

## NEW MULTI-SOLID THERMODYNAMIC MODEL FOR IMPROVED CLOUD POINT PREDICTION OF WAXY CRUDES

\*A. Adeyanju Olusiji and O. Oyekunle Layioye

*Chemical Engineering Department, University of Lagos, Lagos, Nigeria.*

*\*corresponding author: e-mail- [sijideyanju@yahoo.com](mailto:sijideyanju@yahoo.com)*

Received July 10, 2010, Accepted November 15, 2010

---

### Abstract

A thermodynamic framework is developed for calculating the cloud point also known as WAT (Wax Appearance Temperature) or WDT (Wax Disappearance Temperature) in petroleum mixtures. The method involves the use of experimental data to generate a correction's correlation for the liquid molar volume shift parameter during liquid-solid equilibrium. Application of the method to the five ternary systems with the 72 equilibrium data points gives an AAD (Absolute Average Deviation) between 0.843 – 0.979. Also, the method gives a better performance in re-producing the experimental cloud point for real petroleum fluids. Its use is simple, accurate and has wide range of validity.

**Keywords:** Cloud point; Molar volume shift parameter; Multi-solid model; Stability analysis; Thermodynamic equilibrium.

---

### 1. Introduction

The oil industry has experienced a series of wax-precipitation problems as evidenced in wax deposition in producing sands, well bores and in the surface transmission lines. Wax deposition is most likely to occur in the well bore, in the surface transmission lines as well as dehydration difficulties with slightly waxy crude oils. However, wax deposits in the reservoir sand may result in serious production losses that are difficult to overcome. The cloud point, the temperature at which wax begins to precipitate also known as WAT (Wax Appearance Temperature) or WDT (Wax Disappearance Temperature) is essential in determining which crudes will form deposits under field conditions as well as for establishing the minimum required dehydration temperature for avoiding wax/oil/water rag layer detrimental to water settling.

It is an important and serious problem that often occurs in oil production operations as the production goes on, in which the operating condition falls below the cloud point temperature and pressure. The effect of pressure in comparison with the effect of temperature is not so much to be taken into consideration. So, only the effect of temperature has been evaluated.

In this work for the first time, a developed volume correction was applied to multi-solid model for the prediction of Wax Disappearance Temperature (WDT), which is also equal to the WAT (Wax Appearance Temperature). The predictive UNIQUAC model was used to model the non ideality of the solid (wax) phase and the liquid phase in equilibrium. For validating the proposed model some experimental data have been used which were for 72 equilibrium data points. Also Experimental determined WAT (Wax Appearance Temperature) from separator liquid in the literature <sup>[1]</sup> were used for the validation.

### 2. Experimental Data

In this work five ternary systems, which include C<sub>14</sub>-C<sub>15</sub>-C<sub>16</sub> (ternary 1), C<sub>15</sub>-C<sub>16</sub>-C<sub>17</sub> (ternary 2), C<sub>16</sub>-C<sub>17</sub>-C<sub>18</sub> (ternary 3), C<sub>18</sub>-C<sub>19</sub>-C<sub>20</sub> (ternary 4) and C<sub>19</sub>-C<sub>20</sub>-C<sub>21</sub> (ternary 5) have been used <sup>[2]</sup>. These systems contain 72 mixtures that the amount of WDT (Wax Disappearance Temperature) in Kelvin (K) at atmospheric pressure and composition of mixtures have been reported in Table 1-4.

