Improved Equation for Prediction of Saturated Liquid Density

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An extensive evaluation of the available methods for predicting the saturated liquid density of pure hydrocarbons as a function of temperature has been made with as much of the available literature data as could be found. Results of these evaluations are given, and the revised Rackett equation with one constant determined from experimental data is shown to be more accurate. With the list of constants given for use in the modified Rackett equation, one can predict accurately the variation of the saturated liquid density over the entire temperature range from the triple point to the critical point.

For many physical properties needed for design purposes, data and correlations which do not have important limitations are relatively scarce. This is not true, however, in the case of liquid densities, since both correlations and data are plentiful. Selection of the best, and simultaneously most general, method for correlating liquid densities thus proved to be an involved and lengthy task. The results of this study together with a set of completely new constants for the recommended equation are presented.

DATA SOURCES

An extensive literature search has been made to locate saturated liquid density data for pure hydrocarbons, as well as other organic and inorganic compounds. For the data published prior to 1940, the physical property review of Egloff (*25*) was used while the data from 1940 to 1971 were obtained from the original sources. (The data sources are given as part of Table IV.)

In the compilation of the data set, only experimental data values were considered to be useful; the data calculated or obtained by extrapolation from a nomograph were not used. The final data set included 2795 data points for 64 hydrocarbons, 652 points for 36 other organic compounds, and 148 points for 11 inorganic liquids.

EVALUATION OF AVAILABLE CORRELATIONS

Thirteen relatively new correlations for predicting the effect of temperature on saturated liquid density were considered. These methods along with the form of their predictive equations are given in Table I. There are also a number of other correlations available in the literature. In a critical review of such correlations in 1966 (*45*), the methods of Benson (*15*), Watson (*99*), Lydersen et al. (*55*), Goldhammer (*35*), Fishtine (*29*), Guggenheim (*37*), Wada (*98*), and Ritter et al. (*77*) were somewhat less accurate than the equations of Francis (*31*, *32*). Therefore, the above methods were not re-evaluated in this study.

Preliminary evaluation studies were made on the more recent correlations using only the data for the saturated liquid densities of hydrocarbons at low temperatures (40°C below the critical and lower). Many of the methods being tested were developed with this type of data, and thus this test was designed to be a good indicator of the relative values of the correlations. Results for this evaluation are given in Table II.

The Ehrlich, Riedel, and Holmes correlations were evaluated with normal hydrocarbon data. Although they gave reasonable results, they were not so good as the Francis correlation and were therefore not considered further. Harmans' correlation has been generalized only for hydrocarbons up to C_7. Although good for the applicable compounds, this method was not considered sufficiently general and was not evaluated further.

Average errors for the methods of Bradford and Thodos, Lyckman, Eckert and Prausnitz, and Narsimham were too large to warrant further study. In addition, the method of Halm and Stiel was not included in the evaluations listed in Table II, since the authors stated that, for normal fluids, their results were no better than those of Lyckman, Eckert, and Prausnitz. On the other hand, the correlations given by Yen and Woods, Gunn and Yamada, Harlacher, and Francis are all excellent. In particular, it should be noted that the method of Gunn and Yamada is superior to any of the other corresponding states approaches. The Francis equations, however, are considerably better than any of the other correlations and, therefore, the method of Francis was selected for further evaluation.

Modified Rackett Equation. The remaining correlation in Table I which has not been discussed is the Rackett equation. Rackett's equation can be written in the following form:

$$\frac{1}{\rho_s} = V_c Z_c^{(1-T_r)^{2/7}} = \left(\frac{RT_c}{P_c}\right) Z_c^{[1+(1-T_r)^{2/7}]} \tag{1}$$

This equation is the simplest in form of all the equations considered and requires no arbitrary constants for its evaluation. One simply needs the critical constants T_c, P_c, and Z_c. It is able to predict reasonable results from the triple point to the critical point for most substances. The functional form well describes the smooth, almost linear, behavior of density in the low reduced temperature range, and the sharp decrease in density near the critical point. On the other hand, in the evaluation with 36 hydrocarbons and with Z_c, T_c, and P_c values from ref. *1*, the average error of 2.40% is considerably poorer than the results of the better correlations.

