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# Hansen solubility parameters for polyethylene glycols by inverse gas chromatography

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**Abstract**

Inverse gas chromatography (IGC) has been applied to determine solubility parameter and its components for nonionic surfactants—polyethylene glycols (PEG) of different molecular weight. Flory–Huggins interaction parameter ($\chi$) and solubility parameter ($\delta_2$) were calculated according to DiPaola-Baranyi and Guillet method from experimentally collected retention data for the series of carefully selected test solutes. The Hansen's three-dimensional solubility parameters concept was applied to determine components ($\delta_d$, $\delta_p$, $\delta_h$) of corrected solubility parameter ($\delta_T$). The molecular weight and temperature of measurement influence the solubility parameter data, estimated from the slope, intercept and total solubility parameter. The solubility parameters calculated from the intercept are lower than those calculated from the slope. Temperature and structural dependences of the entopic factor ($\chi_S$) are presented and discussed.

*Keywords:* Inverse gas chromatography; Solubility parameter; Hansen solubility parameters

## 1. Introduction

The concept of the solubility parameter was proposed by Scatchard, Hildebrand and Scott and initially applied to systems whose cohesion arises only from dispersion forces. This solubility parameter is the square root of cohesive energy density (CED) [1].

$$\delta = (\mathrm{CED})^{1/2} = \left[\frac{\Delta H - RT}{V_\mathrm{m}}\right]^{1/2} = \left[\frac{\Delta E}{V_\mathrm{m}}\right]^{1/2} \qquad (1)$$

where $\delta$ is the solubility parameter, $R$ the gas constant, $T$ the temperature, $\Delta H$ the enthalpy of vaporization, $V_\mathrm{m}$ the molar volume, and $\Delta E$ the energy of vaporization. The units of solubility parameter, published in literature are $(\mathrm{cal/cm^3})^{1/2}$, $(\mathrm{J/m^3})^{1/2}$, $(\mathrm{MPa})^{1/2}$. Preferred unit used by authors is $(\mathrm{MPa})^{1/2}$.

The cohesive energy of a liquid is the energy of all the intermolecular interactions in a mole of the liquid, thus it is the energy necessary to break all interactions during vaporization of the liquid.

The solubility parameter concept is related to the solution thermodynamics. When two substances are mixed at constant temperature and pressure, the change in the Gibbs energy of mixing is expressed as [2]

$$\Delta G_\mathrm{M} = \Delta H_\mathrm{M} - T\Delta S_\mathrm{M} \qquad (2)$$

where $\Delta G_\mathrm{M}$ is the free energy of mixing, $\Delta H_\mathrm{M}$ is the heat of mixing, and $\Delta S_\mathrm{M}$ denotes the entropy of mixing.

Two substances show total miscibility if the free energy of mixing is negative. The entropy of mixing is usually positive, so positive or negative value of energy of mixing depends on value of heat of mixing. The heat of mixing depends upon the difference of cohesive energies of solution and unmixed components.

$$\Delta H_\mathrm{M} = [V_\mathrm{A}(\delta_\mathrm{A} - \delta_\mathrm{B})^2(1-\phi_\mathrm{A})^2]^{1/2} \qquad (3)$$

where $V_\mathrm{A}$ is the volume and $\phi_\mathrm{A}$ is the volume fraction of component A in the mixture, $\delta_\mathrm{A}$ is the solubility parameter of component A, and $\delta_\mathrm{B}$ is the solubility parameter of component B. The heat of mixing is the smaller if the values of solubility parameter of two materials are comparable [3,4].

Eq. (3) is an approximation that involves drastic assumption. It is assumed that the interaction forces act between the centers of the molecules, the mixing is random and distribution is

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temperature independent. Additivity of the interaction forces is also assumed—the interaction between a pair of molecules is not influenced by the presence of other molecules. Besides, the constant pressure change of volume on mixing is assumed to be zero; the numbers of nearest neighbours of a molecule in solution and in the pure state are considered to be the same [2].

The thermodynamics of polymer solution can be described in terms of Flory–Huggins theory.

On the basis of theory of solution, Flory and Huggins have defined the athermal solution, with the excess internal energy $U^E = 0$, the excess enthalpy $H^E = 0$ and the excess entropy $S^E \neq 0$. The proposed model of athermal solution refers to solutions that are formed with molecules similar in their chemical nature but different in molecular size. The Flory–Huggins theory has facilitated a description of the solution comprising a high-molecular-weight polymeric component and a low-molecular-weight solvent. According to Flory–Huggins, theory each polymer segment and each single solvent molecule occupied a lattice site. Flory and Huggins used a statistical mechanical treatment taking into account the fact that the polymer segments must occupy adjacent sites [2].