Table 1 Experimental WDT (K) data for C<sub>14</sub>-C<sub>15</sub>-C<sub>16</sub> ternary system 1

Mixture	Composition (molar %)			Exp. WDT (K)
	C <sub>14</sub>	C <sub>15</sub>	C <sub>16</sub>	
1	5	10	85	286.5
2	10	15	75	285.2
3	15	10	75	284.7
4	12	16	72	285.5
5	14	10	76	284.1
6	35	25	40	282.2
7	25	20	55	282.4
8	20	10	70	285.1
9	34	14	52	284.3
10	23	16	59	284.9
11	45	30	25	281.5
12	42	52	6	283.1
13	50	23	27	282.7
14	75	13	12	281.5

Table 2 Experimental WDT (K) data for C<sub>15</sub>-C<sub>16</sub>-C<sub>17</sub> ternary system 2

Mixture	Composition (molar %)			Exp. WDT (K)
	C <sub>15</sub>	C <sub>16</sub>	C <sub>17</sub>	
1	5	5	90	299.7
2	7	8	85	298.3
3	12	10	78	297.8
4	20	15	65	297.3
5	13	16	71	298.4
6	15	10	75	298.3
7	20	25	55	295.4
8	40	45	15	293.1
9	32	17	49	294.3
10	21	18	61	295.5
11	12	56	32	293.7
12	15	70	15	291.4
13	45	30	25	292.6
14	25	40	35	292.8
15	85	5	10	289.6
16	5	80	15	290.3

Table 3 Experimental WDT (K) data for C<sub>16</sub>-C<sub>17</sub>-C<sub>18</sub> ternary system 3

Mixture	Composition (% mol.)			Exp. WDT (K)
	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	
1	5	7	88	302.4
2	10	12	78	301.7
3	15	10	75	300.2
4	12	9	79	301.9
5	34	23	43	298.6
6	45	13	42	296.9
7	50	23	27	296.5
8	25	50	25	297.4
9	21	70	9	297.1
10	15	60	25	298.2
11	23	17	60	299.1
12	41	18	41	297.3
13	80	16	4	295.3
14	57	32	11	296.5

Table 4 Experimental WDT (K) data for C<sub>18</sub>-C<sub>19</sub>-C<sub>20</sub> ternary system 4

Mixture	Composition (% mol.)			Exp. WDT (K)
	C <sub>16</sub>	C <sub>17</sub>	C <sub>18</sub>	
1	10	10	80	309.4
2	12	9	79	307.8
3	16	23	61	306.3
4	20	25	55	304.5
5	18	45	37	304.1
6	14	70	16	302.4
7	10	80	10	303.1
8	45	23	32	301.8
9	40	45	15	302.4
10	60	30	10	303.5
11	34	35	31	305.5
12	12	70	18	306.3

Table 5 Experimental WDT (K) data for C<sub>19</sub>-C<sub>20</sub>-C<sub>21</sub> ternary system 5

Mixture	Composition (% mol.)			Exp. WDT (K)
	C <sub>19</sub>	C <sub>20</sub>	C <sub>21</sub>	
1	6	12	82	311.9
2	10	15	75	311.4
3	12	12	76	311.6
4	20	25	55	309.3
5	25	15	60	310.4
6	30	40	30	307.7
7	40	45	15	305.2
8	21	17	62	309.4
9	34	12	54	307.5
10	60	30	10	307.1
11	23	21	56	308.7
12	40	40	20	308.3
13	45	41	14	304.9
14	70	15	15	302.2
15	20	70	10	305.8
16	10	80	10	306.7

## 2.1 The Multi-Solid model based on modified volume correction approach

The solid saturation,  $S$ , can be expressed as

$$S = \frac{f_s V_s}{[f_s V_s + (1 - f_s) V_L]} \quad (1)$$

$$\frac{V_s}{V_T} = \frac{f_s V_s}{[f_s V_s + (1 - f_s) V_L]} \quad (2)$$

$$\frac{V_T - V_L}{V_T} = \frac{f_s (V_T - V_L)}{[f_s (V_T - V_L) + (1 - f_s) V_L]} \quad (3)$$

Also, from the material balance

$$V_T = (1 - f_s) V_L + f_s (V_T - V_L) \quad (4)$$

From experimental value knowledge of  $V_T$ , and solving equ [3] and [4] simultaneously, gives the values of  $V_L$  and  $f_s$  and this enable the values of  $V_s$  to be determined, and then  $V_s = V_T - V_L$ .