Therefore, it was decided to evaluate a modified form of the Rackett equation:

$$\frac{1}{\rho_s} = \left(\frac{RT_c}{\rho_c}\right) Z_{RA}^{[1+(1-T_r)^{2/7}]} \tag{2}$$

Here Z_{RA} is a particular constant for the Rackett equation which is to be determined from the experimental data. This approach does compromise the very desirable property of the original equation of not requiring any unique constant. However, one can always use the Z_c value for a compound for which no Z_{RA} is available and still obtain a reasonable value for the density as shown in Table II.

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Table I. Summary of Correlations Evaluated

Lyckman et al. (*54*)

$$\rho_c/\rho_s = V_r = V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)}$$

where $V_r^{(i)}$'s are generalized functions of T_r.

Halm and Stiel (*39*)

$$1/\rho_s = V_s = V^{(0)} + \omega V^{(1)} + \chi V^{(2)} + \omega^2 V^{(3)} + \chi V^{(4)} + \omega\chi V^{(5)},$$

where $V^{(i)}$'s are generalized functions of T_r

and $\chi = \log P_r@T_r(0.6) + 1.70\ \omega + 1.552$

Holmes (*44*)

$$\rho_s/\rho_c = (1 - \omega)\rho_r^{(0)} + \omega\rho_r^{(1)}$$

where $\rho_r^{(i)}$'s are generalized functions of T_r and P_r

Gunn and Yamada (*38*)

$$1/\rho_s = V_s = [V_r^{(0)}(1 - \omega V_r^{(1)})] \cdot [V@T_r = (0.6)]/(0.3862 - 0.0866\ \omega)$$

where $V_r^{(i)}$'s are generalized functions of T_r

Francis (*31, 32*)

$$\rho_s = A - BT - C/(E - T) \text{ (low temperature)}$$

$$(\rho_s - \rho_c)^H = C(T_c - T) \text{ (high temperature)}$$

where A, B, C, E, and H are specified constants for each compound

Harmans (*43*)

$$\rho_s/\rho_c = (0.43875 - 0.625\ Z_c)\,f(T_r)$$

where $f(T_r)$ is a generalized, density function plot

Bradford and Thodos (*16*)

$$\rho_s/\rho_c = 1.0 + (2.924 - 7.34\ Z_c)(1 - T_r) - (1.139 - 3.796\ Z_c) \times (1 - T_r)^2 + (2.785 - 3.544\ Z_c)(1 - T_r)^{(0.160+0.586 Z_c)}$$

Riedel (*76*)

$$\rho_s/\rho_c = 1 + (1.69 + 0.984\ \omega)(1 - T_r)^{1/3} + 0.85\ (1 - T_r)$$

Yen and Woods (*104*)

$$\rho_s/\rho_c = 1 + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + (0.93 - B)(1 - T_r)^{4/3}$$

where A and B are specified constants for each compound (constants have been generalized as functions of Z_c)

Harlacher (*42*)

$$\rho_s/\rho_c = 1 + K(1 - T_r)^{1/3} + L(1 - T_r)^{2/3}$$

where K and L are specified constants for each compound (constants have been generalized as functions of the parachor and ω)

Ehrlich (*26*)

$$[(\rho_s/\rho_c) - 1]^3/[(\rho_s/\rho_c)(1 - T_r)] = A + B(1 - T_r) + C(1 - T_r)^2$$

where A and B are specified constants for each compound.

Narsimham (*62*)

$$\rho_s/\rho_c = 1 + [(0.422 \log P_c + 0.981)/(1 - T_b/T_c)^{0.40}](1 - T_r)^{0.40}$$

Rackett (*73*).

$$1/\rho_s = [RT_c/P_c]Z_c^{[1+(1-T_r)^{2/7}]}$$

To determine values of Z_{RA} from the experimental data, Equation 2 was rearranged into the following form:

$$\log Z_{RA} = \frac{\log (1/\rho_s) + \log (P_c/RT_c)}{1 + (1 - T_r)^{2/7}} \quad (3)$$

or

$$\log \rho_s = \log P_c/RT_c - [1 + (1 - T_r)^{2/7}] \log Z_{RA} \quad (4)$$

Table II. Summary of Evaluation of Correlations with Low-Temperature Hydrocarbon Data

