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THE ESTIMATION OF MODIFIED NON-SPECIFIC SOLUBILITY PARAMETER OF LIQUIDS BY CORRELATION WITH REFRACTIVE INDEX AND MOLAR ENERGIES OF VAPORIZATION

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ABSTRACT

For apolar liquids, the modified non-specific solubility parameter δ' has been correlated with a form of the Lorentz-Lorenz refractive index function and the molar energy of vaporization per unit molar volume, and two expressions have been developed. Using one form of these expressions, and by introducing the contribution of dipole moment per unit molar volume, expressions for the estimation of modified non-specific solubility parameter of polar liquids have also emerged. These expressions however, have different values of the constants C and K for different families of liquids in order to yield estimated modified non-specific solubility parameter δ'_{est}; not significantly different from the experimental values, δ'_{exp}, for liquids. The K values obtained from a consideration of energy of vaporization per unit molar volume, for polar, associated liquids (alcohols) and polar non-associated liquids seem to lend support for the proposition of structural differences in these groups of liquids.

KEYWORDS: Solubility parameter, refractive index, vaporization energy.

INTRODUCTION:

The concept of modified non-specific solubility parameter, was introduced in the mid-1980s to supersede the previously popular solubility parameter concept., Defined as consisting of dispersion and dipolar forces, and including induced dipoles, it forms part of a new predictive equation for the solubility of solid alkanes, solid nitriles, tertiary amines, polycyclic aromatic hydrocarbons, chlorinated benzenes, biphenyls, polymers and drugs. (Haulait-Pirson et al 1987, Huyskens et al 1985, 1994, Ruelle et al 1991, 1993, 1992.1992,1993, Uzomah 1994) The predictive equation emphasizes the importance of placing entropy and stability constants for substrate-substrate and substrate-solvent hydrogen bonding that describe the hydrophobicity of the system, and has proved superior to the previously popular Hansen's three parameter predictive equation (Uzomah et al 1994,) . Part of the predictive equation (Haulait-Pirson et al 1987, Huyskens et al 1985, 1994, Ruelle et al 1991, 1992, 1992, 1993, 1993, Uzomah et al 1994, involving modified non-specific solubility parameter, δ', is given in eq. (1).

$$D = - \phi^2_B v_B (\delta'_B - \delta'_S)^2/RT \quad ....(1)$$

when D describes that changes in the non-specific cohesion forces when a solute dissolves in a solvent, v_B is molar volume, ϕ_b is volume fraction of substrate in solution, R and T are gas constant and Kelvin temperature respectively. Methods of determination of modified non-specific solubility parameter have been described by Huyskens (1985).

Ruelle et al (1991, 1992, 1992, 1993, 1993), have suggested that this non-specific cohesion term can be represented by the Scatchard - Hildebrand expression, the only difference being that in this case dispersion and dipolar forces only are involved while hydrogen bonding forces are excluded. The negative sign of this expression comes from the fact that the cohesion forces lead to a lowering of the enthalpy. Again, the D term is one of the two terms in the predictive equation that are affected significantly by change in temperature. In particular, as the temperature increases the D term becomes less negative and hence the volume fraction, ϕ_B, of solute dissolved increases.

The original data on modified non-specific solubility parameter from Huyskens et al (1987) laboratory were limited and some values have been revised. Recently Ruelle et al (1991, 1992, 1992, 1993, 1993), using the concept of thermodynamics of mobile order, extended the use of the predictive equation to the solubility of drugs, aromatic hydrocarbons, chlorinated benzenes, and biphenyls while high-lighting the hydrophobic effects of associated liquids in solubility and in addition, up-dated the list of modified non-specific solubility parameter values of over 100 solvents. From Huyskens laboratory came simple correlation expressions with high degree of accuracy between modified non-specific solubility parameters and molar volumes of liquids with the same molecular property e.g. alkanes, ketones, esters and ethers. The significance of such correlations which give estimated values for liquids greater than 95% accuracy for the groups of liquids studied is that they give estimated data very close to the experimental data. This allows for correct estimation of modified non-specific solubility parameter of liquids in the same group with the same molecular property whose modified non-specific solubility parameters are not known. Of

