Generalized Correlation of Saturated Liquid Densities

B. C.-Y. Lu,[1] J. A. Ruether, C. Hsi, and C.-H. Chiu
Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada

The Guggenheim equation is used to represent saturated liquid densities of 23 nonpolar and slightly polar compounds in the reduced temperature range from 0.2 to 1.0. The scaling volume is used in the calculation instead of the critical volume. The two parameters of the equation are generalized linearly in terms of the acentric factor. The average deviation of the calculated densities and literature values for a total of 595 data points tested is 0.27%. The proposed correlation provides an accurate and simple means of predicting the temperature effect on saturated liquid densities.

Numerous methods have been proposed in the literature for correlating and predicting density data for pure liquids at saturation states. In a recent paper, Spencer and Danner (*18*) evaluated 13 relatively new correlations, covering the period from 1954 to 1971, for predicting the effect of temperature on saturation liquid density and suggested that the correlations given by Yen and Woods (*21*), Gunn and Yamada (*6*), Harlacher (*7*), and Francis (*4*) are all excellent, and that the method of Gunn and Yamada is superior to any of the other corresponding states approaches. The reduced temperature range covered by the method of Gunn and Yamada extends from 0.2 to 1.0.

The purpose of this investigation is to develop a generalized but simpler correlation over the same reduced temperature range.

Guggenheim Equation

After reviewing a number of equations in the literature, Martin (*12*) suggested the following equation in 1959 for correlating saturated liquid densities

$$\rho_{rs} = \frac{\rho_s}{\rho_c} = 1 + A(1 - Tr)^{1/3} + B(1 - Tr)^{2/3} + C(1 - Tr) + D(1 - Tr)^{4/3} \quad (1)$$

The equation holds up to the critical temperature and has been employed subsequently by Yen and Woods (*21*) in 1966 without the use of the fourth term on the right hand of Equation 1. These authors fitted literature data for 62 pure components with an average deviation of less than 0.3%.

Guggenheim (*5*) in 1945 suggested a simpler empirical formula for representing saturated liquid argon. It is of the following form:

$$\rho_{rs} = 1 + \alpha(1 - Tr) + \beta(1 - Tr)^{1/3} \quad (2)$$

where $\alpha = 3/4$ and $\beta = 7/4$.

In this investigation, Equation 2 is used for representing saturated liquid densities for nonpolar and slightly polar compounds, but with the quantities α and β treated as two adjustable parameters. In addition, it is intended to correlate these two parameters in terms of the three-parameter corresponding states formulation of Curl and Pitzer (*1*) and Pitzer et al. (*14*).

The Correlation

Saturated liquid densities of 23 pure nonpolar and slightly polar compounds have been correlated by means of Equation 2. The total number of points included in the correlation is 595. By use of the approach of Gunn and Yamada, the scaling volume V_{sc} or the scaling density ($\rho_{sc} = 1/V_{sc}$) is used in Equation 2, rather than the critical volume, in the calculation of the reduced saturated density. The scaling volume as defined by Gunn and Yamada is given by the following relationship:

$$V_{sc} = \frac{V_{0.6}}{0.3862 - 0.0866\,\omega}$$

The quantity $V_{0.6}$ is the molar volume of the liquid evaluated at a reduced temperature of 0.6. The scaling densities, together with the critical temperatures and the acentric factors of the 23 compounds tested, are listed in Table I. The critical densities of these compounds are also listed for the purpose of comparison.

The parameters α and β of the 23 compounds are determined by a least-squares method. Values of these parameters are also listed in Table I and are further correlated in the following forms linear in the acentric factor:

$$\alpha = 0.73098 + 0.28908\,\omega \quad (3)$$

and

$$\beta = 1.75238 + 0.74293\,\omega \quad (4)$$

These equations were obtained by a weighted least-squares technique. The weighting coefficient W_i for compound i was assigned as follows:

$$W_i = \frac{(NDP)_i}{\sum_i (NDP)_i/NC} \quad (5)$$

where $(NDP)_i$ is the number of data points for compound i, and NC is the number of compounds in the correlation.

Results and Conclusions

Equation 2 gives a satisfactory fit for all 23 compounds. The maximum and average deviations, with the α and β values of Table I used in the evaluation, are listed in Table II. The average deviation between the calculated and the literature density values is only 0.15%. With the direct use of critical density in Equation 2 instead of the scaling density, the average deviation would be slightly increased to 0.18 from 0.15%. These small deviations indicate the suitability of Equation 2 for representing the data.

