

LIQUID DENSITY OF PURE AND MULTICOMPONENT FLUIDS BY SCALED- VARIABLE-REDUCED-COORDINATE (SVRC) METHOD

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ABSTRACT

The Scaled-Variable-Reduced-Coordinate (SVRC) method with a proposed set of mixing rules are applied to calculate the liquid density of several system of liquid mixture and satisfactory results are obtained. The ability and accuracy of the proposed method are compared with other widely used method such as Hankinson-Thomson method and Spencer and Danner modification of Rackett method. The results of SVRC method with the proposed mixing rule and comparison with other methods indicate that the proposed model is as good as the best available methods.

NOMENCLATURE

AAPD	:	The average absolute percent deviation
k_{ij}	:	Binary interaction coefficient defined by eq. (22)
l_{ij}	:	Binary interaction coefficient defined by eq. (23)
MW	:	Molecular weight
N	:	Number of data points
T	:	Temperature, K
T_c	:	Critical point temperature, K
T_t	:	Triple point temperature, K
V	:	Molar volume, $m^3/mole$
V_c	:	Molar volume, $m^3/mole$, at the critical point
V_t	:	Molar volume, $m^3/mole$, at the triple point
x	:	Mole fraction
Z_c	:	Compressibility factor at the critical point
α	:	Scaling exponent
ρ	:	Liquid density, kg/m^3 , at given T
ρ_c	:	Liquid density, kg/m^3 , at the critical point

- ρ_t : Liquid density, kg/m^3 , at the triple point
 ω : Acentric factor

INTRODUCTION

The prediction of the physical properties of a fluid system is an essential part of any computer simulation package or in model development of any chemical engineering process. One of these physical properties is liquid density. Several correlations have been suggested in the literature for the prediction of liquid density [2-7, 11-15, 18-21, 23, 25-26, 28, 31]. Unfortunately, an evaluation of the popular equations of state such as Soave-Redlich-Kwong [27] and Peng-Robinson [22] has shown that their ability for predicting liquid density is not accurate enough. In addition, a direct calculation of liquid density is more desirable.

Spencer and Danner [28] have studied the capabilities of several correlations, and results of their evaluation are presented in Table 1. Even though the Ehrlich [5], Riedel [25] and Holmes [18] method give relatively acceptable results but since their errors are large in comparison with the Francis correlation and they are therefore not used in a further evaluation. Harmans [15] correlation is applicable

Table 1: Capability of Several Liquid Density Correlations for Pure Compounds (Spencer and Danner, 1972)

Method	No. of Compounds Tested	No. of Points Tested	Average Absolute % Deviation
Lyckman et al.	36	1597	4.22
Holmes	6	353	1.80
Gunn and Yamada	36	1597	0.59
Francis	36	1597	0.43
Harmans	11	824	0.68
Bradford and Thodos	36	1597	2.19
Riedel	9	641	1.16
Yen and Woods	24	1357	0.91
Harlacher	32	1473	0.81
Ehrlich	5	248	1.30
Narsimhan	32	1473	2.04
Rackett	36	1597	2.24

to hydrocarbons heavier than C₇ only and therefore, because of this limitation, it is not considered further. Obviously, due to their large errors, the Bradford and Thodos [3], Lyckman [20] and Narsimham [21] correlations are also omitted.

The Rackett equation [23] is a very simple equation which requires only the critical temperature, T_c , critical volume, V_c , and critical compressibility, Z_c . In addition it is capable of predicting liquid density over the range from the triple point to the critical point. However, the large error of 2.24 is not tolerable; Spencer and Danner [28] therefore proposed a modification to this equation and increased its accuracy considerably. They replaced the critical compressibility factor, Z_c , by Z_{RA} which was determined for each compound. Table 2 presents the comparison results for the Francis, Rackett and the Spencer and Danner modification of the Rackett equations and shows that the Spencer and Danner method gives excellent results for hydrocarbons but its accuracy is not as good as the Francis method. It should be noted that the Francis method requires four parameters whereas the Spencer and Danner Method requires only one parameter.