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the over 100 liquids whose modified non-specific solubility parameter are known, only about 60 liquids have their solubility parameter determined experimentally. It is therefore a worthwhile venture to dispose on correlations which would enable the calculation of their values from other solvent characteristics

CORRELATION BETWEEN THE MODIFIED NON-SPECIFIC SOLUBILITY PARAMETER OF APOLAR SOLVENTS AND THEIR REFRACTIVE INDEX AND MOLAR ENERGY OF VAPORIZATION

The cohesion force in apolar solvents is determined by the dispersion forces. In the gas phase at a given pressure, the intermolecular attraction between two apolar solvents is largely determined by the polarizability of the molecules. Assuming that the polarizability of gaseous molecules does not differ significantly from that in the liquid phase, it is therefore proper to assume that the modified non-specific solubility parameter, δ'_S of these liquids should be related to the polarizability. Huyskens (1989,) had earlier developed a relationship between the one-term Hildebrand solubility parameter and one form of Lorentz-Lorenz refractive index term $(n^2_D - 1)/(n^2_D + 2)$ where n_D is the refractive index of solvent for the sodium line for apolar solvents. In the same contribution, the same author (Huyskens, 1989), related the molar energy of vaporization ΔH_v, to another function of Lorentz - Lorenz refractive index term $[n^2_D-1)/[n^2_D+2)]^2$ for 30 apolar liquids. The modified non-specific solubility parameter δ'_s is known not to be significantly different from Hildebrand parameter for apolar liquids. It is thus justified to relate the modified non-specific solubility parameter δ'_S to the refractive index term and the molar energy of vaporization ΔH_v. The experimentally determined modified non-specific solubility parameter for 17 apolar liquids is correlated with the refractive index, n_D and the molar energy of vaporization per unit molar volume in expressions (2)and (3).

$\delta'_s = 61.4(\pm 3.3)(n^2_D - 1)/(n^2_D + 2)$ (MPa½) ....(2)

$\delta'_s = 58.6(\pm 6.8)\ \Delta H_v/V_s$ (Mpa½) ......(3)

Table 1 lists the experimental modified no specific solubility parameter, δ'_s (MPa½), molar energ of vaporization ΔH_v(kJmol^{-1}), molar volume (cm³mol-¹) and refractive index of sodium line n_D for 1 apolar liquids. Table II compares the estimated valu of modified non-specific solubility parameter, δ'_S fro the expressions (2) and (3) with the experimental values.

For polar solvents and as suggested by (Huysker (1998) the contribution of the polarity of solve molecule to the correlation is taken care of by th addition of a function of the dipole moment to get th expressions (4) and (5).

$\delta'_s = a + b\ (n^2_D - 1)/(n^2_D + 2) + cy/V_S$ .....(4)

$\delta'_s = P + Q\ \Delta H_v/V_S \quad + K\ \mu_g/V_S$ .....(5)

were a. b.c. P, Q and K are constants, and μ_g is the ga dipole moment of liquids. The procedure consists first plotting the experimental modified solubili parameter δ'_S for the 17 apolar liquids separately a functions of

(1) refractive index $(n^2_D-1)/(n^2_D + 2)$

(ii) molar energy of vaporization $\Delta H_v/V_S$

to obtain by mean square method, expressions and (7) respectively:

$\delta'_s = 4.97 + 41.28\ (n^2_D-1)/(n^2_D + 2)$ .....(6)

Regression coefficient r = 0.962)

$\delta'_s = 8.01 + 28\ 86\ \Delta H_v/V_S$ ....(7)

(regression coefficient r = 0.974)

Having established such relationships which allow t contribution of dispersion force from refractive ind and the molar energies of vaporization to the modifi non-specific solubility parameter, δ^1_s, it is therefo possible to estimate these contributions to oth solvents where dipole and hydrogen- bonding a operative. Huyskens (1989) had previously defined t residual energy of vaporization, ΔH_{res}, of these solve

Table 1

The Refractive Indices n_D^{25}, Molar Volume V_s, Experimental Modified Non-specific Solubility Parameter of some Apolar Solvents (μ_S =0.0).

