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PHYSICAL PROPERTIES OF HEAVY PETROLEUM FRACTIONS AND CRUDE OILS

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1. ABSTRACT

Equations are provided for calculating boiling point, density, refractive index, critical temperature, pressure and density, acentric factor, surface tension and solubility parameter of single carbon number (SCN) hydrocarbon groups for C_6-C_{50} existing in crude oils and hydrocarbon-plus fractions. Results show good consistency among various properties and improvement over the values previously reported. These methods should enhance equation-of-state (EOS) predictions when experimental data are lacking.

2. INTRODUCTION

In predicting various thermodynamic properties of petroleum mixtures necessary to design of processes for both production and refining of crude oils, accurate knowledge of basic physical properties such as molecular weight, boiling point and critical constants is important. Most available correlations for prediction of such parameters are based on properties of light hydrocarbons (< C_{20}) and their application to heavy fractions leads to significant errors.

Katz and Firoozabadi [1] presented a generalized set of boiling point, specific gravity and molecular weight for the petroleum fractions from C_6 through C_{45}. Whitson [2] found inconsistency in the Katz and Firoozabadi tabulated molecular weight data (for hydrocarbon fractions C_{22} through C_{45}) after analyzing and comparing these data with sources from which they were developed. Whitson modified the original tabulated physical properties by employing Riazi and Daubert [3] correlations to extrapolate data from C_{22} to C_{45}. He also tabulated critical properties and acentric factors of C_6 through C_{45}. Later Ahmed [4] correlated these data through 5-term polynomials in terms of carbon number of SCN groups.

Correlation of Riazi-Daubert [3] used by Whitson are based on physical properties of pure hydrocarbons from C_5 to C_{20}. However, these correlations when applied to heavier compounds may lead to significant errors. Perhaps the best way to obtain properties of narrow-cut petroleum fractions is through "pseudocompound method" using the paraffin/naphthene/aromatic (PNA) content of the mixture and pure hydrocarbon properties as described by Daubert [5]. The main objective of this work is to present simple equations for accurate estimation of basic physical properties of SCN groups from C_6 through C_{50}.

3. TECHNICAL DEVELOPMENT

As described by Whitson [2], boiling point, specific gravity and molecular weight of SCN groups reported by Katz and Firoozabadi from C_6 through C_{22} are accurate and show internal consistency. These data may be used as the basis for estimation of these and other properties for heavier SCN groups.

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Properties of narrow-cut petroleum fractions such as a SCN group may be estimated using properties of pure hydrocarbons from paraffin, naphthene and aromatic groups with PNA composition in the following form

$$\theta = x_p\theta_p + x_n\theta_n + x_a\theta_a \tag{1}$$

where x_p, x_n, and x_a are the fraction of paraffins, naphthenes, and aromatic content of the mixture. θ is physical property of the mixture to be estimated. θ_p, θ_n and θ_a are the same property for pure hydrocarbons from paraffin, naphthene and aromatic groups having the same molecular weight as the mixture. These properties can be estimated from molecular weight (M) by

$$\theta = \theta_\infty - \exp(a - bM^c) \tag{2}$$

where θ is a property such as T_b and θ_∞ is the limiting value for that property as $M \to \infty$. This equation is based on the equation originally proposed by Kreglewski and Zwolinski [6] for properties of n-alkanes. It can be shown that different properties of homologous hydrocarbon groups are well predictable by eq. 2 especially for compounds from C_{20} through C_{50}. Constants in eq. 2 for basic properties of n-alkanes, n-alkylcyclopentanes and n-alkylbenzenes are given in Tables 1, 2 and 3, respectively.

