

A New Correlation for Prediction of Wax Disappearance Temperature of Hydrocarbon Mixtures at Various Pressures

Gholamreza Moradi *¹, Majid Mohadesi¹ and Mojtaba Mokhtari²

¹ Chemical Engineering Department, Faculty of Engineering, Razi University, Kermanshah, Iran

² Chemical and Petroleum Engineering Department, Sharif University of Technology, Tehran, Iran

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Abstract

Wax precipitate is one of the most serious issues the oil industry is currently facing, since it can cause some troubles such as increasing of the pressure losses in pipe which subsequently increases the required power for pumpage. To remove this problem, prediction of wax disappearance temperature (WDT) seems necessary. In this study, the pressure influence on the wax disappearance temperature in multi-component mixtures has been surveyed and some correlations have been proposed to predict the wax disappearance temperature instead of using thermodynamic models. The accuracies of the correlations as AARD are 0.30 %, 0.27 % and 0.68 % for binary, ternary and multi-component mixtures, respectively.

Keywords: Wax precipitation, Thermodynamic model, Wax disappearance temperature (WDT)

Introduction

Heavy alkane compounds which have been solved in light compounds under specific operating conditions (temperature, pressure and composition) might precipitate as a wax solid phase at the other conditions. Wax precipitation occurs when temperature decreases to the cloud point temperature. Formation of solid layers on the pipe-line walls increases the pressure drop and therefore the power required for pumpage will increase [1].

Changes in temperature, pressure and oil-gas content might create wax. In designing oil-gas processes, thermodynamic models are used to predict wax appearance temperature (WAT) or wax disappearance temperature (WDT) and also the amount of wax [2].

Various thermodynamic models have been used to predict wax appearance temperature and the amount of precipitated wax in atmospheric pressure. Won [3,4] proposed two modified regular solution for wax precipitation. Also Hansen et al. [5] proposed a modified regular solution, which used Flory's theory of multi-component

polymer solutions [6] for activity coefficient of liquid phase. Furthermore Pedersen et al. [7] developed the Won modified model [3] for WAT calculations. Lira-Galeana et al. [8] presented a multi solid phase for wax precipitation. They assumed each solid phase was a pure component. Vafaie-Sefti et al. [9] applied multi-solid phase model (originally developed by Lira-Galeana et al. [8]) to predict the equilibrium phase in the oil mixtures.

Liquid and gas phases were described by using Peng-Robinson EOS [10]. Also Dalirsefat and Feyzi [11] used modified multi-solid phase thermodynamic model (based Lira-Galeana et al. model [8]) for prediction WAT and wax precipitate amount. They utilized Modified Peng-Robinson (MPR) equation [12] for calculating the fugacity of liquid and gas phases. Coutinho [13] modified a predictive UNIQUAC model (originally developed by Abrams and Prausnitz [14]) for non-ideality of solid and liquid equilibrium.

Also he presented a predictive model [15] for wax formation in jet and diesel fuel.

He used modified UNIFAC for liquid phase and UNIQUAC equation for solid phase [15]. Coutinho et al. [16] and also Coutinho and Ruffier-Me'ray [17] studied wax deposition using experimental and thermodynamics methods.

They used the predictive UNIQUAC model for modeling wax formation in hydrocarbon liquids [16]. Bhat and Mehrotra [18] measured and predicted phase behavior of wax-solvent mixtures using Flory free-volume model [13] for liquid phase and predictive UNIQUAC model [19] for solid phase. Zuo et al. [2] developed solid-solution model to predict wax in crude oils and gas condensates. Esmailzadeh et al. [1] investigated various activity coefficient models and showed that predictive Wilson model [20] is appropriate to explain the ideal behavior of the solid phase (prediction of wax precipitate in the atmospheric pressure). Ji et al. [21] succeeded to achieve wax disappearance temperature for binary and multi systems by applying UNIQUAC thermodynamic model. They estimated firstly thermodynamic properties of the normal paraffins for their calculations.

Moreover, Ghanaei et al. [22] have recently investigated a new predictive thermodynamic model for wax formation under high-pressure conditions. By using various thermodynamic models, they achieved WDT for C_{14} - C_{15} and C_{14} - C_{16} mixtures at various pressures (0.1-100MPa) and they compared their results with the literature data [23].

In this study, some correlations have been obtained to predict WDT of binary mixtures through using the experimental data reported in the literature [23] and then these correlations have been extended to multi-component mixtures. Without any need to perform thermodynamic calculations and by using the achieved equations, WDT can be estimated for mixtures at different pressures. The predicted results illustrate high accuracy of the correlations.

