An Empirical Correlation for the Solubility of Paraffin Waxes in Base Oils

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ABSTRACT. An empirical correlation was developed for the prediction of solubility of three types of paraffin waxes in various base oils. The correlation was developed using the superposition approach and was proposed as

$$T_s = e^A (B \ln C + D)$$

The range of melting points for the three waxes was 43 to 60°C which correspond to molecular weight range of 336 to 441.

Development of the empirical correlation and the experimental data was performed as a function of: Type of wax and base oil; the concentration of the wax in the base oil; and solubility temperature.

The developed correlation shows satisfactory agreement with the experimental data with a average deviation of 5.9% and a maximum deviation of 17.9%.

1. Introduction

The deposition of paraffin waxes in crude oils and petroleum products causes severe problems in pipelining and storage. These and other problems are described by many researchers (Shock *et al.*[1], EnDean[2], Newberry[3], Al-Ahmad *et al.*[4] and Sifferman[5]. Determination of the solubility temperatures of paraffin waxes in crude oils and petroleum products are extremely essential in order to obtain the proper operating conditions to control the paraffin wax deposition for efficient and economical pumping and storage. Extensive research has been carried out to investigate the solubility behaviour of paraffin wax in pure solvents (hydrocarbons) and defined mix-

tures (Al-Ahmad *et al.*[4]). However, only a limited amount of work has been published on the solubility of waxes in undefine mixture (Berne and Work[6], Nathan[7], Gudmundsson and Bott[8]).

Solubility of paraffin wax (melting point of 43°C) in base oils with molecular weight range between 317 – 447 was studied by Al-Ahmad *et al.*[4]. Measurements were made with wax concentrations up to 30 wt%. The study resulted in an empirical correlation of the prediction of the paraffin wax solubility. Further analysis was made by Al-Ahmad *et al.*[9] to cover higher wax concentration (up to 50%). Two regimes (lower and higher than 15 wt% wax solutions) were found for solubility data where two empirical correlations have been developed.

The solubility of refined paraffin waxes in petroleum fractions was studied by Berne and Work[6]. They concluded that the solubility of any paraffin wax in any non-aromatic saturated petroleum could be determined from their empirical correlation. Further analysis of this problem was presented by Nathan[7], where solubility measurements were performed for five paraffinic waxes with melting of (66.5 – 84.5°C) in a number of solvents (including, hexane, heptane, mineral oil, crude oil (MW 220), kerosene, ... etc.). He found that solubilities of the waxes in hydrocarbon solvents can be calculated using ideal solubility relations, however, in chlorinated and oxygenated solvents large deviations from ideality was found (due to nonideal behaviour of the solvent).

The study Gudmundsson *et al.*[8] focused on measuring of a paraffin wax solubility in a commercial kerosene. They performed comparison between data and the Berne and Work correlation[6] and the ideal solubility equation used by Nathan[7]. They concluded that perfect fit between the data and both correlation and the ideal solubility equation was found for wax concentration less than 10 wt%. However, for wax concentrations between 10 and 50 wt%, the theoretical equation gave more accurate results.

Wardhaugh and Boger[10] show that the crystallization of wax in crude oils produce non-Newtonian characteristics.

McClafin and Whitfil[11] show that paraffin deposition can be prevented or greatly retarded by using chemical surfactants. Al-Fariss[12] studied the parameters which affect the formation and strength of the gel structure in pipelines. Study of flow improvers for transportation was done by Van Engelen *et al.*[13], Sifferman[5]. Burger *et al.*[14] stated that wax deposition is due to lateral transport by diffusion, shear dispersion and Brownian diffusion.

Based on previous studies[4,9] it was found essential to continue the work with various paraffin waxes having different melting points.

The objective of this study is to develop a generalized empirical correlation to determine the solubility of paraffin waxes in base oils which takes account of the type of wax as well as type of oil.

2. Experimental Apparatus

The three paraffin waxes used in this study have melting points of 43, 56 and 60°C which correspond to average molecular weights of 336, 386 and 441 respectively (measured by vapour pressure osmometry according to ASTM-D2503). The waxes were referred to as wax 1, 2 and 3 respectively. The wax solubility was measured in three base oils having molecular weights of 317, 346 and 447, which were referred to as oil 1, 2 and 3 respectively. Physical properties of the three oils are given in Table 1.

TABLE 1. Properties of base oils*.

