Generalized Correlation of the Constants of the Benedict-Webb-Rubin-Friend Equation for Paraffinic Isomers

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Canjar, Smith, Volianitis, Galluzzo, and Cabarcos (*1*) developed for normal paraffinic hydrocarbons a correlation of the constants of the Benedict-Webb-Rubin-Friend equation of state:

$$P = dRT - d^2\left\{ [A_o + ad\,(1-\alpha d^3)] - (B_o - db)\,RT + \frac{1}{T^2}[C_o - cd\,(1+\gamma d^2)\exp -\gamma d^2] \right\} \quad (1)$$

Later Griskey and Canjar (*2*) developed a similar correlation for 2-methyl paraffins.

The present work attempted to further generalize the 2-methyl correlation to other isomeric paraffins. The first attempt to do so was unsuccessful. However when the 2-methyl paraffin constants were recorrelated, forms were obtained that applied to several isomeric paraffins. Equations (2) through (9) illustrate these forms:

$$\left(\frac{N_T{}^o}{N_T}\right)(C \times 10^{-6}) = D^*\left(\frac{T_c}{T_c{}^o}\right) - D^{**} \quad (2)$$

$$\left(\frac{N_s N_T{}^o}{N_T N_s{}^o}\right) A_o{}^{1/3} = E^{**} - E^*\left(\frac{T_c{}^o}{T_c}\right)^2 \quad (3)$$

$$B_o = F^*\left(\frac{T_c}{T_c{}^o}\right) + F^{**} \quad (4)$$

$$a = G^*\left(\frac{T_c}{T_c{}^o}\right)^{1/2} - G^{**} \quad (5)$$

$$(b \times 100)^{1/3} = J^*\left(\frac{T_c}{T_c{}^o}\right) - J^{**} \quad (6)$$

$$\log_{10}(\alpha \times 10^3) = K^*\frac{T_c}{T_c{}^o} - K^{**} \quad (7)$$

$$\log_{10}(\gamma \times 10^2) = L^*\frac{T_c}{T_c{}^o} - L^{**} \quad (8)$$

$$\log_{10}\left(\frac{C_o}{C_o{}^o}\right) = M^*\log_{10}\left(\frac{T_c}{T_c{}^o}\right) - M^{**} \quad (9)$$

Each of the slopes (asterisked constants) in Equations (2) through (8) is the same for all of the isomeric paraffins correlated. The intercepts (double asterisked constants) however differ for each paraffin type as do both slope and intercept in Equation (9).

Correlation constants are given in Table 1. Pressures calculated with these constants differed on the average by less than 1% from experimental values for 3-methyl-pentane (*3*) 2,2-dimethylbutane (*4*), and 2,3-dimethylbutane (*5*). Average deviations and appropriate density and temperature ranges were 0.08% (3.2 to 6.0 g. mole/liter, 250° to 275°C.) for 3-methylpentane, 1.01% (1.5 to 5.0 g. mole/liter, 250° to 275°C.) for 2,3-dimethylbutane, and 0.6% (1.8 to 5.0 g. mole/liter, 225° to 275°C.) for 2,2-dimethylbutane. Calculated critical pressures deviated from observed values (*6*) for these compounds by 0.44, 0.34, and 0.11 atm., respectively.

Deviation of calculated from observed critical pressures (*6, 7*) for 3-methylhexane and 3-methylheptane were 0.40 and 0.36 atm., while for 2,3-dimethylpentane and 2,3-dimethylhexane these deviations from observed values (*6, 7*) were 0.32 and 0.30 atm. Calculated critical pressures deviated by 0.11 and 0.09 atm. from observed values (*6, 7*) for 2,2-dimethylpentane and 2,2-dimethylhexane.

Constants obtained from the correlation appear to be able to reproduce with good precision compressibility data and critical points of the compounds correlated (3-methylpentane, 3-methylhexane, 3-methylheptane, 2,2-dimethylbutane, 2,2-dimethylpentane, 2,2-dimethylhexane, 2,3-dimethylbutane, 2,3-dimethylpentane, 2,3-dimethylhexane). These results therefore indicate that the correlation of the present work is applicable to 3-methyl, 2,2-dimethyl, and 2,3-dimethyl paraffins at least up through the octanes.

