spectrum is very important to study the interactions and the chemical changes appearing in the mixture. The NMR spectrum of a molecule serves not only "fingerprint" but it usually.

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allows to drive quite detailed conclusion regarding its isomeric structure, the influence of a solvent, formation of inter and intramolecular hydrogen bonds etc.[12]. Poly(propylene glycol) monobutyl ethers (PPGMBE) were tested extensively as lubricants for automobile engines [13]. 2-(Methylamino)ethanol (MAE) is a secondary amine often used in industrial operations. In the MAE molecule, a methyl group substitutes a hydrogen atom of the amino group of a monoethanolamine (MEA, a primary amine). However, the methyl group is supposed to enhance the reaction kinetics as it increases the basicity of the amine without appreciably increasing the hindrance around the nitrogen atom. The viscosity and density data of 2-(Methylamino) ethanol (MAE) are important for development of the proper design of the absorption and stripping operations [14]. Alcohols are widely used solvents with their characteristic protic and self associative nature. Moreover, the refrigerant properties of alcohols and their mixtures with other compounds are related to the hydrogen bonding capability of the alcohols [10].

In this study, we have investigated the interaction between the poly (propylene glycol) monobutyl ether 1000(PPGMBE) with 2-(Methylamino) ethanol (MAE) and 1- butanol at varying concentrations and temperatures using thermodynamic and spectroscopy (^{1}H NMR) techniques. Deviation in viscosity ($\Delta\eta$) and excess Gibb's free energy of activation of viscous flow (ΔG^{*E}) have been calculated from the experimental values. The values of excess parameters were fitted to Redlich – Kister polynomial equation.

II. Experimental

A. Materials

Poly(propylene glycol) monobutyl ethers (PPGBME) 1000, 2-(Methylamino) ethanol (MAE) (98.5%) and 1-butanol (99%) were obtained from Sigma-Aldrich Chemicals Ltd. and no further purification was done.

B. Apparatus and Procedures

Mixtures were prepared by weighing the liquids in specially designed ground glass stoppered weighing bottles,

taking extreme precautions to minimize preferential evaporation. An OHAUS (AR2140) single pan balance having a stated precision of 0.1 mg was used throughout. The maximum possible error in the mole fraction is estimated to be ±0.0001.

C. Viscosity Measurement

The viscosities have been measured using Brookfied LVDV-II+Pro programmable viscometer (Brookfied Engineering Laboratories, Inc., USA). The experimental assembly allows measurement of viscosities in the range of 0.15 cP to 3065 cP (with CPE-40) and 4.6 cP to 92,130 cP (with CPE-52) with an accuracy of ±1.0% of full scale range and repeatability of ±0.2%. Apparatus requires only 0.5 ml of the sample for measurement of viscosity.

D. Density Measurement

The density of each liquid mixture has been measured using a pyknometer. The pyknometer consists of a long tube graduated in 0.01 ml scale, fitted to a specific gravity bottle of capacity 8 ml. A certain mass of the solution is allowed to expand at the desired temperature and the densities were calculated from the fixed mass and the volume at various temperature. An average of four to five measurements was taken for each sample mixtures.

E. Temperature Maintenance

Circulating water bath with programmable temperature controller (TC-502, Brookfield Engineering Laboratories, Inc., USA), having variable pump speeds, has been used for water circulation in water jackets of the apparatuses. The temperature controller covers the temperature measurement range of 20°C to 200°C, with temperature stability of ±0.01°C.

