An Analytical Expression for Correlating Z Values for Liquids at Low Reduced Temperatures

CHU HSI and BENJAMIN C.-Y. LU

Department of Chemical Engineering
University of Ottawa, Ottawa, Ontario, Canada

Recently, the three-parameter tabular correlation of Pitzer et al. (1955) for calculating compressibility factor of pure normal fluids has been extended to lower temperatures in the region where $0.5 \leqq T_r \leqq 0.8$ and $0 \leqq P_r \leqq 9$ (Lu et al., 1973). The compressibility factor is expressed linearly in the acentric factor as follows:

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{1}$$

with values of $Z^{(0)}$ and $Z^{(1)}$ reported in tabular forms at regular intervals of T_r and P_r. For the purpose of facilitating machine computations and for obtaining other thermodynamic properties, an attempt has been made in this study to represent the tabulated values of $Z^{(0)}$ and $Z^{(1)}$ of the extended correlation for liquids by a set of generalized polynomials in terms of T_r and P_r.

In the low P_r region, the absolute values of $Z^{(0)}$ and $Z^{(1)}$ for liquids are relatively smaller, and larger percentage errors were frequently obtained when various polynomials were tested. For this reason, $Z^{(0)}$ and $Z^{(1)}$ values were divided by P_r at constant T_r to amplify at low P_r conditions the $Z^{(0)}/P_r$ and $Z^{(1)}/P_r$ values, which were further smoothed slightly by a graphical procedure. These values were correlated in terms of P_r at constant T_r by means of Equations (2) and (3):

$$\frac{Z^{(0)}}{P_r} = A_0(T_r) + A_1(T_r)P_r + A_2(T_r)P_r^2 + A_3(T_r)P_r^3 \tag{2}$$

$$\frac{Z^{(1)}}{P_r} = B_0(T_r) + B_1(T_r)P_r + B_2(T_r)P_r^{1/2} + B_3(T_r)P_r^{1/3} \tag{3}$$

in which A_i and B_i are functions of T_r and were further correlated by means of Equations (4) and (5)

$$A_i(T_r) = A_{i0} + A_{i1}\,T_r + A_{i2}\,T_r^2 + A_{i3}\,T_r^3 + A_{i4}\,T_r^4 \tag{4}$$

$$B_i(T_r) = B_{i0} + B_{i1}\,T_r^{-1} + B_{i2}\,T_r^{-2} + B_{i3}\,T_r^{-3} + B_{i4}\,T_r^{-4} \tag{5}$$

Although different functions and various degrees of polynomials were tested, the best fit of the data was obtained by means of the above equations. Values of the coefficients A_{ij} and B_{ij} thus obtained are listed in Table 1.

The Z values of 20 compounds were evaluated using Equations (2) to (5) and compared with the literature values. The total number of experimental points included in the comparison is 418. These points are identical to those tested previously (Lu et al., 1973). A summary of the comparison is presented in Table 2 in which the percentage deviation is defined by $100\ [Z_{\text{calc}} - Z_{\text{expt.}}]/Z_{\text{expt.}}$. The results of the previous investigation are also listed in this table for comparison. The average absolute deviation of the calculated Z values is 1.51% which is slightly better than that reported previously (1.63%). Maximum and bias deviations are also included in Table 2. The average bias deviation indicated is the mean of the deviations taken with their signs.

Recently, revised acentric factors, based on the original defining equation of Pitzer, have been determined by Passut and Danner (1973) for hydrocarbons. New ω values are now available for 15 compounds out of the 20 compounds tested in this investigation. When these new values were used together with the A_{ij} and B_{ij} values of Table 1, the overall deviations obtained between the calculated and the literature Z values were found to be slightly less than those obtained by means of the ω values listed in Table 2. The largest variations in ω occurred in the values for 2,2-dimethylbutane and cyclohexane, and the average absolute and bias deviations are significantly reduced for these two compounds (from 4.00% to 2.31% for 2,2-dimethylbutane and from 2.29% to 0.78% for cyclohexane). Nevertheless, the overall improvement is small. As $Z^{(1)}$ values are smaller than the corresponding $Z^{(0)}$ values, the contribution of the $\omega Z^{(1)}$ term is much smaller than the $Z^{(0)}$ term. As a consequence, the Z values for liquids are not very sensitive to small variations in ω values. A summary of the calculated results for these fifteen hydrocarbons is presented in Table 3.

The lowest pressure at which the proposed analytical expression is valid is the saturation pressure at $T_r = 0.50$.

The analytical form of the $Z^{(0)}$ and $Z^{(1)}$ values for the

TABLE 1. COEFFICIENTS OF EQUATIONS (4) AND (5)

$i \backslash j$	0	1	2	3	4
			A_{ij}		
0	0.5491037	−1.0263205	0.5607605	0.4746418	−0.3892862
1	−0.0793657	0.2874317	−0.2337027	−0.1460924	0.1622860
2	0.0117884	−0.0411863	0.0312967	0.0201921	−0.0205371
3	−0.0006344	0.0022008	−0.0016370	−0.0010687	0.0010535
			B_{ij}		
0	0.1035120	−0.1306114	−0.0076666	0.0044728	0.0021196
1	−0.0527853	0.0265455	0.0087712	−0.0012631	−0.0014799
2	0.7225370	−0.4307156	−0.0819024	0.0333729	0.0105455
3	−0.8339128	0.5459108	0.0527897	−0.0291080	−0.0118169

