Effect of ultrasonication in treatment of crude oil

A Tripathy[a], G Nath[b]* & R Paikaray[c]

[a]Department of Applied Science and Humanities, ABES Engineering College, Ghaziabad 201 009, India
[b]Department of Physics, Veer Surendra Sai University of Technology, Sambalpur, 768 018, India
[c]Department of Physics, Ravenshaw University, Cuttack 753 003, India

The demand of petroleum oil has proven its importance in energy sector as well as in the streamlining the economic scenario of the country. In production sector of crude oil, the problem has been observed when the ambient temperature is lower than the wax appearance temperature (WAT), which results the oil become cool leading to deposition of wax. The present paper focuses effect of ultrasonic energy on crude oil sample to reduce the deposition of wax. The propagation of ultrasonic wave in waxy crude oil in presence of suitable blend makes it possible to proper analyse the reduction of wax by suitable mathematical theory. The treatment of ultrasonic energy in wax reduction process involves experimentation and computation of some basic parameter which are explaining the basic mechanism of reduction of wax deposition. The variation of acoustic parameters, their excess values have been discussed in terms of molecular interactions present in the solvent mixture, which explains the physio- chemical behaviour of the crude oil at WAT due to complex formation. The treatment of crude oil with the optimum suitable blend makes it possible to reduce the wax percentage.

Keywords: Crude oil, Wax appearance temperature, Solvent mixture, Ultrasonic velocity, Acoustic parameter

1 Introduction

Wax deposition and its control continue to be a challenging problem in the oil and gas industry. This is because crude oil contains a mixture of waxes which precipitate out of solution at low temperature and pressure conditions. The presence of these waxes thickens the crude oil and a continuous build-up of wax could eventually clog the pipeline which could lead to a complete loss of production, resulting in shut down which would cost the company a lot of money[1-11]. Paraffin wax produced from crude oil consists primarily of long chain, saturated hydrocarbons (linear alkanes/ n-paraffin) with carbon chain lengths of C_{18} to C_{75+}, having individual melting points from 40 °C to 70 °C is referred as "macro crystalline wax" and naphthenic hydrocarbons (C_{18} to C_{36}) is referred as "microcrystalline wax." Macro crystalline waxes lead to paraffin problems in production and transport operations while microcrystalline waxes contribute the most to tank-bottom sludge. At high enough temperatures these large molecular weight waxes are dissolved in the crude and remain in solution. No precipitation occurs at these temperatures but as the temperature drops below the wax appearance

temperature, wax gets deposited along the wall of the pipeline and some paraffin also is dispersed in the crude oil forming insoluble waxy crystals as shown in Fig. 1.

The deposition process involves two distinct stages: nucleation and growth. Nucleation is the forming of paraffin clusters of a critical size that are stable in the hydrocarbon fluid. This insoluble wax itself tends to disperse in the crude. Prior to solidification, the solid wax crystals in the liquid oil, change the flow properties from a newtonian low viscosity fluid to a very-complex non-newtonian flow gel. Determination of a WAT significantly higher than the temperatures expected to be encountered during production indicates the potential for wax deposition problems. The rheological and thermodynamic properties of wax precipitation are influenced by wax appearance temperature. There are several studies and different techniques that are used to determine the WAT, like American Society for Testing and Materials (ASTM) visual methods, cold finger, differential-scanning calorimetric, cross-polarized microscopy and light transmittance. The present paper focuses on the effect of ultrasonic energy on crude oil sample in presence of blended solvents of MEK and bromobenzene. The velocity of the ultrasonic wave depends on the

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*Corresponding author (E-mail: ganesh_nath99@yahoo.co.in)

density of the medium; thus, the transit time for the wave will change at the WAT. Experiments were conducted on three solvent to crude oil ratios (10:1, 15:1 and 20:1) for temperature range of 10 °C to 70 °C. To confirm the rheological changes at WAT in the crude oil, a light microscope was used to view the oil sample, allowing the wax crystals to show up as bright spots on a black background.

