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Study of the Effect of Molecular Size and Shape in Molecular Interaction of Binary Liquid Mixture Using Viscosity Method

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ABSTRACT

Viscosity is a measure of fluid behaviour. An ideal solution in the usual sense should show no change in volume on mixing. Therefore, expected ideal behaviour, the fluidities should be additive. Viscosity depends on free volume. Change in free volume depends on the type of interaction between the constituents. Generally excess thermodynamic functions have been used as a qualitative or quantitative guide to predict the extent of complex formation in a binary liquid mixture. In present study a series of aliphatic alcohols namely ethanol, n-propanol, n- butanol, n-pentanol, isopropyl alcohol and isoamyl alcohol are chosen as one component of binary mixture. Other components of the binary mixture are either one of these n-heptane, cyclohexane, toluene and xylene. Viscosity studies of these mixtures in a range of 0-100% composition are done. There is always a negative deviation in viscosity. The result indicates that the size and shape play important role in interaction.

KEYWORDS : Viscosity, Ideal solution, Binary mixture, Free volume, Viscosity deviation

INTRODUCTION:

Viscosity is a measure of the resistance of a fluid which is being deformed by either shearing stress or tensile stress. Viscosity describes a fluid's internal friction. A binary liquid mixture is a mixture of two different liquids miscible with each other. A binary mixture of miscible liquids deviates from the ideal behavior of liquids. Discussion of the viscosity behavior of binary liquid solutions commonly starts from the concept of an ideal solution. Binary liquid mixtures of non-electrolytes are least understood system. Generally excess thermodynamic functions have been used as a qualitative and quantitative guide to predict the extent of complex formation in binary liquid mixture of non electrolyte[1]. Viscosity data of the mixture as a function of composition indicate the existence or non-existence of the interaction[2, 3, 4] among them. A number of workers have utilized the direct approach developed by Gruenberg and Nissan[4] and Katti and Chaudri[5] to estimate the strength of interaction in binary mixtures of non-electrolyte from viscosity data.

The project is a study of the molecular interactions in binary liquid mixtures of

- N-heptane with ethanol, propanol, n-butanol, n-pentanol, isopropyl alcohol and isoamyl alcohol
- Toluene with ethanol, propanol, n-butanol, n-pentanol, isopropyl alcohol and isoamyl alcohol.
- Cyclohexane with ethanol, propanol, n-butanol, n-pentanol, isopropyl alcohol and isoamyl alcohol
- Xylene with ethanol, propanol, n-butanol, n-pentanol, isopropyl alcohol and isoamyl alcohol

N-heptane, Toluene, Cyclohexane and Xylene are non-electrolytes. N-heptane is an aliphatic compound, Cyclohexane is a cyclic compound. Toluene and Xylene are aromatic compounds. In set A, N-heptane is a constant component. In set B, Toluene is a constant component. In set C & set D Cyclohexane and Xylene are constant component respectively. For each system, studies have been done over a composition range of 0-100% by weight. The report gives viscosity data of twenty four binary mixtures of four sets A, B, C, &D.

EXPERIMENTAL:

Materials used in the project are all AR grade chemicals. Chemicals are used as received; no further distillation and drying are done. Binary mixtures are prepared by mass. The mass measurements were performed on CA-123 Contech make single pan analytical balance with precision ±0.001gm. The required properties are measured on the same day. Viscosity measurements of all liquids are done at 308K (35°C) in a viscosity temperature bath (constant temperature bath). Viscometer used is Ubbelohde Viscometer. Specific gravity of all the binary liquid mixtures is measured using a specific gravity bottle and CA-123 Contech analytical balance with precision ±0.001gm. The viscometer was calibrated with standards (Distilled water & Ethanol) whose viscosities are reported in the literature. Several semi empirical relations have been proposed to estimate the dynamic viscosities (η) of the binary liquid mixtures in terms of pure component data.