TABLE 2. DEVIATIONS OF CALCULATED LIQUID COMPRESSIBILITY FACTORS FROM LITERATURE VALUES

Compound	ω	T_r range	P_r range	No. of points	Tables Avg. deviation % Abs.	Tables Avg. deviation % Bias	Tables Max. dev. %	Equation Avg. deviation % Abs.	Equation Avg. deviation % Bias	Equation Max. dev. %	References
Methane	0.013	0.788-0.796	0.319-0.599	2	0.97	+0.71	+1.68	1.45	+1.45	+1.54	Vennix et al. (1970)
n-butane	0.201	0.731-0.771	0.093-8.167	23	0.68	+0.42	+2.35	0.54	+0.22	+1.30	Olds et al. (1970)
i-butane	0.192	0.762	0.189-8.507	17	0.78	−0.07	+1.97	0.63	−0.27	−1.32	Gonzalez and Lee (1966)
Neopentane	0.195	0.717	0.216-8.621	16	1.47	−1.02	−5.94	1.80	−1.55	−6.81	Gonzalez and Lee (1968)
n-hexane	0.290	0.735-0.784	0.187-8.674	14	1.01	+0.95	+6.10	0.81	+0.76	+4.86	Kelso and Felsing (1940)
2-methylpentane	0.295	0.750-0.800	0.187-8.674	14	1.75	−1.75	−4.31	1.57	−1.57	−2.26	Kelso and Felsing (1940)
3-methylpentane	0.277	0.739	0.182-8.420	9	1.02	−0.69	−1.94	1.14	−1.14	−1.99	Day and Felsing (1951)
2,2-dimethylbutane	0.266	0.763	0.326-8.143	14	3.74	−3.74	−4.60	4.00	−4.00	−4.70	Felsing and Watson (1943b)
n-heptane	0.359	0.506-0.783	1.828-7.311	15	0.35	−0.23	−0.88	0.32	−0.26	−0.77	Dolittle (1963)
n-octane	0.395	0.523-0.787	0.041-8.614	107	0.66	−0.04	−6.12	0.27	−0.12	−1.43	Benson and Winnick (1971) Felsing and Watson (1942)
2,2,4-trimethylpentane	0.310	0.686-0.778	0.197-7.874	28	2.30	−2.30	−3.44	2.77	−2.77	−3.41	Felsing and Watson (1943a)
2,2,3,3-tetramethyl-butane	0.377	0.704-0.723	0.408-6.290	13	2.10	+2.10	+3.44	1.73	+1.73	+2.08	Felsing et al. (1947)
Cyclohexane	0.186	0.562	0.340-8.503	17	2.22	+2.21	+2.87	2.29	+2.29	+2.97	Reamer and Sage (1957)
Propene	0.143	0.761	0.144-8.955	19	0.63	+0.20	+2.64	0.60	+0.13	+1.67	Sage and Lacey (1959)
1-butene	0.203	0.741	0.107-8.576	18	0.93	−0.70	−4.29	0.73	−0.72	−1.43	Sage and Lacey (1959)
1-pentene	0.238	0.745-0.787	0.140-7.795	20	11.29	−11.29	−14.93	11.45	−11.45	−14.41	Day and Felsing (1951)
Argon	0.0	0.596-0.795	0.313-6.250	13	0.94	−0.83	−2.18	1.03	−0.53	−2.22	Michels et al. (1958), Din (1956a)
Nitrogen	0.04	0.634-0.792	0.149-8.955	15	1.33	−1.28	−2.52	1.18	−1.18	−2.68	Din (1956b)
Hydrogen sulfide	0.100	0.743	0.129-7.657	25	0.77	+0.77	+2.48	0.59	+0.59	+1.27	Sage and Lacey (1959)
Carbon dioxide	0.225	0.776-0.799	0.280-1.120	19	0.73	+0.10	−1.86	0.26	−0.24	−0.58	Jenkin (1920)
			Overall	418	1.63	−0.78	−14.93	1.51	−0.92	−14.41	

TABLE 3. DEVIATIONS OF CALCULATED LIQUID COMPRESSIBILITY FACTORS FROM LITERATURE VALUES FOR 15 HYDROCARBONS USING NEW ω VALUES

Compound	ω Passut and Danner (1973)	Equation Avg. deviation % Abs.	Equation Avg. deviation % Bias	Max.
Methane	0.0072	1.74	+1.74	+1.83
n-butane	0.1928	0.77	+0.64	+1.77
i-butane	0.1756	0.78	+0.50	+1.75
Neopentane	0.1970	1.87	−1.64	−6.91
n-hexane	0.2957	0.67	+0.48	+4.51
2-methylpentane	0.2791	1.67	−1.67	−2.35
3-methylpentane	0.2750	1.04	−1.04	−1.91
2,2-dimethylbutane	0.2310	2.31	−2.31	−3.40
n-heptane	0.3506	0.30	+0.19	+0.67
n-octane	0.3942	0.26	−0.07	−1.33
2,2,4-trimethylpentane	0.3033	2.43	−2.43	−3.16
Cyclohexane	0.2144	0.78	+0.78	+1.45
Propene	0.1477	0.62	−0.09	+1.41
1-butene	0.1874	0.49	+0.01	+0.95
1-pentene	0.2450	11.75	−11.75	−14.75
	Overall	1.53	−1.01	−14.75
Deviations obtained with ω values of Table 2		1.68	−1.18	−14.41

gas phase region is not included in this investigation because gas phase exists only in the very low P_r region for T_r below 0.8. The generalized second virial coefficients reported earlier (Chang and Lu, 1972) appears to be adequate for representing the data.

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