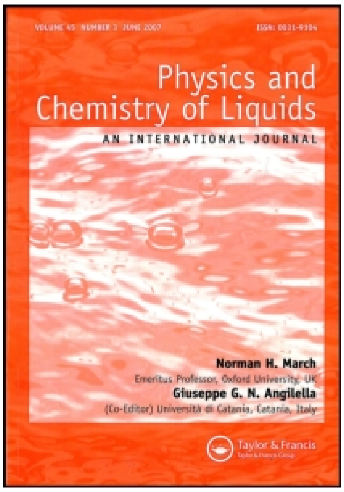

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Property correlations for chlorofluoro carbons and alternatives using structural parameters

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Because of their wide ranging applications, the properties of chlorofluoro carbons (CFCs) and their alternatives are studied and correlated in terms of the parameters derived from molecular structures. The properties correlated are of physical, thermodynamic and transport in nature. The input parameters include molar refraction (R_M), molecular connectivity (χ) and van der Waals equation coefficients (a and b), all of which are easily estimated from molecular structures. The correlations developed for the 11 properties studied showed average absolute deviations ranging between 3.5% and 13.7%. The correlation coefficients calculated for the equations developed ranged between 0.9557 and 0.9921.

Keywords: correlations; chlorofluoro carbons; structural parameters

1. Introduction

Application of chlorofluorocarbons (CFCs) and their alternatives in the areas of refrigeration, fire extinguishing, aerosol, propellant, microelectronics and chemical vapour deposition is well known. The deleterious influence of CFCs on ozone depletion in stratosphere resulting in global warming and health hazards led to the attempts on finding alternatives to these compounds. Such compounds should be non toxic, stable and cheap. Because of the non-participation of the fluorine atom in the ozone-destruction reactions, CFC-alternatives should ideally contain hydrogen, fluorine and carbon atoms. Since such HFC compounds could not be identified, partially fluorinated alkanes like hydrofluorochlorocarbons (HCFCs) and brominated derivatives (halons) are being synthesised presently.

The presence of halogen, carbon and hydrogen atoms and the way in which they are interconnected influences the molecular properties of CFCs and alternates. CFCs have high densities and low boiling points, viscosities and surface tensions. Fluoro hydrocarbons have higher refractive indices, dielectric constants and densities than their fluorocarbon counter parts. Due to the constraints like the lack of finances and the personnel for the property generation, the analysis based on the quantitative structure–property relationships (QSPR) is often resorted to. Such an approach is based on the assumption that the structure of a compound determines its properties

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by means of the molecular descriptors. A large majority of the molecular descriptors used in the QSPR analysis are often derived from program packages using complex quantum chemical calculations. Hence, in the present article, we report the property relationships derived from molecular structures. The properties selected for study are important to process development and equipment design.

2. Properties selected for study

Because of their use in the process equipment design, properties studied are: the critical pressure (P_C), critical temperature (T_C), normal boiling point (T_b), critical volume (V_C), heat of vapourisation at normal boiling point (ΔH_{Vb}, kcal mol^{-1}), melting point (T_m, K), liquid heat capacity (C_{PL}), liquid thermal conductivity (λ_L), surface tension (σ_L), kinematic viscosity (ν_L) and the natural logarithm of the solubility of the compound in water, all at 25°C.

2.1. *Critical properties and normal boiling and melting points*

The critical properties form the foundation to the widely employed principle of corresponding states applied to property correlations. They are also used in the determination of acentric factor, one of the most commonly used third parameters employed to represent the non-ideal nature of compounds. Equilibrium, thermal and volume property correlations also need the critical properties.

