THERMODYNAMIC AND RHEOLOGICAL PROPERTIES OF SOLID-LIQUID SYSTEMS IN COAL PROCESSING

by

Vinayak N. Kabadi
Palakkal Mohandas
Jinsong Wang

Chemical Engineering Department
North Carolina A&T State University
Greensboro, NC 27411

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A GROUP CONTRIBUTION METHOD FOR THE PREDICTION OF VISCOSITY OF COAL DERIVED LIQUIDS

BACKGROUND:

Models available are not very accurate (up to 45% error)

No method available which considers molecular structure to predict viscosity, specifically for coal liquids

Most corresponding states methods use certain specific constants apart from T_c , P_c , ω

Available group contribution methods cannot be extended to coal liquid model compounds (structures like Thiophene, Pyridine, furan, etc. are not considered at all)

GROUP CONTRIBUTION METHOD:

(Van Velzen et. al, Ind. Eng. Chem. Fundam, 11, 20, 1972)

Limited applicability to coal liquids

- * Pyridine, thiophene, furan, pyrrole, polyhydroxy phenyl groups are not defined**
- * Does not consider condensed ring structures and heteroatom groups attached to condensed ring structures**
- * Overall error = 26.93% for model aromatic compounds**

CRITERIA FOR THE NEW MODEL:

- * Up to 10-15% error in the viscosity of coal liquids
- * Use benzene ring as the basic building block
- * Must consider the effect of molecular structure
- * Must be feasible to extend to any type of coal liquid using functional group analysis
- * Group contributions using functional groups as building blocks
- * Must be reasonably simple

LOW PRESSURE VISCOSITY DATA SET:

Model Compounds

No. of Compounds = 142
No. of Data Points = 2339
Temperature range = $0.35 \leq T_r \leq 0.70$

Binary Mixtures

No. of Mixtures = 73
No. of Data Points = 2408

Ternary and Multi Component

No. of Mixtures = 6
No. of Data Points = 48

NEW VISCOSITY MODEL FOR PURE LIQUID AROMATICS:

$$\log \eta = A + \frac{B}{T}$$

where η is absolute viscosity in centipoise

T is absolute temperature in °K

A and B are obtained by group contribution method as follows

$$A = 10 \left[\left(\sum_i \Delta A_i \theta_i \right)_{ring} (N^{**})^{0.467} + \sum_i \Delta A_i n_i^{\alpha_i} - 1 \right] + \Delta A_{alk}$$

$$B = \left(\sum_i \Delta B_i \phi_i \right)_{ring} (N^*)^{-0.5} + \sum_i \Delta B_i n_i^{\beta_i} + \Delta B_{alk}$$

In both the above expressions, the first summation is over group contributions of various ring structures. Types of ring groups considered are aromatic (ar), cyclopentane (cp), cyclohexane (ch), pyridine (py), thiophene (th), cyclopentene (cpe), cyclohexene (che), pyrrole (pyr), furan (fu) and tetrahydrofuran (thf). Primary contribution of each of these rings (ΔA_i) is given in Table 1. θ_i and ϕ_i represent multiplication factors to the primary group contributions. ΔA_i and ΔB_i corresponding to the way ring i is attached to other rings in a composite fused ring structure. Factors θ_i and ϕ_i for various ring configurations are given in Table 2. Let N_t be the total number of rings in the molecule.

For $N_t = 1$, $N^* = 1$ and $N^{**} = 1$

For $N_t > 1$

$$N^* = (N_{ar} + N_{cp} + 1.9N_{ch} + .68N_{py} + 2.8N_{th} + 0.75N_{cpe} + N_{che} + N_{pyr} + N_{fu} + N_{thf})$$

$$N^{**} = (N_{ar} + 0.75N_{cp} + 1.33N_{ch} + 0.8N_{py} + 2.4N_{th} + N_{cpe} + N_{che} + N_{pyr} + N_{fu} + N_{thf})$$

The contributions corresponding to phenyl linkages as in biphenyl and terphenyl must be added in the summations over the ring contributions.

For both A and B, the second summation is over all the other non-ring groups in Table 1. n_i represents number of groups of type i, and α_i and β_i are exponents which are all unity except for the -OH group for which $\alpha_i = 0.1$ and $\beta_i = 0.5$

Model for $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$:

$(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$ are contributions to A and B of all the alkyl groups attached to the rings excluding the α -alkyl groups. These groups are treated equivalent to alkyl groups in normal paraffins. From experimental data on normal paraffins following model for A_{par} and B_{par} was obtained

$$A_{\text{par}} = 10[0.5246 + 0.1657e^{-0.2083n_c} - 1]$$

$$B_{\text{par}} = 2392.82[1 - e^{-0.08n_c}]$$

where n_c is the number of carbon atoms in the paraffin.

