

Chapter 4

VOLUMETRIC AND VISCOMETRIC STUDIES



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VOLUMETRIC AND VISCOMETRIC STUDIES

4.1. INTRODUCTION

Viscometric measurements often yield valuable information regarding the molecular interactions in pure liquids as well as in liquid mixtures. A familiar approach is the hypothesis that there is a direct correlation between the viscosity and the thermodynamic behaviour of the solution. Very often it is essential to know the viscosity of the liquid mixtures to solve some practical problems regarding their heat content, mass transport, fluid flow, molecular structure etc. Many scientists^{1,2} worked on the transport properties of the liquid mixtures by measuring their viscosities.

Licer and Kosanovic³ have discussed the shapes of plots of viscosity against mole fraction for binary liquid mixtures in terms of complex formation between the component molecules. Plots of the type, where the viscosity varied linearly are said to be characteristic of systems in which complexes are not formed, or in which complexes of low stability occur. However, the plots of the type which varied non-linearly are considered to be characteristic of systems in which complexes are formed. According to Licer and Kosanovic³, S-shaped curves of the type suggested by the chloroform + acetone and o-tetrachloroethane + acetone systems are indicative of complex formation and viscosity of the complex may be greater than that of the more viscous component and the maxima noticed curves are said to indicate the formation of stable complexes.

A few studies indicating the variation of viscosities of the binary liquid mixtures with the mole fraction of the component, depends on the type and degree of interactions between the unlike molecules. Positive deviations with the maxima from a rectilinear dependence^{3,4} may occur if strong specific interactions are present between unlike molecules which are responsible for complex formation. Negative deviations occur where dispersion forces are primarily responsible for interactions between the component molecules.

The study of excess thermodynamic functions such as excess viscosity (η^E), excess molar volume (V^E), excess Gibbs free energy of activation of viscous flow (G^{*E})

and Grunberg-Nissan interaction parameter (d^1) of binary liquid mixtures are useful in understanding the nature of intermolecular interactions between the components present in the liquid mixtures.⁵⁻⁸

Some expressions relating to the viscosity of binary liquid mixtures and of the pure components are considered. The excess functions are calculated using the equations (4.1 and 4.2)

$$\eta^E = \eta - (X_1\eta_1 + X_2\eta_2) \quad \dots \quad 4.1$$

$$V^E = V - (X_1V_1 + X_2V_2) \quad \dots \quad 4.2$$

η , η_1 and η_2 are viscosities of the liquid mixture and of the pure components 1 and 2 respectively. V , V_1 and V_2 are molar volumes of the liquid mixture and of the pure components 1 and 2 respectively. X_1 and X_2 are the mole fractions of the pure components 1 and 2 in the liquid mixture. The molar volume of the liquid mixture is calculated by the equation (4.3)

$$V = \frac{X_1M_1 + X_2M_2}{\rho} \quad \dots \quad 4.3$$

where, M_1 and M_2 are the molecular weights of the components 1 and 2; ρ is the density of the mixture. Grunberg and Nissan⁹ formulated equation 4.4 to assess the molecular interactions leading to viscosity changes.

$$\ln \eta = X_1 \ln \eta_1 + X_2 \ln \eta_2 + X_1 X_2 d^1 \quad \dots \quad 4.4$$

d^1 is a constant proportional to W/RT , where W is the interchange energy, R is the gas constant and T is the absolute temperature. This proportionality constant relating d^1 and W requires knowledge of vapor pressure,¹⁰ which are not generally available. Although the molecules of the two components of a regular solution are interchangeable as far as size and shape are concerned, there may be a change in the lattice energy when a molecule of a component 1 is introduced into the lattice of the component 2. The interaction parameter d^1 is a useful parameter, considered as a measure of strength of interactions between the component molecules of the mixture and is also considered as the stability of the complex formed between the components. If d^1 is positive, the interactions between the components in the liquid mixture are strong and if it is negative

the molecular interactions are weak. Katti and Chaudhri¹¹ developed a similar equation (4.5), involving viscosity as well as molar volume for non-ideal solutions.

$$\ln \eta V = X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2 + X_1 X_2 W_{\text{vis}}/RT \quad \dots \quad 4.5$$

where X_1 and X_2 are the mole fractions of the components 1 and 2, and W_{vis} is an empirical parameter, $X_1 X_2 W_{\text{vis}}$ represents another function of G^{*E} called “excess Gibbs free energy of activation of viscous flow” (Eq. 4.6).

$$G^{*E} = RT [\ln \eta V - (X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2)] \quad \dots \quad 4.6$$

Reed and Taylor¹² and Meyer *et al.*¹³ reported that G^{*E} can be considered as reliable criteria to detect or exclude the presence of interactions between unlike molecules in the liquid mixtures. According to these authors, the magnitude of the positive values of G^{*E} is an excellent indicator of the presence of the specific interactions and if the values of G^{*E} are negative, it indicates the presence of weak interactions between the components of the liquid mixtures.

The dependence of η^E , V^E and G^{*E} on the mole fraction of 2-(2-Methoxy ethoxy) ethanol (MC) (X_{MC}) for all the binary liquid mixtures were fitted to the following Redlich-Kister equation by the least-squares method.

$$Y^E = x(1-x) \sum_{i=1}^4 A_i (2x-1)^i \quad \dots \quad 4.7$$

Where Y^E is η^E , V^E and G^{*E} parameters.

From the variations of η , η^E , V^E , G^{*E} and d^1 values with the composition of the liquid mixtures, the molecular interactions present in the liquid mixtures under study are discussed in the following sections of this chapter.