At a given temperature, the vapour pressure of a liquid provides a measure of the concentration of the molecules in the vapour phase above the liquid surface. As the temperature of the liquid is increased, its vapour pressure increases. The temperature at which the liquid vapour pressure equals 1 atm characterises its behaviour and is termed as the normal boiling point (T_b). T_b depends on the intermolecular forces and can be related to structural parameters like molar refraction (R_M) and parachor [P]. T_b is also used in the estimation of critical temperature (T_c). The solid state of substances is characterised by the regularity of arrangement of its elements in its crystal lattice. These elements oscillate around the equilibrium positions around the lattice points and the amplitude of oscillation increases with rise in temperature. At a temperature called the melting point (T_m), the lattice disintegrates, wherein the elements abandon their fixed positions in the lattice, causing the change in the state of substance from solid to liquid. Normal melting point is the temperature at which the substance melts at a pressure of 1 atm. Methods of estimating T_m are less accurate, compared to those of T_b and T_c. This could be attributed to uncertainties involved in the estimation of the entropy of melting which figures in the definition of T_m as the ratio of the enthalpy of melting to the entropy of melting.

2.2. *Heat of vapourisation, heat capacity and surface tension*

The process of vapourisation or the volatility of a liquid is dependent on the strength of intermolecular forces of attraction. As the temperature is increased, the kinetic energy of molecules increases giving rise to the escape of more molecules from the liquid surface. The enthalpy of vapourisation of a liquid (ΔH_V) is the amount of heat needed to convert a unit mass without changing the temperature. ΔH_V is a function of temperature and decreases with increasing temperature. It is used as an input in estimating some other physico-chemical properties and also and in the development of chemical spill models. ΔH_{V} is generally estimated from the well-known Clausius–Clapeyron equation or its modified forms. Heat of vapourisation at normal boiling point (ΔH_{Vb}), the most commonly used version of ΔH_{V} is calculated by several methods like those based on group contributions, or the models using properties like the dipole moment, density and critical volume. The heat of vapourisation values at other temperatures can be estimated from ΔH_{Vb}, employing Watson's equation using normal boiling point, molecular mass and specific gravity per mole of mass as inputs.

Heat capacity of a substance is the heat absorbed to change its temperature by 1°. As the temperature of the liquid is increased, its heat capacity increases. However, this increase is insignificant over normal temperature ranges. Heat capacities of gases and liquids are required in the calculation of several thermo chemical and engineering parameters. Most of the estimation methods are dependent on structural contributions at 298 K, and are accurate to within ±10% of the experimental values. The experimental values of heat capacities are usually fitted by polynomial functions of temperature.

Surface tension of a compound is a measure of the work to be done to expand the surface of a liquid by unit area. It results from the imbalance of the forces acting between the molecules in the bulk of the liquid and its surface. It is usually expressed in dynes cm^{-1}. For most of the organic liquids the values of surface tension range between 25 and 40 dynes cm^{-1}, exceptions being water (72 dynes cm^{-1}) and polyhydric alcohols (up to 65 dynes cm^{-1}). It plays an important role in the absorption of aqueous emulsions on solid surfaces and chemical spill spreads on land or water. Methods of estimating surface tension of liquids (σ_{L}) depend on parachor calculated from group contributions and properties like critical temperature and pressure, liquid density and acentric factor. These estimation methods are usually accurate to within 5–15% from the measured values.

2.3. *Transport properties*

Thermal conductivity serves as an index to the ease with which the heat of conduction propagates through solids, liquids or vapours. It is the proportionality constant in Fourier's law of heat conduction and is usually expressed in the units of $\mathrm{W\,m^{-1}\,K}$ or $\mu\mathrm{cal\,m^{-1}\,s^{-1}\,K^{-1}}$. The polar compounds have conductivities up to three times of their non-polar counter parts. Typical values of liquid thermal conductivities (λ_{L}) range between 250 and 400 $\mu\mathrm{cal\,m^{-1s}\,K^{-1}}$ λ_{L} increases linearly with temperature. Pressure has little influence on λ_{L}. Inter molecular forces play dominant role in the estimation of thermal conductivities of liquids. Most of the λ_{L} estimation methods depend on properties like critical temperature, normal boiling point, heat capacity and densities. Some methods use structural parameters in addition to the physical properties. While typical errors for these methods are about 5% for non-polar compounds, polar compounds are represented by errors as large as 15%.

