solution rate due to monomer diffusion are governed by Brownian motion below an order of micron in particle radius, while they are dominated by the convections above the order. Since the r dependence of r/δ is relatively small in the Brownian motion range, Equation (20) can be practically used instead of Equation (19) if the size distribution ranges not so far from the radius which gives the minimum of r/δ in the Brownian motion range.

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NOTATION

C = concentration of monomers in bulk solution
C_r' = concentration of monomers at interface of solid/solution
$c(x, t)$ = concentration of monomers at radial distance x and time t
D = diffusion coefficient of monomers
d = density of a particle
d_∞ = density of fluid
Δd = density difference ($= |d - d_\infty|$)
g = acceleration of gravity
K = mass transfer coefficient of monomers
k = Boltzmann constant
m = mass of a particle
$\dot{n}$ = number of moles of monomers passing per unit time through the spherical surface at x from the center of a particle
Re = Reynolds number ($= 2rud_\infty/\mu$)
r = particle radius
$\dot{r}$ = dr/dt
r_c = critical radius between Brownian motion range and convection range
Sc = Schmidt number ($= \mu/Dd_\infty$)
Sh = Sherwood number ($= 2rK/D$)
T = absolute temperature
t = time
u = effective slip velocity of a particle
$\overline{u_c^2}$ = mean square relative velocity of a particle due to convections
$\overline{u_t^2}$ = mean square relative velocity of a particle due to thermal movement (Brownian motion) of the particle
V_m = molar volume of particle
x = distance from the center of a spherical particle
δ = thickness of a stagnant boundary layer (Mullin, 1972)
θ = dimensionless constant in Equation (9)
μ = viscosity of fluid

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Saturated Liquid Densities of Normal Fluids

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Process design calculations require liquid densities for estimating storage capacities, sizing pipelines, in calculating vapor-liquid equilibria, etc. Corresponding states theory correlations play an important role in predicting these densities at various conditions. Pitzer's corresponding states theory (Lewis and Randall, 1961) has been very successful in accurately correlating thermophysical properties of normal (nonpolar and a few slightly polar) fluids. However, his correlation for the saturated liquid compressibility factor was found to be poor by Lyckman et al. (1965). Improved correlation by Lyckman et al. (1965) and a recent development of Halm and Stiel (1970) were still considered to be somewhat less accurate by Spencer and Danner (1972) in their comprehensive study of saturated liquid density correlations. In a critical review of these correlations, Reid et al. (1977) recommend the correlation of Gunn and Yamada (1971) for its accuracy over a large temperature range. This correlation of Gunn and Yamada requires critical temperature, Pitzer's acentric factor, and an experimental density at a reduced temperature of 0.6 and thus is not purely predictive. They have also developed a predictive relationship (scaling volume as a function of T_c, P_c, and ω) whose accuracy is not available.

The objective of this study was to develop an accurate and predictive saturated liquid density correlation for

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normal fluids, which is applicable over a wide temperature range.

ANALYSIS

In its presentation of corresponding states theory, Pitzer's (Lewis and Randall, 1961) acentric factor ω is given by the following equation:

$$\omega = -\log(P_r)_{T_r=0.7} - 1.0 \qquad (1)$$

Then the vapor pressure correlation has a linear form in acentric factor as described by

$$\log(P_r) = (\log P_r)^0 + \omega(\log P_r)^1 \qquad (2)$$

Note that vapor pressure varies by a factor of thousands over the entire liquid range, and both equations given above involve logarithms of the reduced vapor pressure. Saturated liquid compressibility factor also varies similarly from melting point to the critical temperature. Therefore, a properly reduced saturated liquid compressibility factor would probably have a linear dependency on the acentric factor similar to Equation (2).

