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Thermodynamic characterization of poly (caprolactonediol) by inverse gas chromatography

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Abstract Specific retention volumes, V_g^0, were determined for 21 solute probes on poly (caprolactonediol) (PCLD) in the temperature range 323.15–403.15 K by inverse gas chromatography. The retention diagrams drawn between ln V_g^0 versus $1/T$ are linear for all the solutes since PCLD with ten repeating units in its chain behaving like a non polymeric material under the conditions applied. The stationary phase with melting temperature ~321 K is in the liquid state in the GC column over the temperature range studied and hence found to be suitable to determine infinite dilution partial molar thermodynamic properties of mixing for solutes on PCLD. The V_g^0 values have been used to calculate weight fraction activity coefficients Ω^∞ and Flory–Huggins interaction parameters, χ_{12}^∞. The average partial molar enthalpy of solution, $\overline{\Delta H}_1^S$, and partial molar enthalpy of mixing, $\overline{\Delta H}_1^\infty$, are calculated using V_g^0 and Ω^∞ respectively. The average molar enthalpy of vaporization ΔH_1^V for solutes have been calculated using $\overline{\Delta H}_1^\infty$ and $\overline{\Delta H}_1^S$ values and compared with the literature values at 363.15 K which is the average column temperature. The partial molar entropy of mixing, $\overline{\Delta S}_1^\infty$ calculated at 363.15 K are in good correlation with the average $\overline{\Delta H}_1^\infty$ values. The total solubility parameter due to Guillet and the Hansen solubility parameters (HSP) are calculated for PCLD using χ_{12}^∞ values. In the present work the Hansen solubility parameters have been calculated using a new method following the Hansen theory and Huang method with less weight on polar and hydrogen bonding components. The errors in the solubility HSP are lower and the correlation coefficients are better in both the methods compared to unweighted three dimensional model.

Keywords Poly (caprolactonediol) · Inverse gas chromatography · Thermodynamic properties · Hansen solubility parameters

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Introduction

Inverse gas chromatography (IGC) has been recognized as a versatile, fast and reliable technique to measure thermodynamic and physical properties of a probe solute at infinite dilution in polymers and nonvolatile solvents [1–8]. In IGC method the nonvolatile material is placed in the column and characterized using volatile solute probes. This technique is simpler and economical than the static method, and requires only small amounts of polymer and solute. The measured retention property provides information on the interaction between solute and the nonvolatile solvent. Retention diagrams obtained by IGC method can be utilized to identify the regions of phase changes in polymers and to evaluate percent of crystallinity [9]. The IGC method can be used to study the phase transitions and surface energies of polymers and polymer blends using suitable solute probes [10, 11]. A knowledge of phase transitions in a polymer is necessary to understand the polymer properties and for selection of polymers for various applications. Flory–Huggins interaction parameters of small molecules in polymer melt obtained by this technique are useful in order to analyze fundamental processing steps such as devolatilization, bulk polymerization and plasticization of polymers. Thermodynamic theory has been developed and applied to determine the solubility parameters of polymers with the knowledge of Flory–Huggins interaction parameters. Hildebrand solubility parameter and Hansen three component solubility parameters are useful in predicting the solubility behavior of a polymer in various solvents and plasticizers [12–14]. The solubility parameter data is also useful to correlate its compatibility with other polymers and in designing coating formulations. Numerous papers have been published on characterization of non volatile materials such as inorganic salts, fibres, clays, pharmaceutical powders, cellulose, pigments, polymers and polymer blends [15, 16].

The main purpose of this paper is to characterize poly (caprolactonediol) (PCLD) by employing packed column IGC technique. The PCLD can be used as a plasticizer to biodegradable polymers in order to monitor the morphology and properties biodegradable polymer. A plasticizer usually decreases the intermolecular forces between the polymer chain resulting in a softened and flexible polymeric matrix. The applications of poly (caprolactonedtriol) as plasticizer agent for cellulose acetate films and resulting changes in physico-chemical properties of cellulose acetate are reported [17]. The interaction of PCLD in molten state with a variety of solute probes is of considerable interest. The structure of PCLD shown in the Fig. 1 reveals that it has three interacting groups such as hydroxyl groups at the ends, pendant carboxyl groups and ether groups in the chain. Since the interaction of the polymer with the solutes is complex, the probes with different functional groups have been used in this study. Further, our survey of literature indicate that the application of IGC method for the determination of thermodynamic parameters of solutes on PCLD has not been reported. Therefore, the retention data for 21 solute probes on PCLD as a function temperature has been determined. The Hansen solubility parameter and Flory–Huggins interaction parameters are required to asses the compatibility of PCLD as plasticizers to biodegradable polymers.

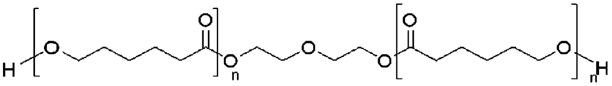

Fig. 1 Structure of the Poly (caprolactonediol)

IGC theory

In IGC the retention is mainly governed by the surface and bulk interactions of the solute with the stationary phase. This interaction can be characterized with the measured specific retention volume, V_g^0, which can be related to thermodynamic quantities. The thermodynamic theory of IGC is described in detail elsewhere [18]. The specific retention volumes, V_g^0 at 273.15 can be calculated using the relation

$$V_g^0 = (t_\mathrm{R} - t_0)JF\frac{273.15}{wT_r}\left(\frac{P_0 - P_\mathrm{w}}{P_0}\right) \tag{1}$$

where t_R is the retention time of probe solutes and t_0 is the retention time of inert species (i.e. methane marker). F is the flow rate of the carrier gas measured at room temperature T_r, w is the mass of the stationary phase. P_w is the water vapour pressure at T_r and T_c is the column temperature. The flow rate of the carrier was measured at the column outlet at T_r using soap film flow meter. The carrier was saturated with water vapour existing in the soap film flow meter before flow rate measurement. Therefore P_w is subtracted from P_o in Eq. 1. J is the James and Martin correction factor which depends on the inlet, P_i, and outlet, P_o, pressures calculated using the following relation [19].

$$J = \frac{3}{2}\left[\frac{(P_\mathrm{i}/P_\mathrm{o})^2 - 1}{(P_\mathrm{i}/P_\mathrm{o})^3 - 1}\right] \tag{2}$$

When the stationary phase is in a fixed state (liquid or solid) the logarithm of the V_g^0 versus the reciprocal of temperature gives a straight line. The slope of the straight line is related to the partial molar enthalpy of solution, $\overline{\Delta H}_1^S$, as follows

$$\frac{\partial \ln V_g^0}{\partial\left(\frac{1}{T}\right)} = -\frac{\overline{\Delta H}_1^S}{R} \tag{3}$$

where R is the gas constant. The partial molar weight fraction activity coefficients for the solute at infinite dilution, Ω_1^∞, can be related to V_g^0 by the following relation

$$\ln \Omega_1^\infty = \ln\left(\frac{273.15\,R}{V_g^0 P_1 M_1}\right) - \frac{P_1(B_{11} - V_1)}{RT} \tag{4}$$

where M_1 is the molar mass of solute, V_1, P_1 and B_{11} are molar volume, saturated vapour pressure and second virial coefficients of solute at temperature T. V_1, P_1 and B_{11} were estimated in the temperature range 323.15–403.15 K following the standard methods reported in the literature and the necessary parameters required in the evaluation are taken from the literature [20, 21]. The second viral coefficients were calculated by utilizing the Tsonopoulos method [22].