The generalized correlation (Equations 3 and 4) also gives satisfactory results for the 23 compounds tested. The maximum and average deviations obtained are listed in Table II. For the same 595 points, the average deviation is 0.27%. (Should the generalized correlation be obtained through the direct use of critical density, the average deviation would be increased from 0.27 to 0.74%.) Average deviations for each compound are generally less than 0.5% with the exception of ethane (0.68%). For most of the pure liquids, the maximum deviation is less than 0.9%, whereas those greater than 1% generally occur in the vicinity of the critical point; this is probably

---

[1] To whom correspondence should be addressed.

due to the experimental difficulty encountered in this region. Should the required scaling density be unavailable, the direct use of critical density in the proposed correlation would slightly increase the average deviation for the same data points from 0.27 to 0.75%.

A deviation plot is shown in Figure 1 for nine compounds which were chosen because the data spanned a wide range of reduced temperature, or because the deviations were unusually large. For comparison the method of Gunn and Yamada was tested by using the same data points. The results are presented in Table II. The proposed correlation provides an accurate and simple means of predicting the temperature effect on the saturated liquid densities.

Table I. Acentric Factors, Critical Temperatures, Critical Densities, Scaling Densities, and Values of α and β for 23 Compounds

Compound	Acentric factor	Critical temp, °C	Critical density, g/cm^3	Scaling (*6*) density, g/cm^3	α	β
Argon	0.0 (*11*)	−122.29 (*13*)	0.5312 (*13*)	0.5308	0.80250	1.72966
Methane	0.013 (*15*)	−82.61 (*2*)	0.1620 (*2*)	0.1619	0.65061	1.79446
Nitrogen	0.04 (*3*)	−146.96 (*2*)	0.3110 (*2*)	0.3125	0.72228	1.78697
Carbon monoxide	0.041 (*15*)	−140.23 (*10*)	0.301 (*10*)	0.3052	0.82584	1.74587
Ethylene	0.089 (*11*)	9.20 (*10*)	0.217 (*10*)	0.21512	0.76346	1.81615
Ethane	0.105 (*15*)	32.34 (*2*)	0.2122 (*2*)	0.20678	0.73069	1.82885
Propane	0.152 (*15*)	96.81 (*17*)	0.220 (*17*)	0.22072	0.77719	1.86696
Cyclohexane	0.186 (*3*)	280.2 (*19*)	0.2718 (*19*)	0.27327	0.84002	1.86791
Isobutane	0.192 (*15*)	134.98 (*10*)	0.221 (*10*)	0.22641	0.98727	1.83657
Benzene	0.215 (*3*)	288.94 (*10*)	0.302 (*10*)	0.30570	0.82341	1.89319
Carbon dioxide	0.225 (*3*)	31.04 (*10*)	0.4679 (*10*)	0.4704	0.95331	1.86488
2,3-Dimethylbutane	0.246 (*11*)	227.35 (*22*)	0.2411 (*22*)	0.23914	0.71801	1.97568
Bromobenzene	0.25 (*11*)	397.0 (*22*)	0.4853 (*22*)	0.49052	0.78678	1.94146
n-Pentane	0.252 (*3*)	196.5 (*9*)	0.232 (*9*)	0.23202	0.76901	1.95881
Chlorobenzene	0.252 (*11*)	359.2 (*22*)	0.3654 (*22*)	0.36883	0.79514	1.94027
Toluene	0.252 (*15*)	319.9 (*19*)	0.2913 (*19*)	0.29375	0.86622	1.90100
2,2,3-Trimethylbutane	0.256 (*11*)	257.96 (*10*)	0.252 (*10*)	0.24329	0.72502	1.97691
Ethyl ether	0.276 (*11*)	193.55 (*10*)	0.265 (*10*)	0.26365	0.82131	1.95285
n-Hexane	0.29 (*15*)	234.8 (*22*)	0.2344 (*22*)	0.23387	0.77083	1.99124
O-xylene	0.30 (*15*)	359.0 (*17*)	0.280 (*17*)	0.29034	0.78244	1.98440
Ethylbenzene	0.342 (*11*)	343.94 (*10*)	0.284 (*10*)	0.28422	0.93385	1.93982
n-Heptane	0.352 (*15*)	267.0 (*10*)	0.232 (*10*)	0.23343	0.81240	2.02994
n-Octane	0.393 (*11*)	295.61 (*10*)	0.232 (*10*)	0.23300	0.79719	2.07290

Table II. Deviations of Calculated Saturated Liquid Densities from Literature Values