TABLE 1. GENERALIZED FUNCTIONS IN THE EQUATION 8

T_r	$(\ln U)^0$	$(\ln U)^1$
.300	−1.1824	−.4131
.320	−1.2292	−.4847
.340	−1.2733	−.5311
.360	−1.3152	−.5586
.380	−1.3552	−.5725
.400	−1.3936	−.5770
.420	−1.4305	−.5753
.440	−1.4659	−.5700
.460	−1.4997	−.5630
.480	−1.5319	−.5555
.500	−1.5623	−.5485
.520	−1.5908	−.5425
.540	−1.6174	−.5376
.560	−1.6420	−.5340
.580	−1.6646	−.5315
.600	−1.6852	−.5298
.620	−1.7038	−.5288
.640	−1.7205	−.5280
.660	−1.7355	−.5273
.680	−1.7487	−.5265
.700	−1.7605	−.5254
.720	−1.7708	−.5240
.740	−1.7797	−.5222
.760	−1.7872	−.5201
.780	−1.7933	−.5179
.800	−1.7978	−.5156
.820	−1.8002	−.5133
.840	−1.8001	−.5112
.860	−1.7966	−.5090
.880	−1.7888	−.5067
.900	−1.7751	−.5036
.920	−1.7538	−.4991
.940	−1.7227	−.4920
.960	−1.6791	−.4805
.980	−1.6198	−.4626
.982	−1.6040	−.4590
.984	−1.5900	−.4510
.986	−1.5780	−.4410
.988	−1.5640	−.4280
.990	−1.5480	−.4120
.992	−1.5330	−.3920
.994	−1.5150	−.3670
.996	−1.4890	−.3370
.998	−1.4540	−.3020
.999	−1.4250	−.2830
1.000	−1.2430	−.2629

Selecting critical compressibility factor as the parameter to reduce saturated liquid compressibility factor Z_{s1}, correlating equation becomes

$$\ln(Z_r) = \ln\frac{(Z_{s1})}{(Z_c)} = a_1 + b_1\omega \qquad (3)$$

A correlation developed as given in Equation (3) has a very limited use, since critical compressibility factors for many compounds are not known. Therefore, Z_c must be eliminated from Equation (3).

Pitzer (Lewis and Randall, 1961) has presented a relationship between critical compressibility factor and the acentric factor as given by

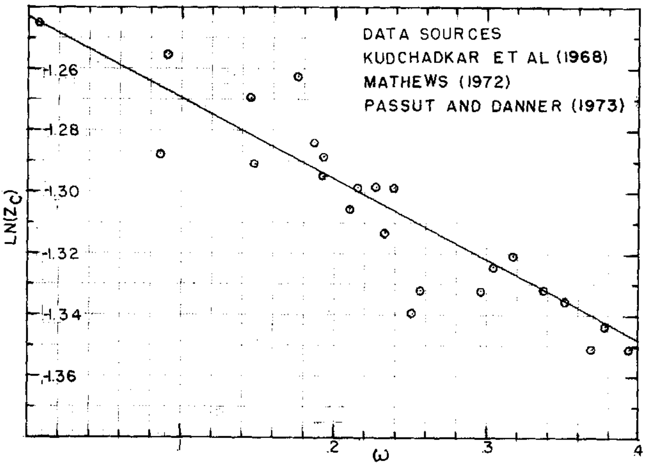

Fig. 1. The critical compressibility factor as a function of the acentric factor.

TABLE 2.

Compound	T_c, k	P_c, kPa	ω
Methane	190.55	4604.3	.0072
Ethane	305.43	4880.1	.0908
Propane	369.82	4249.2	.1454
N-Butane	425.16	3796.9	.1928
N-Pentane	469.60	3368.8	.2510
N-Hexane	507.40	3012.3	.2957
N-Heptane	540.20	2735.8	.3506
N-Octane	568.78	2486.3	.3942
N-Nonane	594.56	2309.7	.4437
N-Decane	617.40	2099.5	.4902
I-Butane	408.13	3648.0	.1756
I-Pentane	460.39	3381.2	.2273
Ethylene	282.36	5031.8	.0856
Propylene	365.00	4619.5	.1477
1,3 Butadiene	425.00	4329.9	.1814
Cyclopentane	511.60	4507.8	.1923
Me-Cyclopentane	532.73	3784.5	.2395
Me-Cyclohexane	572.12	3471.5	.2333
Benzene	562.09	4898.0	.2100
Toluene	591.72	4108.6	.2566
Diethyl ether	466.70	3637.6	.2816
Carbon Tetrachloride	556.40	4557.4	.2020
Carbon dioxide	304.19	7381.5	.2310
Ethyl mercaptan	499.00	5495.1	.1860