RESULTS:

Viscosity of a liquid can be calculated by the formula [6, 7, 8]

$$\eta = \rho (At - B/t) \ldots\ldots (1)$$

Where, η = viscosity of liquid

ρ = specific gravity or density of liquid

A, B= characteristic constants of the viscometer.

t = efflux time or flow time in seconds.

Efflux time of water and Ethyl alcohol are measured at 308K (35°C). From the literature, viscosity values of both the liquids at 308K (35°C) are taken. Using literature data of viscosity and density, viscometer constants are determined by solving equation (1). Values of viscometer constant are used to calculate experimental viscosity of the mixtures.

On the basis of Arrhenius equation, the relation between the viscosity of binary liquid mixtures and of pure components is given by [6, 7, 8]

$$\eta_{Theo} = X_1\eta_1 + X_2\eta_2 \ldots\ldots\ldots (2)$$

Where, η_{Theo} = theoretical dynamic viscosity of mixture.

X_1 & X_2 = mole fractions of pure components 1 & 2 respectively.

η_1 & η_2 = dynamic viscosities of pure components 1 & 2 respectively.

$$\Delta\eta = \eta_{exp} - \eta_{Theo} \ldots\ldots\ldots\ldots\ldots (3)$$

The experimental values of η (η_{exp}) for various mixtures are calculated from the observed value of efflux time knowing viscometer constant. η_{exp} thus obtained have been used to calculate the values of the viscosity deviations at different mole fraction. Table No.1 gives the name of different chemicals used in this work.

Table No. 1: Chemical Name, Mol.Wt and Density of Materials Used

Sr. No.	Chemical name	Mol. Wt.	Density
1	n-heptane	100	0.684 g/cm^3
2	Toluene	92	0.867 g/cm^3
3	Cyclohexane	84	0.777 g/cm^3
4	Xylene	106	0.787 g/cm^3
5	Ethanol	46	0.789 g/cm^3
6	Propanol	60	0.80 g/cm^3
7	1-Butanol	74	0.81 g/cm^3
8	1-Pentanol	88	0.814 g/cm^3
9	Isopropyl alcohol(2-Propanol)	60	0.786 g/cm^3
10	Isoamyl alcohol(3-methyl-1-butanol)	88	0.810 g/cm^3

Table no. 2:- Viscosity deviation of Binary mixtures of Cyclohexane and different alcohols

Composition	$\Delta\eta$ n-Ethanol	$\Delta\eta$ n-Propanol	$\Delta\eta$ n-Butanol	$\Delta\eta$ n-Pentanol	$\Delta\eta$ 2-Propanol	$\Delta\eta$ Isoamylalcohol
100:0	_____	_____	_____	_____	_____	_____
80:20	-0.1239	-0.3577	-0.4727	-0.2157	-0.4563	-0.6002
60:40	-0.1915	-0.4157	-0.6780	-0.1735	-0.6845	-0.9195
40:60	-0.1703	-0.3101	-0.6038	-0.1965	-0.7201	-0.9446
20:80	-0.0885	-0.1398	-0.3364	-0.1711	-0.5302	-0.4855
0:100	_____	_____	_____	_____	_____	_____

Table no. 3:- Viscosity deviation of Binary mixtures of Xylene and different alcohols

Composition	$\Delta\eta$ n-Ethanol	$\Delta\eta$ n-Propanol	$\Delta\eta$ n-Butanol	$\Delta\eta$ n-Pentanol	$\Delta\eta$ 2-Propanol	$\Delta\eta$ Isoamylalcohol
100:0	_____	_____	_____	_____	_____	_____
80:20	-0.2812	-0.5071	-0.6109	-0.1339	-0.6554	-0.8740
60:40	-0.2950	-0.7078	-0.9229	-0.1734	-0.9423	-1.3709
40:60	-0.2105	-0.6303	-0.9734	-0.1101	-0.9605	-1.5971
20:80	-0.1258	-0.3844	-0.6219	-0.0780	-0.6999	-1.0755
0:100	_____	_____	_____	_____	_____	_____

