Ultrasonic Study on Solvent Dewaxing Process of Crude Petroleum Oil

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Abstract: ***The purpose of solvent dewaxing is to prevent corrosion, protect catalyst in subsequent processes, and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricant and grease stocks. The solvent dewaxing process separates aromatics, naphthenes, and impurities from the product stream by dissolving or precipitation. When powerful ultrasound of higher frequency is applied to a system, it is possible to produce physico chemical changes in organic solvent mixture. The ultrasonic velocity and density measurement has been undertaken in presence of high intense ultrasonic beam at 3MHz in binary mixture of MIBK with toluene. The solvent dewaxing process is discussed in terms of molecular interaction by calculating acoustic parameters and their deviated values.The variation of different acoustic parameter with temperature and concentration shows the effect of ultrasonic wave in dewaxing process of crude oil.***

Keywords: Crude oil, solvent dewaxing, acoustic parameter, molecular interaction

1. Introduction

Many studies were conducted in an attempt to understand and solve the problem of wax deposition in oil reservoir and oil transmission lines. Several studies of experimental and numerical modeling were developed in order to predict the phenomenon of deposition of wax. An important feature in the study of wax is its solubility in oil. Solubility is a property that is defined the conditions of temperature and pressure at which these compounds precipitate from solution in the form of crystals. Studies show that the solubility of wax depends strongly on temperature and decreases with the decrease of the temperature. The pressure on the other hand, seems not to significantly affect the solubility.Deposition of wax in a region changes the thermo dynamical equilibrium for which the temperature falls below the cloud point. Above the cloud point the flow is Newtonian and below the cloud point the flow is non –Newtonian due to increase of viscosity.As a result of which the oil becomes thicker and clogs fuel filters and injectors in engines. Thus a suitable solvent mixture is used which increases the cloud point temperature.As a result of which the interaction of solvent mixture with wax decreases the viscosity converting the Non-Newtonian flow into Newtonian flow.When ultrasonic wave propagates in the treatment medium, it generates compressions and rarefactions.The compression cycle exerts a positive pressure on the medium by pushing molecules together.The rarefaction cycle exerts a negative pressure by pulling molecules from each other, and micro bubbles can be generated and grow due to such negative pressure. When these micro bubbles grow to an unstable dimension, they can col-lapse violently and generate shock waves, resulting in very high temperature and pressure in a few microseconds. As wax content long chain hydro carbon so solvent dew axing process is more selective for removing both heavier normal and non-normal hydrocarbons from wax. These hydrocarbons can more interact with some solvent mixture in presence of high intense ultrasonic wave [1]. Pure toluene is excellent oil solvent and has good solvent power for wax. But use of pure toluene provides a tight lattice of wax which will create the difficulty for filtration [2]. In contrast, MIBK shows low solvent power to paraffinic compound and as such it precipitates the wax well. But if a mixture of MIBK and toluene used as solvent for wax separation, the better separation may expected [3]. Dewaxing of crude oil with MIBK-toluene mixture indicated that with increasing MIBK in the mixture, the filtration time increases (i.e. the filtration viscosity increases) and the oil yield decreases. With increasing MIBK, the viscosity of the oil index increases but the solid point remains constant [4].This dewaxing process can be well understood if the interaction between the MIBK and toluene can be studied at different temperature. This interaction can be studied with the help of some thermo acoustic parameters. Since the ultrasonic wave is fundamentally related to the structure of atom or molecules, so the propagation of this wave certainly explains the different thermodynamic characteristics of solvent mixture [5-6].

2. Material and Method

High purity and analytical grade samples of MIBK 99% (GC) and Toluene 99.0 %(GC) are procured from SD chemicals, India. The entire chemical used in the study are purified by standard procedure [7-9] and redistilled before use. To minimize the contact of this deliquescent regent with moist air, the product was kept in sealed bottles in desiccators. The purities of the sample were confirmed by GLC. Binary mixtures were prepared by mass in air tight bottles. The mass measurements were performed on high precession digital balance with an accuracy of ± 1mg. The uncertainty in mole fraction was ± 0.001.The densities of pure liquids and their mixture were determined by using double arm pyknometer with accuracy of the order of ± 0.01 kg/m^3.

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3. Experimental Method

The ultrasonic velocity of the above liquids and their mixtures were measured for temperature 30^0C,40^0Cand 50^0C using multi-frequency ultrasonic interferometer operating at a frequency 3MHz (Mittal Enterprises, New Delhi,Model-MX-3).The accuracy in the measurement of ultrasonic velocity was within $\pm$ 0.01 ms^{-1}. The working principle used in the measurement of velocity of sound through medium was based on the accurate determination of the wave length of ultrasonic waves of known frequency produced by quartz crystal in the measuring cell [10].The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell within $\pm$0.01 K using a constant temperature bath and the temperature was monitored with a platinum resistance thermometer with an accuracy of $\pm$0.001 K.Then binary mixture of each concentration was treated with wax collected from the crude oil supplied by GAIL, Vijaipur, Guna, MP.Finally the weight % of wax obtained, treated with pure MIBK and that of mixture of MIBK with toluene get compared.

