A Corresponding States Equation for Saturated Liquid Densities.

I. Applications to LNG.

AMYN S. TEJA

Department of Chemical Engineering
University of Delaware
Newark, DE 19711

Presented here is a Corresponding States Method for predicting saturated liquid densities of both pure components and mixtures The method is based on the known properties of two reference fluids and requires the critical properties and the acentric factor of the pure component(s) as input parameters. The method is tested for predicting the orthobaric densities of LNG mixtures using methane and *n*-butane as the reference fluids. Very accurate predictions (well within the accuracy of the experimental data) are obtained for such mixtures using, at most, only one adjustable coefficient to characterize each binary system. The method is extremely simple to use and is suitable for design applications.

SCOPE

The three-parameter Corresponding States principle of Pitzer and co-workers has been widely used for calculating the volumetric and thermodynamic properties of fluids and fluid mixtures. Pitzer's original tabular correlations have recently been extended and represented by analytical equations by Lee and Kesler. Both the original correlations and the extended Lee-Kesler form express the property of interest of any fluid in terms of the corresponding property of a simple fluid and that property of another reference fluid. An extension of the principle based on two (nonspherical) reference fluids is proposed here, and the applicability of the proposed method is demonstrated by calculating very accurate values of the saturated liquid densities of LNG mixtures. That the method can be extended to other substances using different reference fluids, and to other thermodynamic properties, using analogous expressions, will be demonstrated in subsequent papers.

CONCLUSIONS AND SIGNIFICANCE

This article describes a method for analytically representing saturated liquid densities using an extension of Pitzer's three-parameter Corresponding States principle. The extended principle uses two reference fluids, neither of which need be a simple fluid with zero acentric factor. Similar relationships can be written for other thermodynamic functions.

The method was found to give extremely accurate predictions of saturated liquid densities of the components of LNG and of LNG mixtures. The extension of the equations to mixtures was achieved via the van der Waals one-fluid model. Results show that it is possible to predict the saturated liquid densities of LNG mixtures to well within the accuracy of the experimental measurements (<0.1%). The method is extremely easy to use and is in a form particularly convenient for computer use.

Saturated liquid densities of pure components and of mixtures are needed in a wide variety of process design calculations. Frequently, these properties are required for conditions at which no data exist and numerous correlations have therefore appeared in the literature. Such correlations for pure liquids have been reviewed recently by Spencer and Adler (1978).

In cases where data does not exist or when data needs to be extrapolated, the three-parameter Corresponding States principle of Pitzer et al. (1955) is widely used for prediction and correlation. But Pitzer's correlations for saturated liquid densities and similar correlations by Gunn and Yamada (1971) and Lyckman et al. (1965) are either valid only over a limited range of reduced temperature or cover such a variety of substances that they are not suitable when very accurate values of the saturated liquid densities are required, as in the case of LNG mixtures.

An extended form of Pitzer's three-parameter principle is proposed here, using two (nonspherical) reference fluids. The method is capable of widespread application and yet, can lead to very accurate predictions of the properties of a limited class substances with a suitable choice of references.

THE PROPOSED METHOD

The principle which is extended in this study was originally proposed by Pitzer et al. (1955) who showed that the compressibility factor (expressed as a function of reduced temperature and reduced pressure) can be written as a linear function of the acentric factor as

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

where $Z^{(0)}$ is the compressibility factor of a simple fluid with zero acentric factor at the same reduced conditions and $Z^{(1)}$ is a complicated deviation function. Other thermodynamic properties can be written in a similar way. In particular, Gunn and

Teja is on leave from: Department of Chemical Engineering, Loughborough University of Technology, Loughborough, Leics. LE11 3TU England.

0001-1541-80-3685-0337-$00.75.

Yamada (1971) showed that the saturated liquid volumes of pure components can be written as

$$(V/V_{sc}) = V_R^{(0)} + \omega V_R^{(1)} \tag{2}$$

where V_{sc} is a scaling volume and $V_R^{(0)}$, $V_R^{(1)}$ are complicated functions of reduced temperature.