			Absolute % deviation						
			Individual, Eq 2		Generalized		Gunn and Yamada		
Compound	Data points	Temp range, °C	Av	Max	Av	Max	Av	Max	Ref.
Argon	36	−189 to −128	0.23	0.83	0.30	1.07[a]	0.46	0.95	*2, 13*
Methane	60	−180 to −83	0.08	0.59	0.46	0.66	0.59	2.54[a]	*8, 16, 20*
Nitrogen	15	−210 to −149	0.22	0.96	0.23	1.01[a]	0.47	1.89[a]	*2*
Carbon monoxide	24	−205 to −147	0.21	0.90	0.27	0.78	0.40	0.97	*2*
Ethylene	14	−145 to 7	0.17	1.27	0.18	1.22[a]	0.43	2.59[a]	*19*
Ethane	9	−184 to −140	0.01	0.03	0.68	0.72	0.79	0.91	*8*
Propane	40	−190 to 94	0.18	0.90	0.20	0.87	0.19	0.62	*2, 17*
Cyclohexane	12	15 to 99	0.11	0.63	0.30	0.42	0.45	0.59	*19*
Isobutane	5	30 to 125	0.20	0.27	0.45	0.71	0.44	0.65	*19*
Benzene	30	0 to 284	0.17	0.82	0.23	1.12	0.25	0.83	*22*
Carbon dioxide	19	−57 to 30	0.24	1.83	0.42	2.47[a]	0.36	1.43[a]	*2*
2,3-Dimethylbutane	26	0 to 225	0.11	0.26	0.35	0.71[a]	0.37	1.53[a]	*22*
Bromobenzene	28	0 to 370	0.07	0.19	0.15	0.28	0.09	0.47	*22*
n-Pentane	52	−137 to 195	0.23	2.33	0.29	2.48[a]	0.30	3.27[a]	*17, 19, 22*
Chlorobenzene	35	−45 to 329	0.13	0.37	0.16	0.32	0.10	0.24	*19, 22*
Toluene	8	−23 to 100	0.04	0.08	0.07	0.20	0.18	0.20	*19*
2,2,3-Trimethylbutane	7	−10 to 50	0.03	0.06	0.33	0.41	0.11	0.19	*17*
Ethyl ether	42	−123 to 192	0.16	1.06	0.15	1.00[a]	0.13	1.61[a]	*19, 22*
n-Hexane	23	0 to 220	0.06	0.37	0.17	0.34	0.20	0.53	*22*
O-xylene	12	0 to 110	0.03	0.06	0.33	0.38	0.17	0.38	*17*
Ethylbenzene	28	−90 to 126	0.13	0.31	0.21	0.67	0.08	0.18	*17, 19*
n-Heptane	40	−90 to 265	0.21	0.56	0.23	0.67	0.22	0.90	*17, 22*
n-Octane	30	0 to 290	0.12	0.64	0.23	0.60	0.27	0.87	*22*
Total	595	Grand av	0.15		0.27		0.30		

[a] Maximum deviation occurred in the vicinity of the critical point.