The Flory–Huggins theory takes into account a considerable divergence in molecular size for describing the entropy of mixing. The change in the entropy of mixing for this reference system is called the combinatorial entropy $\Delta S_M^{\text{comb}}$[2]:

$$\Delta S_M^{\text{comb}} = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \tag{4}$$

where $\phi_1$ and $\phi_2$ are the volume fractions of the solvents (1) and the polymer (2).

The difference between the entropy of mixing for a real solution and an ideal solution is called the excess entropy and the difference between the entropy of mixing for a real solution and $\Delta S_M^{\text{comb}}$ is described as the residual entropy:

$$\Delta S^R = \Delta S_M - \Delta S_M^{\text{comb}} = \Delta S_M + R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \tag{5}$$

The residual energy of mixing is expressed as

$$\begin{aligned} G^R &= \Delta G_M - (-T\Delta S_M^{\text{comb}}) \\ &= \Delta G_M - RT(x_1 \ln \phi_1 + x_2 \ln \phi_2) \end{aligned} \tag{6}$$

The derivative of $G^R$ with respect to the amount of component (1) gives the residual chemical potential of the liquid:

$$\begin{aligned} (\mu_1 - \mu_1^0)^R &= \left(\frac{\partial G^R}{\partial n_1}\right)_{n_2,T,p} \\ &= (\mu_1 - \mu_1^0) - RT\left[\ln \phi_1 + \phi_2\left(1 - \frac{V_1}{V_2}\right)\right] \end{aligned} \tag{7}$$

By rearranging the Eq. (7), the relation that defines interaction parameter between polymer and solvent molecules, is obtained:

$$\frac{(\mu_1 - \mu_1^0)^R}{RT\phi_2^2} = \frac{(\mu_1 - \mu_1^0)}{RT\phi_2^2} - \left[\ln \phi_1 + \left(1 - \frac{V_1}{V_2}\right)\phi_2\right] = \chi \tag{8}$$

$\chi$ is called the Flory–Huggins interaction parameter.

In Eq. (8)

$$\phi_1 = \frac{x_1 V_1^*}{x_1 V_1^* + x_2 V_2^*} \tag{9}$$

$$\phi_2 = \frac{x_2 V_2^*}{x_1 V_1^* + x_2 V_2^*} \tag{10}$$

are the apparent volumes fractions.

The Gibbs free energy of mixing, based on Eq. (6) is expressed as:

$$\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi\phi_1\phi_2(n_1 + mn_2) \tag{11}$$

where $\Delta G_M$ is the free energy of mixing, $n_1$ is the number of moles of solvent, $n_2$ is the number of moles of polymer, $\phi_1$ and $\phi_2$ are the volume fractions of solvent and polymer, respectively, $m$ is the ratio of molar volumes of polymer and solvent, and $\chi$ is the Flory–Huggins interaction parameter [5].

Flory and Huggins polymer–solvent interaction parameter $\chi$ reflects intermolecular interaction between a high-molecular-weight polymer and a low-molecular-weight solvent. As mentioned earlier, negative value of energy of mixing $\Delta G_M$ indicates spontaneous mixing between polymer and solvent. The first two terms in Eq. (11) represent entropic factor of mixing, and they are always negative. Therefore, for mutual solubility/mixing process between polymer and solvent, the third term must also be negative or very small, if positive. Interaction parameter has been considered as a Gibbs free energy parameter, and such assumption allows dividing interaction parameter $\chi$ into entropy $\chi_S$ and enthalpy $\chi_H$ components [2,6]:

$$\chi = \chi_S + \chi_H \tag{12}$$

The enthalpy term can be calculated from the Hildebrand–Scatchard regular solution theory and entropy term, according to Flory–Huggins theory, should have a value of approximately 0.2–0.4 [7], 0.3–0.4 or 0.34 [5,7].

According to Hildebrand–Scatchard theory, the enthalpy component is related to solubility parameters of two components, by relation:

$$\chi_H = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{13}$$

where $\delta_1$ and $\delta_2$ are the solubility parameter solvent and polymer, respectively and $V_1$ is the solvent molar volume [5].

The use of Eq. (13) with Flory–Huggins Eq. (12) gives

$$\chi = \left(\frac{V_1}{RT}\right)(\delta_1 - \delta_2)^2 + \chi_S \tag{14}$$

Guillet and co-workers [6,8] proposed the method for estimating the solubility parameter of polymers by modification of Eq. (14):

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_i} = \frac{2\delta_2}{RT}\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_i}\right) \tag{15}$$

The most widely used concept is that proposed by Hansen, called three dimensional solubility parameters or Hansen solubility parameters (HSP) [9]. According to the Hansen theory, the cohesive energy can be considered as a sum of contributions from dispersive ($E_\mathrm{d}$), polar ($E_\mathrm{p}$) and hydrogen bonding ($E_\mathrm{h}$) interactions:

$$-E_\mathrm{coh} = -E_\mathrm{d} - E_\mathrm{p} - E_\mathrm{h} \qquad (16)$$

And the total solubility parameter ($\delta_T$) is expressed as

$$\delta_T^2 = \delta_\mathrm{d}^2 + \delta_\mathrm{p}^2 + \delta_\mathrm{h}^2 \qquad (17)$$

where $\delta_\mathrm{d}$, $\delta_\mathrm{p}$, $\delta_\mathrm{h}$ denotes dispersive, polar and hydrogen bonding contribution, respectively.