Viscosity is considered to be a measure of resistance to the fluid flow and can be defined as the ratio of the shear stress to the velocity gradient in the direction normal to that of the flow. For normal liquids, viscosity is expressed in centipoises. It is an important input in the design calculations, quality control of materials flow and pumpability of liquids or spreading of chemical spills. For most of the organic liquids, viscosity ranges between 0.3 cP and 20 cP. Liquid viscosities decrease exponentially with temperature. Hence, majority of liquid viscosity estimation methods depend on the familiar Andrade or Antoine equations or their modified forms. Some of such methods use structural contributions combined with physical properties like density, dipole moment, normal boiling point, acentric factor and critical temperature and pressure. Because of complex forces involved in the liquid structure, the viscosity estimation methods are less accurate than those developed for other properties and typical errors for such methods range between 10% and 20%.

2.4. *Solubility*

Solubility of chemicals in water is one of the most important factors in aquatic life. They are also biodegradable in surface water and sewage treatment plants. Solubilities are generally expressed in parts per million (by mass), gram per kilogram and as mass percents in some cases. In general, compounds of similar substances dissolve into one another. Examples for this principle include the miscibility of non polar liquids like oil in gasoline and dissolution of polar–polar systems like water and alcohols. Solubility is one of the properties difficult to model with sufficient accuracy and usually the logarithmic values of solubilities are chosen for study. Most of the solubility estimation methods based on properties like water–octanol partition coefficients, pH, etc. show large deviations. In contrast, models using the structure–dependent parameters provide estimates accurate to within 25–30% of the true values.

3. Input parameters used in the study

Because of their wider application in property correlations, significance and the ease with which they are calculated from the group contributions, we have used molar refraction (R_M), molecular connectivity of zero, first and second orders (${}^0\chi, {}^1\chi, {}^2\chi$) and the van der Waal's equation constants a and b in the present study.

3.1. *Molar refraction*

Molar refraction is a measure of dispersion forces. It is an extensively used parameter in the correlations of various properties like the activity coefficients at infinite dilution, surface tension, viscosity, thermal conductivity, standard heats of formation, combustion and Gibbs free energy of formation, toxicities of pesticides and drug activities. These properties are determined by the intermolecular forces. Dutt and Prasad [1] discussed the application of R_M in the correlation of such properties. R_M can be calculated by using the well-known Lorentz–Lorenz equation

$$R_M = \frac{n^2 - 1}{n^2 + 1} \frac{\text{Molecular weight}}{\text{Density}} \tag{1}$$

where n represents the refractive index of the substance. Molar refraction is an additive and constitutive property estimated readily from the atomic and group

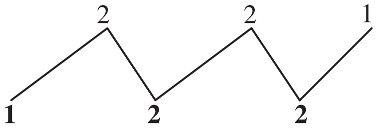

Figure 1. Hydrogen suppressed valency graph for the compound $CH_3CH_2CH_2CH_2CH_2CH_3$ (C_6H_{14}).

contributions proposed by several investigators, the most popular being that of Dreisbach [2]. R_M is used in the property correlations and quantitative structure activity relationship (QSPR) analysis. R_M remains nearly constant with changes in temperature and pressure by virtue of the density factor Equation (1) that balances these effects. Pauling and Pressman [3], in one of the earlier studies on the interaction of small benzoic acid molecule with the macro molecular antibodies suggested a dominant role for the dispersion forces represented by molar refraction of substituents.

3.2. *Molecular connectivity indices*

Kier and Hall [4] developed a valence-based topological parameter named molecular connectivity to provide information on the connectivity of the atoms by bonds within a molecule. They have developed a method of calculating the molecular connectivities of different orders (zero, first, second etc.) by expanding Randic's formulation for hydrogen-suppressed graph in describing hydrocarbons. For example, the hydrogen-suppressed graph of a hydrocarbon by the group connectivity as $CH_3CH_2CH_2CH_2CH_2CH_3$ can be represented by the hydrogen-suppressed graph showing simple vertex connectivities as in Figure 1.