Table 2: Capability of Three Liquid Density Correlations for Pure Compounds (Spencer and Danner, 1972)

Average Absolute % Deviation

Group of Compound	No. of Compounds Tested	No. of Points	Francis	Rackett	Spencer and Danner
Hydrocarbons	37	1948	1.01	2.50	0.53
Organics	36	652	0.43	5.50	0.60
Inorganics	11	148	0.58	0.53	0.74

Recently, Shaver et al. [26] have proposed a unified framework for the prediction of saturated properties using the Scaled-Variable-Reduced-Coordinate (SVRC) approach, specifically for the saturated liquid density of pure fluids. Because of its generality and relatively high precision it will be discussed in detail in the following section. Finally, a set of mixing rules will be proposed to extend their approach to systems of binary and multi-components mixtures.

THE SCALED-VARIABLE-REDUCED-COORDINATE APPROACH

Shaver et al. [26] proposed their Scaled-Variable-Reduced Coordinate model for saturated liquid density of pure fluids as:

$$\rho = \left[\rho_c^\alpha - \Theta (\rho_c^\alpha - \rho_t^\alpha) \right]^{(1/\alpha)} \quad (1)$$

where:

$$\Theta = \frac{(1 - A^{\varepsilon^B})}{(1 - A)} \quad (2)$$

$$\alpha = \alpha_c - (\alpha_c - \alpha_t) \left[\frac{(1 - A^\varepsilon)}{(1 - A)} \right] \quad (3)$$

$$\alpha_c = C_5 + C_6 \cdot T_t^{(C_7 + C_8 \cdot \omega)} \quad (4)$$

$$\Delta\alpha = \alpha_c - \alpha_t = C_1 + C_2 \cdot T_t^{(C_3 + C_4 \cdot Z_c)} \quad (5)$$

$$\varepsilon = \frac{(T_c - T)}{(T_c - T_t)} \quad (6)$$

A, B, and C₁ through C₈ are the model parameters and were determined by Shaver et al. [26] from experimental data and their values are given in Table 3.

**Table 3: The SVRC Model Parameters
(Robinson et al. 1988)**

Parameter	Value
B	0.325
C ₁	3.63493
C ₂	-3.73713
C ₃	0.32786
C ₄	-0.90951
C ₅	+0.36141
C ₆	+2.95802
C ₇	+16.4993
C ₈	-25.4640

EXTENSION OF THE SVRC MODEL TO MULTICOMPONENT SYSTEMS

In order to extend the SVRC model to multicomponent systems, several mixing rules were tested. For each set of mixing rules, liquid densities were predicted and compared with experimental data and the percent deviation for each data point was calculated. Then the average of the absolute percent deviations was calculated. The set of mixing rules giving the least average absolute deviation is the desired one. Based on our evaluation, we propose the following mixing rules.

$$V_{cm} = \sum_i^n \sum_j^n x_i x_j V_{c_{ij}} \quad (7)$$

$$T_{cm} = \frac{1}{V_{cm}^{1/10}} \sum_i^n \sum_j^n x_i x_j V_{c_{ij}}^{1/10} T_{c_{ij}} \quad (8)$$

$$\rho_{c_{ij}} = \left(\frac{\sqrt[3]{\rho_{c_i}} + \sqrt[3]{\rho_{c_j}}}{2} \right)^3 \quad (16)$$

$$\rho_{t_{ij}} = \left(\frac{\sqrt[3]{\rho_{t_i}} + \sqrt[3]{\rho_{t_j}}}{2} \right)^3 \quad (17)$$

$$V_{c_{ij}} = (1/8) \left(\sqrt[3]{V_{c_i}} + \sqrt[3]{V_{c_j}} \right)^3 \quad (18)$$

$$T'_{c_i} = \frac{T_{c_i}}{1 + \frac{C}{MW_i \cdot T}} \quad (19)$$

$$C = \eta 2.6 \left(1 + \frac{|\eta|}{\eta} \right) \quad (20)$$

$$\eta = \sum_i^n (0.11 - \omega_i) \cdot MW_i \left[\frac{T_{c_i}}{T} \right]^4 \quad (21)$$