Generally the temperature difference between the WAT and the gel point will not exceed 30°C. It is known that the increase of (density of liquid (oil)/ density of solid (wax)) at this temperature range will not exceed 2% [3], so the (density of liquid (oil)/ density of solid (wax)) can be treated as a constant. Then the weight fraction of solid (wax) and Liquid (oil) can be determined. These were used directly in the matching procedure of the experimental results to the predicted results.

Both the phase behaviour properties ( $f_s$ ,  $x_i$  and  $y_i$ ) and the volumetric properties ( $V_L$  and  $V_s$ ) were used in the matching procedure for characterization of the pseudo-component parameter for better volumetric prediction [4]. During wax precipitation defining the shift parameter as  $q_i = (V_{iL,E} - V_{iL,C})$ ,

The proposed corrective shift parameters  $q_i = (V_{iL,E} - V_{iL,C})$  for pure n-alkanes, and n-alkyl-cyclohexanes acknowledged to be responsible [5,19] for the wax precipitation in petroleum fluid at a temperature below the Wax Appearance Temperature (WAT) of these well defined components when plotted against the Pseudo-molecular weight of the Liquid components, M. The pseudo molecular weight is defined as:

$$M = \sum_{i=1}^c M_i x_i \tag{5} \text{ and,}$$

$$q = \sum_{i=1}^c q_i \tag{6}$$

Then the molar volume shift parameter q, at different temperature was observed to follow a power function in M as,

$$q = 1 - a / M^b \tag{7}$$

Where a, and b are positive correlation coefficients. The molar volume shift-parameter correlation, Equ. 7 was fit to the plot of q against M and the correlation correlations, a, and b, were determined with regression analysis. The coefficients are given in Table 6.

Table 6 Correlation coefficient of different hydrocarbon

Component Type	Correlation Coefficient	
	a	b
n-alkanes	2.158	0.12182
n-alkyl-cyclohexanes	2.804	0.18874

For precipitating components, the thermodynamic equilibrium can be written as At equilibrium (i.e. at WAT or WDT)

$$f_i^z(P, T, z_i) = f_{i,pure}^L(P, T) \gamma_i^L x_i^L \tag{8} \text{ thus}$$

$$f_{i,pure}^L(P, T) \gamma_i^L x_i^L - f_{i,pure}^S(P, T) > 0 \tag{9}$$

This equals

$$\gamma_i^L x_i^L - \frac{f_{i,pure}^S(P, T)}{f_{i,pure}^L(P, T)} > 0 \tag{10}$$

Applying the molar volume shift parameter, q

The new activity coefficient,  $\gamma_i^*$  can now be written as,

$$\gamma_i^* = \gamma_i^L \exp\left(\frac{-q_i P}{RT}\right) \tag{11}$$

Then equ. [11] becomes,

$$\gamma_i^* \exp\left(\frac{-q_i P}{RT}\right) x_i^L - \frac{f_{i,pure}^S(P, T)}{f_{i,pure}^L(P, T)} > 0 \tag{12} \text{ and,}$$

$$\frac{f_{i,pure}^S(P, T)}{f_{i,pure}^L(P, T)} = \exp\left[\frac{\Delta h_i^f}{RT_i^f} \left(1 - \frac{T_i^f}{T}\right) - \frac{\Delta C_{pi}}{R} \left(1 - \frac{T_i^f}{T}\right) - \frac{\Delta C_{pi}}{R} \ln \frac{T_i^f}{T}\right] + \int_{P_i}^P \Delta v_i dP \tag{13}$$

Neglecting Poynting correction term, that is, last term on the right side of equ. (1), we obtain the expression for the pure solid component fugacity:

$$\frac{f_{i,pure}^S(P,T)}{f_{i,pure}^L(P,T)} = \exp \left[ \frac{\Delta h_i^f}{RT_i^f} \left( 1 - \frac{T_i^f}{T} \right) - \frac{\Delta C_{pi}}{R} \left( 1 - \frac{T_i^f}{T} \right) - \frac{\Delta C_{pi}}{R} \ln \frac{T_i^f}{T} \right] \quad [14]$$

The fusion and transitional properties used are as presented by "O. Adeyanju and L. Oyekunle, unpublished observations".

