Evaluation of Solubility Parameters for Nonvolatile Branched Hydrocarbons by Inverse Gas Chromatography

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ABSTRACT: Flory-Huggins interaction parameters determined by inverse gas chromatographic (IGC) technique have been used for the estimation of solubility parameters of nonvolatile branched hydrocarbon solvents. A family of isosteric branched hydrocarbons consists of one apolar stationary phase, 19,24-dioctadecyldotetracontane (C78), and four polar stationary solvents formed by replacing one of the $-CH_3$ groups of C78 by $-OH$ (POH), $-CN$ (PCN), $-SH$ (PSH), $-CF_3$ (MTF), and two other polar solvents formed by replacing four $-CH_3$ groups of C78 with four $-CF_3$ (TTF) and $-OCH_3$ (TMO) are investigated. The three-dimensional Hansen solubility parameters of the solvents have been estimated following the approaches of Voelkel and the method of Huang at five different temperatures. In the three components estimated by Voelkel method, the dispersion component is decreasing rapidly, whereas the polar, and hydrogen bonding components of the solubility parameters are increasing with temperature. In the components of solubility parameter estimated by Huang method, the dispersion and hydrogen bonding components are slowly decreasing with temperature, however, the polar components are almost constant with temperature. The components of solubility parameters for different solvents have been discussed in terms of solvent polarity. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1761–1769, 2008

Key words: Flory-Huggins interaction parameter; Hansen solubility parameters; inverse gas chromatography; isosteric branched hydrocarbons

INTRODUCTION

Inverse gas chromatography (IGC) has proved to be an effective technique for the measurement of solubility parameters of nonvolatile materials used as stationary phases.[1–7] This technique is widely used for characterization of polymers and polymer blends,[8] surfactants,[9] biopolymers, solid food and petroleum products,[10] and biological materials.[11,12] Solubility parameter concept initially used for understanding the solubility of liquid mixtures has now been found applications in solid/liquid systems, and its importance in cosmetics, pharmacy, coatings, and paint industries.[12] In IGC method, the investigated nonvolatile material has been placed in the column and characterized using volatile solute probes. The measured retention properties provide information on interactions between solute probes and nonvolatile materials. The choice of proper solute probes representing the ability to participate in dispersion, polar, and hydrogen bonding interactions are important in the calculation of solubility parameter. According to Hildebrand et al.,[13,14] the solubility parameter for the volatile solute is related to enthalpy of vaporization ΔH_1^v and molar volume V_1^0 as follows:

$$\delta_1 = \left(\frac{\Delta H_1^v - RT}{V_1^0} \right)^{1/2} \tag{1}$$

However, the application of eq. (1) is not possible for nonvolatile substances. Using Flory-Huggins interaction parameter,[15] Guillet and DiPaola-Baranyi[1,2] proposed an alternative method for the determination of solubility parameter of nonvolatile substances. Price[3] and Voelkel and Janas[5] have further developed this method by incorporating Hansen's method[16] of three-dimensional solubility parameters. Huang et al.[17,18] proposed a new approach to estimated the Hansen solubility parameters of the polymers both by linear and direct methods. They have employed the three components of the solubility parameter of solute probes in the regression to obtain the corresponding solubility parameters of the polymers. The aim of this work is to determine the Hansen solubility parameters of a series of seven branched isosteric paraffin solvents having different polarity by employing IGC results. These paraffin solvents are used as stationary phases in GC columns. One stationary solvent is nonpolar and other six are polar containing different functional groups. All the

TABLE I
Physical Properties of the Seven Stationary Solvents

Stationary solvents	m.p. (°C)	M (g/mol)	$\rho^{\dagger}$ (g/cm³)	$V^{\dagger}$ (cm³/mol)	$\alpha \times 10^4$ (K⁻¹)
C78	69–75	1096.1	0.7714	1420.9	7.62
POH	70–74	1098.1	0.7820	1404.2	7.79
PCN	66–68	1107.1	0.7826	1414.7	7.64
PSH	70–74	1114.2	0.7870	1415.7	7.64
MTF	69–74	1150.1	0.7922	1451.8	7.74
TTF	54–58	1312.0	0.8772	1495.7	7.92
TMO	65–68	1104.0	0.8039	1420.9	7.62

Melting point, m.p., molecular weight, M, density, $\rho^{\dagger}$, and molar volume, $V^{\dagger}$ at 403.15 K, and α the coefficient of thermal expansion.

stationary solvents have the same form and nearly same size. In the polar stationary solvents, the polar–polar interactions are considered to be negligible and the polar groups are in the milieu of methylene groups in the solvent melt.[19] Usually this situation is different in small molecules, for example in 1-hexanol, the hydroxyl groups interact with another hydroxyl groups in the liquid. Therefore, the difference between the solubility parameter of a polar liquid and the nonpolar liquid may be used to study the effect of functional group on the solubility parameter. An evaluation of the components of solubility parameters by Voelkel's method and Huang's method for seven solvents has been reported here and the results are compared.

METHODS

The following stationary solvents 19,24-dioctadecyldotetracontane (C78), 18,23-dioctadecylhentetracontan-1-ol (POH),1-cyano-18,23-dioctadecylhentetracontane (PCN), 18,23-dioctadecyl-1-untetracontanethiol (PSH), 1,1,1-trifloro-19,24-dioctadecyldotetracontane (MTF), 19,24-bis (18,18,18-trifluorooctadecyl)-1,1,1,42,42,42-hexafluorodotetracontane (TTF), and 17,22-bis-(16-methoxyhexadecyl)-1,38-dimethoxyoctatriacontane (TMO) are examined. The physical properties of the stationary solvents collected from earlier articles[19–21] are given in Table I. The details of packing of the stationary solvents in packed columns and method of measurement of retention data was reported earlier.[19] Three groups of solute probes were selected to represent different intermolecular interactions, namely n-alkanes from C5 to C10, dodecane, cyclopentane, and cyclohexane for dispersion; the polar solutes such as 1-hexene, benzene, toluene, ethylbenzene, 1-chlorobutane, trichloromethane, tetrachloromethane, fluorobenzene, chlorobenzene, pyridine, carbondisulphide, 1,4-dioxane, and cyclohexanone for dipolar interaction; and alcohol solutes like 1-butanol, 2-butanol, 2-methyl-2-propanol, 1-nitropropane, 1-butanethiol, and cyclohexanol for hydrogen bonding interaction have been used. The Hansen solubility parameters for all these solutes are taken from the literature.[12] The

selected solute probes have a wide range of values in the three components of the solubility parameters. This will explain the possibility to evaluate the three-dimensional solubility parameters of solvents using the selected probe solutes. The total solubility parameters for the solute probes have been calculated using the relation proposed by Hansen

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{2}$$

where δ_d, δ_p and δ_h are the solubility parameters due to dispersion, polar, and hydrogen bonding, respectively. The results at 363.15 K are given in Table II for the solute probes.

