

Liquid Volumes from Generalized Cubic Equations of State: Take It with Care

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Résumé — **Volumes liquides à partir d'équations d'état cubiques généralisées : à prendre avec précaution** — Les volumes en phase liquide de plusieurs fluides importants sur le plan industriel ont été calculés en utilisant sept équations d'état cubiques généralisées. L'équation d'état de Redlich-Kwong et trois de ses formes dérivées, et l'équation d'état de Patel-Teja et deux de ses formes dérivées sont considérées dans cet article.

Les sept équations sont appliquées à 27 fluides, notamment des alcanes, alcènes, composés aromatiques, alcools, éthers, esters, oxydes organiques et composés inorganiques.

Cette étude analyse la précision de ces équations pour prédire les volumes en phase liquide, et donne un certain nombre de recommandations quant à l'équation à utiliser dans une situation donnée.

Mots-clés : volume liquide, masse volumique liquide, équation d'état cubique, corrélations généralisées.

Abstract — **Liquid Volumes from Generalized Cubic Equations of State: Take It with Care** — *Liquid phase volumes of several industrially important fluids have been calculated using seven generalized cubic equations of state. The Redlich-Kwong equation of state and three of its modifications and the Patel-Teja equation of state and two of its modifications are considered in the study.*

The seven equations are applied to 27 fluids including alkanes, alkenes, aromatics, alcohols, ethers, esters, organic oxides and inorganic compounds.

The study analyzes the accuracy of these equations for predicting liquid phase volumes and gives some recommendations on which equation to use for a given situation.

Keywords: liquid volume, liquid density, cubic equations of state, generalized correlations.

NOTATION

a_c, b, c, d	parameters in the general EOS
A, B, C, D	parameters in the EOS (Eq. (4))
% D	average percent deviation
% D	absolute average percent deviation
GC	Valderrama-Abu-Shark generalized correlation
m	parameter in the EOS for $\alpha(T_R)$
M	molecular weight
N	number of data points for each substance
P	pressure
P_c	critical pressure
p^{cal}	calculated pressure
p^{exp}	experimental pressure
PR	Peng-Robinson EOS
PT	Patel-Teja EOS
PTV	Patel-Teja-Valderrama EOS
PTVC	Patel-Teja-Valderrama-Cisternas EOS
R	ideal gas constant
RK	Redlich-Kwong EOS
SRK	Soave-Redlich-Kwong EOS
SVDW	Soave-van der Waals EOS
T	temperature
T_b	normal boiling temperature
T_c	critical temperature
T_R	reduced temperature (T/T_c)
T_{bR}	reduced normal boiling temperature (T_b/T_c)
V	volume
V_c	critical volume
V_L	liquid volume
Z	compressibility factor ($Z = PV/RT$)
Z_c	critical compressibility factor ($Z_c = PV_c/RT_c$)

Greek Letters

α	reduced temperature function in the general EOS
ω	acentric factor
$\Omega_a, \Omega_b, \Omega_c$	parameters in the a, b, c constants of the EOS

INTRODUCTION

Accurate predictions of liquid volumes are required in many design problems such as condensers and reboilers, the sizing of storage vessels, the calculation of tower heights, material and energy balances involving liquids, and vapor-liquid

equilibrium correlation. Although several good empirical and generalized correlations are available for the calculation of saturated liquid volumes (Rackett, 1970; Spencer and Danner, 1972; Shah and Yaws, 1976; Spencer and Adler, 1978; Danner and Daubert, 1983; Campbell and Thodos, 1985; Reid *et al.*, 1987; Valderrama and Abu-Shark, 1989), calculations of saturation properties through equations of state (EOS) present several advantages, specially in simulation of phase equilibrium problems. Liquid volumes also find important uses in nowadays popular modeling of high pressure processes in which the density of the liquid is of importance (Catchpole and von Kamp, 1997).

Common and industrially important EOS are the cubic equations derived from van der Waals EOS. Among the many cubic EOS nowadays available, those of Redlich and Kwong (1949), of Soave (1972), of Peng and Robinson (1976) and of Patel and Teja (1982), among others, have proven to combine the simplicity and accuracy required for the prediction and correlation of volumetric and thermodynamic properties of fluids (Wilson, 1966; Mihajlov *et al.*, 1981; Trebble and Bishnoi, 1986). Non-cubic equations such as the successful EOS proposed by Benedict, Webb and Rubin (1940) are also used in some applications and are included in modern computer simulation programs (Chemstations, 1999).