The partial molar free energy $\overline{\Delta G_1^{\infty}}$ and the average partial molar enthalpy of mixing, $\overline{\Delta H_1^{\infty}}$, for the solute at infinite dilution can be calculated according to the following thermodynamic relations.

$$\overline{\Delta G_1^{\infty}} = RT \ln \Omega_1^{\infty} \tag{5}$$

$$\overline{\Delta H_1^{\infty}} = R \frac{\partial \ln \Omega_1^{\infty}}{\partial \left(\frac{1}{T}\right)} \tag{6}$$

The partial molar entropy at any temperature can be obtained as follows.

$$\overline{\Delta S_1^{\infty}} = \frac{\left(\overline{\Delta H_1^{\infty}} - \overline{\Delta G_1^{\infty}}\right)}{T} \tag{7}$$

The molar enthalpy of vaporization is related to $\overline{\Delta H_1^{\infty}}$ and $\overline{\Delta H_1^{S}}$ [23]

$$\Delta H_1^{V} = \overline{\Delta H_1^{\infty}} - \overline{\Delta H_1^{S}} \tag{8}$$

The Flory–Huggins interaction parameter for the solute at infinite dilution in the polymer is related to V_g^0 as follows, [24]

$$\chi_{12}^{\infty} = \ln \frac{273.15\, R \upsilon_2}{P_1 V_g^0 V_1} - 1 - \frac{P_1 (B_{11} - V_1)}{RT} \tag{9}$$

where υ_2 is the specific volume of the polymer. The interaction parameter, χ_{12}^{∞}, is considered as the residual chemical potential which consists of enthalpic, χ_H^{∞}, and residual entropic, χ_S^{∞}, contributions.

$$\chi_{12}^{\infty} = \chi_H^{\infty} + \chi_S^{\infty} \tag{10}$$

the χ_H^{∞} is readily related to solubility parameter difference between the solute, δ_1, and the polymer, δ_2, by regular solution theory and the following equation can be obtained

$$\chi_{12}^{\infty} = \frac{V_1 (\delta_1 - \delta_2)^2}{RT} + \chi_S^{\infty} \tag{11}$$

According to Hildebrand et al. [25] the solubility parameter or the square root of cohesive energy density (CED) for the volatile solute is related to enthalpy of vaporization, ΔH_1^V and molar volume as follows

$$\delta_1 = \left(\frac{\Delta H_1^{v} - RT}{V_1}\right)^{1/2} = \left(\frac{\Delta E_1}{V_1}\right)^{1/2} = (\mathrm{CED})^{1/2} \tag{12}$$

where ΔE_1 is the energy of vaporization. However the application of the above equation to polymers and nonvolatile substances is not possible. Guillet and DiPaola-Baranyi [1, 2] proposed an alternative method for the determination of solubility parameter of nonvolatile substances using Flory–Huggins interaction parameter obtained from IGC data. Therefore the rearrangement of Eq. 11 gives the following linear relationship which can be applied to calculate δ_2 of the stationary phases.

$$\left(\frac{\delta_1^2}{RT}-\frac{\chi_{12}^{\infty}}{V_1}\right)=2\left(\frac{\delta_2}{RT}\right)\delta_1-\left(\frac{\delta_2^2}{RT}+\frac{\chi_S^{\infty}}{V_1}\right) \tag{13}$$

δ_1 values required in Eq. 13 are obtained by Hildebrand’s regular solution theory [25]. Plotting left hand side of Eq. 13 as a function of δ_1 at each temperature, it is possible to obtain δ_2 from the slope at the respective temperatures. This relation has been widely used in IGC to estimate δ_2 for the stationary solvent [3, 6, 26–28].

The Hildebrand solubility parameter may not be able to describe adequately the solubility behavior when polar and hydrogen bonding solvents are included in the system. Hansen addressed this problem by introducing the three dimensional solubility parameter model [12] or Hansen solubility parameters (HSP). According to Hansen theory the total cohesive energy is approximated as a sum of contributions from dispersive (E_d), polar (E_p) and hydrogen bonding (E_h) interactions. Therefore the total solubility parameter is expressed as

$$\delta_T^2=\delta_\mathrm{d}^2+\delta_\mathrm{p}^2+\delta_\mathrm{h}^2 \tag{14}$$

where $\delta_{\mathrm{d},1}$, $\delta_{\mathrm{p},1}$ and $\delta_{\mathrm{h},1}$ are the Hansen solubility parameters representing dispersive, polar and hydrogen bonding contributions.

Flory–Huggins interaction parameter is related to the weighted Hansen solubility parameter differences between the polymer and the solute by Hansen theory as follows [12].

$$\chi_{12}^{\infty}=\frac{V_1}{RT}\left[\left(\delta_{\mathrm{d}2}-\delta_{\mathrm{d}1}\right)^2+0.25\left(\delta_{\mathrm{p}2}-\delta_{\mathrm{p}1}\right)^2+0.25\left(\delta_{\mathrm{h}2}-\delta_{\mathrm{h}1}\right)^2\right] \tag{15}$$

The rearrangement of Eq. 15 and with the addition of χ_S^{∞}/V_1 term gives the following relation

$$\left(\frac{\delta_1'^2}{RT}-\frac{\chi_{12}^{\infty}}{V_1}\right)=\left(\frac{2\delta_{\mathrm{d},2}}{RT}\right)\delta_{1,d}+\left(\frac{0.5\,\delta_{\mathrm{p},2}}{RT}\right)\delta_{1,\mathrm{p}}+\left(\frac{0.5\,\delta_{\mathrm{h},2}}{RT}\right)\delta_{1,\mathrm{h},}-\left(\frac{\delta_2'}{RT}+\frac{\chi_S^{\infty}}{V_1}\right) \tag{16}$$

where

$$\delta_1'^2=\delta_{\mathrm{d},1}^2+0.25\,\delta_{\mathrm{p},1}^2+0.25\,\delta_{\mathrm{h},1}^2 \tag{17}$$

$$\delta_2'^2=\delta_{\mathrm{d},2}^2+0.25\,\delta_{\mathrm{p},2}^2+0.25\,\delta_{\mathrm{h},2}^2 \tag{18}$$

