

The fall in overall rate constant value may be attributed to the fact that at higher acid concentration the side reactions (viz., furanization and some ring-opening reactions (Gelling, 1983; Burfield et al. (1984)) predominate over the epoxidation process, resulting in a sharp fall in the overall rate constant value of epoxidation.

The maximum extent of epoxidation was also found to vary with the acid concentration (Figure 6). When the concentration of the acid was very high, e.g., 5 mol/dm<sup>3</sup>, the maximum extent of epoxidation was about 40%, and when the acid concentration was 3.6 mol/dm<sup>3</sup>, the maximum yield was about 57%. When reactions were continued beyond these maxima, the products contained mainly hydrofuran rings and ring-opened groups such as formate and hydroxyl.

When the acid concentration was about 2.3 mol/dm<sup>3</sup>, 70% epoxidation was achieved. However, further decrease in the acid concentration resulted in a much slower rise in the level of maximum epoxidation. This observation may be explained by the phenomena of hydrofuranization and ring opening of epoxy groups, both of which were found to be accelerated in the presence of excess acid (Perera et al., 1988; Burfield et al., 1984). It was also explained by Gelling (1985) and Perera et al., (1988) that the higher the block length of epoxy groups the greater is the tendency of furanization, and this was the reason that the epoxidation rate at higher than 70% was very slow even by further lowering of acid concentration.

The point of intersection of the two curves at the highest position i.e., corresponding to 3.3 mol/dm<sup>3</sup> acid concentration, should give the highest rate of conversion with the lowest extent of side reaction. However, experimentally  $k$  was found to be  $1.166 \times 10^{-3} \text{ min}^{-1}$  and  $(C_E)_{\text{max}}/C_{R0}$  to be 0.634 with a negligible amount of hydroxyl and about 5% hydrofuran rings, but there was no IR absorption due to formates ( $1720\text{--}1725 \text{ cm}^{-1}$ ).

## Conclusion

In conclusion, it can be summarized that the epoxidation of NR with performic acid produced in situ is a feasible

process with well-defined kinetics. The control of ring expansion is possible by judicious choice of reaction temperature and acid concentration. Total control of acidolytic ring opening of the epoxy group is possible. From the experimental curves (Figure 6) it is possible to predict the overall rate constant and maximum extent of epoxidation for a given acid concentration.

**Registry No.** Formic acid, 64-18-6; acetic acid, 64-19-7.

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# Group Contribution Method for the Prediction of Liquid Densities as a Function of Temperature for Solvents, Oligomers, and Polymers

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A new group contribution method, GCVOL, for the prediction of liquid densities as a function of the temperature is proposed. A table for 36 different group volume parameters is given. Using the proposed method liquid densities for even strongly polar solvents can be predicted with an error of approximately 1% in the temperature range between the melting temperature and the normal boiling point. Densities of amorphous polymers are predicted with an average error of 2.7%. The proposed method is able to describe densities for the complete molecular range, covering solvents, oligomers, and polymers.

## Introduction

Most methods for estimating saturated liquid densities are based upon the law of corresponding states or upon group contributions. The estimation of density using the principle of corresponding states generally requires knowledge of the critical properties. For polymers, critical properties, even though they can be estimated using

well-known techniques, do not have any meaning. Group contribution, on the other hand, can be used to estimate polymer densities. Unfortunately existing group contribution tables are usually only valid either for polymers or for low-molecular-weight solvents. No method exists which can successfully predict densities for oligomers (with molecular weights in between solvents and polymers). Fur-

thermore, most group contribution tables for predicting saturated densities are only given at one temperature (usually 25 °C).

The purpose of this work is to develop a group contribution method to predict densities as a function of temperature for the whole molecular weight range, covering solvents, oligomers and polymers.

## Background

**Corresponding-State Models.** Various models exist for predicting saturated liquid densities as a function of the temperature using the principle of corresponding states. Traditionally these models have been used in either of two forms: the Rackett equation (Rackett, 1970) and the method of Bhurud (1978) are examples of predictive methods that only depend on critical properties or some other commonly tabulated property such as the normal boiling temperature. The modified Rackett equation (Spencer and Danner, 1972) and the HBT method (Hankinson and Thomson, 1979), on the other hand, both require an extra characteristic parameter adjusted to already known density data. In the latter case one can often predict the density with errors below 1%, whereas the errors in the first case can get as high as 5–10%. The difference between these two approaches lies more in the use of some experimental density data than in differences in the functional form of the predictive model. Our model is as the Rackett equation a purely *predictive* model.

In the Rackett equation (Rackett, 1970), the saturated liquid volume,  $V$ , is found from the following equation:

$$V = V_c Z_c^{(1-T_r)^{2/7}} \quad (1)$$

where  $Z_c$  is the critical compressibility,  $V_c$  is the critical volume, and  $T_r$  is the reduced temperature. In the calculation of the  $V$ , we use critical data taken from the DIPPR compilation (Daubert and Danner, 1989).