Table no. 4:- Viscosity deviation of Binary mixtures of n-heptane and different alcohols

Composition	$\Delta\eta$ n-Ethanol	$\Delta\eta$ n-Propanol	$\Delta\eta$ n-Butanol	$\Delta\eta$ n-Pentanol	$\Delta\eta$ 2-Propanol	$\Delta\eta$ Isoamylalcohol
100:0	_____	_____	_____	_____	_____	_____
80:20	-0.4666	-0.7333	-0.7498	-0.2810	-0.7854	-0.9176
60:40	-0.4064	-0.8653	-0.9456	-0.3155	-1.1067	-1.3743
40:60	-0.3900	-0.8064	-0.9768	-0.2072	-1.1507	-0.8348
20:80	-0.2303	-0.6743	-0.5834	-0.2295	-0.9499	-1.0854
0:100	_____	_____	_____	_____	_____	_____

Table no. 5:- Viscosity deviation of Binary mixtures of Toluene and different alcohols

Composition	$\Delta\eta$ n-Ethanol	$\Delta\eta$ n-Propanol	$\Delta\eta$ n-Butanol	$\Delta\eta$ n-Pentanol	$\Delta\eta$ 2-Propanol	$\Delta\eta$ Isoamylalcohol
100:0	_____	_____	_____	_____	_____	_____
80:20	-0.3073	-0.6809	-0.5896	-0.2122	-0.6295	-0.7803
60:40	-0.2957	-0.8371	-0.9197	-0.2066	-0.9904	-1.3002
40:60	-0.2559	-0.8497	-1.5025	-0.2581	-0.9911	-1.5560
20:80	-0.1753	-0.6641	-0.8175	-0.2488	-0.8487	-1.3748
0:100	_____	_____	_____	_____	_____	_____

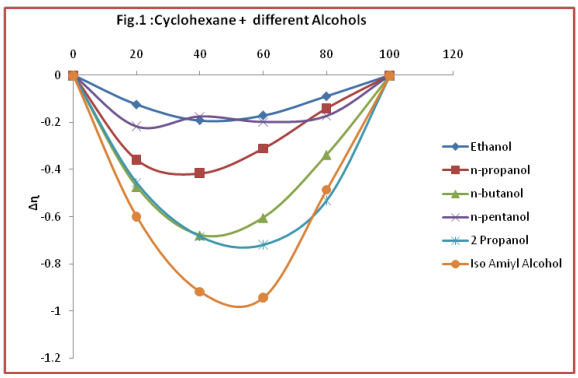
CONCLUSION:

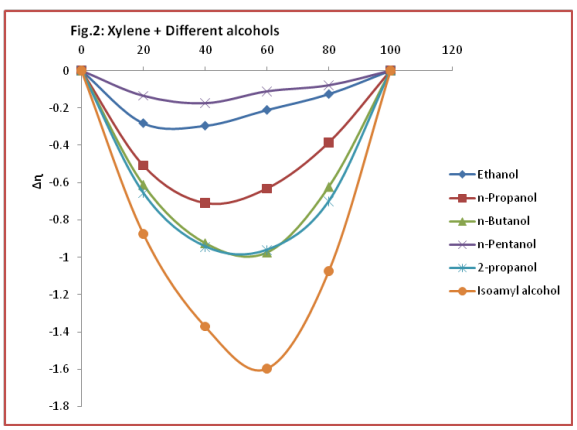
Liquid state of matter has some special properties. Viscosity is reciprocal of fluidity. In gaseous state, the molecules move over considerable distances before colliding with one another whereas in liquid state, the molecules move over an infinitesimally small distance before colliding with one another [1, 6, 7]. This is due to the effect that each molecule in a liquid is tightly surrounded by almost 10-12 neighbors forming sort of spherical cage. It is evident that the centre of caged molecule can move about in a very small volume. This volume for a mole of molecules is known as free volume. The flow of the liquid is due to this free volume. The liquid molecules keep on moving continuously into these vacancies. As a consequence, the vacancies also keep on moving, otherwise liquid will not be able to flow. This process requires energy.