1- Technical development

1-1- WDT function

• Pressure and molecular weight dependency

Ghanaei et al. [22] succeeded to gain WDT for C_{14} - C_{15} and C_{14} - C_{16} binary mixtures at pressures between 0.1 and 100MPa using various thermodynamic models and complex thermodynamic calculations. Their results showed good agreement with experimental data in literature [23].

By taking into consideration the data of literature [23] wax disappearance temperature for the pure components (C_{14} , C_{15} and C_{16}) in various pressures (0.1-100MPa) showed that WDT increases almost linearly by increasing pressure (Fig. 1).

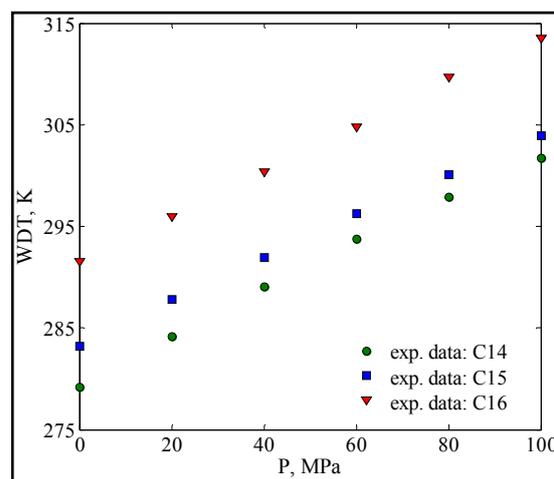


Figure 1: Variation of WDT vs. pressure for several carbons number (data from Milhet et al. [23])

Fig. (1) illustrates the almost linear increase in WDT as a result of increase in pressure for pure components (C_{14} , C_{15} and C_{16}). On the other hand, trend of WDT changes for the pure components with molecular weight in various pressures has been shown in Fig. (2) (data were extracted from Milhet et al. [23]). By considering the almost linear increase in WDT by increasing the pressure proves this fact that WDT in each pressure can be gained by adding WDT in atmospheric pressure (WDT^0) and one term belonged to the

pressure and the molecular weight. Hence, Eq. (1) was developed to predict WDT of pure components at various pressures. Considering this fact that at 0.1 MPa pressure, wax disappearance temperature equals WDT^P ($WDT^P|_{P=0.1} = WDT^\circ$), therefore $P - 0.1$ is used instead of P in the pressure term in order to increase the accuracy of the equation:

$$WDT^P = a M_w^b (P - 0.1)^c + WDT^\circ \quad (1)$$

By fitting Eq. (1) with the experimental reference data [23], the coefficients a , b and c of Eq. (1) was obtained as follows (Eq. 2):

$$WDT^P = 2.0215 M_w^{-0.3628} (P - 0.1)^{0.9393} + WDT^\circ \quad (2)$$

In Eq. (2), Pressure and temperature are in terms of MPa and K respectively.

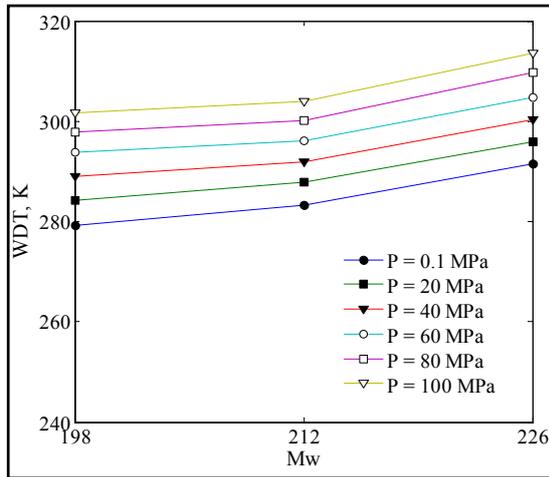


Figure 2: Variation of WDT vs. molar mass for several pressures (data from Milhet et al. [23])

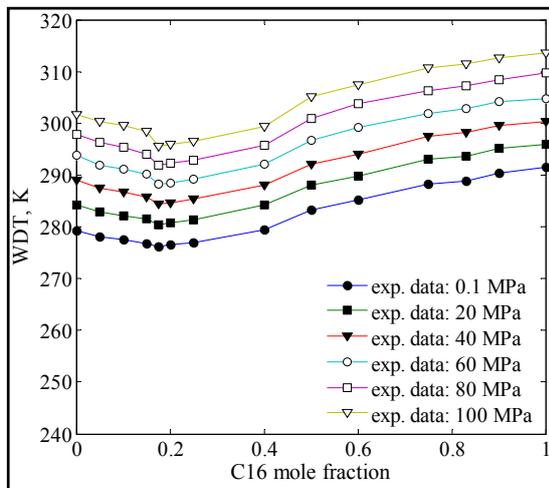


Figure 3: Variation of WDT vs. molar fraction of C_{16} in binary mixture (C_{14} - C_{16}) for several pressures (data from Milhet et al. [23])