### Predictive UNIQUAC activity coefficient model

$$\ln \gamma_i^s = \ln \left( \frac{\Phi_i}{x_i^s} \right) + 1 - \frac{\Phi_i}{x_i^s} - \frac{Z}{2} q_i \left( \ln \left( \frac{\Phi_i}{\theta_i} \right) + 1 - \frac{\Phi_i}{\theta_i} \right) + q_i - q_i \ln \left( \sum_{j=1}^n \theta_j \tau_{ji} \right) - q_i \sum_{j=1}^n \frac{\theta_j \tau_{ij}}{\sum_{k=1}^m \theta_k \tau_{kj}} \quad [15]$$

$$\tau_{ji} = \exp \left( - \frac{\lambda_{ji} - \lambda_{ii}}{q_i RT} \right) \quad [16]$$

In this equation, the  $\lambda_{ji}$  is the interaction energy [14,15]. Similar to UNIFAC model,  $\theta_i$  and  $\Phi_i$  are calculated by (17) and (18). The correlations for the r and q values with the n-alkane chain length are:

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \quad [17]$$

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \quad [18]$$

$$r_i = 0.0148C_{ni} + 0.00996 \quad [19]$$

$$q_i = 0.0185C_{ni} - 0.0211 \quad [20]$$

The interaction energy,  $\lambda_{ii}$  is estimated from the heat of sublimation of pure orthorhombic crystal,

$$\lambda_{ii} = - \frac{2}{Z} (\Delta H_{subi} - RT) \quad [21]$$

With Z being the coordination number. For orthorhombic crystals, the value of 6 is considered for Z. the interaction energy between two non identical molecules is given by:

$$\lambda_{ij} = \lambda_{ji} = \lambda_{jj} \quad [22]$$

where j is the n-alkane with the shorter chain of the pair ij. Heat of sublimation can be calculated by:

$$\Delta H_i^{sub} = \Delta H_i^{vap} + \Delta H_i^f + \Delta H_i^{tr} \quad [23]$$

Where vapourization enthalpy is assessed using the PERT2 correlation by Morgan and Kobayashi [6]. The critical properties needed in Morgan and Kobayashi correlations can be calculated by the following correlations:

$$\Delta H_{tr} = \Delta H_{tot} - \Delta H_f \quad [24]$$

$$\Delta H_{tot} = 3.7791C_n - 12.654 \quad [25]$$

By using stability analysis calculations, and material balance for precipitating components<sup>[7-14]</sup>, the mole fraction and composition of solid phase can be determined. The algorithm and material balance equations have been reported in the literatures<sup>[16,17,18]</sup>.

### 3. Results and discussion

The plots of Experimental WDT (Wax Disappearance Temperature) also known as cloud point against the calculated cloud point for the five ternary system are shown in figs. 1-5. The figures show that the developed technique gives a better prediction of the experimental data judging from the closeness of the experimental and calculated cloud point for each mixture. These were confirmed by low values of Average Absolute Deviation (AAD) calculated for the five ternary systems.

