Correlations of Molecular Connectivity with Critical Volume and Acentricity

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Introduction

The ability to accurately estimate molecular properties based on molecular structure is important and central to many chemical investigations. Numerous correlations based on theory and/or empiricism have been applied to the estimation process.

Structural information based on a knowledge of chemical bonding, branching, size, and shape can be classified in the general category of topology. An approach to the quantitative evaluation of molecular structure referred to as a branching index has been described by Randic (1975). Molecular connectivity, which is a topological descriptor, was developed from the branching index and carries significant structural information to yield a close correlation with properties (Kier and Hall, 1976).

Petroleum scientists and engineers have defined a set of mathematical expressions that allow estimation of properties directly correlatable with critical properties by application of the principle of corresponding states (Reid et al., 1977; Smith and Watson, 1937; Watson and Nelson, 1933; Watson et al., 1935; Chueh and Prausnitz, 1967; Schick and Prausnitz, 1968; Grieves and Thodos, 1963; Storvick and Sandler, 1977). Deviations of property values predicted using the principle of corresponding states are caused by molecular size and shape. These deviations have been accounted for in part by the introduction of a new parameter termed the acentric factor, ω, developed by Pitzer (1955; Pitzer et al., 1955). The acentric factor is defined (Curl and Pitzer, 1958) as

$$\omega = -\log P_r - 1.000 \quad (\text{with } P_r = P/P_c \text{ at } T_r = 0.7) \tag{1}$$

According to Reid and Sherwood (1966), no generally reliable methods for estimation of critical volume have been suggested. Since the critical volume is difficult to measure (Chueh and Prausnitz, 1967) and since the acentric factor has proved to be valuable for improving the accuracy of corresponding state predictions (Passut and Danner, 1973), these properties are used herein to illustrate the potential of molecular connectivity for estimating properties.

Molecular Connectivity

A complete description of molecular connectivity, a calculated topological parameter, has been set forth by Kier and Hall (1976). Molecular connectivities have been used to correlate a variety of physicochemical properties, such as water solubility and boiling point (Hall et al., 1975), density (Kier et al., 1976), and partition coefficient (Murray et al., 1975) of many chemical compound classes. Linear relationships between molecular connectivity and gas chromatographic retention indices have been published for aliphatic alcohols, ketones, ethers, and esters (Kier and Hall, 1979), alkanes (Randic, 1975; McGregor, 1979), polycyclic aromatic hydrocarbons (PAH) (Kaliszan and Lamparczyk, 1978), and nitrated polycyclic aromatic hydrocarbons (nitro-PAH) (White, 1985; Doherty et al., 1984). Recently, White (1986) has used the concept of molecular connectivity to accurately predict the boiling point and heat of vaporization of over 100 planar PAH. Furthermore, it has been shown that in the case of planar PAH, the first-order molecular connectivity, $^1\chi$, is linearly related to both the van der Waals volume and the Hückel molecular orbital (HMO) delocalization energy (White, 1986).

The calculation of molecular connectivity is a fundamental treatment of the molecular structure based on a valence-weighted graph of the structural formula of a compound. First a skeletal structure of the compound is drawn. Each atom in the structure, except hydrogen, is assigned a valence delta, δ, which is equal to the number of outer-shell electrons (valence electrons) in the atom minus the number of hydrogens bonded to that atom. All molecular connectivity calculations are then based on this valence-weighted graph of the compound. The calculations are best illustrated by example. The calculations of $^0\chi$,