• Composition dependency

Figs. (3) and (4) show the changes in WDT of C_{14} - C_{15} and C_{14} - C_{16} mixtures on the basis of mole fraction of the heavier substance in 0.1, 20, 40, 60, 80 and 100MPa (data were extracted from Milhet et al. [23]). It is obvious that trend of WDT changes with mole fraction are so alike in various pressures. WDT changes based on mole fraction have a negative diversion from the straight line that attaches $WDT|_{x_1=1}$ and $WDT|_{x_2=1}$ together. By considering the similarity between Figs. (3) and (4) and diagram of $\ln \gamma$ versus mole fraction, an equation similar to Redlich-Kister [24] with several extra terms was used in this research as presented in Eq. (3):

$$\overline{WDT}^P = x_1 x_2 [d x_1 x_2 + e x_1 + f] + x_1 WDT_1^P + x_2 WDT_2^P \quad (3)$$

In Eq. (3), \overline{WDT}^P is the WDT of the mixture at P pressure, x_1 and x_2 are the light and heavy mole fractions and WDT_1^P and WDT_2^P are WDT for light and heavy components at P pressure, respectively. After fitting Eq. (3) with the Milhet et al. [23] experimental data (144 data points), d , e and f parameters were determined and Eq. (4) was achieved:

$$\overline{WDT}^P = x_1 x_2 [40.0764 x_1 x_2 - 53.5956 x_1 + 2.5806] + x_1 WDT_1^P + x_2 WDT_2^P \quad (4)$$

Eq. (4) was used to predict the WDT of the binary mixture.

Although Eq. (3) has been presented for binary mixtures, it can also be used for n-component mixtures. To generalize Eq. (3) to the multi-component mixtures, $(1-x_1)$ was replaced with x_2 in Eq. (3). Also, the last two terms of the Eq. (3) was shown with $\sum_{i=1}^n x_i WDT_i^P$. Eq. (5) shows the generalization of Eq. (3) for multi-component mixtures:

$$\overline{WDT}^P = x_1 (1-x_1) [h x_1 (1-x_1) + k x_1 + m] + \sum_{i=1}^n x_i WDT_i^P \quad (5)$$

where x_1 is the lightest component that can form wax precipitate. For determination the parameters of Eq. (5), the data of Metivaud et al. [25] were used (29 data points). These data are containing ternary mixtures of several hydrocarbons. After fitting of Eq. (5) with these data, h , k and m parameters were determined as follows:

$$\overline{WDT}^P = x_1(1-x_1)[23.2x_1(1-x_1) - 4.4631x_1 - 10.8033] + \sum_{i=1}^n x_i WDT_i^P \quad (6)$$

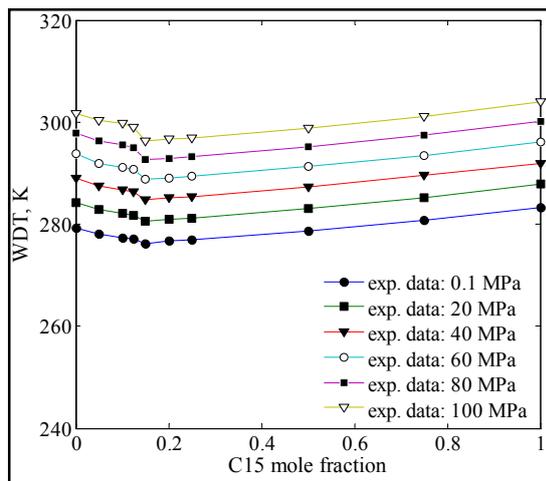


Figure 4: Variation of WDT vs. molar fraction of C_{15} in binary mixture (C_{14} - C_{15}) for several pressures (data from Milhet et al. [23])

1-2- Prediction of WDT

Eqs. (2) and (4) were used to predict the WDT of binary mixtures. Moreover, for prediction of wax disappearance temperature of multi-component mixtures Eqs. (2) and (6) were used. The only experimental data which is required for these calculations is WDT of the pure components at atmospheric pressure (equations in Appendix A of Ji et al. [21] are used to estimate it). The calculations procedure to predict WDT of mixtures is as follows:

- First, WDT^P is calculated for the pure component in the desired pressure (Eq. (2)).
- For binary mixtures: by using WDT_1^P and WDT_2^P and also the mole fraction of each component of the mixture, WDT is calculated for the mixture (Eq. (4)).
- For multi-component mixtures: by using WDT_i^P and x_i for each component of mixture WDT is calculated (Eq. (6)).