More recently, Lee and Kesler (1975) showed that Eqn. (1) can also be written as

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}}\{Z^{(r)} - Z^{(0)}\} \tag{3}$$

where the compressibility of any fluid of acentric factor ω is expressed in terms of a simple fluid contribution $Z^{(0)}$ and a reference fluid contribution $Z^{(r)}$. Lee and Kesler used the properties of (mainly) argon to obtain an analytic equation for the simple fluid and the properties of (mainly) n-octane to obtain an equation for the reference fluid. The Lee-Kesler correlation is accurate for the estimation of the thermodynamic properties of nonpolar fluids (Reid et al. 1977) and has recently been expressed in terms of saturated volumes by Lin and Daubert (1979) as follows

$$\frac{V}{(RT_c/P_c)} = V_R^{(0)} + \frac{\omega}{\omega^{(r)}}\{V_R^{(r)} - V_R^{(0)}\} \tag{4}$$

Both Equations (3) and (4) retain Pitzer's original proposal of a Taylor series expansion of a thermodynamic function about the properties of a simple reference fluid of zero acentric factor.

The new equation proposed here no longer retains the simple fluid as one of the references. Equation (4) is rewritten as

$$\frac{V}{RT_c/P_c} = \frac{V^{(r1)}}{RT_c^{(r1)}/P_c^{(r1)}} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}} \times \left\{\frac{V^{(r2)}}{RT_c^{(r2)}/P_c^{(r2)}} - \frac{V^{(r1)}}{RT_c^{(r1)}/P_c^{(r1)}}\right\} \tag{5}$$

where the superscripts $r1$ and $r2$ refer to two reference fluids which are chosen so that they are similar to the pure component of interest or, in the case of mixtures, to the key components of interest. If one of the references chosen is a simple fluid of zero acentric factor, Eqn. (5) reduces to

$$\frac{V}{RT_c/P_c} = \frac{V^{(0)}}{RT_c^{(0)}/P_c^{(0)}} + \frac{\omega}{\omega^{(r)}}\left\{\frac{V^{(r)}}{RT_c^{(r)}/P_c^{(r)}} - \frac{V^{(0)}}{RT_c^{(0)}/P_c^{(0)}}\right\} \tag{6}$$

which is similar to Eqn. (4), except that the reduction is carried out with RT_c/P_c instead of V_c. This is likely to be more useful in practice, since critical volumes are often not known with great accuracy. If accurate critical volumes are available, as in the case of the components of LNG, Eqn. (5) can be expressed as

$$Z_c V_R = Z_c^{(r1)} V_R^{(r1)} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}}\left\{Z_c^{(r2)} V_R^{(r2)} - Z_c^{(r1)} V_R^{(r1)}\right\} \tag{7}$$

or, in the case of saturated liquid densities

$$\frac{Z_c}{\rho_R} = \frac{Z_c^{(r1)}}{\rho_R^{(r1)}} + \frac{\omega - \omega^{(r1)}}{\omega^{(r2)} - \omega^{(r1)}}\left\{\frac{Z_c^{(r2)}}{\rho_R^{(r2)}} - \frac{Z_c^{(r1)}}{\rho_R^{(r1)}}\right\} \tag{8}$$

Here $\rho_R^{(r1)}$ and $\rho_R^{(r2)}$ are the reduced saturated densities of two reference fluids at the same reduced temperature. Any two fluids may be selected as the reference fluids. The choice is not a matter of principle but is dictated by the component(s) whose properties are to be calculated.

Equations (7) and (8) can readily be extended to mixtures using the van der Waals one-fluid model to replace the critical properties T_c, V_c, Z_c, and ω of any fluid by the pseudocritical properties T_{cm}, V_{cm}, Z_{cm} and ω_m of a hypothetical equivalent substance as

$$T_{cm}V_{cm} = \sum_i \sum_j x_i x_j T_{cij} V_{cij} \tag{9}$$

$$V_{cm} = \sum_i \sum_j x_i x_j V_{cij} \tag{10}$$

$$Z_{cm} = \sum_i x_i Z_{ci} \tag{11}$$

$$\omega_m = \sum_i x_i \omega_i \tag{12}$$

The one-fluid model can be used to obtain the saturated liquid densities of mixtures provided values can be assigned to the cross-parameters T_{cij} and V_{cij} $(i \neq j)$. For LNG mixtures, the most successful mixing rules are (Reid and Leland 1960, Teja 1978)