**Group Contribution Methods.** The best known group contribution method for predicting the density of amorphous polymers is the one given by Van Krevelen (Van Krevelen and Hoftyzer, 1972). The density,  $\rho$ , of a polymer is calculated from the following simple equation:

$$\rho = \frac{MW}{V} = \frac{MW}{\sum n_i \Delta v_i} \quad (2)$$

where the molecular weight, MW, and the molar volume,  $V$ , both apply to the repeat unit of the polymer. The molar volume is calculated from a sum over all group volume increments,  $\Delta v_i$ . Van Krevelen gives a table of 20 different group volume increments encompassing alkane, aromatic, ether, ester, chloride, fluoride, and sulfur groups. Van Krevelen assumed that it was impossible to use the same table of group volume increments both for polymers and for solvents, and the given group volume increments were therefore optimized from experimental densities at 25 °C for 40 amorphous polymers. The error in reproducing these densities using the set of optimized group volume increments is 1.5%.

The temperature dependency of the polymer densities is described by Van Krevelen quite empirically by the following equation:

$$V(t) = V(25\text{ °C}) + (t - 25\text{ °C}) V_w \times 10^{-3} \quad (3)$$

where  $V(t)$  is the molar volume at the temperature  $t$ ,  $V(25\text{ °C})$  is the molar volume at 25 °C calculated using the group volume increments, and  $V_w$  is the van der Waals volume as listed by Bondi (1968).

Another group contribution method for calculating the density of liquids at 25 °C is the method of Fedors (1974).

It was especially developed to be used for calculating the solubility parameter for polymers. The density of solvents and polymers is calculated using eq 2. Fedors lists a very large table of group volume increments, also covering a number of inorganic metals. Fedors does not list any comprehensive analysis of the accuracy of his method.

## GCVOL: The New Group Contribution Method for Predicting Saturated Liquid Density

**Model.** We propose the following simple model for predicting the molar volume of a liquid:

$$V = \sum n_i \Delta v_i \quad (4)$$

where  $n_i$  is the number of group  $i$ , and the temperature dependency of the molar group volume,  $\Delta v_i$ , is given by the following simple polynomial function:

$$\Delta v_i = A_i + B_i T + C_i T^2 \quad (5)$$

where the temperature,  $T/K$ , can vary between the melting point and the normal boiling point if the model is used to predict densities of solvents, and between the glass transition temperature and the degradation temperature if used to predict density data for amorphous polymers. To predict density data for polymers, only groups present in the repeat unit of the polymer need to be included in eq 4, whereas all groups used to define the chemical formula of low-molecular-weight solvents and oligomers have to be included. Group volume temperature constants are given for 36 different groups in Table I.

**Determination of Group Volumes.** Group volumes were optimized independently at temperatures spaced 10 K apart in the temperature range 200–500 K using liquid volume data for solvents below their normal boiling temperature taken from the DIPPR data compilation (Daubert and Danner, 1989).

In the following paragraph the mathematical framework for the calculation of the group volumes will be given. The below-mentioned procedure avoids nonlinear optimization, which otherwise would be the obvious choice. Using normal statistics the following equation can be set up for each temperature:

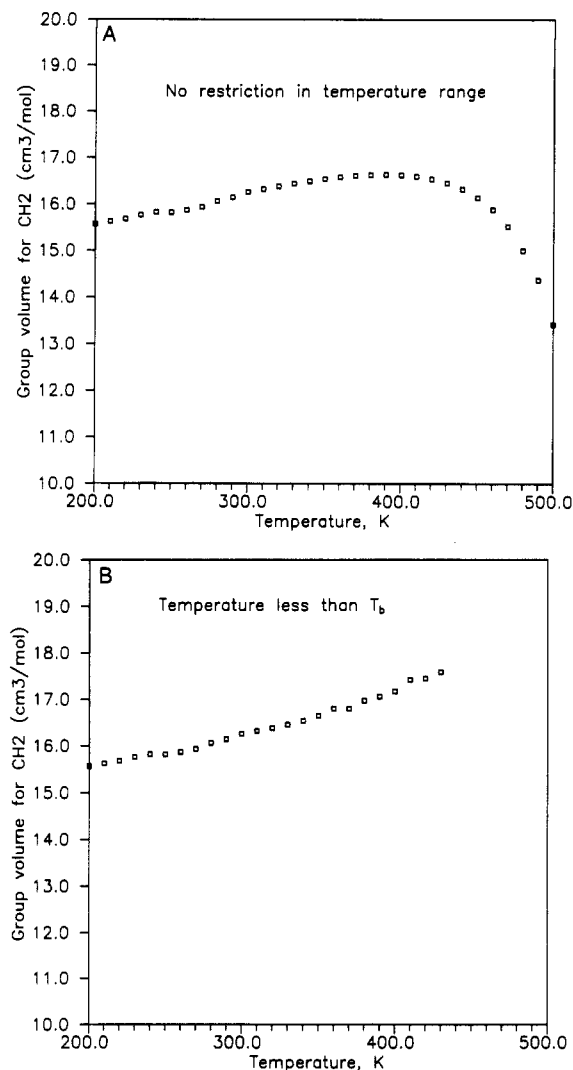
$$G^T \cdot W \cdot G \cdot \Delta v = G^T \cdot W \cdot v^{\text{exp}} \quad (6)$$

where the matrix  $G$  contains the group specification of each solvent included in the optimization, one solvent for each row ( $G^T$  is the transposed matrix);  $\Delta v$  is the molar group volume parameter vector;  $v^{\text{exp}}$  is the experimental molar volume; and  $W$  is a diagonal matrix, containing the weighing factors used for each pure component. These factors were obtained from the errors in the experimental volumes listed in the DIPPR data compilation (Daubert and Danner, 1989); high errors lead to low weighing factors. This equation reduces to a *quadratic* set of linear equations, where the number of unknowns corresponds to the number of molar group volumes to be found. These equations can be solved using simple Gauss elimination.