The standard chemical potential difference at 363.15, 383.15, 403.15, 423.15, and 443.15 K for the selected solute probes were calculated using the equation given below[22]

$$\Delta\mu = \Delta H^{\dagger} - T\Delta S^{\dagger} + \Delta C_P\left[T - T^{\dagger} - T\ln\left(\frac{T}{T^{\dagger}}\right)\right] \tag{3}$$

where $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$ are the partial molar enthalpy and partial molar entropy differences for the solute between an ideal dilute solution and an ideal gas phases at $T^{\dagger}$, and ΔC_P is the partial molar heat capacity differences for the solute between an ideal dilute solution and an ideal gas phase. The values of $\Delta H^{\dagger}$ and $\Delta S^{\dagger}$ at $T^{\dagger} = 403.15$ K, and ΔC_P which is assumed to be temperature independent are taken from the data reported earlier.[19–21]

In IGC, the retention is mainly governed by the interaction between the stationary phase and the solute probe. This interaction can be characterized with $\Delta\mu$ and related to Flory-Huggins interaction parameter χ_{12}^{∞} as follows:

$$\chi_{12}^{\infty} = \left(\frac{\Delta\mu_1}{RT}\right) - \ln P_1^0 - \frac{P_1^0}{RT}\left(B_{11} - V_1^0\right) + \ln r - \left(1 - \frac{1}{r}\right) \tag{4}$$

where P_1^0, V_1^0, and B_{11} are the vapor pressure, molar volume, and second viral coefficient for the pure solute at temperature T, and r is the molar volume ratio

TABLE II
Solubility Parameter Components of Solutes

Solutes	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$	δ_T (MPa)$^{1/2}$	$d\delta_d/dT$	$d\delta_p/dT$	$d\delta_h/dT$
n-Pentane	11.237	0.000	0.000	11.237	−0.050	0.000	0.000
n-Hexane	12.382	0.000	0.000	12.382	−0.039	0.000	0.000
n-Heptane	13.149	0.000	0.000	13.149	−0.033	0.000	0.000
n-Octane	13.586	0.000	0.000	13.586	−0.029	0.000	0.000
n-Nonane	13.914	0.000	0.000	13.914	−0.028	0.000	0.000
n-Decane	14.029	0.000	0.000	14.029	−0.026	0.000	0.000
n-Dodecane	14.479	0.000	0.000	14.479	−0.002	0.000	0.000
1-Hexene	12.622	1.038	0.000	12.664	−0.032	−0.000	0.000
Cyclopentane	13.802	0.000	1.543	13.888	−0.040	0.000	−0.004
Cyclohexane	14.657	0.000	0.174	14.658	−0.033	0.000	−0.000
Benzene	16.113	0.000	1.742	16.207	−0.004	0.000	−0.004
Toluene	16.011	1.338	1.753	16.162	−0.003	−0.000	−0.004
Ethylbenzene	16.036	0.576	1.233	16.093	−0.027	−0.000	−0.003
1-Chlorobutane	13.883	5.185	1.727	14.920	−0.036	−0.005	−0.004
1-Nitropropane	14.793	11.764	4.824	19.506	−0.028	−0.008	−0.010
1-Butanol	14.037	5.420	13.772	20.398	−0.030	−0.004	−0.031
2-Butnaol	13.476	5.365	12.497	19.146	−0.036	−0.005	−0.031
2-Methyl-2-butanol	13.348	5.789	11.567	18.587	−0.030	−0.005	−0.027
1-Butanethiol	14.366	5.049	3.930	15.727	−0.030	−0.004	−0.009
Trichloromethane	15.457	2.937	4.948	16.493	−0.036	−0.003	−0.012
Tetrachloromethane	15.558	0.000	0.522	15.567	−0.035	0.000	−0.001
Fluorobenzene	16.299	5.787	1.739	17.383	−0.037	−0.005	−0.004
Chlorobenzene	17.178	4.135	1.765	17.757	−0.028	−0.003	−0.004
Pyridine	17.163	8.460	5.204	19.830	−0.028	−0.005	−0.011
Carbon disulphide	17.868	0.000	0.522	17.876	−0.041	0.000	−0.001
1,4-Dioxane	16.792	1.716	6.469	18.077	−0.034	−0.001	−0.014
Cyclohexanone	15.992	6.044	4.488	17.676	−0.028	−0.004	−0.009
Cyclohexanol	15.774	3.947	11.925	20.164	−0.025	−0.002	−0.024

Dispersion, δ_d, polar, δ_p, hydrogen bonding, δ_h, and total, δ_T at 363.15 K. The temperature gradients of δ_d, δ_p, and δ_h.

between the stationary phase and the solute. For poor solvents χ_{12}^{∞} values are higher and for good solvents the values are less than 0.5. The solute properties P_1^0, V_1^0, ΔH_1^v, and B_{11} at the five temperatures are estimated using the constants and standard methods reported in the literature.[23,24] The χ_{12}^{∞} values are given in Table III.

The interaction parameter is considered as the residual chemical potential that consists a sum of enthalpic χ_H^{∞} and residual entropic χ_S^{∞} contributions.

$$\chi_{12}^{\infty} = \chi_H^{\infty} + \chi_S^{\infty} \quad (5)$$

The χ_H^{∞} is readily related to solubility parameters of the two components by regular solution theory, and the following equation can be obtained:

$$\chi_{12}^{\infty} = \frac{V_1^0 (\delta_1 - \delta_2)^2}{RT} + \chi_S^{\infty} \quad (6)$$

where δ_2 is the solubility parameter of the solvent as stationary phase. According to Guillet et al.,[1,2] the rearrangement of eq. (6) will give the following linear relationship, which can be used to calculate δ_2 of the nonvolatile substance.