In Figure. 1, the hydrogen-suppressed valencies δ of the group CH_3 $(4-3=1)$ and CH_2 $(4-2=2)$ are shown at the vertices. For such a graph, Kier and Hall [4] have calculated the connectivity indices ${}^{m}\chi_t$ as sum of terms over all the distinct connected sub groups:

$$ {}^{m}\chi_t = \sum_{j=1}^{n_m} {}^{m}S_j, \tag{2} $$

where n_m is the number of type t sub groups of order m. The term ${}^{m}S_j$ is defined in terms of the reciprocal square root of the vertex valencies δ by the expression

$$ {}^{m}S_j = \pi_{j=1}^{m+1}(\delta_i)_j^{-1/2}, \tag{3} $$

where j denotes the particular set of edges that substitute the graph. Thus the molecular connectivity of zeroth-order is given as

$$ {}^{0}\chi = \sqrt{\frac{1}{1.1}} + \sqrt{\frac{1}{2.1}} + \sqrt{\frac{1}{2.1}} + \sqrt{\frac{1}{2.1}} + \sqrt{\frac{1}{2.1}} + \sqrt{\frac{1}{1.1}} = 4.829. \tag{4} $$

Similarly, molecular connectivities of first and second orders could be estimated as

$$^{1}\chi = \sqrt{\frac{1}{1.2}} + \sqrt{\frac{1}{2.2}} + \sqrt{\frac{1}{2.2}} + \sqrt{\frac{1}{2.2}} + \sqrt{\frac{1}{1.2}} = 2.914 \tag{5}$$

$$^{2}\chi = \sqrt{\frac{1}{1.2.2}} + \sqrt{\frac{1}{2.2.2}} + \sqrt{\frac{1}{2.2.2}} + \sqrt{\frac{1}{2.2.1}} = 1.707. \tag{6}$$

Kier and Hall [4] have applied molecular connectivity indices as powerful tools in developing many meaningful property correlations. They have extended their approach to the molecules containing heteroatoms like halogens, nitrogen and oxygen. The computed molecular connectivity indices for such molecules have been used by them in a variety of structural activity/property relationships.

3.3. *van der Waals constants*

van der Waals proposed one of the earliest equations to describe the non ideal behaviour of the gases by incorporating the constants a and b in the ideal gas law. The proposed equation is

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \tag{7}$$

where p, v and T denote the pressure, molar volume and temperature. The constants a and b are introduced as corrections to the pressure and volume of the molecule considered. The constant a depends on the inter atomic forces within the molecule. The constant b nearly equals four times the occupied volume of the molecules contained in a mole of the gas. Both the constants a and b are shown to be constitutive and additive. Bretsznajder [5] reported the atomic contributions towards the values of $\sqrt{a} \times 10^2$ and $b \times 10^5\,\mathrm{cm}^3$.

4. The method

The method followed in the present study includes:

1. The data collected on the properties of CFCs and their alternatives [6] are plotted versus. the parameters derived from their molecular structures.
2. For any set of compounds, each of the properties studied versus. the structural parameter data has been fitted by the mathematical models provided in the standard Excel program.
3. The model yielding the lowest average absolute deviation for any set of compounds for each of the property studied has been chosen for reporting the results.

5. Results and discussion

The input parameters derived from molecular structures used in the present work for various property correlations are: molar refraction (R_{M}), molecular connectivity indices ($^{\circ}\chi$, $^{1}\chi$, $^{2}\chi$), van der Waals equation coefficients (a and b) in addition to the

Table 1. Inputs and the percent average absolute deviations ($\bar{e}$) obtained for critical properties and normal boiling point of fluorohydrocarbons using Equations (10–13).