Table 1
Physical properties of n-alkanes

Property θ	Carbon number range	Constants in eq. 2				% deviation
		θ_∞	a	b	c	
T_b	C_5-C_{40}	1070	6.98291	0.02013	2/3	0.04
S	C_5-C_{19}	0.85	92.22793	89.82301	0.01	0.12
d_{20}	C_5-C_{40}	0.859	88.01379	85.7446	0.01	0.04
I	C_5-C_{40}	0.2833	87.6593	86.62167	0.01	0.002
$T_{br}= T_b/T_c$	C_5-C_{20}	1.15	-0.41966	0.02436	0.58	0.027
$-P_c$	C_5-C_{20}	0	4.65757	0.13423	0.5	0.78
d_c	C_5-C_{20}	0.26	-3.50532	1.5×10^{-6}	2.38	0.83
$-\omega$	C_5-C_{20}	0.3	-3.06826	-1.04987	0.2	1.2
σ	C_5-C_{20}	33.2	5.29577	0.61653	0.32	0.25

Data Source: T_b, n, and d are taken from TRC [7]. All other properties are taken from API [8].
Unit: T_b and T_c are in °K., d and d_c are in g/cm^3, P_c is in bar and σ is in dyne/cm.

Original boiling point (T_b) , specific gravity (S) and molecular weight (M) data reported by Katz and Firoozabadi from C_6 - C_{22} are given in Table 4. Methods recommended by Riazi and Daubert [9] have been used to estimate PNA composition of these SCN groups and they are also given in Table 4. Equations 1 and 2 with Tables 1-4 are the basis for calculation of all basic properties of SCN groups from C_6 - C_{50}.

Boiling point and specific gravity from Table 4 are related to carbon number (N_c) of SCN groups by following relations:

$$T_b = 1090 - \exp(6.9955 - 0.11193N_c^{2/3}) \tag{3}$$

Table 2
Physical properties of n-alkylcyclopentanes

Property θ	Carbon number range	Constants in eq. 2				% deviation
		θ_∞	a	b	c	
T_b	C_6-C_{41}	1028	6.95649	0.02239	2/3	0.05
S	C_7-C_{25}	0.853	97.72532	95.73589	0.01	0.02
d_{20}	C_5-C_{41}	0.857	85.1824	83.65758	0.01	0.04
I	C_5-C_{41}	0.283	87.55238	86.97556	0.01	0.003
$T_{br} = T_b/T_c$	C_5-C_{18}	1.2	0.06765	0.13763	0.35	0.25
$-P_c$	C_6-C_{18}	0	7.25857	1.13139	0.26	0.9
$-d_c$	C_6-C_{20}	-0.255	-3.18846	0.1658	0.5	0.11
$-\omega$	C_6-C_{20}	0.3	-8.25682	-5.33934	0.08	0.54
σ	C_6-C_{25}	30.6	14.17595	7.02549	0.12	0.3

Table 3
Physical properties of n-alkylbenzenes

Property θ	Carbon number range	Constants in eq. 2				% deviation
		θ_∞	a	b	c	
T_b	C_6-C_{42}	1015	6.91062	0.02247	2/3	0.14
-S	C_6-C_{20}	-0.8562	224.7257	218.518	0.01	0.1
$-d_{20}$	C_6-C_{42}	-0.854	238.791	232.315	0.01	0.037
-I	C_6-C_{42}	-0.2829	137.0918	135.433	0.01	0.008
$T_{br} = T_b/T_c$	C_6-C_{20}	1.03	-0.29875	0.06814	0.5	0.12
$-P_c$	C_6-C_{20}	0	9.77968	3.07555	0.15	0.7
$-d_c$	C_6-C_{20}	-0.22	-1.43083	0.12744	0.5	0.8
$-\omega$	C_6-C_{20}	0	-14.97	-9.48345	0.08	0.68
σ	C_6-C_{20}	30.4	1.98292	-0.0142	1.0	1.7

$$S = 1.07 - \exp(3.65097 - 3.8864 N_c^{0.1}) \quad (4)$$

Equations 3 and 4 reproduce values of T_b and S from Table 4 with average deviations of 0.2% (1°K) and 0.1%, respectively. T_b is also related to molecular weight by eq. 2 using data given in Table 4.