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{V_1^0}\right) = 2\left(\frac{\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^{\infty}}{V_1^0}\right) \quad (7)$$

where δ_1 is the solubility parameter of the test solute and are calculated using eq. (2). Plotting left-hand side of eq. (7) as a function of δ_1 at each temperature, it is possible to obtain δ_2 at the respective temperatures from the slope. This relation has been widely used in IGC to estimate δ_2 for the stationary solvents. Price[3] used this equation for several stationary solvents and noticed a curvature in the plot when alkanes along with polar solutes are applied, and therefore suggested the possibility to overestimate δ_2. Price proposed to calculate the slope of eq. (7) separately for alkanes and polar solutes and estimated the dispersion and polar components of the solubility parameter of the solvent. Voelkel and Janas[5] extended this approach with the inclusion of alcohol solutes and obtained the hydrogen bonding component of the solubility parameter. Therefore the values of δ_d, δ_p and δ_h are derived from the slopes of the eq. (7) by using the following relationships:

$$\delta_d = \frac{m_{n\text{-alkanes}} \times RT}{2}$$

$$\delta_p = \frac{(m_1 - m_{n\text{-alkanes}}) \times RT}{2} \quad (8)$$

$$\delta_h = \frac{(m_2 - m_{n\text{-alkanes}}) \times RT}{2}$$

TABLE III

χ_{12}^{∞} **Values for the Solutes in the Seven Solvents at the Five Temperatures**

Solutes	363.15	383.15	403.15	423.15	443.15
C78					
n-Pentane	0.484	0.467	0.426	0.402	0.378
n-Hexane	0.413	0.388	0.365	0.355	0.355
n-Heptane	0.377	0.349	0.331	0.327	0.336
n-Octane	0.306	0.305	0.298	0.292	0.287
n-Nonane	0.277	0.276	0.272	0.271	0.262
n-Decane	0.251	0.250	0.247	0.242	0.240
n-Dodecane	0.267	0.222	0.209	0.189	0.180
1-Hexene	0.685	0.655	0.624	0.593	0.573
Cyclopentane	0.338	0.317	0.298	0.283	0.249
Cyclohexane	0.261	0.250	0.238	0.229	0.205
Benzene	0.528	0.484	0.484	0.419	0.432
Toluene	0.426	0.404	0.391	0.378	0.353
Ethylbenzene	0.403	0.382	0.368	0.351	0.335
1-Chlorobutane	0.605	0.570	0.550	0.502	0.473
1-Nitropropane	2.647	2.070	1.905	1.770	1.791
1-Butanol	2.230	2.154	1.879	1.623	1.441
2-Butnaol	2.488	1.843	1.606	1.384	1.231
2-Methyl-2-butanol	2.135	1.782	1.529	1.280	1.111
1-Butanethiol	0.652	0.542	0.485	0.452	0.423
Trichloromethane	0.580	0.609	0.579	0.545	0.511
Tetrachloromethane	0.644	0.334	0.305	0.292	0.284
Fluorobenzene	0.750	0.660	0.603	0.559	0.504
Chlorobenzene	0.710	0.506	0.480	0.454	0.430
Pyridine	1.327	1.252	1.157	1.077	1.006
Carbon disulphide	0.571	0.574	0.533	0.509	0.470
1,4-Dioxane	1.358	1.149	1.052	0.978	0.890
Cyclohexanone	1.327	1.268	1.167	1.095	1.024
Cyclohexanol	1.784	1.738	1.487	1.285	1.141
POH					
n-Pentane	0.605	0.577	0.537	0.498	0.452
n-Hexane	0.538	0.513	0.481	0.456	0.434
n-Heptane	0.495	0.474	0.449	0.428	0.411
n-Octane	0.461	0.442	0.422	0.405	0.391
n-Nonane	0.437	0.419	0.401	0.386	0.372
n-Decane	0.416	0.397	0.381	0.367	0.355
n-Dodecane	0.384	0.365	0.352	0.342	0.331
1-Hexene	0.718	0.678	0.639	0.610	0.587
Cyclopentane	0.452	0.427	0.401	0.365	0.341
Cyclohexane	0.386	0.364	0.340	0.311	0.293
Benzene	0.559	0.506	0.497	0.419	0.416
Toluene	0.460	0.430	0.408	0.386	0.351
Ethylbenzene	0.444	0.415	0.395	0.365	0.342
1-Chlorobutane	0.636	0.596	0.564	0.518	0.482
1-Nitropropane	2.026	1.864	1.724	1.605	1.644
1-Butanol	1.824	1.700	1.561	1.392	1.272
2-Butnaol	1.563	1.446	1.310	1.162	1.046
2-Methyl-2-butanol	1.575	1.438	1.287	1.102	0.993
1-Butanethiol	0.574	0.543	0.503	0.480	0.456
Trichloromethane	0.593	0.564	0.526	0.490	0.455
Tetrachloromethane	0.443	0.423	0.395	0.366	0.343
Fluorobenzene	0.734	0.659	0.609	0.550	0.503
Chlorobenzene	0.551	0.508	0.487	0.449	0.418
Pyridine	0.896	0.888	0.870	0.854	0.826
Carbon disulphide	0.677	0.644	0.594	0.561	0.533
1,4-Dioxane	1.008	0.920	0.859	0.807	0.756
Cyclohexanone	0.990	0.925	0.902	0.877	0.837
Cyclohexanol	1.503	1.324	1.188	1.067	0.983
PCN					
n-Pentane	0.627	0.604	0.558	0.530	0.495
n-Hexane	0.554	0.532	0.499	0.487	0.474