According to Huang and Denin [29] the unweighted three dimensional solubility parameter model is given by

$$\left(\frac{\delta_1^2}{RT}-\frac{\chi_{12}^{\infty}}{V_1}\right)=\left(\frac{2\delta_{\mathrm{d},2}}{RT}\right)\delta_{\mathrm{d},1}+\left(\frac{2\delta_{\mathrm{p},2}}{RT}\right)\delta_{\mathrm{p},1}+\left(\frac{2\delta_{\mathrm{h},2}}{RT}\right)\delta_{\mathrm{h},1}-\left(\frac{\delta_2^2}{RT}+\frac{\chi_S^{\infty}}{V_1}\right) \tag{19}$$

as the errors in the application of this model is at higher side, Huang and Deanin proposed a modified form of Eq. 19 as follows

$$\frac{RT\chi_{12}^{\infty}}{V_1} = (\delta_{1d} - \delta_{2d})^2 + b\left[(\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2\right] + \frac{RT\chi_S^{\infty}}{V_1} \tag{20}$$

where b is a constant which modifies the weighting of the polar and hydrogen bonding interactions. The b values are obtained by plotting $\left[\frac{RT\chi_{12}}{V_1} - (\delta_{1d} - \delta_{2d})^2\right]$ versus $\left[(\delta_{1p} - \delta_{2p})^2 + (\delta_{1h} - \delta_{2h})^2\right]$ and are given in Table 9. The b values are decreasing with increase of temperature which indicate that the polar and hydrogen bonding components require smaller weights at higher temperatures. The coefficients used to reduce polar and hydrogen bonding components is a variable parameter in the Huang method, Eq. 20, and whereas in the Hansen method, Eq. 15, it is treated as a fixed value. Huang and Deanin suggested that the b value depends on the nature of interaction between the solute probe and the polymer. The interactions in turn depend on temperature and type of polymer and hence the b value may be considered as a variable parameter. Initially δ_{d2}, $\delta_{p,2}$ and $\delta_{h,2}$ values are evaluated using unweighted model, Eq. 19, which are then used in the calculation of b. Eq. 20 can be changed into the following relation

$$\left(\frac{\delta_1'^2}{RT} - \frac{\chi_{12}^{\infty}}{V_1}\right) = \left(\frac{2\delta_{d,2}}{RT}\right)\delta_{d,1} + \left(\frac{2b\delta_{p,2}}{RT}\right)\delta_{p,1} + \left(\frac{2b\delta_{h,2}}{RT}\right)\delta_{h,1} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S^{\infty}}{V_1}\right) \tag{21}$$

where

$$\delta_1'^2 = \delta_{d,1}^2 + b\left(\delta_{p,1}^2\right) + b\left(\delta_{h,1}^2\right) \tag{22}$$

$$\delta_2'^2 = \delta_{d,2}^2 + b\left(\delta_{p,2}^2\right) + b\left(\delta_{h,2}^2\right) \tag{23}$$

The Hansen solubility parameter components of the polymer $\delta_{d,2}$, $\delta_{p,2}$ and $\delta_{h,2}$ in the Eqs. 16, 19 and 21 are obtained by multiple regression. Equation 14 has been used to calculate the total solubility parameter of the polymer, δ_2.

Experimental

The dual column AIMIL (model 5700, AIMIL Ltd, New Delhi) gas chromatograph combined with a module for WinAcds software coupled to personal computer has been used for the measurement of retention times. This equipment is fitted with a Flame Ionization Detector (FID) with a provision for fixing packed columns. The equipment has an LCD processor to control the temperature of the detector, injector and oven. The injector and detector temperatures were set at 100 and 150 °C respectively. Retention times were measured at constant oven temperatures at intervals of 10 °C in the temperature range from 50 to 130 °C. High purity nitrogen after passing through Nucon gas purifier was used as a carrier gas with a flow rate set at 12 mL/min. For the FID detector high signal to noise ratio was obtained using high purity hydrogen and oxygen gases. The two gases are passed through the Nucon gas purifiers to remove moisture and hydrocarbons. The flow rate of H_2 and O_2 are adjusted to obtain the optimum flame.

The analytical grade PCLD, purchased from Sigma-Aldrich Pvt. Ltd. has been used directly for the preparation of column packing. The number average molar mass of the polymer is $\overline{M_n} \sim 1250$ and density at 25 °C is 1.071 g/cm^3. The melting point of the polymer is found to be 48 °C. The chromosorb G/AW-DMCS with particle diameter 150–180 µm purchased from Fluka was used as inert support material in the preparation of column packing. 21 research grade compounds purchased from S.D fine, Merck and Finar are used as probe solutes.

For the preparation of column packing an exact amount of the support (weighed with a precision of ±0.01 g) was wetted with a 3% solution of PCLD (weighed with a precision of 1 mg) prepared using tetrahydrofuran solvent. The evaporation of the solvent was established in a rota evaporator initially at 60–70 °C and then under a slow stream of N_2 in a slowly rotating cylindrical evaporator at 140 °C. The exact weights of the inert support and PCLD have been used to calculate the percent of PCLD present in the stationary phase. The percentage of PCLD has been found to be 14.6%. The stainless steel tube column of 3 mm internal diameter and 2 m length obtained from NUCON was cleaned with methanol and acetone and then dried in the oven for 10 h. The column was weighed before and after packing. The packing was done using mechanical vibrator and applying vacuum. Both ends of the column were closely plugged with glass wool. The column was conditioned at 140 °C for 10 h with N_2 flow rate maintained at 20 mL/min. 0.2 µl of the sample is injected using Hamilton syringe. Each sample is injected three times and the average of the three retention times was used in the calculation of V_g^0.

Results and discussion

The specific retention volumes, V_g^0 and the weight fraction activity coefficients, Ω^∞ for 21 solutes at nine temperatures in the temperature range 323.15–403.15 K are given in Tables 1 and 2 respectively. The V_g^0 and Ω^∞ values are decreasing with increase of temperature for all the solutes, however for $CHCl_3$ the Ω^∞ values are small and nearly constant with change of temperature. The Ω^∞ values are increasing with increase of chain length in *n*-alkane series and in esters series (methyl acetate, ethyl acetate and 1-butyl acetate) where as in 1-alcohols and 2-alcohols the Ω^∞ values are decreasing with increase of chain length. According to Guillet [30] the solutes with $\Omega^\infty < 5$ are good solvents for the PCLD. The linear plots of $\ln V_g^0$ versus $1/T$ for some typical solutes representing different functional groups are shown in Fig. 2. The average partial molar enthalpy of solution $\overline{\Delta H_1^S}$ and the average partial molar enthalpy of mixing $\overline{\Delta H_1^\infty}$ are calculated from the slopes of the linear fit of $\ln V_g^0$ versus $1/T$ and $\ln \Omega^\infty$ versus $1/T$ and using Eqs. 3 and 6 respectively. The results of average molar enthalpy of vaporization ΔH_1^V are obtained using Eq. 8. $\overline{\Delta H_1^S}$, $\overline{\Delta H_1^\infty}$ and ΔH_1^V are presented in Table 3. The average ΔH_1^V values are compared in Table 3 with the ΔH_1^V values calculated by Watson method [20] at 363.15 K, which is the average column temperature. The agreement is good for non-polar solutes and in polar and hydrogen bonding solutes the differences are higher. The partial molar free energy, $\overline{\Delta G_1^\infty}$ and the partial molar entropy, $\overline{\Delta S_1^\infty}$ are calculated using Eqs. 5