Dispersion forces are present between all molecules, whether they are polar or nonpolar. These are the attractive forces arising as a result of temporary dipoles induced in atoms or molecules. Polar forces are due to permanent dipole or induced dipole interactions. Hydrogen bonding interactions occur when a hydrogen atom on one molecule is bound to an electronegative atom on a second molecule [10].

According to Hansen's interpretation of solubility parameter, estimation of interactions between different materials appears to be more precise. Materials having sufficiently close three-dimensional solubility parameters should be compatible.

The solubility parameter determined for different materials can be used for estimation of various physicochemical parameters, e.g. surface free energy and surface tension [11]. The solubility parameter concept has also been used to estimate the miscibility of different species [12]. Two materials having close values of solubility parameter are likely to be compatible and should be miscible when mixed together. Thus, the solubility parameter has been used in coatings industry for selection of solvents in paint formulation [13,14] or matching a binder to pigment [15], in printing industry for selection of the best cleaning agent for binder(s) [16] as well as for characterization of different additives (plasticizers, antistatic agents) used in polymers [17]. The latest literature reports show that the solubility parameter found an application in the investigation of the miscibility of the polymeric blends [18], prediction of permeation properties of organic solvents in polymeric materials [19] and also selection of effective extraction solvents for the extraction process in analytical chemistry [20].

By using Hildebrand concept the solubility parameter for volatile compounds can be calculated from Eq. (1). It is impossible for low- or non-volatile compounds. Therefore, different methods were elaborated to facilitate the estimation of solubility parameter for this group of materials. These were as follows: swelling measurements [7]; group additive methods [21–23], where knowledge of the molecular structure of a material is required; viscosity measurements [9] and inverse gas chromatography (IGC) [6,8,24–27].

In inverse gas chromatography method, the investigated material (stationary phase) is placed into the chromatographic column. The volatile compounds (test solutes) are injected into the column and transported over the examined material by a carrier gas. Each test solute interacts with investigated material. Magnitude of this interaction reflects in the value of specific retention volume ($V_\mathrm{g}$) and is further presented as the Flory–Huggins interaction parameter ($\chi$).

This method has been applied for characterization of a wide range of materials, e.g. polymers [26,28,29], surfactants [25,30], pharmaceutical powders and pharmaceutical products [31,32], and porous solids [33]. The relationship between chromatographic and thermodynamic data is given below [27]:

$$\chi = \ln\left(\frac{273.15R}{p_1^0 V_\mathrm{g} M_{\mathrm{r},1}}\right) - \frac{p_1^0}{RT}(B_{11} - V_1) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1}{V_2}\right) \qquad (18)$$

where $M_{\mathrm{r},1}$, $p_1^0$, $B_{11}$, $V_\mathrm{g}$, $V_1$, $V_2$, $\rho_1$, $\rho_2$ are the molecular mass, saturated vapor pressure of the test solute, second virial coefficient of the test solute, specific retention volume of the test solute, molar volume of the test solute, molar volume of the examined material, density of the test solute and density of the examined material (surfactant, polymer) at the temperature of measurement, respectively.

Further examinations on the selection of test solutes for IGC experiments were also carried out with the use of Principle Component Analysis methods [34]. It has been shown that it is possible to reduce the number of test solutes without the lost of information.

The aim of this work was the determination of Hansen solubility parameters by inverse gas chromatography for non-ionic surfactants—different polyethylene glycols (PEGs): PEG 2000, PEG 10,000 and PEG 35,000. These are the non-ionic surface active agents used in many industrial applications, e.g. pharmaceutical, cosmetic and paint industry. Surfactants' selection process for a given might be difficult and time consuming. The knowledge of the values of solubility parameter or sometimes better Hansen solubility paramaters facilitates selection process. However, the appropriate physicochemical parameters are not always easily available or the literature data are non-reliable. Therefore, the experimental techniques allowing the determination of solubility parameters for new materials and enlarging the existing database should be examined.

## 2. Materials and methods

The examined surfactants were polyethylene glycols with nominal molecular weight: 2000, 10,000 and 35,000 (MERCK). Measurements were carried out using iGC SMS (Surface Measurements Systems, London, UK) gas chromatograph equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). Helium was used as a carrier gas at flow rate 20 ml/min.