The resulting temperature-dependent molar group volumes,  $\Delta v$ , were then fitted to a polynomial function (eq 5) using the lowest degree possible.

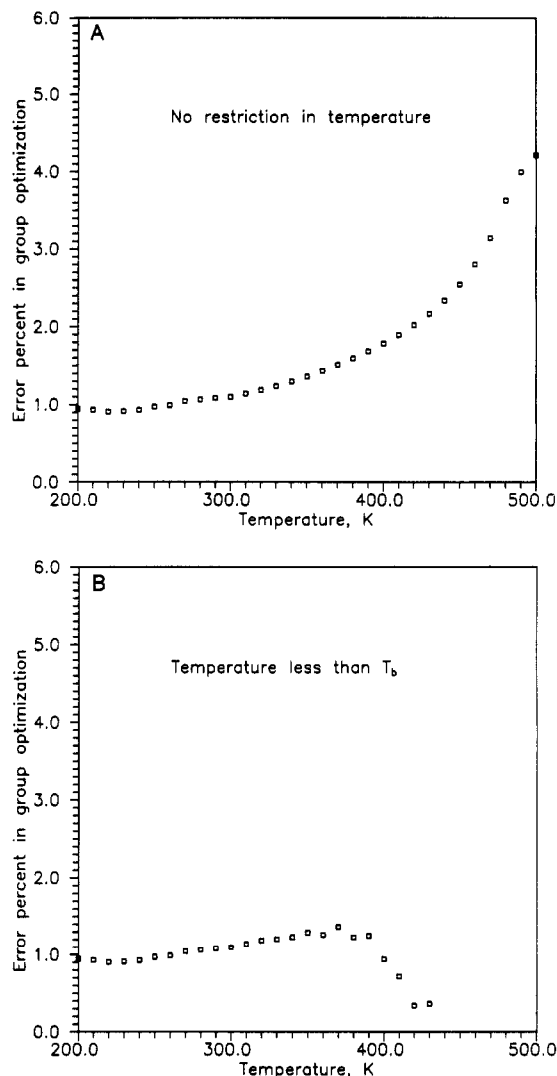
The primary groups to be determined were the alkyl groups, which were determined from 56 different noncyclic alkanes. Secondly, the arene groups were determined from 37 different alkylbenzenes. The remaining groups were determined from solvents, which could be defined using only alkyl or arene groups and *one* additional functional group.

**Selection of Temperature Range.** The range 200–500 K was selected because many solvents are in liquid form within this range.



**Figure 1.** Group volume for CH<sub>2</sub> as a function of the temperature. (A) All liquid solvent data contributed to the determination of the group volume. (B) Only solvents below their normal boiling temperature contributed to the determination of the group volume.

At first no restriction was made regarding the state of the solvent; i.e., the solvent could be close to the critical point and its volume data would still be included in the determination of the corresponding group volumes. However, optimization of the alkane group volumes (CH<sub>3</sub>, CH<sub>2</sub>, CH, and C) showed that this simple group contribution scheme could not be used in the complete range up to the critical temperature. This can be seen in Figure 1, which shows the molar group volume for the CH<sub>2</sub> group as a function of the temperature under two different conditions: In Figure 1A volume data for alkanes in the near-critical region have been included and in Figure 1B only volume data for alkanes below their normal boiling temperature have been included in the determination of the CH<sub>2</sub> group volume. In Figure 2 the corresponding errors in the prediction of the alkane volumes are given for the same two conditions. One would expect the molar volume for the CH<sub>2</sub> group to increase as a function of the temperature; therefore the results from condition A do not appear physically valid. Furthermore, the error in predicting the alkane volume data for condition A is an increasing function of temperature. For condition B the errors are constant until around 400 K, where it drops below 1%. A drop in the error can readily be understood, since higher temperatures will result in fewer alkanes being below their normal boiling temperature, and therefore



**Figure 2.** Errors in the prediction of the liquid volumes as a function of the temperature. (A) All liquid solvent data contributed to the determination of the group volume. (B) Only solvents below their normal boiling temperature contributed to the determination of the group volume.

better correlation of the data. On the basis of this investigation it was therefore decided only to include volume data below the normal boiling point into the determination of the corresponding group volumes.