4.2: VOLUMETRIC AND VISCOMETRIC STUDIES OF BINARY LIQUID MIXTURES OF METHYL CARBITOL (EC) WITH AMINES AT 308.15 K.

ABSTRACT

Densities and viscosities of binary liquid mixtures of 2-(2-Methoxy ethoxy) ethanolMethyl carbitol (MC) with n-butyl amine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), n-octylamine (NOA) and cyclohexylamine (CHA) have been measured at 308.15 K. From the experimental data the excess volume (V^E), excess viscosity (η^E) and the excess molar Gibbs free energy of the activation of viscous flow (G^{*E}) have been computed and presented as function of composition. The interaction parameter d^1 of the Grunberg and Nissan has been calculated. The observed variations of the properties for the above mixtures conclude that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive (η^E), (G^{*E}) and d^1 values. The excess volume, excess Viscosity and excess molar Gibb's free energy of the activation of viscous flow have been fitted to Redlich –Kister equation to derive the coefficients and standard deviations.

4.2.1: INTRODUCTION

The formation of hydrogen bond in solutions and its effect on the physical properties of the mixtures have received much attention. Hydrogen bonding plays an important role in fundamental sciences and in industrial applications. Although many experimental and theoretical studies have been directed towards understanding of hydrogen bonding, it remains an area of active research. Knowledge of physico – chemical properties of liquid mixtures formed by two or more components associated through hydrogen bonds is important from theoretical and process design aspects.

Properties such as densities, viscosities and the excess properties and their variation with composition of the binary mixtures are useful to design engineering processes and in chemical and biological industries. The investigation on the possible

changes in these properties of mixtures has been found to be an excellent qualitative and quantitative way to elicit the information about molecular structure and intermolecular forces present in the liquid mixtures.

In comparison of similar studies of binary liquid mixtures¹⁴⁻¹⁸, the author presents here some new experimental data on the density ρ , and viscosity η , for the binary liquid mixture system of 2- (2-Methoxy ethoxy) ethanol (MC) with different amines (n-butyl amine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), n-octylamine (NOA) and cyclohexylamine (CHA) at 308.15 K.

These systems are particularly chosen in view of their importance in chemical engineering design and polymer processing industries. Moreover; such data for these systems are not available in the literature.

In the present study, 2- (2-Methoxyethoxy)ethanol(MC) is chosen because it finds a wide range of applications, namely, as a solvent, a solublizing agent in many industries¹⁹ and has unique solvating properties associated with its quasi-aprotic character²⁰. MC, ether alcohol, shows physico-chemical characteristics mid way between protic and aprotic dipolar solvents. As it is a quite-toxic solvent²¹, it must be handled with care. 2-(2-Methoxyethoxy) ethanol (MC) is amphiprotic, apotentially acidic medium with a low auto protolysis constant ($Pk_{\text{autoprot}} = 20.5$ at 20°C)²² and low dielectric constant ($\epsilon = 16.94$ at 25°C). It is therefore, hardly dissociating solvent²³⁻²⁷ either for ionogen or inophore solutes. Because of its dipolar character ($\mu=2.3\text{D}$)²⁸ 2-(2-Methoxy ethoxy)ethanol (MC) shows a tendency to Polymerize and form a hydrogen-bonded network.

The molecular interaction studies of 2-(2-Methoxyethoxy) ethanol (MC) are of interest because of investigating the effect of simultaneous presence of ethereal and alcoholic oxygen atoms in the same molecule. The presence of etheric oxygen enhances the ability of the-OH group of the same molecule to form hydrogen bonds with other organic molecules²⁹⁻³².

On the other hand the other components chosen are amines. It is popularly believed that alcohols and amines in dilute aqueous solutions behave as soluble hydrocarbons and it has been said that the functional group provides only a minor

n-octylamine (NOA).

2. Branched amines: sec-butylamine (SBA) and tert-butylamine (TBA).

3. Cyclic amines: cyclohexylamine (CHA)

Which are known as industrially important liquids of special interest in the recent years. In chemical industry there exists a continuing need for reliable thermodynamic data of binary systems. A survey of the literature shows that very few attempts⁴²⁻⁴⁴ have been made to study the excess properties for mixtures containing alkoxyalcohols (carbitols). Amines and alkoxy alcohols⁴⁵⁻⁴⁶ in their pure state exhibit self-association through hydrogen bonding. Amines are proton acceptors, which allow them to have specific interactions. Further, amines form water insoluble compounds of medicinal importance. The molecular interaction study of alkoxy alcohols (carbitols) is of interest because of investigating the effect of simultaneous presence of ether and alcoholic functional groups in the same molecule. The presence of ethereal oxygen enhances the ability of the –OH group of the same molecule to form hydrogen bonds with other organic molecules.^{29,31,47} These characteristics of amines and alkoxy alcohols (carbitols) make them interesting for our study and the results are presented here.

4.2.2: MATERIALS & METHODS

The details of the materials and their purification methods along with the experimental methods of determination of density, viscosity etc. are explained in chapter -3 (Materials and experimental methods) of this thesis.

The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 3.1) and formed good agreement in general.

4.2.3: RESULTS & DISCUSSIONS:

The experimental results of the measurement of densities (ρ) and Viscosities (η) of binary liquid mixtures are presented in Table 4.2.1.to 4.2.6. The molar volume (V), excess volume (V^E), excess viscosity (η^E), excess Gibbs free energy of activation of

viscous flow (G^{*E}), and Grunberg–Nissan interaction parameter $(d^1)^{9-10}$ were calculated from the measured data using the equations 4.1 to 4.6 as explained in section 4.1 and in Tables 4.2.1 to 4.2.6. The Redlich- Kister equation parameters A_i , obtained by a non-linear least square polynomial fitting procedure as calculated by using equation 4.7 are also given in Table 4.2.7 together with standard deviation (σ) values.