The PEGs were dissolved in methanol, mixed with inert solid support (Chromosorb P AW-DMDCS 100/120 mesh, Supelco) and then the solvent was evaporated using a rotary evaporator. The loading of the column was about 20%, i.e. column filling contains 20% of the appropriate excipient and 80% of the support. The amount of PEG that has been coated onto support was determined by Soxhlet extraction. The column parameters are described in Table 1.

Table 1
The column parameters

| | Loading (%) | PEG mass (g) |
|---|---|---|
| PEG 2000 | 19.6 | 0.092 |
| PEG 10000 | 20.2 | 0.095 |
| PEG 35000 | 20.8 | 0.098 |

The packing material was packed into the glass columns (30 cm length, 2 mm i.d.). The column was ended by glass wool. The measurements were made above mp (melting point) of each PEG. The temperature of measurements were 85, 95 and 105 °C. Each column was conditioned at each temperature overnight before use.

Different organic solvents, selected to represent the ability of different intermolecular interactions, were used as the test solutes: dispersive–(*n*-alkanes); polar–acetonitrile, toluene, 2-butanone, 2-pentanone, 1,2-dichloroethane and 1-nitropropane; hydrogen bonding—ethanol, 1-propanol, 1-butanol, 1,4-dioxane, pyridine and chloroform.

For each probe, three injections of vapor of each test solute were made. The retention data were calculated from the maximum of the symmetric peak and then used to calculate Flory–Huggins interaction parameter ($\chi$) from Eq. (18).

Second virial coefficients ($B_{11}$) were calculated from the relation [35]:

$$\frac{B_{11}}{V_C} = 0.500 - 1.144\left(\frac{T_C}{T}\right) - 0.480\left(\frac{T_C}{T}\right)^2 - 0.042\left(\frac{T_C}{T}\right)^3 \qquad (19)$$

where $V_C$ and $T_C$ are the critical molar volume and the critical temperature of the solute, and $T$ is the column temperature (K).

Solute vapor pressures ($p_1^0$) were calculated using the Antoine equation [36]

$$\log p_1^0 = A - \frac{B}{(t+C)} \qquad (20)$$

where $p_1^0$ is the vapor pressure in mmHg, $t$ is the temperature (°C) and $A$, $B$, $C$ are constants.

Solubility parameter was calculated by using the Eq. (15) proposed by Guillet et al., where $\delta_1$ is the solubility parameter of the consecutive test solute. Plotting the left hand of this equation versus $\delta_1$ lead to $\delta_2$ of the examined material calculated from the slope and the intercept of the straight line.

However, value of solubility parameter $\delta_2$ can be estimated from the intercept of Eq. (15). To use this way of calculation, one should make any assumption concerning the value of the entropic factor $\chi_S$. The values of this component most often found in the literature are 0.2–0.4 or 0.6. We have not used the one constant $\chi_S$ value but checked the influence of changing entropic factor (0.2, 0.3, 0.34 and 0.4) on the resulting $\delta_2$ value.

$$\text{Intercept} = \left(\frac{\delta_2^2}{RT} + \frac{\chi_S}{V_i}\right) \qquad (21)$$

Eq. (21) may also be used for estimation of value of entropic factor by using solubility parameter value ($\delta_2$) calculated earlier from the slope of Eq. (15). It may be done assuming that there is also just one value of solubility parameter, and it cannot depend on the way of calculation. It leads to value of $\chi_S$ varying from test solute to test solute.

According to Flory–Huggins theory, value of $V_i$ should be the smallest among molar volumes of the solvents or examined materials (e.g. polymers, surfactants) [37]. In this work, it was the value for acetonitrile $V_i = 52.6\ \text{cm}^3/\text{mol}$.

The components of total solubility parameter were calculated from the slope of straight line, plotted according to Eq. (15) for the respective group of solvents representing different intermolecular interactions. These values were calculated by using the following relationships [38]:

$$\begin{aligned} &\text{(a)}\quad \delta_d = \frac{m_{n\text{-alkanes}} \times RT}{2} \\ &\text{(b)}\quad \delta_p = \frac{(m_1 - m_{n\text{-alkanes}}) \times RT}{2} \\ &\text{(c)}\quad \delta_h = \frac{(m_2 - m_{n\text{-alkanes}}) \times RT}{2} \end{aligned} \qquad (22)$$

where $m_{n\text{-alkanes}}$ is the value of the slope for *n*-alkanes; $m_1$ the value of the slope for aromatic hydrocarbones, ketones, 1-nitropropane, acetonitrile, and 1,2-dichloroethane; $m_2$ the value of the slope for alcohols, 1,2-dioxane, pyridine and chloroform. The value of the total solubility parameter was obtained from Eq. (17).