2 Materials and Instruments

High purity and analytical grade samples of MEK 99% and bromobenzene 99.0% were procured from CDH chemicals, India and was used without further purification. Crude oil samples were obtained from Indian Oil Corporation Limited having density at 15 °C 820-860 kg/ m^3, wax content 20.27 wt%, sulphur content as 0.051-1.5 wt% using standard ASTM methods.

3 Characterisation of Crude Oil by SEM and NMR

The crude oil freshly collected was stored in an air tight bottle under room temperature. The SEM of crude oil shows that the wax initially mixed with the different hydrocarbons are found to be in crystal form of length 250 μm as shown in Fig. 2.
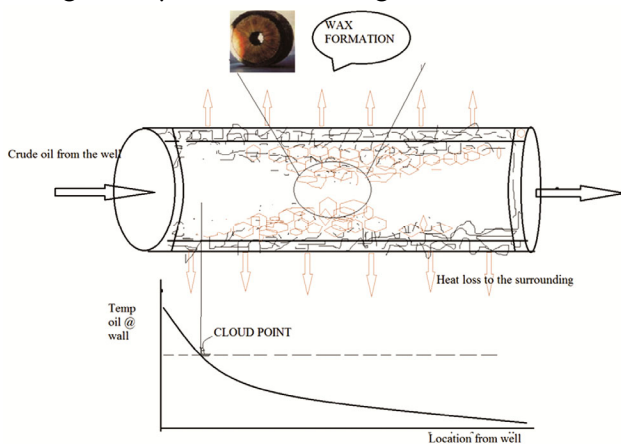

Fig. 1 – Deposition of wax on the inner wall of the pipeline during transport.
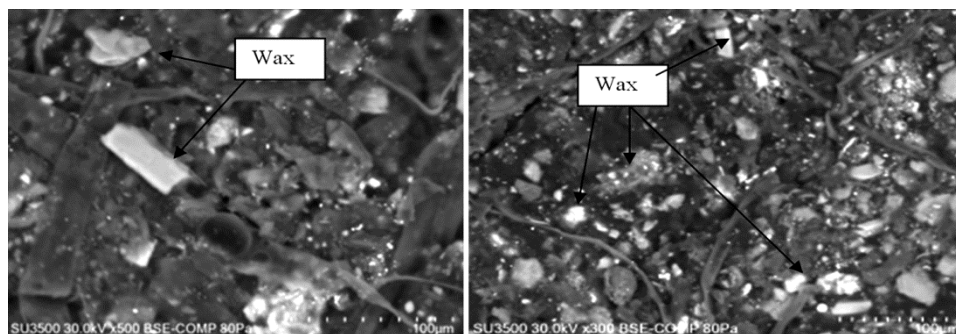
The NMR study in Fig. 3, assumes that all narrow resonances are paraffinic. Even long chain of aliphatic hydrocarbons can also be predicted. More carbon number could be predicted from the narrow responses. Paraffin waxes are mixtures of saturated *n*- and iso-alkanes, naphthenic, and alkyl- and naphthenic-substituted aromatic compounds. $_1$H NMR spectra were recorded in CDCl$_3$ on a Bruker 400 MHz spectrometer using TMS as internal standard. By determining the number, type and relative positions of hydrogen and carbon atoms through $_1$H NMR spectra, several parameters were calculated, which provide information to predict the structure of the average molecule in a given fraction, such as asphalting, wax etc. The amount of energy absorbed at each frequency/magnetic field strength is proportional to the number of protons absorbing. Consequently, the area under each set of spectral lines is proportional to the relative number of protons absorbing. The ratio of the heights of the steps on the integration curve tells us the ratio of the numbers of protons resonating at each frequency.

4 Experimental Procedure

The mass measurements of chemicals for binary mixture were performed on high precession digital balance with an accuracy of ±1 mg. 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. The ultrasonic velocity of the above liquids and their mixtures were measured at frequency 2 MHz using multi-frequency ultrasonic interferometer operating at different frequencies (Mittal Enterprises, New Delhi, Model-MX-3) having accuracy in the measurement of ±0.01 ms^{-1}. The temperature of the solution was controlled by circulating water at a desired temperature through the jacket of double walled cell within ±0.01 K using a constant temperature bath with an accuracy of ±0.001 K as