The variation of the parameters η , v^E , η^E and G^{*E} with mole fraction of 2-(2-Methoxy ethoxy) ethanol (X_{MC}) for the systems under study are shown graphically in Figs: 4.2.1 to 4.2.4 respectively.

From Tables: 4.2.1 to 4.2.6 and Fig: 4.2.1 it is observed that the viscosity of binary liquid mixtures under study varied non-linearly with the mole fraction of 2-(2-Methoxyethoxy) ethanol (X_{MC}). This suggests the presence of intermolecular interactions between unlike molecules of these mixtures. A similar observation was made by Narayana Swamy et al.¹⁴ from the viscosity studies of binary liquid mixtures of MC + amines.

It is clear from the Fig. 4.2.2 that the negative V^E values are obtained over the entire composition range for all these systems except MC+NOA and MC+CHA which indicates the presence of strong molecular interactions between the unlike components of the mixtures. It is also observed from Fig. 4.2.2 and Table: 4.2.1 to 4.2.6 that the V^E values fall in the sequence.

MC + NOA > MC + NHA > MC + CHA > MC + TBA > MC + SBA > MC + NBA.

From Fig.: 4.2.2, it is further observed that the negative/ Positive V^E Vs X_{MC} plots were found to be large and symmetrical showing a maximum between 0.7 to 0.8 mole fractions of MC (X_{MC})

According to Subha, et. al.¹⁵ several effects may contribute to the sign and values of V^E and the following three effects may be considered as being important.

1. Break up of hydrogen bonds and dipolar interactions in MC and intermolecular Interactions in amines.
2. The possible intermolecular interactions like hydrogen bonding or electron donor - acceptor interactions between unlike molecules.
3. Interstitial accommodation of one component molecules into the other unlike

component molecules due to their differences in size and shape.

The overall signs of these excess functions depend on the combined effects of these three effects. From the Fig.4.2.2 it is noticed that in the case of MC +NOA and MC + NHA positive V^E values are observed. An interpretation to this behavior can be given using the experience made with the quantitative evaluation of alcohol + amine mixtures by the ERAS model proposed by the earlier workers⁴⁸⁻⁵². The first effect leads to positive excess volume and the latter two effects leads to negative excess volume. The actual volume change would depend upon the relative strengths of these three effects. In the present study the observed negative values of V^E show that the main contribution to V^E is due to hydrogen bond formation between hydroxyl & ethereal groups of BC and amino group of amines groups of unlike molecules and the difference in size of the unlike molecules. Moreover, the negative values of V^E may also be partly due to the specific acid-base interactions between MC and amine molecules by considering MC as Lewis acid and amines as Lewis bases.

Very recently Nam-Tram⁵³ emphasized the importance of acid-base interactions between tert-butyl alcohol and N,N dimethyl formamide / N,N- dimethyl acetamide order to evaluate the interaction energy of alcohol-amine systems. From the examination of the results in Tables: 4.2.1 to 4.2.6 and Fig.:4.2.2, it is observed V^E fall in the sequence:

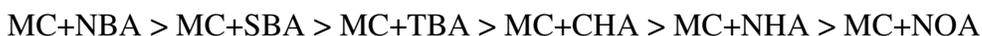
$MC+NOA > MC+NHA > MC+CHA > MC+TBA > MC+SBA > MC+NBA$.

From the Fig .4.2.2, it is also observed that the negative excess volumes of normal amines with MC increase with increase in chain length of amines, this can be explained by considering amines as proton acceptors and MC as proton donar. As the chain length of normal amines increases proton accepting ability of these amines increase and electron density will be more and more on nitrogen atom of NH_2 group due to inductive effect. So, as the chain length of the amines increase, the interaction ability (hydrogen bonding ability) of amines increase with increase in BC component. In the case of branched amines, negative V^E values increase with increase in branching. This is very clear that as the amines become more and more branched, the proton accepting ability increases due to the increase in $-CH_3$ groups on the carbon atom attached to amine group. However, the

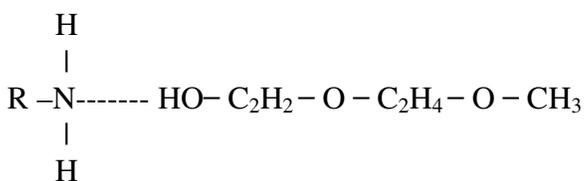
slight positive V^E values are observed at higher MC mole fraction (X_{MC}) in case of NOA & CHA indicating lesser specific interactions at these mole fractions. A similar observation was made by Haraschita, et.al.⁵⁴ from the V^E studies of γ - Picoline + sec-butanol and + tert- butanol.

In the case of cyclohexylamine, V^E values are less positive than the corresponding normal hexyl amine, which may be due to steric and other effects because of cyclic nature of cyclohexylamine.

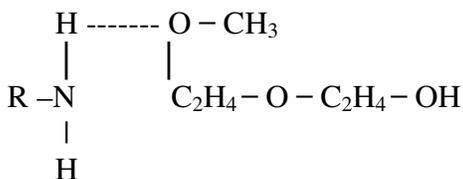
From Fig. 4.2.3, it is noticed that of η^E values are positive over the whole composition range for all the systems under study. A correlation between the signs of η^E and V^E has been observed for a number of binary systems⁵⁵⁻⁵⁶ where η^E being Positive and V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating η^E values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules thereby resulting in positive η^E values. The positive values of η^E for the mixtures of MC + amines fall in the order.