2- Results and discussion

2-1- Binary systems, various pressures

The results of calculating WDT through using various thermodynamic models for binary systems of C_{14} - C_{15} and C_{14} - C_{16} were mentioned in this section. Tables (3) to (12) of Ghanaei et al. [22] were shown WDT of C_{14} - C_{15} and C_{14} - C_{16} mixtures and also their Average Absolute Relative Deviation (AARD). The results prove that the AARD of 'new model' is less than any other models (the models who studied by Ghanaei et al. [22]) and equals to 0.36 % [22]. The results of WDT calculations by using Eqs. (2) and (4) for C_{14} - C_{15} and C_{14} - C_{16} systems were shown in Tables (1) and (2), respectively. The Average Absolute Relative Deviation (AARD) of the models presented in Ghanaei et al. [22] work and 'our correlation' were summarized in Table (3). As shown in this Table, AARD for C_{14} - C_{15} and C_{14} - C_{16} mixtures are 0.25 % and 0.33 %, respectively. So the WDT average error for the method proposed by this article is equal to 0.30 % which is less than investigated methods mentioned in Ghanaei et al. [22] work.

2-2- Multi-component systems, atmospheric pressure

The ternary data of Metivaud et al. [25] (C_{14} - C_{15} - C_{16} , C_{16} - C_{17} - C_{18} , C_{18} - C_{19} - C_{20} and C_{19} - C_{20} - C_{21}) were used for evaluation the accuracy of 'our correlation'. The result of calculating WDT at atmospheric pressure for ternary mixtures, by using Eqs. (2) and (6) are monitored in Tables (4) to (7).

Ji et al. [21] have investigated several models (ideal solid solution, multi-pure-solid, Continuo's UNIQUAC and HWWAX) for ternary mixtures of C_{14} - C_{15} - C_{16} and C_{18} - C_{19} - C_{20} in atmospheric pressures. They used the some data of Metivaud et al. [25] for comparison the results. To perform thermodynamic calculations, they first estimated the thermodynamic properties of the components and then WDT.

Table 1: Results of WDT calculations in K for the $\{(1-x) n-C_{14} + x n-C_{15}\}$ binary system as a function of pressure using ‘our correlation’ (experimental data from Milhet et al. [23])

x	0.1 MPa	20 MPa	40 MPa	60 MPa	80 MPa	100 MPa	AARD %
	WDT (K)						
0.000	279.2	284.1	288.7	293.1	297.4	301.6	0.10
0.050	277.2	282.1	286.6	291.0	295.3	299.6	0.29
0.100	275.8	280.7	285.3	289.6	293.9	298.2	0.52
0.125	275.3	280.2	284.8	289.2	293.4	297.7	0.53
0.150	275.0	279.9	284.4	288.8	293.1	297.3	0.22
0.200	274.6	279.5	284.0	288.4	292.7	296.9	0.34
0.250	274.6	279.4	284.0	288.3	292.6	296.8	0.42
0.500	277.6	282.5	287.0	291.3	295.6	299.8	0.20
0.750	281.6	286.4	290.9	295.2	299.4	303.6	0.54
1.000	283.2	288.0	292.4	296.7	300.9	305.1	0.18

Table 2: Results of WDT calculations in K for the $\{(1-x) n-C_{14} + x n-C_{16}\}$ binary system as a function of pressure using ‘our correlation’ (experimental data from Milhet et al. [23])

x	0.1 MPa	20 MPa	40 MPa	60 MPa	80 MPa	100 MPa	AARD %
	WDT (K)						
0.000	279.2	284.1	288.7	293.1	297.4	301.6	0.10
0.050	277.6	282.5	287.1	291.4	295.7	300.0	0.15
0.100	276.6	281.6	286.1	290.4	294.7	299.0	0.24
0.150	276.2	281.1	285.6	290.0	294.3	298.5	0.08
0.175	276.2	281.1	285.6	289.9	294.2	298.4	0.50
0.200	276.2	281.1	285.6	290.0	294.2	298.4	0.43
0.250	276.6	281.5	286.0	290.3	294.6	298.8	0.35
0.400	279.3	284.2	288.6	292.9	297.2	301.3	0.29
0.500	281.8	286.6	291.0	295.3	299.6	303.7	0.44
0.600	284.4	289.2	293.6	297.8	302.0	306.1	0.34
0.750	287.8	292.6	296.9	301.2	305.3	309.4	0.23
0.830	289.3	294.0	298.4	302.6	306.8	310.8	0.13
0.900	290.3	295.1	299.4	303.6	307.8	311.8	0.12
1.000	291.5	296.2	300.5	304.7	308.8	312.9	0.10