Liquid	n_D^{25}	V_S (b) (cm^{3}mol^{-1})	ΔH_v (exp)(c) (KJ mol^{-1})	δ'(exp)(b) (Mpa½)
n-Pentane	1.3560	116.1	23.95	14.18
n-Hexane	1.3735	131.6	29.07	14.56
n-Heptane	1.3861	147.5	34.07	14.66
n-Octane	1.3957	163.5	39.01	14.85
n-Nonane	1.4037	179.5	43.96	15.07
n-Decane	1.4085	195.9	48.89	15.14
n-Dodecane	1.4198	228.6	58.81	15.34
n-Tetradecane	1.4284	260.3	68.69	15.49
n-Pentadecane	1.4297	277.7	73.67	15.56
n-Hexadecane	1.4327	294.1	78.61	15.61
n-Heptadecane	1.4351	310.7	83.73	15.67
2,2,4-Me_3 Pentane	1.3915	166,1	35,73	14,52
Carbon tetrachloride	1.4610	97.1	30.30	17.04
Benzene	1.4990	89.4	31.40	18.95
P-Xylene	1.4948	123.9	50.00	17.30
1,3,5-Me_3 Benzene	1.4973	139.8	45.00	17.00
Cyclohexane	1.4248	108.8	29.16	15.43

(a) From Ref (13) For the values given at 20°C a correction factor of 0.9975 was applied to obtain the value at 25°C

(b) From Ref (6)

(c) The molar energies of vaporization were calculated from the molar enthalpies of vaporization taken from Ref. (13).

TABLE 2

The Experimental and the Estimated Modified Non-specific Solubility parameter δ'_s from Equations (4) and (5) Respectively for Apolar Solvents.

Solvent	δ'_s (exp) MPa$^{1/2}$	δ'_s(MPa$^{1/2}$)- Eq. (4)	δ'_s(MPa$^{1/2}$) Eq. (5)
n-Pentane	14.18	13.99	13.96
n-Hexane	14.56	14.39	14.39
n-Octane	14.66	14.67	14.68
n-Nonane	14.85	14.88	14.90
n-Decane	15.07	15.06	15.08
n-Decane	15.14	15.17	15.21
n-Tetradecane	15.34	15.41	15.44
n-Pentadecane	15.49	15.60	15.63
n-Hexadecane	15.56	15.63	15.67
n-Heptadecane	15.61	15.69	15.72
2,2,4 - Me_3 - Pentane	14.52	14.79	14.22
Carbon tertrachloride	17.04	16.30	17.01
Benzene	18.95	17.09	18.15
P -xylene	17.30	17.02	17.56
1,3,5 -Me_3 Benzene	17.00	17.06	17.30
Cyclohexane	15.43	15.52	15.14

with specific interactions by the difference between the molar energy of vaporization ΔH_v and the molar energy of dispersion, $\Delta H_{disp.}$

From the definition of modified non-specific solubility parameter: consisting of dispersive and dipolar forces only, it is evident that the larger value of the modified non-specific solubility parameter for these polar solvents relative to those of apolar solvents with same molar volume is attributable to the influence of dipole moments of such liquids. For polar liquids therefore, one tries to obtain the values of the constants c and k of equations (4) and (5). This is done by taking the average gaseous dipole moment, μ_g, of the homologous series of these organic solvents: eg nitroalkanes 3.57D dimethylsulphoxide 4.02D, ketones 2.70D, nitriles 3.51D, aliphatic ethers 1.23D,dioxane 0.45D, tetrahydrofuran 1.73D, aromatics 0.50D, aliphatic alcohols 1.69D, and equating $y_1 = c\mu_g/V_s$ and $y_2 = k\mu_g/V_s$ followed by rearangements into equations (4) and (5) to obtain the expressions (8) and (9) respectively