	Input parameters							% Dev			% Dev			% Dev			
Compound	R_M (Cc mol^{-1})	$^\circ\chi$	$^1\chi$	$_2\chi$	$100 \times a$	$10^5 \times b$	Pc (atm)	Lyd^{++}	Equation (10)	T_c (K)	Lyd	Equation (11)	V_c (cc mol^{-1})	Lyd	Equation (12)	T_b (K)	% Dev Equation (13)
CCl_3F	21.385	4.500	2.000	1.995	22.2	455.0	43.50	−5.0	8.7	471.2	0.2	3.9	247.0	0.4	−0.1	296.97	−2.6
CCl_2F_2	16.556	4.500	2.000	2.016	19.7	410.0	40.60	−11.0	2.2	385.2	0.1	−3.1	217.0	0.9	0.5	243.36	−6.8
$CClF_3$	10.245	4.500	2.000	1.796	17.2	365.0	38.20	−15.0	−4.0	303.1	0.1	−8.8	181.0	−1.7	3.5	191.75	−0.3
$CBrF_3$	14.051	4.500	2.000	1.964	18.8	430.0	39.10	−28.4	−1.6	340.2	−1.0	−8.7	200.0	−2.5	0.2	215.59	−8.7
CF_4	6.528	4.500	2.000	2.043	–	–	36.96	−13.9	−7.4	227.5	−0.7	−24.2	141.0	−8.5	−6.8	145.19	2.3
$CHCl_2F$	16.379	3.577	1.732	1.712	17.9	369.0	51.00	−0.9	3.5	451.7	0.4	11.1	197.0	−5.1	7.8	282.07	−0.1
$CHClF_2$	10.880	3.577	1.732	1.630	15.4	324.0	49.12	5.7	−0.2	369.2	−0.3	7.7	165.0	−6.7	10.4	232.04	6.0
CHF_3	6.561	3.577	1.732	1.746	12.9	279.0	47.70	1.7	−3.2	299.1	−1.7	3.4	133.0	−38.1	8.8	191.12	17.9
C_2Cl4F2	31.105	7.000	3.300	4.522	33.6	710.0	34.00	3.2	6.0	551.2	−0.6	3.6	370.0	4.3	3.4	365.95	7.2
C_2Cl_3F3	26.028	7.000	3.250	4.567	31.1	665.0	33.70	2.8	5.2	487.3	0.4	2.9	325.0	0.0	−0.2	320.72	2.6
C_2Cl_2F4	21.140	7.000	3.250	4.548	28.6	620.0	32.20	−0.7	0.7	418.9	0.1	0.3	293.0	−0.3	−0.6	276.92	−1.4
C_2Br_2F4	26.973	7.635	3.250	4.544	31.8	750.0	34.00	−8.3	−0.6	487.7	−1.0	0.7	329.0	−2.1	3.5	320.41	0.7
C_2ClF_5	16.320	7.000	3.250	4.619	26.1	575.0	30.80	−3.6	−3.8	353.2	−0.2	−2.6	259.0	−1.5	−2.1	234.45	−5.2
C_2F_6	11.440	7.000	3.250	4.729	23.6	530.0	29.40	−6.0	−8.7	292.9	−0.4	−4.4	232.0	−3.1	−0.8	194.95	−6.2
$\bar{e}$								7.6	4.0		0.5	6.1		5.4	3.5		4.8

Note: Lyd. ++: Lydersen method.

Table 2. Percent average absolute deviations ($\bar{e}$) calculated for ΔH_{vb}, T_m, C_{pL}, λ_L, σ_L, ν_L and S_L using Equations (14–20).