$$V_{cij}T_{cij} = \xi_{ij}(T_{cii}V_{cii}T_{cjj}V_{cjj})^{\frac{1}{2}} \tag{13}$$

$$V_{cij} = \eta_{ij}(V_{cii}^{1/3} + V_{cjj}^{1/3})^3/8 \tag{14}$$

where ξ_{ij} and η_{ij} are binary interaction coefficients. In all mixtures studied here, it suffices to use one adjustable coefficient to characterize each binary system (Teja 1978). No additional coefficients are required to predict the properties of ternary and higher mixtures.

Here, we use the procedure outlined above to obtain very accurate predictions of the orthobaric densities of LNG mixtures. Subsequent articles will show that a similar procedure can be adopted for other thermodynamic properties.

APPLICATIONS TO LNG

Very accurate values of the orthobaric liquid densities are required as a basis for the custody transfer of LNG. Since it is not possible to measure this property for all mixtures and at all conditions of interest, a reliable and accurate method for the prediction of the densities of LNG mixtures is of great practical importance to the LNG industry. Haynes et al. (1977) estimated that an error of 1% in density can result in an inequity of approximately \$40,000 per 125,000 m^3 shipload of LNG.

Very accurate measurements of the orthobaric densities of LNG components and some of the mixtures of interest have now become available (Haynes and Hiza 1977, Haynes et al. 1976, Hiza et al. 1977, Rodosevich and Miller 1973). These measurements have a total uncertainty of less than 0.1% and enable prediction methods to be developed and tested. Haynes et al. (1977) optimized and tested several methods using these data. The methods include an extended corresponding states approach using shape factors (Mollerup and Rowlinson 1974, Teja and Rowlinson 1973), a hard sphere equation (Rodosevich and Miller 1974), an equation based on the cell model (Albright 1973) and an empirical method due to Klosek and McKinley (1968).

Of all the methods tested, the extended corresponding states procedure with shape factors (hereafter referred to as the shape factor approach) was found to be the most versatile, since it could be applied over the greatest range of pressure, temperature and composition. But, the shape factor approach is complex, and therefore difficult to use. It also requires very accurate values of two binary interaction coefficients. The method outlined in this article can very easily be applied to LNG mixtures. It is comparable in accuracy to the shape factor approach, at least for the calculation of saturated liquid densities, and is more easily applied. In addition, it requires less information per binary, and is suitable for computer calculation, since it requires input parameters which are readily available in most physical properties packages.

Methane and n-butane were chosen as the two reference fluids in all calculations presented here. Methane is a key component in LNG mixtures and n-butane was the largest molecule in all LNG mixtures where accurate data are available. As will be seen, it is extremely simple to change references in the calculations so that other (larger) molecules can very easily be accommodated.

The saturated liquid densities of methane and n-butane were

TABLE 1. REFERENCE FLUID CONSTANTS FOR EQN. (15)

	Methane	n-Butane
b_1	1.8364291	1.8586895
b_2	0.6606329	3.0518061
b_3	−0.09322854	−5.0703878
b_4	0	2.9597219

TABLE 2. CRITICAL CONSTANTS AND ACENTRIC FACTORS OF THE COMPONENTS OF LNG

Substance	$T_c(K)$	$V_c(m^3kmol^{-1})$	P_c(bar)	Z_c	ω
Methane	190.555	0.098425	46.4	0.2883	0.012
Ethane	305.42	0.1481	48.8	0.2848	0.114
Propane	369.82	0.2030	42.5	0.2806	0.162
Isobutane	408.15	0.2630	36.48	0.2827	0.177
n-Butane	425.16	0.2551	37.97	0.2740	0.199
Nitrogen	126.2	0.0898	33.9	0.2901	0.020

represented as functions of reduced temperature by an equation of the type

$$\rho_R = 1 + b_1(1 - T_R)^{0.35} + \sum_{i=2}^{4} b_i(1 - T_R)^{(i+1)/3} \qquad (15)$$

