

Solubility Parameter of Fluids from Molecular Thermodynamic Model

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The modified square well potential is combined with perturbed-hard-trimer-chain (PHTC) EOS to predict the solubility parameters of several fluids including alkanes, refrigerants and molten polymers. The performance of the proposed model has been evaluated by predicting the solubility parameters of 12 hydrocarbons, 3 refrigerants and 12 polymers. Out of 263 data points for hydrocarbons and refrigerants, the average absolute deviations percent (AAD%) of the predicted densities and solubility parameter from the experimental ones were found to be 1.74% and 1.09%, respectively. Additionally, out of 1993 data points of 12 polymers, the AADs% of the predicted densities were found to be 0.43% and out of 60 data points examined, the AAD% of the predicted solubility parameters from the experimental ones were found to be 0.56%, respectively.

Keywords: Solubility parameter, Square-well, Equation of state, Miscibility

INTRODUCTION

The solubility parameter is used in industries [1,2] such as oil exploration, processing and transportation, oil and natural gas storage, supercritical extraction, and polymer foam and mixing. In order to design a chemical, it is important to choose the best solvent. Hildebrand and Scott [3] were the first to work on the solubility parameter introduced by Scatchard [4].

Group contribution methods have been used to calculate solubility parameters by various research groups [5-7]. To calculate the hydrogen bonding component, the lattice fluid theory (LFT) method was investigated by Panayiotou [8]. The internal energy of supercritical gas was used to calculate the Hildebrand solubility parameter (HSP) of supercritical fluids by Allada [9]. Further, the HSP for CO₂ in a wide range of pressures and temperatures has been correlated by Williams *et al.* [10].

Gharagheizi *et al.* [11] calculated the effects of Hansen sphere model on the solubility parameter. Stefanis *et al.* [12] evaluated a method for predicting the partial solubility parameter using equation of state. The HSPs of hydrocarbons have been evaluated using PC-SAFT (perturbed-chain statistical associating fluid theory) EOS [13]. In the other works, the relation between solubility parameter and the internal pressure has been calculated [14,15].

The solubility parameter was introduced by Hildebrand and Scott [16], which is useful parameter for predicting solubility of polymers [17-20]. There is much interest now in the use of solubility parameters for rationally designing new processes, such as supercritical extraction or new materials such as drugs and polymer alloys [21].

In the present study, a perturbed-hard-trimer-chain (PHTC) equation of state in conjunction with a theoretical-based model is employed to model the solubility parameter of several fluids including alkanes, refrigerants, and polymers.

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THEORY

Perturbed Hard-Trimer-Chain Equation of State (PHTC EOS)

The PHTC EOS has been previously applied to predict the volumetric properties of amorphous and molten polymers by Alavianmehr *et al.* [22], whose general expression is:

$$Z^{PHTC} = \left(\frac{P}{\rho k_B T} \right)^{PHTC} = Z^{HS} + Z^{Pert} \quad (1)$$

where P is the pressure, ρ is the number (molar) density, and $k_B T$ is the thermal energy per molecule. The hard-sphere long-chain part of the above-mentioned equation is as follows [23]:

$$Z^{HS} = \left(\frac{P}{\rho k_B T} \right)^{HS} = 3(1 + b \rho g^{HS}(\sigma)) - 2 \left\{ 1 + \eta \frac{\partial \ln g^{HS}(\sigma)}{\partial \eta} \right\} \quad (2)$$

Here, $g^{HS}(\sigma)$ denotes the radial distribution function (RDF) of hard-spheres at contact which is developed by Carnahan-Starling (CS) [24]. The exact expression can be evaluated from the general relationship:

$$g^{HS}(\sigma) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (3)$$

where, η is the packing fraction of hard-core-chain defined by:

$$\eta = \frac{m \pi \rho \sigma^3}{6} \quad (4)$$

In Eq. (4), m is the segment number and b represents the van der Waals co-volume which is theoretically related to the hard-core diameter by the following equation:

$$b = \frac{2 \pi \sigma^3}{3} \quad (5)$$

The second term in the right hand of Eq. (1) represents an attractive part of the van der Waals equation of state

which is introduced as the perturbation term:

$$Z^{Pert} = \left(\frac{P}{\rho k_B T} \right)^{Pert} = - \frac{m^2 a(T) \rho}{k_B T} \quad (6)$$

