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Properties of materials as determined by inverse gas chromatography❖

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The application of inverse gas chromatography (IGC) in the determination of the physicochemical properties of various materials is presented and discussed. The special attention is focused on the determination of solubility parameters.

1. INTRODUCTION

The term *inverse gas chromatography* indicates that the material of interest is placed in a chromatographic column and the behavior of selected test solutes is studied. Retention parameters and the shape of chromatographic peak of these solutes are affected by the nature and magnitude of interactions between them and the examined material. The basic tools for IGC are inexpensive, widely available and well suited for routine laboratory applications. The use of standard gas chromatographs or slightly modified gas chromatographs enables the collection of retention data of the test solutes over the broad temperature range.

Inverse gas chromatography should be divided into inverse gas liquid and inverse gas solid chromatography. The criterion of such discrimination is the state of the examined material placed in the column. The retention in gas-solid chromatography seems to be a simpler case. In gas-liquid IGC the final retention of test solute results from different ways of interaction with the column packing: (i) partition between gas and liquid phase; (ii) adsorption at the gas-liquid

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interface; (iii) adsorption at the liquid-solid interface. The net retention volume (V_N) could be, therefore, presented as:

$$V_N = V_L K_L + K_{GL} A_{GL} + K_{LS} A_{LS} \qquad (1)$$

where K_L, K_{GL}, K_{LS} denote the partition coefficient and the adsorption coefficient at the gas-liquid and liquid-solid interface, respectively.

Eq. (1) is valid at the liquid phase loading higher than 10% (w/w), i.e. when the contribution from the structured liquid-phase layer can be neglected and the retention results only from interactions with the bulk liquid [1]. However, much important and significant contribution might result from the adsorption at the support surface. Careful deactivation of the support surface and the use of higher liquid loading can minimize this undesirable effect.

The dominating retention mechanism depends on the temperature of IGC experiment. For polymeric materials, generally two groups of parameters are determined by means of IGC. One group is related to the surface parameters, such as surface free energy, surface acid/base properties. The other one is related to bulk parameters. The pertinence of IGC measurements to surface or bulk properties clearly depends on whether or not the probe molecules can diffuse into the bulk during experiment. Retention volume measured at the temperature of IGC experiment higher than T_g of the examined polymer (or blend) results from the sum of surface and bulk sorption. Below T_g mainly from the adsorption of probe molecules on the surface of the stationary phase. Therefore, the surface properties can be determined only below T_g. However, Mukhopadhyay and Schreiber proposed a procedure facilitating the determination of the surface property above T_g [2]. They found that increasing the carrier gas flow rate to approx. 50 mL/min. enabled the separation of the net retention volume of probe molecules into surface and bulk retention components. Nastasovic and Onija [3] discussed the parameters influencing precision and accuracy of T_g determination by IGC. These are: (i) inert support type, (ii) coating thickness, (iii) sorbate type; (iv) flow rate.

IGC may be carried out in two different modes: (i) at infinite dilution (or at zero surface coverage) i.e. where the Henry's law obeys, (ii) at finite concentration. At infinite dilution the minor amounts (vapors) of test solutes are injected onto the column and the absence of the adsorbate-adsorbate interactions may be neglected and adsorption-desorption phenomena occur in the monolayer.

There are several points crucial to the validity of IGC method at infinite dilution [4]: (i) the peaks of non-polar and polar test solutes as well as marker should be reproducible, sharp and symmetrical; (ii) the retention volume of a given probe should remain constant under changing gas flow rate; (iii) the

surface contamination (by the permanently sorbing molecules of test solutes) should be avoided; (iv) the volume of injected vapor of the test solute should confirm the work in the zero surface coverage region and the absence of interactions between test solute molecules.