The least squares coefficients (b_i) for methane and n-butane between their triple and critical points have been obtained by Haynes and Hiza (1977) and are given in Table 1. The critical constants and acentric factors of the reference fluids and of the other fluids studied here are given in Table 2. The critical constants of the reference fluids are those recommended by Haynes and Hiza (1977) for use with Eqn. (15) and the constants given in Table 1. Acentric factors for the reference fluids and the critical constants of the fluids studied were taken from standard compilations (Reid et al. 1977). The acentric factors of the fluids studied differ slightly from the conventional values calculated from vapor pressures. The values given in Table 2 were obtained as follows: Eqn. (8) is first rearranged to give

$$\omega = \omega^{(r1)} + (\omega^{(r2)} - \omega^{(r1)}) \times \left\{\frac{Z_c}{\rho_R} - \frac{Z_c^{(r1)}}{\rho_R^{(r1)}}\right\} \Big/ \left\{\frac{Z_c^{(r2)}}{\rho_R^{(r2)}} - \frac{Z_c^{(r1)}}{\rho_R^{(r1)}}\right\} \qquad (16)$$

Hence if a single value of the orthobaric density of a *pure* fluid is available, the acentric factor for that fluid can be calculated using Eqn. (16).

Since the temperature range of interest for LNG mixtures is 90K-140K, a density value near the mid-point of this range was chosen for the calculation of acentric factors for each component of interest. An advantage of calculating ω's in this way is that allowance is made for slight errors in the chosen values of the critical points used in the calculations. It is well known that the success of any method based on the corresponding states principle depends on the accuracy of the values of the critical constants and acentric factors used. The procedure adopted here makes all the equations consistent for very accurate calculations. A similar procedure using a vapor pressure equation and the boiling point was used by Lee and Kesler in their calculations. The values of the acentric factors calculated above are not very different from conventional values reported by Passut and Danner (1973).

TABLE 3. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED LIQUID DENSITIES OF PURE COMPONENTS

Component	# Of Data	Temp. Range of Data (K)	Reference	AAD*%	Max. Dev. %
Methane**	11	105-160	Haynes & Hiza (1977)	0.01	0.01
Ethane	22	100-270	Haynes & Hiza (1977)	0.17	0.33
Propane	16	100-290	Haynes & Hiza (1977)	0.15	0.27
i-Butane	12	115-300	Haynes & Hiza (1977)	0.14	0.19
n-Butane**	12	135-300	Haynes & Hiza (1977)	0.01	0.02
Nitrogen	18	95-120	Haynes (1976)	0.22	0.54
Methane	4	91-115	Rodosevich & Miller (1973)	0.04	0.06
Ethane	4	91-115	Rodosevich & Miller (1973)	0.20	0.25
Propane	4	91-115	Rodosevich & Miller (1973)	0.14	0.17
Nitrogen	4	91-115	Rodosevich & Miller (1973)	0.12	0.20
			Overall AAD = 0.15%		

** Data used to obtain Eqn. (15)

* AAD = $100 \times |\rho_{calc} - \rho_{exp}|/\rho_{exp}$

TABLE 4. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED LIQUID DENSITIES OF BINARY MIXTURES

Mixture	# Of Data	Data Ref.	Temp. Range of Data (K)	Comp. Range of Data (x_1)	η_{12}	AAD%	Max. Dev. %
CH_4-C_2H_6	39	1,2*	91-140	0.35-0.95	0.994	0.04	0.12
CH_4-C_3H_8	26	1,2	90-130	0.29-0.97	1.000	0.03	0.10
CH_4-iC_4H_{10}	11	1,2	95-125	0.49-0.95	1.013	0.05	0.11
CH_4-nC_4H_{10}	8	1	105-140	0.92	1.003	0.07	0.17
CH_4-N_2	29	1,2	91-140	0.51-0.95	1.018	0.05	0.14
C_2H_6-C_3H_8	12	1	105-140	0.50-0.67	1.000	0.04	0.12
C_2H_6-iC_4H_{10}	6	1	105-130	0.69-0.72	1.007	0.03	0.07
C_2H_6-nC_4H_{10}	8	1	115-140	0.65-0.67	1.010	0.04	0.07
C_2H_6-N_2	4	1	105-120	0.94	1.000	0.10	0.14
C_3H_8-iC_4H_{10}	8	1	105-130	0.49-0.51	1.000	0.02	0.03
C_3H_8-nC_4H_{10}	8	1	110-150	0.59-0.61	1.000	0.09	0.14
C_3H_8-N_2	6	1	100-115	0.92-0.98	1.000	0.08	0.12
iC_4H_{10}-nC_4H_{10}	4	1	125-140	0.47	1.000	0.04	0.06
					Overall AAD = 0.046%		

* Ref 1, Hiza et al. (1977); Ref. 2, Rodosevich & Miller (1973).