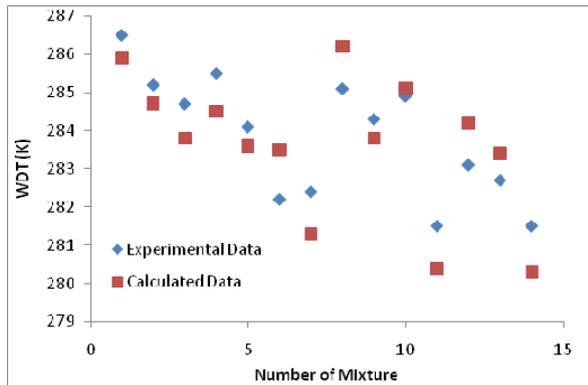


Fig. 1 Comparison of the experimental data and calculated results for ternary 1 ( $C_{14}$ - $C_{15}$ - $C_{16}$ )

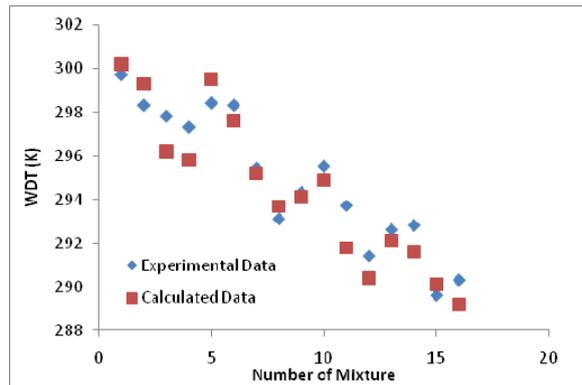


Fig. 2 Comparison of the experimental data and calculated results for ternary 2 ( $C_{15}$ - $C_{16}$ - $C_{17}$ )

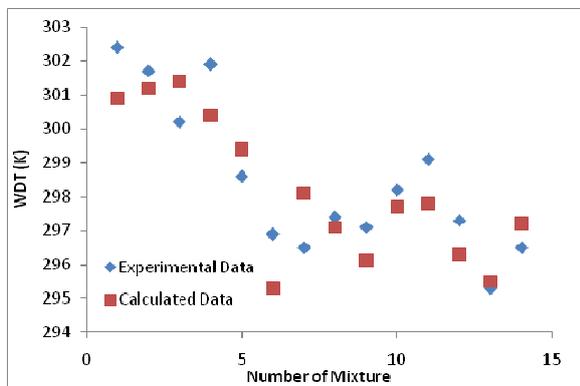


Fig.3 Comparison of the experimental data and calculated results for ternary 3 ( $C_{16}$ - $C_{17}$ - $C_{18}$ )

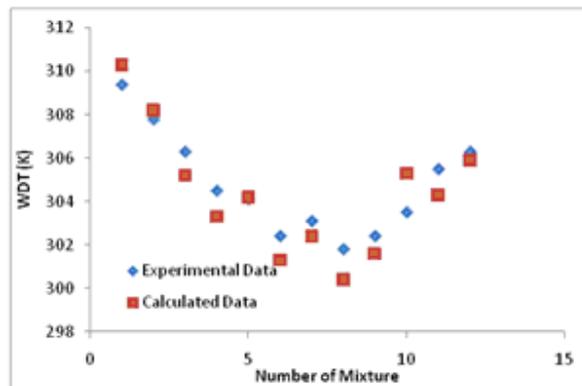


Fig. 4 Comparison of the experimental data and calculated results for ternary 4 ( $C_{18}$ - $C_{19}$ - $C_{20}$ )

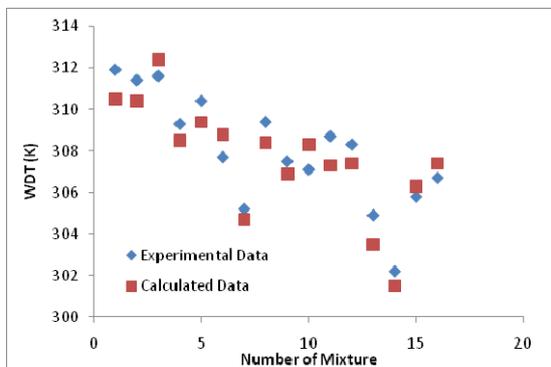


Fig. 5 Comparison of the experimental data and calculated results for ternary 5 ( $C_{19}$ - $C_{20}$ - $C_{21}$ )

The Average Absolute Deviations defined as,

$$AAD = \left( \frac{1}{n} \right) \sum_{i=1}^n |Cal_i - Exp_i|$$

For each of the ternary system have been reported in Table 8, the results show that using the proposed corrective shift parameter with the multi-solid model to model the equilibrium point gives better results in comparison with the normal multi-solid model without the corrections.