Table 3: Comparison of AARD for different models (Ghanaei et al. [22]) and ‘our correlation’

NDP	AARD %						
	model 1	model 2	model 3 without k_{ij}	model 3 with k_{ij}	‘new model’	‘our correlation’	
mixtures of C_{14} - C_{16}	84	0.83	2.32	0.32	1.24	0.37	0.33
mixtures of C_{14} - C_{15}	60	0.59	2.00	0.39	1.57	0.35	0.25
Total	144	0.73	2.19	0.35	1.38	0.36	0.30

Table 4: Experimental WDT data [25] and ‘our correlation’ calculations for C_{14} - C_{15} - C_{16} ternary, at 0.1MPa

Experimental data				Predictions and Absolute Relative Deviation (ARD %)	
Mole fraction			WDT (K)	‘our correlation’	
C_{14}	C_{15}	C_{16}		WDT (K)	ARD %
0.06	0.57	0.37	283	285	0.63
0.14	0.23	0.63	285	286	0.31
0.17	0.06	0.77	286	287	0.26
0.24	0.33	0.43	282	284	0.56
0.21	0.56	0.23	281	282	0.42
0.27	0.66	0.07	280	280	0.17
0.37	0.05	0.58	283	284	0.43
0.32	0.24	0.44	282	283	0.45
0.43	0.33	0.24	279	281	0.77
0.57	0.17	0.26	278	281	1.01
0.73	0.14	0.13	276	279	1.16
AARD %					0.56

Table 5: Experimental WDT data [25] and 'our correlation' calculations for C₁₆-C₁₇-C₁₈ ternary, at 0.1MPa

Experimental data				Predictions and Absolute Relative Deviation (ARD %)	
Mole fraction			WDT (K)	'our correlation'	
C ₁₆	C ₁₇	C ₁₈		WDT (K)	ARD %
0.10	0.10	0.80	298	298	0.00
0.10	0.75	0.15	294	295	0.34
0.10	0.80	0.10	295	295	0.00
0.11	0.39	0.50	296	297	0.34
0.20	0.20	0.60	296	296	0.00
0.20	0.60	0.20	294	294	0.00
0.33	0.33	0.34	293	294	0.34
0.40	0.10	0.50	294	294	0.00
0.40	0.40	0.20	292	293	0.34
0.60	0.20	0.20	291	292	0.34
0.80	0.10	0.10	290	290	0.00
AARD %					0.16

Table 6: Experimental WDT data [25] and 'our correlation' calculations for C₁₈-C₁₉-C₂₀ ternary, at 0.1MPa

Experimental data				Predictions and Absolute Relative Deviation (ARD %)	
Mole fraction			WDT (K)	'our correlation'	
C ₁₈	C ₁₉	C ₂₀		WDT (K)	ARD %
0.02	0.02	0.96	309	309	0.09
0.05	0.05	0.90	309	309	0.13
0.05	0.90	0.05	305	305	0.13
0.10	0.10	0.80	308	308	0.14
0.10	0.40	0.50	306	306	0.04
0.10	0.55	0.35	306	305	0.20
0.14	0.73	0.13	304	304	0.04
0.15	0.15	0.70	307	307	0.12
0.20	0.20	0.60	306	306	0.07
0.20	0.60	0.20	305	304	0.43
0.26	0.26	0.48	306	305	0.39
0.33	0.33	0.34	304	304	0.09
0.40	0.10	0.50	305	304	0.22
0.43	0.43	0.14	303	302	0.25
0.48	0.15	0.37	304	303	0.22
0.60	0.20	0.20	302	302	0.00
0.79	0.11	0.10	301	301	0.03
0.90	0.05	0.05	301	301	0.12
AARD %					0.15

Table 7: Experimental WDT data [25] and 'our correlation' calculations for C₁₉-C₂₀-C₂₁ ternary, at 0.1MPa