$$y_1 = \delta'_s - (a + b\,(n^2_D - 1)/(n^2_D + 2) \quad (8)$$

$$y_2 = \delta'_s - (P + Q\,\Delta H_v / V_s) \quad (9)$$

The expressions for the constants C and K assume that the magnitudes of the change in modified non - specific solubility parameter, δ'_S for polar solvents depends on the dipole moment per unit molar volume of the solvent. By substituting the values of a and b, and p and q in (8) and (9) respectively, one obtains the y_1 and y_2 values for each solvent; from which $C = v_s y_1/\mu_g$, and $K = V_s\, y_2/\mu_g$ are calculated. Table 3 lists the molar volume V_S(cm^3 mol^{-1}), the experimental modified non- specific solubility parameter δ'exp (MPa$^{1/2}$), the refractive index for sodium D line n_D and dipole moment,μ(D). The values of the constants C and k (cm^{3}mol^{-1} MPa$^{1/2}$/D) of the solvents are reported in Table 4. Due to the large variation in the values of C and K ranging from in m-xylene 36.3 to in dioxane 522.1 and in m -xylene 12.0 to in dibutyl ether 531.1 respectively, it seems inappropriate to take a single mean value of each constant for the whole spectrum of solvents. Rather , it becomes necessary to take the mean value of each constant for each family of solvents within which the constants are reasonably similar to obtain an estimated value of modified non - specific solubility parameter that is approximately equal to the experimental data. The non-inclusion of the values of K for the alcohols so far will be explained below.

AROMATIC HYDROCARBONS

The values of the constants C and K are affected by the amount of substitution on the benzene, with disubstituted benzene - the xylenes having lower values with respect to those of monosubstituted benzenes. The mean value of the constants are C = 143.1 and K = 162.1, large deviations from the mean are generally observed, to be greater than 100 units.

CHLOROHYDROCARBONS

The values of the constants C and K seemed also to be affected by the type of parent hydrocarbon, whether aliphatic or aromatic and on the degree of substitution , exhibiting large deviations from the mean values C =181.5, and K =14.6 especially in 1,2 - dichlorobenzene;1,2-dichloroethane; and chlorobutane respectively. The basis for the negative values of K for dichloremethane and 1,2-dichlorobenzeene is not clear. The K values represent one of the least for all classes of solvents studied.

ESTERS

The C and K value are approximately similar being independent of the alkyl residues. This is probably in line with Huyskens et al (1994) proposition that the modified non-specific solubility parameter for esters depends on the concentration of the active sites ie. the -COO- group. The mean values obtained are C=370.0 (highest for all families of solvents) and K = 219.6

KETONES

The C values are approximately the same, with a mean value of C =227.6. However the values showed significant variation in particular in diethyl ketone and diisopropyl ketone, but with a mean K value of 68.5

ETHERS

The number of ether groups-O-(α) seems also to be important in the calculation of C. The C value is more appropriately defined by $C = V_s.y_1/\alpha\mu_g$. For monoethers1 while it is 2 for dioxane. The mean value of C =434.0, with significant deviation from the mean value in tetrahydrofuran. A significant deviation of mean K=449.8, is only observed in tetrahydrofuran and represents the highest K value of all families of solvents studied

ALCOHOLS

The values of the constant, C, are approximately the same with a mean value of C=104.6±34.8, the largest deviations being encountered in cyclohexanol. However, the K values are negative for all alcohols(ΔH_v=35.00 kJmol^{-1})ranging from -14.4 in decan-1-o1 to 327.9 in methanol, giving a mean value of K = 263.9, the largest deviations being encountered in low and high molar volume alcohols.

NITROGEN DERIVATIVE AND DIMETHYLSULPHOXIDE

The C values in this family of highly polar solvents is fairly constant with mean value 163.2±22.0, while the

Table 3

The Refractive Indices n_D[a] Molar volumes V_S Molar Energies of Vaporization ΔH_v, Experimental Modified Non-specific Solubility Parameter δ'_{exp} Mean Dipole Moment μ of some Polar Solvents.