In the above equations T_{c_i} represents the true critical temperature of component i and T'_{c_i} is the "effective" critical temperature; MW is molecular weight; V_c is critical volume, and x is mole fraction. If C in equation (19) is set equal to zero, the "effective" critical temperature, T'_{c_i} , becomes equal to the true critical temperature. The binary interaction parameters k_{ij} and l_{ij} are defined by equations (22) and (23),

respectively. The subscript m stands for mixture, c for critical point and t for triple point.

$$k_{ij} = 1 - \frac{8 \left(\sqrt{V_{c_i} V_{c_j}} \right)}{\left(\sqrt[3]{V_{c_i}} + \sqrt[3]{V_{c_j}} \right)^3} \quad (22)$$

$$l_{ij} = 1 - \frac{8 \left(\sqrt{V_{t_i} V_{t_j}} \right)}{\left(\sqrt[3]{V_{t_i}} + \sqrt[3]{V_{t_j}} \right)^3} \quad (23)$$

The working equations for the calculation of the liquid density of a multi-components system are the same as those for the pure component with mixture properties as described above i.e.

$$\rho_m = \left[\rho_{c_m}^{\alpha_m} - \Theta_m (\rho_{c_m}^{\alpha_m} - \rho_{t_m}^{\alpha_m}) \right]^{(1/\alpha_m)} \quad (24)$$

where:

$$\Theta_m = \frac{(1 - A^{\varepsilon_m^B})}{(1 - A)} \quad (25)$$

$$\alpha_m = \alpha_{c_m} - (\alpha_{c_m} - \alpha_{t_m}) \left[\frac{(1 - A^{\varepsilon_m})}{(1 - A)} \right] \quad (26)$$

$$\alpha_{c_m} = C_5 + C_6 \cdot T_{t_m}^{(C_7 + C_8 \cdot \omega_m)} \quad (27)$$

$$\Delta\alpha_m = \alpha_{c_m} - \alpha_{t_m} = C_1 + C_2 \cdot T_m^{(C_3 + C_4 \cdot Z_{c_m})} \quad (28)$$

$$\varepsilon_m = \frac{(T_{c_m} - T)}{(T_{c_m} - T_{t_m})} \quad (29)$$

It should be noted that the values of A, B and C₁ through C₈ are the same as those presented in Table 3 for pure components. The average absolute percent deviation, AAPD, is calculated by equation (30).

$$\text{AAPD} = \frac{1}{N} \sum_i^N \left| \left(\frac{\rho_{\text{EXP}} - \rho_{\text{CAL}}}{\rho_{\text{EXP}}} \right)_i \right| \quad (30)$$

In the above equation, N is the number of data point tested and the subscripts EXP and CAL represent experimental and calculated values, respectively.

RESULTS

In order to compare the SVRC model with other accurate methods, a computer program and data base were prepared. Using the computer program, the liquid densities of several pure fluid were predicted by the SVRC of Shaver et al. [26], Hankinson-Thomson [13], and Spencer-Danner modification [28] of the Rackett equation and the calculated values were compared with the experimental data. A summary of the results of this comparison is presented in Table 4. In addition, Figs 1 through 5 also present graphical comparison of some of the selected pure fluids. These figures represent the typical accuracy obtained for pure fluids.

The analysis of Table 4 indicates that the SVRC method gives a smaller error for hydrocarbons than both the Hankinson-Thomson and Spencer-Danner methods. For water, however the Hankinson-Thomson gives more accurate results than the other two methods. As it is noticed from Table 4, the SVRC method gives overall best results.