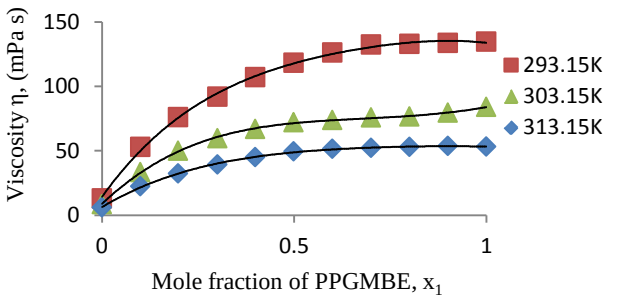
F. ^1H NMR Measurements

^{1}H-NMR spectra were obtained at room temperature (25°C) using Bruker DRX- 400 spectrometer operating at 400 MHz, no other NMR solvent was added. A steam capillary coaxial tube loaded with D_2O was used for the external lock of the NMR magnetic field/frequency and its signal was used as the ^{1}H NMR external reference at 4.70ppm and 4.85ppm.

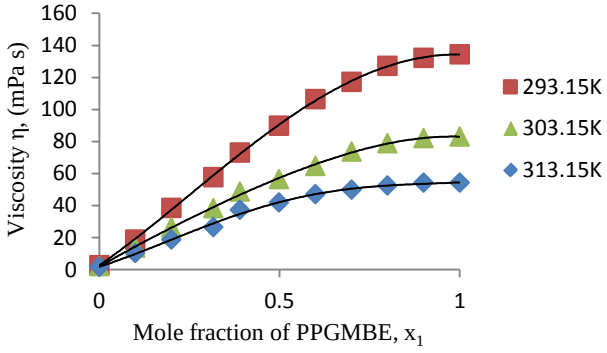
III. Result And Discussion

A. Thermodynamic Studies

Adjustable parameters along with standard deviation calculated using Redlich – Kister polynomial equation for excess parameters are given in tables I and II for both the mixtures. The experimental values of density (ρ_m) and viscosity (η_m) of poly (propylene glycol) monobutyl ether 1000(PPGMBE) with 2-(Methylamino) ethanol (MAE) and 1-Butanol mixtures at temperatures 293.15K, 303.15K and 313.15K are found to vary nonlinearly with the change in concentration. The values increase on increasing the addition of polymer in the mixture. The density values increases sharply at lower concentrations for both the mixtures (Figs 1 and 2).

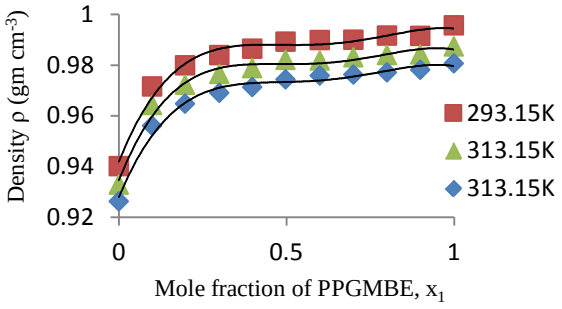


(a)



(b)

Fig. 1 Viscosity (η) versus the mole fraction of PPGMBE1000 (x_1) for binary mixtures (a) PPGMBE1000 + MAE and (b) PPGMBE + 1-butanol at 293.15K, 303.15K and 313.15K.



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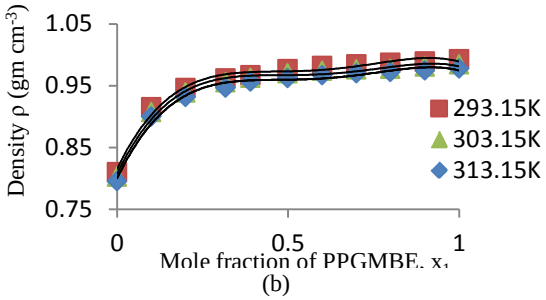


(b)

Fig. 2 Density (ρ) versus the mole fraction of PPGMBE1000 (x_1) for binary mixtures (a) PPGMBE1000 + MAE and (b) PPGMBE + 1-butanol at 293.15K, 303.15K and 313.15K.