One temperature-dependent parameter, $a(T)$ which appears in the proposed PHTC EOS is related to the attractive forces between non-bonded segments. This parameter is usually determined using the corresponding states correlations based on the molecular scaling parameters reflecting dispersive energy parameters, ε and the hard-core diameter, σ . As a matter of fact, $a(T)$ can be expressed in terms of the universal function of reduced temperature. In the present work, the attractive parameter is correlated with the hard-core diameter and the non-bonded interaction energy between two trimer spheres (or two segments formed by the trimer cores), according to the following equation:

$$a(T) = \frac{2 \pi}{3} \sigma^3 \varepsilon F_a \left(\frac{k_B T}{\varepsilon} \right) \quad (7)$$

where, F_a is the universal function of the reduced temperature ($k_B T / \varepsilon$) which can be written as the following empirical relation [25]:

$$F_a(k_B T / \varepsilon) = 1.8681 \exp[-0.0619(k_B T / \varepsilon)] + 0.6715 \exp[-1.7317(k_B T / \varepsilon)^{3/2}] \quad (8)$$

Solubility Parameter Concept

The value of the solubility parameter (δ) is a measure of the square root of the internal energy per unit volume that is defined as the cohesive energy density. The solubility of the substance is related to its molecular structure with the following equation [3]:

$$\delta = \left(\frac{\Delta E_{vap}}{V_{saturated}} \right)^{1/2} = \left(\frac{\Delta U_{vap}}{V_{saturated}} \right)^{1/2} = \left(\frac{\Delta H_{vap} - RT}{V_{saturated}} \right)^{1/2} \quad (9)$$

where, $\Delta V_{saturated}$, ΔH_{vap} and ΔE_{vap} are the molar volume,

enthalpy of vaporization and cohesive energy, respectively, and ΔU_{vap} is the energy change upon isothermal vaporization of the saturated liquid to the ideal-gas state [26].

Molecular Thermodynamic Model

The internal pressure, π_T , and the solubility parameter, δ^2 , are related to each other based on the following equation [27]:

$$\delta^2 = \pi_T + \frac{A}{\rho} \quad (10)$$

where, A is a constant.

Based on the perturbation theory [28] the following expression is suggested for the internal pressure:

$$\pi_T = \pi_T^{\text{ref}} + \pi_T^{\text{pert}} \quad (11)$$

In the above equation, the superscripts "ref" and "pert" refer to the reference fluid and perturbed term, respectively.

On the other hand, the relation between the internal pressure and the inter-particle pair potential, $u(r)$, is given by the following equation [29]:

$$\pi_T = -2\pi\rho^2 \int_0^\infty u(r) \left[g(r) + \rho \left(\frac{\partial g(r)}{\partial \rho} \right)_{r,T} \right] r^2 dr \quad (12)$$

where, $g(r)$ is the RDF, r is the intermolecular distance and ρ is the density.

By simple differentiation with respect to the volume, Eq. (12) was obtained from the total energy equation [29]. Meanwhile, by combining these equations, it is possible to link the solubility parameter to the molecular theory based on the statistical mechanical expression for fluids.

In the proposed model, the reference fluid is assumed to be a chain composed of spherical segments. The pair potential for the segment of the chain is given by a modified square-well potential proposed by Chen, and Kreglewski [30]:

$$u^{\text{ref}}(r) = \begin{cases} \infty & r < \omega\sigma \\ 3\varepsilon & \omega\sigma < r < \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases} \quad (13)$$

where, r is the distance between molecules, σ is the hard-core diameter, ε is the non-bonded interaction energy between pair-wise trimmers, λ is the well width and ω is the optimized parameter in modified square-well potential.

The radial distribution function proposed by Carnahan-Starling [24] (Eq. (3)) is used in the reference term of the proposed model.

For the perturbation term, the LJ (12-6) inter-particle pair potential function together with as simplified RDF expression proposed by Xu and Hu [31] were employed. The LJ (12, 6) potential function for pure fluids is defined as:

$$u^{\text{pert}}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (14)$$

The required RDF expression for use in the perturbed section, taken from Xu and Hu, [31] reads as follows:

$$g(r) = H(r-r^*) + (r^* - \sigma^3) D(r-r^*) / 3r^{*2} \quad (15)$$

where H is the Heaviside function [32]

$$\begin{cases} H(x-a) = 1, & x > a \\ H(x-a) = 0, & x < a \\ H(x-a) = 1/2 & x = a \end{cases} \quad (16)$$

Here, $r^* = 1.150d$ is the distance between molecules in the first coordination shell, and $r^{**} = 1.575d$ is the outer radius of the first coordination shell [33] and D is Dirac delta function, viz:

$$\begin{cases} D(x-a) = 0, & x \neq a \\ D(x-a) = \infty, & x = a \end{cases} \quad (17)$$