In experiments at finite concentration a known quantity of liquid solute is injected which allows the determination of adsorption isotherms [5]. The problems of IGC at finite concentration (FC-IGC) were disussed by Papirer and Balard [6, 7], Thielmann and Burnett [8] as well as Charmas and Leboda [9]. The interesting possibility of FC-IGC is the assessment of the surface heterogeneity through the distribution functions of adsorption energy of the probe. It gives an insight into the heterogeneous nature of solid surfaces resulting both from their way of formation and their past. Charmas et al. indicated the following advantages of IGC method in comparison to the traditional adsorption techniques: (i) no need to pump out the preliminary sample under vacuum, (ii) the possibility to study the temperature effects, (iii) measurements are accurate at low surface concentrations, (iv) physical and chemical adsorption can be studied, (v) commercially available gas chromatographs could be used. The use of FC-IGC is often reported in literature [10-14].

2. THEORETICAL

Many of the properties and processing characteristics of mixtures (i.e. polymer blends, compositions, modified fillers) depend on whether they are miscible or not. However, mixture parameters that characterize polymer-polymer, polymer-filler interactions are generally required.

Flory-Huggins interaction parameter (χ) is an important factor of miscibility of polymer blends and solutions which has been determined by a number of methods (e.g. SANS, DSC, IGC) and reported in different papers. It reflects interaction between low-molecular-weight solvent and high-molecular-weight polymer, and it has been considered as a Gibbs free energy parameter. According to such assumption the interaction parameter χ can be divided into enthalpy χ_H and entropy χ_S components [15]:

$$\chi = \chi_H + \chi_S \tag{2}$$

χ_S is positive and usually should be between 0.2 and 0.6. For complete miscibility between polymer and solvent the interaction parameter χ should be

less than 0.5. Also the entropy term is about 0.3, therefore the enthalpy term χ_H must be very small to complete miscibility's criterion [15].

At infinite dilution of the probe and for high molecular weight of the stationary phase the Flory-Huggins interaction parameter can be determined from [16, 19]:

$$\chi_{12}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \tag{3}$$

1 denotes the solute and 2 denotes the examined material, M_1 is the molecular weight of the solute, p_1^o is the saturated vapor pressure of the solute, B_{11} is the second virial coefficient of the solute, V_i^o is the molar volume, ρ_1 is the density, R is the gas constant.

When mixture of components is used as a stationary phase in a chromatographic column, subscripts 2 and 3 are used to represent the first and second mixtures' component, respectively:

$$\chi_{1m}^{\infty} = \ln\left(\frac{273.15 \cdot R}{p_1^o \cdot V_g \cdot M_1}\right) - \frac{p_1^o}{R \cdot T} \cdot \left(B_{11} - V_1^o\right) + \ln\left(\frac{\rho_1}{\rho_m}\right) - \left(1 - \frac{V_1^o}{V_2^o}\right) \cdot \varphi_2 - \left(1 - \frac{V_1^o}{V_3^o}\right) \cdot \varphi_3 \tag{4}$$

where φ_2 and φ_3 are the volume fractions of components [15].

Voelkel and Fall [20] have shown that the significant variation in the second virial coefficient data possibly collected from different sources may affect the final result, i.e. the value of physicochemical parameter. Conder and Young [21] indicated that permissible uncertainty in estimation of the second virial coefficient of solute should be ±10% (at 20–50^{0}C). The second virial coefficient was also tabulated for a limited group of compounds in a few handbooks, e.g. [22].

Due to uncertainty of the basic physicochemical data one should take into account the possible error of estimation of inverse gas chromatographic parameter which may, in several cases, exceed 10%.

Applying the Flory–Huggins equation of polymer solutions to a ternary system with two polymers and one probe, the interaction parameter χ_{1m}^{∞} can be related to the probe–polymer interaction parameters and the polymer–polymer interaction parameter by the following equation [23]:

$$\chi_{1m}^{\infty} = \varphi_2 \cdot \chi_{12}^{\infty} + \varphi_3 \cdot \chi_{13}^{\infty} - \varphi_2 \cdot \varphi_3 \cdot \chi_{23}^{'} \tag{5}$$

where φ_2 and φ_3 are the volume fractions of the polymers.