TABLE 5. COMPARISON OF CALCULATED AND EXPERIMENTAL SATURATED LIQUID DENSITIES OF THREE TERNARY MIXTURES USING BINARY COEFFICIENTS ONLY. THE EXPERIMENTAL DATA ARE THOSE OF RODOSEVICH AND MILLER (1973)

Mixture	# of Data	Temp. Range of Data	AAD%	Max. Dev. %
0.8466 CH_4 + 0.1025 C_2H_6 + C_3H_8	4	100-115	0.05	0.07
0.8409 CH_4 + 0.1086 C_2H_6 + N_2	4	91-115	0.06	0.07
0.9055 CH_4 + 0.0497 C_3H_8 + N_2	2	91-108	0.03	0.03
		Overall AAD = 0.05%		

TABLE 6. COMPARISON OF SATURATED LIQUID DENSITIES OF A SIX-COMPONENT LNG MIXTURE CALCULATED USING THE PROPOSED METHOD WITH THOSE CALCULATED USING THE SHAPE FACTOR APPROACH

0.6975 CH_4 + 0.156 C_2H_6 + 0.092 C_3H_8 + 0.029 nC_4H_{10} + 0.014 iC_4H_{10} + 0.0115 N_2

Temp. (K)	Density (kmol m^{-3}) Using shape factors	Density (kmol m^{-3}) Using proposed method	AAD%
95	24.3315	24.3612	0.12
100	24.0648	24.0956	0.13
105	23.7942	23.8265	0.14

TABLE 7. COMPARISONS OF CALCULATED AND EXPERIMENTAL SATURATED LIQUID DENSITIES FOR SELECTED BINARY MIXTURES WHEN ETHANE AND *n*-PENTANE ARE USED AS THE REFERENCE FLUIDS

Mixture	η_{12}	AAD%	Max. Dev.
C_2H_6-C_3H_8	1.000	0.05	0.07
C_2H_6-iC_4H_{10}	1.010	0.07	0.09
C_3H_8-iC_4H_{10}	1.000	0.10	0.12
C_3H_8-nC_4H_{10}	1.000	0.12	0.16

RESULTS AND DISCUSSION

Results of the calculations of the saturated liquid densities of the pure components of LNG are shown in Table 3. The overall absolute average deviation of the pure component densities is 0.15%. The method can easily be adapted for other pure substances, using different reference fluids if expressions (which can be very simple) are available for the saturated liquid densities of the references chosen.

Results of the calculations of the saturated liquid densities of binary mixtures formed from the components of LNG are given in Table 4. For all binary mixtures, ξ_{12} was set equal to 1.0. This value is close to the optimum for low molecular weight alkane mixtures using the mixing rule given in Eqn. (13) as discussed by Teja (1978). In most cases η_{12} was also 1.0. Values of η_{12} are given in Table 4. The overall average absolute deviation for the 169 data points is 0.046%, well within the experimental error of the data. Mixtures containing a high concentrations of N_2 can be handled by this approach as can be seen from the range of concentrations of the data used. This is not true of methods such as that of Klosek and McKinley as pointed out by Haynes et al. (1977) and Rodosevich and Miller, (1973).

Calculations of the saturated liquid densities of three ternary mixtures are given in Table 5. The only mixture parameters used in the calculations were the binary η_{12} values for methane-ethane and methane-nitrogen mixtures. All other binary interaction coefficients were set equal to 1.0. The overall absolute average deviation of 0.05% for the 11 data points is very encouraging.