The following expression is proposed as relationship

Table 1. Optimized Pure-component Parameters for the Studied Fluids

	M_w (g mol ⁻¹)	ε/k_B (K)	σ (nm)	m	λ	ω
Hydrocarbons						
n-Pentane	72	277	0.371	3.17	2.24	0.600
n-Hexane	86	278	0.385	3.27	2.39	0.600
n-Heptane	100	280	0.397	3.6	2.05	0.620
n-Octane	114	285	0.410	3.65	2.60	0.600
n-Nonane	128	293	0.426	3.97	2.52	0.600
n-Decane	142	295	0.440	3.40	3.29	0.580
n-Dodecane	170	300	0.457	3.74	2.99	0.600
Toluene	92	240	0.341	4.32	3.06	0.580
Cyclohexane	84	270	0.355	3.78	2.53	0.590
Benzene	78	260	0.333	3.43	2.61	0.600
2-methylpentane	86	270	0.384	3.61	2.20	0.600
2-methylbutane	72	275	0.370	3.84	1.92	0.600
R143a	84.04	110	0.289	3.70	2.90	0.640
R12	120.91	127	0.284	5.44	3.22	0.580
R13	104.46	125	0.293	3.55	3.16	0.530
Polymers						
PVME	58	100	0.240	6.44	4.54	0.610
PVC	62.45	165	0.240	4.81	3.68	0.400
PVAc	86	206	0.290	4.80	3.63	0.595
PS	104	240	0.325	5.10	3.83	0.570
PMMA	100	190	0.290	5.99	4.44	0.550
PC	254.3	1140	0.53	2.26	2.70	0.350
PTFE	100	50	0.170	19.4	4.90	0.588
PSF	442	390	0.403	13.26	6.90	0.350
PET	192	97	0.260	17.86	8.30	0.584
PDMS	74	175	0.300	3.81	2.90	0.625
PBD	54	104	0.250	6.21	4.50	0.612
PA6	113	240	0.330	4.86	4.50	0.591