When a polymer blend is used the interaction between the two polymers is expressed in terms of $\chi_{23}^{'}$ as an indicator of the miscibility of the polymer blend. Large positive values of $\chi_{23}^{'}$ indicates the absence or negligible interactions between components, a low value indicates favorable interactions, while negative value indicates strong interactions (the polymer pair is miscible).

If the parameters χ_{12}^{∞} and χ_{13}^{∞} are known (from the IGC experiment with the appropriate component "2" or "3") the interaction parameter $\chi_{23}^{'}$ may be calculated from the equation [24, 25]:

$$\chi_{23}^{'} = \frac{\chi_{23}^{\infty} \cdot V_1^{o}}{V_2^{o}} = \frac{1}{\varphi_2 \cdot \varphi_3} \cdot \left(\ln \frac{V_{g,m}}{W_2 \cdot v_2 + W_3 \cdot v_3} - \varphi_2 \cdot \ln \frac{V_{g,2}}{v_2} - \varphi_3 \cdot \ln \frac{V_{g,3}}{v_3} \right) \tag{6}$$

Here, the second subscript of V_g identifies the nature of the column.

$$\chi_{23}^{'} = \frac{1}{\varphi_2 \cdot \varphi_3} \cdot (\chi_{12}^{\infty} \cdot \varphi_2 + \chi_{13}^{\infty} \cdot \varphi_3 - \chi_{1m}^{\infty}) \tag{7}$$

The values of Flory-Huggins $\chi_{23}^{'}$ parameter depend on chemical structure of the solute and it is a common phenomenon [26]. It has been interpreted as arising for preferential interaction with one of two types of components.

There were a lot of attempts to solve the problem [27-29] of so-called "probe dependence" of polymer-polymer interaction and to develop a method to evaluate the probe-independent interaction.

Feraz, Hamou and Djadoun [28] used IGC ($\chi_{23}^{'}$ parameter) and DSC (T_g of blends) to interpret the miscibility of polymer blend of poly(styrene-co-acrylic acid) with poly(ethyl methacrylate) or poly(isobutyl methacrylate) or poly(ethyl methacrylate-co-4-vinyl pyridine) or poly(isobutyl methacrylate-co-4-vinyl pyridine). SAA/PIBMA was found to be immiscible as confirmed by the observation of two glass transition temperatures and the positive $\chi_{23}^{'}$ values. SAA/PME, SAA/EM4VP, SAA/EM4VP and SAA/IBM4VP were miscible as evidenced from the negative $\chi_{23}^{'}$ values and single composition – dependent glass transition temperature.

Zhao and Choi [29] suggested employing single common reference volume (V_o) instead of individual molar volumes of the solutes used in the IGC experiments for the calculations of the χ_{12}^{∞} parameter. As the reference volume Zhao and Choi proposed to use the molar volume of repeated unit of polymer at the experimental temperature [29, 30]:

$$\chi_{1m}^{\infty} = \frac{V_0}{V_1} \cdot \left(\ln \frac{273.15 \cdot R \cdot (W_2 \cdot v_2 + W_3 \cdot v_3)}{V_g \cdot V_1 \cdot p_1^0} - 1 + \frac{V_1}{M_2 \cdot v_2} + \frac{V_1}{M_3 \cdot v_3} - \frac{(B_{11} - V_1)}{R \cdot T} p_1^0 \right)$$

(8)

Milczewska and Voelkel [31, 32] used the IGC method to investigate other compositions – polymers filled with modified inorganic materials. The authors expressed the magnitude of interaction between the polymer and the filler by using the Flory-Huggins parameters. They calculated interaction parameter χ_{12}^{∞} by the classical way from equations (3) and (4) and the polymer-filler interaction parameters from equation (5). Later [30, 33] they used the procedures proposed by Farooque and Deshpande, Zhao and Choi, and Huang to calculate the values of χ_{23}' parameters independent of solute type. The results (values of χ_{23}') obtained from the applied procedures allowed to minimize the $\Delta\chi$ effect.