In some applications, liquid volumes predicted by cubic EOS are corrected using an empirical correction factor. This method gives origin to the *translated equation of state*, an approach first suggested by Martin (1979) and developed by Peneloux *et al.* (1982). The concept has been used, with relative success, by several authors to calculate volumetric, thermodynamic and phase equilibrium properties (Jhaveri and Youngren, 1984; Soave and Fredenslund, 1985; Jingshan and Xiaogong, 1986; Watson *et al.*, 1986). Although effective, most of the translated EOS require the calculation of the correction factor from experimental data. Therefore, the translated equations are not of the generalized type of interest in this article.

In this work, seven predictive-type cubic EOS are used for the calculation of saturated liquid volumes of several industrially important fluids, including alkanes, alkenes, aromatics, alcohols, ethers, esthers, organic oxides and inorganic compounds. Calculations are carried out for wide ranges of temperature, from the normal boiling point to near the critical temperature. Calculated values are compared to literature data and conclusions on the accuracy of one or another equations are drawn from the results.

1 PRESENTATION OF THE EQUATIONS

The seven generalized EOS analyzed in this work have been well described in the literature. They are: Redlich-Kwong (RK; Redlich and Kwong, 1949), Soave-Redlich-Kwong

(SRK; Soave, 1972), Soave-van der Waals (SVDW; Soave, 1984), Peng-Robinson (PR; Peng and Robinson, 1976), Patel-Teja (PT; Patel and Teja, 1982), Patel-Teja-VC (PTVC; Valderrama and Cisternas, 1986), and Patel-Teja-Valderrama (PTV; Valderrama, 1990). All these EOS can be expressed by the following general expression:

$$P = \frac{RT}{(V-b)} - \frac{a_c \alpha(T)}{V(V+d) + c(V-d)} \quad (1)$$

For the RK equation:

$$\begin{aligned} a_c &= R T_c^{2.5} / P_c \\ \alpha(T_R) &= [1/T^{0.5}] \end{aligned} \quad (2)$$

For all the other equations:

$$\begin{aligned} a_c &= \Omega_a (R^2 T_c^2 / P_c) \\ \alpha(T_R) &= [1 + m(1 - T_R^{0.5})]^2 \end{aligned} \quad (3)$$

The parameters c , d , Ω_a , and m assume different expressions for each EOS as described in Table 1. For computer calculations, the general expression (1) can be written in terms of the compressibility factor ($Z = PV/RT$), as follows:

$$\begin{aligned} Z^3 + (C + D - B - 1)Z^2 \\ + (A - BD - BC - C - CD - D)Z \\ + (BCD - AB + CD) = 0 \end{aligned} \quad (4)$$

In this equation:

$$A = aP/R^2T^2 \quad B = bP/RT \quad C = cP/RT \quad D = dP/RT \quad (5)$$

The mean deviations of the values predicted by the EOS were compared to those calculated by a generalized equation from the literature (Valderrama and Abu-Shark, 1989). The generalized correlation gives the liquid volume as a function of the critical properties (P_c , T_c and V_c) and of the normal boiling temperature (T_b):

$$V_L = (RT_c / P_c) [(0.3445P_c / RT_c)^{1.0135}]^{[1 + (1 - T_R)^{2/7}] / [1 + (1 - T_{bR})^{2/7}]} \quad (6)$$

In this equation, R is the ideal gas constant, T_R is the reduced temperature ($T_R = T/T_c$), and T_{bR} is the reduced temperature at the normal boiling point ($T_{bR} = T_b/T_c$). The values of the several properties involved in Equation (6) are shown in Table 2.

2 RESULTS

The seven EOS have been used to predict the saturated liquid volume of the 27 selected fluids. Predicted values were compared to data given by Schlunder (1983). The fluids considered in the study and the range of temperature and pressure for the data set are shown in Table 3.