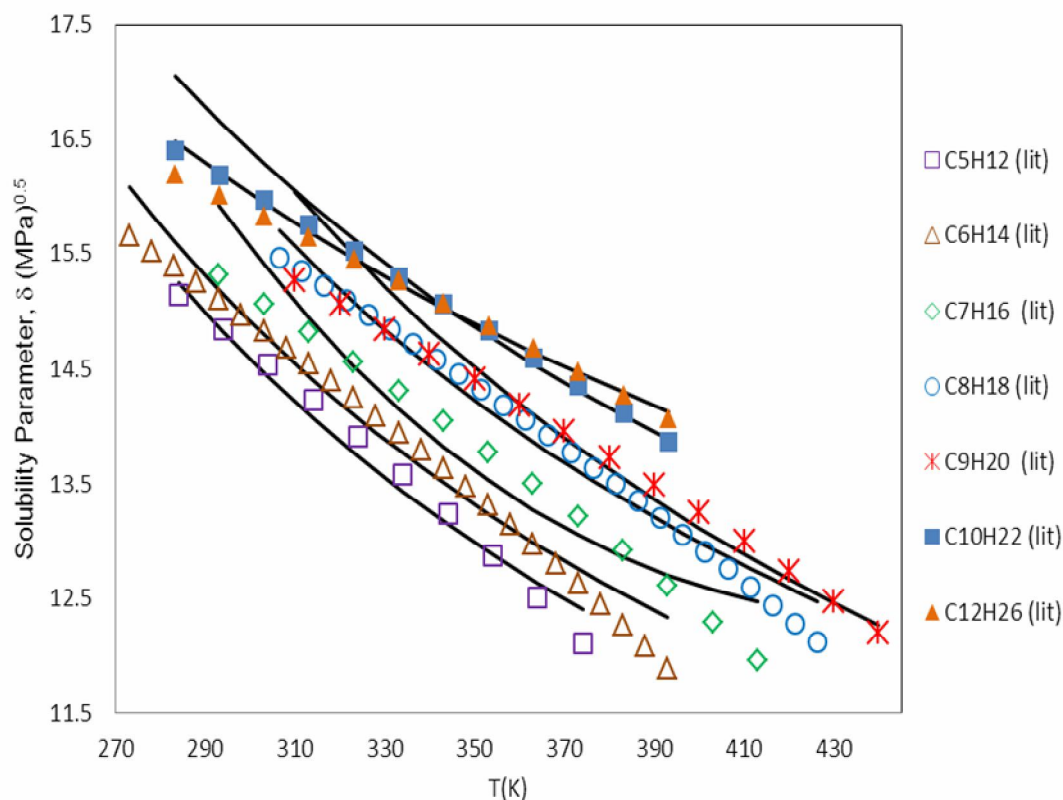


Fig. 1. Saturated behaviour of solubility parameters of selected alkanes at several temperatures. The markers represent the literature [40] and the solid lines are those estimated from the proposed model for C_5H_{12} (\square), C_6H_{14} (Δ), C_7H_{16} (\diamond), C_8H_{18} (\circ), C_9H_{20} ($*$), $C_{10}H_{22}$ (\blacksquare) and $C_{12}H_{26}$ (\blacktriangle).

between the hard sphere diameter, d , and the soft sphere diameter of LJ (12, 6), σ by Li and Lu [34]:

$$d = \left[\frac{1 + 0.2977 kT / \varepsilon}{1 + 0.3316 kT / \varepsilon + 0.0010477 (kT / \varepsilon)^2} \right] \sigma \quad (18)$$

Finally, the solubility parameter is employed to predict the miscibility of polymers through polymer-polymer interaction parameter χ . Molecular mixing of two high molecular weight polymers can occur only when χ is very close to zero [35,36]. This approach suffers from two distinct and important limitations: it requires that χ to be always zero or positive and it imposes the condition that the solubility parameter is precisely calculated (or known) in order to determine the magnitude of this difference. The

polymer-polymer interaction parameter χ can be calculated according to the following expression [37,38]:

$$\chi = \frac{V_r}{RT} (\delta_1 - \delta_2)^2 \quad (19)$$

where V_r is the molar volume of the rubbery phase of the repeat unit, and δ_1 , δ_2 are the solubility parameters of the two polymers.

RESULTS AND DISCUSSION

To utilize the proposed PHTC EOS the values of five pure-component parameters, m , σ , ε , λ and ω for all studied fluids are determined. Physically, these parameters reflect the segment number, hard-core diameter, non-bonded