Table 1 The specific retention volumes, V_g^0, (cm^3/g) of solutes on poly caprolactonediol in the temperature range 323.15–403.15 K

Solutes	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
n-Pentane	15.08	13.37	12.12	11.57	10.69	9.76	8.82	8.39	7.63
n-Hexane	28.46	24.21	20.88	17.84	16.46	14.23	12.23	11.15	10.22
n-Heptane	56.91	46.72	36.37	29.75	25.02	21.69	17.99	15.89	13.64
n-Octane	125.97	95.19	69.81	54.27	43.63	35.43	29.26	23.91	19.07
Acetone	93.86	79.26	60.54	47.13	38.20	31.29	28.74	23.13	19.17
Ether	26.70	23.30	20.19	17.49	15.71	14.50	12.99	12.07	10.54
Methanol	117.74	85.53	63.37	49.24	40.27	32.03	26.12	22.34	18.47
Ethanol	170.30	130.69	93.50	69.89	55.01	42.50	33.98	28.13	22.55
1-Propanol	399.94	286.00	193.15	148.70	108.40	87.51	59.39	47.77	37.06
1-Butanol			414.35	291.90	211.83	145.87	108.64	81.54	64.53
Benzene	242.01	185.79	136.50	104.23	81.90	64.48	52.84	43.91	33.84
Toluene	517.99	399.67	285.60	206.19	155.07	119.70	93.19	73.39	54.58
2-Propanol	194.04	150.84	106.37	93.13	65.94	46.68	36.86	29.97	22.88
2-Butanol	363.63	303.12	196.21	151.46	110.86	83.32	63.58	49.44	40.64
Dichloromethane	131.91	95.66	83.33	64.99	53.20	43.81	35.55	30.23	23.83
Trichloromethane	310.59	216.57	164.90	117.65	90.69	70.50	55.46	45.49	37.93
Methyl acetate	98.10	80.83	62.34	48.98	40.27	33.60	27.43	23.39	18.83
Ethyl acetate	162.05	128.60	95.30	72.47	57.34	46.16	36.86	30.23	23.83
1-Butyl acetate		545.21	364.91	260.40	175.37	138.54	104.97	79.70	59.19
1,4-Dioxane	497.57	383.93	296.51	242.07	167.39	136.60	104.71	82.60	65.32
THF	157.37	139.27	101.48	74.28	58.37	49.72	40.26	33.13	28.18

and 7 at 363.15 K and are given in Table 3 . $\overline{\Delta H_1^\infty}\big/RT$ is correlated with $\overline{\Delta S_1^\infty}\big/R$ and $\overline{\Delta G_1^\infty}\big/RT$ in Figs. 3 and 4 with correlation coefficients $r = 0.912$ and, $r = 0.802$ respectively. The higher correlation coefficients observed in $\overline{\Delta H_1^\infty}\big/RT$ versus $\overline{\Delta S_1^\infty}\big/R$ is due to compensation of correlated errors between the two properties [31]. Therefore it may be concluded, in spite of lower r value, that the free energy- enthalpy plots are better criteria for evaluation of extra thermodynamic relationships than entropy-enthalpy plots.

The Flory–Huggins interaction parameter χ_{12}^∞ has been evaluated using Eq. 9 and the values are given in Table 4. for some typical solutes the effect of temperature on χ_{12}^∞ has been shown in Fig. 5, which indicate that χ_{12}^∞ is decreasing nonlinearly with temperature. At any one temperature χ_{12}^∞ values are increasing with increase of chain length in *n*-alkanes whereas in the alcohols the trend is reversed. The trend in aromatic compounds is similar to *n*-alkanes, where χ_{12}^∞ values are increasing with increase of size of the compound. As shown in Fig. 6, the χ_{12}^∞ is not linear with the chain length of 1-alcohols the difference in χ_{12}^∞ values between 1-propanol and 1-butanol is very small. The lower χ_{12}^∞ values in

Table 2 The weight fraction activity coefficients, ln Ω^{∞}, of solutes on poly caprolactonediol in the temperature range 323.15–403.15 K

Solutes	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
n-Pentane	2.637	2.474	2.309	2.114	1.958	1.771	1.759	1.631	1.561
n-Hexane	2.873	2.699	2.536	2.404	2.197	2.113	2.033	1.910	1.796
n-Heptane	3.063	2.872	2.762	2.628	2.490	2.343	2.261	2.134	2.051
n-Octane	3.155	2.997	2.898	2.770	2.636	2.515	2.400	2.316	2.276
Acetone	2.272	2.107	2.066	2.027	1.968	1.917	1.769	1.768	1.752
Ether	2.467	2.314	2.191	2.089	1.969	1.838	1.753	1.645	1.614
Methanol	2.407	2.313	2.227	2.119	1.980	1.898	1.808	1.688	1.620
Ethanol	2.303	2.111	2.019	1.913	1.777	1.694	1.594	1.481	1.419
1-Propanol	2.058	1.880	1.799	1.625	1.538	1.376	1.415	1.308	1.260
1-Butanol			1.727	1.590	1.469	1.423	1.334	1.265	1.168
Benzene	1.219	1.122	1.095	1.053	1.005	0.973	0.920	0.870	0.910
Toluene	1.366	1.216	1.173	1.146	1.103	1.054	1.018	0.988	1.033
2-Propanol	2.111	1.888	1.794	1.516	1.477	1.469	1.375	1.273	1.257
2-Butanol	2.044	1.713	1.674	1.497	1.407	1.318	1.243	1.174	1.072
Dichloromethane	0.382	0.393	0.244	0.226	0.179	0.143	0.138	0.100	0.152
Trichloromethane	–0.081	–0.053	–0.089	–0.038	–0.045	–0.041	–0.034	–0.052	–0.073
Methyl acetate	1.349	1.200	1.144	1.092	1.017	0.947	0.917	0.914	0.928
Ethyl acetate	1.447	1.305	1.259	1.212	1.150	1.090	1.058	1.018	1.032
1-Butyl acetate		1.357	1.327	1.264	1.287	1.177	1.132	1.106	1.123
1,4-Dioxane	1.207	1.050	0.923	0.767	0.803	0.697	0.674	0.641	0.623
THF	1.254	1.032	1.031	1.047	1.012	0.916	0.887	0.859	0.812