**Basis of Group Volumes.** The group volume increment values will always to some extent be correlated. A basis was therefore established using density data for a linear polyethylene since it only contains CH<sub>2</sub> groups, the CH<sub>3</sub> end-groups making insignificant contributions. The temperature dependence of the CH<sub>2</sub> group between 140 and 180 °C was found from density data for a completely amorphous polyethylene, and subsequently the three alkane group volumes (CH<sub>3</sub>, CH, and C) were adjusted to density data for low-molecular-weight alkanes.

Using the polyethylene data seems legitimate since it results in a physically realistic value for the CH<sub>2</sub> group volume. This can be seen from Figure 3, where the CH<sub>2</sub> group volume at 20 °C is given for a series of cycloalkanes as a function of the number of carbon atoms. As the number of carbon atoms in the cycloalkane increases, the cycloalkane loses the strained conformation which is dominant especially for the lower cycloalkanes, and the molar volume for a CH<sub>2</sub> unit goes asymptotically toward the value we have selected using the data for linear polyethylene. From Figure 3 it is also clear why the proposed

Table I. Group Contributions for Saturated Molar Volume

group	no.	group volume temp const			sample group assignment
		A, cm <sup>3</sup> /mol	10 <sup>3</sup> B, cm <sup>3</sup> /(mol K)	10 <sup>5</sup> C, cm <sup>3</sup> /(mol K <sup>2</sup> )	
CH <sub>3</sub>	1	18.960	45.58	0	butane: 2 CH <sub>3</sub> , 2 CH <sub>2</sub>
CH <sub>2</sub>	2	12.520	12.94	0	2-methylpropane: 3 CH <sub>3</sub> , 1 CH
CH	3	6.297	-21.92	0	2,2-dimethylpropane: 4 CH <sub>3</sub> , 1 C
C	4	1.296	-59.66	0	
ACH	5	10.090	17.37	0	benzene: 6 ACH
ACCH <sub>3</sub>	6	23.580	24.43	0	toluene: 5 ACH, 1 ACCH <sub>3</sub>
ACCH <sub>2</sub>	7	18.160	-8.589	0	ethylbenzene: 1 CH <sub>3</sub> , 5 ACH, 1 ACCH <sub>2</sub>
ACCH	8	8.925	-31.86	0	cumene: 2 CH <sub>3</sub> , 5 ACH, 1 ACCH
ACC	9	7.369	-83.60	0	tert-butylbenzene: 3 CH <sub>3</sub> , 5 ACH, 1 ACC
CH <sub>2</sub> =	10	20.630	31.43	0	1-hexene: 1 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>2</sub> =, 1 CH=
CH=	11	6.761	23.97	0	2-hexene: 2 CH <sub>3</sub> , 2 CH <sub>2</sub> , 2 CH=
C=	12	-0.3971	-14.10	0	2-methyl-2-butene: 3 CH <sub>3</sub> , 1 CH=, 1 C=
CH <sub>2</sub> OH	13	39.460	-110.60	23.31	1-hexanol: 1 CH <sub>3</sub> , 4 CH <sub>2</sub> , 1 CH <sub>2</sub> OH
CHOH	14	40.920	-193.20	32.21	2-hexanol: 2 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CHOH
ACOH	15	41.200	-164.20	22.78	phenol: 5 ACH, 1 ACOH
CH <sub>3</sub> CO	16	42.180	-67.17	22.58	methyl ethyl ketone: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>3</sub> CO
CH <sub>2</sub> CO	17	48.560	-170.40	32.15	diethyl ketone: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> CO
CHCO	18	25.170	-185.60	28.59	diisopropyl ketone: 4 CH <sub>3</sub> , 1 CH, 1 CHCO
CHO	19	12.090	45.25	0	1-hexanal: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CHO
CH <sub>3</sub> COO	20	42.820	-20.50	16.42	butyl acetate: 1 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>3</sub> COO
CH <sub>2</sub> COO	21	49.730	-154.10	33.19	butyl propionate: 2 CH <sub>3</sub> , 3 CH <sub>2</sub> , 1 CH <sub>2</sub> COO
CHCOO	22	43.280	-168.70	33.25	methyl isobutyrate: 3 CH <sub>3</sub> , 1 CHCOO
COO	23	14.230	11.93	0	poly(methyl methacrylate): 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 C, 1 COO
ACCOO	24	43.060	-147.20	20.93	methyl benzoate: 1 CH <sub>3</sub> , 5 ACH, 1 ACCOO
CH <sub>3</sub> O	25	16.660	74.31	0	ethyl methyl ether: 1 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>3</sub> O
CH <sub>2</sub> O	26	14.410	28.54	0	diethyl ether: 2 CH <sub>3</sub> , 1 CH <sub>2</sub> , 1 CH <sub>2</sub> O
CHO	27	35.070	-199.70	40.93	diisopropyl ether: 4 CH <sub>3</sub> , 1 CH, 1 CHO
CO	28	30.120	-247.30	40.69	di-tert-butyl ether: 6 CH <sub>3</sub> , 1 C, 1 CO
CH <sub>2</sub> Cl	29	25.29	49.11	0	1-chlorobutane: 1 CH <sub>3</sub> , 2 CH <sub>2</sub> , 1 CH <sub>2</sub> Cl
CHCl	30	17.40	27.24	0	2-chloropropane: 2 CH <sub>3</sub> , 1 CHCl
CCl	31	37.62	-179.1	32.47	2-chloro-2-methylpropane: 3 CH <sub>3</sub> , 1 CCl
CHCl <sub>2</sub>	32	36.45	54.31	0	1,1-dichloroethane: 1 CH <sub>3</sub> , 1 CHCl <sub>2</sub>
CCl <sub>3</sub>	33	48.74	65.53	0	1,1,1-trichloroethane: 1 CH <sub>3</sub> , 1 CCl <sub>3</sub>
ACCl	34	23.51	9.303	0	chlorobenzene: 5 ACH, 1 ACCl
Si	35	86.71	-555.5	97.90	hexamethyldisiloxane: 6 CH <sub>3</sub> , 1 SiO, Si
SiO	36	17.41	-22.18	0	poly(dimethylsiloxane): 2 CH <sub>3</sub> , 1 SiO