Solvent	n^{25}_D	V_s (b) (cm^{3}mol^{-1})	ΔH_v © (kJmol^{-1})	δ'_{exp} (MPa$^{1/2}$)
AROMATIC HYDROCARBONS (μ = 0.500)				
Toluene	1.4933	106.8	30.67	18 10
o-xylene	1.5054	121.2	39.31	17 50
m-xylene	1.4972	123.2	38.92	17 20
Ethylbenzene	1.3688	123.1	35 90	17.30
CHLOROHYDROCARBONS (μ = 1.70D)				
Dichloromothane	1.4246	64.5	29 17	20 53
Trichloromethane	1.4486	80.7	28.87	18 77
1,2, -Dichloroethane	1.4246	78.8	30.75	20 99
1-Chlorobutane	1.4021	105.0	31 57	18.57
1,2-Dichlorobenzene	1.5491	113 1	43 26	18.77
ESTERS (μ = 1.70D)				
Methyl formate	1 3433	62.1	26.90	22 96
.Methyl formate	1 3575	79.8	29 84	21 71
Ethyl acetate	1 3686	98.5	32.22	20 79
Hexyl acetate	1.3905	165:5	41.70	19.17
Butyl propionate	1.4010	148.6	41 39	18.95
Ethyl propionate	1.3840	115.5	34.63	20.05
n-Propyl acetate	1.3844	114.9	34.81	20.22
Butyl acetate	1.3941	132.5	37.40	19.73
Butyl acrylate	1.4090	143.4	40.13	19.23
KETONES (μ=2.70D)				
Acetone	1.3588	74	29.46	22.16
Methylethylketone	1.3788	90.2	31.59	21.10
Diethylketone	1.3920	106.4	44.27	20.28
Methylisobutylketone	1.3880	125.8	43.81	20.02
Diisopropylketone	1.4501	140.4	30.03	19.45
ETHERS ((μ=1.2.3D)				
Diethyl ether	1.3505	104.8	26.56	29.50
Diisopropyl ether	1.3830	141.8	30.03	18.30
Tetreahydrofuran	1.4072	81.4	25.82	19.30
Dibutyl ether	1.3969	170.3	34.43	17.40
Dioxane	1.4203	85.8	32.64	20.90
ALCOHOLS[e] ((μ=1.69D)				
Methanol	1.3265	40.7	35.05	19.25
Ethanol	1.3594	58.7	37.96	17.81
Propan-1-o1	1.3837	75.1	41.08	17.29
Propan-2-o1	1.3752	76.9	39.59	17.60
Butan-1-o1	1.3971	82.0	43.38	17.16
Butan-2-o1	1.3949	92.4	42.30	16.60
Pentan-1-o1	1.4080	108.6	49.75	16.65
Hexan-1-o1	1.4161	125.2	50.64	16.40
Heptan-1-o1	1.4206	141.9	55.71	16.39
Octan-1-o1	1.4260	153.3	57.14	16.38
Decan-1-o1	1.4336	191.9	56.30	16.35
2 Methylpropan-1-o1	1.3958	92.8	43.23	16 40
2-Methylpropan-2-o1	1.3877	94.3	41.05	15.78
Furfuryl alcohol	1.4866	86.5	51.09	18.99
Cyclohexanol	1.4029	106.0	47.41	17.88
NITROGEN DERIVATIVE AND DIMETHYLSULPHOXIDE ((μ=3.57/3.51D)				
Nitromethane	1.3795	53.7	36.02	24.90
Ntroethane	1.3892	71.5	37.36	22.44
1-Niropropane	1.3994	90.7	39.11	21.80
Ehanoicacid nitrile	1.3408	52.5	31.09	23.54
1-Butanoic acid nitrile	1.3807	87.5	37.75	22.5
Pentanoic acid nitrile	1.3936	104.3	40.65	21.22
Dimethyl sulphoxide	1.4741	71.3	42.80	23,80

(a) From Ref. (13) (b) From Ref (6) (4) (c) From Ref. (13) with adjustment as in Tble (1), (d) obtained from individual dipole moments of liquids from Ref. (1); (e) δ' for alcohols are estimated values.

TABLE 4

The Constants C and K of Equations (4) and (5) . Dipole Moments (μ) the Experimental And Estimated Modified Non-specific Solubility Parameter $\delta/_{est}$ Polar Solvents

