Generalized Method for Prediction of Saturated Liquid Volumes Using Van der Waals Volumes

Jinsong Wang and V. N. Kabadi
Chemical Engineering Dept., North Carolina A&T State University, Greensboro, NC 27411

Rackett (1970) developed an equation to estimate saturated liquid volumes which was later modified by Spencer and Danner (1972). The modified Rackett equation represents a simple and very widely used method to predict saturated liquid volumes. In addition to being fairly accurate, this equation is mathematically continuous and renders expressions for first and second derivatives of saturated liquid volume needed for computations of thermodynamic properties such as enthalpies and heat capacities from certain liquid state equations of state that use saturated liquid volume like the Tait equation (Thomson et al., 1982). There are other methods available in the literature to calculate saturated liquid volumes. Prominent among them is COSTALD (Hankinson and Thomson, 1979). The modified Rackett equation is almost as accurate as COSTALD and somewhat simpler to use. The objective of this work is to further enhance the applicability of the modified Rackett equation by developing a correlation for the parameter Z_{RA} with Van der Waals volume of the molecule and with a volume parameter calculated by summing the UNIFAC volume parameters (R) of individual groups making up the molecule. The modified Rackett equation of Spencer and Danner is written as

$$V_s = RT_c Z_{RA}^{[1+(1-T_r)^{2/7}]}/P_c \tag{1}$$

Z_{RA} is a parameter which has a unique value for each compound. Z_{RA}s for a number of compounds have been tabulated by Spencer and Danner. Yamada and Gunn (1973) proposed a method to estimate Z_{RA}

$$Z_{RA} = 0.29056 - 0.08775\,\omega \tag{2}$$

Although useful, Eq. 2 results in considerable errors in predicted saturated volumes. It is the objective of this work to develop an accurate predictive correlation for Z_{RA} based on molecular parameters. Van der Waals volume (V_w) of the molecule with the group contributions proposed by Bondi (1968) is used as the correlating parameter. Alternatively, if successful, the UNIFAC group volume parameter R, which is closely related to Bondi's group contributions to Van der Waals volume would provide a good correlating parameter for Z_{RA}. The method so conceived will be consistent with the recent predictive vapor pressure correlation of Wang and Kabadi (1995) in which the molecular shape parameter is calculated from the UNIFAC volume and surface area parameters R and Q.

Correlation of Z_{RA} with V_w

The data used in this work included 124 compounds classified into various families. The experimentally regressed Z_{RA}s for most of these compounds (88 compounds) were obtained from Reid et al. (1987). Z_{RA}s of other 36 compounds were regressed using liquid density data obtained from the API Monograph Series (1978–1985), and Kudchadker et al. (1978), and Kudchadker and Kudchadker (1978). These compounds included high molecular weight aromatics and heterocycles, phenols, and some amines. V_w were computed using the group contribution tabulations of Bondi (1968). A polynomial fit for Z_{RA} with V_w gave the following expression

$$Z_{RA} = 0.16870 + 0.53719\,Z_w + 28.38709\,Z_w^2 \tag{3}$$

where

$$Z_w = (P_c V_w)/(RT_C) \tag{4}$$

Equation 3 was obtained using data for all the compounds except alcohols and phenols, and represents an excellent correlation as seen from Figure 1 where Z_{RA}s calculated from Eq. 3 and experimental values are plotted. Bondi's van der Waals volume tabulations include a compound specific correction factor for OH group because of hydrogen bonding. Using the experimental Z_{RA}s and Eq. 3, an average contribution for the OH group was regressed as 4.55 cm^3/mol which is a correction of -3.49 cm^3/mol to the value of 8.04 cm^3/mol tabulated by Bondi. Table 1 shows a comparison between Eq. 2 and Eq. 3 for estimation of Z_{RA}. The compounds are divided into various homologous series and average percent errors corresponding to each series are tabulated. An average

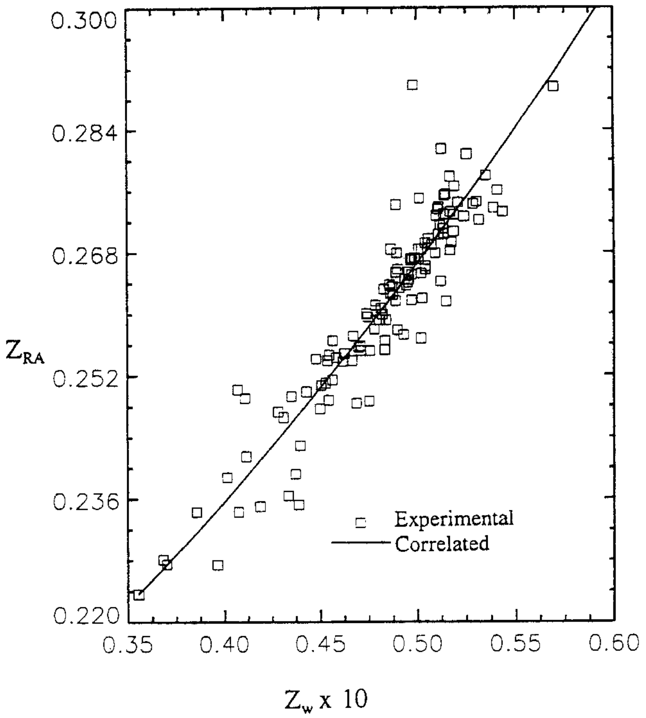

Figure 1. For 124 organic liquids, Z_{RA}s regressed from experimental data and those from correlation in Eq. 3 are plotted against the compressibility factor Z_w defined by Eq. 4.