TABLE III *Continued*

Solutes	363.15	383.15	403.15	423.15	443.15
n-Heptane	0.508	0.492	0.463	0.460	0.451
n-Octane	0.422	0.409	0.384	0.388	0.383
n-Nonane	0.445	0.434	0.409	0.417	0.413
n-Decane	0.421	0.411	0.402	0.399	0.393
n-Dodecane	0.381	0.374	0.372	0.372	0.371
1-Hexene	0.678	0.659	0.632	0.614	0.610
Cyclopentane	0.470	0.448	0.419	0.402	0.386
Cyclohexane	0.409	0.384	0.359	0.347	0.338
Benzene	0.490	0.457	0.451	0.390	0.420
Toluene	0.401	0.384	0.369	0.361	0.356
Ethylbenzene	0.392	0.370	0.355	0.348	0.343
1-Chlorobutane	0.559	0.528	0.508	0.481	0.465
1-Nitropropane	1.695	1.605	1.496	1.418	1.501
1-Butanol	2.050	1.815	1.602	1.410	1.281
2-Butnaol	1.791	1.499	1.365	1.185	1.084
2-Methyl-2-butanol	1.802	1.566	1.359	1.157	1.034
1-Butanethiol	0.523	0.513	0.491	0.475	0.457
Trichloromethane	0.475	0.458	0.440	0.441	0.432
Tetrachloromethane	0.430	0.413	0.385	0.378	0.366
Fluorobenzene	0.629	0.587	0.539	0.509	0.480
Chlorobenzene	0.457	0.428	0.417	0.414	0.404
Pyridine	1.081	1.026	0.954	0.910	0.863
Carbon disulphide	0.633	0.659	0.596	0.596	0.569
1,4-Dioxane	1.091	1.000	0.922	0.864	0.817
Cyclohexanone	1.002	0.951	0.887	0.846	0.804
Cyclohexanol	1.723	1.456	1.257	1.106	1.008
PSH					
n-Pentane	0.586	0.559	0.536	0.504	0.464
n-Hexane	0.520	0.505	0.482	0.462	0.445
n-Heptane	0.482	0.471	0.453	0.438	0.424
n-Octane	0.455	0.445	0.431	0.419	0.408
n-Nonane	0.435	0.425	0.413	0.401	0.391
n-Decane	0.419	0.407	0.396	0.385	0.375
n-Dodecane	0.396	0.382	0.373	0.363	0.355
1-Hexene	0.761	0.728	0.694	0.670	0.645
Cyclopentane	0.438	0.417	0.384	0.369	0.354
Cyclohexane	0.372	0.355	0.335	0.320	0.309
Benzene	0.583	0.541	0.529	0.458	0.472
Toluene	0.500	0.470	0.444	0.425	0.409
Ethylbenzene	0.496	0.469	0.432	0.422	0.405
1-Chlorobutane	0.673	0.635	0.582	0.568	0.542
1-Nitropropane	2.180	2.035	1.865	1.747	1.772
1-Butanol	2.458	2.138	1.879	1.632	1.459
2-Butnaol	2.126	1.851	1.606	1.389	1.249
2-Methyl-2-butanol	2.109	1.819	1.571	1.333	1.177
1-Butanethiol	0.634	0.605	0.570	0.525	0.517
Trichloromethane	0.683	0.644	0.605	0.574	0.541
Tetrachloromethane	0.441	0.423	0.402	0.379	0.363
Fluorobenzene	0.772	0.713	0.663	0.609	0.562
Chlorobenzene	0.602	0.561	0.540	0.506	0.484
Pyridine	1.354	1.255	1.154	1.085	1.010
Carbon disulphide	0.661	0.646	0.590	0.565	0.529
1,4-Dioxane	1.274	1.169	1.073	1.007	0.925
Cyclohexanone	1.365	1.267	1.167	1.097	1.014
Cyclohexanol	2.102	1.763	1.508	1.321	1.173
MTF					
n-Pentane	0.318	0.382	0.426	0.469	0.496
n-Hexane	0.363	0.356	0.352	0.342	0.335
n-Heptane	0.321	0.318	0.323	0.32	0.316
n-Octane	0.289	0.289	0.304	0.302	0.300
n-Nonane	0.266	0.265	0.272	0.275	0.282
n-Decane	0.246	0.245	0.247	0.256	0.267
n-Dodecane	0.203	0.212	0.216	0.215	0.207

TABLE III *Continued*

Solutes	363.15	383.15	403.15	423.15	443.15
1-Hexene	0.594	0.581	0.551	0.527	0.528
Cyclopentane	0.304	0.300	0.290	0.265	0.265
Cyclohexane	0.245	0.235	0.230	0.213	0.209
Benzene	0.449	0.412	0.422	0.344	0.372
Toluene	0.352	0.338	0.337	0.312	0.301
Ethylbenzene	0.338	0.322	0.324	0.297	0.289
1-Chlorobutane	0.502	0.486	0.462	0.437	0.427
1-Nitropropane	1.974	1.846	1.707	1.591	1.644
1-Butanol	2.31	2.005	1.746	1.511	1.351
2-Butnaol	1.976	1.699	1.474	1.271	1.125
2-Methyl-2-butanol	1.918	1.650	1.420	1.188	1.044
1-Butanethiol	0.510	0.485	0.439	0.415	0.394
Trichloromethane	0.551	0.510	0.507	0.484	0.464
Tetrachloromethane	0.315	0.297	0.306	0.289	0.282
Fluorobenzene	0.611	0.559	0.514	0.482	0.439
Chlorobenzene	0.465	0.462	0.418	0.406	0.384
Pyridine	1.170	1.097	1.029	0.973	0.906
Carbon disulphide	0.566	0.565	0.531	0.502	0.468
1,4-Dioxane	1.107	1.024	0.937	0.861	0.812
Cyclohexanone	1.172	1.091	1.018	0.947	0.886
Cyclohexanol	1.944	1.633	1.395	1.202	1.076
TTF					
n-Pentane	0.541	0.518	0.500	0.469	0.429
n-Hexane	0.484	0.475	0.454	0.435	0.417
n-Heptane	0.426	0.420	0.405	0.390	0.375
n-Octane	0.404	0.400	0.389	0.377	0.365
n-Nonane	0.390	0.386	0.376	0.365	0.353
n-Decane	0.381	0.375	0.366	0.356	0.346
n-Dodecane	0.402	0.390	0.382	0.374	0.366
1-Hexene	0.622	0.604	0.585	0.564	0.543
Cyclopentane	0.463	0.453	0.431	0.405	0.390
Cyclohexane	0.409	0.396	0.377	0.357	0.345
Benzene	0.434	0.414	0.430	0.365	0.380
Toluene	0.334	0.336	0.342	0.329	0.314
Ethylbenzene	0.339	0.341	0.346	0.332	0.319
1-Chlorobutane	0.493	0.475	0.450	0.430	0.407
1-Nitropropane	1.575	1.490	1.392	1.304	1.374
1-Butanol	2.239	1.946	1.710	1.473	1.313
2-Butnaol	1.887	1.623	1.420	1.208	1.076
2-Methyl-2-butanol	1.849	1.582	1.356	1.140	0.997
1-Butanethiol	0.547	0.535	0.513	0.494	0.472
Trichloromethane	0.606	0.584	0.556	0.533	0.505
Tetrachloromethane	0.415	0.404	0.390	0.377	0.367
Fluorobenzene	0.531	0.503	0.471	0.441	0.411
Chlorobenzene	0.438	0.433	0.424	0.415	0.401
Pyridine	1.017	0.963	0.913	0.867	0.824
Carbon disulphide	0.766	0.745	0.707	0.680	0.657
1,4-Dioxane	0.964	0.901	0.842	0.787	0.740
Cyclohexanone	0.911	0.866	0.817	0.770	0.724
Cyclohexanol	1.932	1.615	1.386	1.199	1.069
TMO					
n-Pentane	0.545	0.608	0.496	0.476	0.439
n-Hexane	0.474	0.468	0.438	0.434	0.419
n-Heptane	0.429	0.429	0.403	0.408	0.397
n-Octane	0.396	0.398	0.376	0.387	0.380
n-Nonane	0.370	0.374	0.352	0.368	0.361
n-Decane	0.348	0.353	0.332	0.351	0.346
n-Dodecane	0.311	0.319	0.297	0.326	0.322
1-Hexene	0.512	0.510	0.511	0.499	0.488
Cyclopentane	0.391	0.383	0.361	0.345	0.311
Cyclohexane	0.328	0.318	0.300	0.293	0.265
Benzene	0.382	0.360	0.368	0.320	0.339

