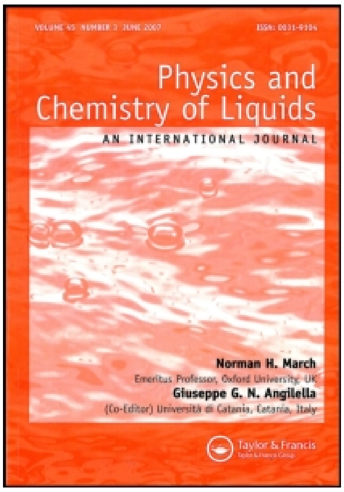

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N. V. K. Dutt[a]; D. H. L. Prasad[a]
[a] Chemical Engineering Division Indian Institute of Chemical Technology, Hyderabad, India

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ATOMIC AND STRUCTURAL CONTRIBUTIONS TO MOLAR REFRACTION AND EXTENSION TO MIXTURES

N. V. K. DUTT and D. H. L. PRASAD*

Chemical Engineering Division
Indian Institute of Chemical Technology
Hyderabad - 500 007, India

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Molar refraction of pure liquids has been calculated for well over a thousand substances, from an evaluated set of atomic and structural contributions. On an overall basis, the calculated values are in agreement with the experimental data, showing an average absolute deviation of 0.6%, and an average of maximum deviations of 2.1%. The effect of temperature on molar refraction has also been studied and found to show an average absolute deviation of 0.8%.

Molar refraction of binary liquid mixtures has been estimated from the molar refraction of pure liquids (calculated from atomic and structural contributions) and the mole fraction by applying the linear rule. The results for 25 randomly studied mixtures showed an average absolute deviation of 0.4%.

The effect of estimating molar refraction of pure liquids (or liquid mixtures) as described above on the values of the various physico-chemical properties, calculated employing molar refraction (or its equivalent for polar substances - molar polarization at the critical temperature) is found to be less than 2.8%.

Keywords: Molar refraction; atomic and structural contributions; physico-chemical properties

1 INTRODUCTION

Based on some of the theoretical considerations [1, 2], the numerical value of molar polarization, calculated at the critical temperature

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*Author for correspondence.

(P_{MC}) has been proposed as a new third parameter [3] in the theorem of corresponding states, for the correlation of thermodynamic properties in 1970. Since that time, P_{MC} and/or its equivalent for non-polar substances R_M (the molar refraction) has been used as a characteristic property, in the development of simple and reliable relationships for many physico-chemical properties including: viscosity of pure gases and mixtures [4–6], viscosity of pure liquids and mixtures [7], thermal conductivity of organic liquids [8], Prandtl number of gases [9], latent heat of vaporization at the normal boiling point [10], liquid heat capacity [11], second virial coefficient [12, 13], surface tension of liquids [14], infinite dilution activity coefficient of hydrocarbons in water [15], standard heats of combustion, formation and Gibbs free energy [16–18], boiling, melting and critical temperatures of fatty acids [19], and even the activity of drugs [20] and pesticides [21]. Essentially, the data on molar refraction (R_M) in the case of non-polar substances and dipole moment (μ) and critical temperature (T_C) , additionally in the case of polar substances, are required for the determination of the characteristic property or properties for use in any of the generalized correlations just mentioned for various thermophysical and thermochemical properties. Experimental values of R_M are usually calculated from the measurements on the density and refractive-index at the same temperature. Dreisbach [22] made such calculations (at a few temperatures each) for a large number of hydrocarbons and related compounds. Frequently it may not be possible to determine the experimental value due to non-availability of the materials, facilities etc. The aim here is to suggest a practically useful method, based on atomic and structural contributions for the estimation of molar refraction for use when experimental data are not available. An experimental-cum-analytical study has also been carried out to extend the ideas to mixtures.