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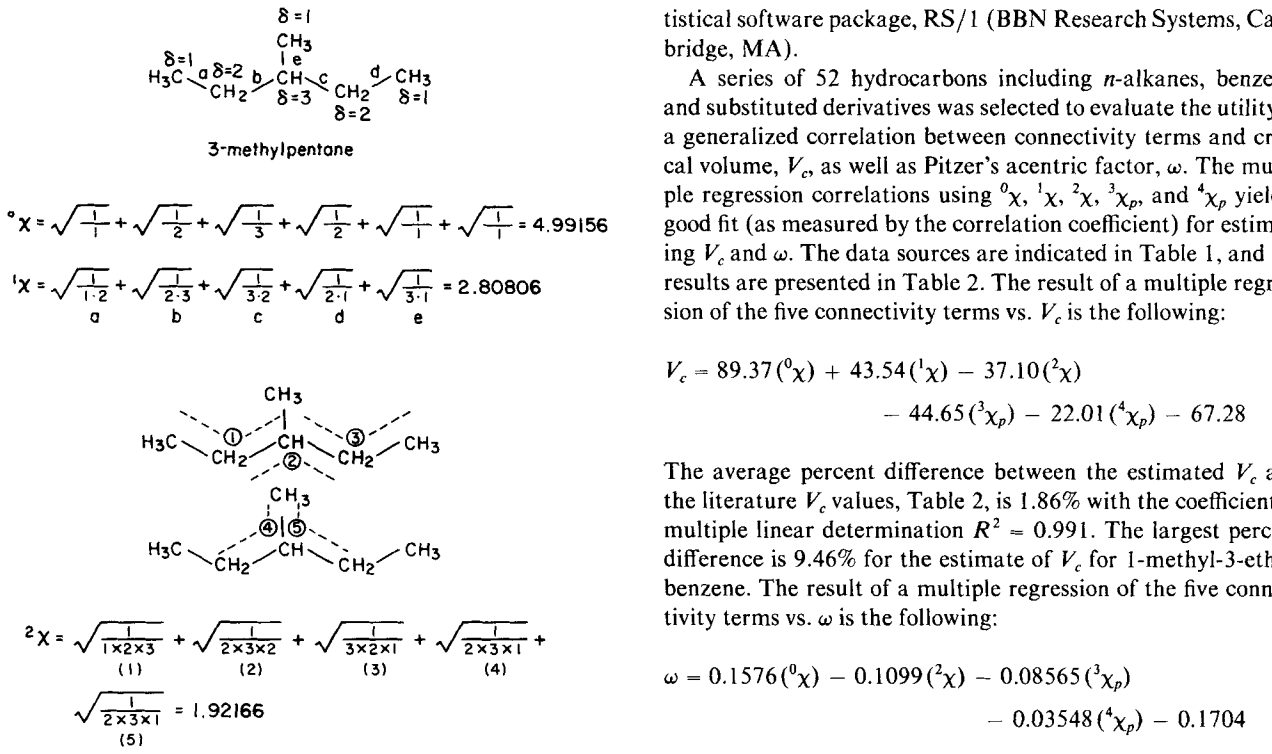

Figure 1. Example calculations of zero-, first-, and second-order molecular connectivities of 3-methylpentane.

zero-order, $^1\chi$, first-order, and $^2\chi$, second-order molecular connectivity are shown for 3-methylpentane in Figure 1. The simplest expression of the molecular structure, $^0\chi$, is equal to the sum of the reciprocal square roots of the valence deltas of the atoms taken one at a time. The $^0\chi$ calculation is essentially a carbon counter that is sensitive to the degree of saturation of an organic compound. Thus, the $^0\chi$ calculation for 3-methylpentane is the same as $^0\chi$ for 2-methylpentane, and for hexane. Bonding information results when the atoms are taken two at a time or one bond at a time for the calculation of $^1\chi$. The calculated $^1\chi$ is equal to the sum of the reciprocal square roots of the product of the valence deltas taken two at a time where the two atoms are bonded. Similarly, $^2\chi$ is the sum of the reciprocal square roots of the product of the valence deltas of the atoms taken three at a time where the terminal members of the triad are both bonded to the same central atom. The $^2\chi$ calculation gives information about branching in the molecular structure. For further definitions, examples, and tabulated values of connectivity terms, see Kier and Hall (1976).