It can be predicted that in view of the strong proton donating ability of MC and strong proton accepting ability of amines, the overall negative V^E values and overall positive η^E values in all these systems may be regarded as an evidence for the formation of two sets of hydrogen bonds between MC and amines. Among them the first set of hydrogen bond formation is between N atom of amino group of amine and H atom of –OH group of 2-(2-Methoxy ethoxy) ethanol



(MC) and second set of hydrogen bond formation is between H atom of amino group of amines and oxygen atom of etheric group of 2-(2-Methoxy ethoxy) ethanol (MC). Among the two the first set of hydrogen bond formation predominates.



From the Tables 4.2.1 to 4. 2.6 & Fig 4.2.4, it is also observed that the values of G^{*E} are found to be positive which is an indication of the presence of strong specific interactions between the unlike molecules and are in the following order



Fort and Moore⁵⁷ and Ramana moorthy⁵⁸ reported that for any binary liquid mixture, the positive value of d^1 indicates the presence of strong interactions and the negative value of d^1 indicates the presence of weak interactions between the components. On this basis the d^1 values in the present study for all the systems confirm the presence of strong interactions between the component molecules. A similar observation was made by Subha et al.¹⁶ from the d^1 values of the binary liquid mixtures of propionic acid with alcohols.

CONCLUSIONS

The present study reports the volumetric and viscometric properties of 2-(2-Methoxy ethoxy) ethanol (MC) with n- butyl amine, sec- butyl amine, tert- butyl amine, n-hexyl amine, n – Octyl amine and cyclo hexyl amine over the entire composition range at 305.15 K. From the results, it is observed that the variation of the properties of the mixtures studied supports the view that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive η^E , G^{*E} and d^1 values.

4.3: VOLUMETRIC AND VISCOMETRIC STUDIES OF BINARY LIQUID MIXTURES OF ETHYL CARBITOL (EC) WITH AMINES AT 308.15 K.

ABSTRACT

Densities and viscosities of binary liquid mixtures of 2 - (2-Ethoxy ethoxy) ethanol (EC) with n-butyl amine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), n-octylamine (NOA) and cyclohexylamine (CHA) have been measured at 308.15 K. From the experimental data the excess volume (V^E), excess viscosity (η^E) and the excess molar Gibbs free energy of the activation of viscous flow (G^{*E}) have been computed and presented as function of composition. The interaction parameter d^1 of the Grunberg and Nissan has been calculated. The observed variations of the properties for the above mixtures conclude that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive (η^E), (G^{*E}) and d^1 values. The excess volume, excess Viscosity and excess molar Gibb's free energy of the activation of viscous flow have been fitted to Redlich – Kister equation to derive the coefficients and standard deviations.

4.3.1: INTRODUCTION

Binary liquid mixtures due to their unusual behavior have attracted considerable attention⁵⁹ in recent years. In chemical process industries materials are normally handled in fluid form and as a consequence, the physical, chemical and transport properties of fluids assume importance. Thus the data on some of the properties associated with the liquids and liquid mixtures like density and viscosity find extensive application in solution theory and molecular dynamics⁶⁰. Such results are necessary for interpretation of data obtained from thermo chemical, electrochemical and kinetic studies.^{61, 62}

Alkoxy ethanols are very interesting classes of substance from a practical point of view, as oxygenated compounds are increasingly used as additives to gasoline due to their octane enhance and pollution- reducing properties.^{63, 64} In addition, hydroxyl ethers

are non-toxic amphiphilic molecules. Very effective as surfactants with a large number of applications.^{65,66} On the other hand, the investigation of mixtures involving alkoxy ethanols make possible the study of self-association via inter and intra molecular hydrogen bonds related to the presence of the ether and OH groups in the same molecule. So, different spectroscopic techniques have been used to investigate the existence of intra molecular hydrogen bonds in these compounds⁶⁷⁻⁶⁹. They are present at all conditions, even in vapour phase, whereas intermolecular H-bonds appear at higher concentrations of the cellosolve in liquid state. In solutions formed by alkoxy ethanols and alkanes, the formation of the intra molecular H-bonds leads to enhanced dipole-dipole interactions in comparison to those present in mixtures with homomorphic alkanols⁷⁰.

In the literature of liquid-state chemistry, binary mixtures containing 2-(2-Ethoxy ethoxy) Ethanol have attracted considerable interest in view of the widely varying type of molecular interactions with liquids. The study of molecular interactions in 2-(2-Ethoxy ethoxy) Ethanol with amines is of interest in its own right and because they serve as simple block elements of biologically and industrially important amphiphilic materials.⁷¹

A literature survey revealed that the thermodynamic properties of binary mixtures containing alkoxy alcohols (Carbitols) are very few.⁴²⁻⁴⁴ Amines and alkoxy alcohols⁴⁵⁻⁴⁶ in their pure state exhibit self-association through hydrogen bonding. Amines are better electron donors, which allow them to have specific interactions. Further, amines form water insoluble compounds of medicinal importance. The molecular interaction study of alkoxy alcohols (carbitols) is of interest because of investigating the effect of simultaneous presence of ether and alcoholic functional groups in the same molecule. The presence of ether oxygen enhances the ability of the -OH group of the same molecule to form hydrogen bonds with other organic molecules.^{29,31} These characteristics of amines and alkoxy alcohols (carbitols) make them interesting for our study. In continuation of our physico-chemical property studies of binary liquid mixtures^{13,17,18,47,72} and survey of the literature it is noticed that no attempts have been made to study excess volumes and viscosity of binary liquid mixtures of 2-(2-Ethoxyethoxy) ethanol (Ethyl carbitol) with a series of amines which include n-butyl

amine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), N-octylamine (NOA), and cyclohexylamine (CHA) at 308.15 K aiming for a wider understanding of the intermolecular interactions involved and the results are presented here.