A firm conclusion as to extrapolation beyond the octanes cannot be directly reached because neither compressibility

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TABLE 1. CORRELATION CONSTANTS

	A_o	B_o	$C \times 10^{-6}$	a	b	$C \times 10^{-6}$	$\sigma \times 10^3$	$\gamma \times 10^2$
3-methylpentane	12.203	0.081505	2.2125	5.9716	0.11224	0.95556	2.2500	6.2500
3-methylhexane	14.310	0.091423	3.1564	7.5854	0.14321	1.3252	2.8155	7.4461
3-methylheptane	16.113	0.10077	4.5701	9.0636	0.17715	1.7411	3.4778	8.7819
2,2-dimethylbutane	11.842	0.19214	3.3595	10.108	0.14000	1.7483	2.1890	5.6500
2,2-dimethylpentane	12.423	0.20246	5.1237	11.786	0.17721	2.2586	2.7640	6.7990
2,2-dimethylhexane	13.040	0.21265	7.4893	13.394	0.21991	2.8283	3.4803	8.1150
2,3-dimethylbutane	16.430	0.19000	2.5534	4.6956	0.07900	1.1346	3.5948	7.5000
2,3-dimethylpentane	17.375	0.20202	3.8374	6.6451	0.10956	1.5786	4.7170	9.2730
2,3-dimethylhexane	17.468	0.21106	5.7002	8.0669	0.13713	2.0233	5.7860	10.880

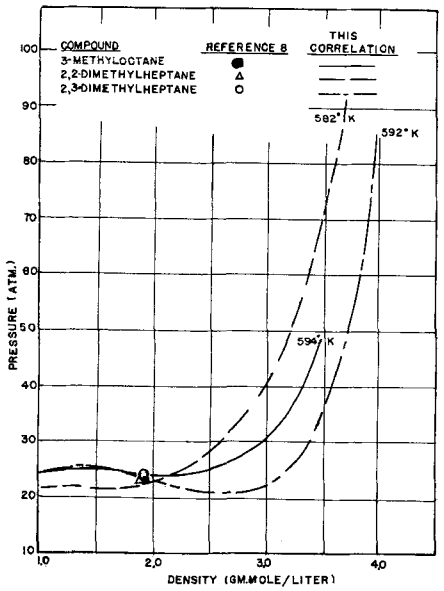

Fig. 1. Comparison of extrapolated critical isotherms with estimated critical points.

nor critical data exist for such compounds. An indirect comparison did however indicate possible application of the correlation for higher molecular weight compounds. The comparison first involved estimating critical temperatures for 3-methyloctane, 2,2-dimethylheptane, and 2,3-dimethylheptane by the method of Thodos (8) which generally yields estimated values within 2% of experimental data. These estimated critical temperatures were then used with Equations (2) through (9) to obtain appropriate Benedict equation constants for each of the nonanes tested. Isotherms corresponding to the estimated critical temperatures were then calculated. These isotherms are plotted in Figure 1. Also shown are the critical points as per the estimation technique of Thodos (8). As can be seen agreement is quite good considering both the rapid change in isotherm shape near the critical point and the per cent deviations in the estimation method of Thodos (for example critical temperatures can be off by 5° to 12°K. for the compounds considered). These results therefore give some backing to extrapolation of the correlations of this work.

Additional correlation for other isomeric paraffins could also possibly be developed with the forms of Equations (2) through (9). In order to do this however additional experimental data would have to be available. The procedure for accomplishing such correlations would be as follows:

1. Determine the Benedict equation constants for at least the first compound in the isomeric paraffin series.
2. The intercepts of Equations (2) through (8) can then be determined by passing the slopes (constant for all isomeric types) through the Benedict equation constants.
3. The slope and intercept of Equation (9) can be established if a check point (critical point or compressibility data point) is available for another member of the isomeric paraffin series.

The constants of the present paper hold only for the critical and superheated vapor regions. It is recommended that these constants not be used to estimate properties for the vapor-liquid dome.