In literature, the interaction studies in solutions are most done in terms of excess thermodynamic function. These

functions are found to be sensitive not only towards the intermolecular forces but also on the difference in size and shape of the molecules [15]. The results of variation in viscosity deviations ($\Delta\eta$) of binary systems consisting of PPGMBE1000 with MAE and 1-butanol at temperatures of 303.15K, 308.15K, and 313.15K are presented in fig. 3, which shows positive deviations over the entire range of mole fraction. $\Delta\eta$ values are found to decrease with increasing temperature for both the systems. The viscosity of the mixture strongly depends on the entropy of mixture,

TABLE I

ADJUSTABLE PARAMETERS A_i FOR REDLICH-KISTER POLYNOMIAL EQUATION WITH STANDARD DEVIATION ($\sigma(Y^E)$) FOR DEVIATION IN VISCOSITY ((ΔH) AND EXCESS GIBBS'S FREE ENERGY OF ACTIVATION OF FLOW (ΔG^{*E}) FOR BINARY MIXTURES OF PPGMBE 1000 + 1-BUTANOL AT TEMPERATURE 293.15. 303.15 AND 313.15K

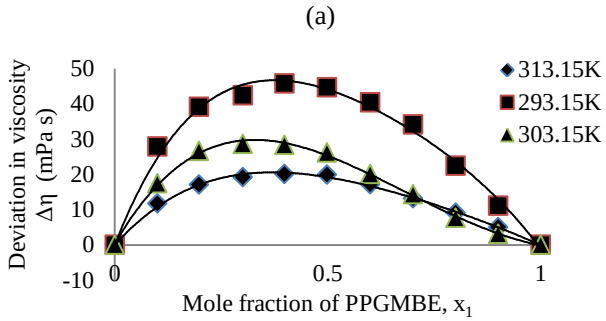
Parameters	Temp(K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
Δη(mPa . s)	293.15	79.3325	-45.2640	68.9286	-18.0657	-112.7048	0.3885
	303.15	53.0774	-22.1574	47.1962	-2.6730	-59.3609	0.4439
	313.15	55.4940	-15.4940	-31.2051	3.7633	27.9934	0.6984
ΔG^{*E} *(kJ mol^{-1})*	293.15	21.6161	19.4456	20.3052	-0.1688	-2.3986	0.0430
	303.15	19.3525	10.5260	13.7794	21.9458	12.9954	0.0677
	313.15	21.9697	18.5753	16.5562	10.1274	3.8374	0.03643

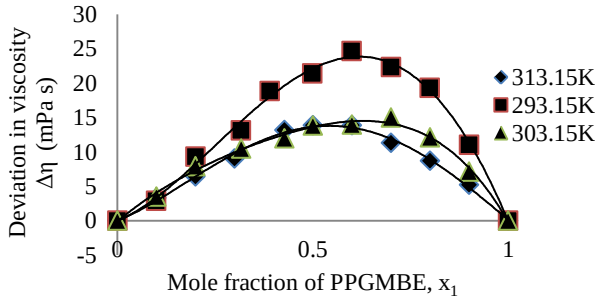
TABLE II

ADJUSTABLE PARAMETERS AI FOR REDLICH-KISTER POLYNOMIAL EQUATION WITH STANDARD DEVIATION ($\sigma(Y^E)$) FOR DEVIATION IN VISCOSITY ((ΔH) AND EXCESS GIBBS'S FREE ENERGY OF ACTIVATION OF FLOW (ΔG*E) FOR BINARY MIXTURES OF PPGMBE 1000 + 1-MAE AT TEMPERATURE 293.15. 303.15 AND 313.15K

Parameters	Temp (K)	a_1	a_2	a_3	a_4	a_5	$\sigma(Y^E)$
Δη(mPa . s)	293.15	118.4596	42.4915	11.2453	114.9665	77.5232	0.8556
	303.15	112.2222	-5.6152	136.7271	164.9991	-209.9957	0.4734
	313.15	79.4516	24.3559	-18.3493	34.3043	76.7605	0.1537
ΔG^{*E} *(kJ mol^{-1})*	293.15	16.5736	7.3478	5.2532	23.1680	20.1478	0.0279
	303.15	16.5695	16.8001	-4.3431	10.3431	34.4671	0.0251
	313.15	17.2974	11.9866	10.3032	16.4588	12.7944	0.0274