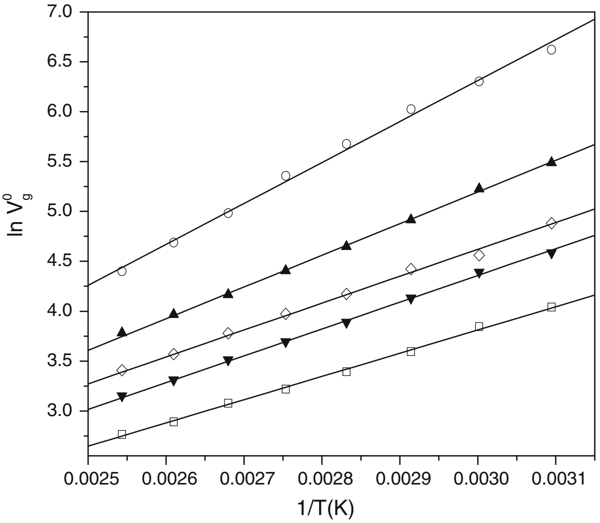

Fig. 2 Retention diagram of some selected solutes on poly (caprolactonediol): *n*-octane (*opened square*), 1-butanol (*opened circle*), methyl acetate (*filled inverted triangle*), benzene (*filled triangle*) and dichloromethane (*opened diamond*) in the temperature range 323.15–403.15 K

Table 3 The partial molar free energy, $\overline{\Delta G_1^\infty}$, and partial molar entropy, $\overline{\Delta S_1^\infty}$, at 363.15 K

Solutes	$\overline{\Delta H_1^\infty}$ (kJ mol^{-1})	$\overline{\Delta G_1^\infty}$ (kJ mol^{-1})	$\overline{\Delta S_1^\infty}$ (JK^{-1} mol^{-1})	$\overline{\Delta H_1^S}_{\text{Sorp}}$ (kJ mol^{-1})	ΔH_1^V (Cal) (kJ mol^{-1})	ΔH_1^V (The) (kJ mol^{-1})
n-Pentane	15.069	5.912	25.217	–8.909	23.978	22.065
n-Hexane	14.476	6.633	21.597	–13.979	28.455	27.389
n-Heptane	13.680	7.518	16.968	–19.358	33.037	32.293
n-Octane	12.354	7.959	12.104	–25.125	37.479	36.990
Acetone	6.902	5.942	2.644	–21.653	28.554	26.898
Ether	11.879	5.945	16.340	–12.260	23.239	22.685
Methanol	10.980	5.978	13.774	–27.584	38.563	33.221
Ethanol	11.777	5.365	17.656	–32.161	43.938	37.685
1-Propanol	10.816	4.644	16.998	–34.135	44.951	42.520
1-Butanol	13.371	4.435	24.607	–26.398	39.769	45.606
Benzene	4.416	3.034	3.806	–30.509	34.926	30.201
Toluene	4.456	3.330	3.099	–29.267	33.723	34.381
2-Propanol	11.269	4.459	18.752	–28.643	39.913	39.014
2-Butanol	11.948	4.248	21.203	–22.332	34.279	41.684
Dichloromethane	3.867	0.540	9.160	–25.989	29.856	26.128
Trichloromethane	–0.285	–0.135	–0.412	–34.781	34.496	28.876
Methyl acetate	5.782	3.071	7.469	–27.775	33.557	28.026
Ethyl acetate	5.576	3.472	5.794	–24.349	29.926	31.018
1-Butyl acetate	4.763	3.886	2.417	–23.469	28.233	38.872
1,4-dioxane	7.610	2.424	14.279	–22.412	30.022	37.049
THF	4.920	3.055	5.135	–30.865	35.786	30.491

Average partial molar enthalpy of solution, $\overline{\Delta H_1^S}$, average partial molar enthalpy of mixing, $\overline{\Delta H_1^\infty}$, calculated average enthalpy of vaporization, ΔH_1^V(Cal) and theoretical enthalpy of vaporization ΔH_1^V(The) at 363.15 K

cyclohexanone when compared to cyclohexane is due to the interaction of –C=O group with the polymer molecule.

The solubility parameter for the PCLD has been obtained by the Guillet and DiPaola-Baranyi method at an interval of 10 °C in the temperature range from 323.15 to 403.15 K. The Hansen solubility parameters are also obtained for poly caprolactonediol using Eq. 16, which has been derived in this work based on Hansen theory, and using Eqs. 19 and 20 due to Huang. According to Guillet's procedure the δ_1 of 21 solute probes are linearly fitted as a function of the left hand side of Eq. 13. From the slope of the linear plot δ_2 is obtained directly and the values are given in Table 5 along with the statistical results of the fit. The correlation coefficient of the linear fit is greater than 0.994 at all the temperatures. The δ_2 values are decreasing with increase of temperature.

The Hansen solubility parameters for the 21 solutes at 298.15 K are taken from the literature [12]. The $\delta_{d,1}$, $\delta_{p,1}$ and $\delta_{h,1}$ values at the experimental temperatures are calculated using the relations proposed by Hansen and Beerbower [32].

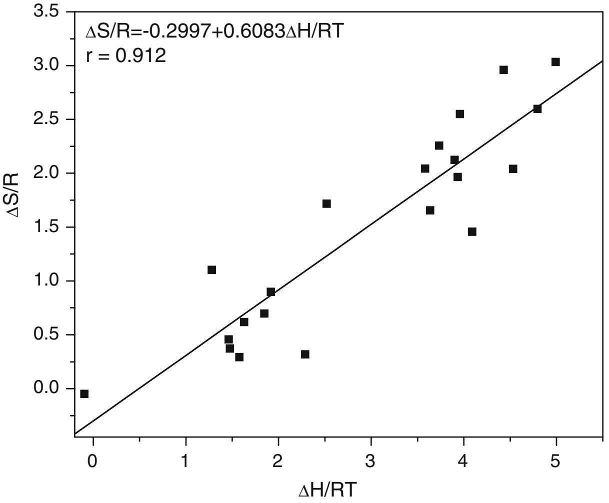

Fig. 3 The correlation between partial molar entropy, Δ*S*/*R* at 363.15 K and average partial molar enthalpy, Δ*H*/RT for solutes on Poly (caprolactonediol)