$$T_b = 1080 - \exp(6.97996 - 0.01964 M^{2/3}) \quad (5)$$

Equation 5 can be rearranged for estimating molecular weight from T_b. Equations 3 and 4 are used to generate a set of T_b and S data for SCN from C_6 to C_{50}. These data are shown in Table 5. Molecular weights are calculated by eq. 5 using T_b calculated from eq. 3. Molecular weights given in Table 5 for SCN from C_{23} - C_{45} differ with those reported by Whitson. M and S given in Table 5 are related through eq. 2 by:

$$S = 1.07 - \exp(3.56073 - 2.93886 M^{0.1}) \quad (6)$$

This equation predicts S within 0.4% for SCN from C_6-C_{50}. If eq. 2 is applied to specific gravity with values of M from Whitson's table, an average error of 1% is obtained indicating that T_b, S, M data in Table 5 shows better consistency than those reported by Whitson for SCN for C_{23} - C_{45}. One good simple relation for molecular weight of SCN groups is given below which is in good agreement with experimental data as shown by Pedersen et al. [10].

Table 4
Boiling point, specific gravity, molecular weight and PNA composition of SCN groups

SCN	T_b/°K	S (60/60)	M	PNA composition		
				x_p	x_n	x_a
6	337	0.690	84	0.822	0.108	0.070
7	366	0.727	96	0.674	0.181	0.145
8	390	0.749	107	0.589	0.220	0.192
9	416	0.768	121	0.515	0.253	0.232
10	439	0.782	134	0.467	0.269	0.265
11	461	0.793	147	0.429	0.280	0.291
12	482	0.804	161	0.392	0.291	0.317
13	501	0.815	175	0.354	0.302	0.344
14	520	0.826	190	0.319	0.310	0.371
15	539	0.836	206	0.292	0.308	0.400
16	557	0.843	222	0.274	0.306	0.420
17	573	0.851	237	0.254	0.303	0.444
18	586	0.856	251	0.244	0.296	0.460
19	598	0.861	263	0.235	0.288	0.477
20	612	0.866	275	0.227	0.278	0.495
21	624	0.871	291	0.221	0.265	0.514
22	637	0.876	300	0.211	0.259	0.530

T_b, S and M are taken from Katz-Firoozabadi (1978).
PNA compositions are predicted through methods recommended by Riazi and Daubert [9].

$$M = 14\,N_C - 4 \tag{7}$$

Molecular weights of SCN groups for C_6 through C_{45} from Table 4, Table 5 and eq. 7 are shown in Fig. 1. As it is seen from this figure, new values of molecular weights given in Table 5 are in better agreement with eq. 7.

Equations 1 and 2 together with Tables 1-4 are used to estimate various physical properties of SCN groups from C_6 through C_{22} and then these calculated properties are used in eq. 2 to obtain the constants for SCN fractions. These constants are given in Table 6. Physical properties of SCN groups from C_6 through C_{50} generated from eq. 2 with constants in Table 6 are presented in Table 5. Data on liquid solubility parameters (δ) used to obtain the constants in Table 6 for eq. 2 are those recommended by Won [11]. These data have been also used by Pedersen et al. [10] and are correlated to molecular weight in the following form

$$\delta = 5.30789 + 0.48649\ ln\ M \tag{8}$$

Equation 8 predicts δ with an error of 1% while eq. 2 with constants in Table 6 predicts δ with an average deviation of 0.1%.

In calculation of critical temperature from eq. 2, calculated T_b should be divided by calculated reduced boiling point (T_{br}). Equation 2 with constants given in Table 6 predicts critical pressure of 1.013 bar (1 atm) for molecular weight of 1382 (N_C=99). At this molecular weight calculated, T_{br} is 0.996 which is very close to unity, the value expected for the compound with atmospheric critical pressure. These predictions show internal consistency among T_b, T_c and P_c for very heavy fractions. As there is no experimental data for critical properties of heavy fractions, direct evaluation of values reported in Table 5 for critical properties and acentric factor is not possible.