Table 4 shows the average percent deviation and the absolute average percent deviation of the values predicted by

TABLE 1

Values of c , d , Ω_a , Ω_b and m in the general EOS defined in Eqs. (1)-(3)

EOS	d	c	Ω_a	Ω_b	Ω_c	m	Reference
RK	0	0	0.42478	0.0866	**	**	Redlich and Kwong, 1949
SVDW	0	0	0.42188	0.1250	**	$0.499 + 1.593\omega - 0.1956\omega^2 - 0.025\omega^3$	Soave, 1979
SRK	b	0	0.42679	0.0865	**	$0.480 + 1.574\omega - 0.176\omega^2$	Soave, 1972
PR	b	b	0.45724	0.0778	**	$0.3746 + 1.5423\omega - 0.2699\omega^2$	Peng and Robinson, 1976
PT	b	c	*	*	*	$0.3290 + 1.3098\omega - 0.2959\omega^2$	Patel and Teja, 1982
PTVC	b	c	$0.694 - 1.063Z_c + 0.683Z_c^2 - 0.210Z_c^3 + 0.00375Z_c^4$	$0.026 - 0.181Z_c + 0.061Z_c^2$	$0.578 - 1.904Z_c$	$-6.608 + 70.43Z_c - 159.0Z_c^2$	Valderrama and Cisternas, 1986
PTV	b	c	$0.6612 - 0.7616Z_c$	$0.0221 + 0.2087Z_c$	$0.5777 - 1.8718Z_c$	$0.4628 + 3.5823(\omega Z_c) + 8.1942(\omega Z_c)^2$	Valderrama, 1990

* For the PT equation, the parameters Ω_a , Ω_b and Ω_c assume specific values for each substance. Also, for the PT equation, the expression in terms of the acentric factor for the parameter m is valid for non-polar fluids only.

** Those parameters do not exist for the associated equations.

TABLE 2

Critical and basic properties for all fluids considered in this study.
The data was taken from Reid *et al.* (1987)

No.	Fluid	M	T_b (K)	T_c (K)	P_c (MPa)	Z_c	ω
1	Methane	16.04	111.7	190.6	4.60	0.288	0.008
2	Propane	44.10	231.1	369.8	4.24	0.281	0.152
3	<i>n</i> -Hexane	86.18	341.9	507.4	2.97	0.260	0.296
4	<i>n</i> -Decane	142.29	447.3	617.6	2.11	0.247	0.490
5	Benzene	78.11	353.3	562.1	4.89	0.271	0.212
6	Toluene	92.11	383.7	591.8	4.11	0.264	0.257
7	<i>m</i> -Xylene	106.12	412.3	617.0	3.55	0.260	0.331
8	Acetylene	26.04	189.2	308.3	6.14	0.271	0.184
9	Ethylene	28.05	169.4	282.4	5.04	0.276	0.085
10	Propylene	42.08	225.4	365.0	4.62	0.275	0.148
11	Methanol	32.04	337.8	512.6	8.10	0.224	0.559
12	1-Propanol	60.10	370.4	536.7	5.17	0.253	0.624
13	Ethanol	46.07	351.5	516.2	6.38	0.248	0.635
14	Ethyl Ether	74.12	307.7	566.7	3.64	0.262	0.281
15	Methyl Tert-Butyl Ether	88.10	331.2	503.4	3.41	0.273	0.266
16	Ethylene Oxide	44.05	283.5	469.0	7.19	0.258	0.200
17	Propylene Oxide	58.08	307.5	482.2	4.92	0.228	0.269
18	Methyl Acetate	74.08	330.1	506.8	4.69	0.254	0.324
19	Ethyl Acetate	88.11	350.3	523.2	3.83	0.252	0.363
20	Chloroform	119.38	334.3	536.4	5.47	0.293	0.216
21	Aniline	93.13	457.5	699.0	5.31	0.242	0.382
22	Acetic Acid	60.05	391.1	594.4	5.78	0.200	0.454
23	Acetone	58.08	329.4	508.1	4.70	0.232	0.309
24	Ammonia	17.03	239.7	405.6	11.28	0.242	0.250
25	Carbon Dioxide	44.01	194.7	304.2	7.38	0.274	0.225
26	Carbon Monoxide	28.01	81.70	132.9	3.50	0.295	0.049
27	Water	18.02	373.2	647.3	22.50	0.229	0.344

TABLE 3

Range of temperature and pressure of the literature data (Schlunder, 1983)
for the 27 fluids used in this study