Property	Test procedure	Oil 1	Oil 2	Oil 3
Molecular weight, gm/gm mole		317	346	447
Color	ASTM - D1500	1.5	3.0	4.5
Pour point, °C (max.)	ASTM - D97	– 18	–9	–6
Flash point (COC °C, min)	ASTM - D92	199	218	232
Mean average boiling point, °C		351	385	455
Viscosity at 40°C	ASTM - D445	18.5 / 21	55 / 61	128 / 139
Viscosity index		100	300	700
Density, gm / cm³		0.84	0.88	0.89

*Obtained from Riyadh Refinery.

To investigate the solubility behaviour of various waxes in the base oils, the cloud point was determined using cloud point test cabinet (Fig. 1). The measurement procedure was performed according to ASTM-D97 (IP15). Details of experimental set up and procedure were given by Al-Ahmad *et al.*[4]. The performed experiments included nine sets, which include the solubility of the three waxes in the three base oils. In each set wide range of wax concentrations were investigated, *i.e.*, from 5 to 30 wt%.

3. Development of the Proposed Correlation

The parameters included for the analysis of solubility data were: wax concentration and its molecular weight, and oil molecular weight. Superposition technique was implemented for the development of the correlation[15] and regression analysis was used to estimate the values of the constants in each step, leading finally to the following form :

$$T_s = e^A (B \ln C + D)$$

where: T_s is the solubility temperature in °C,

$$A = 0.434 \, M_o - 0.752 \, M_w,$$
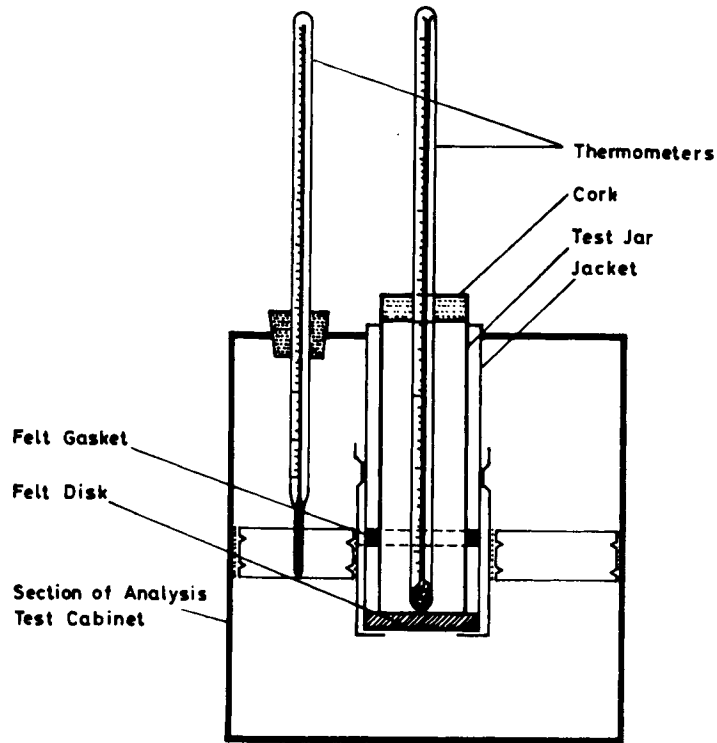
FIG. 1. Experimental set-up for solubility temperature determination (ASTM-D97).

$B = 8.0 \times 10^{-5} M_o 1.738,$

$D = 1.946 \times 10^{-10} M_o 3.632,$

C is the wax concentration in wt%,

M_o is oil molecular weight,

M_w is wax molecular weight,

4. Results and Discussion

Results of solubility measurement are shown in Fig. 2, 3 and 4 for waxes 1, 2 and 3 in base oils, 1, 2 and 3 covering wax concentrations from 5 to 30 wt%.