absolute error of 1.32% was obtained when Z_{RA} computed from Eq. 3 were compared with experimentally regressed Z_{RA} for all 124 compounds. The same comparison using Eq. 2 gave an error of 2.64%.

Table 1. Predicted Z_{RA}s Values Regressed from Experimental Data

Homologous Ser.	No. of Points	% Errors (Absolute) Eq. 2	Eqs. 3,4	Eqs. 6,7
Paraffins	34	1.692	0.756	1.327
Halogenated Paraffins	6	4.815	1.986	2.404
Cycloparaffins	4	0.316	0.167	0.412
Olefins	13	1.549	1.751	2.585
Aromatics	26	2.781	0.899	1.485
Aromatic Derivatives	4	1.474	0.327	2.518
Heterocycles	8	2.021	1.182	1.061
Alcohols	8	4.834	2.546	3.272
Phenols	9	6.954	2.078	3.978
Amines	7	2.673	3.383	2.539
Ethers	3	0.717	1.814	1.027
Sulfides	2	1.259	0.267	1.957
Total	124	2.636	1.322	1.925

*All errors reported in this work are calculated as: (|exp − calc|/exp) * 100; exp = experimental value; calc = calculated value.

Correlation for Z_{RA} Using UNIFAC R

With the success of Eq. 3, a further attempt was made to replace the group Van der Waals volumes by the UNIFAC group volume parameters R (Fredenslund et al., 1975). Although the latter were obtained from Bondi's tabulations and an arbitrary normalization factor, the UNIFAC procedure to estimate molecular volumes includes some simplifications of the more rigorous approach of Bondi. Bondi's procedures involve a number of exceptions and corrections that depend on the molecular types; UNIFAC Rs, on the other hand, were averaged to a single constant per group and do not include any molecular factors. Some examples of these differences are:

(1) Different cycloparaffins, i.e., cyclopropane, cyclopentane, and cyclohexane are listed with their own characteristic Van der Waals volumes by Bondi. In the UNIFAC procedure, methyl groups in cycloparaffins are considered equivalent to paraffinic methyl groups and molecular volume parameter for a cycloparaffin is calculated by simply summing the Rs over all the methyl groups.

(2) In fused multiring aromatic compounds, the condensed carbons between aromatic rings are assigned different contributions from other aromatic carbons in Bondi's tabulations. No such distinction is made in the UNIFAC procedure.

(3) Bondi's procedure involves a number of correction factors such as correction for OH groups in alcohols, correction for cis- and trans-isomers, correction for amine group in various molecular types, and so on. The UNIFAC procedure assigns a single constant value R per group and includes no exceptions and corrections.

UNIFAC group contribution correlation is widely used in vapor-liquid equilibrium calculations. Although, the group parameters R and Q are based on Bondi's tabulations of Van der Waals volumes and surface areas, they are more readily available (Reid et al., 1987) and easier to use. To obtain a correlation for Z_{RA} using UNIFAC Rs, first the molecular volume parameter was defined as

$$V_U = \sum R_k \tag{5}$$

where R_k is the UNIFAC R of group k and the summation is over all the groups in the molecule.

The correlation for Z_{RA} was then obtained as

$$Z_{RA} = 0.13041 + 40.4063\, Z_U \tag{6}$$

where

$$Z_U = P_c V_U / (R T_c) \tag{7}$$

Equation 6 again represented excellent fit as seen from Figure 2 where experimental and calculated Z_{RA}s are plotted against Z_U. As with the previous correlation, the R value of OH group was corrected to 0.528 which is a correction of −0.472 from the original UNIFAC value of 1.00. The accuracy of Eq. 6 to estimate Z_{RA} is compared with Eq. 2 and Eq. 3 in Table 1. For the same 124 compounds, Eq. 6 gave an overall percent error of 1.93 compared to 2.64 for Eq. 2 and 1.32 for Eq. 3. Thus, Eq. 6, although better than Yamada's method is not as good as the method using Van der Waals volumes of Bondi.