° Percent deviation = (Calculated density − Experimental

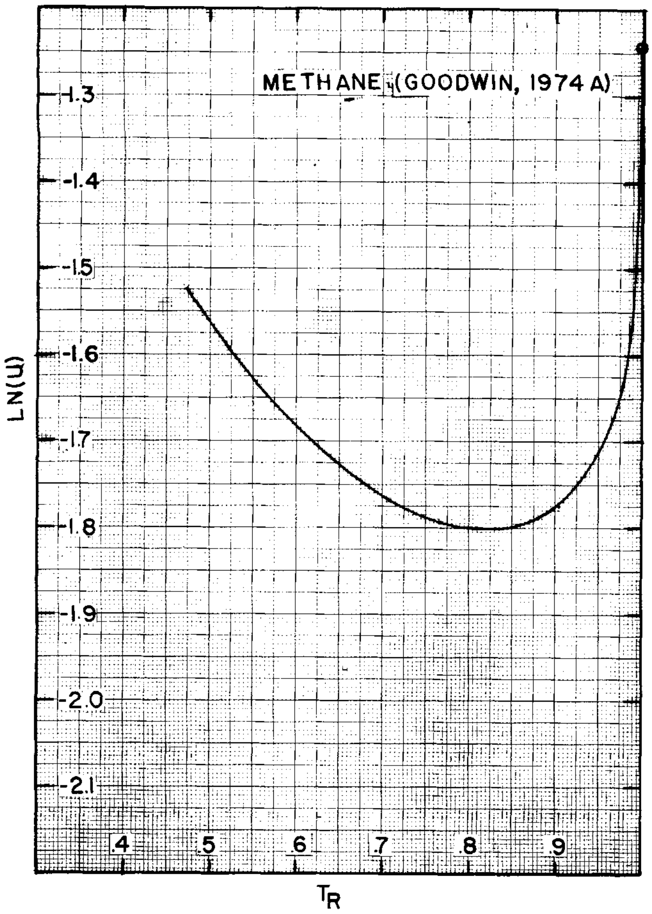

Fig. 2. Plot of $\ln(U)$ vs. T_r for methane.

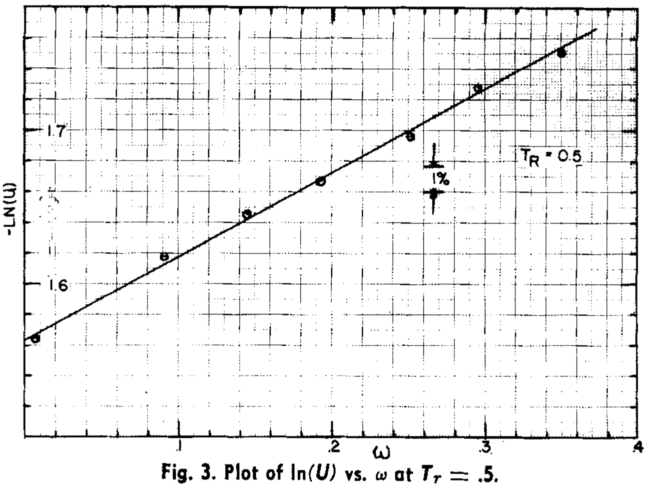

Fig. 3. Plot of $\ln(U)$ vs. ω at $T_r = .5$.