No.	Fluid	Range of T (K)	Range of P (MPa)
1	Methane	111-190	0.1-4.5
2	Propane	231-367	0.1-4.0
3	<i>n</i> -Hexane	341-507	0.1-3.0
4	<i>n</i> -Decane	447-618	0.1-2.1
5	Benzene	353-563	0.1-4.9
6	Toluene	384-594	0.1-4.1
7	<i>m</i> -Xylene	412-617	0.1-3.5
8	Acetylene	192-309	0.1-6.2
9	Ethylene	169-281	0.1-5.0
10	Propylene	225-365	0.1-4.6
11	Methanol	338-512	0.1-7.8
12	1-Propanol	373-533	0.1-4.7
13	Ethanol	351-513	0.1-6.0
14	Ethyl Ether	308-463	0.1-3.5
15	Methyl Tert-Butyl Ether	331-503	0.1-3.4
16	Ethylene Oxide	284-469	0.1-7.2
17	Propylene Oxide	308-482	0.1-5.0
18	Methyl Acetate	331-507	0.1-4.7
19	Ethyl Acetate	350-523	0.1-3.8
20	Chloroform	335-536	0.1-5.5
21	Aniline	458-699	0.1-5.3
22	Acetic Acid	391-595	0.1-5.8
23	Acetone	329-508	0.1-4.7
24	Ammonia	240-400	0.1-9.9
25	Carbon Dioxide	217-304	0.1-7.4
26	Carbon Monoxide	82-133	0.1-3.5
27	Water	373-647	0.1-2.2

TABLE 4

Deviation in saturated liquid volume calculations using several EOS.

The values are percent deviation defined by Eq. (6).

GC corresponds to the deviations given by a generalized correlation given by Eq. (5)

No.	Fluid	RK	SVDW	SRK	PR	PT	PTVC	PTV	GC
1	Methane	7.6	-38.7	-8.6	-0.5	-12.0	-8.9	-0.9	3.6
2	Propane	-21.8	-40.1	11.5	2.6	-3.7	-6.6	-2.3	0.9
3	<i>n</i> -Hexane	-19.7	-46.6	-14.8	-15.9	-2.8	-0.1	2.4	1.2
4	<i>n</i> -Decane	5.2	-51.2	-19.7	-6.7	0.1	-27.8	3.4	0.9
5	Benzene	-13.8	-44.4	-14.2	-0.3	-2.6	-1.1	-4.9	0.9
6	Toluene	-9.1	-49.0	-12.3	-5.3	-4.4	-2.2	0.8	0.9
7	<i>m</i> -Xylene	-22.4	-48.9	-17.3	-7.6	-2.5	-1.2	1.7	1.9
8	Acetylene	-10.5	-40.2	-8.9	-0.8	-0.7	5.1	3.9	3.6
9	Ethylene	-8.8	-40.0	-7.9	2.5	-3.4	2.6	-8.5	3.7
10	Propylene	-13.6	-14.7	-8.9	-3.6	-5.7	3.1	-1.5	2.8
11	Methanol	-57.8	-81.5	-41.0	-25.5	-12.1	2.1	-7.4	4.3
12	1-Propanol	-47.2	-69.9	-36.8	16.4	-3.1	-37.8	-6.4	1.0
13	Ethanol	-23.8	-63.7	-29.9	-16.1	-5.5	-15.5	-7.2	3.6
14	Ethyl Ether	-24.0	-50.9	-18.8	-4.9	2.5	-1.0	-1.3	1.8
15	Methyl Tert-Butyl Ether	-17.2	-45.6	-12.6	-3.3	2.1	2.5	4.6	2.1
16	Ethylene Oxide	-20.4	-50.9	-18.7	-8.0	11.3	-2.1	-0.5	3.9
17	Propylene Oxide	-32.1	-64.1	-13.3	-29.1	-16.0	0.7	1.8	4.9
18	Methyl Acetate	-23.9	-53.9	-28.7	-18.1	-5.8	-1.9	1.0	2.8
19	Ethyl Acetate	-24.7	-54.2	-19.3	-9.5	9.5	-1.7	0.9	0.6
20	Chloroform	-10.0	-35.0	-6.4	3.0	2.2	-8.1	-6.3	4.9
21	Aniline	-21.3	-45.8	-16.8	-7.1	-1.4	1.1	5.7	4.2
22	Acetic Acid	-35.7	-62.2	-17.2	-16.6	-9.8	8.2	11.0	2.7
23	Acetone	-30.0	-63.2	-26.3	-15.7	-12.5	0.4	2.3	0.9
24	Ammonia	-40.3	-67.4	-31.0	-16.1	-17.7	-3.3	-13.9	4.1
25	Carbon Dioxide	-15.9	-41.1	8.9	-1.0	-2.5	-3.2	-0.2	2.5
26	Carbon Monoxide	-2.8	-31.3	-3.3	6.7	1.0	-3.7	-3.7	4.5
27	Water	-39.6	-76.5	-33.0	-22.5	3.9	-4.6	-2.2	5.0
	% D	-22.2	-52.3	-16.5	-7.5	3.4	3.9	1.0	2.7
	% D	22.1	52.3	18.0	8.6	9.8	5.8	3.9	2.7