Solubility parameter data are useful in the description and interpretation of different phenomena occurring between materials like their miscibility, compatibility or adsorption. The solubility parameter called *Hildebrand solubility parameter* or *Hildebrand parameter* [34] is applied only for regular solutions

$$\delta = \left(E_{coh} / V \right)^{1/2}$$

(9)

where: E_{coh} is the cohesive energy and V is the molar volume. It describes the degree of the forces holding the molecules of a liquid together. The solubility parameter is expressed in the following units $(cal/cm^3)^{1/2}$, $(J/m^3)^{1/2}$, $MPa^{1/2}$, $atm^{1/2}$.

The solubility parameter reflects the van der Waals interactions between molecules, forming a liquid. However, such definition could not be used for other systems where, besides dispersive interactions, polar and hydrogen bonding interactions will be present.

The most widely accepted concept of solubility parameter, related to more complex systems has been proposed by Hansen [35, 36, 37]:

$$E = E_d + E_p + E_h \tag{10}$$

Therefore the total cohesive energy is the sum of energy contributions which are carried by dispersive (non-polar) E_d, polar E_p, and hydrogen bonding E_h interactions.

The total solubility parameter (corrected solubility parameter) δ_T is therefore defined as follows:

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{11}$$

where δ_d, δ_p, and δ_h denote the dispersive, polar and hydrogen bonding contributions, respectively. It is also known as the three dimensional solubility parameter or Hansen solubility parameter (HSP).

Guillet and co-workers [38, 39] have proposed the IGC method for estimation of the uggins interaction parameter and solubility parameter for polymers:

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

It is a straight line equation. The left hand side contains the values of Flory--Huggins interaction parameter, the test solute (see equation (3), the solubility parameter of the test solute (δ_1) and its molar volume. Plotting the left hand side of such equation versus the solubility parameter of test solute (δ_1) one obtains the slope ($a = 2\delta_2/RT$) enabling the calculation of the solubility parameter of the examined material.

Introducing the entropic factor of interaction parameter into equation (12) one obtains:

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(12)i}^\infty}{V_{1i}} = \frac{2\delta_2}{RT}\delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_{1i}}\right) \tag{13}$$

where "i" denotes the consecutive test solute.

Components of solubility parameter. The procedure proposed by Guillet [40], has been applied by Price [41] for estimation of the low-molecular weight compounds' solubility parameter.

Price reported that the experimental relation between the left hand-side of equation (13) and the solubility parameters of test solutes is different from the linear relationship. The significant curvature of left hand-side of equation (13) vs. δ_1 relation was observed. The downward curvature was found for alkanes and the upward curvature for other compounds. Therefore, the tendency for alkanes leads to underestimation of δ_2 while the tendency for polar compounds may cause the overestimation value of δ_2.

According to the three-component solubility parameter theory of Hansen, Price assumed that different types of intermolecular interactions between the examined material and the test solute will influence the value of solubility parameter. Price proposed to estimate the solubility parameter as the sum of two terms:

$$\delta_T^2 = \delta_d^2 + \delta_a^2 \tag{14}$$

resulting from dispersive and polar intermolecular interactions of the examined material/test solute.

However, in complex systems, additional, hydrogen bonding interaction should be taken under consideration. The extension of Price's concept, enabling calculation of all components of the total solubility parameter is the procedure proposed by Voelkel and Janas [42]. They have extended a group of test solutes used in the IGC experiments, by addition of solutes, representing hydrogen bonding interactions.

The values of each component of the total solubility parameter are calculated from the slope of straight line by using the following relationships:

$$\delta_d = \frac{m_{n-alkanes} \times RT}{2} \tag{15}$$

$$\delta_p = \frac{(m_1 - m_{n-alkanes}) \times RT}{2} \tag{16}$$

$$\delta_h = \frac{(m_2 - m_{n-alkanes}) \times RT}{2} \tag{17}$$

where $m_{n-alkanes}$ – the value of the slope for n-alkanes; m_1 – the value of the slope for aromatic hydrocarbons, ketones, 1-nitropropane, acetonitrile, 1,2-dichloro-ethane; m_2 – the value of the slope for alcohols, 1,2-dioxane and pyridine.

