R & D NOTES

Critical Properties, Potential Force Constants, and Structure of Organic Molecules

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INTRODUCTION

Recently, it was shown (Sanchez, 1983) that the surface tension (σ) of a liquid in its normal liquid range is related to its isothermal compressibility (κ) and mass density (ρ) by

$$\sigma = (A_o \rho/\kappa)^{1/2} \tag{1}$$

where A_o is a temperature-independent constant for a wide variety of inorganic, organic, and polymeric liquids. For hydrocarbons as well as oxygen and nitrogen containing organics, A_o varies only by about 20%. It was argued that if molecules interact through a pair potential, such as Lennard-Jones 6-12 potential, then

$$A_o \sim \epsilon_o \sigma_o^2/Z \tag{2}$$

where ϵ_o and σ_o are the force constants that characterize the attractive and repulsive parts of the potential, and Z is the number of electrons in the molecule. The small variation in A_o for organics implies that the product $\epsilon_o \sigma_o^2$ is proportional to the number of C, O, and N atoms in the molecule since the groups CH_3, CH_2, NH_2, OH, etc., are nearly isoelectronic. An additional implication is that any combination of thermodynamic properties that is proportional to A_o might itself be relatively invariant. This notion is pursued in the next section for critical properties.

CRITICAL PROPERTY CORRELATION

For a van der Waals fluid or from dimensional considerations, it is easy to show that the critical temperature T_c, pressure P_c, and volume V_c are related to ϵ_o and σ_o by $T_c \sim \epsilon_o$, $P_c \sim \epsilon_o/\sigma_o^3$ and $V_c \sim \sigma_o^3$ Therefore, both $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ are proportional to $\epsilon_o\sigma_o^2$.

For the normal alkanes, the linearity in the $T_cV_c^{2/3}$ product with carbon number is striking. The correlation for both $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ with carbon number is illustrated in Figure 1. The slopes of the two lines indicate that the $T_cV_c^{2/3}/Z$ and $P_cV_c^{5/3}/Z$ values are about 530 and 1,140, respectively (when T_c is expressed in K, P_c in MN/m^2, and V_c in cm^3/mol).

A close examination of other organics indicates that many have values of $T_cV_c^{2/3}/Z$ and $P_cV_c^{5/3}/Z$ similar to those of the normal alkanes. Some representative values of $T_cV_c^{2/3}/Z$ and $P_cV_c^{5/3}/Z$ are benzene (540, 1,200), acetic acid (570, 960), acetone (560, 1,100), ethyl amine (550, 1,200), *n*-butyraldehyde (560,1,200), 1-butanol (590, 1,300), 1-butene (510, 1,200), and aniline (590, 1,200). Aliphatic and aromatic hydrocarbons, acids, alcohols, amines, ketones and aldehydes all have similar values of $T_cV_c^{2/3}/Z$ in the range 500 to 600. Esters and ethers have somewhat lower values that are usually in the range 470 to 500. Almost all organics have $P_cV_c^{5/3}/Z$ values between 1,000 and 1,300.

The linear dependence of $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ on the number of C, N, and O atoms suggests that these quantities can be estimated by a group contribution method. In Table 1 values of the group contributions Δ_i and δ_i to $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$, respectively, are tabulated:

$$T_cV_c^{2/3} = \sum_i \Delta_i \tag{3}$$

$$P_cV_c^{5/3} = \sum_i \delta_i \tag{4}$$

Notice that the ratio of $P_cV_c^{5/3}$ to $RT_cV_c^{2/3}$ is just the critical compressibility factor Z_c. Thus

$$Z_c = \frac{P_cV_c}{RT_c} = \sum\delta_i/R\sum\Delta_i \tag{5}$$

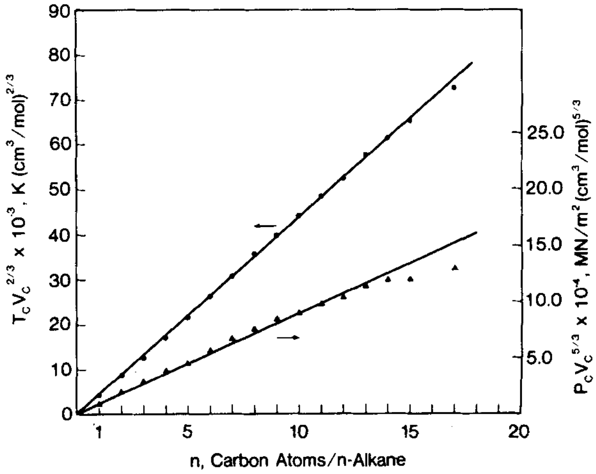

Figure. 1. Variation of the critical property combinations $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ with chain length for the normal alkanes. Critical constants obtained from (Reid et al., 1977).