However, estimated values of boiling point through eqs. 1-2 and Tables 1-3 are compared with the original and accurate values of Katz-Firoozabadi [1] data. As shown in Fig. 2, values of boiling point from eqs. 1-2 are very close to those reported by Katz and Firoozabadi. Evaluation of values of critical properties reported in Table 5 can be made through prediction of directly measurable thermodynamic properties. However, a comparison between values of T_c given in Table 5 with those reported by Whitson [2] and values calculated through Kesler-Lee correlations [12] is presented in Fig. 3. Whitson data for critical properties are based on Riazi-Daubert [3] correlations. Both Kesler-Lee and Riazi-Daubert correlations become unreliable for compounds heavier than C_{20}.

Table 5
Recommended values for physical properties of single carbon number fractions.

Carbon Number	M	T_b	S	n_{20}	d_{20}	T_c	P_c	d_c	ω	σ	δ
6	82	337	0.690	1.395	0.686	513	33.3	0.254	0.255	18.6	7.25
7	95	365	0.727	1.407	0.723	546	31.4	0.255	0.303	21.2	7.41
8	107	390	0.749	1.417	0.743	575	29.2	0.256	0.346	23.0	7.53
9	121	416	0.768	1.426	0.762	603	26.8	0.256	0.394	24.4	7.63
10	136	440	0.782	1.435	0.777	628	24.2	0.255	0.444	25.4	7.71
11	149	461	0.793	1.442	0.790	650	22.6	0.255	0.486	26.0	7.78
12	163	482	0.804	1.448	0.802	671	20.9	0.254	0.530	26.6	7.83
13	176	500	0.815	1.453	0.812	688	19.5	0.254	0.570	27.0	7.88
14	191	520	0.826	1.458	0.822	708	18.1	0.254	0.614	27.5	7.92
15	207	539	0.836	1.464	0.831	725	16.7	0.253	0.661	27.8	7.96
16	221	556	0.843	1.468	0.839	740	14.3	0.253	0.701	28.1	7.99
17	237	573	0.851	1.472	0.847	755	13.4	0.252	0.746	28.3	8.02
18	249	586	0.856	1.475	0.852	767	12.7	0.252	0.779	28.5	8.05
19	261	598	0.861	1.478	0.857	777	12.1	0.252	0.812	28.6	8.07
20	275	611	0.866	1.481	0.862	788	11.4	0.251	0.849	28.8	8.09
21	289	624	0.871	1.484	0.867	798	10.7	0.251	0.886	28.9	8.11
22	303	637	0.876	1.486	0.872	808	10.2	0.250	0.923	29.0	8.13
23	317	648	0.881	1.489	0.887	817	9.6	0.250	0.959	29.1	8.15
24	331	660	0.885	1.491	0.880	826	9.2	0.250	0.995	29.2	8.17
25	345	671	0.888	1.493	0.884	834	8.7	0.249	1.031	29.3	8.18
26	359	681	0.892	1.495	0.888	842	8.3	0.249	1066	29.3	8.20
27	373	691	0.896	1.497	0.891	849	7.9	0.249	1.101	29.4	8.21
28	387	701	0.899	1.499	0.895	856	7.5	0.248	1.135	29.4	8.22
29	400	710	0.902	1.501	0.898	863	7.2	0.248	1.167	29.5	8.24
30	415	720	0.905	1.503	0.901	869	6.9	0.247	1203	29.5	8.25
31	429	728	0.909	1.504	0.904	875	6.6	0.247	1.237	29.6	8.26
32	443	737	0.912	1.506	0.906	881	6.3	0.247	1.270	29.6	8.27
33	457	745	0.915	1.507	0.909	886	6.0	0.246	1.303	29.7	8.28
34	471	753	0.917	1.509	0.912	891	5.8	0.246	1.336	29.7	8.29
35	485	760	0.920	1.510	0.914	896	5.6	0.246	1.369	29.7	8.30
36	499	768	0.922	1.511	0.916	901	5.4	0.245	1.402	29.8	8.31
37	513	775	0.925	1.512	0.918	905	5.1	0.245	1.434	29.8	8.32
38	528	782	0.927	1.514	0.920	909	4.9	0.245	1.468	29.8	8.33
39	542	789	0.929	1.515	0.922	913	4.8	0.245	1.500	29.8	8.34
40	556	795	0.931	1.516	0.924	917	4.6	0.244	1.532	29.9	8.35
41	570	802	0.933	1.517	0.926	921	4.4	0.244	1.563	29.9	8.35
42	584	808	0.934	1.518	0.928	924	4.3	0.244	1.595	29.9	8.36
43	599	814	0.936	1.519	0.930	927	4.1	0.243	1.628	29.9	8.36
44	614	820	0.938	1.520	0.932	931	4.0	0.243	1.661	29.9	8.37
45	629	826	0.940	1.521	0.933	934	3.8	0.243	1.695	29.9	8.38
46	641	831	0.941	1.522	0.935	936	3.7	0.242	1.721	30.0	8.38
47	656	836	0.943	1.523	0.936	939	3.6	0.242	1.754	30.0	8.39
48	670	841	0.944	1.524	0.938	942	3.5	0.242	1.784	30.0	8.39
49	684	846	0.946	1.524	0.939	944	3.4	0.242	1.815	30.0	8.40
50	698	851	0.947	1.525	0.940	947	3.3	0.241	1.845	30.0	8.40