## 3. Results and discussion

It is important to carry out IGC experiments in the temperature range where the retention mechanism is dominated by the bulk retention. The checking can be done by the injection of test solutes (here: hexane and toluene) onto the column at the different temperatures of IGC column. The inflection of the curve indicates the melting point or better $T_g$ (region) of the examined material. The temperature in our experiments varied between 45 and 105 °C (isothermal conditions). The exemplary relations between retention data of the test solute and temperature are shown in Fig. 1.

Regions where melting process occur determined with the use of two different test solutes agree and give comparable values of $T_g$. The melting point regions for all PEGs determined by IGC

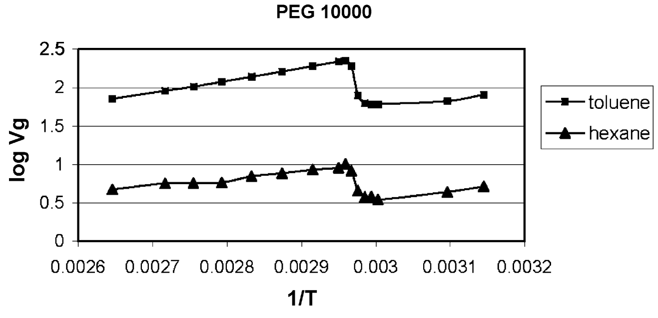

Fig. 1. The example of retention diagram for toluene and hexane on polyethylene glycol 10000.

Table 2
Melting point range for PEG 2000, 10,000 and 35,000

| | Melting point data (°C) |
|---|---|
| PEG 2000 | 50–53 |
| PEG 10,000 | 62–65 |
| PEG 35,000 | 64–66 |

Table 3
$\chi$ parameter values found for the test solute/PEG 2000 pairs

| Test solute | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| C6 | 2.349 | 2.206 | 2.161 |
| C7 | 2.244 | 2.065 | 1.935 |
| C8 | 2.298 | 2.130 | 1.973 |
| C9 | 2.388 | 2.201 | 2.010 |
| Toluene | 0.601 | 0.568 | 0.517 |
| 2-Butanone | 0.884 | 0.838 | 0.776 |
| 2-Pentanone | 0.894 | 0.844 | 0.769 |
| 1-Nitropropane | 0.414 | 0.390 | 0.359 |
| Acetonitrile | 1.595 | 1.579 | 1.746 |
| 1,2-Dichloroethane | −0.345 | −0.321 | −0.312 |
| Ethanol | 1.119 | 1.033 | 0.945 |
| Propanol | 0.919 | 0.841 | 0.743 |
| Butanol | 0.853 | 0.774 | 0.669 |
| Pyridine | 0.133 | 0.120 | 0.088 |
| 1,4-Dioxane | 0.299 | 0.271 | 0.228 |
| Chloroform | −0.843 | −0.782 | −0.740 |

method are in agreement with literature data. At temperature above melting point for all PEGs, a straight-line relationship can be observed. This region corresponds to bulk absorption of the test solute in surfactant (stationary phase). The melting point region for all PEGs are collected in Table 2.

Retention data of test solutes are first converted into the values of Flory–Huggins interaction parameter $\chi$. Data found for the examined PEGs are given in Tables 3–5.

Table 4
$\chi$ parameter values found for the test solute/PEG 10000 pairs

| Test solute | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| C6 | 2.317 | 2.306 | 2.261 |
| C7 | 2.195 | 2.134 | 2.009 |
| C8 | 2.213 | 2.150 | 1.945 |
| C9 | 2.302 | 2.139 | 1.915 |
| Toluene | 0.544 | 0.506 | 0.468 |
| 2-Butanone | 0.816 | 0.751 | 0.724 |
| 2-Pentanone | 0.827 | 0.768 | 0.739 |
| 1-Nitropropane | 0.261 | 0.258 | 0.237 |
| Acetonitrile | 0.692 | 0.711 | 0.693 |
| 1,2-Dichloroethane | −0.480 | −0.440 | −0.439 |
| Ethanol | 1.055 | 0.966 | 0.903 |
| Propanol | 0.841 | 0.777 | 0.705 |
| Butanol | 0.754 | 0.687 | 0.595 |
| Pyridine | 0.050 | 0.003 | 0.008 |
| 1,4-dioxane | 0.187 | 0.172 | 0.137 |
| Chloroform | −1.002 | −0.919 | −0.855 |