The results show that for the three oils, the solubility temperature increases with the increase of the wax concentration and molecular weight (Fig. 2-4). The rate of change in solubility temperature seems higher in the lower range of concentration. The rate of change in solubility temperature is particularly small above the melting point of wax itself. This shows that in the present range of concentrations, the physical properties of wax dominate those of oil, so that the wax starts to solidify near its melting point.
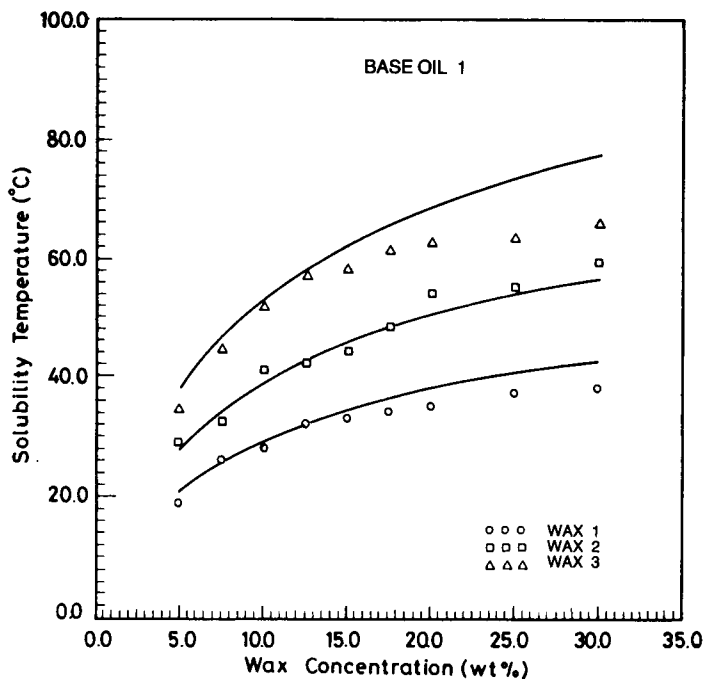
FIG. 2. Variation in solubility temperature of waxes (1, 2, 3) in oil 1, as function of wax concentration and type.
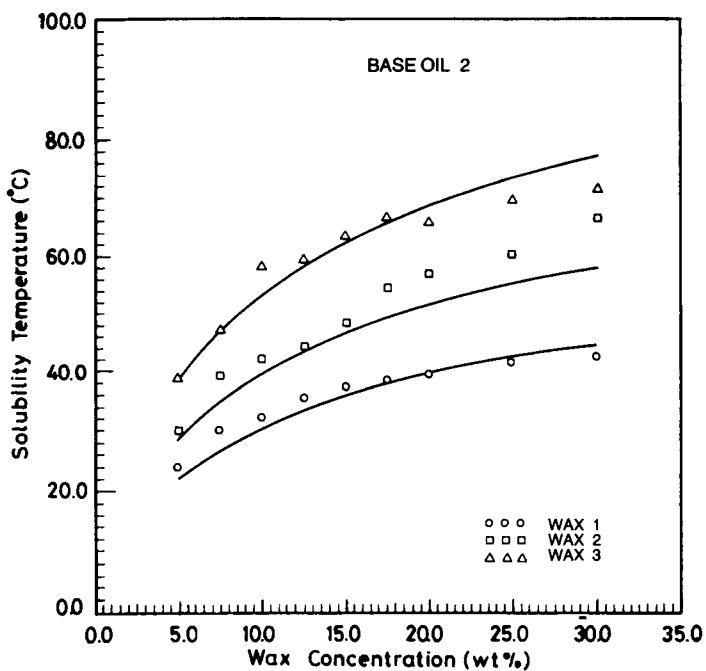

FIG. 3. Variation in solubility temperature of waxes (1, 2, 3) in oil 2, as function of wax concentration and type.
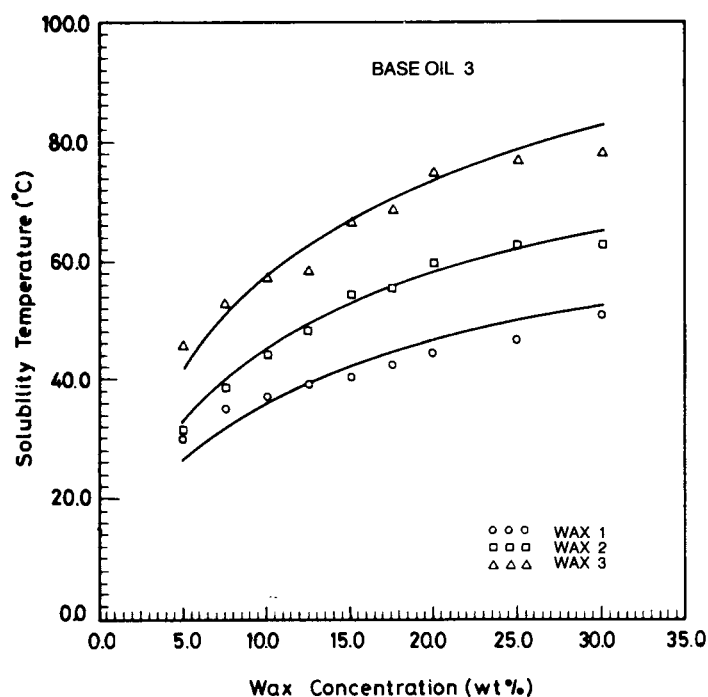
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FIG. 4. Variation in solubility temperature of waxes (1, 2, 3) in oil 3, as function of wax concentration and type.