While determining the solubility parameter, especially in calculation of HSP values, a proper selection of the test solutes is extremely important. These groups consist of test solutes representing different types of intermolecular interactions – dispersive, polar and hydrogen bonding. It should be noted, that ability for only one type of the intermolecular interactions, dispersive ones, can be attributed just to alkanes. Unfortunately, there are no test solutes representative only for polar or hydrogen bonding interactions. As the criterion of a classification of the test solutes to proper group, a prevailing tendency for a definite type of intermolecular interaction should be taken into the consideration.

Components of the solubility parameter can be calculated by using the model proposed by Lindvig et. al. [43], combining the experimental data of the Flory--Huggins interaction parameter χ_{12}^{∞} with the components of solubility parameter for material:

$$\chi_{12}^{\infty} = \alpha \frac{V_1}{RT} \left(\left(\delta_{1,d} - \delta_{2,d} \right)^2 + 0,25 \left(\delta_{1,p} - \delta_{2,p} \right)^2 + 0,25 \left(\delta_{1,h} - \delta_{2,h} \right)^2 \right) \qquad (18)$$

where α, V_1, R, T are the corrective coefficient, molar volume of the test solute, gas constant and temperature of measurement respectively. In this relation, literature data for components of different, test solutes ($\delta_{1,d}$, $\delta_{1,p}$, $\delta_{1,h}$) and solubility parameter of material ($\delta_{2,d}$, $\delta_{2,p}$, $\delta_{2,h}$) can be used for estimation of the Flory-Huggins interaction parameter. For purpose of IGC, experimentally obtained χ_{12}^{∞} values can be used for the determination of HSP for the examined material by applying the above relation (equation (18)) [44]. Experimentally obtained values of χ_{12}^{∞} parameter and solubility parameters ($\delta_{1,d}$, $\delta_{1,p}$, $\delta_{1,h}$) data of test solutes can be used for calculation of values of the solubility parameter components. In calculation of HSP data according to the modified Guillet's procedure the intensity of interaction between the examined material and the test solute is very important. Therefore, the method where all data of Flory-Huggins interaction parameter are taken for HSP calculations is justified.

HSPs may be determined by means of different methods including IGC when the examined material is liquid at the temperature of experiment. However, engineers often require the data for "room" temperature or e.g. 25^0C. Extrapolation of the values of δ_2 or HSP determined above T_g is possible but it is a dangerous operation. It may cause a large error while moving from the liquid

material to the solid one. For solids, determination of the solubility parameter from equation (9) is impossible. Consequently, indirect methods must be used, to estimate their energy of interaction with a series of carefully chosen model compounds. Several methods have been indicated, including densitometry, the measure of solubility according to the Martin's solution model. Another possibility is the calculation of the solubility parameter from the group contribution method [45].

Determination of the solubility parameter for solid materials by means of inverse gas chromatography is based on the model of adsorption described by Snyder and Karger and requires the knowledge of adsorption energy value

$$\ln V_g = -\left(E^A/RT\right) + const \tag{19}$$

for the respective test solutes [46-48].