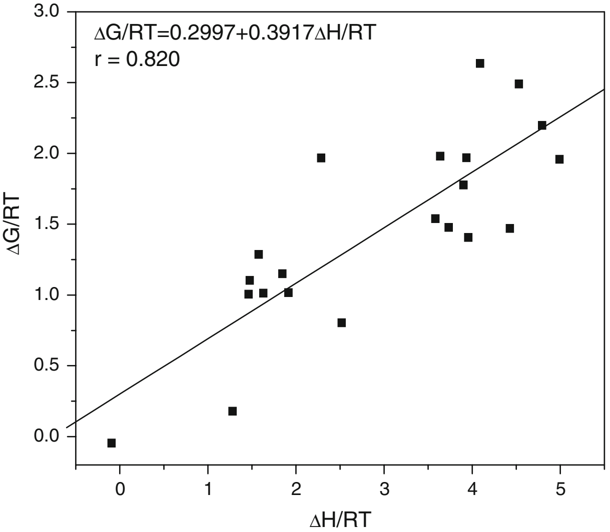

Fig. 4 The correlation between partial molar free energy, Δ*G*/RT at 363.15 K and average partial molar enthalpy, Δ*H*/RT for solutes on Poly (caprolactonediol)

$$\begin{aligned} d\delta_{\mathrm{d}}/dT &= -1.25\alpha\delta_{\mathrm{d}} \\ d\delta_{\mathrm{p}}/dT &= -\alpha\delta_{\mathrm{p}}/2 \\ d\delta_{\mathrm{h}}/dT &= -\left(1.22\times10^{-3}+\alpha/2\right)\delta_{\mathrm{h}} \end{aligned} \tag{24}$$

Table 4 Flory–Huggins interaction parameter at infinite dilution, χ_{12}^{∞}, of solutes on poly caprolactonediol in the temperature range 323.15–403.15 K

Solutes	323.15	333.15	343.15	353.15	363.15	373.15	383.15	393.15	403.15
n-Pentane	1.048	0.866	0.682	0.465	0.287	0.076	0.038	–0.118	–0.218
n-Hexane	1.344	1.153	0.974	0.825	0.600	0.497	0.397	0.253	0.117
n-Heptane	1.575	1.371	1.246	1.098	0.944	0.781	0.682	0.537	0.436
n-Octane	1.698	1.528	1.416	1.275	1.127	0.992	0.862	0.762	0.706
Acetone	0.325	0.142	0.083	0.026	–0.052	–0.124	–0.294	–0.318	–0.358
Ether	0.531	0.359	0.215	0.091	–0.052	–0.208	–0.320	–0.457	–0.520
Methanol	1.056	0.945	0.841	0.714	0.555	0.453	0.340	0.198	0.106
Ethanol	0.952	0.743	0.635	0.511	0.357	0.254	0.134	–0.001	–0.085
1-Propanol	0.731	0.538	0.442	0.253	0.150	–0.029	–0.007	–0.133	–0.200
1-Butanol			0.423	0.272	0.137	0.077	–0.028	–0.113	–0.227
Benzene	–0.012	–0.121	–0.161	–0.216	–0.279	–0.324	–0.392	–0.458	–0.434
Toluene	0.122	–0.040	–0.094	–0.133	–0.189	–0.250	–0.299	–0.343	–0.312
2-Propanol	0.757	0.518	0.408	0.113	0.056	0.029	–0.085	–0.207	–0.246
2-Butanol	0.721	0.375	0.322	0.129	0.022	–0.082	–0.175	–0.262	–0.383
Dichloromethane	–0.451	–0.457	–0.624	–0.661	–0.728	–0.784	–0.811	–0.871	–0.843
Trichloromethane	–0.788	–0.773	–0.822	–0.785	–0.806	–0.818	–0.826	–0.861	–0.899
Methyl acetate	0.164	–0.001	–0.074	–0.143	–0.236	–0.326	–0.376	–0.400	–0.409
Ethyl acetate	0.232	0.074	0.012	–0.051	–0.130	–0.207	–0.258	–0.319	–0.325
1-Butyl acetate		0.115	0.073	–0.002	0.007	–0.116	–0.175	–0.215	–0.213
1,4-Dioxane	0.137	–0.032	–0.172	–0.340	–0.317	–0.436	–0.474	–0.521	–0.554
THF	0.044	–0.196	–0.217	–0.219	–0.273	–0.386	–0.431	–0.478	–0.542

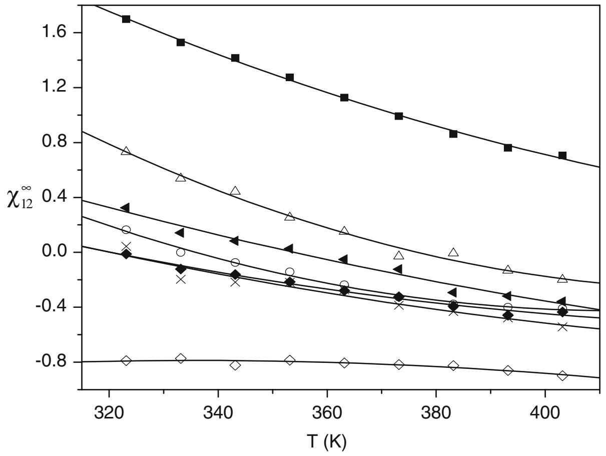

Fig. 5 Variation of χ_{12}^{∞} values with temperature on Poly (caprolactonediol) for some selected solute probes: *n*-octane (*filled square*), 1-propanol (*opened triangle*), methyl acetate (*opened circle*), benzene (*filled diamond*), acetone (*left triangle*), THF (*multiplication*) and trichloromethane (*opened diamond*)

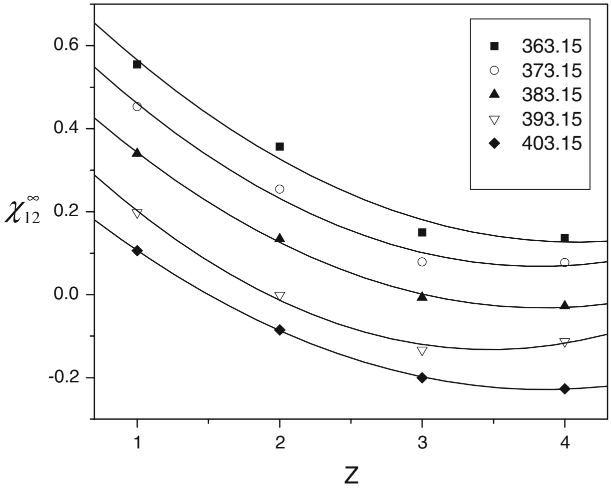

Fig. 6 Variation of χ_{12}^{∞} with carbon number, *Z*, of 1-alcoholos on Poly (caprolactonediol)

Table 5 The results of the statistical analysis, of Eq. 13, slope $\left(\frac{\delta_2}{RT}\right)$,intercept $\left(\frac{\delta_2^2}{RT}+\frac{\chi_S^{\infty}}{V_1^0}\right)$, correlation coefficient, *r*, and solubility parameter, δ_2, of PCLD