CONCLUSIONS

1. A generalized correlation of the constants of the Benedict-Webb-Rubin-Friend equation of state has been developed and applied to 3-methyl, 2,2-dimethyl, and 2,3-dimethyl paraffins.
2. Pressures calculated with correlation constants used deviated on the average by less than 1% from experimental data. In addition calculated critical pressures had an average deviation of 0.27 atm. from experimental values.
3. A procedure is outlined for extending the correlation to other isomeric paraffin series.

NOTATION

$A_o, B_o, C_o, a, b, c, \alpha, \gamma$ = constants of the Benedict-Webb-Rubin-Friend equation of state
C_o^o = C_o value for initial compound of each isomeric type (for example 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane
D^* = constant of Equation (2) with a value of 2.91526
D^{**} = constant of Equation (2) with values of 1.95971, 1.78066, and 1.16697 respectively for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins.
E^* = constant of Equation (3) with a value of 1.72315
E^{**} = constant of Equation (3) with values of 4.02540, 4.26535, and 4.00247 respectively for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
F^* = constant of Equation (4) with a value of 0.160342
F^{**} = constant of Equation (4) with values of —0.078837, 0.0296581, and 0.031801 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
G^* = constant of Equation (5) with a value of 52.9749
G^{**} = constant of Equation (5) with values of 47.0034, 48.2793, and 42.8677 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
J^* = constant of Equation (6) with a value of 3.06105
J^{**} = constant of Equation (6) with values of 0.821987, 1.06945, and 0.65092 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
K^* = constant of Equation (7) with a value of 1.5742
K^{**} = constant of Equation (7) with values of 1.22202, 1.01853, and 1.2340 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
L^* = constant of Equation (8) with a value of 1.2294
L^{**} = constant of Equation (8) with values of 0.433519, 0.35434, and 0.47735 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
M^* = constant of Equation (9) with values of 6.92499, 7.7496, and 6.53947 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
M^{**} = constant of Equation (9) with values of 0.026186, 0.0066454, and —0.0060904 for 3-methyl, 2,3-dimethyl, and 2,2-dimethyl paraffins
N_T = total number of carbon atoms in a given compound
N_T^o = total number of carbon atoms in the initial compound of each isomeric type (for example 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane
N_S = number of carbon atoms in the straight chain of a given compound
N_S^o = number of carbon atoms in the straight chain in the initial compound of each isomeric type (for example 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane)
P = pressure, atm.
R = gas constant
T = temperature, °K.
T_c = critical temperature, °K.
T_c^o = critical temperature for the initial compound of each isomeric type (for example 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane)
d = density, g.-moles/liter

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Thermodynamics and Interfacial Tension of Multicomponent Liquid-Liquid Interfaces

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Sternling and Scriven have shown that the derivative of interfacial tension with respect to solute concentration is an important parameter influencing the hydrodynamic stability at an interface across which mass transfer is taking place. This work is concerned with a molecular thermodynamic study of that derivative.

With surface thermodynamics and an extension of the solution theory of Schuchowitzky, an expression is derived which relates the interfacial tension to the solute concentration in terms of physically meaningful parameters. These in turn are related to molecular properties of the solute and solvent species.

New experimental data are reported for the interfacial tension of nine ternary systems; these consist of an aqueous phase and an organic phase where both phases are dilute solutions of an alcohol. The organic phases are hexane, benzene, and carbon tetrachloride and the alcohols are methanol, ethanol, and n-propanol.

The theoretical equations predict interfacial tensions which are in good agreement with the new experimental results and with experimental data of Vignes on aqueous-organic systems which are dilute solutions of organic acids.

In recent years researchers in chemical engineering (for example *4, 5, 6, 7, 9, 15, 19, 22, 24, 25, 26, 32, 42*) have shown a renewed interest in the role of surface and interfacial phenomena in situations involving the transfer of matter across liquid-liquid and liquid-vapor interfaces. Sternling and Scriven (37) have investigated the conditions under which the diffusive transport of material across an interface leads to hydrodynamic (Marangoni)

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