

# Thermodynamics of the Deposition of Complex Waxes and Asphaltenes in Crude Oil

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**Abstract:** The thermodynamics of wax formation in crude oils is examined and additional insights obtained into the problem. We show that a correlation for cloud point, or wax appearance temperature, obtained for pure-substance waxes may be extended to mixtures of hydrocarbons, thereby generalising the usefulness of the correlation. We apply the colligative equation for freezing point depression to quantify the analogous activity of wax inhibitors. The limits of applicability of an empirical formula that relates wax molecular weight and wax density are examined. We extend the analysis to the high molecular weight asphaltenes.

**Keywords:** Colligative properties, wax appearance temperature, wax inhibitors, wax specific volume.

## 1. INTRODUCTION

A big issue in flow assurance engineering of pipelines that carry crude oil is wax deposition. The temperature at which wax begins to form is called the cloud point or the wax appearance temperature ( $T_w$ ), and at that stage less than 0.1% of the oil will be present as solid. The pour point is the temperature at which the wax content is high enough to preclude pouring, and even at this stage the percentage of the oil present as wax is only 1-2%. Wax in this quantity is sufficient to impart a matrix structure to the oil and this is the basis of the observed effect.

The  $T_w$  for a crude oil is analogous to the freezing point for a pure organic substance. There is of course the difference that for a crude oil solid appearance occurs over a temperature range whereas for a single organic substance the temperature remains constant until the phase change from liquid to solid is complete. Nevertheless, comparisons between  $T_w$  of oils and freezing points of pure substances can lead to some helpful ideas. This will be the first point to be discussed in this piece of work, and further related points, including the action of wax inhibitors and the effect on wax density, will follow.

## 2. WAX APPEARANCE TEMPERATURE

Elsharkawy *et al.* [1] found the following correlation between wax appearance temperature and molar mass:

$$T_w = 382.72 \text{ K} - 20242.593 \text{ g mol}^{-1} \text{ K}/M, \quad (1)$$

where  $M$  is the gram molar mass. Elsharkawy *et al.* applied this correlation to particular wax components of known carbon number, and obtained the constants from knowledge

of the freezing points of pure organic substances. In this discussion we examine the hypothesis that a particular wax will conform to Eq. (1) where  $M$  is a weighted average molecular weight. In so doing make the following supporting arguments: First, the correlation was obtained simply by fitting freezing points to molar masses; its derivation did not invoke the phase rule therefore in its extension to a multi-component system there is no violation of the principles of thermodynamics. (There is arguably such a violation in the application of the Clausius-Clapeyron equation to biodiesels, a practice that has been deprecated [2]). Secondly, the concept of average molecular weight of a complex mixture of hydrocarbons is a well established one.

Kok *et al.* [3] give measured  $T_w$  values for a variety of crude oils from sources including Algeria, Libya, Angola, Venezuela and France. The values are in the range 19-42°C. The correlation (1) gives the values  $M = 223 \text{ g mol}^{-1}$  for  $T_w = 19^\circ\text{C}$  (292 K) and  $M = 299 \text{ g mol}^{-1}$  for  $T_w = 42^\circ\text{C}$  (315 K). For purposes such as prediction of flue gas emissivities [4], liquid fuels from petroleum across the entire boiling range from gasoline to residue are considered to have an empirical formula  $\text{CH}_2$ . We carry this same empirical formula across to crude oil, in which case for  $M = 223 \text{ g mol}^{-1}$  it corresponds to a molecular formula of  $\text{C}_{16}\text{H}_{32}$  and for  $M = 299 \text{ g mol}^{-1}$  it corresponds to a molecular formula of  $\text{C}_{21}\text{H}_{42}$ . The carbon number range of such waxes encompasses  $\text{C}_{16}$  and  $\text{C}_{21}$ ;  $\text{C}_{16}$  is at the low end, and the range extends to about  $\text{C}_{30}$ .

As a limiting case, which might even be seen as *reductio ad absurdum*, we estimate the molar mass at a  $T_w$  of absolute zero as

$$M = (20242.593/382.72) = 53 \text{ g mol}^{-1},$$

which is in between the molar masses of butane ( $58 \text{ g mol}^{-1}$ ) and propane ( $44 \text{ g mol}^{-1}$ ). It can be inferred that waxes

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comprising alkanes with such low carbon numbers will not under any conditions be formed.