	No. of compounds treated	No. of data points	Av % dev[a]
Lyckman et al. (*54*)	36	1597	4.22
Holmes (*44*)	6[b]	353	1.80
Gunn and Yamada (*38*)	36	1597	0.59
Francis (*32*)	36	1597	0.43
Harmans (*43*)	11[b]	824	0.68
Bradford and Thodos (*16*)	36	1597	2.19
Riedel (*76*)	9[b]	641	1.16
Yen and Woods (*104*)[c]	24	1354	0.91
Harlacher (*42*)[c]	32	1473	0.81
Ehrlich (*26*)	5[b]	248	1.30
Narsimham (*62*)	32	1473	2.04
Rackett (*73*)[d]	36	1597	2.40

[a] $(100/N)\ \Sigma \left|\frac{\text{calculated value} - \text{experimental value}}{\text{experimental value}}\right|$. [b] Predominantly normal hydrocarbons. [c] Specific constants for each compound were used in this evaluation. Generalized forms for the constants gave poorer results. [d] Using Z_c as in Equation 1.

Table III. Comparison of Two Forms of Rackett Equation and Francis Equation

			Average percent deviation[a]		
	No. of compds treated	No. of data points	Francis equation	Rackett equation (Equation 1)	Modified rackett equation (Equation 2)
Hydrocarbons	37	1948	1.01	2.50	0.53
Organics	36	652	0.43	5.50	0.60
Inorganics	11	148	0.58	2.26	0.74

[a] $(100/N)\ \Sigma \left|\frac{\text{calculated value} - \text{experimental value}}{\text{experimental value}}\right|$.

The best values of Z_{RA} were then determined by performing a linear regression of the following form:

$$\log Z_{RA} = \frac{\Sigma X_i Y_i}{\Sigma (X_i^2)} \quad (5)$$

where

$$X_i = 1 + (1 - T_{r_i})^{2/7} \quad (6)$$

$$Y_i = \log \left(\frac{P_c}{RT_c\rho_{s_i}}\right) \quad (7)$$

where ρ_{s_i} and T_{r_i} are the respective values for each data point. Although by this linearization technique, one is actually minimizing the sum of the difference in the logs of the predicted and experimental densities, the density values in general vary only from 0.2 to 0.8 g/cm^3 and thus no important uneven weighting of the data is encountered.

By this method, values of Z_{RA} were calculated and the modified Rackett equation was evaluated for the 36 hydrocarbons (1597 data points). The average error of only 0.38% was better than even the Francis equation had been able to do. This is significant in as much as the low-temperature Francis equation contains four specific constants for each compound, while the Rackett form requires only one constant. Furthermore, if the appropriate coefficients are not available for some material, the Francis equation cannot be used. If the Z_{RA} of the Rackett equation is not tabulated, however, Z_c can be used to predict a reasonable value.

A new data set was next constructed consisting of 37 of the 64 hydrocarbons, 36 other organic compounds, and 11 inorganic materials. These data covered the entire temperature range of the compounds from their triple points to their critical