Table 5
$\chi$ parameter values found for the test solute/PEG 35000 pairs

| Test solute | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| C6 | 2.567 | 2.592 | 2.202 |
| C7 | 2.418 | 2.315 | 1.947 |
| C8 | 2.408 | 2.308 | 1.854 |
| C9 | 2.456 | 2.240 | 1.837 |
| Toluene | 0.769 | 0.731 | 0.347 |
| 2-Butanone | 0.947 | 0.979 | 0.134 |
| 2-Pentanone | 0.953 | 0.932 | 1.109 |
| 1-Nitropropane | 0.508 | 0.469 | 0.149 |
| Acetonitrile | 0.994 | 0.993 | 0.661 |
| 1,2-Dichloroethane | −0.173 | −0.145 | −0.481 |
| Ethanol | 1.254 | 1.169 | 0.833 |
| Propanol | 1.034 | 0.938 | 0.603 |
| Butanol | 0.949 | 0.829 | 0.487 |
| Pyridine | 0.308 | 0.122 | −0.130 |
| 1,4-Dioxane | 0.487 | 0.424 | 0.035 |
| Chloroform | −0.683 | −0.621 | −0.902 |

For all examined PEGs, the highest values of the Flory–Huggins interaction parameter were found for nonpolar test solutes, *n*-alkanes. These high values reflect the poor compatibility/miscibility of *n*-alkanes with the examined polymers. For polar and hydrogen bonding test solvents, $\chi$ data are considerably lower than those for nonpolar test solutes. In case of the polar test solvents, 1,2-dichloroethane exhibits negative values of $\chi$, which reflects stronger interaction with examined PEGs. It can be noticed that the strongest interactions (good compatibility with polymer) are found for chloroform. This test solvent exhibits the most negative value at all temperatures for all examined PEGs. Relatively strong interactions were also found for pyridine-solvent representing ability to hydrogen bonding interactions. Values of pyridine/examined PEGs pairs are close to zero.

Solubility parameter value ($\delta_2$) for PEGs, calculated from the slope according to Eq. (15), decrease with increasing molecular weight. Solubility parameter values decrease with increasing temperature of IGC measurement. Values of corrected solubility parameter for all PEGs are higher than those calculated from the slope. Relation between corrected solubility parameter values and temperature or molecular weight of PEGs is not so evident as for $\delta_2$. Slight decrease of $\delta_T$ solubility parameter's with increasing of the temperature is found for PEG 2000. However, for PEG 10,000 and 35,000 a slight increase of $\delta_T$ solubility parameter is observed with increase in temperature and molecular weight (Fig. 2). The lowest value of total solubility parameter obtained for PEG 2000 at 105 °C is equal to 18.0 $(\mathrm{MPa})^{1/2}$ and the highest obtained for PEG 35,000 also at the same temperature is equal to 24.9 $(\mathrm{MPa})^{1/2}$ (Table 6).

Similar behavior is observed for dispersive ($\delta_d$) and hydrogen bonding component ($\delta_h$) determined for PEG 2000. Values of $\delta_d$ and $\delta_h$ parameters decrease with increasing temperature of measurement whereas for PEG 10,000 and 35,000, values of these components increase with increasing temperature.

Value of polar component of solubility parameter for all PEGs ($\delta_p$) increases both with the increase of temperature and molecular weight of surfactant. The increase of $\delta_p$ and $\delta_h$ with increasing temperature of measurement for PEG 10,000 and PEG 35,000 is probably due to different arrangement of PEGs chain on the surface of the support. The effect of variable arrangement

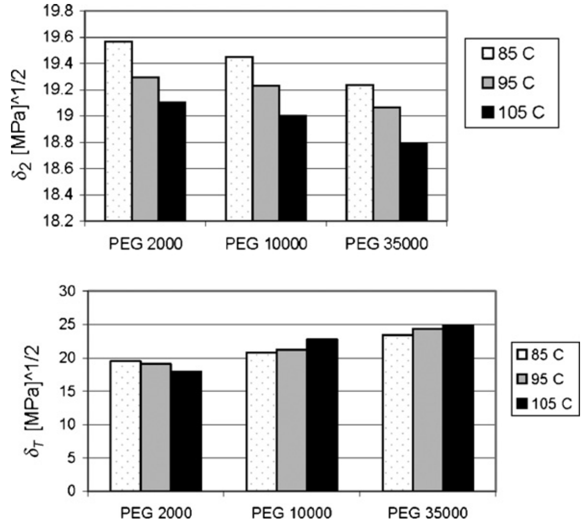

Fig. 2. Values of solubility parameter calculated from the slope and corrected solubility parameter at 89, 95 and 105 °C.

may influence the availability of etheric oxygen atoms by the molecule of test solute.

Comparison of solubility parameter data estimated from the intercept is presented in Fig. 3. It can be noticed that for PEG 10,000 and 35,000, values of solubility parameter at the same temperature and for the same value of entropic factor are very similar. Values of solubility parameter for PEG 2000 calculated from the intercept at all temperatures are higher than those found for PEG 10,000 and 35,000. For all PEGs values of solubility parameter calculated from the intercept, assuming different values of $\chi_S$, are lower than those calculated from the slope.