### 3. WAX INHIBITORS

These behave analogously to freezing point depressants, to which the following equation applies:

$$\Delta T_f = K_f c_m, \quad (2)$$

where  $\Delta T_f$  is the number of degrees by which the freezing point is lowered ( $^{\circ}\text{C}$ ),  $c_m$  is the concentration of solute ( $\text{mol kg}^{-1}$ ), and  $K_f$  is the freezing point depression constant ( $^{\circ}\text{C kg mol}^{-1}$ ). In principle  $K_f$  is a property of the solvent only and independent of the solute, although of course if the solute dissociates into ions note has to be taken of that in assigning a value to  $c_m$ . Literature values of  $K_f$  in the units given above include 1.86 for water, 20.2 for cyclohexane and 5.1 for benzene. In attempting to apply a similar equation to wax inhibition in crude oil we encounter the difficulty that there are few if any ( $\Delta T_f c_m$ ) data points for crude oil in the public domain. Even for those data that are available, Eq. 2 cannot be fully tested without knowledge of the molar mass of the inhibitor. Wax inhibitors are often polymers added in very small proportions to the oil. A patent filed in 1997 [5] describes how such an inhibitor present at 400 ppm in an organic solution simulating a crude oil effected a  $0.8^{\circ}\text{C}$  depression in  $T_w$ . If, arbitrarily but not unreasonably for the purpose of a rough calculation, we assume that the polymer molar mass is about the same as the average molar mass of the crude oil itself, each about  $400 \text{ g mol}^{-1}$  corresponding to about  $\text{C}_{28}$ , a value for  $K_f$  can be obtained, as shown in Box 1.

$$400 \text{ ppm by weight of inhibitor} \equiv 0.4 \text{ g kg}^{-1}$$

$$0.4 \text{ g kg}^{-1} \equiv 10^{-3} \text{ mol kg}^{-1}$$

Applying Eq. 2:

$$0.8 = K_f \times 10^{-3}$$

$$K_f = 800^{\circ}\text{C kg mol}^{-1}$$

**Box 1.**

This is a much higher value than those for simple compounds such as water and cyclohexane, and notwithstanding the many approximations made it can be seen as a general result that  $K_f$  values for crude oils are an order of magnitude or more higher than those for simple compounds. Depression of freezing point and lowering of  $T_w$  are colligative effects, depending only on the number of particles. There will be many fewer "particles" (i.e., molecules) per kg with crude oil than with a simple organic. Introducing a mole of solute particles into a  $\text{C}_{30}$  compound will have an effect about an order of magnitude higher than introducing this amount into a  $\text{C}_3$  compound such as propanol. That is the reason for the very high value calculated in Box 1, the order of magnitude of which can be seen as being typical.

### 4. POSSIBLE EXTENSION TO ASPHALTENES

Asphaltenes are of high average molar mass, typically  $1000\text{-}1500 \text{ g mol}^{-1}$ , and also contribute to pipeline blockage. They contain aromatic clusters and accordingly have a smaller proportion of hydrogen than waxes:  $\text{CH}_{1.2}$  is a roughly correct empirical formula for asphaltenes. The

molecular formula corresponding to this empirical formula and to  $M = 1000 \text{ g mol}^{-1}$  is  $\text{C}_{75}\text{H}_{90}$ . This carbon number is well beyond the range for the waxes, and separation mechanisms are not the same for the two. The asphaltenes are present in crude oil in colloidal suspension and their deposition is due to destabilisation of that as the physical conditions experienced by the oil change. This differs from wax deposition which, as we have seen, is closely analogous to simple freezing. We shall return to asphaltenes in the next section.

### 5. WAX SPECIFIC VOLUME

Elsharkawy *et al.* [1] give the following formula for wax specific volume:

$$V = a + bM \ln(M/M_H) \text{ cm}^3 \text{ mol}^{-1} \quad (3)$$

where  $V$  is the specific volume ( $\text{cm}^3 \text{ mol}^{-1}$ ) of the wax,  $M$  as previously defined,  $M_H$  is the molar mass of the hydrogen atom, and the coefficients have the values  $a = 45.865 \text{ cm}^3 \text{ mol}^{-1}$ ,  $b = 0.1641 \text{ cm}^3 \text{ g}^{-1}$ . For  $M = 400 \text{ g mol}^{-1}$ , corresponding to about  $\text{C}_{30}$ , formula (3) gives  $V = 440 \text{ cm}^3 \text{ mol}^{-1}$  and a density of  $0.91 \text{ g cm}^{-3}$ . This is a typical value for a paraffin wax. More interestingly, one would expect that, since in formula (3) the specific volume is on a molar basis, the wax density could be used to determine the molecular weight. This requires that the correlation be examined for the range of  $M$  values across which it can be so used. This is detailed in Box 2.