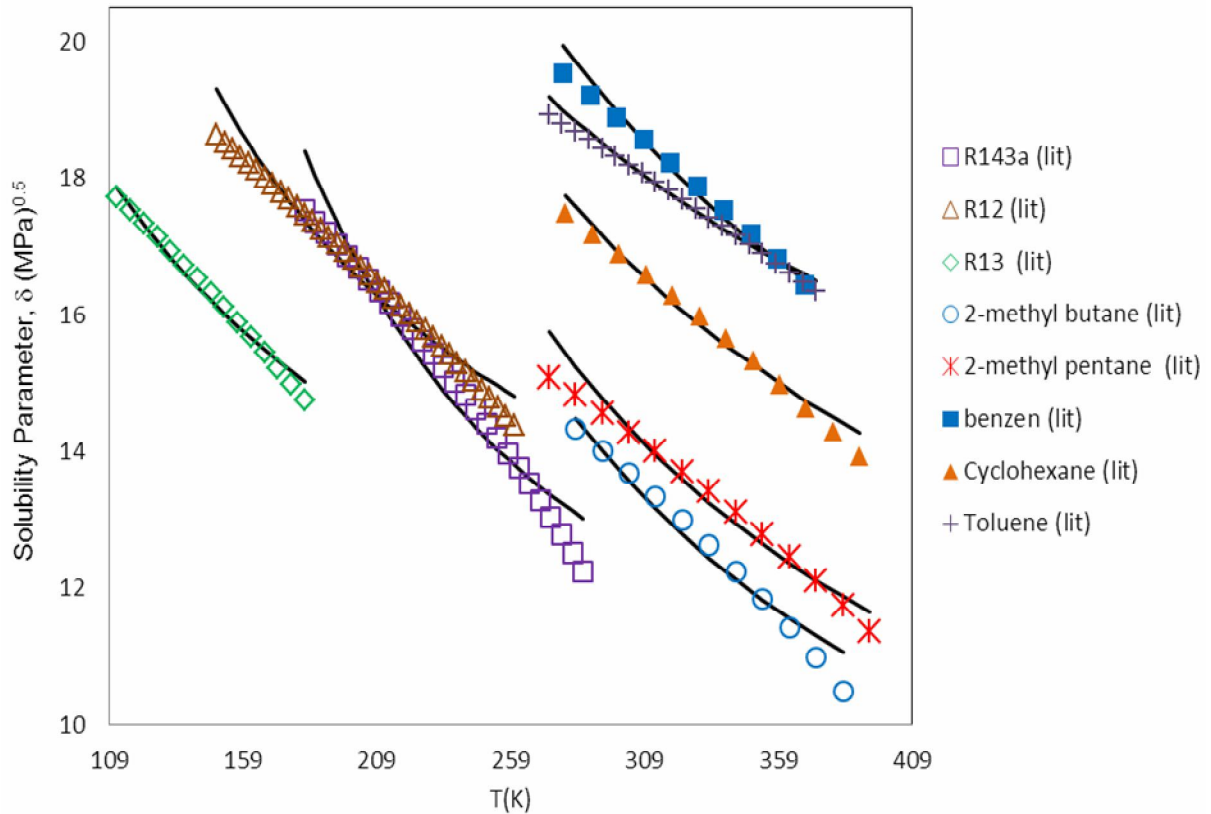


Fig. 2. Saturated behaviour of solubility parameter of selected hydrocarbons at several temperatures. The markers representing the literature [40] and the solid lines are those estimated from the proposed model for R134a (\square), R12 (Δ), R13 (\diamond), 2-methyl butane (\circ), 2-methyl pentane ($*$) Benzene (\blacksquare), Cyclohexane (\blacktriangle) and Toluene ($+$).

interaction energy between pair-wise trimers, the well width and optimized parameter in modified square-well potential, respectively. In this work, these parameters were optimized for each fluid by fitting the proposed model with experimental PVT and solubility parameter data from low to moderate pressures [35,39-42]. To achieve this goal, the following objective function (OF) was minimized using the least-squares method:

$$OF = \min \frac{1}{n} \sum_{i=1}^n \left\{ \left| \frac{\rho_i^{\text{Lit.}} - \rho_i^{\text{Calc.}}}{\rho_i^{\text{Lit.}}} \right| + \left| \frac{\delta_i^{\text{Lit}} - \delta_i^{\text{Calc}}}{\delta_i^{\text{Lit}}} \right| \right\} \quad (20)$$

where, n represents the number of density and solubility

parameter data at atmospheric and moderate pressures for a given system. The numerical values of optimized pure-component parameters of the studied systems are reported in Table 1.

Figures 1 and 2 show the saturated behaviour of the calculated solubility parameters for some selected hydrocarbons. The markers represent the literature data [41] and the solid lines are those reproduced using our proposed model. As Figs. 1 and 2 depict, there is a rather non-linear trend and also some fairly smooth curves associated with literature data. Table 2 contains the average absolute deviations percent (AAD in %) of the predicted density and solubility parameter of the hydrocarbons and refrigerants from the literature data [35,41]. As indicated in Table 2, out

Table 2. AAD (%) of Estimated Density (ρ), and the Solubility Parameter (δ) from the Literature Data [41,42]

Hydrocarbons	P_{\min} - P_{\max} (MPa)	T_{\min} - T_{\max} (K)	NP ^a	AAD% ^b	AAD% ^c
n-Pentane	0.039-0.61	284-374	10	1.88(4.82)	0.93(2.44)
n-Hexane	0.0060-0.40	273-393	25	1.68(5.13)	1.15(3.71)
n-Heptane	0.0047-0.30	293-413	13	1.07(2.45)	1.73(4.33)
n-Octane	0.0029-0.21	306-426	25	1.69(5.10)	0.91(2.99)
n-Nonane	0.00012-0.15	310-440	14	1.90(5.30)	1.34(5.02)
n-Decane	6×10^{-5} -0.020	283-393	12	0.63(-0.90)	1.04(3.96)
n-Dodecane	4.72×10^{-6} -0.005	283-393	12	0.49(1.62)	0.47(1.76)
Toluene	0.00091-0.047	273-373	21	0.78(1.91)	0.42(1.43)
Cyclohexane	0.0053-0.27	279.5-389.5	12	1.42(2.45)	0.82(2.54)
Benzene	0.0048-0.16	278.7-368.7	10	0.66(2.04)	0.66(2.13)
2-methylpentane	0.0089-0.49	273-393	13	2.61(-4.41)	1.42(4.34)
2-methylbutane	0.052-0.89	283-383	11	2.77(7.54)	1.57(5.47)
R143a	0.0069-0.91	182-286	27	2.78(8.81)	2.08(6.26)
R12	8.16×10^{-5} -0.2	149-260	38	2.97(7.63)	1.19(3.60)
R13	3.37×10^{-5} -0.72	206-278	20	2.79(6.60)	0.61(2.86)
Overall			263	1.74	1.09

^aNP represents the number of data points examined. ^bAAD% = $100/NP \sum_{i=1}^{NP} |\rho_{i, \text{Calc.}} - \rho_{i, \text{Lit.}}| / \rho_{i, \text{Lit.}}$

^cAAD% = $100/NP \sum_{i=1}^{NP} |\delta_{i, \text{Calc.}} - \delta_{i, \text{Lit.}}| / \delta_{i, \text{Lit.}}$. Parenthesis report the percent of maximum deviation.