Table IV. Z_{RA} Values for Modified Rackett Equation

Compd	Z_{RA}	Av. % dev.[a]	No. of data points	Data sources
Hydrocarbons				
Methane	0.2876	0.60	161	*2, 3, 7, 21, 25, 46, 50, 57*
Ethane	0.2789	1.27	111	*2, 5, 7, 12, 25, 32, 46, 48, 52, 56, 93*
Propane	0.2763	0.32	202	*2, 9, 19, 23, 25, 41, 53, 74, 75, 81, 83*
n-Butane	0.2728	0.42	100	*2, 14, 19, 20, 25, 32, 53, 64, 71, 81*
2-Methylpropane	0.2750	0.31	129	*2, 8, 11, 14, 19, 20, 25, 32, 53, 64, 79, 81, 97*
n-Pentane	0.2685	0.22	107	*2, 19, 25, 46, 53, 78, 80–82, 92*
2-Methylbutane	0.2716	0.42	63	*2, 4, 25, 46, 47*
n-Hexane	0.2635	0.47	65	*2, 25, 46, 49, 72, 89, 100*
2,3-Dimethylbutane	0.2694	0.39	4	*2*
n-Heptane	0.2611	0.19	55	*2, 25, 32, 46, 48, 59, 72, 92*
2-Methylhexane	0.2629	0.71	18	*59*
3-Methylhexane	0.2609	0.95	18	*59*
3-Ethylpentane	0.2665	0.66	19	*59*
2,2-Dimethylpentane	0.2673	0.87	34	*59*
2,3-Dimethylpentane	0.2596	1.10	19	*59*
2,4-Dimethylpentane	0.2654	0.82	38	*59, 70*
3,3-Dimethylpentane	0.2735	0.35	18	*59*
2,2,3-Trimethylbutane	0.2697	0.62	17	*59*
n-Octane	0.2567	0.51	53	*2, 18, 25, 28, 46, 72, 78*
2-Methylheptane	0.2581	0.36	18	*59*
3-Methylheptane	0.2575	0.98	19	*59*
4-Methylheptane	0.2589	0.18	17	*59*
3-Ethylhexane	0.2584	1.11	19	*59*
2,2-Dimethylhexane	0.2640	0.38	18	*59*
2,3-Dimethylhexane	0.2622	0.63	19	*59*
2,4-Dimethylhexane	0.2657	1.07	19	*59*
2,5-Dimethylhexane	0.2615	0.14	17	*59*
3,3-Dimethylhexane	0.2599	1.45	18	*59*
3,4-Dimethylhexane	0.2633	0.38	18	*59*
2-Methyl-3-ethylpentane	0.2611	1.06	18	*59*
3-Methyl-3-ethylpentane	0.2666	0.55	20	*59*
2,2,3-Trimethylpentane	0.2647	1.24	18	*59*
2,2,4-Trimethylpentane	0.2672	0.48	24	*59, 70*
2,3,3-Trimethylpentane	0.2686	0.57	20	*59*
2,3,4-Trimethylpentane	0.2656	0.35	19	*59*
2,2,3,3-Tetramethylbutane	0.2746	0.44	24	*59*
n-Nonane	0.2547	0.24	35	*2, 18, 25, 72*
2,2,5-Trimethylhexane	0.2637	0.31	17	*2, 25, 32*
n-Decane	0.2503	0.40	38	*2, 25, 32, 72*
n-Dodecane	0.2466	0.13	40	*2, 25, 32*
Ethene	0.2810	0.50	22	*2, 25, 46*
Propene	0.2785	0.72	176	*2, 19, 25, 27, 40, 46, 53, 61, 81, 95, 101*
1-Butene	0.2736	0.49	83	*2, 10, 19, 20, 25, 53, 61, 65, 81, 97*
cis-2-Butene	0.2705	0.16	21	*2, 25, 46, 61, 97*
trans-2-Butene	0.2721	0.18	20	*2, 20, 25, 61, 97*
2-Methylpropene	0.2727	0.45	108	*2, 32, 41, 61, 97*
1-Pentene	0.2944	1.57	21	*102*
1,3-Butadiene	0.2713	0.25	72	*2, 22, 25, 85*
Ethyne	0.2712	0.05	12	*2, 25*
Propyne	0.2703	0.29	27	*2, 25, 96*
Cyclopropane	0.2716	0.06	22	*87*
Cyclopentane	0.2687	3.11	15	*51*
Cyclohexane	0.2729	0.14	27	*2, 25, 32, 70*
Methylcyclohexane	0.2699	0.40	32	*2, 25, 32*
Benzene	0.2696	0.21	121	*2, 17, 25, 32, 34, 36, 46, 66, 86*
Methylbenzene	0.2646	0.33	76	*2, 17, 25, 32, 46, 94*
Ethylbenzene	0.2626	0.26	23	*2, 25, 68*
1,2-Dimethylbenzene	0.2633	0.80	15	*2, 25, 32, 46, 86*
1,3-Dimethylbenzene	0.2593	0.49	69	*2, 25, 32, 46, 86, 92*
1,4-Dimethylbenzene	0.2589	0.36	53	*2, 25, 32, 46, 86*
n-Propylbenzene	0.2599	0.16	24	*2, 25, 92*
Isopropylbenzene	0.2617	0.06	19	*2, 25, 68*
Biphenyl	0.2743	0.45	20	*2, 25, 58*
Naphthalene	0.2610	0.10	31	*2, 25, 60*
Overall		0.50	2795	
Organics				
Acetic acid	0.2230	1.95	27	*91*
Acetone	0.2459	0.14	17	*91*