2 PRESENT WORK

The best method of determining the values of molar refraction (R_M) and molar polarization (P_M) is from the measured values of refractive-index (n), density (ρ) and the dielectric constant ($\in$) at any temperature, and the definitions of the characteristic properties.

$$R_M = (n^2 - 1) / (n^2 + 2) \quad (M/\rho) \tag{1}$$

$$P_M = (\varepsilon - 1) / (\varepsilon + 2) \quad (M/\rho) \tag{2}$$

where M is the molecular weight. The equation

$$P_M = R_M + (4\pi N \mu^2 / 9kT) \tag{3}$$

with N as the Avogadro's number and k as the Boltzmann constant can be used to calculate the dipole moment (μ) for use in the calculation of the characteristic property - molar polarization at the critical temperature from

$$P_{MC} = R_M + P_P \tag{4}$$

where

$$P_P = (4\pi N \mu^2 / 9kT_C) \tag{5}$$

When the parameters required in the calculation of the characteristic property (P_{MC}) are not available, or experimental measurements cannot be carried out for any reason, estimation methods become handy. The properties R_M and μ can be calculated respectively from atomic and structural contributions, and vectorial summation of the moments of the bonds. Methods for the estimation of T_C are also available [23, 24]. In view of the wide variety of applications in the correlations mentioned in the introduction, it is thought desirable to:

i) study in depth the estimation of R_M of pure liquids from atomic and structural contributions,

ii) estimate the effect of R_M on the calculation of physico-chemical properties, and

iii) test the application of the linear rule in mole fraction for the estimation of R_M of mixtures.

After a careful scrutiny and evaluation of the atomic and structural contributions to R_M proposed by: Eisenlohr, Vogel and several others mentioned in Bresznajder [23], and elsewhere, the values given in Table I have been selected and recommended for use. A summary of comparison of the values of R_M calculated from the recommended

TABLE I Contributions of Atoms and Groups for the Calculation of Molar Refraction

Atom / Group	*Contribution to R_M*
Argon	4.200
Bromine	8.865
Carbon (single bond and alone)	2.592
Carbon (single bond)	2.418
Carbon (double bond)	1.733
Carbon (triple bond)	2.398
Carbon (conjugated)	1.270
Chlorine	5.967
Fluorine	0.950*
Hydrogen	1.100
Iodine	13.900
Krypton	6.370
Nitrogen (in aliphatic primary amine)	2.450
Nitrogen (in aromatic primary amine)	3.210
Nitrogen (in aliphatic secondary amine)	2.650
Nitrogen (in aromatic secondary amine)	3.590
Nitrogen (in aliphatic tertiary amine)	3.000
Nitrogen (in aromatic tertiary amine)	4.360
Nitrogen (in hydroxyl amine)	2.480
Nitrogen (in hydrazine)	2.470
Nitrogen (in aliphatic cyanide)	3.050
Nitrogen (in aromatic cyanide)	3.790
Nitrogen (in aliphatic oxime)	3.390
Nitrogen (in primary amine)	2.650
Nitrogen (in secondary amide)	2.270
Nitrogen (in tertiary amide)	2.710
NO (in nitrile)	5.910
NO (in nitroso-amine)	5.370
NO_2 (in alkyl nitrile)	7.440
NO_2 (in alkyl nitrate)	7.590
NO_2 (in nitroparaffin)	6.720
NO_2 (in nitroaromatic)	7.300
NO_2 (in nitramine)	7.510
Oxygen (in hydroxyl)	1.525
Oxygen (in ether)	1.643
Oxygen (in ketone)	2.211
Oxygen (in ester)	1.640
Sulfur (in SH)	7.690
Sulfur (in RSR)$^+$	7.970
Sulfur (in RCNS)$^+$	7.910
Sulfur (in RSSR)$^+$	8.110
Xenon	10.160

$^+$ R stands for alkyl group

* This value is for one fluorine atom attached to carbon. The value of 1.1 is to be used for each fluorine atom in polyfluorides.