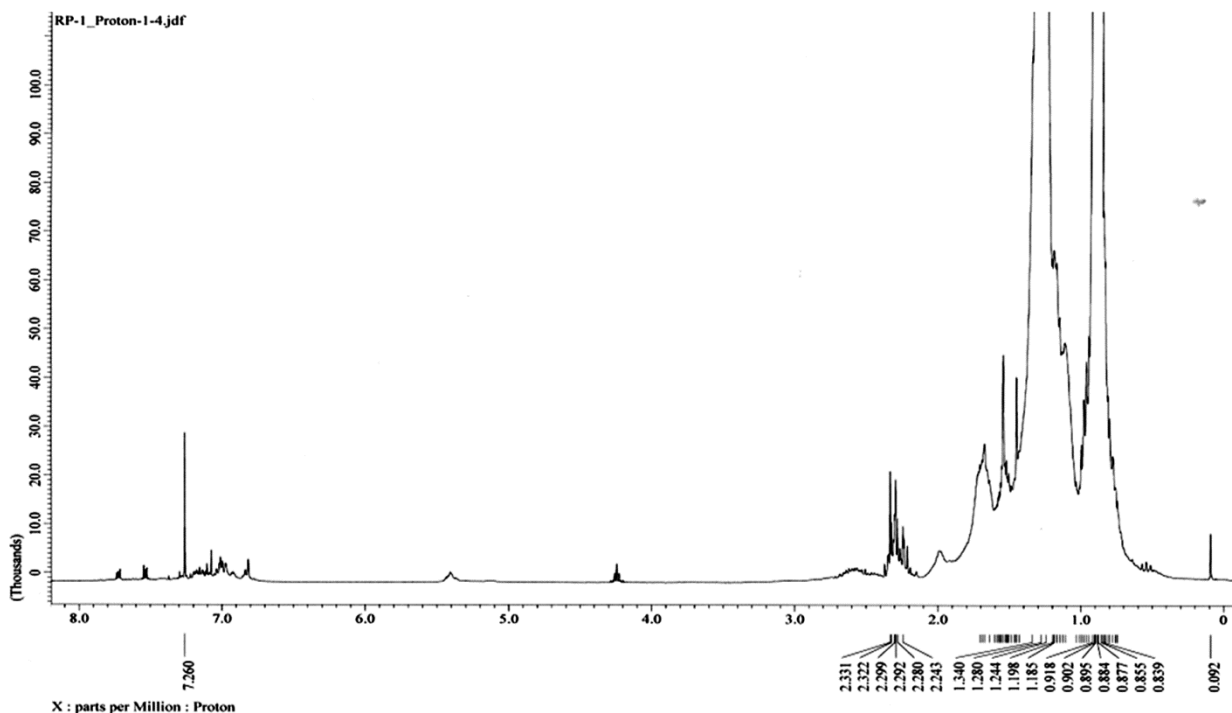Fig. 2 – SEM image of wax present in Indian oil.

Fig. 3 – NMR spectra of wax present in Indian oil.

shown in Fig. 4(a). Experiments were conducted on three solvent to crude oil ratios (10:1, 15:1 and 20:1) at temperature range 10 °C to 70 °C for 45 min.

4.1 Separation of wax

Each crude oil sample was weighed out and mixed with acoustically determined blended solutions of MEK and bromobenzene mixture at a predetermined mass ratio and then heated in a hot water bath and stirred until a thermal equilibrium was achieved. The entire sample was kept in the ultrasonic bath operating at a frequency 125 kHz and power 60 W to allow for well dispersion of the chemicals with the oil in presence of high frequency ultrasonic wave[12-15]. The solution of oil in solvent was then chilled from 70 ºC to 10 ºC in a chiller for 45 min. The separated wax from the mother solution was filtered using Whatman paper of 45 µm. The wax was then left for drying for 24 h in a desiccator. The yield point of the wax was calculated from the recovery of wax after the treatment of solvent mixture by the following relation:

$$Y = \frac{W_e}{W_o} \times 100 \qquad \qquad \dots (1)$$

Where Y is the yield as a percentage of the total weight of the sample;
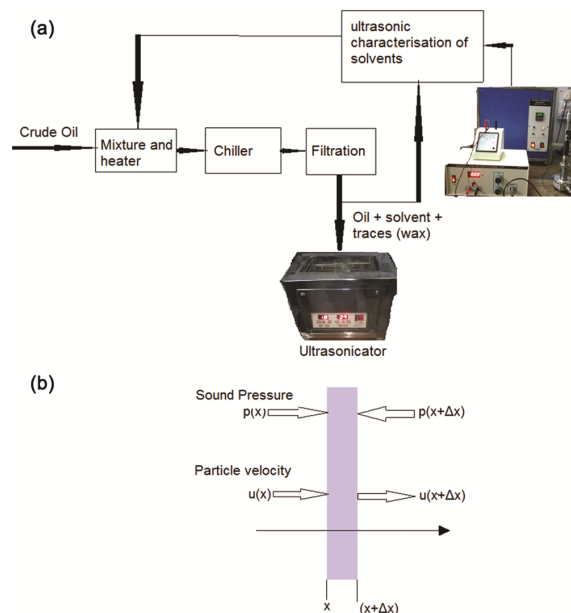

Fig. 4 – (a) Step wise procedure for ultrasonic assisted dewaxing of crude oil and (b) mathematical model for the pressure wave in the medium.

W_e = the weight of the extract and

W_o = the weight of the crude oil sample.

Figure 4(a) is step wise procedure for ultrasonic assisted dewaxing of crude oil.

5 Theory

When a high-frequency ultrasonic wave propagates in a medium, it produces an oscillatory motion in it and surface is displaced by the component of the motion normal to the surface. As a consequence of this movement, the pressure in a layer near the surface is increased or decreased by the action of contraction or expansion, respectively. Subsequently the transient pressure change will move the neighbouring particles of the fluid beyond this layer and causes the periodic motion that propagates is a sound wave. Assuming the sound wave propagating in a fluid in an equilibrium state with pressure P_0, and density ρ_0 the particles making up the medium begin to have translational vibration with velocity 'u' parallel to the propagating direction as shown in Fig. 4(b). This increases the pressure accompanying the density change:

$$u = -\nabla\phi = \text{velocity gradient} \qquad \text{... (2)}$$

For one dimensional motion of a volume element, pressure difference between the pressure acting on both sides is:

$$P(x) - P(x + \Delta x) \approx -\left(\frac{\partial P}{\partial x}\right)\Delta x \qquad \text{... (3)}$$

This force is effectively applied to a mass of $\rho_0\Delta x$.

Thus equation of motion for acceleration $\dfrac{du}{dt}$ is:

$$\rho_0\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x}\right) = -\frac{\partial P}{\partial x} \qquad \text{... (4)}$$

When $u \approx 0$,

$$\rho_0\frac{\partial u}{\partial t} = -\frac{\partial P}{\partial x} \qquad \text{... (5)}$$

Mass inflowing through the plane x is $\rho_0 u(x)$ per unit area and unit time, the mass out flowing through $x + \Delta x$ is:

$$\rho_0 u(x + \Delta x) = -\rho_0\left(\frac{\partial u}{\partial x}\right)\Delta x = \text{incremental mass in the}$$

element between x and $x + \Delta x$ per unit area per unit time $= \dfrac{\partial \rho}{\partial t}\Delta x$

From equation of continuity we have:

$$\frac{\partial \rho}{\partial t} = -\rho_0\frac{\partial u}{\partial x} \qquad \text{... (6)}$$

The change in pressure is expressed as a function of the fractional change of density $\dfrac{\rho}{\rho_0}$.

From equation of state:

$$P = K\frac{\rho}{\rho_0} \qquad \text{... (7)}$$

where $K =$ Bulk modulus

From Eq. (2) in Eq. (5):

$$P = \rho_0\frac{\partial \phi}{\partial t}$$

Hence acoustic pressure can be easily obtained from velocity potential. Combining Eq. (5), Eq. (6) and Eq. (7) to eliminate u and ρ, we have:

$$\frac{\partial^2 P}{\partial x^2} - \frac{1}{c^2}\frac{\partial^2 P}{\partial t^2} = 0 \qquad \text{... (8)}$$

where $c^2 = \dfrac{K}{\rho_0} = \dfrac{\partial P}{\partial \rho} \qquad \text{… (9)}$

is the constant which depends on the characteristics of the medium like speed of the ultrasonic wave, compressibility, density of the medium, frequency and energy of the ultrasonic wave. The other acoustic parameters which are related to dewaxing process of crude oil were computed from the experimentally measured values of ultrasonic wave velocity in the medium[16-18]. The acoustic parameters have been evaluated with the help of the following relationship[7-10].