(Continued on next page)

Table IV. *(Continued)*

Compd	Z_{RA}	Av. % dev.[a]	No. of data poiuts	Data sources
Acetonitrile	0.1957	0.49	13	*91*
Bromobenzene	0.2899	1.30	28	*91*
n-Butyric acid	0.2740	0.19	10	*91*
Carbon disulfide	0.2801	0.13	14	*88*
Carbon tetrachloride	0.2721	0.16	27	*91*
Chlorobenzene	0.2651	0.25	28	*91*
Chloroform	0.2748	0.25	15	*91*
Diethylamine	0.2630	0.06	4	*90*
Ethyl acetate	0.2538	0.38	24	*91*
Ethylamine	0.2190	2.10	6	*69*
Ethyl bromide	0.2897	0.61	7	*91*
Ethyl chloride	0.2667	0.08	18	*67*
Ethyl formate	0.2586	0.28	23	*91*
Ethyl propionate	0.2545	0.21	27	*91*
Fluorobenzene	0.2660	0.45	10	*24*
Iodobenzene	0.2649	0.12	20	*91*
Isobutyric acid	0.2414	0.09	9	*91*
Methanol	0.2318	1.76	23	*33*
Methyl acetate	0.2550	0.40	23	*91*
Methyl *n*-butyrate	0.2562	0.37	28	*91*
Methyl chloride	0.2229	2.45	23	*103*
Methyl ethyl ether	0.2669	0.90	10	*91*
Methyl formate	0.2577	0.28	21	*91*
Methyl isobutyrate	0.2585	0.28	27	*91*
Methyl propionate	0.2556	0.38	26	*91*
Perfluoro *n*-butane	0.2704	0.43	5	*30*
Phosgene	0.2793	0.22	16	*67*
Propionic acid	0.2491	0.25	7	*91*
Propionitrile	0.2169	0.09	12	*91*
n-Propyl acetate	0.2524	0.43	27	*91*
n-Propyl alcohol	0.2485	0.78	19	*91*
n-Propyl formate	0.2589	0.22	27	*91*
Trichlorofluoromethane	0.2746	0.20	27	*13*
Trimethylamine	0.2715	0.07	4	*90*
Overall		0.60	652	
Inorganics				
Ammonia	0.2465	0.16	17	*67*
Argon	0.2912	0.43	13	*6*
Carbon dioxide	0.2736	0.72	14	*67*
Carbon monoxide	0.2917	2.04	15	*91*
Chlorine	0.2761	0.09	8	*91*
Hydrogen	0.3199	0.97	13	*84*
Hydrogen sulfide	0.2851	1.18	11	*103*
Neon	0.3064	0.52	8	6
Nitrogen	0.2905	0.51	20	*67, 84*
Oxygen	0.2909	0.73	16	*67, 84*
Xenon	0.2810	0.66	13	*63*
Overall		0.74	148	

[a] $(100/N)\ \Sigma \left|\dfrac{\text{calculated value} - \text{experimental value}}{\text{experimental value}}\right|$.

points. Only 37 hydrocarbons could be included owing to the lack of Francis equation coefficients for the remaining 27. The two forms of the Rackett equation (Equations 1 and 2) and the Francis equations were evaluated with this expanded data set. Table III shows that over the entire temperature range, the modified Rackett equation is by far the best for the hydrocarbons and quite good for the other organic and inorganic materials.