Which is related with liquid's structure and enthalpy. Consequently, it depends on molecular interactions between the components of the mixtures. Therefore the viscosity deviation values provide the information about the molecular interaction as well as the size and shape of the molecules. The positive values of Δη for both the systems indicate the presence of specific interaction [16].





(b)

Fig. 3 Deviation in viscosity (Δη)versus the mole fraction of PPGMBE1000 (x1) for binary mixtures (a) PPGMBE1000 + MAE and (b) PPGMBE + 1-butanol at 293.15K, 303.15K and 313.15K.

Fig.4 shows that ΔG*E values are positive for PPGMBE1000 + MAE and PPGMBE + 1-butanol mixtures. The positive values of ΔG*E reflects the presence **of strong** interaction. Singh et al. [17] have also reported similar variations in the ΔG*E values for binary mixtures of butylamine + 1-butanol.

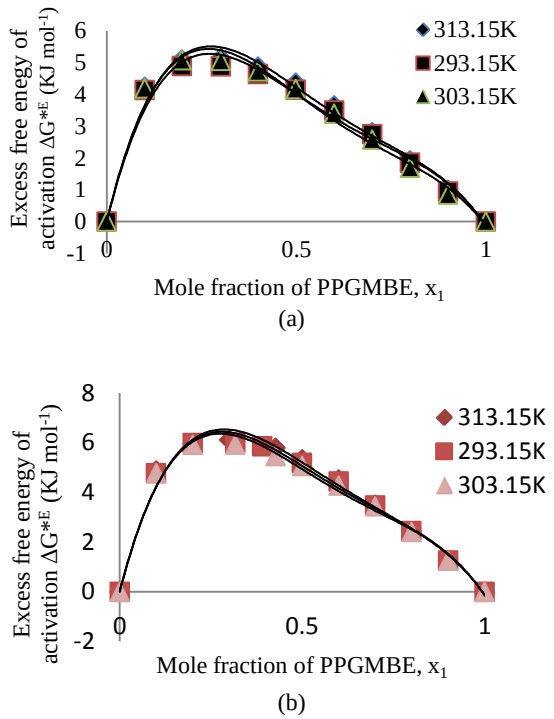


Fig. 4 Excess Gibb's free energy of activation of flow (ΔG*E) versus the mole fraction of PPGMBE1000 (x1) for binary mixtures: (a) PPGMBE 1000 + MAE and (b) PPGMBE 1000+ 1-butanol at 293.15K, 303.15K and 313.15K.

1 H NMR Spectroscopy Study

Interaction can be easily identified by observation of spectral parameters like selective line broadening or chemical shift displacements of 1H-NMR signals, which is a direct molecular probe, has been used to elucidate the change in electronic environment of various protons of PPGMBE + MAE and PPGMBE+1-butanol binary mixtures. Such an investigation will be of great importance, because of the ability of this technique to identify the protons involved in interaction, if any, with more precision and accuracy [18].