T (K)	$2\left(\frac{\delta_2}{RT}\right)$	$\left(\frac{\delta_2^2}{RT}+\frac{\chi_S^{\infty}}{V_1^0}\right)$	*r*	δ_2 (MPa)$^{1/2}$
323.15	0.01445 ± 0.00024	–0.1404 ± 0.0048	0.997	19.41 ± 0.33
333.15	0.01399 ± 0.00020	–0.1301 ± 0.0039	0.998	19.37 ± 0.29
343.15	0.01293 ± 0.00021	–0.1171 ± 0.0039	0.997	18.44 ± 0.30
353.15	0.01239 ± 0.00020	–0.1097 ± 0.0037	0.997	18.19 ± 0.30
363.15	0.01184 ± 0.00021	–0.1020 ± 0.0037	0.997	17.87 ± 0.32
373.15	0.01125 ± 0.00020	–0.0936 ± 0.0038	0.996	17.45 ± 0.34
3831.5	0.01071 ± 0.00021	–0.0863 ± 0.0037	0.996	17.06 ± 0.35
393.15	0.01021 ± 0.00023	–0.0795 ± 0.0039	0.995	16.69 ± 0.38
403.15	0.00969 ± 0.00024	–0.0727 ± 0.0039	0.994	16.24 ± 0.41

where α is the thermal expansion coefficient which has been calculated using molar volumes at 25 °C and the molar volumes at experimental temperatures. The solubility parameter components calculated using Eq. 24 at 90 °C and the temperature gradients of solubility parameter components are given in Table 6. The three components of the solubility parameter $\delta_{d,1}$, $\delta_{p,1}$ and $\delta_{h,1}$ of the 21 solutes are fitted as a function of the left hand side of the Eqs. 16, 19 and 21 by multiple regression analysis. The coefficients of the multiple regression are used to obtain the dispersive component, δ_{d2}, polar component, $\delta_{p,2}$, hydrogen bonding component, $\delta_{h,2}$ of the polymer. The three components, δ_{d2}, $\delta_{p,2}$ and $\delta_{h,2}$ are used in Eq. 14 to calculate the total solubility parameter of the polymer, δ_2. The solubility parameter values $\delta_{d,2}$, $\delta_{p,2}$, $\delta_{h,2}$, δ_2 and the corresponding statistical data obtained when Eqs. 16, 19 and 21 are applied, have been presented in Tables 7, 8 and 9

Table 6 The three components of the Hansen solubility parameters of solutes, dispersion, $\delta_{d,1}$, polar, $\delta_{p,1}$, and hydrogen bonding, $\delta_{h,1}$, and total, $\delta_{T,1}$, at 363.15 K

Solutes	$\delta_{d,1}$ (MPa)$^{1/2}$	$\delta_{p,1}$ (MPa)$^{1/2}$	$\delta_{h,1}$ (MPa)$^{1/2}$	$\delta_{T,1}$ (MPa)$^{1/2}$	dδ_d/dT (MPa)$^{1/2}$ K^{-1}	dδ_p/dT (MPa)$^{1/2}$ K^{-1}	dδ_h/dT (MPa)$^{1/2}$ K^{-1}
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	13.398	0.000	0.000	13.398	–0.029	0.000	0.000
n-Octane	13.586	0.000	0.000	13.586	–0.029	0.000	0.000
Benzene	16.113	0.000	1.742	16.207	–0.035	0.000	–0.004
Toluene	16.011	1.338	1.753	16.162	–0.031	0.001	–0.004
Dichloromethane	14.828	5.833	5.164	16.75	–0.052	–0.007	–0.014
Trichloromethane	15.096	2.912	4.902	16.137	–0.042	–0.003	–0.012
Methanol	12.290	11.385	18.872	25.235	–0.043	–0.014	–0.053
Ethanol	13.066	8.191	16.519	22.598	–0.042	–0.009	–0.044
1-Propanol	13.647	6.400	14.997	21.263	–0.036	–0.006	–0.037
1-Butanol	13.972	5.411	13.746	20.333	–0.031	–0.004	–0.032
2-Propanol	13.143	5.690	13.996	20.025	–0.041	–0.006	–0.037
2-Butnaol	13.476	5.365	12.497	19.146	–0.036	–0.005	–0.031
Diethyl ether	11.072	2.626	4.213	12.134	–0.053	–0.004	–0.014
Tetrahydrofuran	14.329	5.365	6.895	16.782	–0.038	–0.005	–0.017
Acetone	12.603	9.623	5.922	16.927	–0.045	–0.012	–0.017
Methyl acetate	13.006	6.737	6.508	16.028	–0.038	–0.007	–0.017
Ethyl acetate	13.297	4.964	6.173	15.477	–0.039	–0.005	–0.016
1-butyl acetate	13.964	3.528	5.508	15.420	–0.028	–0.003	–0.012
1,4-dioxane	16.545	1.707	6.431	17.833	–0.038	–0.001	–0.015

The temperature gradients of $\delta_{d,1}$, $\delta_{p,1}$ and $\delta_{h,1}$ are also given

Table 7 The Hansen solubility parameters of PCLD calculated using Eq. 16: dispersion, $\delta_{d,2}$, polar, $\delta_{p,2}$, hydrogen bonding, $\delta_{h,2}$ total solubility parameter, δ_2 and correlation coefficient, *r*

T (K)	$\delta_{d,2}$ (MPa)$^{1/2}$	$\delta_{p,2}$ (MPa)$^{1/2}$	$\delta_{h,2}$ (MPa)$^{1/2}$	$\delta_{T,2}$ (MPa)$^{1/2}$	*r*
298.15[a]	20.67	7.56	5.61	22.61	
323.15	18.59 ± 0.67	7.42 ± 1.65	5.59 ± 0.87	20.78 ± 1.98	0.991
333.15	18.28 ± 0.58	7.20 ± 1.49	6.09 ± 0.80	20.57 ± 1.79	0.993
343.15	17.42 ± 0.65	7.30 ± 1.69	5.69 ± 0.91	19.73 ± 2.03	0.990
353.15	16.66 ± 0.68	6.40 ± 1.82	6.34 ± 0.99	18.94 ± 2.18	0.989
363.15	15.79 ± 0.73	6.64 ± 2.00	6.28 ± 1.10	18.25 ± 2.40	0.986
373.15	15.09 ± 0.76	6.64 ± 2.14	6.19 ± 1.19	17.61 ± 2.57	0.983
383.15	14.43 ± 0.76	7.26 ± 2.21	5.87 ± 1.24	17.19 ± 2.65	0.982
393.15	13.63 ± 0.81	6.67 ± 2.44	6.24 ± 1.39	16.41 ± 2.92	0.977
403.15	12.85 ± 0.79	6.12 ± 2.50	6.55 ± 1.45	15.67 ± 2.99	0.976

[a] Extrapolated data

Table 8 The Hansen solubility parameters of PCLD calculated using Eq. 19: dispersion $\delta_{d,2}$, polar $\delta_{p,2}$, hydrogen bonding $\delta_{h,2}$ total solubility parameter δ_2, and correlation coefficient r