Property Estimates with Connectivity

Thermodynamic properties, either measured or estimated by viable methods, have been tabulated by Reid et al. (1977). These values are sufficiently close to critically assessed experimental values to demonstrate the accuracy of estimates from correlations with molecular connectivity, and they were used in the correlations given here. All calculations of multiple regressions and the associated statistical parameters were performed on a PRO-350 computer (Digital Equipment Corp.) using a statistical software package, RS/1 (BBN Research Systems, Cambridge, MA).

A series of 52 hydrocarbons including *n*-alkanes, benzene, and substituted derivatives was selected to evaluate the utility of a generalized correlation between connectivity terms and critical volume, V_c, as well as Pitzer's acentric factor, ω. The multiple regression correlations using $^0\chi$, $^1\chi$, $^2\chi$, $^3\chi_p$, and $^4\chi_p$ yield a good fit (as measured by the correlation coefficient) for estimating V_c and ω. The data sources are indicated in Table 1, and the results are presented in Table 2. The result of a multiple regression of the five connectivity terms vs. V_c is the following:

$$V_c = 89.37(^0\chi) + 43.54(^1\chi) - 37.10(^2\chi) - 44.65(^3\chi_p) - 22.01(^4\chi_p) - 67.28 \quad (2)$$

The average percent difference between the estimated V_c and the literature V_c values, Table 2, is 1.86% with the coefficient of multiple linear determination $R^2 = 0.991$. The largest percent difference is 9.46% for the estimate of V_c for 1-methyl-3-ethylbenzene. The result of a multiple regression of the five connectivity terms vs. ω is the following:

$$\omega = 0.1576(^0\chi) - 0.1099(^2\chi) - 0.08565(^3\chi_p) - 0.03548(^4\chi_p) - 0.1704 \quad (3)$$

The average percent difference between the estimated and literature values for ω is 3.54% with $R^2 = 0.972$. The largest percent difference was 19.31% for the estimate of ω for 1-methyl-2-ethylbenzene. A method for estimating ω, proposed by Edmister (1958), is given in Eq. 4:

$$\omega = \{3/7\,[\theta/(1-\theta)]\log P_c\} - 1 \quad (4)$$

where $\theta = T_b/T_c$, and P_c is in atmospheres. Values calculated from experimental data for ω using Eq. 4 are compared in Table 2 with values estimated using the regression with molecular connectivity in Eq. 3. The average percent difference for ω predicted by Eq. 4 is 2.72; the largest percent difference is 19.53% for the estimate of ω for 2, 3-dimethylpentane. A parameter table, Table 3, is included to assist the reader in further evaluating the results of the linear multiple regressions.

Conclusions

The potential for estimating molecular and thermodynamic properties through correlations with molecular connectivity has been demonstrated. Both critical volume and Pitzer's acentric factor are difficult to measure, yet can be estimated with reasonable reliability for the 52 hydrocarbons investigated. Equation 4 predicts ω surprisingly well and should be very useful where good data exist for T_b, T_c, and P_c. Once a correlation with χ is established, however, only the structural formula is required to calculate the connectivity terms used in the regression equation. One problem with this method is the need for further developments in the connectivity approach to account for cis-trans isomerism, or chair-boat configurations, or other conformational contributions to the structural expression.

The goodness of fit required of a correlation with properties is obviously determined by the accuracy required for the estimated value of any property. Single linear regressions (equations for