Comparison with Experimental Density Data

Saturated liquid density data were compiled for 40 mostly ring compounds with a total of 787 data points. Most of these

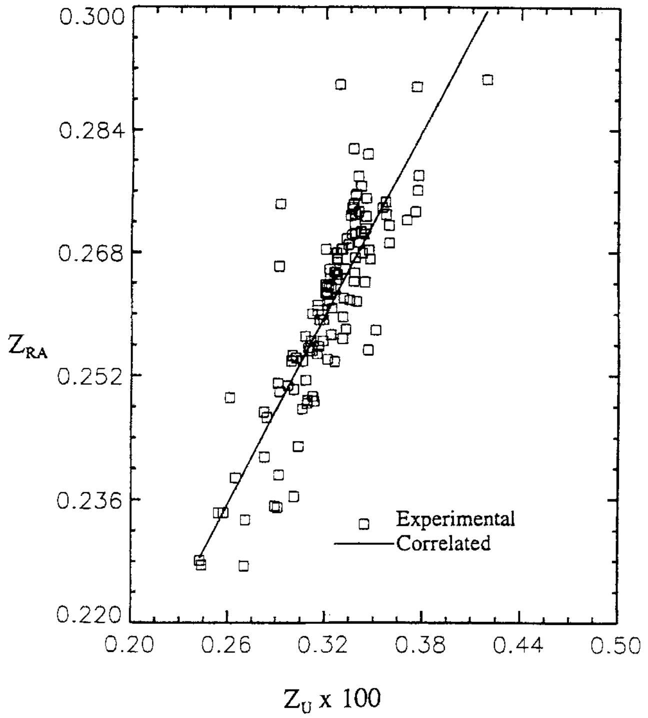

Figure 2. For the same 124 compounds, Z_{RA}s regressed from experimental data and those from correlation in Eq. 6 are plotted against the compressibility factor Z_U defined by Eq. 7.

data were obtained from the API Monograph Series (1978-1985). Data on benzene were from Chao (1978), toluene from Goodwin (1989), and phenol, cresols, and xylenols data were obtained from Kudchadker et al. (1977, 1978), and Kudchadker and Kudchadker (1978). Saturated liquid volumes were computed using modified Rackett equation with regressed Z_{RA}, Z_{RA} from Eqs. 3 and 4, Z_{RA} from Eqs. 6 and 7, and Z_{RA} from Eq. 2. Results are shown in Table 2. The compounds are again divided into homologous series and average errors in estimated volumes are listed for each family of compounds. As expected, usage of regressed Z_{RA}s results in the minimum overall error of 0.87%. However, of the three estimation methods for Z_{RA}, the two presented here perform appreciably better than the method of Yamada. The method based on Van der Waals volumes (Eqs. 3 and 4) gave an overall error in density of 3.15%. Using the UNIFAC Rs instead of Bondi's list of contributions (Eqs. 6 and 7) resulted in an error of 3.66%, whereas Yamada's correlation performed worst with an average error of 5.81%. This exercise showed that deviations of estimated Z_{RA}s from regressed values also result in proportional deviations in predicted liquid volumes. Although the density data set used here is not representative of various families of organic compounds, such an exercise could be carried out with a more extensive density data set, and undoubtedly the results will be quite similar to the results of Table 2.

Yamada's correlation, moreover, has a limitation in that it uses acentric factor as a correlating parameter. For high molecular weight compounds, when accurate vapor pressure data are not available, acentric factors obtained from different sources could easily vary by as much as 10%. Also, in predicting acentric factors by correlations, average errors of around 10% are quite common. A pair of correlations are presented here that eliminate this limitation and provide methods that allow estimation of Z_{RA} from simply the group composition of the molecule; and furthermore, these correlations are more accurate for density estimation than currently available predictive correlations.

Acknowledgment

Support for this work from US DOE, Pittsburgh Energy Technology Center, through grant no. DE-FG22-91PC91300 is gratefully acknowledged.

Notation

P_c = critical pressure
R = gas constant
T_c = critical temperature
T_r = reduced temperature
V_s = saturated liquid volume, cm^3/mol
V_U = volume parameter defined by Eq. 5
V_w = Van der Waals volume, cm^3/mol
Z_{RA} = modified Rackett parameter
ω = acentric factor

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Table 2. Predicted Molar Volumes vs. Experimental Data

Homologous Ser.	No. of Compounds	No. of Points	Regressed Z_{RA}	% Errors (Absolute) Z_{RA} (Eq. 2)	Z_{RA} (Eqs. 3,4)	Z_{RA} (Eqs. 6,7)
Phenols	9	124	0.536	10.97	3.079	5.906
Amines	4	120	1.393	6.085	7.413	6.412
Heterocycles	5	96	3.210	2.904	3.875	2.926
Alkylbenzenes	6	141	0.196	1.698	1.055	1.111
Two-ring compounds	11	243	0.383	5.458	2.172	3.101
Three-ring compounds	5	63	0.323	10.14	2.504	3.027
Total	40	787	0.867	5.811	3.148	3.664

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Manuscript received May 30, 1995.