Compound	ΔH_{vb} (Kcal mol^{-1})	% Dev Equation (14)	T_m (K)	% Dev Equation (15)	C_{pL} (Cal mol^{-1})	% Dev Equation (16)	$\lambda_L \times 1000$	% Dev Equation (17)	σ_L Dynes cm^{-1}	% Dev Equation (18)	ν_L (cm^2 s^{-1})	% Dev Equation (19)	1000 × Ln(S)	% Dev Equation (20)
CCl_3F	5.9206	−2.9	162.15	2.1	28.573	−20.6	50.0	2.5	18.0	−15.3	0.2863	−9.5	2.3979	−10.1
CCl_2F_2	4.8001	−4.9	115.15	−13.2	28.051	−7.5	41.0	−5.7	9.0	−6.2	0.1983	9.6	3.3322	9.2
$CClF_3$	3.7052	1.5	92.15	−8.2	–	–	20.0	−14.0	–	–	0.1502	12.0	2.1972	12.4
$CBrF_3$	4.2263	−6.1	105.15	−11.7	30.934	8.3	25.0	−3.7	4.0	−16.9	0.0975	−16.8	3.4012	17.5
CF_4	2.8594	0.9	89.15	5.3	–	–	–	–	–	–	–	–	0.4055	−4.4
$CHCl_2F$	5.9550	0.1	138.15	−4.0	26.348	−0.3	63.0	9.7	18.0	1.7	0.2489	7.7	6.8565	10.3
$CHClF_2$	4.4910	1.5	113.15	2.6	24.141	15.9	52.0	16.9	8.0	27.9	0.1926	7.6	5.7038	−7.4
CHF_3	4.0067	19.6	117.95	24.9	10.873	−19.6	8.0	−23.8	–	–	–	–	4.6052	0.7
$C_2Cl_4F_2$	7.5417	5.8	299.15	22.7	45.41	5.3	40.0	−4.0	23.0	2.6	0.7405	4.8	4.7875	−10.6
$C_2Cl_3F_3$	6.5714	2.8	238.15	10.3	40.849	−4.1	38.0	6.7	19.0	3.1	0.4345	−0.5	2.8332	−8.6
$C_2Cl_2F_4$	5.5563	−2.5	178.15	−11.4	41.531	0.6	34.0	−5.4	12.0	−2.2	0.2610	2.2	2.5649	−8.4
$C_2Br_2F_4$	6.4958	4.5	162.65	−33.3	43.132	0.9	27.0	−0.7	18.0	15.3	0.3329	−35.0	–	–
C_2ClF_5	4.6511	−7.9	167.15	−10.7	44.006	10.7	26.0	−33.6	5.0	−45.5	0.2014	25.0	1.7918	−14.3
C_2F_6	3.8601	−12.1	172.55	0.0	–	–	26.54	6.8	–	–	–	–	–	–
$\bar{e}$		5.0		11.4		8.6		10.4		13.7		11.1		11.0

total number of atoms (N_t) and the number of fluorine (N_f), halogen (N_{hal}), hydrogen (N_h) and carbon (N_c)atoms.

For each of the several properties of the present study, the percent deviation (e) between the experimental and calculated values defined by

$$e = 100\left(\frac{P_{\exp} - P_{\mathrm{cal}}}{P_{\exp}}\right) \tag{8}$$

and the average absolute deviation ($\bar{e}$) obtained over a set of N compounds

$$\bar{e} = \frac{\Sigma IeI}{N} \tag{9}$$

are listed in Tables 1 and 2.

The inputs used for the property correlations and the average absolute deviations estimated for the critical properties and normal boiling point using Equations (10–13) are reported in Table 1. The table also lists the percent deviations (e) calculated for each of the compounds studied. Equations (10–13) are

$$\begin{gathered} P_c = 2.1072^0\chi^2 - 27.333^0\chi + 120.04 \\ N = 14; \quad \bar{e} = 4.0\%; \quad R = 0.9629 \end{gathered} \tag{10}$$

$$\begin{gathered} T_{\mathrm{C}} = 11.393R_M - 39.025\mathrm{Ln}(^2\chi) + 236.013 \\ N = 14; \quad \bar{e} = 6.1\%; \quad R = 0.9574 \end{gathered} \tag{11}$$