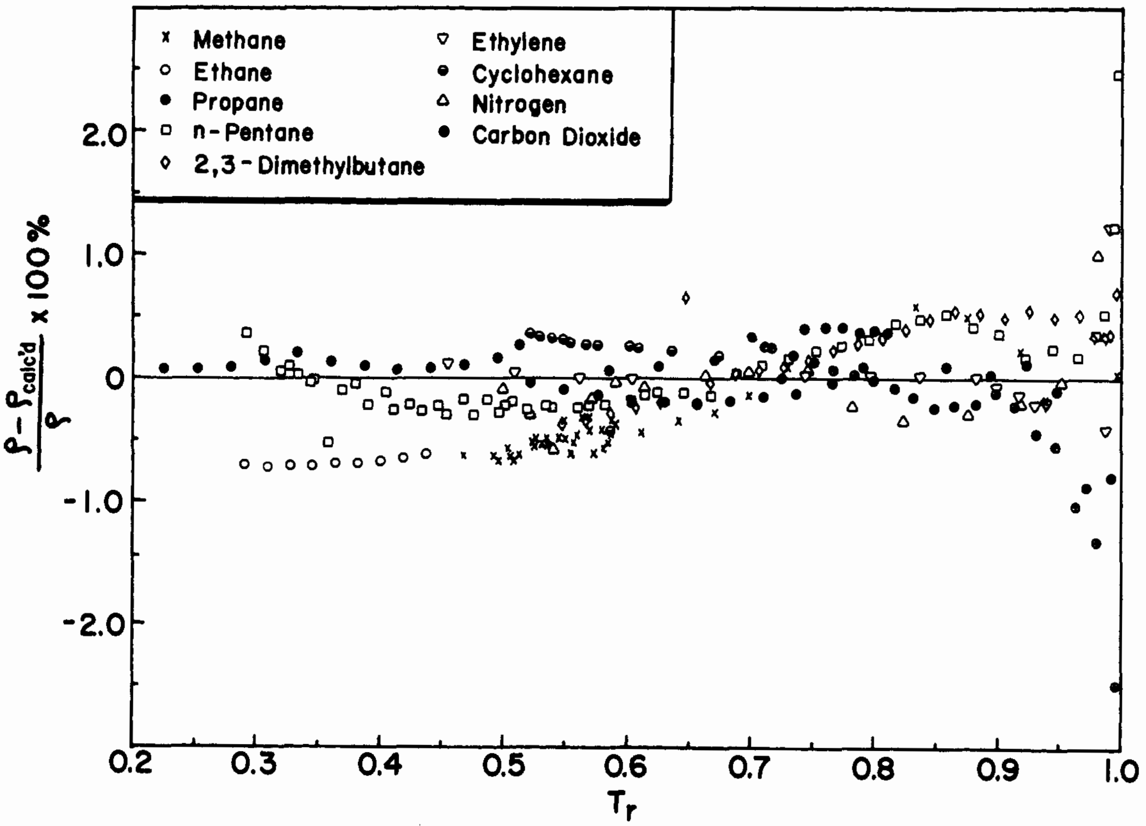

Figure 1. Plot of deviations between calculated densities and literature values for nine compounds as function of reduced temperature

Nomenclature

A, B, C, D = parameters, Equation 1
α, β = adjustable parameters, Equations 2–4
ρ = density
ω = acentric factor
T = absolute temperature
V = volume
W = weighting coefficient

Subscripts

i = component identification
r = reduced property
rs = reduced saturation density
sc = scaling property

Literature Cited

(1) Curl, Jr., R. F., Pitzer, K. S., *Ind. Eng. Chem.*, **50**, 265 (1958).
(2) Din, F., "Thermodynamic Functions of Gases," Butterworths, London, England, 1956.
(3) "Engineering Data Book," Natural Gas Processors Suppliers Association, Tulsa, Okla., 1967.
(4) Francis, A. W., *Chem. Eng. Sci.*, **10**, 37 (1959); *Ind. Eng. Chem.*, **49**, 1779 (1957).
(5) Guggenheim, E. A., *J. Chem. Phys.*, **13**, 253 (1945).
(6) Gunn, R. D., Yamada, T., *AIChE J.*, **17**, 1341 (1971).
(7) Harlacher, E. A., PhD thesis, The Pennsylvania State University, University Park, Pa., 1968.
(8) Klosek, J., McKinley, C., Proceedings of the First International Conference on LNG, Session No. 5, Chicago, Ill., 1968.
(9) Kobe, K. A., Lynn, Jr., R. E., *Chem. Rev.*, **52**, 117 (1953).
(10) Kudchadker, A. P., Alani, G. H., Zwolinski, B. J., *ibid.*, **68**, 659 (1968).
(11) Lyckman, E. W., Eckert, C. A., Prausnitz, J. M., *Chem. Eng. Sci.*, **20**, 703 (1965).
(12) Martin, J. J., "Thermodynamic and Transport Properties of Gases, Liquids, and Solids," p 110, Amer. Soc. Mech. Eng. and McGraw-Hill, New York, N.Y., 1959.
(13) Michel, A., Levett, J. M., DeGroaff, W., *Physica*, **24**, 659 (1958).
(14) Pitzer, K. S., Lippmann, D. Z., Curl, Jr., R. F., Huggins, C. M., Petersen, D. E., *J. Amer. Chem. Soc.*, **77**, 3433 (1955).
(15) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," 2nd ed., McGraw-Hill, New York, N.Y., 1966.
(16) Roche, Y., Perret and Bochirol, The Second International Conference and Exhibition on Liquefied Natural Gas, Session No. 2, Paper No. 8, Paris, France, 1970.
(17) Rossini, F. D., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.
(18) Spencer, C. F., Danner, R. P., *J. Chem. Eng. Data*, **17**, 236 (1972).
(19) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, N.Y., 1950.
(20) Vennix, A. J., Leland, Jr., T. W., Kobayashi, R., *J. Chem. Eng. Data*, **15**, 238 (1970).
(21) Yen, L. C., Woods, S. S., *AIChE J.*, **12**, 95 (1966).
(22) Young, S., *Sci. Proceed. Roy. Dublin Soc.*, **12**, 374 (1909–1910).

Received for review July 25, 1972. Accepted January 25, 1973. The authors are indebted to the National Research Council of Canada for financial support.