Comparing A's and B's of paraffins and alkylbenzenes, it was observed that intercept A for an alkylbenzene is equivalent to that of a paraffin with carbon number three less than that of the alkylbenzene whereas slope B for an alkylbenzene is equivalent to that of a paraffin with same number of carbon atoms as the alkylbenzene.

From this the following procedure is developed to calculate $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$.

Let n_t be the sum of all the ring carbon atoms and the alkyl chains carbon atoms in the molecule.

Let n_r be the sum of all the ring carbon atoms and the carbon atoms in α -alkyl groups. Then $(\Delta A)_{\text{alk}}$ and $(\Delta B)_{\text{alk}}$ are contributions of $(n_t - n_r)$ alkyl groups in the molecule and are given as

$$(\Delta A)_{\text{alk}} = (A_{\text{par}})_{n_c=n_t-3} - (A_{\text{par}})_{n_c=n_r-3}$$

$$(\Delta B)_{\text{alk}} = (B_{\text{par}})_{n_c=n_t} - (B_{\text{par}})_{n_c=n_r}$$

RESULTS:

Comparison of model results with experimental data is shown in Table 3. An average percent error of 11.64% for 2605 data points indicates good agreement.

Table 1
PRIMARY GROUPS AND THEIR CONTRIBUTIONS

Groups		ΔA	ΔB
benzene	0.6122	1000
cyclohexane	0.4903	1435
cyclohexene	0.5684	1140
pyridene	0.6100	1140
cyclopentane	0.5934	965
thiophene	0.5934	1068
cyclopentene	0.4772	1240
tetrahydrofuran	0.6203	900
furan	0.5962	900
pyrrole	0.4618	1675
biphenyl bridge	-0.841	400
hydroxyl	-0.2756	1541
amine	-0.1622	1030
α -alkyl	-0.015	47
N-alkyl	-0.0696	0.0
o-alkyl	0.10023	-966

— attached to a ring
— attached to nitrogen
— attached to oxygen

TABLE 2

†

GROUP MULTIPLIERS θ_i AND Φ_i FOR VARIOUS RING CONFIGURATIONS

sub-group	multipliers for $\Delta A, \theta_i$	multipliers for $\Delta B, \Phi_i$
1.000	1.000
0.3375	1.060
-0.0666	0.76
-0.1413	1.23
0.1746	1.15
0.0309	1.365
-0.229	1.40
0.000	1.80

† same multipliers hold for all the different types of rings in the same configuration (see table 1)

Table 3

ERROR ANALYSIS FOR HOMOLOGOUS SERIES

Homologous Series	No. Of Points	%error
n-Alkanes	567	7.45
Alkylbenzenes	483	12.39
Fused/multi ring compounds	550	9.34
Cyclohexanes	253	15.92
Phenols	232	19.67
Amines	259	14.98
Thiophenes	37	2.24
Pyridines	141	10.22
Cyclopentanes	77	10.58
Sidechain-linked compounds	6	7.29
Entire Data Bank	2605	11.64

ILLUSTRATION OF VISCOSITY CALCULATION USING THE MODEL:

Compound: Flouranthene

Required to calculate viscosity at 179.1 °C of 452.25 °K

Step 1: Analysis of number of types of rings

Total number of rings = 4

Type of rings: Aromatic = 3, cyclopentane = 1

$$N^* = 3 + 1 = 4$$

$$N^{**} = 3 + 0.75 = 3.75$$

Step 2: Analysis of ring configurations and calculation of their contributions to A and B

Rings
ΔA_i	0.6122	0.5934	0.6122	0.6122
$\Delta \theta_i$	0.3375	-0.229	0.1746	0.1746
ΔB_i	1000	950	1000	1000
ϕ_i	1.06	1.40	1.15	1.15
$\Delta A_i \theta_i$	0.20661	-0.1359	0.1069	0.1069
$\Delta B_i \phi_i$	1060	1330	1150	1150

$$\left(\sum_i \Delta A_i \theta_i \right)_{ring} = 0.2845, \quad \left(\sum_i \Delta B_i \phi_i \right)_{ring} = 4690$$

Step 3: From the equations for A and B, A= -4.7256, B=2345

Step 4: With these A and B and T=452.25 °K

$$\eta = 1.583 \text{ cp}$$

From literature, experimental value is 1.528 cp, Error = 3.6%

EXTENSION OF THE MODEL TO MIXTURES:

1. Kendall and Monroe (KM) Mixing rule:

$$\mu_M = \left\{ \sum x_i \mu_i^{1/3} \right\}^3$$

2. Quadratic Mean (QM) Mixing rule:

$$\mu_M = \sum_i \sum_j x_i x_j (\mu_i \mu_j)^{1/2}$$

TABLE 4

ERROR ANALYSIS FOR BINARY SYSTEMS OF COAL LIQUID MODEL COMPOUNDS

SYSTEM	No.Pts	QUADRATIC		KENDALL-MONROE	
		experimental	model	experimental	model
Aromatics—Aromatics	553	1.70	9.27	1.68	9.22
Aromatics—Naphthenes	187	10.45	6.43	10.22	6.38
Aromatics—Multiring compds	162	4.95	6.19	4.56	5.91
Aromatics—Phenols	18	88.73	59.57	67.93	45.20
Aromatics—Thiophenes	11	0.28	2.39	0.28	2.39
Naphthenes—Multiring compds	11	2.84	47.87	2.32	50.82
Phenols—Phenols	69	2.09	36.37	1.86	36.38
Phenols—Pyridenes	548	25.44	23.12	21.21	23.84
Phenols—Amines	335	13.06	31.10	13.30	30.88
Pyridenes—Amines	64	12.95	16.76	13.11	16.90
Paraffins—Ring compounds	59	8.55	10.54	8.20	10.25
Systems with Biphenyls	118	7.30	35.93	7.34	35.73
Systems with guaiacols	78	36.68	30.58	34.57	28.88
Entire Data bank	2213	13.03	19.38	11.72	19.30

EQUATION OF STATE AT HIGH PRESSURES FOR LIQUID AROMATIC COMPOUNDS

OBJECTIVES:

1. To develop an equation of state for high pressure liquid aromatic compounds, such as the ones that occur in coal liquids.
2. In addition to high pressure compressibilities, the equation should predict other thermodynamic properties of liquids such as enthalpies and heat capacities with reasonable accuracy.
3. Extend the equation to liquid mixtures, using the available low pressure models.

ACHIEVEMENTS:

1. A new saturated vapor pressure equation, which will be used in high pressure equation of state, was developed based on 127 organic compounds, 2971 data points.
2. A new correlation for saturated density, which will be used in high pressure equation of state was developed based on 124 organic compounds.
3. An extensive literature search was carried out for the high pressure liquid thermodynamic properties of organic compounds.

HIGH PRESSURE EQUATION OF STATE:

The most promising of the equations in the literature is the Tait equation (Thomson et al. AICHE J., 28, 671, 1982)

$$V = V_s \left(1 - C \ln \frac{B + P}{B + P_s} \right)$$

where V_s is the saturated liquid volume at the saturation pressure P_s , B and C are parameters which for a given compound are functions of only temperature.

Using the detailed density and heat capacity data of benzene and toluene compiled by Goodwin (J. Phys. Chem. Ref. Data 17, 1541, 1988; Ibid 18, 1565, 1989), Thomson equation was tested and following were the conclusions of the investigations.

1. Densities computed from Thomson equation agreed reasonably well with experimental data (errors < 1 % for $T_r < 0.9$)
2. Errors in density exhibited definite trend with temperature showing a point of inflexion for benzene at about 450 °K.
3. Trends in error with temperature, would indicate that larger errors would be expected for enthalpies and heat capacities because enthalpy is a function of first derivative of density with temperature and heat capacity is a function of the second derivative.
4. This was confirmed when experimental and calculated heat capacities of benzene were compared. Errors in calculated heat capacities (in excess of the values at saturation pressure) were found to exceed 100 % over the entire temperature range, with a very good agreement observed at 450 °K as expected.
5. To identify the source of the temperature dependence of the density errors, the methods used for P_s (Lee-Kesler equation) and V_s (Rackett equation) were tested. Although, these methods were found to give some

errors, no systematic trends were observed. Next B and C were regressed at different temperatures from experimental data. Definite deviations were observed between these values and equivalent curves in Thomson equation.

6. Based on above results, the following three tasks were undertaken
 - (a) Develop a better generalized correlation for vapor pressures to be valid from melting point to critical point.
 - (b) Improve and generalize the Rackett equation for saturated densities.
 - (c) Obtain better expressions for Tait B and C using density and heat capacity data.