Using the density  $\rho$ , which is the inverse of the specific volume expressed on a mass basis, we can write

$$V = M \text{ g mol}^{-1} / \rho \text{ g cm}^{-3},$$

$$M/\rho = a + bM \ln(M/M_H), \text{ or}$$

$$M(1/\rho - a \ln(M/M_H)) - b = 0, \quad (4)$$

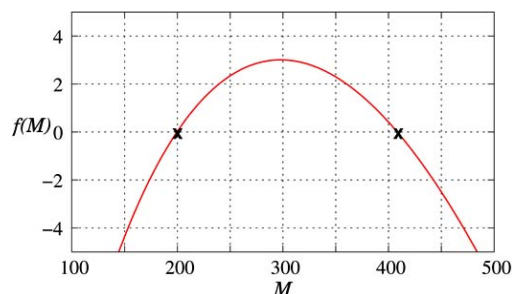
where  $a = 45.865 \text{ cm}^3 \text{ mol}^{-1}$ ,  $b = 0.1641 \text{ cm}^3 \text{ g}^{-1}$ . To examine the roots of Eq. 4 graphically we express it as

$$f(M) = M(1/\rho - a \ln(M/M_H)) - b, \quad (5)$$

where  $\rho = 0.91$  as given above.

**Box 2.**

$f(M)$  is plotted against  $M$  in Fig. (1). Evidently there are two values of  $M$  for which formula 4 holds,  $M \sim 200 \text{ g mol}^{-1}$  and  $M \sim 410 \text{ g mol}^{-1}$ , corresponding to waxes of about  $\text{C}_{14}$  and  $\text{C}_{29}$  respectively.



**Fig. (1).** On a function plot of Eq. 5 the two zeros of  $f(M)$  are marked by crosses.

We may generalize the result in Box 2 to obtain the range of densities over which formula 4 is valid. By the implicit function theorem the density may be regarded as a function of the molar mass and we may write

$$\rho(M) = M / (b + aM \ln(M/M_H)). \quad (6)$$

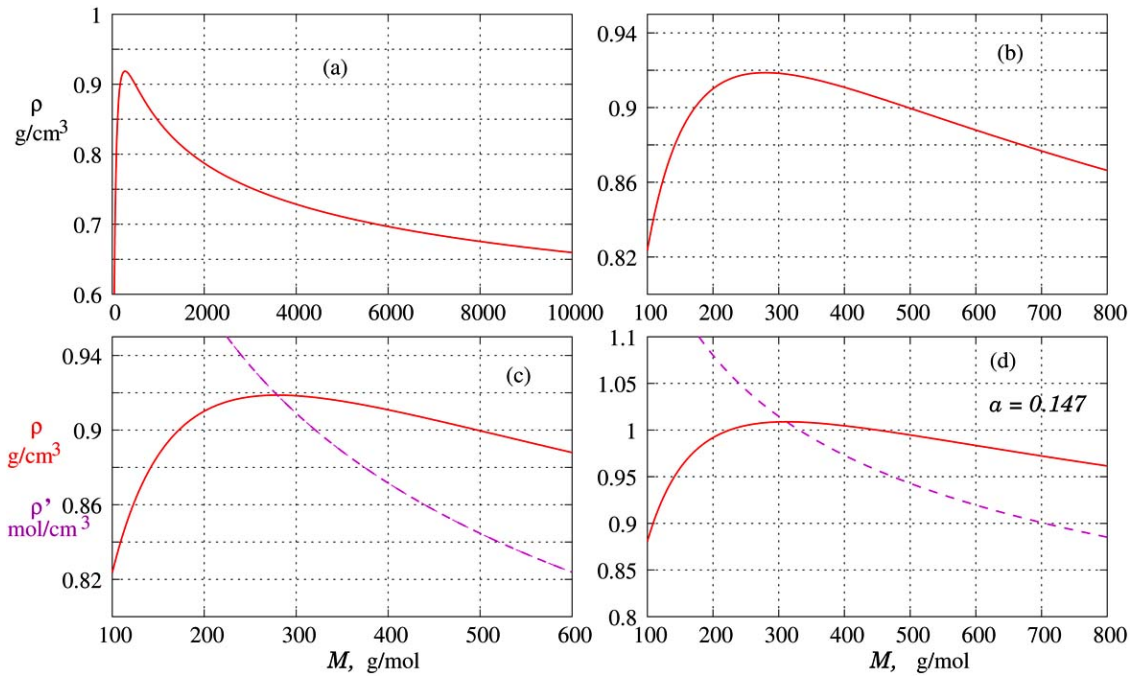


Fig. (2). Red curves: function plot of Eq. 6, dashed magenta curves: function plot of Eq. 7.