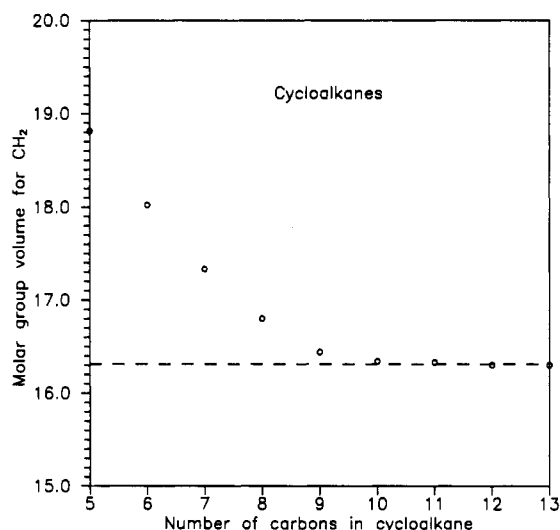


Figure 3. Molar group volume for the CH<sub>2</sub> group as a function of the number of carbons in the cycloalkane at 20 °C. The dashed line corresponds to the value for the CH<sub>2</sub> group used in this work. Experimental data are from the *Polymer Handbook* (Brandrup and Immergut, 1989).

model is not recommended to be used to describe density data for cycloalkanes.

### Prediction of Liquid Densities

**Solvents.** Figure 4 is a graph of the error in the prediction of the saturated liquid density for 1-hexanol as a function of the temperature. Up to around the normal

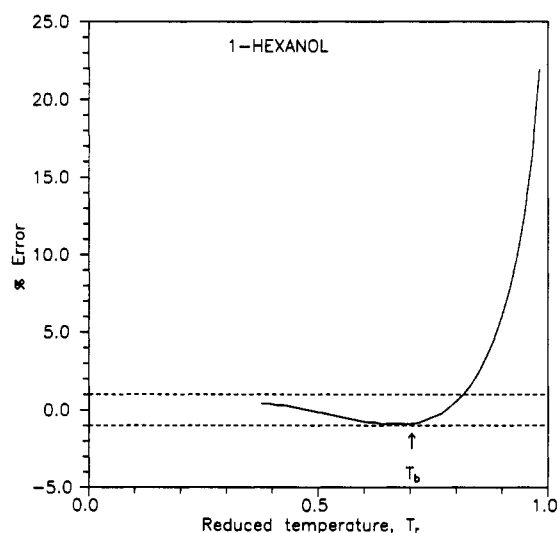


Figure 4. Percent error in the prediction by the GCVOL model of the liquid volume of 1-hexanol as a function of the reduced temperature. Experimental data are taken from the DIPPR data compilation (Daubert and Danner, 1989).

boiling point the errors are within the experimental error. As the temperature reaches the near-critical area, the errors become unacceptably high. This behavior is typical for the GCVOL model, and we therefore recommend to use the model only in the temperature range between the melting point and the normal boiling point.

In Table II we have compared the GCVOL model with the widely used Rackett (1970) model in the calculation

**Table II. Average Mean Deviation<sup>a</sup> between Experimental and Predicted Saturated Specific Volumes for Low-Molecular-Weight Solvents. Experimental Data Are from the DIPPR Data Compilation (Daubert and Danner, 1989)**

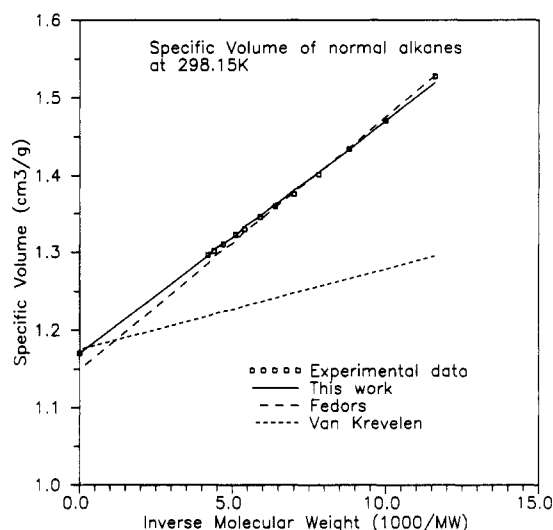
chemical family	no. of compds	Rackett		this work	
		$T_m - T_b$	298.15 K	$T_m - T_b$	298.15 K
alkanes	55	4.4	4.5	1.4	1.1
aromatics	33	2.5	2.5	1.1	0.8
alkenes	36	5.3	5.3	1.0	0.7
alcohols	38	7.5	4.3	0.8	0.7
ketones	8	5.4	5.4	0.7	0.7
aldehydes	9	6.9	6.9	1.0	0.7
esters	22	4.1	4.1	1.2	1.1
esters <sup>c</sup>	20	3.3	3.3	1.8	1.3
ethers	13	6.7	7.7	1.2	0.5
chlorides	23	4.1	4.0	0.9	0.5
siloxanes <sup>b</sup>	5	na	na	0.1	0.0