NEW VAPOR PRESSURE EQUATION:

An accurate vapor pressure correlation is needed for P_s in Tait equation. No accurate vapor pressure correlations is available from melting point to critical point. Based on the formula of Pitzer (J. Am. Chem. Soc. 77, 3433, 1955) and Wagner equation (Cryogenics 13, 470, 1973), we developed a new saturated vapor pressure equation.

$$\ln(P/P_c) = f^{(B)}(T_r) + \Phi f^{(c)}(T_r)$$

$$f^{(B)}(T_r) = (a_B x + b_B x^{1.5} + C_B x^3 + d_B x^6) / T_r$$

$$f^{(c)}(T_r) = (a_c x + b_c x^{1.5} + C_c x^3 + d_c x^6) / T_r$$

where $f^{(B)}(T_r)$ is the vapor pressure of benzene, $f^{(c)}(T_r)$ represents departure from vapor pressure of benzene and $x = (1 - T_r)$.

Regressed constants for these equations are given below.

$a_B = -6.958$, $b_B = 1.2776$, $c_B = -2.5647$, $d_B = -3.4035$, $a_c = -1.2731$,

$b_c = -0.2194$, $c_c = -0.2638$, $d_c = -4.4878$

Φ is a compound specific parameter. Three different methods were devised for Φ (Methods 2-4 below)

Four Methods:

Method 1: Specific constants a, b, c, d regressed for each compound using Wagner's equation.

Method 2: Specific Φ regressed for each compound using experimental data.

Method 3: Φ calculated for each compound from one data point ($Tr = 0.6$)

Method 4: Group contribution method to estimate Φ .

Group contribution method for Φ :

We note the vapor pressure is strongly related to the shape of the molecule. So we defined a parameter Ψ which is called shape factor.

$$\Psi = \frac{S_{compound} / (V_{compound})^{2/3}}{S_{benzene} / (V_{benzene})^{2/3}}$$

V is the summation of R as in UNIFAC.

S is the summation of Q as in UNIFAC with some modifications, and additions of ring, branch, and attachment factors.

Groups, group contributions R and Q and all the relevant addition and multiplication factors are given in Tables 5, 6, and 7.

The following expression was fitted to the values of Φ and Ψ :

$$\Phi = a_1(1 - \Psi) + a_2(1 - \Psi)^2 + a_3(1 - \Psi)^3$$

$$a_1 = -4.2546, a_2 = 4.5345, a_3 = 7.2866$$

Figure 1 shows a very good correlation between regressed Φ and the shape factor Ψ .

Table 5 . List of R and Q of Different Groups

I.D.	Group Symbol	R	Q _(this paper)	Q _(UNIFAC)
g1	CH ₃	0.9011	0.8480	0.848
g2	CH ₂	0.6744	0.5400	0.540
g3	CH	0.4469	0.2280	0.228
g4	C	0.2195	0.0000	0.000
g5	OH	1.0000	1.7700	1.200
g6	aCH ⁽⁺⁾	0.5313	0.4000	0.400
g7	aCC ^(*)	0.5847	0.0000	0.120
g8	aC	0.3652	0.1200	0.120
g9	aCOH	0.8952	1.2562	0.680
g10	CH=CH	1.1167	0.8670	0.867
g11	aCNH ^(*)	0.8978	0.5332	0.516
g12	aCNH ₂	1.0600	1.1975	0.816
g13	aCBr	1.3144	0.9611	0.952
g14	aCCl	1.1562	0.8442	0.844
g15	aCCOOH	1.6665	2.1967	1.344
g16	aC-O-CH ₃	1.5102	1.3462	1.208
g17	aC-O-CH ₂	1.2835	1.1031	0.900
g18	aC-CH=CH ₂	1.7106	1.2068	1.296
g19	aN ^(*)	0.3428	0.3675	0.113
g20	NH ^(*)	0.5326	0.7742	0.369
g21	aO ^(*)	0.2439	0.2706	0.240
g22	aS ^(*)	0.91875	0.6747	0.825

Note, ⁽⁺⁾ : All groups starting with "a" are aromatic groups

^(*) : For these groups UNIFAC R and Q were estimated from other group contributions.