atomic and structural contributions with experimental data for 1290 substances, belonging to 34 series is given in Table II. The overall average absolute deviation is 0.6% and average of maximum deviations for the different series is 2.1%. To cite an example, the R_M of benzyl alcohol, C_6H_5-CH_2-OH, can be calculated by summing up: seven contributions of carbon (7 × 2.418), eight contributions of hydrogen (8 × 1.100), one contribution of oxygen in OH (1 × 1.525) and

TABLE II Comparison of the values of Molar Refraction calculated from Atomic and structural Contributions with Experimental data given in Dreisbach [22]

Series	*Number of compounds*	*Percent Average*	*Absolute Deviation Maximum*
Alkyl-benzenes	120	0.90	1.72
Halo-benzenes	26	0.61	1.65
Styrenes	15	0.81	4.65
Thia-alkyl-benzenes	8	0.82	2.45
Thiophenes	18	0.72	1.69
Alkyl-naphthalenes	30	0.65	1.03
Tetrahydronaphthalenes	24	0.80	1.32
Decahydronaphthalenes	8	0.47	1.68
Aromatic phenols	5	1.34	1.96
Thiophenols	6	0.68	0.89
Aromatic amines	9	0.46	1.30
Aromatic ketones	3	1.65	2.87
Aromatic alcohols	6	0.41	1.03
Cyclopentanes	50	0.48	0.82
Cyclopentenes	13	0.42	1.37
Thiacyclopentenes	7	0.05	0.29
Thiacyclopropanes	3	1.75	2.01
Cyclohexanes	47	0.39	0.98
Cyclohexenes	12	0.25	0.75
Thiacyclohexenes	4	0.55	0.76
Alkanes	175	0.52	1.77
Haloalkanes	23	0.68	3.22
Alkenes	185	0.59	2.64
Haloalkenes	21	1.12	2.27
Diolefins	29	1.17	3.48
Alkynes	38	0.23	0.61
Fluoroalkanes	61	0.65	5.29
Chloroalkanes	75	0.37	1.42
Bromoalkanes	82	0.48	3.66
Iodoalkanes	43	0.45	4.53
Aminoalkanes	101	0.39	6.05
Alkylcyanides	21	0.55	2.99
Thia and Dithia-alkanes	18	0.50	1.64
Organic acids	4	0.11	0.15
OVER ALL	1290	0.58	2.09

three contributions of double bonds (3 × 1.733) to be 32.45, very favourably comparing with the experimentally determined value of 32.41. Experimental values of R_M at different temperatures (details not given in this paper) varied from those calculated from atomic and structural contributions with an average absolute deviation of 0.8%.

The maximum deviations likely to occur due to the use of R_M estimated from atomic and structural contributions instead of its experimental value in the application of the generalized correlations for various physico-chemical properties are summarized in Table III. The table also notes the percent average absolute deviation in the estimation of the particular property while applying the R_M and/or P_{MC} based correlation. While detailed comparisons have been presented in the original papers, it can be mentioned here that the R_M and/or P_{MC}

TABLE III Maximum Contribution to Percent Average Absolute Deviation due to the Calculation of Molar Refraction from Atomic and Structural Contribution on Various Physico-chemical Properties

Property [Reference]	*Percent* Average in *the Method Proposed*	*Absolute Deviation* Likely contribution due to R_M *estimation*
Compressibility factor [1]	1.8	0.2
Fugacity coefficient [2]	2.5	0.3
Isothermal variation of enthalpy [2]	6.9	0.8
Isothermal variation of heat capacity [2]	16.4	1.6
Derivative compressibility factors [2]	4.0	0.5
Velocity of sound in compressed gases [2]	6.4	0.7
Viscosity of gases [4–6]	7.0	0.3
Viscosity of liquids [7]	30.0	1.5
Thermal conductivity of liquids [8]	2.0	0.5
Prandtl number of gases	5.0	0.6
Heat of vaporization at the normal boiling point [10]	3.7	0.5
Second virial coefficient of gases [12, 13]	7.0	0.6
Surface tension of liquids [14]	5.6	0.4
Infinite dilution activity coefficient of hydrocarbons in water [15]	6.1	1.0
Standard heat of combustion [16]	5.7	1.5
Standard heat of formation [17]	7.0	2.2
Standard Gibbs free energy [18]	3.8	2.0
Boiling point of fatty acids [19]	1.7	0.5
Melting point of fatty acids [19]	5.7	0.8
Critical temperature of fatty acids [19]	1.4	0.4
Activity of drugs [20]	21.3	2.0
Activity of pesticides [21]	21.0	2.8