Table 1. Multiple Linear Least-Squares Regression of Selected Hydrocarbons

Compound	Molecular Connectivities*					Crit. Vol.*	Pitzer Acentric Factor**
	$^0\chi$	$^1\chi$	$^2\chi$	$^3\chi_p$	$^4\chi_p$	V_c	ω
Ethane	2.00000	1.00000	—	—	—	148	0.098
n-propane	2.70710	1.41421	0.70710	—	—	203	0.152
n-butane	3.41421	1.91421	1.00000	0.50000	—	255	0.193
n-pentane	4.12132	2.41421	1.35355	0.70710	0.35355	304	0.251
n-hexane	4.82842	2.91421	1.70710	0.95710	0.50000	370	0.296
n-heptane	5.53553	3.41421	2.06066	1.20710	0.67677	432	0.351
n-octane	6.24264	3.91421	2.41421	1.45710	0.85355	492	0.394
n-nonane	6.94974	4.41421	2.76776	1.70710	1.03033	548	0.444
n-decane	7.65685	4.91421	3.12132	1.95710	1.20710	603	0.490
n-undecane	8.36395	5.41421	3.47486	2.20710	1.38389	660	0.535
n-dodcane	9.07106	5.91421	3.82841	2.45710	1.56061	713	0.562
n-tridecane	9.77817	6.41421	4.18196	2.70710	1.73746	780	0.623
n-tetradecane	10.48528	6.91421	4.53551	2.95710	1.91423	830	0.679
n-pentadecane	11.19239	7.41421	4.88906	3.20710	2.09102	880	0.706
2,2-dimethylpropane	4.50000	2.00000	3.00000	0.00000	0.00000	303	0.197
2-methylbutane	4.28445	2.27005	1.80209	0.81649	0.00000	306	0.227
2,2-dimethylbutane	5.20710	2.56066	2.91421	1.06066	0.00000	359	0.272
2,3-dimethylbutane	5.15470	2.64273	2.48803	1.33330	0.00000	358	0.270
2,2,3-trimethylbutane	6.07735	2.94337	3.52072	1.73205	0.00000	398	0.251
2-methylpentane	4.99156	2.77005	2.18252	0.86602	0.57735	367	0.267
3-methylpentane	4.99156	2.80806	1.92166	1.39384	0.28867	367	0.273
2,2-dimethylpentane	5.91421	3.06066	3.31066	1.00000	0.75000	416	0.282
2,3-dimethylpentane	5.86180	3.18073	2.52954	1.78202	0.47140	393	0.256
2,4-dimethylpentane	5.86180	3.12589	3.02339	0.94280	0.94280	418	0.306
3-ethylpentane	5.69867	3.34606	2.09077	1.73205	0.86602	416	0.310
2,2,3-trimethylpentane	6.78445	3.48138	3.67532	2.09077	0.61237	436	0.297
2,2,4-trimethylpentane	6.78445	3.41650	4.15863	1.02062	1.22474	468	0.303
2,3,3-trimethylpentane	6.78445	3.50403	3.49683	2.47417	0.40824	455	0.290
2,3,4-trimethylpentane	6.73205	3.55341	3.34715	2.10313	0.76980	461	0.317
2-methyl-3-ethylpentane	6.56891	3.71874	2.82059	1.99156	1.23148	443	0.330
3-methyl-3-ethylpentane	6.62132	3.68198	2.87132	2.56066	0.75000	455	0.304
2-methylhexane	5.69867	3.27005	2.53607	1.13502	0.61237	421	0.330
3-methylhexane	5.69867	3.30806	2.30209	1.47839	0.69692	404	0.324
2,2-dimethylhexane	6.62132	3.56066	3.66421	1.28033	0.70710	478	0.338
2,3-dimethylhexane	6.56891	3.68073	3.00997	1.88208	0.78867	468	0.346
2,4-dimethylhexane	6.56891	3.66390	3.14296	1.57069	0.97140	472	0.343
2,5-dimethylhexane	6.56891	3.62589	3.36504	1.32136	0.66666	482	0.352
3,3-dimethylhexane	6.62132	3.62132	3.26776	1.88388	0.85355	443	0.321
3,4-dimethylhexane	6.56891	3.71874	2.77106	2.25930	0.80473	466	0.338
3-ethylhexane	6.40577	3.84606	2.47119	1.85462	1.10517	455	0.361
2,2,5-trimethylhexane	7.49156	3.91650	4.49318	1.47168	0.72168	519	0.357
2-methylheptane	6.40577	3.77005	2.88962	1.38502	0.80258	488	0.378
3-methylheptane	6.40577	3.80806	2.65564	1.74740	0.75671	464	0.369
4-methylheptane	6.40577	3.80806	2.68252	1.56294	1.12993	476	0.369
Benzene	3.46410	2.00000	1.15470	0.66666	0.38490	259	0.212
Methylbenzene	4.38675	2.41068	1.65470	0.94045	0.53437	316	0.257
Ethylbenzene	5.09385	2.97134	1.83915	1.25107	0.71371	374	0.301
n-propylbenzene	5.80096	3.47134	2.23 59	1.38149	0.93335	440	0.344
1,2,3-trimethylbenzene	6.23205	3.24401	2.51680	1.87546	0.89779	430	0.390
1,2,4-trimethylbenzene	6.23205	3.23803	2.58771	1.66241	0.89134	430	0.390
1,3,5-trimethylbenzene	6.23205	3.23205	2.66506	1.36602	1.20235	433	0.398
1-methyl-2-ethylbenzene	6.01650	3.38801	2.28003	1.64215	1.00677	460	0.294
1-methyl-3-ethylbenzene	6.01650	3.38202	2.34260	1.49073	0.93206	490	0.360
1-methyl-4-ethylbenzene	6.01650	3.38202	2.33915	1.52885	0.82378	470	0.322
1,4-diethylbenzene	6.72361	3.94268	2.52360	1.83946	1.01066	480	0.403