The energy of adsorption ΔE^A is related to the solubility parameters of both components (i and j) of the system corresponding to their capability of dispersive, polar and hydrogen bonding interactions:

$$-\Delta E^A = V_i\left(\delta_d^i\delta_d^j + \delta_p^i\delta_p^j + \delta_h^i\delta_h^j\right) \tag{20}$$

(ΔE_i^A) for the series of test solutes of (δ_k^i) and V_i values. When N test solutes are used in the IGC experiments one obtains a system of N equations corresponding to equation (20) shown below in the matrix form:

$$
\begin{pmatrix} -\Delta E_1 \\ ... \\ -\Delta E_n \\ ... \\ -\Delta E_N \end{pmatrix} = \begin{pmatrix} V_1\delta_{1d} & V_1\delta_{1p} & V_1\delta_{1h} \\ ... & ... & ... \\ V_n\delta_{nd} & V_n\delta_{np} & V_n\delta_{nh} \\ ... & ... & ... \\ V_N\delta_{Nd} & V_N\delta_{Np} & V_N\delta_{Nh} \end{pmatrix} * \begin{pmatrix} \beta_1 \\ ... \\ \beta_n \\ ... \\ \beta_N \end{pmatrix} + \begin{pmatrix} \varepsilon_1 \\ ... \\ \varepsilon_n \\ ... \\ \varepsilon_N \end{pmatrix} \tag{21}
$$

$$Y = X\beta + \varepsilon \tag{22}$$

where: Y is the column vector containing the N values of experimental measurements of the energy of adsorption ($-E_n$) of N solutes, X is the experimental matrix, formed of elements (X_{nk}), where $X_{nk} = V_n\delta_{nk}$, V_n is the

molar volume of the nth solute and δ_{nk} is one of the Hansen solubility parameters of type k ($k = d, p$, or h) of the respective solute. The β vector contains the real values of HSPs of the adsorbent, i.e. δ_{jd}, δ_{jp}, δ_{jh}.

3. REPRESENTATIVE RESULTS

The good example of the application of IGC is the determination of solubility parameters for the well known drug – Ibuprofen as well as several nanomaterials.

Solubility parameters might be used in pharmaceutical dosage form design [57]. The example of such active component is Ibuprofen. The Hansen Solubility Parameters values for Ibuprofen were determined by means of IGC (δ_d = 12.9±0.2; δ_p = 6.3±0.8; δ_h = 12.3±0.9 and δ_T = 18.9±0.5). The HSPs values indicate that Ibuprofen is a relatively active material with high capability of acting in hydrogen bonding interactions. It is probably connected with the presence of carboxyl group in the Ibuprofen molecule. However, its polar component of solubility parameter indicates rather medium polarity of this material despite the phenyl group in the molecule. Low δ_d value equal to 12.9 is probably related to small contribution of aliphatic parts and the significant influence of carboxyl and phenyl groups reducing the hydrophobic character of aliphatic chains.

Tab. 1. HSPs [MPa$^{1/2}$] values for Aerosil 200®V and nanogoethite by IGC (s.d. for α =0.05).

Parameter	Aerosil 200®V	Nanogoethite
δ_d	18.0±0.2	15.5±0.3
δ_p	10.8±0.7	6.2±0.2
δ_h	9.0±0.8	14.2±0.2
δ_T	22.8±0.5	22.0±0.2

The application of gas-solid inverse gas chromatographic procedure allows the estimation of the activity of this drug at any required temperature, e.g. at the temperature of human body or at "room" i.e. below and/or at 25^{0}C in which it is used during manufacturing. These HSPs values could be further used in the prediction of its behavior in real system. The HSPs values calculated with the

use of additive methods are available only at 25^0C. It is also difficult or even impossible to estimate precision in this case. Estimation of HSPs by the determination of partition coefficients is time consuming and limited to the temperature of experiment, e.g. most often 25^0C. Moreover, it cannot be used for substances completely insoluble in various solvents, e.g. iron oxides. Estimation of HSPs for solid material as nanomaterials such as Aerosil 200$^®$V and nanogoethite through determination of partition coefficients is extremely difficult and leads to significant error due to very low solubility of both oxides in the series of commonly used solvents. Therefore, IGC seems to be an attractive alternative here. The appropriate results for both nanomaterials are given in Table 1.