Table 4: Ability of Three Methods in Prediction of Pure Fluid Densities

Average Absolute % Deviation

Compound	Reference No.	No. of Points	Temp. Range, °F	Pres. Range, Psia	SVRC	Hankinson Thomson	Spencer Danner
CH ₄	1	32	-280 -125	4.9 575	0.6622	1.2968	1.3225
C ₂ H ₆	1	30	-200 70	0.3 563	1.2571	1.5940	1.5041
C ₃ H ₈	1	29	-100 190	2.9 524	0.6981	0.9972	0.9093
C ₄ H ₁₀	1	36	-150 290	0.1 477	0.6138	0.3472	0.2289
C ₃ H ₆	1	28	-160 180	0.3 562	1.3921	0.3504	0.5826
H ₂	1	14	-435 -403	1.0 152	1.0958	6.1871	6.2001
N ₂	1	12	-346 -240	1.8 407	1.0447	0.4027	0.6563
CO ₂	1	31	-70 80	75.1 969	1.2233	0.3674	0.3795
H ₂ O	1	29	33 500	0.1 680	4.0289	1.1007	4.2951
NH ₃	1	34	-108 260	0.9 1484	0.4441	1.1833	0.3821
CH ₃ OH	1	35	-144 -440	0.1 945	0.6951	2.0511	2.9201
Ar	1	24	-309 -196	10.0 603	1.0316	0.2391	0.3676
Ne		12	-416 -383	6.3 311	0.2731	0.5851	0.7971
Average AAPD					1.1123	1.2850	1.5800