Table 3. AAD (%) for Estimated Solubility Parameters (δ) of Polymers from the Literature Data [35] at 0.1 MPa

Polymers	P (MPa)	T _{min} -T _{max} (K)	NP ^a	AAD% ^b
PVME	0.1	393-553	5	0.48(0.95)
PVC	0.1	393-553	5	0.16(0.35)
PVAc	0.1	393-553	5	0.39(0.85)
PS	0.1	393-553	5	0.30(0.88)
PMMA	0.1	393-553	5	0.34(0.57)
PC	0.1	393-553	5	0.35(0.99)
PTFE	0.1	393-553	5	0.84(1.63)
PSF	0.1	393-553	5	1.64(2.86)
PET	0.1	393-553	5	0.39(1.28)
PDMS	0.1	393-553	5	0.93(2.21)
PBD	0.1	393-553	5	0.48(1.54)
PA6	0.1	393-553	5	0.47(1.33)
Overall			60	0.56

^aNP represents the number of data points examined. ^bAAD% = $100/NP \sum_{i=1}^{NP} |\delta_{i,Calc.} - \delta_{i,Lit.}| / \delta_{i,Lit.}$

Parenthesis report the percent of maximum deviation.

of 263 data points examined for studied hydrocarbons and refrigerants, the overall AADs% for density and solubility parameter were found to be 1.74% and 1.09%, respectively.

It is interesting to check how the proposed model predicts the volumetric properties of polymers. In this regard, the model was applied to several polymers. Table 3 shows the AAD% of the predicted solubility parameters of studied polymers from the measurements [35] over the temperature and pressure range within 393-553 K and at 0.1 MPa. The overall AAD% of the predicted solubility parameters from the literature data has also been included in Table 3. For 60 experimental data points examined for the polymers, the AAD% was found to be 0.56%. Figure 3 shows the isobaric behaviour of the calculated solubility parameter for the selected polymers. The markers represent

the literature data [35] and the solid lines are those reproduced using our new model. The model was further evaluated by predicting the densities of polymers. Table 4 also compares the calculated density with those obtained from experimental data points for polymers. As indicated in Table 4, the overall AAD% of the calculated densities from the literature values was found to be 0.43% for 1993 data points.

According to Eq. (19) the polymer-polymer miscibility can occur when the solubility parameters are close to each other. In Fig. 4, the isobaric predicted solubility parameter lines of polymers cross each other in a single specific temperature, indicating the polymer pairs miscibility. Figure 4 indicates that the results are in favour of the good performance of our proposed model. Images indicate the