The solubility temperature of wax increases with the increase of the molecular weights of both the oil and the wax. This behaviour is clearly displayed in Fig. 2, 3 and 4. For example, for wax 1 at concentration of 20 wt%, the solubility temperatures were 35, 39 and 44°C in oils 1, 2 and 3, respectively. Also for oil 1 at the same wax concentration, the solubility temperatures were 35, 54 and 61.5°C for waxes 1, 2 and 3, respectively. The increase in solubility temperature with the increase in wax or oil molecular weights might be due to larger molecular volume, where higher temperatures are required in order to increase the molecular spacing[9].

Assessment of the validity of the developed correlation was achieved by comparison of the measured data and the predictions by the correlations. The comparison is shown in Fig. 2-10.

In Fig. 2-4 the calculated values of solubility temperature as function of wax concentration, wax molecular weight and oil molecular weight, represented by solid curves, are plotted against the measured data. Showing reasonable accuracy of correlation predictions are as shown, obtained over the considered concentration range.

The calculated values of the solubility temperature are also plotted against the measured data in Fig. 5-7 to show the error scatter around the 45° line.
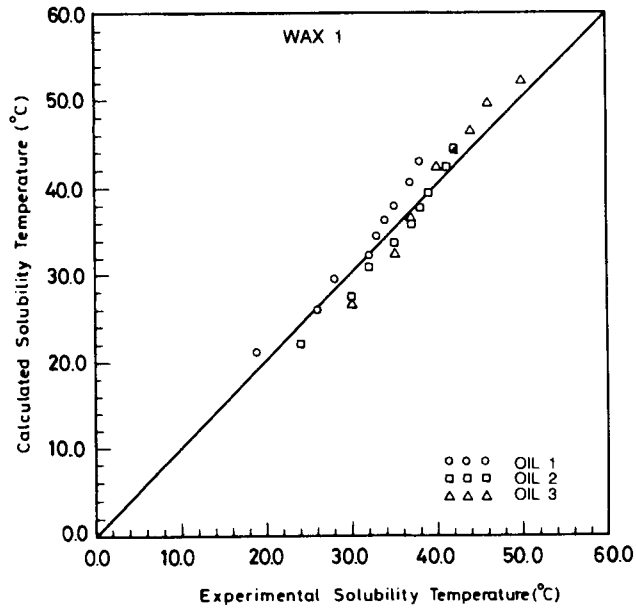
FIG. 5. Experimental and model predictions of variations solubility temperature as a function of wax concentration for wax 1 in oils 1, 2 and 3.
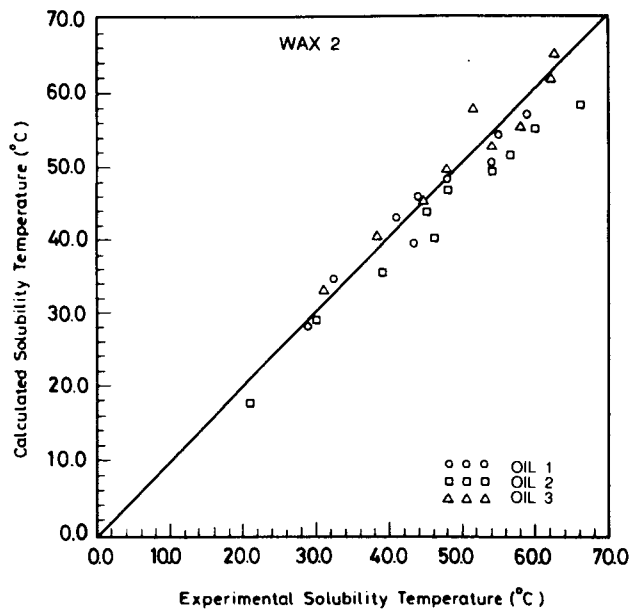