Finally, Table 6 shows the values of saturated liquid densities of a six-component LNG mixture calculated using the proposed method. Also shown are the values calculated by Haynes et al. (1977) using the shape factor approach. Agreement between the two sets of saturated liquid densities is truly remarkable. Values of η_{12} for nitrogen-butane mixtures were set equal to 1.0, since binary data were not available for these mixtures. The advantage of the proposed equation is that it is much easier to use than the shape factor approach. It also offers an advantage over methods which use the excess volume (such as of the Klosek and McKinley method) in that pure component liquid densities do not have to be extrapolated to temperatures below the triple points of the substances.

Although the method has been demonstrated using a nearly spherical fluid (methane) as one of the references, calculations were also carried out using ethane and n-pentane as the two reference fluids. Results similar to those shown in Table 3 were obtained with slightly different values of η_{12} for the binaries and with different values of ω from Eqn. (16). A few results are shown in Table 7. In these calculations, the equations for the reference substances (corresponding to Eqn. 15) were taken from the work of Teja and Singh (1977). It is obvious that comparable results can be obtained using two non-spherical reference fluids. Methane was preferred here since it is a "key" component of LNG mixtures.

ACKNOWLEDGMENT

I wish to thank the faculty and staff of the Department of Chemical Engineering of the University of Delaware for their hospitality during my sabbatical year.

NOTATION

b_1, b_2
b_3, b_4 = constants as given in Table 1
P = pressure
R = gas constant
T = thermodynamic temperature
V = volume (of saturated liquid)
x = mole fraction
Z = compressibility factor

Greek Letters

ξ = binary interaction coefficient = 1.0 in all calculations
η = binary interaction coefficient
ω = acentric factor
ρ = density (of saturated liquid)

Superscripts

(0) = reference fluid of zero acentric factor
(*r*) = reference fluid
(*r*1) = reference fluid 1
(*r*2) = reference fluid 2

Subscripts

c = critical
calc = calculated value
exp = experimental value
i,j = component *i*, *j*
sc = scaling value

LITERATURE CITED

Albright, M. A., "A Model for the Precise Calculation of Liquefied Natural Gas Densities," NGPA Technical Publ. TP-3 (June, 1973).

Gunn, R. D., and T. Yamada, "Corresponding States Correlation of Saturated Liquid Volumes," *AIChE J.*, 17, 1341 (1971).

Haynes, W. M., M. J. Hiza, and N. V. Fredrick, "Magnetic Suspension Densimeter for Measurements of Fluids of Cryogenic Interest," *Rev. Sci. Instrum.*, **47**, 1237 (1976).
Haynes, W. M., M. J. Hiza, and R. D. McCarty, "Densities of LNG for Custody Transfer," Proceedings Fifth Int. Conf. on LNG, Dusseldorf, Vol. 2, Section III, Paper 11 (1977).
Haynes, W. M., and M. J. Hiza, "Measurements of the Orthobaric Liquid Densities of Methane, Ethane, Propane, Isobutane and Normal Butane," *J. Chem. Thermodyn.*, **9**, 179 (1977).
Hiza, M. J., W. M. Haynes, and W. R. Parrish, "Orthobaric Liquid Densities and Excess Volumes for Binary Mixtures of Low Molecular Weight Alkanes and Nitrogen Between 105K and 140K," *J. Chem. Thermodyn.*, **9**, 873 (1977).
Klosek, J., and C. McKinley, "Densities of Liquefied Natural Gas and of Low Molecular Weight Hydrocarbons," Proc. First Int. Conf. on LNG, Chicago (1968).
Lee, B. I., and M. G. Kesler, "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," *AIChE J.*, **21**, 510 (1975).
Lin, C. T., and T. E. Daubert, "Prediction of Partial Molar Volume from the Lee-Kesler Equation of State," *AIChE J.*, **25**, 365 (1979).
Lyckman, E. W., C. A. Eckert, and J. M. Prausnitz, "Generalized liquid volumes and solubility parameters for Regular solution application," *Chem. Eng. Sci.*, **20**, 703 (1965).
Mollerup, J., and J. S. Rowlinson, "The Prediction of the Densities of Liquefied Natural Gas and of Lower Molecular Weight Hydrocarbons," *Chem. Eng. Sci.*, **29**, 1373 (1974).
Passut, C. A., and R. P. Danner, "Acentric Factor. A Valuable Correlating Parameter for the Properties of Hydrocarbons," *Ind. Eng. Chem. Process Des. Dev.*, **12**, 365 (1973).
Pitzer, K. S., D. Z. Lippman, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson, "The Volumetric and Thermodynamic Properties of Fluids II. Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *J. Am. Chem. Soc.*, **77**, 3433 (1955).
Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd Ed., McGraw-Hill, New York (1977).
Reid, R. C., and T. W. Leland, "Pseudocritical Constants," *AIChE J.*, **11**, 228 (1965).
Rodosevich, J. B., and R. C. Miller, "Experimental Liquid Mixture Densities for Testing and Improving Correlations for Liquefied Natural Gas," *AIChE J.*, **19**, 729 (1973).
Rodosevich, J. B., and R. C. Miller, "Calculation of LNG Excess Volumes by a Modified Hard-Sphere Model," *Adv. Cryog. Eng.*, **19**, 339 (1974).
Spencer, C. F., and S. B. Adler, "A Critical Review of Equations for Predicting Saturated Liquid Density," *J. Chem. Eng. Data*, **23**, 82 (1978).
Teja, A. S., and J. S. Rowlinson, "The Prediction of the Thermodynamic Properties of Fluids and Fluid Mixtures," *Chem. Eng. Sci.*, **29**, 529 (1973).
Teja, A. S., "Binary Interaction Coefficients for Mixtures Containing the *n*-Alkanes," *Chem. Eng. Sci.*, **33**, 609 (1978).
Teja, A. S., and A. Singh, "Equations of State for Ethane, Propane, *n*-Butane and *n*-Pentane," *Cryogenics*, **17**, 591 (1977).