$\rho$  is plotted against  $M$  in Fig. (2a). For low densities formula 4 holds for hydrocarbons of very high and very low molecular mass. Note that formula 4 breaks down for  $\rho \gtrsim 0.92 \text{ g cm}^{-3}$ , i.e., above the maximum density for which Eq. 5 has roots. In Fig (2b) the two values of  $M$  for the given density of  $0.91 \text{ g cm}^{-3}$  can be read off more precisely. In Fig. (2c) the dotted line plots

$$\rho' = \frac{\partial \rho(M)}{\partial M} = 1 / a(M_H + \ln(M / M_H)), \quad (7)$$

thus locating the critical value of the density more precisely. Note that the parameter  $b$  does not appear in Eq. 7 thus the critical density is controlled by  $a$ . If we wish to apply formula 4 to hydrocarbons of density greater than  $0.92 \text{ g cm}^{-3}$  the parameter  $a$  must be varied. This is shown in Fig. (2d), where we see that for densities of around  $1 \text{ g cm}^{-3}$   $a$  must be adjusted downwards. We also see from Fig. (2c) and (d) that the molar density decreases as the molecular weight increases.

To extend this to asphaltenes is valid because the correlation simply links density with molecular weight, and the different deposition mechanisms described in the previous section are irrelevant. The development of a corresponding expression for asphaltenes is in Box 3.

Asphaltenes are usually more dense than water, say  $\rho = 1.2 \text{ g cm}^{-3}$ , thus we must find a lower value of the coefficient  $a$  in order to use formula 4. We have

$$V = (0.83 \text{ cm}^3 \text{ g}^{-1} \times M) \text{ cm}^3 \text{ mol}^{-1}$$

Retaining  $b = 45.865$  from the previous correlation and using  $M = 1000 \text{ gmol}^{-1}$  as a typical molar mass for asphaltenes we may estimate the parameter  $a$  using Eq. 4,

$$0.83 \times M = 45.865 + aM \ln(M), \text{ from which}$$

$$a = 0.1135. \text{ Using this in Eqs. 6 and 7 we plot the curves in Fig. (3).}$$

Box 3.

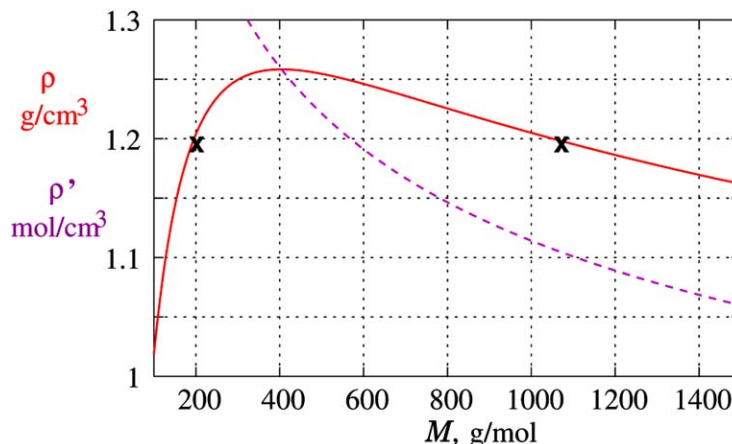


Fig. (3). Red curve: function plot of Eq. 6, dashed magenta curve: function plot of Eq. 7, with  $M = 1000 \text{ g/mol}$  and  $a = 0.1135$ , values that are appropriate for asphaltenes.

We see that the two values of  $M$  for the given density of  $1.2 \text{ g cm}^{-3}$  are  $M \sim 200 \text{ g mol}^{-1}$  and  $M \sim 1070 \text{ g mol}^{-1}$ . The higher value corresponds to asphaltenes of about  $\text{C}_{81}$ .

## 6. CONCLUDING REMARKS

This paper has examined simple expressions previously presented in the literature for the properties of pure waxes. It is hoped that extending thermodynamic relations to apply to waxes and asphaltenes, which are in general complex mixtures of hydrocarbons defined by an average molecular weight, will be of help in the very important matter of flow assurance in oil pipelines.

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