$$\begin{gathered} V_{\mathrm{C}} = N_{\mathrm{hal}}\left[\frac{R_{\mathrm{M}}}{^0\chi} + 27\right] \\ N = 14; \quad \bar{e} = 3.5\%; \quad R = 0.9921 \end{gathered} \tag{12}$$

$$\begin{gathered} T_{\mathrm{b}} = 85.065\left(\frac{R_{\mathrm{M}}}{^1\chi}\right)^{0.5693} + 57.799N_{\mathrm{C}} - 84.68 \\ N = 14; \quad \bar{e} = 4.8\%; \quad R = 0.9681 \end{gathered} \tag{13}$$

(N_{C} = Number of carbon atoms).

Table 2 presents the percent deviations by which the properties other than P_c, T_c, V_c and T_b as represented by Equations (14–20). The equations are:

$$\begin{gathered} \Delta H_{\mathrm{vb}} = 0.9873\frac{R_{\mathrm{M}}}{^0\chi} + 1.3127N_{\mathrm{C}} + 0.0875 \\ N = 14; \quad \bar{e} = 5.0\%; \quad R = 0.9674 \end{gathered} \tag{14}$$

$$\begin{gathered} T_{\mathrm{m}} = 91.703\mathrm{Exp}\left(0.0674\frac{RM}{\chi}\right) + 86.144N_c - 116.01 \\ N = 14; \bar{e} = 11.4\%; R = 0.9830 \end{gathered} \tag{15}$$

$$\begin{gathered} C_{\mathrm{PL}} = 0.0008\left(\sqrt{a} \times 100\right)^3 - 0.13\left(\sqrt{a} \times 100\right)^2 \\ + 6.115\left(\sqrt{a} \times 100\right) - 45.967 \\ N = 11; \quad \bar{e} = 8.6\%; \quad R = 0.9582 \end{gathered} \tag{16}$$

$$\lambda_L = 2.944\left(\frac{N_F}{N_C}\right)^2 - 4.5317\left(\frac{N_F}{N_C}\right) + 0.011R_M^3 - 0.6966R_M^2 + 12.84R_M - 7.372 \tag{17}$$

$$N = 13; \quad \bar{e} = 10.4\%; \quad R = 0.9557$$

$$\sigma_L = -0.0301\left(\frac{R_M N_C}{N_F}\right)^2 + 1.7477\left(\frac{R_M N_C}{N_F}\right) - 2.8492 \tag{18}$$

$$N = 10; \quad \bar{e} = 13 \cdot 7\%; \quad R = 0.9653$$

$$\nu_L = 0.0016R_M^2 - 0.0437R_M - 0.0521\left(\frac{N_F}{N_C}\right) + 0.5683 \tag{19}$$

$$N = 11; \quad \bar{e} = 11.1\%; \quad R = 0.9678$$

(N_F = Number of fluorine atoms)

$$\mathrm{Ln}(S \times 1000) = 18.131\left({}^1\chi\right)^3 - 118.27\left({}^1\chi\right)^2 + 239.07\,{}^1\chi - 0.4626\left(\frac{R_M}{{}^0\chi}\right)^2 + 3.541\left(\frac{R_M}{{}^0\chi}\right) - 153.8478 \tag{20}$$

$$N = 12; \quad \bar{e} = 11.0\%; \quad R = 0.9879.$$

Equations (10–20), using the structural parameters as inputs could be found to provide reasonable representation of the data as seen from the high values of the correlation coefficients (R) ranging between 0.9557 and 0.9921. That the percent of average absolute deviations ($\bar{e}$) calculated for these equations ranging between 3.5 and 13.7 are comparable to those of various property correlations reported in the literature can be supported by the following discussion.