Manuscript received June 6, 1979; revision received October 4, and accepted October 11, 1979.

II. Applications to the Calculation of Swelling Factors of CO_2—Crude Oil Systems

AMYN S. TEJA
and
STANLEY I. SANDLER
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

In an earlier article, a Corresponding States Method was presented for predicting the saturated liquid densities of both pure components and mixtures. The method is based on the known saturated liquid densities of two reference fluids and requires the critical properties and acentric factors of the pure components as input parameters. We use the method here to calculate the swelling factors of CO_2-crude oil mixtures using CO_2 and *n*-dodecane as the reference fluids. The critical properties and acentric factors of the crude oils were estimated from their API gravities and Watson K-factors. Using only one adjustable coefficient to characterize each CO_2-crude oil system, swelling factors were calculated to within 0.5% of their experimental values. The single adjustable coefficient is linearly related to the boiling point of the crude.

SCOPE

The use of carbon dioxide for tertiary oil recovery from petroleum reservoirs is receiving increasing attention. One of the characteristics of carbon dioxide is that it promotes swelling. The extent of the expansion or swelling is measured by the "swelling factor," and these are used to calculate other properties of interest in enhanced oil recovery. Swelling factors are directly related to the saturated liquid densities of CO_2-crude oil mixtures, and we recently proposed a method for calculating saturated liquid densities.

That method is basically an extension of the three-parameter corresponding states principle of Pitzer and co-workers, and uses the properties of two (nonspherical) reference fluids. The method has been used to calculate very accurate values of the saturated liquid densities of LNG mixtures published previously and is extended here, using different reference fluids and different reference equations, to calculate saturated liquid densities, and hence swelling factors, of CO_2-crude oil mixtures. The method can be extended to mixed gas-crude oil systems, and to other thermodynamic properties.

CONCLUSIONS AND SIGNIFICANCE

Described here is an analytic method for calculating saturated liquid densities, and hence swelling factors, of CO_2-crude oil systems, which are of interest in enhanced oil recovery. The method uses an extension of Pitzer's three-parameter corresponding states principle, based on two reference fluids chosen so that their properties are close to the key components of interest. The method gives extremely accurate predictions of the saturated liquid densities of LNG mixtures (Teja 1980), when the critical properties and acentric factors of the components are known.

When the critical properties and acentric factors have to be estimated, as in the case of crude oils in CO_2-crude oil mix-

Teja is on leave from the Department of Chemical Engineering, Loughborough University of Technology, Loughborough, LE11 3TU, England.

0001-1541-80-3686-0341-$00.75.