TABLE 1. GROUP CONTRIBUTION INCREMENTS FOR $T_c V_c^{2/3}$ AND $P_c V_c^{5/3}$

Group		$\Delta_i \times 10^{-3}$ K (cm^3/mol)$^{2/3}$	$\delta_i \times 10^{-3}$ MN/m^2 (cm^3/mol)$^{5/3}$
$-CH_3$	single bonds to C, N, or O	4.41	9.93
$-CH_2-$		4.26	9.31
$-\overset{\vert}{C}H-$		3.47	5.56
$-\overset{\vert}{\underset{\vert}{C}}-$		2.32	4.52
$=CH_2$	double bonds to C, N, or O	3.67	8.62
$=CH-$		3.82	8.82
$=\overset{\vert}{C}-$		4.00	5.66
$=C=$		4.30	8.84
$\equiv CH$	triple bonds to C or N	3.60	8.10
$\equiv C-$		4.27	9.94
—OH (aliphatic alcohol)		6.32	13.3
—OH (aromatic alcohol)		3.20	4.69
—OH (acid)		4.88	5.53
—O— (ether)		2.94	4.59
—O— (ester)		0.46	1.61
=O		5.25	11.6
$-NH_2$		5.95	12.6
$-NH-$		5.34	13.4
$-\overset{\vert}{N}-$		3.73	9.86
—N=		5.90	13.1
N≡		8.08	6.35
Some Common Composite Groups			
$-\overset{\vert}{C}=O$ (ketone)		9.25	17.3
$H\overset{\vert}{C}=O$ (aldehyde)		9.07	20.4
—COOH (acid)		14.1	22.8
—COO— (ester)		9.71	18.9
HCOO— (formate)		9.53	22.0
—CN (nitrile)		12.35	16.3
$-C_6H_5$ (phenyl)		23.1	49.8

DISCUSSION

A linear least squares procedure and 66 compounds were used to determine the Δ_i and δ_i in Table 1. These group contribution parameters were then used to calculate the values of $T_cV_c^{2/3}$, $P_cV_c^{5/3}$, and Z_c for the 22 compounds shown in Table 2. These 22 compounds were *not among* the 66 used to prepare Table 1. Notice that the average error between experimental and calculated values of $T_cV_c^{2/3}$ is about 2.5%. This is very good agreement because estimates of experimental errors in $T_cV_c^{2/3}$ range between 0.5 and 5% (Kudchadker et al., 1968). The average error between experimental and calculated values for both $P_cV_c^{5/3}$ and Z_c is about 5%. Since estimated experimental errors in P_c are much larger than for T_c (Kudchadker et al., 1968) and errors in V_c are magnified in the $P_cV_c^{5/3}$ product (compared to $T_cV_c^{2/3}$), it is not surprising that the group contribution scheme for $P_cV_c^{5/3}$ or Z_c is not as accurate as that for $T_cV_c^{2/3}$. In general, errors between calculated and experimental values appear to be largest for small molecules (e.g., methanol) and nonaromatic cyclic compounds.

In spite of the good agreement, a certain amount of error is inherent in this estimation scheme. This problem is exemplified by the ortho- and metacresols. Structurally these two isomers are identical, and the present estimation method would predict that they should have identical values of $T_cV_c^{2/3}$, $P_cV_c^{5/3}$, and Z_c. Experimentally, these isomers do have identical values of Z_c, but their $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ products differ by about 7%.

Often the critical temperature of an organic is known, but not its critical volume or pressure. The present estimation method can be used to calculate critical volumes and pressures when only the critical temperature is known. It might also be combined with other methods for estimating critical properties (Reid et al., 1977) to obtain a superior estimation scheme. An advantage that the present method has over other estimation methods is that no distinction is made between groups in cyclic and noncyclic compounds.

Theoretical support for the linearity of the $T_cV_c^{2/3}$and $P_cV_c^{5/3}$ products with carbon number (n) for the normal alkanes comes from the lattice fluid model (Sanchez and Lacombe, 1978). This model is a generalization of the well-known lattice gas model in which a molecule occupies n sites on a lattice instead of a single site. For a homologous series of liquids, such as the normal alkanes, this mean field theory predicts that both $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ should vary linearly with n for large n. However, the theory fails to predict the correct n dependencies of T_c, P_c, and V_c individually. The data indicate approximately that $V_c \sim n$, $T_c \sim n^{1/3}$, and $P_c \sim n^{-2/3}$, whereas the theoretical predictions for large n are $V_c \sim n^{3/2}$, T_c is independent of n, and $P_c \sim n^{-3/2}$. Also note from Figure 1 that the linearity appers to break down for the $P_cV_c^{5/3}$product for $n >$ 14.

The observed linearity of $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ with the number of C, N, and O atoms in the organic molecule further confirms that pair potential force constants are coupled in a very specific way. The general interdependence of ϵ_o and σ_o has been commented upon before (Kim and Ross, 1967; Reichenberg, 1973), but the present correlation and that of Sanchez 1983) are the strongest statements made about this interdependence. However, there is one caveat worth mentioning: As illustrated in Table 1, $T_cV_c^{2/3}$ and $P_cV_c^{5/3}$ do not vary exactly in the same way with structure, i.e., δ_i is not strictly proportional to Δ_i. Moreover, the product ZA_o is not strictly proportional to either $T_cV_c^{2/3}$ or $P_cV_c^{5/3}$.