*From Keir and Hall (1976) or calculated. These values are presented with sufficient significant figures to be useful for correlation with more exact data.
**From Reid et al. (1977).

Table 2. Prediction of Critical Volume V_c and Pitzer's Acentric Factor ω Using Molecular Connectivities and Eq. 4 for 52 Selected Hydrocarbons

Compound	V_c*	Predicted by χ* V_c†	Predicted by χ* %Δ**	ω*	Predicted by χ* ω‡	Predicted by χ* %Δ**	Predicted by Eq. 4 ω	Predicted by Eq. 4 %Δ**
n-pentane	304	316.6	−4.14	0.251	0.2572	−2.48	0.257	−2.39
n-hexane	370	374.0	−1.09	0.296	0.3032	−2.43	0.299	−1.01
n-heptane	432	430.8	0.27	0.351	0.3481	0.84	0.352	−0.29
n-octane	492	487.6	0.89	0.394	0.3929	0.27	0.396	−0.51
n-nonane	548	544.4	0.66	0.444	0.4378	1.39	0.447	−0.68
n-decane	603	601.2	0.30	0.490	0.4827	1.49	0.484	1.22
n-undecane	660	657.9	0.30	0.535	0.5276	1.38	0.526	1.68
n-dodecane	713	714.8	−0.25	0.562	0.5725	−1.86	0.560	0.36
n-tridecane	780	771.6	1.08	0.623	0.6174	0.91	0.604	3.05
n-tetradecane	830	828.4	0.19	0.679	0.6622	2.47	0.625	7.95
n-pentadecane	880	885.2	−0.59	0.706	0.7071	−0.16	0.680	3.75
2,2-dimethylpropane	303	310.7	−2.53	0.197	0.2089	−6.06	0.201	−2.03
2-methylbutane	306	311.1	−1.68	0.227	0.2368	−4.31	0.233	−2.64
2,2-dimethylbutane	359	354.1	1.37	0.272	0.2389	12.14	0.238	12.50
2,3-dimethylbutane	358	356.6	0.39	0.270	0.2542	5.84	0.254	5.93
2,2,3-trimethylbutane	398	396.0	0.49	0.251	0.2519	−0.37	0.255	−1.59
2-methylpentane	367	367.1	−0.02	2.67	0.2817	−5.49	0.282	−5.62
3-methylpentane	367	361.2	1.58	0.273	0.2754	−0.87	0.277	−1.47
2,2-dimethylpentane	416	410.5	1.31	0.282	0.2854	−1.21	0.292	−3.55
2,3-dimethylpentane	393	407.6	−3.71	0.256	0.2949	−15.22	0.300	−19.53
2,4-dimethylpentane	418	417.7	−0.08	0.306	0.3068	−0.26	0.307	−0.33
3-ethylpentane	416	413.7	0.55	0.310	0.3188	−2.84	0.306	1.29
2,2,3-trimethylpentane	436	447.4	−2.62	0.297	0.2939	1.03	0.301	−1.35
2,2,4-trimethylpentane	468	460.9	1.50	0.303	0.3107	−2.54	0.306	−0.99
2,3,3-trimethylpentane	455	442.4	2.77	0.290	0.2879	0.70	0.293	−1.03
2,3,4-trimethylpentane	461	454.0	1.51	0.317	0.3151	0.59	0.318	−0.32