FIG. 6. Experimental and model predictions of variations solubility temperature as a function of wax concentration for wax 2 in oils 1, 2 and 3.
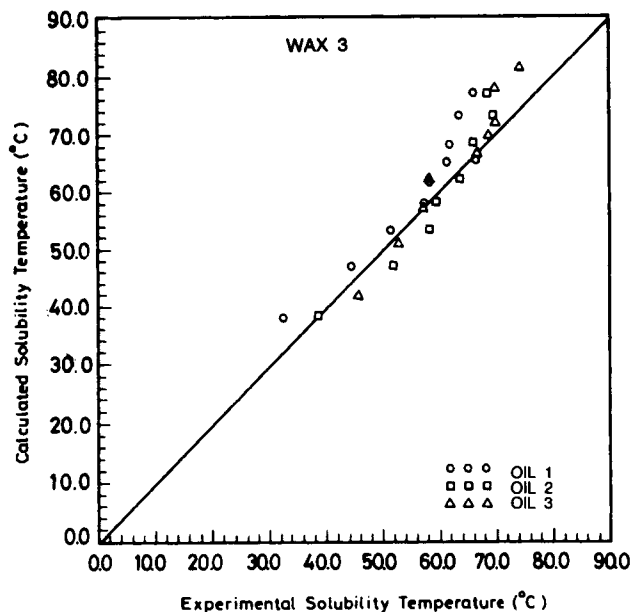
FIG. 7. Experimental and model predictions of variations solubility temperature as a function of wax concentration for wax 3 in oils 1, 2 and 3.

Analysis of data for these figures shows that the average deviation between the measured and the calculated data is only 5.9% while the maximum deviation is 17.9%. Meanwhile 82% of the whole data points have less than 10% error, which means satisfactory predictions of the proposed correlation.

Further assessment of the model was performed by comparison with the results obtained from the correlation developed in this work and that developed previously by Al-Ahmad *et al.*[4].

The correlation in Ref. [4] was developed for wax 1 (of melting point 42°C) in three base oils (oils 1, 2 and 3). The comparison is limited to wax 1 in the three oils.

The results of this test are shown in Fig. 8-10, where the solubility temperature is drawn versus the wax concentration. The figures also include the fits of both correlations.

The new model fits the data for oils 2 and 3 with average deviations of 5.9%, 4.6% and 5.2% respectively and with maximum deviation of 12.2% for the whole set of data points. The old model fits the data for the three oils with average deviations of 3.2%, 4.2% and 5.5% respectively and with maximum deviation of 16.8% for the whole set of data points. Although the predictions of both models are satisfactory, and comparable the new model is superior and general, because it includes the effect of the type of wax, while the old model is limited to single type of wax.
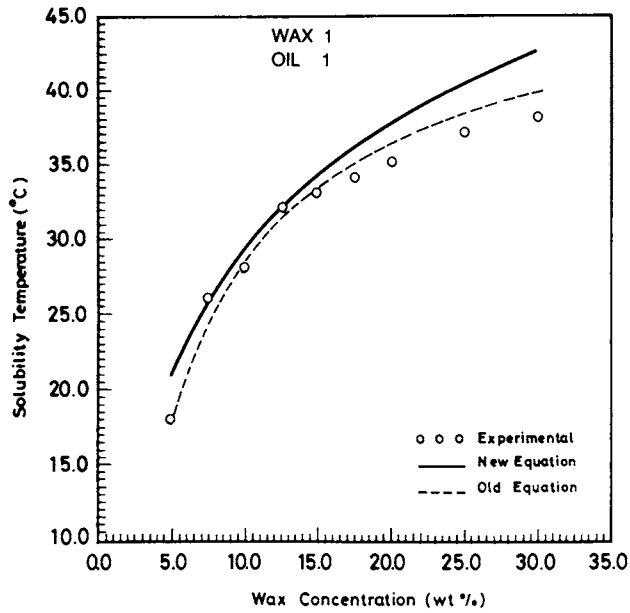
FIG. 8. Comparison of prediction of solubility temperature as a function of wax concentration for wax 1 in oil 1 by the new and old[4] models.

FIG. 9. Comparison of prediction of solubility temperature as a function of wax concentration for wax 1 in oil 2 by the new and old[4] models.