TABLE III *Continued*

Solutes	363.15	383.15	403.15	423.15	443.15
Toluene	0.297	0.294	0.296	0.294	0.282
Ethylbenzene	0.281	0.280	0.282	0.284	0.274
1-Chlorobutane	0.452	0.442	0.426	0.421	0.390
1-Nitropropane	1.621	1.533	1.445	1.365	1.436
1-Butanol	1.661	1.480	1.335	1.170	1.066
2-Butnaol	1.426	1.265	1.135	0.985	0.896
2-Methyl-2-butanol	1.496	1.309	1.155	0.976	0.869
1-Butanethiol	0.430	0.415	0.405	0.397	0.379
Trichloromethane	0.151	0.202	0.232	0.249	0.267
Tetrachloromethane	0.269	0.312	0.273	0.271	0.270
Fluorobenzene	0.474	0.455	0.431	0.405	0.377
Chlorobenzene	0.300	0.320	0.319	0.321	0.312
Pyridine	0.987	0.937	0.887	0.840	0.794
Carbon disulphide	0.565	0.559	0.522	0.506	0.483
1,4-Dioxane	0.958	0.890	0.831	0.774	0.723
Cyclohexanone	0.993	0.934	0.884	0.830	0.783
Cyclohexanol	1.388	1.169	1.028	0.910	0.830

TABLE IV
The Results of Statistical Analysis, Slope (δ_2/RT), Intercept ($(\delta_2^2/RT) + (\chi_S^\infty/V_1^0)$), and Correlation Coefficient, r, of eq. (7) when fitted to all Solutes and the Three Groups of Solutes at 403.15 K for the Seven Stationary Solvents

Solutes	$2(\delta_2/RT)$	$((\delta_2^2/RT) + (\chi_S^\infty/V_1^0))$	r
C78			
Nonpolar	0.0074 ± 0.0003	−0.0469 ± 0.0039	0.992
Polar	0.0076 ± 0.0004	−0.0521 ± 0.0069	0.984
Alcohols	0.0071 ± 0.0009	−0.0452 ± 0.0168	0.965
All solutes	0.0070 ± 0.0002	−0.0435 ± 0.0030	0.990
POH			
Nonpolar	0.0073 ± 0.0003	−0.0475 ± 0.0035	0.994
Polar	0.0089 ± 0.0005	−0.0713 ± 0.0079	0.985
Alcohols	0.00 77 ± 0.0009	−0.0537 ± 0.0161	0.972
All solutes	0.0075 ± 0.0002	−0.0496 ± 0.0028	0.992
PCN			
Nonpolar	0.0074 ± 0.0003	−0.0478 ± 0.0036	0.994
Polar	0.0086 ± 0.0005	−0.0671 ± 0.0083	0.982
Alcohols	0.0077 ± 0.0008	−0.0550 ± 0.0138	0.980
All solutes	0.0075 ± 0.0002	−0.0495 ± 0.0026	0.993
PSH			
Nonpolar	0.0074 ± 0.0003	−0.0477 ± 0.0038	0.993
Polar	0.0077 ± 0.0004	−0.0535 ± 0.0065	0.986
Alcohols	0.0072 ± 0.0009	−0.0484 ± 0.0159	0.971
All solutes	0.0071 ± 0.0002	−0.0453 ± 0.0029	0.991
MTF			
Nonpolar	0.0077 ± 0.0003	−0.0486 ± 0.0035	0.994
Polar	0.0089 ± 0.0005	−0.0678 ± 0.0086	0.982
Alcohols	0.0078 ± 0.0009	−0.0521 ± 0.0151	0.976
All solutes	0.0077 ± 0.0002	−0.0487 ± 0.0028	0.992
TTF			
Nonpolar	0.0072 ± 0.0003	−0.0461 ± 0.0035	0.994
Polar	0.0081 ± 0.0004	−0.0588 ± 0.0007	0.985
Alcohols	0.0076 ± 0.0007	−0.0537 ± 0.0127	0.983
All solutes	0.0074 ± 0.0002	−0.0487 ± 0.0027	0.992
TMO			
Nonpolar	0.0073 ± 0.0003	−0.0467 ± 0.0031	0.995
Polar	0.0087 ± 0.0005	−0.0657 ± 0.0087	0.980
Alcohols	0.0080 ± 0.0008	−0.0577 ± 0.0140	0.980
All solutes	0.0076 ± 0.0002	−0.0509 ± 0.0025	0.994

TABLE V
The Solubility Parameter Components of the Solvents at Different Temperatures