TABLE 5

Deviation in saturated liquid volume calculations near the critical point ($T_R > 0.9$).
The deviations are defined by Eq. (7)

No.	Fluid	RK	SVDW	SRK	PR	PT	PTVC	PTV
1	Methane	-20.2	-41.4	-20.1	-14.0	-32.7	-29.5	-11.1
2	Propane	-44.6	-46.7	-22.4	-5.7	-14.6	-15.8	-13.0
3	<i>n</i> -Hexane	-20.5	-42.6	-10.1	-27.5	-7.0	-5.3	1.5
4	<i>n</i> -Decane	9.6	-55.0	-24.7	-6.9	-0.8	-21.8	0.3
5	Benzene	-17.7	-40.0	-24.2	-3.7	-8.0	-7.1	-1.2
6	Toluene	0.7	-44.4	-15.3	-11.5	-9.8	-8	-1.4
7	<i>m</i> -Xylene	-25.0	-46.3	-21.8	-13.9	-9.3	-8.8	-1.6
8	Acetylene	-14.8	-35.5	-14.3	-5.4	-6.7	3.4	1.2
9	Ethylene	-19.3	-42.9	-17.8	-5.4	-12.9	-6.5	-6.6
10	Propylene	-27.0	12.8	-26.9	-14.2	-20.1	-18	-13.7
11	Methanol	-74.5	-86.5	-48.2	-32.7	-23.7	-15.7	-12.7
12	1-Propanol	-76.5	-93.3	-66.2	64.6	-16.5	-91.5	-17.9
13	Ethanol	-82.9	-75.3	-46.1	-30.4	-18.8	-27.3	-19.5
14	Ethyl Ether	-31.4	-50.7	-24.7	-11.3	-12.2	-8.9	-8.8
15	Methyl Tert-Butyl Ether	-19.8	-42.5	-17.2	-10.7	-5.3	-5.3	0.9
16	Ethylene Oxide	-23.1	-48.4	-22.5	-13.8	38.1	-7.4	-1.3
17	Propylene Oxide	-37.1	-63.0	-35.0	-34.7	-23.3	-8.2	-1.2
18	Methyl Acetate	-28.0	-50.5	-28.6	-18.6	-12.3	-9.2	-0.6
19	Ethyl Acetate	-29.1	-50.4	-25.2	-15.7	-24.5	-9.1	-1.5
20	Chloroform	-27.1	-32.0	-9.1	-1.7	-0.8	-10.4	-15.2
21	Aniline	-26.5	-47.7	-26.8	-17.7	-9.4	-13.0	2.3
22	Acetic Acid	-60.5	-87.3	-30.0	-43.9	-34.8	-15.5	-7.7
23	Acetone	-33.5	-58.6	-31.0	-22.7	-10.4	-6.7	0.5
24	Ammonia	-48.9	-69.1	-38.4	-23.3	-25.5	-8.6	-31.4
25	Carbon Dioxide	-17.9	-8.1	-38.2	36.8	-7.1	-7.2	-2.1
26	Carbon Monoxide	-5.5	-28.3	-6.5	0.9	-1.3	-6.5	-13.5
27	Water	-41.4	-68.1	-38.1	-28.1	32.0	-11.5	-4.2
	% D	-31.2	-50.7	-26.1	-16.3	-12.7	-13.5	-6.6
	% D	32.0	51.7	26.1	19.1	17.8	13.8	6.9

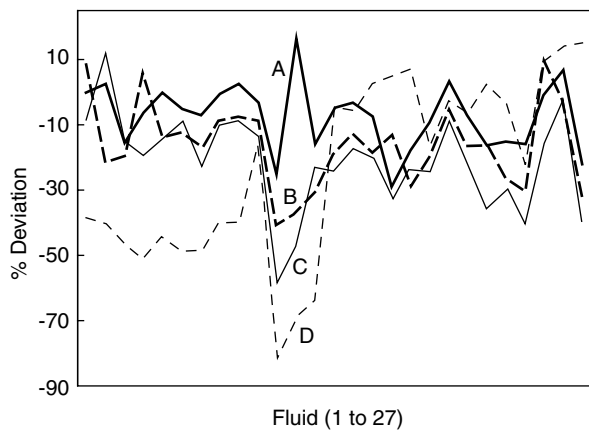


Figure 1

Mean deviation in saturated liquid volumes predicted by four two-parameter EOS: PR (A), SRK (B), RK (C), and SVDW (D).