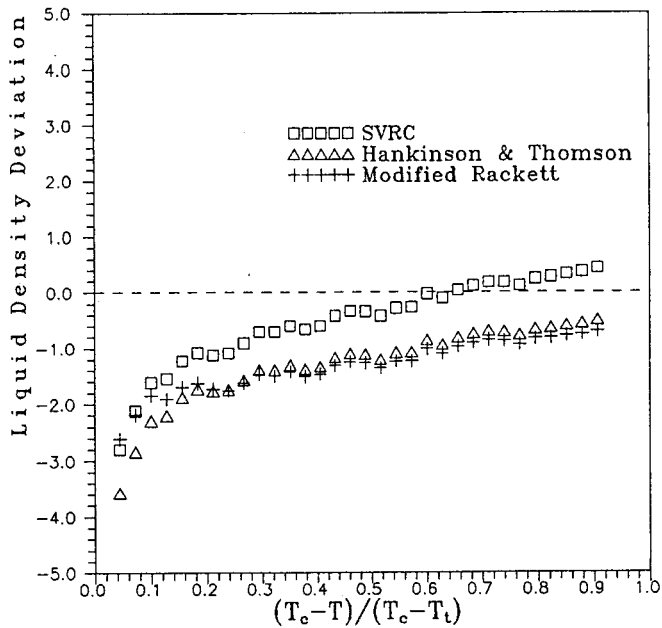


Fig. 1: Ability of three methods in predicting the liquid density of methane

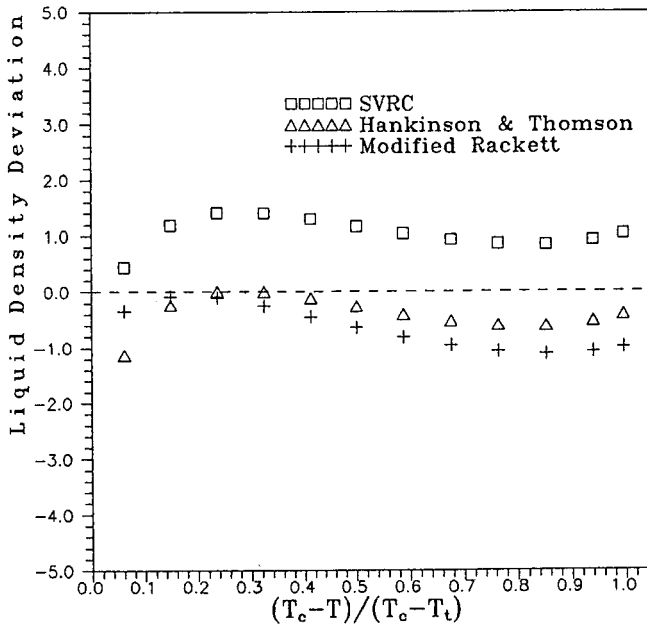


Fig. 2: Ability of three methods in predicting the liquid density of nitrogen

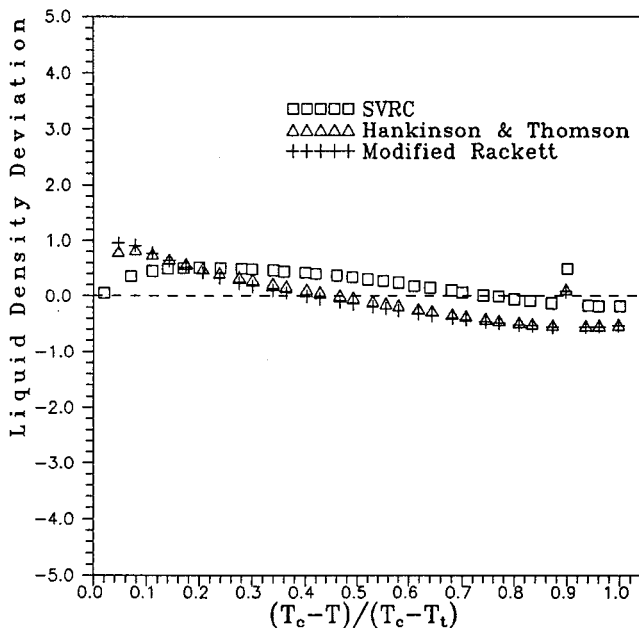


Fig. 3: Ability of three methods in predicting the liquid density of methane carbon dioxide