4.3.2: MATERIALS & EXPERIMENTAL METHODS:

The details of the materials and their purification methods along with the experimental methods of determination of density, viscosity etc. are explained in chapter -3 (Materials and experimental methods) of this thesis.

The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 3.1) and formed good agreement in general.

4.3.3: RESULTS & DISCUSSIONS

The experimental results of the measurement of densities (ρ) and Viscosities (η) of binary liquid mixtures are presented in Table 4.3.1.to 4.3.6. The molar volume (V), excess volume (V^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscous flow (G^{*E}), and Grunberg–Nissan interaction parameter (d^1)⁹⁻¹⁰ were calculated from the measured data using the equations 4.1to 4.6 as explained in section 4.1 section and presented in Tables 4.3.1 to 4.3.6.

The dependence of n^E , V^E and G^{*E} on the mole fraction of 2-(2-Ethoxy ethoxy) ethanol (EC) for all the six systems were fitted to the Redlich – Kister equation as represented in equation 4.7 as explained in 4.1 section by the least square method and the values are given in Table 4.3.7.

The Redlich-kister equation parameters A_i , obtained by a non-linear least squares polynomial fitting procedure as calculated by using the equation 4.1 are also given in Table:4.3.7, together with the standard deviation (σ) values.

The variation of the parameters η , V^E , η^E and G^{*E} with mole fraction of 2-(2-Ethoxy ethoxy) ethanol (X_{EC}) for the systems under study are shown graphically in Fig. 4.3.1 to 4.3.4 respectively.

From Tables: 4.3.1 to 4.3.6 and Fig. 4.3.1 it is observed that the viscosity of binary liquid mixtures under study varied non-linearly with the mole fraction of 2-(2-Ethoxy ethoxy) ethanol (X_{EC}). This suggests the presence of intermolecular interactions between unlike molecules of these mixtures. A similar observation was made by Narayana Swamy et al.¹⁴ from the viscosity studies of binary liquid mixtures of EC + amines

According to Subha, et al.¹⁶ the sign of excess molar volume is influenced by the relative magnitude of contractive and expansive effects which arise on mixing of liquid components. The factors that are responsible for contraction in volume on mixing are

- (i). Strong physical interaction, frequently a kind of chemical interaction.
- (ii) Strong physical interaction such as dipole – dipole (or) dipole – induced dipole or ion pair interaction
- (iii) favorable zoometric fitting of component molecules.
- (iv) Occupation of void spaces of one component by the other which may be due to difference in molecular size of the components in large magnitude.

However, the factors that lead to expansion of volume on mixing of the components are

- (i) Dissociation of one component (or) all the components.
- (ii) Steric hindrance due to branching of chains.
- (iii) Formation of weaker solute- solvent bond than solute- solute and solvent – solvent interaction between the molecules.

The values of excess molar volume for amines with EC are negative in the entire range of composition indicating negative deviations from ideal behavior. It approaches the minimum values in Amines + EC systems at mole fraction of EC at about $X_I \approx 0.5010$ as seen in Fig 4.3.2. This behavior can be expressed in terms of hydrogen bonding that is certainly leading to negative V^E values is observed in the present studies. The overall

negative V^E values noticed in the present study can be explained as follows. For these two components under studies, it has favorable interactions, such as strong hydrogen bonds between the hydroxyl groups of EC and the amino group of amines acting as a hydrogen acceptor. On this basis a volume contraction should be expected on mixing EC & Amines when favorable interactions between groups occur and as consequence, the effects should lead to negative V^E value. Another effect which is expected to act on the V^E property, and which should give a negative contribution to the excess volume is the difference in the molecular size (geometrical effect) between the components in the mixture. In this case the unlike molecules have big difference in the molecular volumes (EC=137.6, NBA=102, SBA =103, TBA= 107, NHA= 134, NOA= 167, CHA= 116 at 25 ° C. Therefore this effect should lead to negative deviation in V^E values. However, the difference in the free volumes between different species could facilitate the penetration of one component into the other and the difference of the free volumes of the two pure species increases, the more negative should be the contribution to V^E .

The overall sign of these excess functions depends on the combined effects of the above three effects, under these circumstances from Fig. 4.3.2, it is noticed that V^E is negative over the whole range of composition except for NOA. From the Fig 4.3.2 it is noticed that in the case of EC + NOA positive V^E values are observed only at higher mole fractions of EC. An interpretation to this behavior can be given using the experience made with the quantitative evaluation of alcohol + amine mixtures by the ERAS model proposed by the earlier workers⁴⁸⁻⁵². The first effect leads to positive excess volume and the latter two effects leads to negative excess volume. The actual volume change would depend upon the relative strengths of these three effects. In the present studies the observed negative values of V^E show that the main contribution to V^E is due to hydrogen bond formation between – OH and – NH₂ groups of unlike molecules and the difference in size of the unlike molecules. Moreover, the negative values of V^E may also be partly due to the specific acid-base interactions between EC and amine molecules by considering EC as Lewis acid and amines as Lewis bases.