<sup>a</sup> Average mean deviation is calculated as

$$\text{AMD} = 100\% \times \frac{1}{n_c} \sum \frac{1}{n_p} \sum \left| \frac{v^{\text{exp}} - v^{\text{pred}}}{v^{\text{exp}}} \right|$$

where  $n_c$  is number of compounds and  $n_p$  is number of points for each compound (usually spaced 10K apart). <sup>b</sup> Experimental data are from Hurd (1946) in temperature range between 0 and 80 °C.

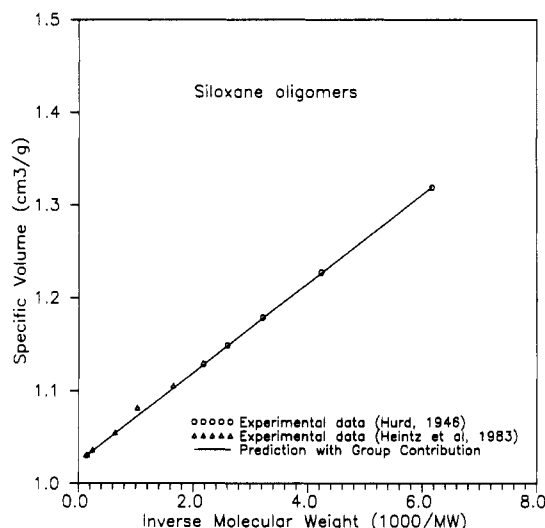
<sup>c</sup> Using only the -COO- group.



**Figure 5.** Specific volume at 25 °C for a series of linear alkanes from hexane to amorphous polyethylene. The ordinate intercept corresponds to polyethylene. Experimental data for low-molecular-weight alkanes is taken from the DIPPR data compilation (Daubert and Danner, 1989), and data for the polymer are taken from Orwoll and Flory (1967).

of the saturated densities for a number of different chemical families. Most of the density data used in Table II went into the optimization of the group volume parameters, but as the number of solvents used in the parameter estimation is very big, we believe that one would obtain the same quality for solvents not included in the data base. The errors in using the Rackett model are typically around 5%, whereas our proposed group contribution model only has errors around 1%. The larger error in the Rackett predictions of the liquid densities might be caused by erroneous critical data.

**Specific Volumes for a Complete Molecular Weight Range.** In Figure 5 the specific volume of a normal alkane series going from hexane to polyethylene is given as a function of the inverse molecular weight. The GCVOL model is compared with two other group contribution models: the Van Krevelen (Van Krevelen and Hoftyzer,



**Figure 6.** Specific volume at 25 °C for a series of siloxanes from hexamethyldisiloxane to poly(dimethylsiloxane).

1972) and the Fedors (1974) methods. As foreseen by Van Krevelen, his model cannot reproduce the relationship between the molecular weight and the specific volume, and the Fedors method has some problems in the polymer end of the molecular weight. As we fixed the value of the group volume for CH<sub>2</sub> to the value in an amorphous linear polyethylene, it is not surprising that the GCVOL method will reproduce correctly the trend in the specific volume.

In Figure 6 the specific volume of a siloxane series going from hexamethyldisiloxane to poly(dimethylsiloxane) is given as a function of the inverse molecular weight. In this series only the experimental data for the five low-molecular-weight siloxanes were used in the determination of the group volume parameters. It is therefore reassuring that the trend in the specific volume as a function of the molecular weight is readily reproduced by the GCVOL model.

Only density data for compounds with one functional group different from alkyl and arene groups were included in the determination of the group volumes. It is therefore encouraging to see how well the GCVOL model predicts the densities for solvents with several different functional groups present. The average mean deviation between experimental and predicted data for diethylene glycol, triethylene glycol, tetraethylene glycol, and polyethylene glycol-400 (containing alkyl groups, an ether group, and an alcohol group) is only 1%. The Fedors (1974) model predicts the same data with an average error of 7%. Experimental data are taken from Müller and Rasmussen (1991).

**Polymers.** The density of a polymer is dependent on whether the polymer is amorphous, glassy, or crystalline. The density of an amorphous polymer is the one that most closely resembles the liquid density of a solvent, and is therefore the only kind that can be predicted accurately by the proposed GCVOL model.