2-methyl-3-ethylpentane	443	461.0	−4.06	0.330	0.3405	−3.18	0.334	−1.21
3-methyl-3-ethylpentane	455	447.4	1.67	0.304	0.3115	−2.47	0.307	−0.99
2-methylhexane	421	426.1	−1.22	0.330	0.3299	0.02	0.333	−0.91
3-methylhexane	404	419.3	−3.78	0.324	0.3233	0.22	0.327	−0.93
2,2-dimethylhexane	478	470.8	1.50	0.338	0.3355	0.74	0.364	−7.69
2,3-dimethylhexane	468	466.9	0.22	0.346	0.3448	0.36	0.349	−0.87
2,4-dimethylhexane	472	471.2	0.18	0.343	0.3503	−2.13	0.345	−0.58
2,5-dimethylhexane	482	479.1	0.59	0.352	0.3581	−1.72	0.357	−1.42
3,3-dimethylhexane	443	457.9	−3.38	0.321	0.3222	−0.38	0.323	−0.62
3,4-dimethylhexane	466	460.3	1.23	0.338	0.3381	−0.04	0.342	−1.18
3-ethylhexane	455	473.9	−4.17	0.361	0.3697	−2.40	0.366	−1.39
2,2,5-trimethylhexane	519	524.4	−1.05	0.357	0.3646	−2.12	0.358	−0.28
2-methylheptane	488	482.6	1.10	0.378	0.3744	0.96	0.378	0.00
3-methylheptane	464	477.8	−2.97	0.369	0.3707	−0.45	0.371	−0.54
4-methylheptane	475	476.8	−0.17	0.369	0.3703	−0.35	0.373	−1.08
Benzene	259	248.3	4.13	0.212	0.1779	16.11	0.221	−4.25
Methylbenzene	316	314.6	0.45	0.257	0.2395	6.79	0.273	−6.23
Ethylbenzene	374	377.5	−0.94	0.301	0.2977	1.09	0.310	−2.99
n-propylbenzene	440	437.1	0.66	0.344	0.3466	−0.76	0.350	−1.74
1,2,3-trimethylbenzene	430	434.0	−0.94	0.390	0.3426	12.16	0.371	4.87
1,2,4-trimethylbenzene	430	440.8	−2.51	0.390	0.3533	9.42	0.380	2.56
1,3,5-trimethylbenzene	433	444.1	−2.55	0.398	0.3591	9.77	0.402	−1.01
1-methyl-2-ethylbenzene	460	437.8	4.82	0.294	0.3508	−19.31	0.304	−3.40
1-methyl-3-ethylbenzene	490	443.7	9.46	0.360	0.3595	0.14	0.331	8.06
1-methyl-4-ethylbenzene	470	444.5	5.43	0.322	0.3605	−11.95	0.332	−3.11
1,4-diethylbenzene	480	507.3	−5.68	0.403	0.4184	−3.82	0.405	−0.50

*From Table 1.
**%Δ = (Literature–Predicted)/Literature × 100, calculated before rounding off predicted value.
†$V_c = 89.37\ (^0\chi) + 43.54\ (^1\chi) - 37.10\ (^2\chi) - 44.65\ (^3\chi_p) - 22.01\ (^4\chi_p) - 67.28$.
‡$\omega = 0.1576\ (^0\chi) - 0.1099\ (^2\chi) - 0.08565\ (^3\chi_p) - 0.03548\ (^4\chi_p) - 0.1704$.

