$$\frac{\Gamma}{\Gamma_\infty} = \frac{\displaystyle\int_0^\eta \exp\left[-\int_0^s \frac{\rho {r_o}^2}{4\mu_s t}\left(\int_0^t \frac{\partial v_z}{\partial z}\,dt'\right)dt\right]ds}{\displaystyle\int_0^\infty \exp\left[-\int_0^s \frac{\rho {r_o}^2}{4\mu_s t}\left(\int_0^t \frac{\partial v_z}{\partial z}\,dt'\right)dt\right]ds} \tag{13}$$

where s, t, and t' are dummy integration variables. [Note that $\partial v_z/\partial z = \partial v_z/\partial z(t')$.] From estimated values for Γ_∞, from the circulation at the tank wall, and from experimental measurements of $\partial v_z/\partial z$ vs. η, Equation (13) was found to closely approximate the measured tangential velocity profiles. Inspection of Equation (13) also indicates directly that reduction of the axial velocity gradient in the core region implies a corresponding reduction in tangential velocity, indicative of vortex inhibition. The precise explanation for the very small axial gradient in the polymer solution is still obscure; it may be related to the large values of μ_e for this system. This is currently under study.

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NOTATION

g = gravitational acceleration
p = isotropic pressure
r = radial coordinate
r_o = radius of solid core, for which v_θ is linear in r
v_i = i^{th} component of velocity vector
z = axial coordinate (points toward tank bottom)
z_s = axial coordinate of free surface (a negative quantity)

Greek Letters

Γ = circulation (rv_θ)
Γ_∞ = circulation at $r = \infty$ (tank wall)
η = dimensionless radial coordinate $(r/r_o)^2$
μ_e = extensional viscosity defined by Equation (7)
μ_s = shear viscosity defined by Equation (10)
π_{ij} = i,j^{th} component of total stress tensor
ρ = density

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An Empirical Method for Evaluating Critical Molar Volumes

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The experimental determination of critical molar volumes has proven to be an unusually difficult problem. As a consequence, experimental values of V_c are known for only a relatively few compounds and with an error which is not always negligible. Furthermore, the critical properties of some compounds must be estimated because their instability at the critical point prevents the experimental determination. On the other hand, even if a great amount of effort has been devoted to the development of empirical methods for estimating this parameter, it is generally admitted that correlation methods for V_c are still less satisfactory than correlations for other critical properties (Reid and Sherwood, 1966).

Lacking experimental data, and with the unreliability of the prevision methods, we have, until now, been prevented from using V_c for estimating thermodynamic and volumetric properties of fluids by the theorem of corresponding states (Pitzer et al., 1955).

The purpose of this work was to examine the best empirical methods for critical volumes and to develop a more precise correlation based on additive group contributions to estimate V_c from the knowledge of the chemical structure and molecular weight.

METHOD FOR V_c EVALUATION

Empirical correlations for evaluating critical volumes have been reviewed by Reid and Sherwood (1966)), Kudchadker et al. (1968*a*), and Spencer and Daubert (1973). Only recent developments or methods of wide applica-

Table 1. Group Contributions to the Critical Molecular Volumes

Functional group	Δv_i
Nonring increment:	
—CH$_3$, —CH$_2$—, —CH—, —C— } in linear chain	3.360
—CH$_3$, —CH$_2$—, —CH—, —C— } in side chain	2.888
=CH$_2$	2.940
=CH	2.940
=C—	2.940
=C=	2.908
≡CH	2.648
≡C—	2.648
Ring increment:	
—CH$_2$—, —CH, —C—	2.813
=CH, =C—, =C=	2.538
Halogen increment:	
F	0.770
Cl	1.237
Br	0.899
I	0.702
Oxygen increment:	
—OH (alcohols)	0.704
—OH (phenols)	1.553
—O— (nonring)	1.075
—O— (ring)	0.790
—O— (epoxid)	−0.252
—C=O (nonring)	1.765
—C=O (ring)	(1.500)
HC=O (aldehyde)	(2.333)
—COOH (acid)	1.652
—COO— (ester)	1.607
Nitrogen increments:	
—NH$_2$	2.184
—NH (nonring)	2.333
—NH (ring)	1.736
—N— (nonring)	1.793
—N— (ring)	1.883
—CN	2.784
—NO$_2$	1.559
Sulfur increments	
—SH	1.537
—S— (nonring)	0.591
—S— (ring)	0.911