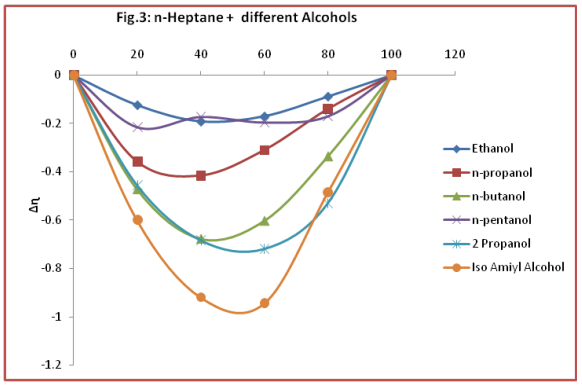
An ideal solution, in the usual sense, shows no volume change on mixing. The assumption that there is no free volume change on mixing leads to the expectation that if the two kinds of molecule are similar in size and shape, as they must be, they are to form an ideal solution. The fluidities should be additive. It is true that free volume is necessary for flow, shrinkage on mixing cause a reduction in free volume and therefore should be associated with an increase in viscosity and a positive viscosity deviation ($\Delta\eta$). On the other hand, increase in density on mixing indicates a decrease in free volume and this should be associated with an increase in viscosity and a negative viscosity deviation ($\Delta\eta$).

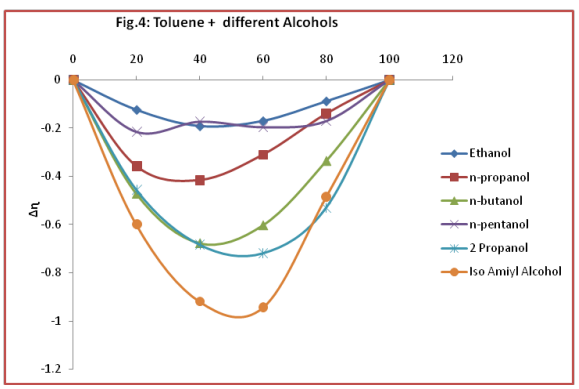
In present set of studies, all the viscosity data indicate a decrease in viscosity value on mixing. Fig. 1-4 gives variation of viscosity ($\Delta\eta$) with respect to composition. For all 24 systems studied data indicate effect of number of carbon atom on $\Delta\eta$ values. As chemicals, we used, are not further distilled and purified; parameters such as enthalpy, entropy and free energy are not calculated. There is always a decrease in viscosity on mixing. Deviation from ideal behavior increase as ethanol is replaced by propanol and butanol but a reversal occurs with n-pentanol. In a liquid system introduction of another liquid molecule cause an increase in free volume hence decrease in viscosity. Data indicate deviations in viscosity ($\Delta\eta$) depends on the number of carbon atoms present in the alcohols and the size of the molecules present in alcohols. With increase in size of alcohol molecule there is increase in free volume of system hence decrease in viscosity. Reversal in $\Delta\eta$ with n-pentanol may be due to comparable size of n-pentanol and the other component of binary mixture. Figures also show deviation of viscosity with respect to composition keeping number of carbon atom same example (n-propanol and 2- propanol) and (n-pentanol and iso amyl alcohol). Data indicate in all the four sets isoamyl alcohol show greater deviation in viscosity in comparison to straight chain n-pentanol whereas n-propanol and 2-propanol viscosity deviation data are well comparable. As n-propanol and 2-propanol are comparable in size and shape, $\Delta\eta$ of binary mixture containing these liquids are also comparable. Data indicate that there are large difference in $\Delta\eta$ value of binary mixture of n pentanol and

that of isoamyl alcohol. Both n-pentanol and isoamyl alcohol cantains same number of carbon atom. Branching in isoamyl alcohol may be causing some difference in packing hence increase in free volume and deviation from ideal behavior.









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