Solvent	C	K	$\mu_{(a)}$ (D)	$\delta_{Exp}^{(b)}$	$\delta'_{est\,Eq}$ (4) (MPa^{½})	$\delta'_{est\,Eq}$ (5)
AROMATIC HYDROCARBONS						
Toluene	224 4	385 0	0 40	18 10	17 59	16.91
o-Xylene	67 4	31 4	0.62	17 50	17 95	18.20
m-Xylene	36 3	17 0	0 37	17 20	17 48	17.62
Ethylbenene	244 3	215.1	0.60	18 02	17.73	17.22
CHLOROHYDROCARBONS						
Dichloromethane	202 1	-19 3	1 60	20 53	20.02	21 42
Trichloromethane	184.1	19 7	1 20	18 77	18.72	18 55
1,2 -Dichloroethane	276.5	76.1	1.56	20 99	19.11	21 37
1-Chlorobutane	181 6	122.9	2 05	18 57	18 57	16 98
1.2 -Dichlorobenzene	63.3	17 7	2.50	18 77	22.11	
ESTERS						
Methyl formate	338 3	89 5	1 70	22 96	23.83	26.52
Mehthyl acetate	360.9	136 5	1 72	21.71	21 99	23.53
Ethyl Acetate	377 5	193.5	1.78	20.79	20.96	21.42
Hexyl acetate	428.7	320.8	1.74	19 17	18.66	17.59
Butyl propionate	345.3	255 3	1.75	18 95	19.35	18.64
Ethyl propionate	368.8	230 1	1 74	20.05	20.19	19.97
n-Propyl acetate	384 1	234.3	1 76	20 22	20.30	20 11
Butyl acetate	380.6	278 3	1 75	19 73	19.74	19.06
Butyl acrylate	346 2	269.4	1 66	19 28	19.45	18.63
KETONES						
Acetone	228.2	72.9	2 69	22 16	22.32	21 99
Methylethyketone	220 2	99.8	2 75	21.10	21 45	21.21
Diethylketone	216.0	10 3	2 69	20.28	20.55	21.75
Methylisobutylketone	247 3	91.3	2.69	20.02	19.58	19.53
Diisopropylketone	232 4	273 9	2.69	19 45	19.34	15.49
ETHERS						
Diethyl ether	518 1	38.9	1.20	19.50	18.84	20.47
Diisopropyl ether	460 3	519 7	1 29	18 30	18 55	18.21
Tetrahydrofuran	297 3	100 5	1 75	19.30	24.47	26.81
Dibutyl ether	372 2	531 1	1.20	17 40	17.97	16.57
Dioxane	522.1	364 4	0 45	20.90	17.70	21.34
ALCOHOLS						
Methanol	143 0	-327 9	1 71	19 25	17.68	21 90
Ethanol	130 0	-307.8	1 70	17 81	17 10	19 07
Propan-1-ol	118 9	-289.1	1 68	17.29	16.18	17.90
Propan-2-ol	144.5	-239 7	1 68	17 60	16.57	17 10
Butan-1-ol	122.3	-242 7	1 68	17 16	16 71	16.80
Butan-2-ol	94 9	-252.7	1.58	16 60	16.64	16 71
Pentan-1-ol	109 0	-281.5	1.70	16.85	16 79	17 10
Hexan-1-ol	79 2	-243.2	1 68	16.40	16.65	16 12
Heptan-1-ol	80.7	-247.7	1 68	16 39	15 59	16.20
Octan-1-ol	75.5	-216.5	1.68	16.38	16.63	15.88
Decan-1-ol	72.5	-14.4	1 68	16.35	16.57	14 17
2-Methylpropan-1-ol	83.2	-277.5	1.79	16.40	16.91	16 36
2-Methylpropan-2-ol	100 4	-267.5	1.66	15 78	15 82	15.92
Furfuryl alcohol	110 3	-310.5	1 92	18 99	19 12	19.20
Cyclohexanol	178.1	-190.6	1.86	17.88	16.88	16.29
NITROGEN DERIVATIVE AND DIMETHYLSULPHOXIDE						
Nitromethane	156 1	-37 2	3.44	24.90	24.97	27.67
Nitro ethane	154.3	-13.0	3.65	22.44	23 07	23.33
1-Nitropropane	173.7	34.2	3.66	21.80	21.59	20.84
Ethanoic acid nitrile	148 1	-23.3	3 92	23.54	26.26	25.45
1-Butanoic acid nitrile	12 0	44.6	4.02	22.25	22.21	20 64
Pentanoic acid nitrile	189.7	58.3	4.07	21.22	21 28	19.44
Dimethyl sulphoxide	128.2	-31.2	4.02	23.80	25.77	25.59

(a) From Ref(1) (b) From Ref (4) (6) (7)

mean K value = 4.62±48, clearly indicating considerable deviation from the mean value. As in the case of chlorohydrocarbons. we cannot satisfactorily explain the basis for the negative values of K for some individual solvents. However, it appears that the lower values of energies of vaporization $\Delta H_V \leq 37.36$ kJmol^{-1} for lower molar volume solvents ie nitromethane, nitroethane, dimethylsulphoxide and acetic acid nitrile may contribute to this. The mean K value (4.62) represents the least of the K values for all classes of solvents.