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NOTATION

A_o = temperature-independent constant
a = van der Waals attraction constant
b = van der Waals repulsion constant
n = number of carbon atoms in a normal alkane
P_c = critical pressure
R = gas law constant
T_c = critical temperature
V_c = critical volume
Z = number of electrons per molecule
Z_c = critical compressibility factor
ϵ_o = attractive force constant in a pair potential
σ_o = repulsive force constant in a pair potential

TABLE 2. COMPARISON OF EXPERIMENTAL[a] AND CALCULATED VALUES

					$T_cV_c^{2/3} \times 10^{-4}$			$P_cV_c^{5/3} \times 10^{-4}$			Z_c		
Formula	Name	T_c K	P_c, MN/m^2	V_c, cm^3/mol	Expt.	Calc. (Eq. 3)	% Error	Expt.	Calc. (Eq. 4)	% Error	Expt.	Calc. (Eq. 5)	% Error
C_3H_6O	Allyl alcohol	545.	5.71	203.	1.88	1.81	−3.7	4.00	4.00	0.0	0.256	0.266	+3.9
$C_3H_8O_3$	Glycerol	726.	6.7	255.	2.92	3.10	+6.2	6.9	6.4	−7.2	0.28	0.25	−11.
C_4H_4O	Furan	490.2	5.50	218.	1.78	1.82	+2.2	4.34	3.99	−8.1	0.294	0.264	−10.2
C_4H_7N	Butyronitrile	582.2	3.79	285.	2.52	2.53	+0.4	4.68	4.49	−4.1	0.223	0.214	−4.0
C_4H_8O	Methyl ethyl ketone	535.6	4.15	267.	2.22	2.23	+0.5	4.59	4.65	+1.3	0.249	0.251	+0.8
$C_4H_{10}O$	Isobutanol	547.7	4.30	273.	2.30	2.29	−0.4	4.94	4.80	−2.8	0.257	0.252	+1.9
$C_4H_{10}O$	*t*-butanol	506.2	3.97	275.	2.14	2.19	+2.3	4.62	4.76	+3.0	0.259	0.262	+0.8
$C_4H_{10}O_2$	1,2-Dimethoxyethane	536.	3.87	271.	2.24	2.32	+3.6	4.39	4.77	+8.7	0.235	0.247	+5.1
C_5H_8	1,2-Pentadiene	503.	4.07	276.	2.13	2.05	−3.8	4.76	4.55	−4.4	0.269	0.267	−0.7
C_5H_8	1-Pentyne	493.4	4.1	278.	2.10	2.08	−1.0	4.9	4.6	−6.1	0.28	0.27	−3.6
$C_5H_{10}O$	Methyl *n*-propyl ketone	564.0	3.89	301.	2.53	2.66	+5.1	5.26	5.58	+6.1	0.250	0.252	+0.8
$C_5H_{12}O$	1-Pentanol	586.	3.8	326.	2.78	2.78	0.0	5.9	6.0	+1.7	0.26	0.26	0.0
$C_6H_{10}O$	Cyclohexanone	629.	3.8	312.	2.89	3.06	+5.9	5.5	6.4	+16.	0.23	0.25	+8.7
$C_6H_{14}O$	Diisopropyl ether	500.0	2.88	386.	2.65	2.75	+3.8	5.89	5.54	−5.9	0.267	0.242	−9.4
$C_6H_{15}N$	Dipropyl amine	550.	3.1	407.	3.02	3.12	+3.0	6.9	7.1	+2.9	0.28	0.27	−3.6
C_8H_{10}	Ethyl benzene	617.1	3.61	374.	3.20	3.18	−0.6	7.01	6.90	−1.6	0.263	0.261	−0.8
C_8H_{16}	Ethyl cyclohexane	609.	3.03	450.	3.58	3.34	−6.7	8.01	7.14	−10.8	0.269	0.257	−4.5
C_9H_{10}	α-Methyl styrene	654.	3.40	397.	3.53	3.52	−0.3	7.29	7.40	+1.5	0.249	0.253	+1.6
$C_9H_{10}O_2$	Ethyl benzoate	697.	3.2	451.	4.10	4.15	+1.2	8.5	8.8	+3.5	0.25	0.26	+4.0
C_9H_{k12}	1,3,5-Trimethyl benzene	637.3	3.13	433.	3.65	3.67	+0.5	7.76	7.32	−5.7	0.256	0.240	−6.0
$C_{10}H_{22}$	*n*-decane	617.6	2.11	603.	4.41	4.29	−2.7	9.08	9.48	+3.9	0.247	0.265	+7.3
$C_{10}H_{15}N$	*n*-butyl aniline	721.	2.8	518.	4.65	4.56	−1.9	9.4	10.3	+6.4	0.25	0.27	+8.0

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[a] Critical constants obtained from (Reid et al., 1977).

Δ_i = group contribution to $T_cV_c^{2/3}$
δ_i = group contribution to $P_cV_c^{5/3}$
ρ = mass density
κ = isothermal compressibility
σ = surface tension

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