Table III shows a comparison between amorphous polymer densities at 25 °C predicted by the three group contribution methods: Van Krevelen (Van Krevelen and Hoftyzer, 1972), Fedors (1974), and the GCVOL model. Considering that the same limited amount of density data went into the optimization of the Van Krevelen group volumes, the predictions by the proposed GCVOL model are satisfactory. It is interesting to note that the Fedors model always overpredicts the density of the polymers, which might point to a general deficiency in the group volumes.

Table III. Predictions of Amorphous Polymer Densities at 298.15 K

polymer	exp <sup>a</sup> density, g/cm <sup>3</sup>	this work		Van Krevelen <sup>b</sup>		Fedors <sup>c</sup>	
		$\rho$ , g/cm <sup>3</sup>	% dev <sup>d</sup>	$\rho$ , g/cm <sup>3</sup>	% dev <sup>d</sup>	$\rho$ , g/cm <sup>3</sup>	% dev <sup>d</sup>
polypropene		0.864	-1.7	0.857	-0.8	0.866	-1.9
polybutene	0.850	0.862	-0.3	0.852	1.0	0.867	-0.9
polypentene	0.860	0.861	-1.3	0.855	-0.6	0.868	-2.1
polyhexene	0.850	0.861	-0.1	0.855	0.7	0.869	-1.0
polyisobutene	0.860	0.864	-0.4	0.860	0.1	0.878	-2.1
poly(5-phenylpentene)	0.860	1.038	1.1	1.042	0.8	1.085	-3.3
poly(methyl acrylate)	1.050	1.205	1.2	1.229	-0.7	1.293	-6.0
poly(ethyl acrylate)	1.220	1.140	-1.8	1.156	-3.2	1.211	-8.1
poly(butyl methacrylate)	1.120	1.078	-2.4	1.036	1.7	1.092	-3.7
poly(hexyl methacrylate)	1.053	1.034	-2.7	1.001	0.6	1.049	-4.1
poly(2-ethylbutyl methacrylate)	1.007	1.037	0.3	1.003	3.6	1.047	-0.6
poly(1-methylpentyl methacrylate)	1.040	1.037	-2.4	1.003	1.1	1.047	-3.3
poly(octyl methacrylate)	1.013	1.005	-3.5	0.997	-0.5	1.019	-5.0
poly(dodecyl methacrylate)	0.971	0.968	-4.2	0.946	-1.8	0.982	-5.8
poly(vinyl propionate)	0.929	1.221	-19.7	1.109	-8.7	1.211	-18.7
poly(isopropyl vinyl ether)	1.020	0.925	-0.1	0.954	-3.2	1.015	-9.8
poly(butyl vinyl ether)	0.924	0.960	-3.5	0.936	-0.9	0.995	-7.3
poly(sec-butyl vinyl ether)	0.927	0.915	1.0	0.938	-1.4	0.992	-7.3
poly(isobutyl vinyl ether)	0.924	0.964	-3.7	0.938	-0.8	0.992	-6.7
poly(pentyl vinyl ether)	0.930	0.946	-3.0	0.925	-0.8	0.978	-6.5
poly(hexyl vinyl ether)	0.918	0.935	-1.1	0.916	1.0	0.965	-4.3
poly(octyl vinyl ether)	0.925	0.920	-0.7	0.905	1.1	0.947	-3.6
poly(2-ethylhexyl vinyl ether)	0.914	0.922	-2.0	0.906	-0.2	0.945	-4.5
av mean dev, %			3.5		1.5		5.8

<sup>a</sup> Experimental data are taken from Van Krevelen and Hoftyzer (1972). <sup>b</sup> Calculated densities are from Van Krevelen and Hoftyzer (1972).

<sup>c</sup> Predictions with the Fedors model is calculated in connection with this work. <sup>d</sup> The percent deviation between experimental and predicted densities is calculated as

$$\% \text{ dev} = \frac{\rho^{\text{exp}} - \rho^{\text{pred}}}{\rho^{\text{exp}}} \times 100\%$$

Table IV gives a comparison between the Van Krevelen (Van Krevelen and Hoftyzer, 1972) model and the GCVOL model for the prediction of the temperature dependency of the specific volume for a number of different amorphous polymers. The predictions by the proposed GCVOL model compares well with those of the Van Krevelen model.

That the same group contribution table can be used to predict the densities of both solvents and polymers is contradictory to the observations by Van Krevelen (Van Krevelen and Hoftyzer, 1972), and might also seem somewhat contradictory to the idea of polymers and solvents as having different free volumes. However, according to the simple group contribution concept put forward in this work, a rather large amount of free volume is created by monovalent end-groups. This is probably because monovalent groups have a much larger degree of freedom than groups with higher valency. An intuitive way of realizing that the monovalent groups create more free volume than the groups with higher valency is to compare the ratio of optimized group volumes and van der Waals volume (given by Bondi, (1968)). As an example, this ratio is much bigger for a CH<sub>3</sub> group than it is for a CH<sub>2</sub> group. Accordingly, the difference in the free volume between hexane and polyethylene can be explained as an end-group effect: Polyethylene has a negligible number of the free-volume-generating CH<sub>3</sub> end-groups compared to the number of bivalent CH<sub>2</sub> groups, whereas hexane has only twice the number of CH<sub>2</sub> groups compared to the number of CH<sub>3</sub> end-groups. Consequently hexane has a much higher degree of free volume than polyethylene.