The percentage deviations (e) calculated for Equations (10–12) representing the critical property data are reported in Table 1, along with those obtained by the application of Lydersen's method [6]. The contents of the Table 1 also include the input property data. A comparison of the errors (e) and the average absolute deviations ($\bar{e}$) reported in Table 1 for Equations (10–12) and those given by Lydersen's method reveals better representation of the P_C and V_C by Equations (10–12) compared to Lydersen's method as seen from the lower $\bar{e}$-values(4.0% vs. 7.6% for P_C and 3.5% vs 5.4% for V_c). In the case of critical temperature, Lydersen's, method proved superior to the present method using Equation (11), the corresponding $\bar{e}$-value being 0.5% for Lydersen's method compared to 4.8% for Equation (11). The superiority of Lydersen's method over Equation (11) could be mainly attributed to using the experimental values of T_b in addition to the molecular group contributions used in calculations. The percent deviations and the percent average absolute deviations ($\bar{e}$) reported for Equations (11), (13) and (15) in the case of T_C, T_b and T_m, show that larger errors are encountered in the estimation of T_m. This could be attributed to the uncertainties involved in the determination of the entropy of melting, which figures in the definition of the melting point as the ratio of the enthalpy of melting to the entropy of melting.

The heat of vapourisation at normal boiling point (ΔH_{vb}) data has been represented by Equation (14) with an $\bar{e}$ of 5.0% as seen from the Table 2. Most of the ΔH_{vb} –estimation methods reported in the literature [7, 8] are found to provide $\bar{e}$-values of 2–3%. Better accuracy yielded by such methods is due to the use of the experimental values of properties like T_b, T_c and P_c as inputs. The $\bar{e}$ of 8.6% reported for Equation (16) in the case of the liquid heat capacity (C_{PL}) is comparable to the average value of 7.1% over 22 compounds reported for a method based on bond-contributions [6]. For a set of 20 compounds, Poling et al. [8] also have reported an average deviation of 6.4% for a group contribution method compared to 5.9% yielded by a corresponding states method using critical temperature and acentric factor and liquid heat capacity at 298 K. Most of the methods of estimating surface tension of pure liquids discussed [7–9], needing T_c, P_c, T_b and densities reported average errors ranging between 5% and 17%. In general, polar compounds showed larger errors compared to non polar compounds. Equation (18), yielding an average deviation of 13.7% falls within the range of 5–17% mentioned. Because of the more complex mechanisms involved, transport properties like viscosity, thermal conductivity and diffusivity are more difficult to model and their estimation methods show larger errors compared to thermo physical properties. Liquid viscosity estimation methods reported by Reid et al. [7], using group contributions and a number of inputs like liquid density, T_c, P_c and heat of vapourisation have yielded average absolute errors ranging between 14.2% and 21.2%, when tested with the data of about 35 liquids. In the present case, a comparable estimate of 11.1% has been provided by Equation (19). Several liquid thermal conductivity estimation methods described in references [7–9], using several properties like specific heat, T_b, T_c, P_c, V_c and those using T_b, T_c and molecular weight in addition to group contributions are reported to yield errors averaging between 6% and 10%, compared to the average deviation of 10.4% given by Equation (17) in the present case. Solubility of compounds in solvents is an important property needed in the waste water disposal equipment like sewage treatment plants. Water is the most commonly used solvent. Lyman et al. [10] described most of the water solubility estimation methods using properties like water-octanol partition coefficients and pH. These methods showed very large deviations. In contrast, models using the structure-dependent parameters provided estimates accurate to 25–30% of the true values. Representation of the solubility data in the present case by the Equation (20) showing an average deviation of 11.0% falls well below the prescribed range (25–30%).

6. Conclusions

The methodology used in the present work using easily estimated structural parameters provided the correlations with reasonable accuracies, as seen from the average deviations ranging between 3.5% and 13.7%. The correlation coefficients for the equations developed are reasonably high, ranging between 0.9557 and 0.9921. The percent average absolute deviations of the correlations developed on the various properties of study are comparable to the literature values.

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