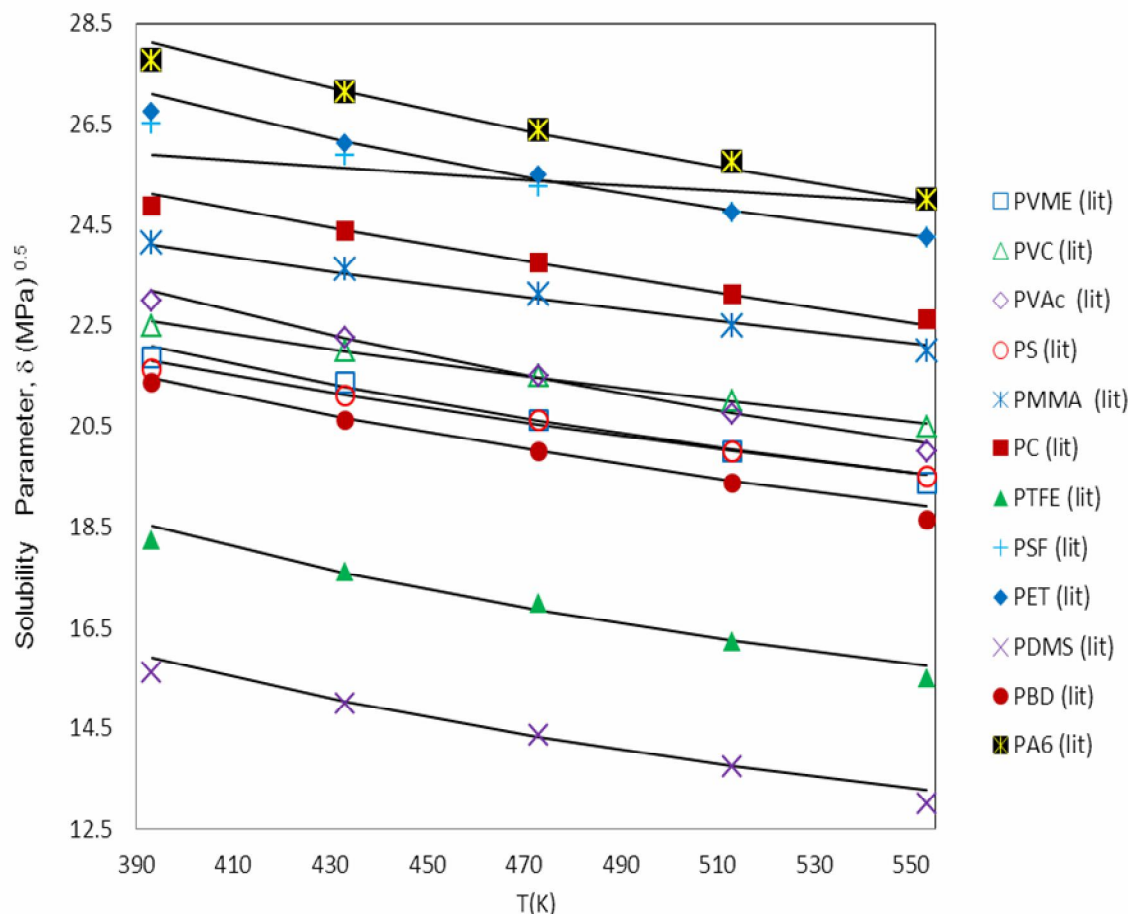


Fig. 3. Isobaric solubility parameter of selected polymers at several temperatures. The markers representing the literature [35] and the solid lines are those estimated from the proposed model for PVME (\square), PVC (Δ), PVAc (\diamond), PS (\circ), PMMA ($*$), PC (\blacksquare), PTFE (\blacktriangle), PSF ($+$), PET (\blacklozenge), PDMS (\times), PBD (\bullet) and PA6 (\blacksquare).

miscibility of four polymer pairs: PA6/PSF, PSF/PET, PS/PVME and PC/PMMA. Based on Utraki [35], it is noteworthy that the tabulated solubility parameters (derived from the solution data under ambient conditions) suggest the PVC/PVAc pair immiscibility.

CONCLUSIONS

In the present study, a Perturbed Hard-Trimer Chain (PHTC) equation of state was developed to model the volumetric properties and solubility parameters of several hydrocarbons, refrigerants and polymers. Inspection of results obtained revealed that the proposed equation of state

is able to model the densities and solubility parameters of the studied systems. The linear dependency of δ for polymers on temperature has also been successfully investigated using the proposed model at several isobars.

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ABBREVIATIONS

R143a

1,1,1-TrifluoroEthane

Table 4. AAD (%) of the Estimated Density (ρ) from the Literature Data [39,40]

Polymers	P_{\min} - P_{\max} (MPa)	T_{\min} - T_{\max} (K)	NP ^a	AAD% ^b
PVME	0.1-120	311.5-415.5	84	0.21(-0.72)
PVC	0.1-120	393-423	52	0.18(-0.56)
PVAc	20-200	377-518	180	0.16(-1.43)
PS	20-200	303-524.75	230	0.40(-2.33)
PMMA	20-200	303.5-505	210	0.74(-3.36)
PC	20-180	443-623.65	126	0.82(-2.62)
PTFE	20-100	293-600.65	195	0.47(-3.49)
PSF	20-100	302.9-454.5	100	0.60(-0.42)
PET	20-200	294.9-521.5	230	0.52(-2.12)
PDMS	20-200	303.5-580.5	240	0.68(-2.59)
PBD	20-200	302.6-471	220	0.24(-1.13)
PA6	0.1-200	373.7-421	126	0.13(-0.38)
Overall			1993	0.43

^aNP represents the number of data points examined. ^b AAD% = $100/NP \sum_{i=1}^{NP} |\rho_{i, \text{Calc.}} - \rho_{i, \text{Lit.}}| / \rho_{i, \text{Lit.}}$.

Parenthesis report the percent of maximum deviation.