Isentropic compressibility: $\beta_S = \dfrac{1}{\rho c^2} \qquad \text{… (10)}$

Intermolecular free length: $L_f = k\beta^{1/2} \qquad \text{… (11)}$

Acoustic impedance : $Z = \rho c \qquad \text{…(12)}$

and their excess values are calculated as:

$$\left(Y^E\right) = Y_{mix} - \left(X_A Y_A + X_B Y_B\right) \qquad \text{... (13)}$$

where X_A, X_B are the mole fractions, Y_A, Y_B and Y_{mix} represent the isentropic compressibility inter molecular free length, acoustic impedance of bromobenzene, MEK and their mixtures respectively. The constant k is temperature dependent which is given as[11] [93.875+ (0.375T)] $\times 10^{-8}$ where T is denoted as absolute temperature.

6 Results and Discussion

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 Figs 5 and 6. From Fig. 5 it is clear that the ultrasonic velocity decreases with increase of mole fraction of MEK. There is a linear variation of velocity with respect to mole fraction of MEK. This may be due to self-association of the molecules and a very strong dipole-induced dipole interaction between the component molecules which is concentration dependent and there is no formation of complex takes place[19]. This shows that the intermolecular interaction occurring in the liquid mixtures results in the decrease of the interspaces between molecules. In order to understand the nature of molecular interactions
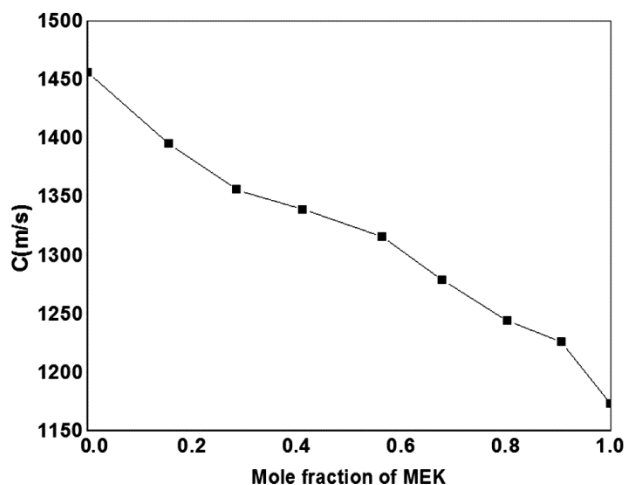

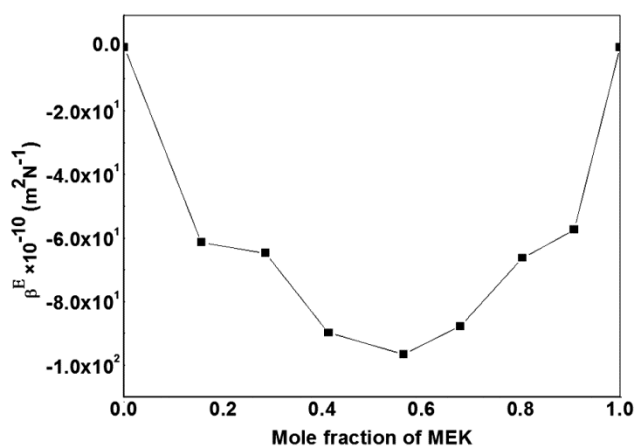Fig. 5 – Variation of ultrasonic velocity with mole fraction of MEK.

Fig. 6 – Variation of deviated compressibility with mole fraction of MEK.

between the components of the liquid mixture, it is of interest to discuss the acoustical properties in terms of excess parameter rather than actual values.