Very recently Nam-Tram⁵³ emphasized the importance of acid-base interactions between tert-butyl alcohol and N, N dimethylformamide / N,N- dimethyl acetamide in

order to evaluate the interaction energy of alcohol-amine systems. From the examination of the results in Tables 4.3.1 to 4.3.6 and Fig 4.3.2 it is observed that the magnitude values of V^E fall in the sequence:



From the Fig. 4.3.2, it is also observed that the negative excess volumes of normal amines with EC increase with increase in chain length of amines. This can be explained by considering amines as proton acceptors and EC as proton donor. As the chain length of normal amines increases proton accepting ability of these amines increases and electron density will be more and more on nitrogen atom of NH_2 group due to inductive effect. So, as the chain length of the amines increase, the interaction ability (hydrogen bonding ability) of amines also increases with increase in EC component. In the case of branched amines, negative V^E values increase with increase in branching. This is very clear that as the amines become more and more branched, the proton accepting ability increases due to the increase in $-CH_3$ groups on the carbon atom attached to amine group. However, the slight positive V^E values are observed at higher BC mole fraction in case of NOA & CHA indicating lesser specific interactions at these mole fractions. A similar observation was made by Haraschita, et.al.⁵⁴ from the V^E studies of γ -Picoline + sec-butanol and + tert-butanol.

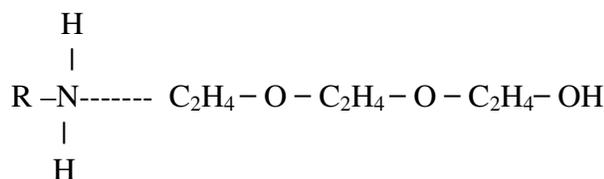
In the case of cyclohexylamine, V^E values are less positive than the corresponding normal hexyl amine, which may be due to steric and other effects because of cyclic nature of cyclohexylamine.

From Figure: 4.3.3, it is noticed that η^E values are positive over the whole composition range for all the systems except NOA under study. A correlation between the signs of η^E and V^E has been observed for a number of binary systems^{55, 56} where η^E being positive and V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating η^E values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to the

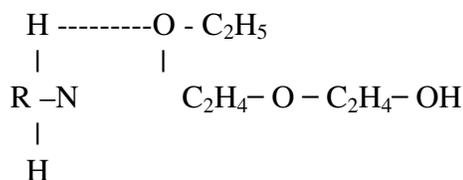
formation of complex species between unlike molecules thereby resulting in positive η^E values. The positive values of η^E for the mixtures of EC + amines fall in the order.



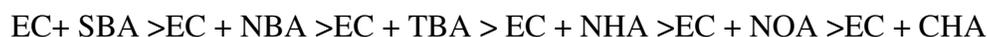
It can be predicted that in view of the strong proton donating ability of BC and strong proton accepting ability of amines, the overall negative V^E values and overall positive η^E values in all these systems may be regarded as an evidence for the formation of two sets of hydrogen bonds between BC and amines. Among them the first set of hydrogen bond formation is between N atom of amino group of amine and H atom of -OH group of 2-(2-Ethoxy ethoxy) ethanol



and second set of hydrogen bond formation is between H atom of amino group of amines and oxygen atom of etheric group of 2-(2-Ethoxy ethoxy) ethanol (EC). Among the two the first set of hydrogen bond formation predominates.



From the Tables. 4.3.2 to 4.3.6 & Fig .4.3.4, it is also observed that the values of G^{*E} are found to be positive which is an indication of the presence of strong specific interactions between the unlike molecules and are in the following order



Fort and Moore⁵⁷ and Ramana moorthy^{58, 73} reported that for any binary liquid mixture, the positive value of d^1 indicates the presence of strong interactions and the

negative value of d^1 indicates the presence of weak interactions between the components. On this basis the d^1 values in the present study for all the systems confirm the presence of strong interactions between the component molecules. A similar observation was made by Subha et.al.¹⁶ from the d^1 values of the binary liquid mixtures of propionic acid with alcohols.

CONCLUSION

The present study reports the volumetric and viscometric properties of 2-(2-Ethoxy ethoxy) ethanol (EC) with n- butyl amine, sec- butyl amine, tert- butyl amine, n- hexyl amine, n – octyl amine and cyclo hexyl amine over the entire composition range at 305.15 K. From the results, it is observed that the variation of the properties of the mixtures studied supports the view that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive η^E , G^{*E} and d^1 values.

4.4: VOLUMETRIC AND VISCOMETRIC STUDIES OF BINARY LIQUID MIXTURES OF BUTYL CARBITOL (BC) WITH AMINES AT 308.15 K.

ABSTRACT

Densities and viscosities of binary liquid mixtures of 2 - (2-Butoxy ethoxy) ethanol (BC) with n-butylamine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), n-octylamine (NOA) and cyclohexylamine (CHA) have been measured at 308.15 K. From the experimental data the excess volume (V^E), excess viscosity (η^E) and the excess molar Gibbs free energy of the activation of viscous flow (G^{*E}) have been computed and presented as function of composition. The interaction parameter d^1 of the Grunberg and Nissan has been calculated. The observed variations of the properties for the above mixtures conclude that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive (η^E), (G^{*E}) and d^1 values. The excess volume, excess Viscosity and excess molar Gibb's free energy of the activation of viscous flow have been fitted to Redlich – Kister equation to derive the coefficients and standard deviations.