R12	DichlorodifluoromEthane	NOMENCLATURE AND UNITS	
R13	ChlorotrifluoromEthane		
PVME	Poly(vinyl methyl ether)	$b(T)$	Van der Waals co-volume, m ³
PVC	Poly(vinylchloride)	P	Pressure, Pa
PVAc	Poly(vinylacetate)	R	Gas constant, J/mol K
PS1301	Poly(styrene)	T	Absolute temperature, K
PMMA	Poly(methylmethacrylate)	k_B	Boltzmann's constant, J/K
PC	Poly(carbonate)	M_w	Molecular weight
PTFE	Poly(tetrafluoroethylene)	$a(T)$	Strengths of attractive forces, J
PSF	Poly(sulfone)	m ⁻³	
PET	Poly(ethyleneterephthalate)	F_a and F_b	Universal functions
PDMS	Poly(dimethylsiloxane)	GREEK LETTERS	
PBD	Poly(butadiene)		
PA6	Poly(- ϵ -caprolactam)	ϵ	Non-bonded interaction energy

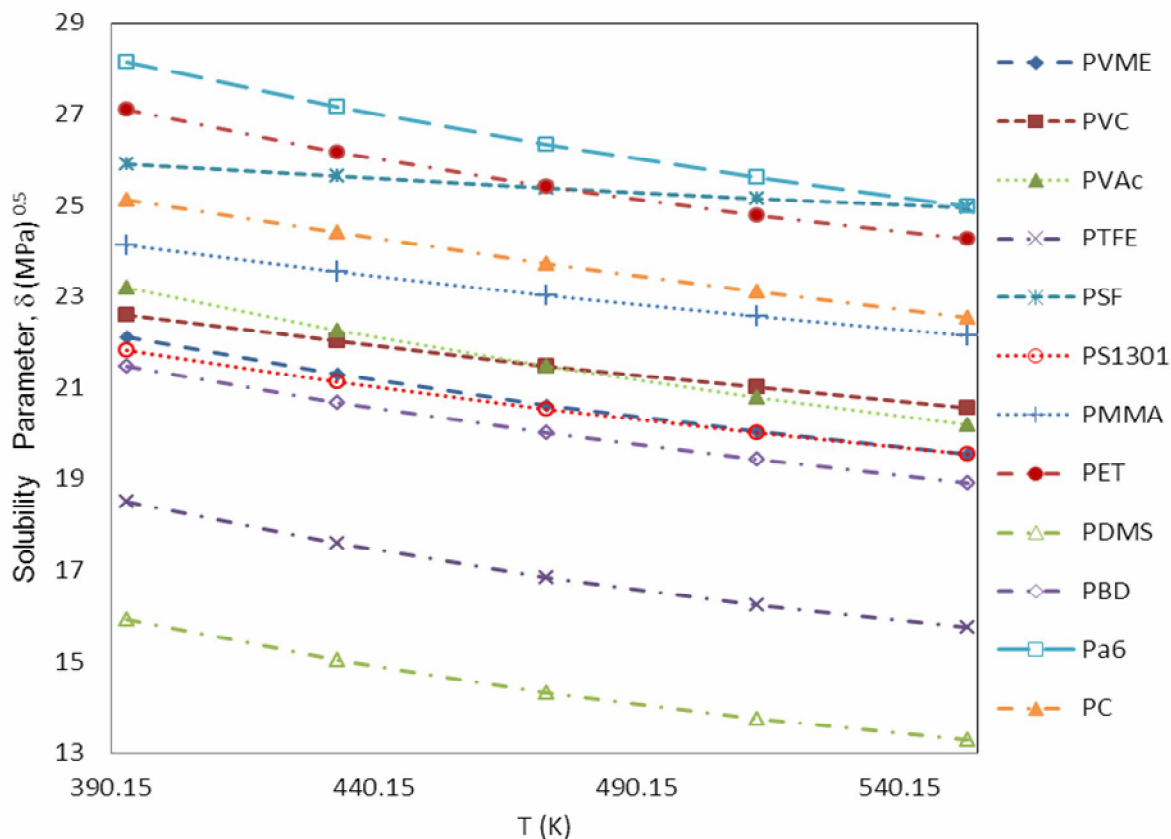


Fig. 4. Isobaric ($P = 0.10132$ MPa) predicted solubility parameter *versus* T (K) for 12 polymers. The figure indicates four pairs of polymers where miscibility is suspected.

parameter, J

σ	Hard-core diameter, nm
η	Packing fraction
ρ	Molar density, mol m ⁻³
ω	Parameter defined in Eq. (13),
λ	Well width of square-well
potential	

SUBSCRIPT

Lit	Literature
Calc	Calculated

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