bility are considered here. For this reason, methods based on unusual or not easily available parameters such as parachor have been discarded. Literature methods are represented by two types of correlations, the first being purely empirical, that is, based on molecular structure alone, while the second has some thermodynamical basis and usually requires as input parameters other critical parameters such as P_c and T_c.

To the first type belongs the Lydersen correlation, which is one of the earlier and still valid methods for V_c:

$$V_c = 40 + \sum_i \Delta v_i \tag{1}$$

The more recent modification of this method is reported by Fedors (1973), which simply states

$$V_c = \sum_i \Delta v_i \tag{2}$$

The main difference with respect to Equation (1) is represented by the rules for group contribution values.

Among the correlations of the second type, the one suggested by Riedel (1954) is

$$V_c = \frac{RT_c}{P_c}\,[3.72 + 0.26(\alpha - 7.0)]^{-1} \tag{3}$$

The Riedel factor α can be calculated by means of a simple relationship proposed by Miller (1963):

$$\alpha = 0.9076\left[1 + \frac{(T_b/T_R)\ln P_c}{1 - (T_b/T_R)}\right] \tag{4}$$

More recently, Viswanath (1968) has proposed the ideal critical volume $V_{ci} = RT_c/P_c$ as a correlating parameter for V_c following the relationship

$$V_c = 10.0 + 0.259\,V_{ci} \tag{5}$$

A first comparison between correlations of the two types for different classes of compounds, chosen among those reported by Kudchadker et al. (1968*a*), clearly shows the superiority of the relationship based on the group contributions method with respect to the other methods (see, for example, Table 2). This fact is not surprising, since the critical molar volume appears to be a typical additive property. The theoretical framework of the additivity principle is discussed in detail by Rouvray (1973). Therefore, in this work the principle of additivity was adopted as the most useful tool for developing a correlation for V_c. The new relationship proposed is

$$V_c = 33 + \sum_i (\Delta v_i \cdot M_i)^{1.029} \tag{6}$$

where M_i is the molecular weight of the structural group considered. The group contributions to Δv_i are listed in Table 1 (values in parentheses are based upon few experimental data; accordingly, they are less reliable than other values).

It is quite evident that structural features predominate over other factors, since different group contributions are

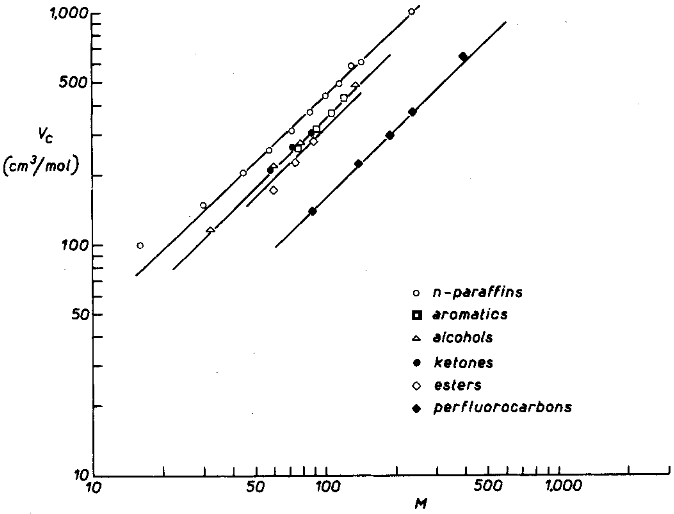

Fig. 1. Relationship between critical molar volume and molecular weight for various classes of compounds.