Experimental data				Predictions and Absolute Relative Deviation (ARD %)	
Mole fraction			WDT (K)	'our correlation'	
C ₁₉	C ₂₀	C ₂₁		WDT (K)	ARD %
0.05	0.05	0.90	313	313	0.00
0.05	0.89	0.06	309	309	0.00
0.10	0.40	0.50	311	310	0.32
0.10	0.80	0.10	310	309	0.32
0.12	0.10	0.78	312	311	0.32
0.19	0.50	0.31	310	309	0.32
0.20	0.21	0.59	311	310	0.32
0.20	0.60	0.20	309	308	0.32
0.29	0.28	0.43	310	309	0.32
0.39	0.10	0.51	310	308	0.65
0.39	0.50	0.11	308	307	0.32
0.49	0.20	0.31	308	307	0.32
0.50	0.40	0.10	307	306	0.33
0.60	0.20	0.20	307	306	0.33
0.80	0.10	0.10	306	305	0.33
0.90	0.05	0.05	305	305	0.00
AARD %					0.28

Table 8: Compression of WDT AARD % for ternary mixtures of Metivaud et al. [22] work by several models, at 0.1 MPa

Model	AARD %				Average
	C ₁₄ -C ₁₅ -C ₁₆ (11 data point)	C ₁₆ -C ₁₇ -C ₁₈ (11 data point)	C ₁₈ -C ₁₉ -C ₂₀ (18 data point)	C ₁₉ -C ₂₀ -C ₂₁ (16 data point)	
P. Wilson* -P. UNIQUC** [1]	0.76	0.58	0.22	0.10	0.36
P. Wilson*- Regular solution** [1]	0.33	0.26	0.42	0.52	0.40
P. Wilson*-Ideal** [1]	0.33	0.26	0.42	0.52	0.40
P. UNIQUAC* -UNIFAC** [1]	1.00	0.58	0.19	0.17	0.42
P. UNIQUAC* -Ideal** [1]	1.00	0.59	0.19	0.17	0.42
P. UNIQUAC*-Regular solution** [1]	1.00	0.59	0.19	0.17	0.42
P. Wilson* -UNIFAC** [1]	0.33	0.26	0.42	0.52	0.48
Regular solution* -UNIFAC** [1]	1.60	1.21	0.66	0.47	0.90
Regular solution* -Ideal** [1]	1.61	1.21	0.66	0.47	0.90
Regular solution *-Regular solution** [1]	1.61	1.21	0.66	0.47	0.90
Ideal* -UNIFAC** [1]	1.66	1.25	0.69	0.49	0.93
UNIFAC* -UNIFAC** [1]	1.67	1.25	0.69	0.49	0.94
Ideal* -Ideal** [1]	1.67	1.25	0.69	0.50	0.94
Ideal *-Regular solution** [1]	1.67	1.26	0.69	0.50	0.94
UNIFAC* -Ideal** [1]	1.68	1.26	0.69	0.50	0.94
UNIFAC*-Regular solution** [1]	1.68	1.26	0.69	0.50	0.94
P. UNIQUAC* -P. UNIQUC** [1]	1.70	1.28	0.71	0.51	0.96
P. Wilson*- P. Wilson** [1]	1.83	1.36	0.75	0.55	1.02
Regular solution* -P. UNIQUC** [1]	2.35	1.95	1.29	1.16	1.59
Ideal* -P. UNIQUC** [1]	2.41	1.99	1.32	1.19	1.63
UNIFAC* -P. UNIQUC** [1]	2.42	2.00	1.33	1.19	1.63
P. UNIQUAC*- P. Wilson** [1]	2.84	2.14	1.32	1.09	1.71
Regular solution*- P. Wilson** [1]	3.51	2.84	1.93	1.76	2.37
Ideal*- P. Wilson** [1]	3.58	2.89	1.97	1.80	2.42
UNIFAC*- P. Wilson** [1]	3.59	2.89	1.97	1.80	2.42
Ideal solid solution [21]	1.49	-	0.44	-	0.84
Multi-pure-solid [21]	1.36	-	1.41	-	1.39
Coutinho UNIQUAC [21]	0.65	-	1.04	-	0.89
HWWAX [21]	0.71	-	0.18	-	0.34
'our correlation'	0.56	0.16	0.15	0.28	0.27

* Solid phase

**Liquid phase

Table 9: Calculated WDT with 'new model' in K and AARD of several mixture as a function of pressure for different compositions (experimental data from Daridon et al. [26])