Table 6 Q Additives (Q_{add}) for Various Molecular Structure

I.D.	Structure	Q_{add}
r1	One aromatic-ring	0.45023
r2	Two aromatic -ring	0.71355
r3	Three aromatic-ring	1.10481
r4	Four aromatic-ring	1.23800
r5	One aromatic -one naphthene (fused)	0.60446
r6	Two aromatic -one naphthene (fused)	1.01571
r7	Cyclohexane (without attachment)	0.102451
r8	Cyclohexane (with attachment)	-0.118173
r9	Isoquinoline	-0.13794

Table 7: Modifications to Q for some additional Group Structures ⁺

Group g	Q_{add}	Θ_a	Θ_b
--CH ₃ branch eg. $\begin{array}{c} \text{--C--} \\ \\ \text{CH}_3 \end{array}$	-0.08289	2, if two branches attached to same carbon 0.5, if a single branch in β position relative to a ring 1.0, all other cases	1.0
--CH ₂ -CH ₃ branch eg. $\begin{array}{c} \text{--C--} \\ \\ \text{CH}_2\text{CH}_3 \end{array}$	-0.1233	Same as for -CH ₃ branch	1.0
Attachments to an aromatic ring in ortho position	0	_____	0.9872
Two attachments to a carbon in a hydro- aromatic ring	0	_____	0.9461
Alkyl groups in the largest straight chain attached to a ring	-0.02157	1.0	1.0

$$^+ Q_M = (Q_g + Q_{add} \Theta_a) n_g \Theta_b$$

Q_M - modified contribution of n_g groups of type g

Q_g - original contribution (Table 4) per group of type g

FIGURE 1

RESULTS:

Comparison of the correlations (Methods 1-4 and Lee-Kesler) with experimental data for different homologous series of compounds is shown in Table 8.

Comparisons of the correlations around the melting point and the boiling point are shown in Table 9.

Results are impressive. Even the generalized correlation (Method 4) performs as well as the Lee-Kesler method, but with applicability over a wider range of temperatures.

Table 8. Comparison of vapor pressure errors (percent) for different methods

	Method 1	Method 2	Method 3	Method 4	Lee-Kesler	No. Pts
1.alkanes	0.260	1.96	2.63	3.07	3.17	906
2.alcohols	0.088	5.75	8.46	16.24	9.62	185
3.alkyl-benzenes	0.210	1.12	1.27	3.37	3.34	706
4.phenols	0.884	4.39	7.60	7.47	4.89	218
5.alkyl cyclo-hexanes	0.141	1.33	1.45	3.78	4.07	174
6.two ring aromatics	0.612	3.10	4.03	6.98	12.60	298
7.three and four ring aromatics	0.724	6.76	9.54	17.23	17.85	173
Total	0.360	2.53	3.45	5.65	5.55	2971

Table 9. Comparison of Correlations In Different Temperature Ranges

Temperature Range	No. Points	Method 2	Method 3	Method 4	Lee-Kesler
$T_m < T < T_m + 30K$	100	8.06%	15.65%	13.70%	20.29%
T nearest to T_b	127	3.15%	2.92%	5.01%	2.54%

NEW CORRELATION FOR SATURATED LIQUID DENSITIES:

Rackett (J. Chem. Eng. Data, 15, 514, 1970)] developed an equation to estimate saturated volumes. The equation was later modified by Spencer and Danner (J. Chem. Eng. Data, 17, 236, 1972). In this correlation specific Z_{RA} was used for each compound. Yamada (J. Chem. Eng Data 18, 234, 1973) proposed a method to estimate Z_{RA} from acentric factors. We developed a method to calculate Z_{RA} from Van der Waals volumes.

$$Z_{RA} = \frac{P_c}{RT_c} (2.768858 + 0.423611V_w + 9.2792939 \times 10^{-4}V_w^2)$$

where P_c is in bars, T_c is in $^{\circ}\text{K}$, $R = 8.314$ bar cc/ mole $^{\circ}\text{K}$ and V_w is in cc/mole.

RESULTS:

Comparisons of Regressed Z_{RA} with ones obtained from the Yamada and our correlation are shown in Table 10. It is observed that Van der Waals volume is a better correlation parameter than acentric factor. For 782 data points for 40 liquids, the correlations gave the following percent errors:

Regressed Z_{RA} - 0.56%, Yamada Z_{RA} - 5.87% , Our Z_{RA} - 3.96%

A better generalized method for saturated liquid densities has thus been developed.

Table 10 Comparison between Yamada Correlations and Our Method for Prediction of ZRA			
	No. of Points	Yamada	Ours
Paraffins	34	1.692	1.429
Halogenated Paraffins	6	4.815	2.833
Cycloparaffins	4	0.316	0.319
Olefins	13	1.549	2.119
Aromatics	26	2.781	2.565
Aromatic Derivatives	4	1.474	1.263
Heterocycles	8	2.021	1.439
Alcohols	8	4.834	1.416
Phenols	9	6.954	3.113
Amines	7	2.673	2.133
Ethers	3	0.717	2.759
Sulfides	2	1.259	0.940
Total	124	2.636	1.953