TABLE 2. ERROR PERCENT OF CRITICAL VOLUMES OF UNSATURED HYDROCARBONS AND POLAR COMPOUNDS CALCULATED WITH VARIOUS METHODS

Classes of compounds	No. of compounds	Viswaneth	Riedel	Fedors	This work
Naphthenes, olefins, acetilenics, aromatics	18	1.12	0.97	1.87	0.96
Ketones	5	6.92	5.59	3.52	3.40
Alcohols	10	9.60	4.74	4.73	2.77
Esters	11	5.36	3.61	3.27	0.94
Eters	10	5.30	4.89	5.98	3.03
Nitrogen compounds	4	20.01	19.47	2.68	4.41
Acids	4	17.45	12.41	1.63	1.46
Sulfur compounds	4	2.81	2.12	0.85	1.05
Organic halides	15	3.77	4.50	5.23	2.68
	81	5.93	4.75	3.62	2.10

TABLE 3. COMPARISON BETWEEN METHODS FOR PREDICTION OF CRITICAL MOLAR VOLUMES OF PARAFFINS

Hydrocarbons	Number of compounds	Error %	
		Lydersen-Kudchadker	This work
n-paraffins	17	2.26	0.96
Isoparaffins	31	1.59	1.78
Average error		1.82	1.49

associated with the same functional group depending on its position on the molecule.

Equation (6) can be justified by observing the graphical representation of some experimental data for various types of compounds reported in Figure 1. For each homologous series, the V_c value is an exponential function of the molecular weight. All straight lines relating V_c to M on a double logarithmic diagram have the same slope; this fact justifies an exponential term equal for all compounds. The first term in Equation (6) has been introduced mainly to have a correct value for V_c for the first members of the homologous series. A comparison between Equation (6) and those found in the literature is summarized in Table 2 for eighty-one unsaturated hydrocarbons and polar compounds chosen among those reported by Kudchadker et al. (1968*b*).

A significant overall superiority of Equation (6) with respect to the other methods is quite evident. V_c predicted from this equation is, for most compounds, within 2% of the experimental value, and the maximum deviation was found to be 8.54% in the case of furan. Among the literature correlations, Viswanath's is the poorest, while Fedors' can be considered the best for polar compounds. Regarding the various classes of compounds, Equation (6) and those of Riedel and Viswanath are almost equivalent, while Fedors' method furnishes less satisfactory results. The correlations proposed by Viswanath and Riedel fail in the case of organic acids and nitrogen compounds and give poor results also for alcohols and ketones. Generally, the discrepancy is larger for the first member of an homologous series, but high errors are found also for high molecular weight compounds. An obvious explanation of this fact would be that no semiempirical method can take into account phenomena such as dimerizations, hydrogen bonding interactions, and dipolar moment associations which play an important role in the case of highly polar compounds. On the contrary, the two methods based on group contributions appear fairly good for almost all types of polar compounds. However, the method proposed in this work is appreciably better than Fedors' for all classes of compound except those containing nitrogen and sulfur.

The reliability of the proposed method for saturated hydrocarbons with respect to the Lydersen correlation for n-paraffins and to the Kudchadker correlation (1968*a*) for isoparaffins is shown in Table 3. It is worthwhile noticing that the Kudchadker correlation for isoparaffins is a quite complicated relationship which requires an input parameter the V_c value of the corresponding n-paraffin.

In conclusion, the main advantage of Equation (6) lies in its simplicity and generality. Another favorable feature calls for comment. Contrary to what is found with the Viswanath and Riedel equations, none of the other critical parameters (P_c, T_c) is required in order to calculate V_c. As a consequence, the applicability of Equation (6) is not prevented by lack of experimental data for P_c and T_c.

NOTATION

M = molecular weight
P_c = critical pressure (atm)
R = universal gas constant (atm cm^3/K mole)
T_b = normal boiling temperature (K)
T_c = critical temperature (K)
V_c = critical volume (cm^3/mole)
V_{ci} = ideal critical volume, RT_c/P_c (cm^3/mole)
Δv_i = group contribution value to V_c
α = Riedel factor, $d(\ln P_R)/d(\ln T_R)$

Indexes

c = calculated values
s = experimental values

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