P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %
M ₁			M ₂			M ₃		
0.1	271.0	0.15	0.1	274.2	0.18	0.1	277.7	0.25
19.9	275.5	0.18	19.9	278.7	0.22	19.5	282.1	0.32
40.2	280.1	0.39	40.7	283.3	0.39	40.0	286.6	0.46
59.9	284.4	0.46	61.9	287.9	0.56	60.1	290.9	0.55
80.0	288.8	0.66	80.3	291.8	0.69	80.0	295.3	0.85
99.8	293.2	0.96	100.0	296.2	1.02	100.3	299.6	1.18
AARD %		0.47			0.51			0.60
M ₄			M ₅			M ₆		
0.1	281.3	0.50	0.1	284.9	0.53	0.1	288.4	0.80
19.8	285.7	0.60	19.5	289.3	0.63	20.0	292.8	0.83
39.6	290.1	0.73	40.0	293.6	0.79	39.9	297.1	0.92
60.0	294.5	0.86	60.1	298.1	0.98	59.1	301.2	0.97
79.0	298.5	1.05	78.8	302.0	1.14	79.5	305.4	1.19
100.3	303.1	1.44	100.0	306.5	1.42	98.0	309.4	1.38
AARD %		0.86			0.92			1.02
M ₇			M ₈			M ₉		
0.1	292.0	0.72	0.1	297.9	0.68	0.1	303.8	0.73
20.0	296.3	0.75	19.2	302.2	0.77	20.0	308.2	0.82
39.9	300.6	0.84	40.1	306.4	0.76	40.0	312.3	0.87
60.1	304.9	0.89	60.1	310.6	0.81	60.1	316.6	0.92
80.0	309.0	1.08	80.0	314.9	0.99	80.3	320.8	0.98
100.0	313.3	1.39	100.0	319.0	1.17	99.3	324.6	1.09
AARD %		0.95			0.86			0.90

Table 10: Calculated WDT with 'HWWAX' model in K and AARD of several mixture as a function of pressure for different compositions (experimental data from Daridon et al. [22])

P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %
M ₁			M ₂			M ₃		
0.1	270.9	0.11	0.1	274.6	0.33	0.1	278.3	0.47
19.9	274.0	0.36	19.9	277.7	0.14	19.5	281.6	0.14
40.2	277.3	0.61	40.7	281.1	0.39	40.0	284.8	0.18
59.9	280.7	0.85	61.9	284.6	0.59	60.1	288.3	0.35
80.0	283.9	1.05	80.3	287.7	0.72	80.0	291.7	0.38
99.8	287.2	1.10	100.0	291.0	0.75	100.3	295.1	0.34
AARD %		0.68			0.49			0.31
M ₄			M ₅			M ₆		
0.1	281.2	0.46	0.1	283.8	0.14	0.1	286.1	0.00
19.8	284.6	0.21	19.5	287.1	0.14	20.0	289.5	0.31
39.6	288.0	0.00	40.0	290.6	0.24	39.9	292.9	0.51
60.0	291.3	0.24	60.1	294.1	0.37	59.1	296.3	0.67
79.0	294.5	0.30	78.8	297.4	0.40	79.5	300.0	0.60
100.3	298.2	0.20	100.0	301.1	0.36	98.0	303.2	0.66
AARD %		0.24			0.28			0.46
M ₇			M ₈			M ₉		
0.1	288.3	0.55	0.1	291.7	1.42	0.1	294.8	2.25
20.0	291.7	0.82	19.2	295.2	1.57	20.0	298.6	2.32
39.9	295.2	0.97	40.1	299.2	1.61	40.0	302.6	2.26
60.1	298.1	1.36	60.1	303.1	1.62	60.1	306.6	2.26
80.0	302.4	1.08	80.0	307.0	1.54	80.3	310.7	2.20
100.0	306.1	0.94	100.0	311.0	1.36	99.3	314.6	2.02
AARD %		0.95			1.52			2.22

Table 11: Calculated WDT with 'our correlation' in K and AARD of several mixture as a function of pressure for different compositions (experimental data from Daridon et al. [22])