CONCLUSION

On the basis of the above evaluations, it has been concluded that the most accurate and simultaneously simplest means of predicting the effect of temperature on the saturated liquid densities is by the modified Rackett equation. In Table IV is given the listing (for all 64 hydrocarbons, 36 organics, and 11 inorganics) of the recommended values of Z_{RA}, the average percent deviation between the predicted and experimental density values, the number of data points used, and the sources of the data. With the Z_{RA} value given, one can predict accurately the variation of the saturated liquid densities over the entire temperature range from their triple point to their critical point. It should be noted, however, that to maintain the high accuracy and internal consistency of the method, the critical properties used for each individual compound should be taken from Chapter 1 of the second edition of the API Technical Data Book—Petroleum Refining (*1*). If a prediction is desired for a substance for which no Z_{RA} is given, the critical compressibility factor, Z_c, may be used in place of Z_{RA}. This will decrease the expected accuracy of the predicted value, but will provide an estimate which in general is in error by no more than 3 or 4%.

NOMENCLATURE

N = number of data points
P = pressure, atm
P_c = critical pressure, atm
P_r = reduced pressure, P/P_c
$P_r@T_r(0.6)$ = reduced saturation pressure at a reduced temperature of 0.6
R = universal gas constant, 82.06 atm cm^3/g-mol K
T = temperature, K
T_b = normal boiling point temperature, K
T_c = critical temperature, K
T_r = reduced temperature, T/T_c
V_c = critical volume, cm^3/g
V_r = reduced volume, V/V_c
V_s = saturated liquid volume, cm^3/g
$V@T_r(0.6)$ = saturated liquid volume at a reduced temperature of 0.6, cm^3/g
Z_c = critical compressibility factor
Z_{RA} = constant of the modified Rackett equation

GREEK LETTERS

ρ_c = critical density, g/cm^3
ρ_r = reduced density
ρ_s = saturated liquid density, g/cm^3
ω = acentric factor

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Activity Coefficients for Systems Sodium Toluenesulfonate–Xylose–Water and Sodium Toluenesulfonate–Urea–Water at 25°C from Isopiestic Measurements

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The osmotic and activity coefficients for the two ternary systems sodium *p*-toluenesulfonate–xylose–water and sodium *p*-toluenesulfonate–urea–water were measured by the isopiestic vapor pressure method at 25°C. The activity coefficients of sodium toluenesulfonate were increased by xylose and decreased by urea. The sulfonate increased the activity coefficients of xylose and decreased those of urea.

Many investigations have been made on the activity coefficients in aqueous ternary solutions because of their importance to the understanding of solute-solute interaction and solute-solvent interaction which includes water structure change by the solute. Thermodynamics of aqueous solutions of organic electrolytes arouse great interest as they generally have larger ionic radii than inorganic electrolytes and have hydrophobic parts in ions which interact peculiarly with water.

Concerning the ternary systems containing organic electrolytes, however, only a few systems have been investigated in which tetraalkylammonium halide (*14*) or sulfonate (*12*) has been one of the components. In the systems tetramethylammonium bromide–urea–water and tetrabutylammonium bromide–urea–water, Wen and Chen (*14*) noted that each solute component is salted in by the other and that the effect increases greatly with the cationic size of the tetraalkylammonium ion.

On the other hand, aromatic sulfonate ions are somewhat different from tetraalkylammonium ions in the locality of ionic charge, and the water-structure breaking effect of the sulfonic group outweighs the structure-making effect of the benzene ring (*13*).

Previously, we reported (*12*) the activity coefficients for the ternary systems, sodium benzenesulfonate–xylose–water and sodium benzenesulfonate–urea–water. In this paper, the osmotic and activity coefficients for the two ternary solutions sodium *p*-toluenesulfonate–xylose–water and sodium *p*-toluenesulfonate–urea–water were measured by the isopiestic vapor pressure method at 25°C. Sodium *p*-toluenesulfonate has a little larger hydrophobic part than sodium benzenesulfonate, and the difference may influence the activity coefficients in the ternary systems. These sulfonates are model compounds of sulfonic acid type of cation exchange resin. Therefore the data for the systems containing sulfonates and sugar will be