T (K)	δ_d (MPa)$^{1/2}$	δ_p (MPa)$^{1/2}$	δ_h (MPa)$^{1/2}$	δ_T (MPa)$^{1/2}$	δ_2 (MPa)$^{1/2}$
C78					
363.15	14.22	−0.86	−2.28	14.43	12.48
383.15	13.31	−0.28	−1.38	13.38	12.14
403.15	12.32	0.47	−0.50	13.34	11.71
423.15	11.38	0.99	0.21	11.42	11.31
443.15	10.80	1.55	0.59	10.63	10.68
POH					
363.15	14.13	0.85	−0.35	14.16	13.63
383.15	13.30	1.13	−0.03	13.35	13.06
403.15	12.30	2.55	0.54	12.57	12.52
423.15	11.40	1.90	1.04	11.60	11.89
443.15	10.46	2.29	1.29	10.78	11.23
PCN					
363.15	14.18	−0.04	−0.96	14.21	13.41
383.15	13.49	0.11	−0.37	13.50	13.01
403.15	12.35	2.08	0.60	12.54	12.52
423.15	11.42	1.58	1.23	11.59	11.94
443.15	10.48	2.16	1.53	10.81	11.27
PSH					
363.15	14.18	−0.80	−2.03	14.35	12.61
383.15	13.28	0.08	−1.13	13.33	12.30
403.15	12.33	0.57	−0.23	12.35	11.88
423.15	11.40	1.11	1.58	11.56	11.43
443.15	10.46	1.75	0.92	10.65	10.87
MTF					
363.15	13.77	0.03	−1.42	13.84	12.77
383.15	13.08	0.28	−0.78	13.11	12.41
403.15	12.87	2.03	0.17	13.03	12.83
423.15	11.49	1.14	0.77	11.56	11.64
443.15	10.24	2.08	1.15	10.51	10.92
TTF					
363.15	13.86	0.33	−1.04	13.90	13.21
383.15	13.22	0.73	−0.37	13.25	12.88
403.15	12.13	1.44	0.67	12.23	12.43
423.15	11.79	2.11	1.63	12.09	12.58
443.15	10.35	2.38	1.75	10.76	11.26
TMO					
363.15	14.02	0.17	0.00	14.02	13.83
383.15	13.36	0.45	0.34	13.39	13.35
403.15	12.25	2.11	1.12	12.48	12.77
423.15	11.33	1.65	1.65	11.57	12.65
443.15	10.43	2.15	2.24	10.88	11.48

δ_d, δ_p, and δ_h are components of solubility parameter due to Voelkel; δ_T is the total solubility parameter; δ_2 is due to Guillet Procedure.

where $m_{n\text{-alkanes}}$ is the value of the slope for nonpolar, m_1 is the values of the slope for polar solutes, and m_2 is the value of the slope for alcohols. Equation (7) has been used here for the three series of solutes probes separately, and the slope and intercept values are calculated at the five temperatures. The slope and intercept values along with the standard errors are given in Table IV for all stationary solvents at 403.15 K. The values of the three Hansen solubility parameters and the total solubility parameter calculated using eq. (2) are summarized in Table V.

Huang et al.[17,18] proposed a modified form of eq. (7) to calculate the three-dimensional solubility parameters of solvents as follows:

$$\left(\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}\right) = \left(\frac{2\delta_{d,2}}{RT}\right)\delta_{d,1} + \left(\frac{2\delta_{p,2}}{RT}\right)\delta_{p,1}$$

$$+ \left(\frac{2\delta_{h,2}}{RT}\right)\delta_{h,1} - \left(\frac{\delta_{t,2}^2}{RT} + \eta\right) \quad (9)$$

$\delta_{d,1}$, $\delta_{p,1}$, and $\delta_{h,1}$ are the dispersion, polar, and hydrogen bonding components of the solutes. The solubility parameter components for the 28 solutes at 298.15 K are taken from the Hansen method.[12] The $\delta_{d,1}$, $\delta_{p,1}$, and $\delta_{h,1}$ values at the five experimental temperatures are calculated using the relations proposed by Hansen and Beerbower.[25]

TABLE VI
The Solubility Parameters Components Dispersion, $\delta_{d,2}$, Polar, $\delta_{p,2}$, Hydrogen Bonding, $\delta_{h,2}$, and Total Solubility Parameters, $\delta_{T,2}$, due to Huang and the Values of $\eta = \chi_S/V_1$