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Fig. 10. Comparison of prediction of solubility temperature as a function of wax concentration for wax 1 in oil 3 by the new and old[4] models.
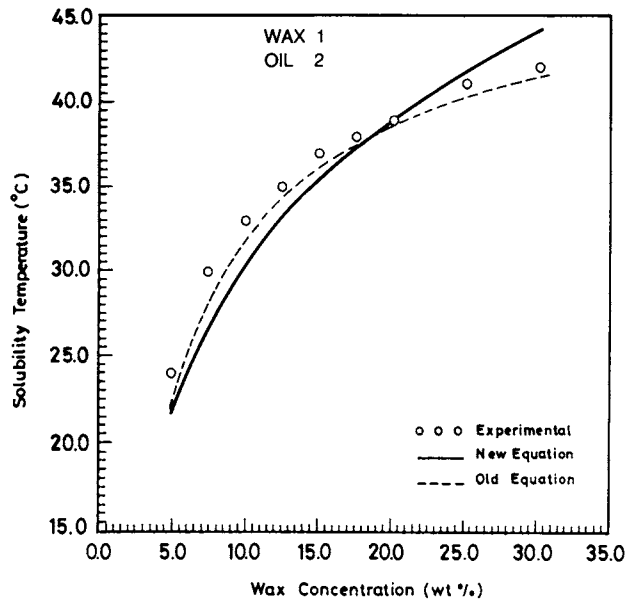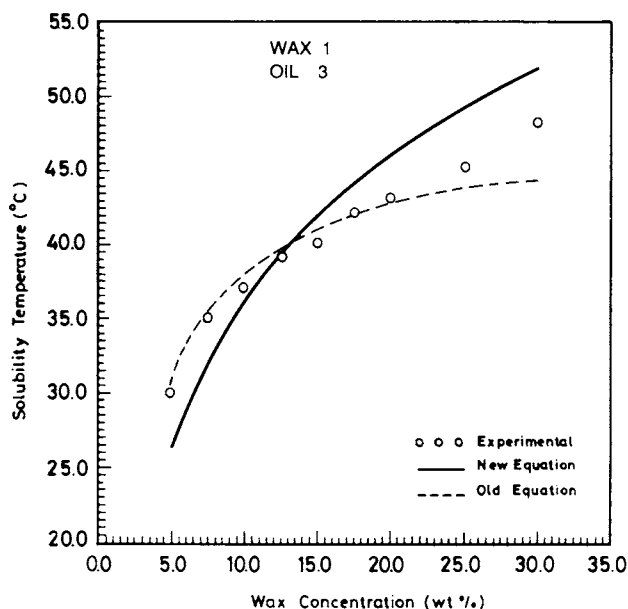
Attempts have been made to test the model with data from literature. When compared with Gudmundsson[8] data, the model gave conservative predictions. This is because of the difference in solvent used, where Gudmundsson used kerosene. Other's data were completely unsuitable for comparison, because of lack of experimental data and parameters to fit in our model.

5. Conclusion

A single satisfactory empirical correlation was developed for the determination of solubility temperature of various paraffin waxes, with wide range of concentrations, in various base oils. The developed correlation is based on experimental measurement using superposition approach.

The proposed correlation gives an overall average obsolute deviation of 5.9% and maximum absolute deviation of 17.9% from the experimental measurement of solubility for three types of paraffin waxes in three types of solvents (base oils). It can predict the solubility temperature in terms of wax molecular weight, wax concentration and solvent molecular weight. .

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معـادلـة تجريبيـة لذوبـانية الشمـوع البـرافينية في الـزيوت الأساسيـة

مالك الأحمد ، و طارق الفارس ، و محمد أبشر و هشام التوني
قسم الهندسة الكيميائية ، كلية الهندسة ، جامعة الملك سعود
الريـــــاض – المملكة العربية السعودية

المستخلص .   تم تطوير معادلة رياضية تصف ذوبانية ثلاثة أنواع من الشموع البرافينية
في مجموعة من الزيوت الأساسية . وقد تم تطوير المعادلة باستخدام تقنية النقل الفائق
(Superposition) مع الشكل التالي

$$T_s = e^A \, (b \ln C + D)$$

والمعادلة تغطي شموع ذات ذوبانية من ٤٣ حتى ٦٠ درجة مئوية مكافأة لوزن جزيئي
يتراوح من ٣٣٦ حتى ٤٤١ . والمعادلة المستخلصة تحوي نوع الشمع ونوع الزيت
الأساسيين ، وكذلك تركيز الشمع في الزيت وذوبانية الشمع . وقد تمت مقارنة المعادلة مع
النتائج المعملية ، وكان متوسط الخطأ ٥٫٩ بالمائة وأعلى خطأ هو ١٧٫٩ بالمائة .