based methods give results either comparable or better than the methods of the same complexity recommended in the literature [24].

To study the applications to mixtures, experimental measurements on mixture refractive-index and density measurements of this work, as well as from the literature, have been analysed. The results, summarised in Table IV, show that the mixture molar-refractions can be calculated from the values of R_M of pure liquids estimated from the atomic and structural contributions, through the use of linear rule in mole fractions, with an average absolute deviation of 0.43%.

TABLE IV Application of Linear Rule in Mole Fraction to the Molar Refraction Calculated from Atomic and Structural Contributions and Comparison with Mixture Experimental Molar Refraction Data

Mixture (No. of Data Points)	Source of *Experimental Data*	% Average *Absolute Deviation*
Acetone + water (9)	[26]	0.64
Acetone + 1, 2-Dichloroethane (4)	*	0.22
Acetone + 1, 1, 1-Trichloroethane (4)	*	0.66
Isobutanol + Methyl-isobutyl-ketone (9)	[25]	0.18
n-Hexadecane + 1-Chlorobutane (6)	[27]	0.17
n-Hexadecane + 1-Chloropentane (6)	[27]	0.18
n-Hexadecane + 1-Chlorohexane (10)	[27]	0.22
n-Hexadecane + 1-Chloro-octane (7)	[27]	0.25
n-Hexadecane + 1-Chlorodecane (10)	[27]	0.36
n-Hexadecane + 1-Chlorododecane (8)	[27]	0.13
n-Hexadecane + 1-Chlorotetradecane (9)	[27]	0.13
n-Hexadecane + 1-Chlorohexadecane (7)	[27]	0.14
n-Hexadecane + 1-Chlorooctadecane (7)	[27]	0.25
1, 2-Dibromoethane + Methylbenzene(9)	[28]	0.44
1, 2-Dibromoethane + 1, 2-Dimethylbenzene (9)	[28]	0.61
1, 2-Dibromoethane + 1, 3-Dimethylbenzene (9)	[28]	0.83
1, 2-Dibromoethane + 1, 4-Dimethylbenzene (9)	[28]	0.75
1, 2-Dichloroethane + 1, 1, 1-Trichloro-ethane (4)	*	0.27
1, 2-Dichloroethane + 1, 1,2,2-Tetrachloroethane (4)	*	0.34
1, 1, 1-Trichloroethane (+ 1,1,2,2-Tetrachloroethane (4)	*	0.65
1, 1, 1-Trichloroethane + p-Xylene (4)	*	1.41
1, 1, 1-Trichloroethane + Benzene (4)	*	0.40
1, 1, 1-Trichloroethane + Toluene (4)	*	0.90
1, 2-Dichloroethane + Toluene (4)	*	0.24
1, 2-Dichloroethane + p-Xylene (4)	*	0.49
OVERALL (25 Mixtures at 164 Data Points)		0.43

* This work

3 RESULTS AND DISCUSSION

The results, summarized in Tables II–IV, show that the calculation of R_M from atomic and structural contributions is a good option because the estimation of R_M for pure substances from atomic and structural contributions, and the use of linear rule in mole fraction in the case of mixtures (additionally) have provided values in good agreement with experimental data. The method of estimating R_M recommended has been shown to have very little effect on the calculation of the various physico-chemical properties related to R_M or P_{MC}. The scheme is therefore recommended for use in the estimation of thermophysical properties for design work.

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