Table 3. Parameters for Multiple Linear Regressions Used to Estimate V_c and ω

Variable	Coefficient Value	T-Value	Significance Level
	Critical Volume V_c, Eq. 2		
${}^0\chi$	89.37	4.7	0.001
${}^1\chi$	43.54	3.1	0.003
${}^2\chi$	−37.10	−3.2	0.003
${}^3\chi_p$	−44.65	−5.2	0.0001
${}^4\chi_p$	−22.01	−2.1	0.04
	Pitzer's Acentric Factor ω, Eq. 3		
${}^0\chi$	0.1576	16.5	0.0001
${}^2\chi$	−0.1099	−12.6	0.0001
${}^3\chi_p$	−0.08565	−8.8	0.0001
${}^4\chi_p$	−0.03548	−2.5	0.02

these regressions are not presented in the text) of ${}^1\chi$ vs. V_c and ω for the series of 52 hydrocarbons in Table 1 yield estimates for these properties that are not as reliable as estimates from the multiple regressions; however, they may be adequate for some applications. If an average percent deviation of 3.2% in V_c and of 6.2% in ω can be tolerated, the generalized single linear regression correlation (including the 52 hydrocarbons) may be used with some confidence. The use of higher order connectivity terms may be expected to reduce the error in the estimate from a generalized multiple-fit regression. In the present cases, the average percent deviation in V_c decreases from 3.2 to 1.86% and in ω decreases from 6.2 to 3.54% when equations resulting from multiple regressions (Eqs. 2 and 3) were used instead of single linear regressions for the 52 hydrocarbons. It is not expected, however, that various homologous series that give dissimilar single regressions (different slopes and intercepts) for the same property may ever be estimated with significant accuracy from a generalized regression regardless of the number of molecular connectivity terms included in the multiple regression. The *n*-alcohols yield a single regression fit vs. V_c that is similar to the single regression fit for hydrocarbons. Thus, V_c can be estimated from a generalized multiple regression fit including *n*-alcohols and hydrocarbons. However, the single regression fit of ω for *n*-alcohols is not similar to that found for hydrocarbons, and a generalized regression including these compound types would not be expected to yield accurate estimates of ω.

Molecular connectivities are easily calculated and are amenable to implementation in computerized methods of property estimation. As it is presently understood, the concept of molecular connectivity can make a significant contribution to available methods for estimation of physical, chemical, and thermodynamic properties. Based on these preliminary results, broad application of the concept of molecular connectivity to engineering sciences is expected.

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Notation

P = vapor pressure
P_c = critical pressure, atm (SI conversion: kPa = atm × 101.325)
P_r = reduced pressure, P/P_c
T = temperature, K
T_b = boiling point, K
T_c = critical temperature, K
T_r = reduced temperature, T/T_c
V_c = critical volume, cm³/gmol

Greek letters

ω = Pitzer's acentric factor
δ = valence of atom minus the number of bonds to hydrogen
χ = the generalized connectivity
${}^0\chi$ = zero-order molecular connectivity
${}^1\chi$ = first-order molecular connectivity
${}^1\chi^v$ = first-order valence molecular connectivity; superscript v designates a calculation for a molecule containing either a heteroatom or an unsaturated bond
${}^2\chi$ = second-order molecular connectivity
${}^3\chi_p$ = third-order path molecular connectivity. In the third order, cluster and chain terms are possible for the first time; subscript p specifies that this is a path term determined in a manner similar to the ${}^2\chi$ calculation.
${}^4\chi_p$ = fourth-order path molecular connectivity. In the fourth order, all types of subgraphs are possible; subscript p specifies that this is a path term determined in a manner similar to the ${}^3\chi_p$ calculation.
$\theta = T_b/T_c$.

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