β^E is negative means that liquid mixture is highly compressed and it is possible only when unlike molecules are more tightly bound or interaction is high as shown in Fig. 6. 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. From Fig. 7 it was observed that when each blended solvent added to the crude oil and subjected to sonication with the help of sonicator operating at 125 kHz and 60 W power at room temperature 303 K followed by centrifuge with rpm 2000 the wax are separated out above the oil. The filter paper of diameter 45 μm was used to separate out the settled wax from the oil and wax was measured for each treatment after dry in vacuum chamber operated at low temperature. The extracted wax measured for each extraction increased[12] under the optimum conditions of MEK and bromobenzene at ratio 3:1 and with change in the ratio of MEK and bromobenzene to 1:1, 2:1, 3:1 the amount of removal of wax increases with increasing the ratio of mixture.

The microscopic image for each treatment has been collected before and after the treatment with ultrasonically blended solvent mixture and the results shows the improvement is more for the 0.45-0.50% mole fraction of MEK and bromobenzene at room temperature which is well agrees with the inflection point of acoustic parameters computed from the ultrasonic velocity data and density of the mixture[20]. The microscopic image shows (Fig. 8) that the wax is
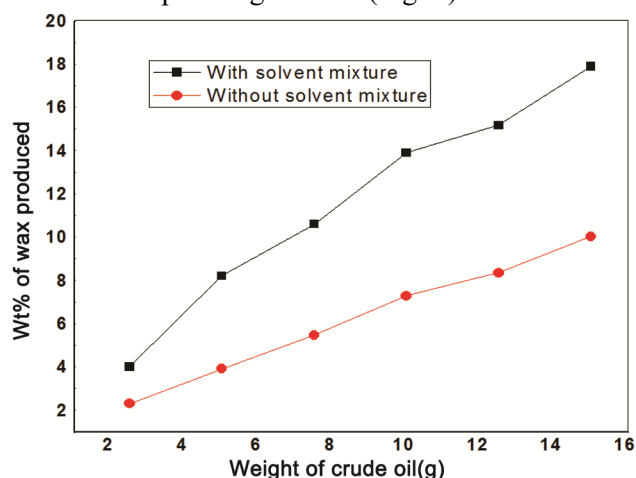

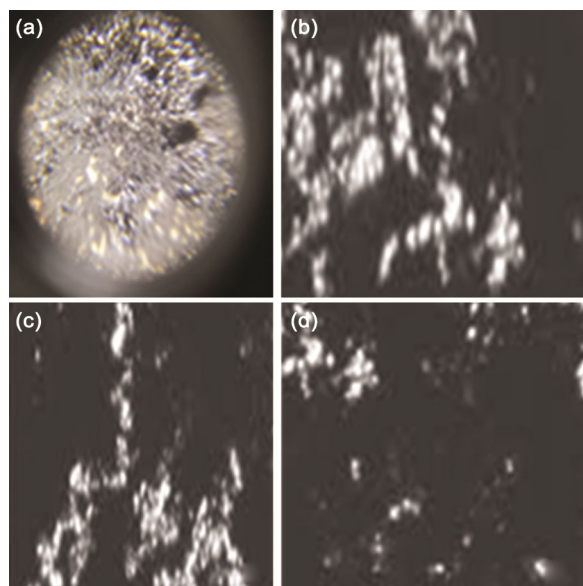Fig. 7 – Wax produced with and without treatment of solvent mixture.

Fig. 8 – Microscopic image of the wax of with ultrarsonicated treated solvent mixture at different oil ratio.

more crystallite form when they treated with solvent mixture of different concentration.

7 Conclusions

The compatibility of solvent mixture was well studied with the ultrasonic assisted high frequency wave by computation of acoustic parametrs.The suitable blend was determined which are well applicable to dewaxing of crude oil. The percentage of wax increases with increase of blended organic solvent up to 0.6-0.75 of chemical solvent mixture concentrations which is quite obvious from the variation of acoustical parameters. The microscopic image of the crude oil verifies strong agglomeration of wax molecules in treated crude oil.Moreover, the greater ratio of solvent to oil increases the solubility preference for the oil rather than that of the wax helping to improve the dewaxing process. This was reflected by the high wax yield obtained from mixtures with 3:1 solvent ratios.

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