Prediction of the Critical Volume from the van der Waals Volume

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The critical volume, V_c, is one of the important parameters used for estimating thermodynamic properties of compounds by a corresponding state-type approach. Unfortunately since experimental data are not always available, a predictive method must be employed. Kudchadker et al. (1968) thoroughly review conventional predictive methods, most of which use different pure-component data as input parameters. Reid et al., on the other hand, offer an up-to-date recommendation of the newer group contribution methods, where only information necessary is on the chemical structure of the compound.

In this work, we propose the following simple method for predicting the critical volume from the van der Waals volumes:

$$V_c = A \times V_{vdw} = 5.36 \times V_{vdw} \tag{1}$$

where A is a universal constant, which as shown below, can be used to predict the critical volume for a wide variety of substances: alkanes, alkenes, cycloalkanes, alcohols, carboxylic acids, amines, aromats and others. We use van der Waals volumes given in the DIPPR data compilation (Daubert and Danner, 1989), which again usually are based on the work by Bondi (1968).

The new predictive method has been compared with two other methods:

1. The Lydersen method (1955), which had been modified by Joback (1984) and reviewed by Reid et al. (1987), estimates V_c by means of the following equation:

$$V_c = A + \Sigma\Delta_V \tag{2}$$

where Δ_V is the *group* contribution to the critical volume. For this method, 40 different group increments have been reported. This method was one of the two methods recommended by Reid et al. (1987).

2. The Fedors method (1979) estimates V_c also by Eq. 1, but now Δ_V denotes *atomic* and structural contributions. For this method, only 18 different increments were necessary. This method has been used in the DIPPR data compilation by Daubert and Danner (1989) to predict critical volumes for nonhydrocarbons.

To compare the applicability of these various estimation procedures, we used experimental critical data for organic compounds with experimental errors less than 5% as evaluated in the DIPPR data compilation by Daubert and Danner (1989). To obtain a fair comparison, only data for those substances to which all estimation procedures may be applied were used. This gave a total of 212 different compounds. The result is compared in Table 1.

Not included in the above-mentioned set of data was the group of phenols, where the average error on using the proposed method was between 20-25%. The Fedors method also results in rather big errors (between 15-20%), whereas the Lydersen/Joback method has errors smaller than 5%, but uses an incremental value for the phenol group which appears unrealistic.

The three methods all give an average percent error between 3 and 4%. This is well below the experimental error of 5%, shown by the majority of the compounds in the DIPPR compilation. Therefore, the three methods can be considered equally

Table 1. Average Mean Deviation between Experimental and Predicted Critical Volumes by Three Methods

Average Mean Dev. %*	No. of Compounds	Fedors	Lydersen/ Joback	This Work
Alkanes	48	2.7	2.3	3.0
Cycloalkanes	22	6.3	4.0	3.8
Alkenes	18	2.5	1.5	2.0
Alkynes	2	1.8	2.0	9.2
Aromats	24	6.4	3.0	3.5
Ketones	5	3.0	2.8	3.1
Alcohols	16	1.4	2.3	3.0
Carboxylic Acids	3	2.6	2.2	2.4
Esters	6	2.7	0.8	1.1
Ethers and Epoxides	12	4.2	4.6	4.8
Halogenides	41	3.0	4.3	3.4
Amines	10	9.4	4.1	4.7
Sulfides	5	2.2	1.0	3.6
Others	16	1.4	2.3	3.0
All Compounds	212	3.8	3.0	3.3

*Average mean deviation is calculated from:

$$\frac{1}{n}\sum\frac{|V_c^{\text{exp}} - V_c^{\text{pred}}|}{V_c^{\text{exp}}}\,100\%$$

well suited in their predictive power.

All of the three methods depend on empirically optimized parameters. In the Lydersen/Joback method there are 40 group volumes, while the Fedors method incorporates 18 structural and atomic contributions. The method proposed in this work has only *one* universal parameter. In the two first-mentioned methods, the empirical parameters are all that are needed to predict the critical volumes whereas the proposed method requires the van der Waals volumes, available from group contributions (Bondi, 1968) for a large number of chemical families. We, therefore, believe that the proposed method is a flexible alternative to other methods.

Literature Cited

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