4. Theory:

The experimental measured values of ultrasonic velocity and computed values of density are used to compute acoustic parameters such as intermolecular free length (L_f), isentropic compressibility (β), acoustic impedance (Z),and their excess values. The above acoustic parameters are determined with the help of the following relationship.

Isentropic compressibility: $$(\beta_S)=\frac{1}{\rho C^2} \qquad (1)$$

Intermolecular free length: $$(L_f)=k\beta^{1/2} \qquad (2)$$

Acoustic impedance: $$(Z)=\rho C \qquad (3)$$

and their excess values are calculated as

$$Y^E=Y_{mix}-(X_A Y_A+X_B Y_B) \qquad (4)$$

where the constant K is temperature dependent which is given as [93.875+ (0.375T)] $\times10^{-8}$ as per literature [8] and T being the absolute temperature.

5. Result and Discussions

The computed values of density of the mixture and measured values of ultrasonic velocity in the binary mixture are used to calculate the different acoustic parameters and their deviated values are shown in Figure1-5.Fig.1 shows the variation of ultrasonic velocity for different temperature with increasing mole fraction of MIBK.With increase of temperature the ultrasonic velocity decreases with increasing values of mole fraction of MIBK.This shows that the intermolecular interaction occurring in the liquid mixtures results in the decrease of the inter space between molecules and this might lead to a decrease in intermolecular free length producing negative values of the excess intermolecular free length as shown in Fig.4. The decrease in intermolecular free length results in a decrease of compressibility (Fig.3) and an increase of velocity.

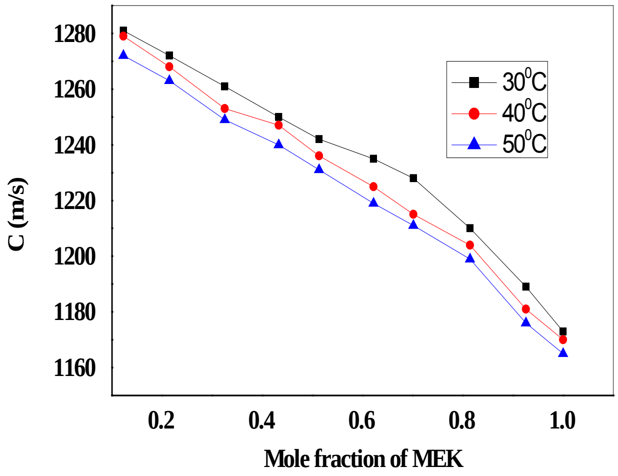

Figure 1

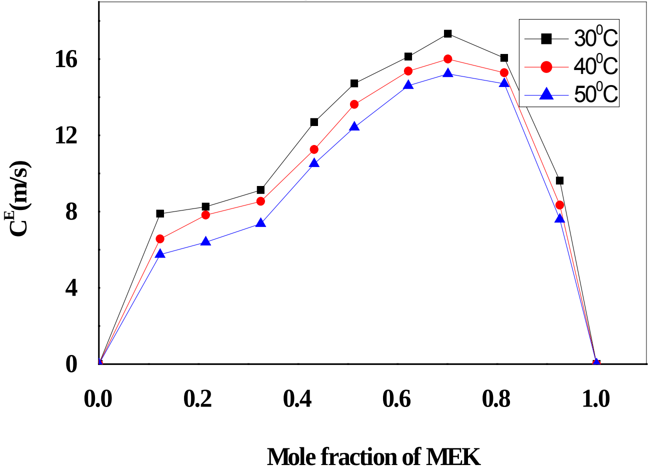

Figure 2

This produces negative values of excess compressibility and positive values of excess speed in the binary mixture (Fig.2). As a result the graph of the variation of excess compressibility with mole fraction of MIBK must show the same trend as that of the excess intermolecular free length and excess velocity graph must show the reverse trend as that of the excess compressibility graph. The excess acoustic impedance (Fig.5) and adiabatic compressibility exhibit opposite trend. This result point out the fact that the variation of excess velocity and excess acoustic impedance must show a reverse trend as that of the excess intermolecular free length and excess compressibility verses mole fraction of MIBK which is obtained in the present study.