$$Z_c = 0.291 - 0.08\,\omega \qquad (4)$$

This relationship was examined again, using the latest compilation of critical compressibility factors as given by Kudchadkar et al. (1968) and that of acentric factors by Passut and Danner (1973). In Figure 1, the logarithm of the critical compressibility factor is plotted against acentric factor, indicating a straight line relationship which can be represented by

$$\ln Z_c = -1.247 - 0.2629\,\omega \qquad (5)$$

Note that Equations (5) and (4) do not differ significantly, as on expanding Equation (5) and neglecting terms of second and higher orders in ω, we get

$$Z_c = 0.2885 - 0.076\,\omega \qquad (6)$$

SUMMARY OF DEVIATIONS OF CALCULATED SATURATED LIQUID DENSITIES FROM LITERATURE DATA

		Percent deviation*								
		Proposed				Gunn-Yamada (1971)				
T_r range	No. of points	Bias	avg.	Max.	T_r at max.	Bias	Avg.	Max.	T_r at max.	Data source
.47/1.00	52	.11	.24	−.59	.955	−.95	.95	−4.41	.997	Goodwin (1974a)
.29/1.00	45	−.26	.46	2.39	.999	−1.12	1.15	−1.45	.999	Goodwin (1974b)
.28/1.00	51	−.08	.26	1.19	1.000	−.65	.69	1.08	1.000	API Project 44
.32/1.00	55	.16	.19	1.00	.980	−.20	.22	−.63	.995	API Project 44
.30/1.00	62	.24	.43	−3.00	1.000	.27	.37	−2.16	1.000	API Project 44
.36/1.00	61	−.50	.50	−1.12	.996	−.25	.27	−.90	.876	API Project 44
.34/1.00	42	.41	.43	1.03	.977	1.23	1.23	2.54	.997	API Project 44
.38/1.00	32	.45	.50	1.22	.981	1.51	1.51	2.43	.986	API Project 44
.37/0.91	26	2.23	2.23	2.45	.411	3.57	3.57	4.02	.374	API Project 44
.40/0.99	37	1.35	1.57	2.58	.900	3.52	3.52	4.40	.991	API Project 44
.47/1.00	24	.92	.92	2.72	1.000	.41	.47	2.88	1.000	API Project 44
.29/1.00	32	.99	1.07	1.57	.627	.96	.96	1.23	.651	API Project 44
.37/1.00	23	−1.09	1.09	−3.76	.996	−1.94	1.94	−6.16	.996	Angus (1972)
.31/0.91	15	.55	.73	1.45	.852	.03	.51	−1.14	.822	Vargaftik (1975), Zordan and Henry (1975)
.41/1.00	17	−1.54	1.54	−2.20	.407	−1.93	1.93	−2.42	.407	Vargaftik (1975)
.49/0.63	9	.83	.83	1.10	.586	.48	.50	.55	.564	API Project 44
.47/0.65	11	1.17	1.17	1.39	.584	1.13	1.13	1.20	.479	API Project 44
.30/1.00	22	−.13	.45	−1.74	.303	−.15	.29	−1.57	.984	Vargaftik (1975)
.51/1.00	21	−.99	.99	−2.37	.996	−1.21	1.21	−2.82	.996	ESDU (1973)
.49/1.00	22	−2.09	2.09	−3.53	.997	−2.03	2.03	−3.13	.997	ESDU (1974)
.35/1.00	33	−.71	.73	−3.51	.997	−.51	.51	−2.57	.997	Timmermans (1950, 1965, (Vargaftik (1975)
.45/1.00	30	−.09	.34	−2.43	.994	−.43	.45	−2.93	.994	Vargaftik (1975)
.72/1.00	13	1.93	1.93	2.57	.888	1.85	1.85	3.16	.986	Vargaftik (1975)
.55/1.00	17	−1.72	1.72	−2.53	.985	2.12	2.12	−2.98	.981	Timmermans (1950, 1965)
Overall	752	.07	.76			.06	1.09			

density) × 100./Experimental density.

For sixty three hydrocarbons, Equations (4) and (5) showed a bias of 0.7 and 0.6%, respectively, and an average deviation of 1.3 and 1.4%, respectively, in predicted values of the critical compressibility factor.