Units: T_b, T_c in K; P_c in bar; d_{20} and d_c in g/cm^3, σ in dyne/cm ; δ in [cal/cm^3]$^{1/2}$

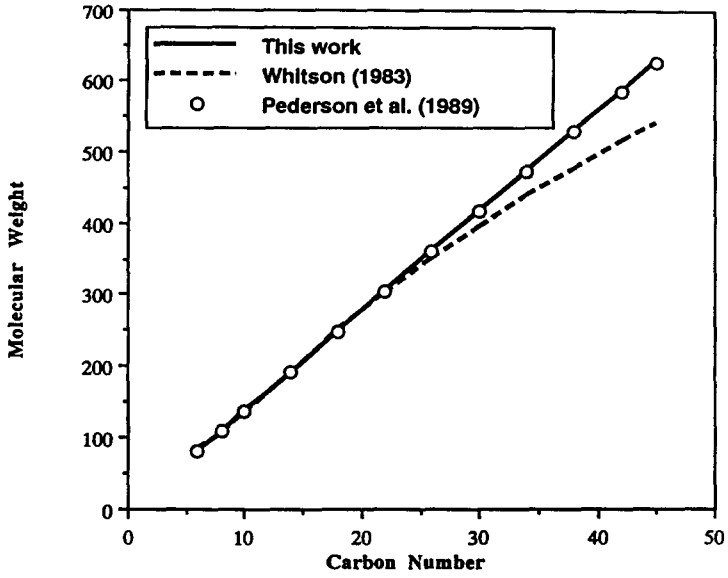

Figure 1. Molecular weight of SCN fractions.

Table 6
Constants in eq. 2 for various properties of SCN groups

Property θ	Constants in eq. 2				% dev.*
	θ_∞	a	b	c	
T_b	1080	6.97996	0.01964	2/3	0.4
S	1.07	3.56073	2.93886	0.1	0.07
d_{20}	1.05	3.80258	3.12287	0.1	0.1
I	0.34	2.30884	2.96508	0.1	0.1
$T_{br}= T_b/T_c$	1.2	-0.34742	0.02327	0.55	0.15
$-P_c$	0	6.34492	0.7239	0.3	1%
$-d_c$	-0.22	-3.2201	0.0009	1.0	0.05
$-\omega$	0.3	-6.252	-3.64457	0.1	1.4
σ	30.3	17.45018	9.70188	0.1	1
δ	8.6	2.29195	0.54907	0.3	0.1

* This is AAD% between values obtained from eq. 2 with constants given in this table and the values originally used. Units: δ is in $[cal/cm^3]^{1/2}$; for other parameters units are given in Table 1.