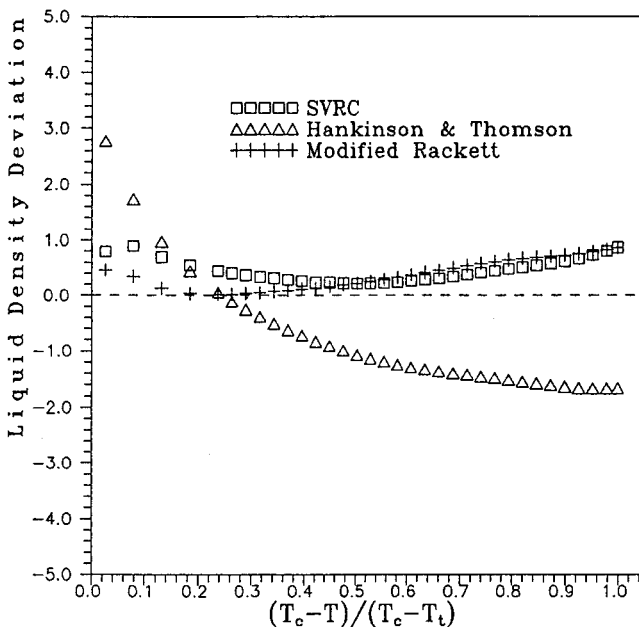


Fig. 4: Ability of three methods in predicting the liquid density of ammonia

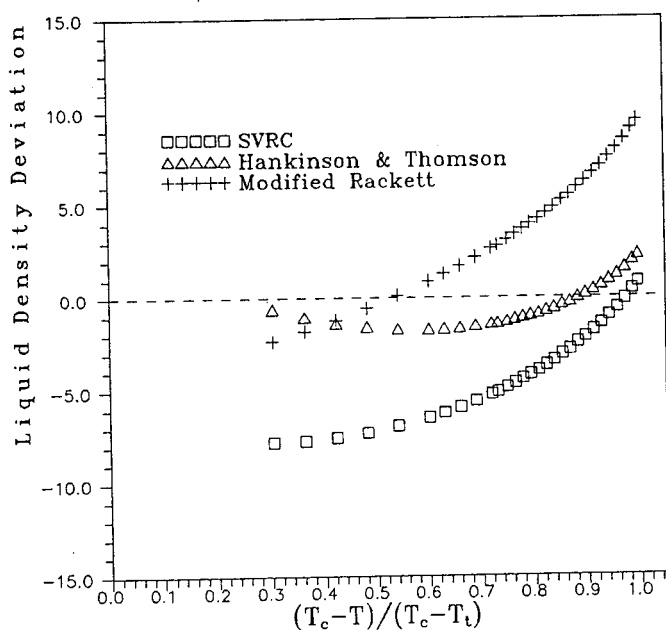


Fig. 5: Ability of three methods in predicting the liquid density of water

In order to test the capability of the proposed model, the liquid density of several multicomponent systems were predicted by the three methods and the predicted values were compared with literature data. A summary of the results of this comparison is presented in Table 5. As can be seen in Table 5, with the exception of carbon dioxide-butane and propane-butane system the Hankinson-Thomson and Spencer-Danner methods give better results compared to the method when the value of C in equation (19) is set to zero. The quality of SVRC method is improved considerably if C is calculated by eqs. (20-21). The overall analysis of Table 5 indicates that the accuracy of the proposed model is as good as other best available methods and can be used for industrial application.

Table 5: Ability of Three Methods for Prediction of Multicomponent Fluid DensityAverage Absolute % Deviation

Compound	Reference No.	No. of Points	Temp. Range, °F	Pres. Range, Psia	SVRC	Hankinson Thomson	Spencer Danner
C ₂ H ₆ C ₃ H ₈	9	22	50 60	2.76 4.14	2.715	2.159	1.690
CO ₂ C ₄ H ₈	24	3	160 160	10.00 10.0	3.420	8.759	13.210
C ₃ H ₈ C ₄ H ₁₀	9	15	50 140	0.60 1.72	0.243	0.504	0.400
C ₂ H ₆ C ₃ H ₈ C ₄ H ₁₀	9	14	60 139	0.69 2.41	0.797	0.512	0.335
N ₂ CH ₄	16	8	-262 -244	0.841 1.013	1.163	0.771	0.783
Ar CH ₄	30	4	-253 -226	0.88 1.57	2.098	1.148	1.085
Ar C ₂ H ₆	16	8	-253 -226	0.59 1.47	10.67	5.081	4.225
Ar CH ₄ C ₂ H ₆	30	8	-253 -226	0.65 1.12	2.0987	0.745	0.543
N ₂ CH ₄ C ₄ H ₁₀	16	4	-253 -226	0.65 1.12	3.248	0.479	0.199
CH ₄ C ₂ H ₆ C ₃ H ₈ C ₄ H ₁₀	17	5	-217 -253	0.118 0.43	6.650	0.094	0.331
N ₂ CH ₄ C ₂ H ₆ C ₃ H ₈ C ₄ H ₁₀	16	4	-235 -253	0.221 0.479	4.566	0.201	0.129
Average AAPD					3.33	1.85	2.08

CONCLUSIONS

A set of mixing rules has been proposed for the SVRC method for the prediction of multicomponent densities. The SVRC along with this set of mixing rules has been evaluated for several binary and multicomponent mixtures. The comparison of calculated results with experimental data indicates that the accuracy of the proposed method is as good as the best available methods such as the Hankinson-Thomson method (COSTALD) or Spencer and Danner modification of the Rackett equation. It should be emphasized that no curve fitting of parameters was required nor were any additional parameters were incorporated in the model. Only the pure component parameters were required in this model. Since the method is so general, it can be recommended for design calculations.

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