4. CONCLUSIONS

IGC is a developing technique due to its theoretical potential and wide application. It is the milestone in testing physicochemical properties of liquid and solid materials. Understanding and quantitative expression of interactions between components of different systems seems to be very important for estimation of the utility of materials for complex applications. One of potential solutions is calculation of cohesive energy of materials, or precisely, solubility parameter value, which can be used for estimation of the magnitude of intermolecular interactions in material. Therefore, the solubility parameter and the Hansen solubility parameters are physicochemical parameters which enable estimation of type and interaction force, responsible for compatibility between materials. The solubility parameter and/or HSP can be applied in the description of the behavior of materials in real systems, including such phenomena as: miscibility, adhesion and wetting [49-57].

5. REFERENCES

[1]   C. F. Poole, S. K. Poole, *Chem. Rev.* 89, 377 (1989).
[2]   P. Mukhopadhyay, H. P. Schreiber, *Macromolecules* 26, 6391 (1993).
[3]   A. Nastasovic, A. E. Onija, *J. Chromatogr. A* 1195 (2008) 1.
[4]   M. N. Belgacem, A. Gandini, in E. Pfefferkorn (Ed.), *Interfacial Phenomena in Chromatography*, Marcel Dekker, New York, 1999, p. 41.
[5]   H. Grajek, J. Chromatogr. A, 1145, 1 (2007).
[6]   E. Papirer, H. Balard, in E. Pfefferkorn (Ed.), *Interfacial Phenomena in Chromatography*, Marcel Dekker, New Ypork, 1999, p. 145.
[7]   H. Balard, *Langmuir* 13, 1260 (1997).
[8]   F. Thielmann, J. Burnett, J. Y. Y. Heng, *Drug. Dev. Ind. Pharm.* 33, 1240 (2007).
[9]   B. Charmas, R. Leboda, *J. Chromatogr. A* 886, 133 (2000).

[10] H. Balard, A. Saada, J. Hartmann, O Aouadj, E. Papirer, *Macromol. Symp.* 108, 63 (1996).

[11] N. A. Katsanos, N. Rakintzikis, F. Roubani-Kalantzopoulou, E. Arvanitopoulou, A. Kalantzopoulou*, J. Chromatogr. A* 845, 103 (1999).

[12] A. van Asten, N. van Veenendaal, S. Koster*, J. Chromatogr. A* 888, 175 (2000).

[13] I. I. Salame, T. J. Bandosz, *J. of Coll. and Int. Sci.* 240 (1), 252 (2001).

[14] H. Balard, D. Maafa, A. Santini, J. B. Donnet, *J. Chromatogr. A* 173, 1198 (2008).

[15] A. F. M. Barton, *CRC Handbook of Solubility Parameter and Other Cohesion Parameters*. CRC Press, Boca Raton, FL, 2000.

[16] J. M. Barrales-Rienda, J. Vidal Gancedo, *Macromolecules* 21, 220 (1988).

[17] A. Voelkel, J. Fall, *Chromatographia* 44, 197 (1997).

[18] A. Voelkel, J. Fall, *Chromatographia* 41, 414 (1995).

[19] J. Fall, K. Milczewska, A. Voelkel, *J. Mater. Chem.* 11, 1042 (2001).

[20] A. Voelkel, J. Fall, *J. Chromatogr. A* 721, 414 (1995).

[21] J. Conder, C. L. Young, *Physicochemical Measurements by Gas Chromatography*, Wiley, Chichester, 1979.

[22] J. H. Dymond, E. B. Smith, *The Virial Coefficients of Pure Gases and Mixtures*. Clarendon Press, Oxford, 1980.

[23] J. C. Huang, *J Appl. Polym. Sci.* 90, 671 (2003).

[24] M. J. El-Hibri, W. Cheng, P. Hattam, P. Munk, in D. R. Lloyd, T. C. Ward, H. P. Schreiber (Editors), *Inverse Gas Chromatography. Characterization of Polymers and Other Materials*. ACS Symposium Series, 391, Washington, 1989, p. 121.

[25] O. Olabisi, *Macromolecules* 8, 316 (1975).