The entropy factor values were calculated according to Eq. (21) and listed in Tables 7–9. $\chi_S$ increase with the increase of molecular weight of PEG and, for each PEG, decrease with the increasing temperature of measurement. $\chi_S$ values depend, of

Table 6
Components of total solubility parameter at 85, 95 and 105 °C

| | Solubility parameter data [MPa]$^{1/2}$ at 85 °C | | |
|---|---|---|---|
| | $\delta_d$ | $\delta_p$ | $\delta_h$ |
| PEG 2000 | 19.4 ± 0.4 | 1.6 ± 0.3 | 1.2 ± 0.4 |
| PEG 10000 | 20.5 ± 0.3 | 2.1 ± 0.3 | 2.4 ± 0.3 |
| PEG 35000 | 22.6 ± 0.3 | 4.8 ± 0.3 | 3.9 ± 0.3 |
| | Solubility parameter data [MPa]$^{1/2}$ at 95 °C | | |
| | $\delta_d$ | $\delta_p$ | $\delta_h$ |
| PEG 2000 | 19.0 ± 0.1 | 1.8 ± 0.1 | 0.8 ± 0.1 |
| PEG 10000 | 20.8 ± 0.4 | 2.9 ± 0.4 | 2.7 ± 0.4 |
| PEG 35000 | 23.2 ± 0.3 | 5.9 ± 0.3 | 4.8 ± 0.3 |
| | Solubility parameter data [MPa]$^{1/2}$ at 105 °C | | |
| | $\delta_d$ | $\delta_p$ | $\delta_h$ |
| PEG 2000 | 17.7 ± 0.3 | 2.9 ± 0.3 | 0.4 ± 0.2 |
| PEG 10000 | 22.0 ± 1.4 | 4.4 ± 1.4 | 4.0 ± 1.4 |
| PEG 35000 | 23.5 ± 0.5 | 6.0 ± 0.5 | 5.7 ± 0.5 |

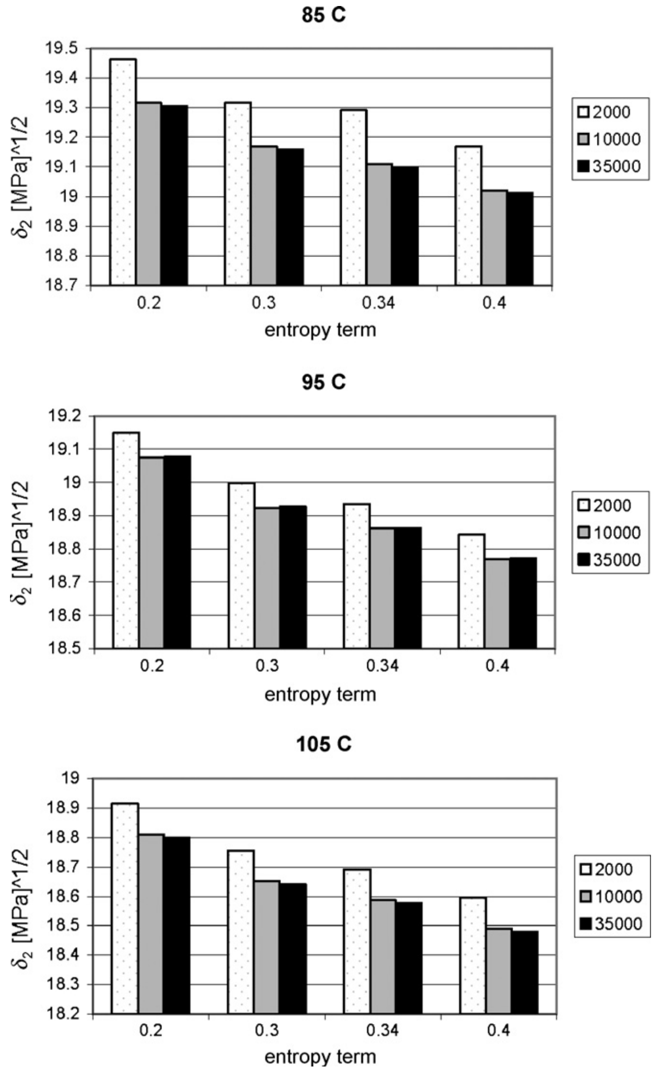

Fig. 3. The comparison of solubility parameter values calculated from the intercept for different values of entropy term at 85, 95 and 105 °C.