The 1H-NMR spectra of binary mixtures have been presented in figs 5 and 6. Fig 5 shows the variation in observed chemical shift for different protons of butanol in the binary mixtures as a function of mole fraction of PPGMBE 1000. An up field shift in δOH, δCH2, and δCH3 has been observed for the system PPGMBE+1-butanol with the increase in PPGMBE concentration. An up field shift is indicative of an increase in electron density around the H nuclei of butanol which is due to (i) breaking the intermolecular hydrogen bonding in butanol (ii) less hydrogen bonding type interactions between the hydroxyl proton of butanol and PPGMBE 1000. Deviations of chemical shift (Δδ) provided important information on relative strengths of chemical interactions between various protons of PPGMBE 1000 and 1-butanol [19]. The Δδ for O-H and CH2 of butanol was found to be negative for all the binary systems investigated over the whole composition range. The position of minima in Δδ, indicates the composition of maximum interaction between components of the binary system for different PPGMBE 1000. Such an upfield shift was also observed by Poppe and Vanhalbeek [20] who pointed out that hydroxy protons involved in hydrogen bonds should be deshielded. Besides temperature coefficients, coupling constants and chemical exchange, it has been shown previously that the chemical shift difference Δδ can also be used as a conformational probe to study hydrogen bond interaction [21]. In agreement with Kumar. et al. [19] this negative Δδ indicates that strong interaction present in binary mixture of PPGMBE+1-butanol.

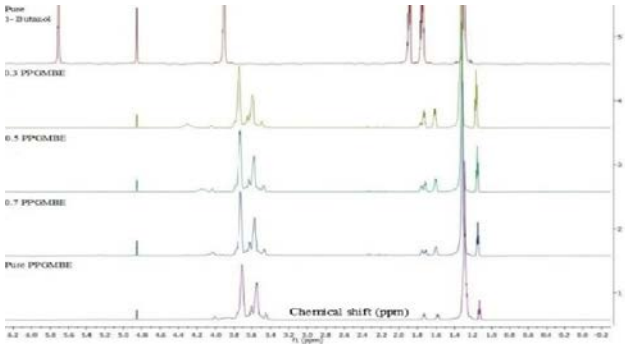


Fig. 5 1D 1H NMR spectra of pure and binary mixture of PPGMBE + 1- butanol at different concentration of PPGMBE1000.

Fig 6 shows the variation in observed spectral parameters for different protons of MAE in the binary mixtures as a function of mole fraction of PPGMBE 1000. No change in chemical shifts but line broadening was observed for the CH3 and CH2 protons in the binary mixture of PPGMBE 1000 + MAE. As the concentration of PPGMBE 1000, increases the line broadening increases and then vanishes. This is due to the fact that the nucleus is rapidly transferred from one magnetization condition to another or disorganizing effect, leading the line broadening. The disorganizing is also reflected on signals multiplicity. This disorganizing effect is due to the interaction between the PPGMBE 1000 and MAE. Therefore, on the basis of actual experimental evidence and literature information about the internal structure of binary mixtures [22]-[25], we can suggest that the addition of pure PPGMBE 1000 to MAE would disrupt their self-associate structure and stabilizes internal structure of mixed solvent and exhibit the existence of strong molecular interactions. This is also supported from the thermodynamic study.

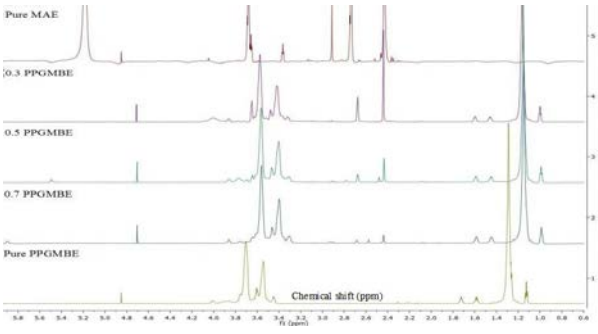


Fig. 6 1D 1H NMR spectrum of pure and binary mixture of PPGMBE 1000 + MAE at different concentration of PPGMBE1000.

IV. Conclusion

It may be concluded that in the present study the observed positive values of excess parameters exhibit the presence of strong molecular association in binary mixtures of PPGMBE with MAE and butanol. 1H NMR spectroscopic techniques provide information about the molecular scale interactions prevailing in these systems. A comparative analysis of thermodynamic and spectroscopic results shows that the strong interaction presents in binary mixture of PPGMBE+1-butanol and PPGMBE + MAE.

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