[26] E. Fernandez-Sanchez, A. Fernandez-Torres, J. A. Garcia-Dominguez, J. M. Santiuste, E. Pertierra-Rimada, *J. Chromatogr.* 457, 55 (1988).

[27] A. M. Farooque, D. D. Deshpande, *Polymer* 33, 5005 (1992).

[28] F. Feraz, A. S. H. Hamou, S. Djadoun, *Eur. Polym. J.* 31, 665 (1995).

[29] L. Zhao, P. Choi, *Polimer* 43, 6677 (2002).

[30] K. Milczewska, A. Voelkel, *J. Appl. Polym. Sci.* 107, 2877 (2008).

[31] A. Voelkel, K. Milczewska, J. Jeczalik, *Macromol. Symp.* 169, 45 (2001).

[32] K. Milczewska, A. Voelkel, J. Jeczalik, *Macromol. Symp.* 194, 305 (2003).

[33] K. Milczewska, A. Voelkel, *J. Polym. Sci Part B: Polym. Phys.* 44, 1853 (2006).

[34] A. F. M. Barton, *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, CRC Press, Boca Raton, 1983.

[35] C. M. Hansen, *J. Paint Technol.* 39, 104 (1967).

[36] C. M. Hansen, *J. Paint Technol.* 39, 505 (1967).

[37] C. M. Hansen, *Ind. Eng. Chem. Prod. Res. Dev*. 8, 2 (1969).

[38] J. E. Guillet, *Polym. Math. Sci. Eng.* 58, 645 (1988).

[39] G. DiPaola-Baranyi, J. E. Guillet, *Macromolecules*, 11, 228 (1978).

[40] K. Ito, J. E. Guillet, *Macromolecules* 12, 1163 (1979).

[41] G. J. Price, in D. R. Lloyd, T. C. Ward, H. P. Schreiber (Editors), *Inverse Gas Chromatography. Characterization of Polymers and Other Materials*, ACS Symposium Series, 391, Washington, 1989, p. 48.

[42] A. Voelkel, J. Janas, *J. Chromatogr. A* 645, 141 (1993).

[43] T. Lindvig, M. L. Michelsen, G. M. Kontogeorgis, *Fluid Phase Equilib.* 203, 247 (2002).

[44] K. Adamska, R. Bellinghausen, A. Voelkel, *J. Chromatogr. A* 1195, 146 (2008).

[45] A. Voelkel, *Crit. Rev. Anal. Chem.* 22, 411 (1991).

[46] R. A. Keller, B. L. Karger, L. R. Snyder, in R. Stock, S. G. Perry (Editors), *Proceedings of the 8th International Symposium*, The Institute of Petroleum (1970), p. 125.

[47] B. L. Karger, L. R. Snyder, C. Eon, *Anal. Chem.* 50, 2126 (1978).

[48] N. Huu-Phuoc, R. P. T. Luu, A. Munafo, P. Ruelle, H. Nam-Tran, M. Buchmann,
      U. W. Kesselring, *J. Pharm. Sci.* 75, 68 (1986).
[49] D. J. David, T. F. Sincock, *Polymer* 33, 4505 (1992).
[50] C. Carr, *Polym. Paint. Col. J.* 181, 112 (1991).
[51] C. D. Vaughan, *J. Soc. Cosmet. Chem.* 57, 319 (1985).
[52] D. Karst, Y. Yang, *J. Appl. Polym. Sci.* 96, 416 (2005).
[53] D. Rasmussen, E. Walmström, *Surf. Coat. Int. PT B-C*, 8, 323 (1994).
[54] C. M. Hansen, *Progr. Org. Coat.* 51, 77 (2004).
[55] B. L. Karger, L. R. Snyder, C. Eon, *J. Chromatogr.* 125, 71 (1976).
[56] J. Poerschmann, *J. Microcolumn Sep.* 12, 603 (2000).
[57] B. C. Hancock, P. York, R. C. Rowe, *Int. J. Pharm.* 148, 1 (1997).

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