Table 8 Average Absolute Deviations (AAD) values

Ternary system	1	2	3	4	5
No. of data points	14	16	14	12	16
AAD of solid model with proposed correction	0.843	0.888	0.979	0.925	0.938
AAD of solid model without proposed correction	1.34	1.58	1.89	2.03	1.26

An application of the proposed method to real petroleum fluids coded Oil 1, 2, 5 and 8 from the literature also gives better results than the normal method without the corrective method. This is shown in Table 9,

Table 9 Experimental and calculated cloud point temperatures

Oil no.	Un-corrected WAT, (K)	Corrected WAT, (K)	Experimental WAT, (K)
1	306.2	304.67	304.15
2	310.1	311.87	312.15
5	316.9	315.02	313.15
8	308.3	309.46	311.15

A corrective shift parameter had been proposed for the determination of cloud point (WAT or WDT) for components in petroleum fluid. The method is based on the experimental supported theory and tested with experimental data. Application of this method to some real petroleum mixtures confirmed the superiority of this method to the normal method.

#### 4. Conclusion

New thermodynamic correction method for the Prediction of Cloud point in petroleum systems has been proposed. The method when validated with five petroleum systems showed that the method predicts the Cloud Point to a higher degree of accuracy than the existing thermodynamic model judging by the lower value of Average Absolute Deviation from the experimental results. The application of the new proposed model is simple and need only few parameters which are dependent on the petroleum system. Also, the method gives a better performance in reproducing the experimental cloud point for real petroleum fluids.

#### Nomenclature

a, b	shift parameter correlation coefficient	T	temperature
C	number of component	T <sub>c</sub>	critical Temperature
C <sub>n</sub>	carbon number	S	solid mole fraction
C <sub>p</sub>	specific heat capacity	V	molar Volume
D	density	V <sub>c</sub>	critical volume
F	fugacity	V <sub>S</sub>	solid volume fraction
H	enthalpy	V <sub>T</sub>	mixture molar volume
I	counter of component	V <sub>L</sub>	liquid volume fraction
M	molecular weight	V <sub>IL,C</sub>	calculated liquid molar volume
M <sub>i</sub>	pseudo molecular weight of Liquid components/pseudo components	V <sub>IL,E</sub>	experimentally determined liquid molar volume
N	total number of components and pseudo components	*	modified liquid molar volume
P	pressure	V <sub>I</sub>	
P <sub>c</sub>	critical pressure	X	liquid mole fraction
		Z	coordination number

Q	dimensionless molar volume parameter	$Z_f$	feed composition
R	gas universal constant		

### Greek letters

$\Delta$	variation	$\varphi$	volume fraction
$\gamma$	activity coefficient	$\Phi$	Segment fraction
$\delta$	solubility parameter	$\phi$	fugacity coefficient
$\bar{\delta}$	average solubility parameter		