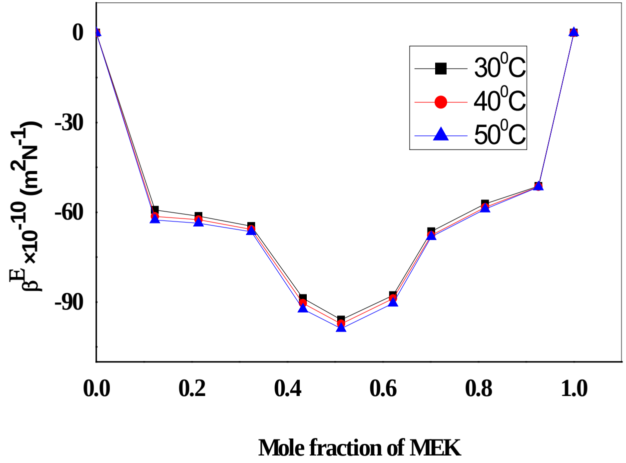

Figure 3

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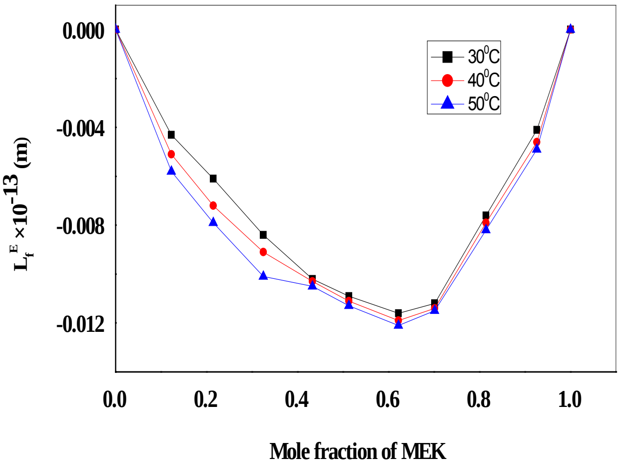

Figure 4

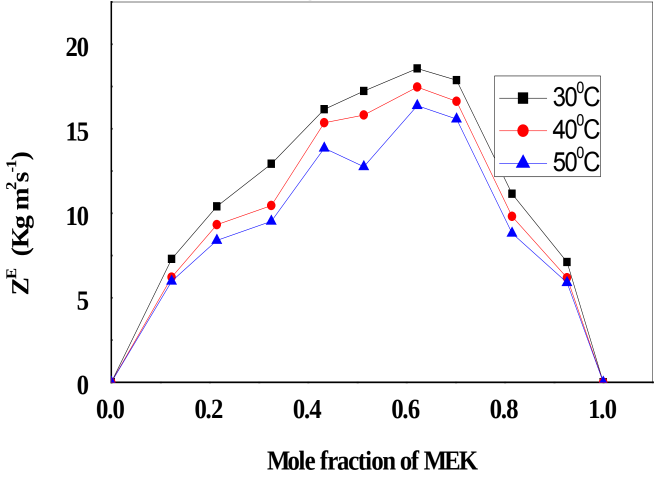

Figure 5

From the figures it is clear that the value of excess compressibility becomes more negative with increase of temperature. This behavior indicates that the strength of interaction between unlike molecules in the present study increases with temperature in the binary mixture. According to Fort and Moore a negative excess compressibility is an indication of strong hetro molecular interaction in the liquid mixtures which is attributable to charge transfer, dipole-dipole, dipole-induced dipole interaction and is attributed to dispersion forces. The mixture of MIBK and toluene is a combination of polar-non polar liquid. In the carbonyl group of MIBK, the carbon atom and the more electronegative oxygen atom are joined together by σ-bond.In the valence band theory a special type of resonance called hyper conjugation is takes place in stabilization of toluene. Due to this resonance the negative charge on the methylene group of toluene molecule is stabilized so that hydrogen atom has a positive charge. Thus in MIBK+ toluene mixtures there may be an interaction between the hydrogen atoms of toluene molecules with the oxygen atom of MIBK which is found to be strong. According to Reddy et al the positive values of C^E and negative values of βs^E are attributed to molecular association and complex formation where as negative values of excess speed and positive values of excess compressibility are attributed to molecular dissociation. In the present case as C^E is positive and βs^E is negative it indicates the molecular association or complex formation.

6. Conclusion

Thus from the analysis of different acoustic parameters and their variation with concentration of MIBK indicates the presence of different intermolecular interaction in the mixture which are fundamentally responsible for explain the dewaxing process of wax contained in the crude oil. Thus there exists interaction due to dipole-dipole and hyper conjugation that leads to molecular association in the binary mixture. Hydrocarbons show regular increases in melting point as the molecular weight increases. It has been noticed that non-polar molecules like toluene are weakly attracted to each other by intermolecular Van der Waal's forces. These force, which operate only over very small distances result from induced polarization of the electron clouds in molecules. Although the electron distribution in a molecule is uniform on average over a period of time, the distribution at any given instant is not uniform. One side of a molecule may by chance have a slight excess of electrons relatives to the opposite side. When that occurs, the molecules have a temporary dipole moment. This temporary dipole in one molecule causes a nearby molecule to adopt a temporarily opposite dipole with the result that a tiny attraction is induced between the two molecules which results in decrease of wt% of wax due to addition of solvent mixture.

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