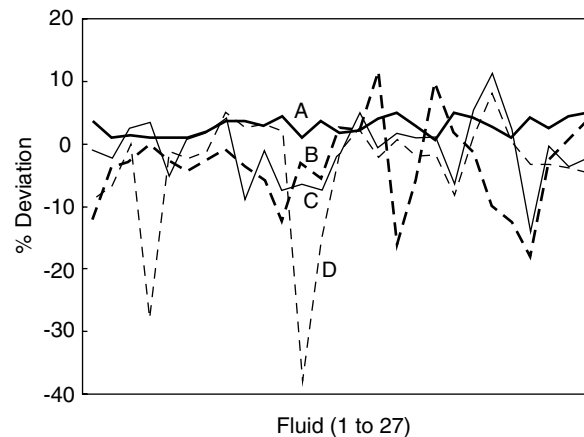


Figure 2

Mean deviation in saturated liquid volumes predicted by a generalized correlation (A) and three three-parameter EOS: PT (B), PTV (C), and PTVC (D).

all the EOS used in this work. The average percent deviation (% D), and the absolute average deviation (% |D|), for a set of N values, are defined as follows:

$$\begin{aligned} \% D &= (100/N) \sum [(P_{\text{calc}} - P_{\text{exp}})/P_{\text{exp}}]_i \\ \% |D| &= (100/N) \sum |[P_{\text{calc}} - P_{\text{exp}}]/P_{\text{exp}}]_i \end{aligned} \quad (7)$$

Table 5 shows the deviations in predicting the volumes near the critical point, a region where most EOS give higher deviations. Figures 1 and 2 summarize all the results for the 27 fluids considered in this work.

3 DISCUSSION

The old and popular RK equation has no adjustable parameters and gives poor results. The SVDW equation, a generalization of the van der Waals equation proposed by Soave (1984), gives the worst results. This is understandable because of the known inaccuracies of the van der Waals equation, despite its tremendous importance in the development of EOS. The popular SRK and PR equations, of extensive application in fluid phase equilibrium calculations, do not satisfy the minimum accuracy required for some applications. As seen in Table 4, deviations go to 36% for SRK and to 29% for PR for some fluids.

The three-parameter equations (PT, PTVC, and PTV) give the best results. The PT equation uses the acentric factor as generalizing parameter, the PTVC uses the critical compressibility factor, and the PTV uses both the critical compressibility factor and the acentric factor. The convenience of using these two parameters has been explained in the literature (Valderrama and Cisternas, 1987), and the reasons given by the authors seem to be justified.

The PTV EOS gives the best results of the seven equations evaluated in this study. However, even the accuracy of this equation is lower than good generalized correlations available in the literature, deviations higher than 10% are found for some fluids. As shown in Table 4, good generalized correlations found in the literature give deviations below 5% for all types of fluids (Valderrama and Abu-Shark, 1989).

All the EOS give higher deviations near the critical point, specially the two-parameter equations. This fact is expected of any cubic equation which predicts a unique critical compressibility factor (Z_c), to fulfill the property of continuity of the critical isotherm at the critical point. That is, when the mathematical condition $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ is applied at the critical point. The SVDW gives $Z_c = 0.375$, the RK and the SRK give $Z_c = 0.333$, and the PR equation gives $Z_c = 0.307$. Table 2 shows the actual values of Z_c , which vary from 0.2 to 0.3.

CONCLUSIONS AND RECOMMENDATIONS

The cubic equations of state used have shown to predict liquid volumes with varying degrees of accuracy, accuracy which increases as the complexity of the equation increases. If accurate values of liquid densities are needed, equations of state are not the best way to go. Based on this study and information from the literature, the following recommendations can be given for the estimation of liquid volumes:

- do not use old equations of state, although they appear to be popular and still in use. They are not good for liquid density estimations;
- if equations of state are to be used, prefer a three-parameter equation such as PT or PTV;

- always prefer generalized semi-empirical correlations such as those proposed in the literature (Valderrama and Abu-Shark, 1989);
- for some heavy and complex fluids (such as decane, propanol, ammonia or chloroform), even the use of the best equation of state or a good generalized correlation does not guarantee high accuracy;
- a general statement about the accuracy of one or another equation or correlation cannot be done. Thus, liquid density estimation, especially through equations of state, *should be taken with care.*

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