P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %	P(MPa)	Calc. WDT (K)	ARD %
M ₁			M ₂			M ₃		
0.1	271.1	0.18	0.1	274.6	0.34	0.1	278.2	0.44
19.9	276.1	0.38	19.9	279.5	0.51	19.5	283.0	0.63
40.2	280.7	0.62	40.7	284.3	0.73	40.0	287.6	0.80
59.9	285.1	0.71	61.9	288.9	0.91	60.1	292.0	0.92
80.0	289.5	0.91	80.3	292.9	1.06	80.0	296.2	1.16
99.8	293.8	1.16	100.0	297.1	1.32	100.3	300.5	1.47
AARD %		0.66			0.81			0.90
M ₄			M ₅			M ₆		
0.1	281.3	0.51	0.1	284.3	0.33	0.1	287.1	0.33
19.8	286.1	0.74	19.5	289.0	0.52	20.0	291.8	0.47
39.6	290.5	0.87	40.0	293.5	0.75	39.9	296.1	0.58
60.0	294.9	1.00	60.1	297.8	0.87	59.1	300.2	0.62
79.0	298.9	1.19	78.8	301.7	1.03	79.5	304.4	0.85
100.3	303.3	1.52	100.0	306.0	1.27	98.0	308.1	0.96
AARD %		0.97			0.80			0.64
M ₇			M ₈			M ₉		
0.1	289.8	0.02	0.1	294.3	0.55	0.1	298.6	0.98
20.0	294.5	0.14	19.2	298.7	0.40	20.0	303.2	0.83
39.9	298.8	0.24	40.1	303.1	0.32	40.0	307.3	0.74
60.1	303.0	0.27	60.1	307.2	0.28	60.1	311.4	0.74
80.0	307.1	0.45	80.0	311.2	0.18	80.3	315.4	0.74
100.0	311.1	0.68	100.0	315.2	0.03	99.3	319.1	0.64
AARD %		0.30			0.29			0.78

2-3- Multi-component systems, various pressures

By using Daridon et al. [26] experimental data the more accurate investigation of 'HWWAX' thermodynamic model [21], the predictive model of Ghanaei

et al. [22] ('new model') and the proposed 'our correlation' (Eq. (6) of this work), have been performed. In Daridon et al. [26] work, hydrocarbon mixtures were studied with different components and compositions and the experimental data of WDT has been

reported for each mixture at various pressures [26]. In this study, the data of Daridon et al. [26] (Tables (3) and (4) of this literature) was used for validation of the proposed correlations.

Tables (9) to (11) show the results of WDT calculations for mixtures in various pressures using 'new model' [22], 'HWWAX' thermodynamic model [21] and the proposed 'our correlation', respectively. The AARD for each of these methods is also mentioned in these Tables. The AARD of calculating WDT is 0.79 %, 0.79% and 0.68 % for the predictive model ('new model') of Ghanaei et al. [22], 'HWWAX' thermodynamic model [21], and also the proposed 'our correlation' respectively. 'HWWAX' thermodynamic model can't properly predict WDT for mixtures with high number of components (Table 10). The algorithm of WDT calculations for 'HWWAX' thermodynamic model, 'new model' and also the equations required for estimating thermodynamic properties are presented in Ji et al. [21] and Ghanaei et al. [22] works. As it is obvious, the equations proposed by this article have an outstanding accuracy and its AARD is equal to 0.68 % for multi-component mixtures.

3- Conclusion

The pressure effect on Wax Disappearance Temperature of multi-component mixtures has been surveyed in this article. First, some- but not so complex-correlations were achieved for binary mixtures through fitting experimental data. Then the achieved equations were generalized to multi-component mixtures. This method enjoys a unique accuracy in addition to avoiding any need for complex and long thermodynamic calculations and

has less average absolute relative deviation than other previously investigated thermodynamic methods. The average absolute relative deviation result of WDT by using 'our correlation' for binary mixtures at various pressures, ternary mixtures at atmospheric pressure and multi-component mixtures at various pressures are 0.30 %, 0.27 % and 0.68 %, respectively.

Nomenclature

a, b, c	parameters of equation 1
d, e, f	parameters of equation 3
h, k, m	parameters of equation 5
Mw	molecular weight
n	number of component
P	pressure, MPa
WDT^o	wax disappearance temperature in atmospheric pressure, K
WDT^P	wax disappearance temperature in P pressure, K
$\overline{WDT^P}$	wax disappearance temperature of mixture in P pressure, K
x	molar fraction
<i>Subscripts</i>	
1	light component
2	heavy component
i	ith component
<i>Acronyms</i>	
AARD	average absolute relative deviation $[(100/m) \sum_{i=1}^m exp_i - calc_i / exp_i], \%$
ARD	absolute relative deviation $[\equiv \sum_{i=1}^m exp_i - calc_i / exp_i], \%$
HWWAX	Heriot-Watt wax
MPR	modified Peng Robinson
NDP	Number of data point
PR	Peng Robinson
UNIFAC	universal functional activity coefficient
UNIQUAC	universal quasi-chemical
WAT	wax appearance temperature, K
WDT	wax disappearance temperature, K

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