The relationship expressed by Equation (5) allows elimination of Z_c in Equation (3), resulting in

$$\ln Z_{s1} = \ln Z_r + \ln Z_c = (a_1 + b_1 \omega) - 1.247 - 0.2629\,\omega \qquad (7)$$

Vapor pressure in Equation (7) can be eliminated by using Equation (2), giving

$$\ln(Z_{s1}/P_r) = \ln U = \ln \frac{(P_c V_{s1})}{(RT)} = (\ln U)^0 + \omega(\ln U)^1 \qquad (8)$$

A saturated liquid density correlation developed in the form of Equation (8), requires critical temperature, critical pressure, and the acentric factor and hence is purely predictive in the sense of Pitzer's corresponding states theory. Equation (8) is also convenient to use because it has a linear form in the acentric factor.

The quantity ln U is plotted vs. reduced temperature in Figure 2 for methane. As temperature increases from melting point, ln U decreases continuously until a reduced temperature of about 0.82 is reached, where it exhibits a minimum and then increases continuously up to the critical point. In developing this correlation, data for seven normal paraffins, methane through n-heptane, were used, and in all cases a minimum such as shown in Figure 2 was observed around a reduced temperature of 0.82. This temperature seems to be unique, since the correlation holds for twenty four organic compounds of different natures. Any physical significance to this minimum is not apparent so far.

CORRELATION

As indicated above, data for methane through n-heptane were used in the evaluation of generalized functions $(\ln U)^0$ and $(\ln U)^1$. To show the validity of Equation (8), values of ln U at a reduced temperature of 0.5 are plotted vs. acentric factor in Figure 3. The width of a 1% band is also shown in Figure 3. Note that a straight line relationship of Equation (8) is demonstrated within a fraction of a percent. The scatter in the data points increases only slightly up to reduced temperatures as high as 0.98. Near the critical point and beyond T_r of 0.98, the scatter in these data amounts to a few percent, which is expected since the values of saturated liquid density near the critical are usually not well known.

Values of the generalized functions $(\ln U)^0$ and $(\ln U)^1$ are given in Table 1 from a reduced temperature of 0.3 to the critical temperature. Note that up to 0.98 T_r, values are listed every 0.02 T_r apart, but beyond that an interval of 0.002 T_r is selected since ln U varies considerably from 0.98 T_r to the critical temperature. The generalized functions $(\ln U)^0$ and $(\ln U)^1$ can be expressed mathematically up to and including the reduced temperature of 0.98 by the following equations:

$$\begin{aligned}(\ln U)^0 = {} & 1.39644 - 24.076\,T_r + 102.615\,T_r^2 \\ & - 255.719\,T_r^3 + 355.805\,T_r^4 \\ & - 256.671\,T_r^5 + 75.1088\,T_r^6 \end{aligned} \qquad (9)$$

$$\begin{aligned}(\ln U)^1 = {} & 13.4412 - 135.7437\,T_r + 533.380\,T_r^2 \\ & - 1091.453\,T_r^3 + 1231.43\,T_r^4 \\ & - 728.227\,T_r^5 + 176.737\,T_r^6 \end{aligned} \qquad (10)$$

Beyond 0.98 T_r, linear interpolation of the tabular values is recommended.

RESULTS

This correlation is compared with the literature values of saturated liquid densities of twenty four organic compounds, and a summary is presented in Table 2. Compounds were selected to represent various classes such as naphthenes, aromatics, unsaturates, etc. Consideration was also given to the availability of data over as wide a temperature range as possible. All data are also evaluated by the Gunn and Yamada (1971) correlation in predictive mode. If we consider overall deviations, both correlations show just about the same bias but differ in average deviations. In this respect, Gunn-Yamada correlation shows an average deviation of 1.09% compared to 0.76% for the proposed correlation.

Both correlations were also evaluated extrapolatively for seventeen compounds. Scaling volumes reported by Gunn and Yamada (1971) were used. For the proposed correlation, one density point around 0.6 T_r was selected. For six hundred and thirty data points, Gunn-Yamada and proposed correlations showed a basis of 0.05 and −0.15%, respectively, and an average deviation of 0.28 and 0.34%, respectively.