## Conclusion

A new group contribution model for the prediction of liquid densities as a function of the temperature has been proposed. A table of 36 different group volume increments for a wide variety of chemical families (noncyclic alkanes,

Table IV. Predictions of Amorphous Polymer Densities as a Function of Temperature

polymer	temp range, K	ref	AMD <sup>a</sup>	
			Van Krevelen	this work
polybutadiene	277-328	a	0.5	1.4
poly(1-butene), isotactic	407-514	b	1.2	0.2
poly(methyl methacrylate), isotactic	328-463	c	8.1	2.2
polypropylene, isotactic	447-571	b	3.2	1.7
poly(butyl methacrylate)	295-473	d	1.0	2.4
polydimethylsiloxane	298-343	e	na	1.0
polyisobutylene	326-383	e	9.4	6.8
poly(methyl methacrylate)	387-432	d	18.3	1.2
poly(4-methyl-1-pentene)	514-592	f	5.5	3.6
polyoxymethylene	462-492	g	6.5	4.8
poly( $\alpha$ -methylstyrene)	413-471	h	0.3	2.4
polystyrene	389-469	h	5.4	3.7
poly(vinyl acetate)	337-393	e	1.1	4.1
polytetrahydrofuran	337-444	i	0.5	1.1
poly(vinyl chloride)	355-370	j	1.5	3.1
total av mean dev, %			4.5	2.7

<sup>a</sup> Barlow, 1978. <sup>b</sup> Zoller, 1979. <sup>c</sup> Quach et al., 1974. <sup>d</sup> Olabisi and Simha, 1975. <sup>e</sup> Beret and Prausnitz, 1975. <sup>f</sup> Zoller, 1977. <sup>g</sup> Starkweather et al., 1988. <sup>h</sup> Quach and Simha, 1971. <sup>i</sup> Tsujita et al., 1973. <sup>j</sup> Hellwege et al., 1962. <sup>k</sup> Average mean deviation is calculated as

$$\text{AMD} = 100\% \times \frac{1}{n} \sum \left| \frac{\rho^{\text{exp}} - \rho^{\text{pred}}}{\rho^{\text{exp}}} \right|$$

aromatics, alkenes, ketones, ethers, esters, chlorides, and siloxanes) has been developed. The model can be used in the complete molecular weight range from solvents, over oligomers, and to polymers.

The liquid densities for solvents between the melting point and the normal boiling point can be predicted with an average error of 1%, which compares favorably with

predictions by the widely used Rackett model (Rackett, 1970). Also densities for solvents with more than one different functional group can be predicted with very good results.

Densities of amorphous polymers in the temperature range of 277–571 K are predicted with an average error of 2.7%, which compares favorably with the group contribution models by Van Krevelen (Van Krevelen and Hof-tyzer, 1972) and Fedors (1974).

**Registry No.** Polypropene, 9003-07-0; polybutene, 9003-28-5; polypentene, 9078-70-0; polyhexene, 50981-41-4; polyisobutene, 9003-27-4; poly(5-phenylpentene), 136489-80-0; poly(methyl acrylate), 9003-21-8; poly(ethyl acrylate), 9003-32-1; poly(butyl methacrylate), 9003-63-8; poly(hexyl methacrylate), 25087-17-6; poly(2-ethylbutyl methacrylate), 25087-19-8; poly(1-methylpentyl methacrylate), 136489-81-1; poly(octyl methacrylate), 25087-18-7; poly(dodecyl methacrylate), 25719-52-2; poly(vinyl propionate), 25035-84-1; poly(isopropyl vinyl ether), 25585-49-3; poly(butyl vinyl ether), 25232-87-5; poly(sec-butyl vinyl ether), 28853-85-2; poly(isobutyl vinyl ether), 9003-44-5; poly(pentyl vinyl ether), 71356-03-1; poly(hexyl vinyl ether), 25232-88-6; poly(octyl vinyl ether), 25232-89-7; poly(2-ethylhexyl vinyl ether), 29160-05-2; polybutadiene, 9003-17-2; poly(1-butene), isotactic, 25036-29-7; poly(methyl methacrylate), isotactic, 25188-98-1; polypropylene, isotactic, 25085-53-4; poly(methyl methacrylate), 9011-14-7; poly(4-methyl-1-pentene), 25068-26-2; polyoxymethylene, 9002-81-7; poly( $\alpha$ -methylstyrene), 25014-31-7; polystyrene, 9003-53-6; poly(vinyl acetate), 9003-20-7; polytetrahydrofuran, 24979-97-3; poly(vinyl chloride), 9002-86-2; cyclopentane, 287-92-3; cyclohexane, 110-82-7; cycloheptane, 291-64-5; cyclooctane, 292-64-8; cyclononane, 3350-30-9; cyclodecane, 293-96-9; cycloundecane, 294-41-7; cyclododecane, 294-62-2; cyclotridecane, 295-02-3.

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