4.4.1: INTRODUCTION

Studies of excess thermodynamic functions are useful tool in understanding the nature of molecular interactions in binary liquid mixtures⁷⁴. In chemical industry, knowledge of the properties of binary liquid mixtures is essential in designs involving chemical separations, heat transfer, mass transfer, and fluid flow⁷⁵⁻⁸⁰. The mixing of two solvents has been reported to result in specific interactions such as hydrogen bonding, dipole–dipole, and charge transfer reactions⁸¹. Strong and weak interactions between unlike molecules in mixtures lead to deviations from ideality. Deviations from ideality in binary liquid mixtures are usually associated with synergism and are attributed to differences in the chemistry and molecular architecture of the mixing solvents⁸²⁻⁸⁷ as well

as the experimental conditions such as temperature and the mixing ratios of the binary liquids.

In chemical industry there exists a continuing need for reliable thermodynamic data of binary systems. A survey of the literature shows that very few attempts⁴²⁻⁴⁴ have been made to study excess properties for mixtures containing alkoxy alcohols (carbitols). Amines and alkoxy alcohols^{43, 44} in their pure state exhibit self-association through hydrogen bonding. Amines are better electron donors, which allow them to have specific interactions. Further, amines form water insoluble compounds of medicinal importance. The molecular interaction study of alkoxy alcohols (carbitols) is of interest because of investigating the effect of simultaneous presence of ether and alcoholic functional groups in the same molecule. The presence of ethereal oxygen enhances the ability of the -OH group of the same molecule to form hydrogen bonds with other organic molecules.⁴⁵⁻⁴⁶ These characteristics of amines and alkoxy alcohols (carbitols) make them interesting for our study. In continuation of our physico chemical property studies of binary liquid mixtures^{15,17,18,31,76} and survey of the literature it is noticed that no attempts have been made to study excess volumes and viscosity of binary liquid mixtures of 2-(2-Butoxy ethoxy) ethanol (Butyl carbitol) with a series of amines which include n-butyl amine (NBA), sec-butyl amine (SBA), ter-butylamine (TBA), n-hexylamine (NHA), N-octyl amine (NOA), and cyclohexylamine (CHA) at 308.15 K aiming for a wider understanding of the intermolecular interactions involved and the results are presented here.

4.4.2: MATERIALS & EXPERIMENTAL METHODS:

The details of the materials and their purification methods along with the experimental methods of determination of density, viscosity etc. are explained in chapter -3 (Materials and experimental methods) of this thesis.

The measurements were made with proper care in an AC room to avoid evaporation loss. The purities of the liquids were checked by comparing the values of densities and viscosities with literature data (Table 3.1) and formed good agreement in general.

4.4.3: RESULTS & DISCUSSIONS

The experimental results of the measurement of densities (ρ) and Viscosities (η) of binary liquid mixtures are presented in Tables. 4.4.1. to 4.4.6. The molar volume (V), excess volume (V^E), excess viscosity (η^E), excess Gibbs free energy of activation of viscous flow (G^{*E}), and Grunberg–Nissan interaction parameter (d^1) were calculated from the measured data using the Equation 4.1 to 4.6 as explained in 4.1 section and presented in Table 4.4.1 to 4.4.6.

The dependence of η^E , V^E and G^{*E} on the mole fraction of 2-(2-Butoxy ethoxy) ethanol (BC) for all the six systems were fitted to the following Redlich-Kister equation as represented by equation 4.7 equation in 4.1 section by the least-squares method and the values are given in Table. 4.4.7.

The parameters A_i , obtained by a non-linear least squares polynomial fitting procedure, are also given in Table.4.4.8, together with the standard deviation (σ) values. The variation of the parameters η , V^E , η^E and G^{*E} with mole fraction of 2-(2-Butoxy ethoxy) ethanol (X_{BC}) for the systems under study are shown graphically in Fig. 4.4.1 to 4.4.4 respectively.

From Tables.4.4.1 to 4.4.6 and Fig.4.4.1 it is observed that the viscosity of binary liquid mixtures under study varied non-linearly with the mole fraction of 2-(2-Butoxy ethoxy) ethanol (X_{BC}). This suggests the presence of intermolecular interactions between unlike molecules of these mixtures. A similar observation was made by Narayana Swamy et al.¹⁶ from the viscosity studies of binary liquid mixtures of BC + amines.

It is clear from the Fig 4.4.2 that the negative V^E values are obtained over the entire composition range for the systems which indicates the presence of strong molecular interactions between the unlike components of the mixtures. It is also observed from Fig. 4.4.2 and Tables 4.4.1 to 4.2.6 that the V^E values fall in the sequence.

BC + NBA > BC + SBA > BC + TBA > BC + CHA > BC +NHA > BC + NOA.

From Fig 4.4.2, it is further observed that the negative/ Positive V^E, V_s, X_{BC} plots were found to be large and symmetrical showing a maximum between 0.7 to 0.8 mole fractions of BC (X_{BC})

According to Subha et al.¹⁴ several effects may contribute to the sign and values of V^E and the following three effects may be considered as being important.

1. Break up of hydrogen bonds and dipolar interactions in BC and intermolecular Interactions in amines.
2. The possible intermolecular interactions like hydrogen bonding or electron donor-acceptor interactions between unlike molecules.
3. Interstitial accommodation of one component molecules into the other unlike component molecules due to their differences in size and shape.