In Table4 also are reported the estimated modified non-specific solubility parameter s^1 est using the full expressions (4) and (5). by substituting the values of the constants a. b. mean C; and P, Q mean K; and the gaseous dipole moments and molar volume o individual liquids.

In Table 4, it is clear that the estimated values o modified non-specific solubility parameter .δ',exp, from both refractive index n_D and molar energies o vaporization are generally comparable for mos families of solvents.

The general increase in C and K values shown i *Table 4 for ketones, ethers, nitriles and nitroalkanes cannot be ascribed to large mean dipole moment o* the class of the solvents.. The values of C for primary alcohols decrease with increasing chain length, as - CH_2 - group is added, and as the mean distance between the polar ends increase. These values can be seen to be considerably lower than those of polar liquids e.g. esters of comparable dipole moment. The same increase is exhibited in K values as chain length of primary alcohols decreases. By a consideration of residual molar energies of vaporization $\Delta H_{res,}$ for alcohols compared to those of nitriles, Huyskens (1989) suggested that the difference is due largely to the varying nature of the cohesion forces involved, hydrogen bonding as opposed to dipolar forces respectively and evoked some kind of structural differences. While hydrogen bonds are explained as directional along one lone pair of electrons of the second oxygen atom with both groups being in contact, but in nitriles and other polar molecules, a direct contact of one molecule with another is not necessary and are not stoichiometric. The difference between the dipolar forces in non-associated polar liquids on one hand and associated polar liquids (alcohols) on the other hand is explained by structural differences.

The modified *non-specific solubility parameter* δ^1 by definition is made up of dispersive and dipolar forces only and excludes hydrogen-bonding forces. It's importance lies in

(1) the use of this single parameter instead of 3-parameters of Hansen in a more accurate predictive equation for polar and non-polar substances whether liquids or solids in solvents;

(11) it can be easily determined;

(111) in part, it agrees with the old rule of the thumb "like dissolves like" when the values δ'_s and δ'_B match

Estimation of modified non-specific solubility parameter from physical properties of liquids to compare with the experimental value would be an attractive exercise. Such correlations should exclude properties of liquid which are influenced by H-bonding eg. Boiling point, surface tension dielectric constant and in part energies of vaporization. Typical physical properties that are not affected by H-bonding eg. polarizability and dipole moments in the gas phase have been utilized for such studies. The use of polar non-associated liquids derives from the well- known relationship with polarizabilities.

CONCLUSION

The Lorentz-Lorentz refractive index function and molar energy of vaporization per unit volume have been correlated with modified non-specific solubility parameter of non-polar liquids to obtain the expressions for $\delta' = 61.4(\pm 3.3\ \mathrm{MPa}^{1/2})\ (n^2_D - 1)/\ (n^2_D + 2)$ and $58.6(\pm 6.8\ \mathrm{MPa}^{1/2})\Delta H_V/V_S$ respectively. Using the computer least square regression analysis two corresponding expressions with good regressions coefficients also emerged. Using the latter set of expressions, and by introducing the contribution of dipole moment, expressions for the estimation of modified non-specific solubility parameter of polar liquids were also developed. Because of the large variation in the constants C and K for the whole spectrum of solvents, it was considered more appropriate to obtain the mean value of the constants for groups of liquids with the same molecular properties eg. esters, ketones, ethers, alcohols, etc. in order to obtain estimated modified non-specific solubility parameter not significantly different from the experimental value. The C and K values did not generally correlate with the mean dipole moment of the family of liquids eg. for highly polar nitro-derivative ($\mu = 3.50$), C=163.2, K=46.2; ethers ($\mu = 1.14$D) C=434, K=449, aromatic hydrocarbons ($\mu = 0.5$D) C=143.1, K=162.1 The K values obtained from $\Delta H_V/V_S$ expression for polar associated liquids seem to agree with the proposition of structural differences in these groups of liquids.

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