T (K)	$\delta_{d,2}$ (MPa)$^{1/2}$	$\delta_{p,2}$ (MPa)$^{1/2}$	$\delta_{h,2}$ (MPa)$^{1/2}$	δ_2 (MPa)$^{1/2}$	r
323.15	16.62 ± 3.51	3.83 ± 2.15	9.73 ± 1.14	19.63 ± 4.27	0.971
333.15	16.15 ± 2.95	3.52 ± 1.88	9.56 ± 1.02	19.09 ± 3.65	0.976
343.15	15.70 ± 2.71	3.45 ± 1.77	9.13 ± 0.96	18.49 ± 3.37	0.977
353.15	15.27 ± 2.57	3.20 ± 1.72	9.19 ± 0.94	18.11 ± 3.23	0.978
363.15	14.66 ± 2.51	3.20 ± 1.72	9.07 ± 0.95	17.53 ± 3.18	0.977
373.15	14.22 ± 2.37	3.13 ± 1.67	8.92 ± 0.93	17.08 ± 3.05	0.977
383.15	13.78 ± 2.23	3.20 ± 1.62	8.71 ± 0.92	16.61 ± 2.91	0.977
393.15	13.17 ± 2.141	2.94 ± 1.63	8.65 ± 0.93	16.03 ± 2.85	0.976
403.15	12.54 ± 1.99	2.66 ± 1.58	8.55 ± 0.91	15.40 ± 2.70	0.976

Table 9 The Hansen solubility parameters of PCLD calculated using Eq. 21: dispersion $\delta_{d,2}$, polar $\delta_{p,2}$, hydrogen bonding, $\delta_{h,2}$ total solubility parameter δ_2, correlation coefficient r, and the b values

T (K)	$\delta_{d,2}$ (MPa)$^{1/2}$	$\delta_{p,2}$ (MPa)$^{1/2}$	$\delta_{h,2}$ (MPa)$^{1/2}$	$\delta_{T,2}$ (MPa)$^{1/2}$	r	b
298.15[a]	20.21	6.20	6.57	22.02		
323.15	18.39 ± 0.70	6.86 ± 1.53	6.09 ± 0.81	20.55 ± 1.87	0.991	0.28 ± 0.06
333.15	17.95 ± 0.62	6.37 ± 1.34	6.79 ± 0.72	20.22 ± 1.64	0.993	0.30 ± 0.05
343.15	17.06 ± 0.67	6.30 ± 1.43	6.53 ± 0.77	19.32 ± 1.76	0.991	0.31 ± 0.05
353.15	16.38 ± 0.69	5.68 ± 1.54	6.90 ± 0.84	18.66 ± 1.89	0.989	0.30 ± 0.05
363.15	15.64 ± 0.74	6.15 ± 1.81	6.63 ± 0.99	18.07 ± 2.19	0.986	0.28 ± 0.05
373.15	15.00 ± 0.76	6.26 ± 1.99	6.43 ± 1.11	17.48 ± 2.40	0.983	0.27 ± 0.06
383.15	14.40 ± 0.76	7.04 ± 2.13	5.99 ± 1.19	17.11 ± 2.56	0.982	0.26 ± 0.06
393.15	13.68 ± 0.80	6.88 ± 2.54	6.14 ± 1.45	16.50 ± 3.03	0.977	0.24 ± 0.06
403.15	12.89 ± 0.79	6.56 ± 2.71	6.75 ± 1.57	15.96 ± 3.23	0.976	0.23 ± 0.07

[a] Extrapolated data

respectively. The comparison of the results presented in Tables 7 and 9 indicate that the errors in the parameters, δ_{d2}, $\delta_{p,2}$, $\delta_{h,2}$ and δ_2 are smaller and the correlation coefficients, r, are better compared to the data set presented in Table 8. This indicate that the errors in three dimensional solubility parameter model are largely reduced when lower weights are used for polar and hydrogen bonding components. The δ_{d2}, $\delta_{p,2}$, $\delta_{h,2}$ and δ_2 values are given in Tables 7 and 9 are nearly similar. The δ_{d2} and δ_2 values in Tables 7 and 9 are decreasing with increase of temperature whereas $\delta_{p,2}$ and $\delta_{h,2}$ values are nearly independent of temperature. The variation of HSP and the total solubility parameter with temperature is shown in Fig. 7 for the two data sets and the plots are extrapolated to 298.15 K. The extrapolated results are included in Table 7 and 9. The comparison of errors in HSP and correlation coefficients obtained Hansen method and Huang method indicate that in both the methods the errors and r values are nearly same. Further it is observed that in both the methods the errors are slightly increasing with increase of temperature.

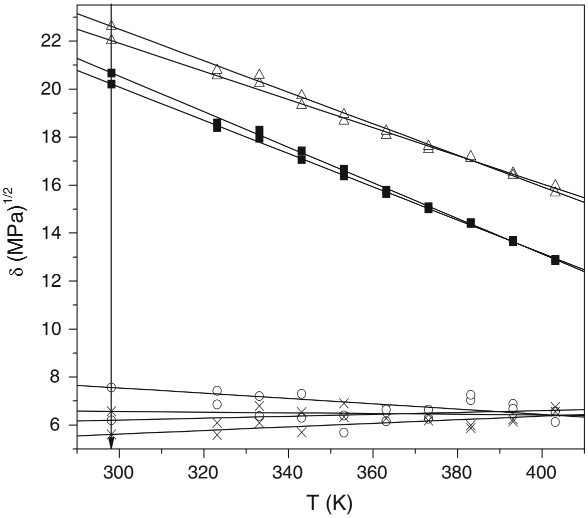

Fig. 7 The variation of Hansen solubility parameters with temperature; dispersive $\delta_{d,2}$ (*filled square*), polar $\delta_{p,2}$ (*opened circle*), hydrogen bonding $\delta_{h,2}$ (*multiplication*), total solubility parameters δ_2 (*opened triangle*). The plots are for the data given in Tables 7 and 9

Conclusion

Specific retention volumes have been determined for 21 solute probes on PCLD as a function of temperature. The results are used to evaluated infinite dilution thermodynamic properties such as weight fraction activity coefficient, partial molar free energy, partial molar enthalpy, partial molar entropy and Flory–Huggins interaction parameter, χ_{12}^{∞}. The χ_{12}^{∞} values are increasing with increase of chain length in *n*-alkanes, whereas in 1-alcohols the trend is reversed. The solubility parameter, δ_2, for the molten PCLD has been obtained as a function of temperature by Guillet method which is decreasing with increase of temperature. The values of Hansen solubility parameters calculated by the new method based on Hansen theory and Huang method are nearly same. The errors in HSP are smaller and nearly similar in both the methods. Among the Hansen solubility parameters the dispersive component $\delta_{d,2}$ is decreasing with increase of temperature the polar component $\delta_{p,2}$ and the hydrogen bonding component, $\delta_{h,2}$, are nearly constant with increase of temperature.

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