Table 7
Values of the entropy term $\chi_S$ calculated from the intercept, at different temperatures, for polyethylene glycol 2000

| | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| Hexane | 0.22 | 0.08 | 0.03 |
| Heptane | 0.24 | 0.09 | 0.03 |
| Octane | 0.27 | 0.10 | 0.04 |
| Nonane | 0.29 | 0.10 | 0.04 |
| 1,2-Dichloroethane | 0.13 | 0.05 | 0.02 |
| Toluene | 0.17 | 0.06 | 0.02 |
| Ethanol | 0.10 | 0.03 | 0.01 |
| Propanol | 0.12 | 0.04 | 0.02 |
| Butanol | 0.15 | 0.05 | 0.02 |
| 2-Butanone | 0.15 | 0.05 | 0.02 |
| 2-Pentanone | 0.16 | 0.06 | 0.02 |
| 1-Nitropropane | 0.15 | 0.05 | 0.02 |
| Pyridine | 0.13 | 0.05 | 0.02 |
| Acetonitrile | 0.09 | 0.03 | 0.01 |
| 1,4-Dioxane | 0.14 | 0.05 | 0.02 |
| Chloroform | 0.14 | 0.05 | 0.02 |

Table 8
Values of the entropy term $\chi_S$ calculated from the intercept, at different temperatures, for polyethylene glycol 10000

| | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| Hexane | 0.32 | 0.27 | 0.24 |
| Heptane | 0.35 | 0.30 | 0.27 |
| Octane | 0.39 | 0.32 | 0.29 |
| Nonane | 0.42 | 0.36 | 0.32 |
| 1,2-Dichloroethane | 0.19 | 0.16 | 0.14 |
| Toluene | 0.25 | 0.21 | 0.19 |
| Ethanol | 0.14 | 0.12 | 0.11 |
| Propanol | 0.18 | 0.15 | 0.13 |
| Butanol | 0.22 | 0.18 | 0.16 |
| 2-Butanone | 0.22 | 0.18 | 0.16 |
| 2-Pentanone | 0.23 | 0.20 | 0.18 |
| 1-Nitropropane | 0.21 | 0.18 | 0.16 |
| Pyridine | 0.19 | 0.16 | 0.14 |
| Acetonitrile | 0.13 | 0.11 | 0.10 |
| 1,4-Dioxane | 0.20 | 0.17 | 0.15 |
| Chloroform | 0.19 | 0.16 | 0.15 |

Table 9
Values of the entropy term $\chi_S$ calculated from the intercept, at different temperatures, for polyethylene glycol 35000

| | 85 °C | 95 °C | 105 °C |
|---|---|---|---|
| Hexane | 0.71 | 0.62 | 0.57 |
| Heptane | 0.78 | 0.68 | 0.63 |
| Octane | 0.86 | 0.74 | 0.70 |
| Nonane | 0.94 | 0.81 | 0.76 |
| 1,2-Dichloroethane | 0.42 | 0.37 | 0.34 |
| Toluene | 0.56 | 0.48 | 0.45 |
| Ethanol | 0.31 | 0.27 | 0.25 |
| Propanol | 0.40 | 0.34 | 0.32 |
| Butanol | 0.48 | 0.42 | 0.39 |
| 2-Butanone | 0.48 | 0.42 | 0.39 |
| 2-Pentanone | 0.52 | 0.45 | 0.42 |
| 1-Nitropropane | 0.47 | 0.41 | 0.38 |
| Pyridine | 0.43 | 0.37 | 0.34 |
| Acetonitrile | 0.28 | 0.24 | 0.23 |
| 1,4-Dioxane | 0.45 | 0.39 | 0.36 |
| Chloroform | 0.43 | 0.37 | 0.35 |

course, on the nature of test solute (solvent) used in IGC experiment. The highest values of the entropy term are observed for *n*-alkanes. The free volume effect and specific interaction influence the entropy term values. When the molecular weight of PEGs increases, the difference between the free volume of solvent and polymer also increases causing the increase of the free volume contribution to $\chi_S$. Highest values of the entropy term were obtained for PEG 35000. It can be assumed, that the large positive value corresponds to an increase of order on forming a polymer–solvent mixture. It can also be noticed, that the entropy term of the interaction parameter might depend on the size and shape of the solvent molecules and also on values of those parameters for polymer groups.

## 4. Summary

This work has shown that inverse gas chromatography can be applied for the estimation of solubility parameter for PEGs. Guillet and co-workers' procedure was used for calculation of the solubility parameter from the slope and intercept, assuming different values of the entropy term. On the basis of Guillet's method, Voelkel and Janas procedure was applied to determine dispersive, polar and hydrogen bonding components. Corrected solubility parameter, were calculated from these components according to the Hansen's equation,. Values of determined solubility parameter ($\delta_2$, $\delta_T$) or HSP ($\delta_p$, $\delta_h$, $\delta_h$) depend on the structure of examined PEGs and the temperature of IGC experiment.

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