T (K)	$\delta_{d,2}$ (MPa)$^{1/2}$	$\delta_{p,2}$ (MPa)$^{1/2}$	$\delta_{h,2}$ (MPa)$^{1/2}$	$\delta_{T,2}$ (MPa)$^{1/2}$	η (mol/cm^3)
C78					
363.15	11.97 ± 0.72	2.25 ± 0.45	4.18 ± 0.33	12.88 ± 0.91	−0.0549
383.15	11.48 ± 0.69	2.28 ± 0.45	4.08 ± 0.34	12.39 ± 0.89	−0.0482
403.15	11.03 ± 0.66	2.35 ± 0.44	3.90 ± 0.35	11.93 ± 0.87	−0.0425
423.15	10.45 ± 0.63	2.39 ± 0.44	3.80 ± 0.34	11.34 ± 0.87	−0.0404
443.15	09.95 ± 0.57	2.34 ± 0.42	3.65 ± 0.35	10.85 ± 0.79	−0.0319
POH					
363.15	12.02 ± 0.76	2.46 ± 0.47	4.89 ± 0.34	13.21 ± 0.96	−0.0578
383.15	11.64 ± 0.70	2.53 ± 0.45	4.62 ± 0.34	12.78 ± 0.93	−0.0513
403.15	11.34 ± 0.74	2.38 ± 0.50	4.44 ± 0.39	12.41 ± 0.97	−0.0459
423.15	10.57 ± 0.62	2.62 ± 0.43	4.12 ± 0.35	11.64 ± 0.83	−0.0385
443.15	10.08 ± 0.56	2.54 ± 0.45	3.89 ± 0.34	11.10 ± 0.77	−0.0334
PCN					
363.15	12.08 ± 0.77	2.72 ± 0.48	4.51 ± 0.34	13.18 ± 0.97	−0.0575
383.15	11.36 ± 0.77	2.50 ± 0.50	4.67 ± 0.38	12.53 ± 0.99	−0.0493
403.15	11.35 ± 0.74	2.61 ± 0.50	4.26 ± 0.39	12.40 ± 0.97	−0.0459
423.15	10.57 ± 0.79	2.83 ± 0.44	3.99 ± 0.35	11.65 ± 0.97	−0.0386
443.15	10.04 ± 0.57	2.74 ± 0.42	3.79 ± 0.35	11.07 ± 0.80	−0.0333
PSH					
363.15	11.88 ± 0.78	2.29 ± 0.78	4.26 ± 0.36	12.83 ± 1.17	−0.0545
383.15	11.48 ± 0.69	2.39 ± 0.45	4.14 ± 0.34	12.43 ± 0.89	−0.0485
403.15	11.04 ± 0.66	2.46 ± 0.44	3.94 ± 0.35	11.97 ± 0.87	−0.0427
423.15	10.47 ± 0.63	2.48 ± 0.44	3.83 ± 0.35	11.42 ± 0.85	−0.0371
443.15	09.97 ± 0.58	2.43 ± 0.42	3.66 ± 0.35	10.89 ± 0.80	−0.0322
MTF					
363.15	11.97 ± 0.71	2.47 ± 0.29	4.24 ± 0.32	12.94 ± 0.83	−0.0554
383.15	11.52 ± 0.68	2.48 ± 0.44	4.14 ± 0.34	12.49 ± 0.88	−0.0490
403.15	11.85 ± 0.77	2.55 ± 0.52	4.36 ± 0.40	12.88 ± 1.01	−0.0495
423.15	10.62 ± 0.60	2.59 ± 0.42	3.89 ± 0.34	11.60 ± 0.81	−0.0382
443.15	09.95 ± 0.57	2.50 ± 0.42	3.68 ± 0.35	10.90 ± 0.79	−0.0322
TTF					
363.15	11.96 ± 0.74	2.79 ± 0.46	4.24 ± 0.35	13.03 ± 0.90	−0.0562
383.15	11.56 ± 0.68	2.99 ± 0.44	4.14 ± 0.33	12.64 ± 0.87	−0.0501
403.15	11.21 ± 0.74	2.81 ± 0.49	4.07 ± 0.38	12.25 ± 0.96	−0.0448
423.15	10.98 ± 0.66	3.20 ± 0.46	4.10 ± 0.37	12.15 ± 0.88	−0.0420
443.15	09.91 ± 0.57	2.93 ± 0.42	3.68 ± 0.35	10.67 ± 0.35	−0.0309
TMO					
363.15	12.18 ± 0.74	2.65 ± 0.46	4.86 ± 0.34	13.38 ± 0.60	−0.0593
383.15	11.74 ± 0.69	2.67 ± 0.45	4.68 ± 0.34	12.92 ± 0.89	−0.0524
403.15	11.40 ± 0.74	2.51 ± 0.50	4.52 ± 0.39	12.52 ± 0.97	−0.0467
423.15	11.47 ± 0.72	2.67 ± 0.51	4.36 ± 0.41	12.56 ± 0.97	−0.0448
443.15	10.09 ± 0.56	2.69 ± 0.41	4.02 ± 0.34	11.19 ± 0.25	−0.0340

$$d\delta_d/dT = -1.25\alpha\delta_d$$
$$d\delta_p/dT = -\alpha\delta_p/2 \qquad (10)$$
$$d\delta_h/dT = -\left(1.22 \times 10^{-3} + \alpha/2\right)\delta_h$$

α values are calculated using molar volumes at 298.15 K and at experimental temperatures. The solubility parameter components calculated using eq. (10) at 363.15 K and the temperature gradients of solubility parameter components are given in Table II. The solubility parameter components of solvents $\delta_{d,2}$, $\delta_{p,2}$, and $\delta_{h,2}$ are obtained by multiple regression of eq. (9). Equation (2) has been used to calculate the total solubility parameter of the solvents, $\delta_{T,2}$. The $\delta_{d,2}$, $\delta_{p,2}$, $\delta_{h,2}$, and $\delta_{T,2}$ results are given in Table VI along with the η values.

RESULTS AND DISCUSSION

The solubility parameters for the seven solvents have been obtained by the Guillet procedure, the Voelkel approach, and the Huang method. According to Guillet's procedure, the δ_1 of all the solute probes are linearly fitted as a function of the left-hand side of eq. (7), and from the slope δ_2 is obtained directly. Guillet's procedure is used to calculate δ_2 for all the solvents and the data are presented in Table V. The statistical analysis presented in Table IV indicates that the correlation coefficients, r, of the linear fit due to Guillet analysis are always greater than 0.990. Voelkel's method has been used to obtain the three components of the solubility parameter. The plots of the left-hand side of eq. (7)
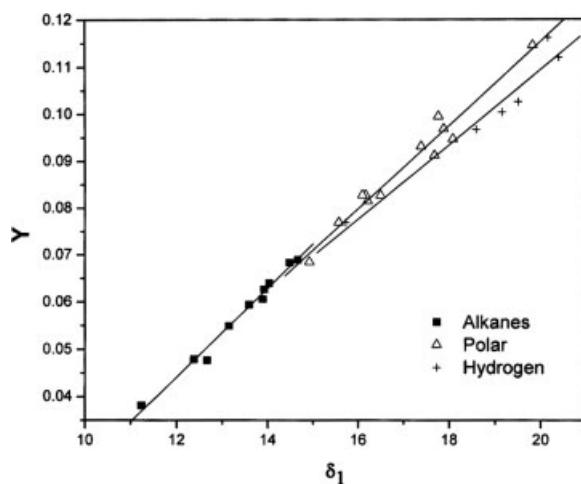
Figure 1 $((\delta_1^2/RT) - (\chi_{12}^{\infty}/V_1^0)) = y$ values as a function of δ_1 (MPa)$^{1/2}$ for the three sets of solute probes on apolar C78 at 403.15 K.

versus δ_1 are linear for each group of solute probes. Such plots are shown in Figures 1 and 2 for an apolar C78 and the polar POH solvents at 403.15 K. The slope and intercept values along with the standard errors for the three groups of solutes are given in Table IV. The correlation coefficients for each group of solutes in all the solvents are nearly similar and the values are as follows: r (nonpolar) > 0.992, r (polar) > 0.984, and r (alcohols) > 0.965. Good correlation coefficients are obtained for nonpolar probes and polar solute probes in comparison to the appropriate values found for alcohol solute probes. The slope values are used in eq. (8) to calculate the components δ_d, δ_p, and δ_h. The three components are used in eq. (2) and the total solubility parameter has been calculated. The method has been extended to calculate the three components of Hansen solubility parameters and δ_T at all other temperatures, and the results are presented in Table V. A comparison of δ_T with δ_h values given in Table V indicates that δ_T is higher than δ_2 at all temperatures and the difference decreases with increase of temperature. The results presented in Table V also indicate that with increase of temperature δ_d values are decreasing rapidly, whereas δ_p and δ_h values are increasing. Further, δ_p and δ_h values are negative at lower temperature and became positive with rise of temperature. In C78 and in less polar solvents, δ_p and δ_h are more negative when compared with highly polar solvents. Price[26] also observed that δ_p values are negative for nonpolar solvents like n-hexadecane and squalane, and positive in case of polar solvents such as n-methyl pyrrolidone and dinonyl phthalate. This behavior may be explained in terms of the sign and magnitude of Flory-Huggins interaction parameter, χ_{12}^{∞}. The χ_{12}^{∞} values are smaller for polar solute probes when compared with nonpolar probes in