The overall sign of these excess functions depends on the combined effects of these three effects from Fig. 4.4.2. It is noticed that BC +NOA and BC +CHA positive V^E . Values are observed. An interpretation to this behavior can be given using the experience made with the quantitative evaluation of alcohol + amine mixtures by the ERAS model proposed by the earlier workers⁴⁸⁻⁵². The first effect leads to positive excess volume and the latter two effects leads to negative excess volume. The actual volume change would depend upon the relative strengths of these three effects. In the present studies the observed negative values of V^E show that the main contribution to V^E is due to hydrogen bond formation between – OH and – NH₂ groups of unlike molecules and the difference in size of the unlike molecules. Moreover, the negative values of V^E may also be partly due to the specific acid-base interactions between BC and amine molecules by considering BC as Lewis acid and amines as Lewis bases.

Very recently Nam-Tram⁵³ emphasized the importance of acid-base interactions between tert-butyl alcohol and N, N dimethylformamide / N, N–dimethylacetamide in order to evaluate the interaction energy of alcohol-amine systems. From the examination of the results in Tables 4.4.1 to 4.4.6 and Fig. 4.4.2 it is observed that the magnitude values of V^E fall in the sequence:

BC +NBA > BC + SBA > BC+TBA > BC + CHA > BC + NHA > BC + NOA.

From the Fig 4.4.2, it is also observed that the negative excess volumes of normal amines with BC increase with increase in chain length of amines. This can be explained by considering amines as proton acceptors and BC as proton donor. As the chain length of normal amines increases proton accepting ability of these amines increases and electron density will be more and more on nitrogen atom of NH_2 group due to inductive effect. So, as the chain length of the amines increases, the interaction ability (hydrogen bonding ability) of amines increases with increase in BC component. In the case of branched amines, negative V^E values increase with increase in branching. This is very clear that as the amines become more and more branched, the proton accepting ability increases due to the increase in $-\text{CH}_3$ groups on the carbon atom attached to amine group. However, the slight positive V^E values are observed at higher BC mole fraction in case of NOA indicating lesser specific interactions at these mole fractions. A similar observation was made by Haraschita et al.⁵⁴ from the V^E studies of γ -Picoline + sec-butanol and + tert-butanol.

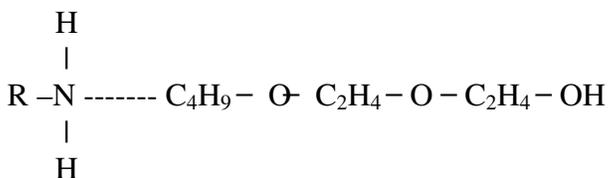
In the case of cyclohexylamine, V^E values are less positive than the corresponding normal hexyl amine, which may be due to steric and other effects because of cyclic nature of cyclohexylamine.

From Fig.4.4.3, it is noticed that η^E values are positive over the whole composition range for all the systems under study. A correlation between the signs of η^E and V^E has been observed for a number of binary systems⁵⁵⁻⁵⁶ where η^E being Positive and V^E is negative and vice-versa. In general, for systems where dispersion and dipolar interactions are operating η^E values are found to be negative whereas charge transfer and hydrogen bonding interactions lead to the formation of complex species between unlike molecules thereby resulting in positive η^E values. The positive values of η^E for the mixtures of BC + amines fall in the order.

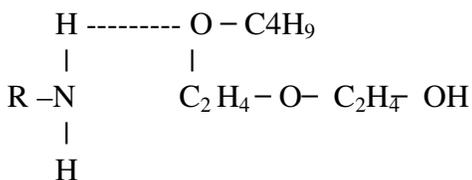
BC + NBA > BC + SBA > BC + TBA > BC + CHA > BC + NHA > BC + NOA

It can be predicted that in view of the strong proton donating ability of BC and strong proton accepting ability of amines, the overall negative V^E values and overall positive η^E values in all these systems may be regarded as an evidence for the formation of two sets of hydrogen bonds between BC and amines. Among them the first set of

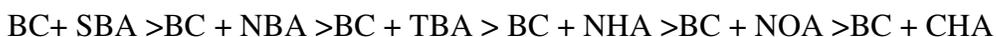
hydrogen bond formation is between N atom of amino group of amine and H atom of –OH group of 2-(2-Butoxy ethoxy) ethanol



and second set of hydrogen bond formation is between H atom of amino group of amines and oxygen atom of etheric group of 2-(2-Butoxy ethoxy) ethanol (BC). Among the two the first set of hydrogen bond formation predominates.



From the Tables 4.4.1 to 4.4.6 & Fig. 4.4.4, it is also observed that the values of G^{*E} are found to be positive which is an indication of the presence of strong specific interactions between the unlike molecules and are in the following order



Fort and Moore⁵⁷ and Ramana moorthy^{58,73} reported that for any binary liquid mixture, the positive value of d^1 indicates the presence of strong interactions and the negative value of d^1 indicates the presence of weak interactions between the components. On this basis the d^1 values in the present study for all the systems confirm the presence of strong interactions between the component molecules. A similar observation was made by Subha et al.¹⁶ from the d^1 values of the binary liquid mixtures of propionic acid with alcohols.

CONCLUSIONS

The present study reports the volumetric and viscometric properties of 2-(2-Butoxy ethoxy) ethanol (BC) with n- butyl amine, sec- butyl amine, tert- butyl amine, n-

hexyl amine, n - Octyl amine and cyclo hexyl amine over the entire composition range at 305.15 K. From the results, it is observed that the variation of the properties of the mixtures studied supports the view that the interactions between unlike molecules predominate over the dissociation effects in the individual components. It is also evident that the presence of strong interactions between unlike molecules is predominant and characterized by the negative V^E and positive η^E , G^{*E} and d^1 values.

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