### References

- [1] Lira-Galeana and Firoozabadi A. and Prausnitz J.M., "Thermodynamics of Wax Precipitation in Petroleum Mixtures", *AIChE Journal*, January 1996, Vol 42, No. 1, 239-247.
- [2] Metivaud, V, Rajabalee, F. Oonk, H.A.J, Mondieig, D. and Haget Y. "Complete Determination of the Solid (RI)-Liquid Equilibria of four Consecutive n-alkanes Ternary Systems in the Range of C<sub>14</sub>H<sub>30</sub>-C<sub>21</sub>H<sub>44</sub> Using only Binary Data," *Canada j. Chem.*, Vol. 77, 1999, 332-339.
- [3] Hongying L. and Jinjug, Z., "A Generalized model for Predicting Non-newtonian Viscosity of Waxy Crudes as a function of Temperature and Precipitated Wax," *Fuel* 82 (2003), 1387-1397.
- [4] Isehunwa O. S. and Falade G. K. : "Improved Characterization of Heptanes-Plus Fractions of Light Crudes" SPE 111918, Presented at the 31<sup>st</sup> Nigeria Annual SPE International Conference and Exhibition, held in Abuja, Nigeria, 6-8 August, 2007.
- [5] Firoozabadi, A., "Reservoir-Fluid Phase Behaviour and Volumetric Prediction with Equation of State," *J. Pet. Tech*, 397, Apr. 1988.
- [6] Morgan, D.L. and Kobayashi, R., "Extension of Pitzer CSP Models for Vapour Pressures and Heat of Vapourization to Long Chain Hydrocarbons," *Fluid Phase Equilib.*, vol. 94, 1984, 51-87.
- [7] Broadhurst, M. G. *J Res. Nat. Bur. Stand.*, 66A (1962), 241.
- [8] Marano, J.J., Holder, G.D., *Ind. Eng. Chem Res.*, 36 (1997), 1895.
- [9] Pan, H., Firoozabadi, A., Fotland, P., *SPE Production & Facilities*, November (1997) 250.
- [10] Pedersen K.S., Skovborg P., Ronningsen H.P., *Energy and Fuels*, 5 (1991) 924.
- [11] Cavett R.H. "Physical Data for Distillation Calculation -Vapour\_Liquid Equilibrium," *Proc. 27<sup>th</sup> API Meeting*, San Francisco, CA (1964).
- [12] Lee B.I. and Kesler M.G.: "A Generalized Thermodynamic Correction Based on Three Parameter Corresponding States," *AIChE J* (1995).
- [13] Pan Huanquan and Firoozabadi Abbas " Pressure and Composition Effect on Wax Precipitation: Experimental Data and Model Results" (1997), SPE 36740 First presented at the SPE 1996 Annual Technical Conference and Exhibition held in Denver, 6-9 October.
- [14] Coutinho, J.A.P., "Predictive Local Composition Model: NRLT and UNIQUAC and their Application to Model Solid-Liquid of n-alkane," *Fluid Phase Equilib.*, Vol. 158-160, 1999, 447-457.
- [15] Coutinho, J.A.P., "Predictive UNIQUAC: A New Model for the Description of Multi-phase Solid-Liquid Equilibria in Complex Hydrocarbon Mixtures," *Ind. Eng. Chem. Res.*, Vol. 37, 1998, 4870-4875.
- [16] Bishop, A., and Philip, P., "Prediction of Potential Wax Deposition Problems During Petroleum Production," *Internal Rep Organic Geochemistry Group*, University of Oklahoma, Normal, 1994.
- [17] Chueh, P.L. and Prausnitz, " Vapour-Liquid Equilibria at High Pressures: Calculation of Partial Molar in Non-Polar Liquid Mixtures," *AIChE J.* 13(6), 1967, 1099.
- [18] Erickson, D.D., Niesen, V.G., and Brown, T.S.: "Thermodynamic Measurements and Prediction of Paraffin Precipitation in Crude Oil," Paper SPE 26604, Tech. Conf. and Exhibit of the Soc. Of Petroleum Engineers, Houston, Oct 3-6, 1993.
- [19] Riazi M.R. and Al-Sahhaf T.A.. "Physical Properties of n-Alkanes and n-AlkylHydrocarbons' Application to Petroleum Mixtures" *Ind. Eng. Chem. Res.*(1995), 34, 41-45.