polar stationary solvents due to dipolar interaction. On the other hand, χ_{12}^{∞} values are higher for polar solute probes when compared with nonpolar probes in apolar stationary solvents due to break down of dipolar interactions in polar solutes. With rise of temperature the χ_{12}^{∞} values are increasing rapidly in nonpolar solute probes when compared with polar and alcohol solute probes.

A comparison of the results presented in Table V with the corresponding data evaluated by Huang's method presented in Table VI indicates some interesting information. The components of solubility parameter and their variation with temperature given in Tables VI appears to be more reasonable, and the trend is similar to that observed in the variation of solute solubility parameters with temperature. Unlike in Voelkel data, the δ_d and δ_h in Table VI are slowly decreasing with increase of temperature, and δ_p values are almost constant in the temperature range. Further, the unusual observations like negative values of δ_p and δ_h and increase in δ_p and δ_h with increase of temperature have not been observed in the parameters calculated by Huang's method. The η values are increasing with increase of temperature in all the solvents.

From the components of solubility parameters evaluated by Huang's method it has been observed that the difference between different solvents is within the error limits. The values of the total solubility parameters $\delta_{T,2}$ are close to δ_2 values calculated by Guillet's method. To make a comparison between different solvents it is proposed to calculate the difference in total solubility parameters $\Delta\delta$, between polar (P) solvents and the nonpolar C78 as follows:

$$\Delta\delta = \delta(P) - \delta(C78) \tag{11}$$
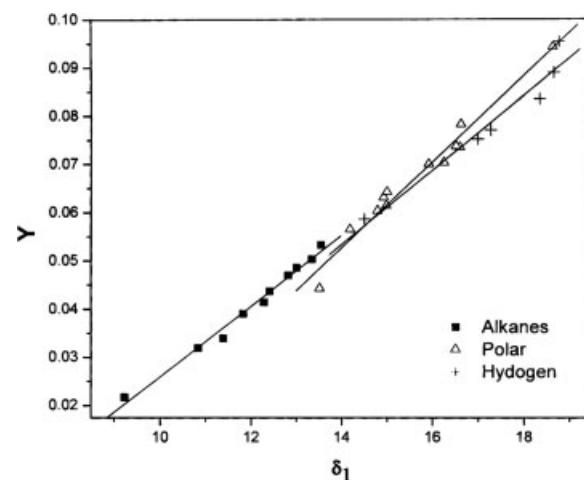
Figure 2 $((\delta_1^2/RT) - (\chi_{12}^{\infty}/V_1^0)) = y$ values as a function of δ_1 (MPa)$^{1/2}$ for the three sets of solute probes on polar POH at 403.15 K.

TABLE VII
The Values of $\Delta\delta$ (MPa)$^{1/2}$ Calculated Using Eq. (11) for the Six Polar Solvents

T (K)	POH	PCN	PSH	TMO	TTF	MTF
Hansen method						
363.15	0.33	0.30	−0.05	0.50	0.15	0.06
383.15	0.39	0.14	0.04	0.53	0.25	0.10
403.15	0.48	0.47	0.04	0.59	0.32	0.95
423.15	0.30	0.31	0.08	1.22	0.81	0.26
443.15	0.25	0.22	0.04	0.63	−0.18	0.05
Guillet method						
363.15	1.15	0.93	0.13	1.35	0.73	0.29
383.15	0.92	0.87	0.16	1.21	0.74	0.27
403.15	0.81	0.81	0.17	1.06	0.72	1.12
423.15	0.58	0.63	0.12	1.34	1.27	0.33
443.15	0.55	0.59	0.19	0.80	0.58	0.24
Voelkel method						
363.15	−0.27	−0.22	−0.08	−0.59	−0.53	−0.41
383.15	−0.03	0.12	−0.05	−0.27	−0.13	0.01
403.15	−0.77	−0.80	−0.99	−0.31	−1.11	−0.86
423.15	0.18	0.17	0.14	0.14	0.67	0.15
443.15	0.15	0.18	0.02	−0.12	0.13	0.25

where δ represents δ_2 or δ_T or $\delta_{T,2}$ due to Guillet, Voelkel, and Huang, respectively. $\Delta\delta$ values are presented in Table VII. The decrease in $\Delta\delta$ with increase of temperature is almost regular with Guillet and Huang data. $\Delta\delta$ is higher in case of more polar solvents when compared with less polar solvents. The order in $\Delta\delta$ is as follows:

$$\text{TMO} > \text{POH} > \text{PCN} > \text{TTF} > \text{MTF} > \text{PSH}$$
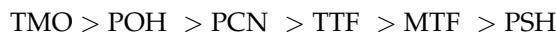
This order of variation has been observed with data calculated using Guillet and Huang methods. However, with the data calculated using Voelkel's approach the regularity in the order is not maintained and in some cases negative $\Delta\delta$ values are obtained.

CONCLUSIONS

Solubility parameters of seven nonvolatile branched hydrocarbons having same size and same form but differ in polarity have been evaluated using IGC results at higher temperatures. The three-dimensional solubility parameter components δ_d, δ_p, and δ_h are estimated by the Voelkel method as well as by Huang's method for all the solvents. The variation of the components with the temperature has been compared between the two methods. It is observed that the trend in the variation of δ_d, δ_p, and δ_h with temperature calculated by Huang's method is similar to

the behavior observed with the solute probes. The $\Delta\delta$, the difference between polar solvents and the nonpolar C78 calculated using Guillet and Hansen data are decreasing with increase of temperature regularly. Further, the $\Delta\delta$ values are higher for polar solvents and smaller for less polar solvents. $\Delta\delta$ values are calculated using Voelkel data are not varying regularly.

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