To summarize, a set of data for various basic physical properties of SCN groups from C_6 through C_{50} are reported. These values show improvement over the values of physical properties previously reported in the literature. Equations are also provided to estimate these properties when the only available information is molecular weight. Based on preliminary evaluation of proposed equations, improvement on equation-of- state predictions for heavy petroleum fractions and crude oils is expected. However, some extensive analysis of PVT calculations for reservoir fluids is needed to show the performance of proposed methods. This would be the next phase of this work.

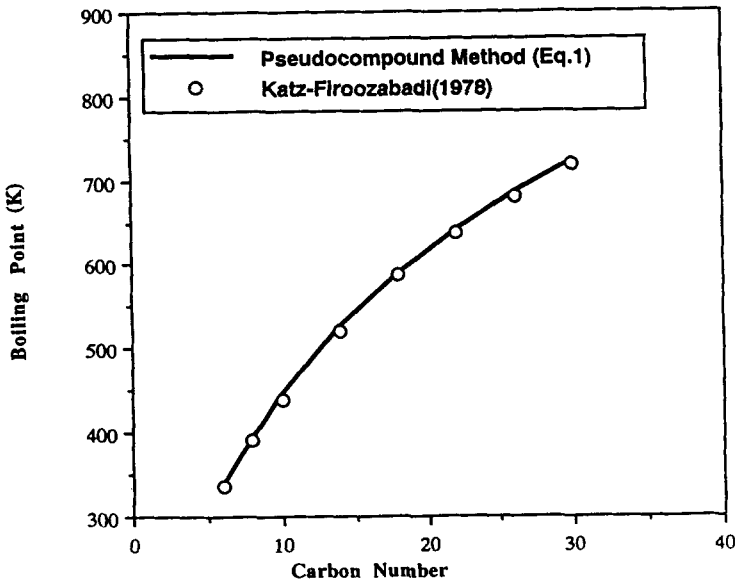

Figure 2. Estimated boiling point of SCN fractions.

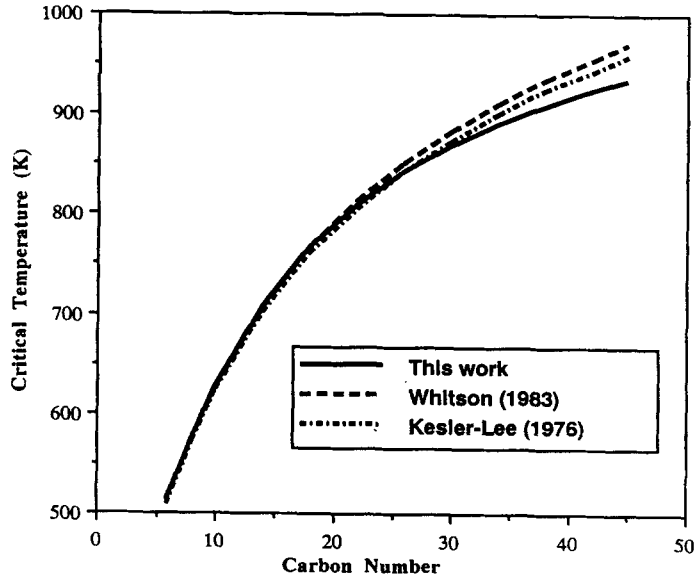

Figure 3. Critical temperature of SCN fractions.

4. NOMENCLATURE

a,b,c = constants specific for each property in eq. 2
d_c = critical density [g/cm^3]
d_{20} = liquid density at 20 °C [g/cm^3]
I = refractive index parameter [$(n^2-1)/(n^2+2)$]

M = molecular weight
n = sodium D-line refractive index of liquid at 20 °C and 1 atm.
N_c = carbon number
P_c = critical pressure [bar]
S = specific gravity at 60F/60F
T_b = normal boiling point [K]
T_{br} = reduced boiling point [T_b/T_c]
T_c = critical temperature [K]

Greek Letters:

θ = a property such as T_b, P_c
θ_∞ = limiting value of θ as $M \rightarrow \infty$
ω = acentric factor
σ = surface tension at 25°C [dyne/cm]
δ = liquid phase solubility parameter [$(cal/cm^3)^{0.5}$]

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