Consistently large deviations shown by compounds such as n-decane or toluene seem to be due to inaccurate corresponding states parameters. For example, in the case of n-decane, deviations of the order of about 1.5% in all data points are observed from the proposed correlation. A close examination of criticals given by Kudchadkar et al. (1968) indicates that though T_c is quite accurate, P_c could be off as much as 20.7 kPa. The saturated liquid density at 0.7016 T_r along with the vapor pressure at 0.7 T_r were used with respective correlations, resulting in $P_c = 2076.8$ kPa and $\omega = 0.4858$ (compared to $P_c = 2099.5$ kPa and $\omega = 0.4902$ as used). These new values of P_c and ω give an average deviation of about 0.1% in density values. A similar case can be made for other compounds. Thus, the proposed correlation is predictive, accurate over a large temperature range, and applicable to normal fluids.

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NOTATION

a_1, a_2 = coefficients in Equations (3) and (7)
b_1, b_2 = coefficients in Equations (3) and (7)
$(\ln P_r)^0$ = generalized functions dependent on T_r only
$(\ln P_r)^1$ = generalized functions dependent on T_r only
$(\ln U)^0$ = generalized function dependent on T_r only
$(\ln U)^1$ = generalized function dependent on T_r only
P_c = critical pressure
P_r = reduced pressure
R = gas constant
T = temperature
T_r = reduced temperature
U = dimensionless saturated liquid volume
V_{s1} = saturated liquid volume
Z_c = critical compressibility factor
Z_r = reduced saturated liquid compressibility factor
Z_{s1} = saturated liquid compressibility factor
ω = Pitzer's acentric factor

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A Modified Naphtali-Sandholm Method for General Systems of Interlinked, Multistaged Separators

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Frequently, as shown by Stupin and Lockhart (1972) and Tedder and Rudd (1978), complex arrangements of interlinked distillation columns, as shown in Figure 1, can separate ternary mixtures into three products more economically than can simple sequential arrangements. For example, with a feed containing components R, S, and T in decreasing order of volatility, the complex arrangements in Figures 1*b* and *c* may be preferred over the arrangement in Figure 1*a* when the feed contains small amounts and large amounts of S, respectively. Complex interlinked arrangements can also be advantageous when feeds contain more than three components, and three or more products are required.

General systems of interlinked distillation columns have been devised by Sargent and Gaminibandara (1975), as shown, for example, in Figure 2 for the separation of a feed(s) into three products. The single-linked arrangement in Figure 1*b* can be obtained from Figure 2 by sending a feed to section 1, deleting sections 2*a* and *b*, combining sections 1 and 3*b* to form column I, letting section 3*a* be column II, and removing products from stages *P*, *L*, and *N*. In a similar manner, it can be shown that other complex and simple arrangements are embedded in the general system of Figure 2.

In this note, we extend the Naphtali-Sandholm method (1971), which was originally formulated to make stage calculations for a single distillation column, to the general interlinked system of Figure 2. The extension retains the technique of total linearization and simultaneous solution of all the equations for the system by a Newton-Raphson type of procedure. As discussed by Browne, Ishii, and Otto (1977), this type of approach is more advantageous than the iterative sequential approach.

CALCULATION PROCEDURE FOR INTERLINKED SYSTEM

For each stage in Figure 2, component material balances, equilibrium relationships, and an enthalpy balance are written in the manner of Naphtali and Sandholm except for some changes in subscripts at stages *P*, *J*, *Q*, and *M*, where interlinks occur. For example, the functions M_{Pj}, for component material balances for stage *P* are

$$M_{Pj} = (1 + S_P)V_{Pj} + (1 + s_P)L_{Pj} - V_{P+1,j} - L_{Jj} - f_{Pj} \tag{1}$$

where the term L_{Jj}, a linking flow rate, appears instead of an $L_{P-1,j}$ term which appears in the original Naphtali-Sandholm equation. To solve the equations for all stages simultaneously by a modified Newton-Raphson procedure, the functions are linearized in the usual manner, and then both the linearized equations and variables are grouped according to stage to form the matrix equation. However,

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