Inverse gas chromatography as a source of physiochemical data

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ABSTRACT

Inverse gas chromatography (IGC) is presented as a useful method for the examination of physicochemical properties of various materials. The advantages of IGC are presented. However, the uncertainties and sources of possible errors are also indicated and discussed.

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1. Introduction

During the last 50 years inverse gas chromatography (IGC) has been the well established and accepted source of physicochemical data for various investigated non-volatile materials. Nowadays, it is very common to find this term in the titles of hundreds of papers every year. The idea of this method was presented many times in various books [1–5] and journals [6–8]. The term inverse indicates that the material of interest is placed in a chromatographic column and the behavior of carefully 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 (probes) over the broad temperature range. These test solutes could be selected from hundreds of volatiles leading to different characteristics of the examined material.

Everything above indicates that the application of inverse gas chromatography is easy, cheap and quick. Let us examine this
statement and try to find the source of possible errors which might lead to vague and physicochemical groundless results.

What one needs to carry out the IGC experiment? One should take care of the following components of “the system”: (i) equipment; (ii) sample preparation; (iii) data correction; (iv) physicochemical model linking retention data with established physicochemical parameter; (v) calculation of parameters describing the interesting property of the examined material.

Inverse gas chromatography could be divided into inverse gas liquid and inverse gas solid chromatography. The obvious 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. However, even here the special attention should be paid on the influence of the materials porosity on the retention parameters. It will be discussed later. 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 interface; (iii) adsorption at the liquid–solid interface. The net retention volume ($V_N$) could be, therefore, presented as

$$V_N = V_G + K_{GL}A_G + K_{LS}A_L$$  

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

Although the basic equations of IGC were derived using the specific retention volume ($V_G$) very often the net retention volume ($V_N$) is used in the literature. Moreover, several authors calculated the specific retention volume as the ratio of the net retention volume and mass of the stationary phase without adjustment to 273.15 K (see Ref. [8] and e.g. [6]).

Poole and Poole [9] reported that 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. 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 influence of the flow rate of carrier gas on $V_N$ value was compensated by the extrapolation data to zero flow rate. However, this concept was not always accepted (see Ref. [8]).

The dominating retention mechanism is often related to the temperature of IGC experiment. Pure adsorption–desorption events occur during retention on the surface of solid adsorbent. However, even in this case one should discriminate the adsorption in micro- and macropores [6,10,11]. Characterization of amorphous materials requires special attention when selecting the temperature of experiment. Here, the detailed examination of retention diagram is required [12,13]. Such diagram can be divided into three isotherms: equilibrium surface adsorption, nonequilibrium sorption and equilibrium absorption. For polymer materials, generally two groups of parameters are characterized by IGC. One group is related to surface parameters, such as surface free energy, surface acid/base properties. The other is related to bulk parameters. In the retention diagrams for semicrystalline polymers phase transition below the melting temperature is also observed [12,14]. The growing research on solid surfaces and interfaces of polymeric systems, such as polymer blends and polymer composites, has accelerated the development of IGC technique. 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 results 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 $T_g$ [15]. They found that increasing the carrier gas flow rate to approximately 50 mL/min enabled the separation of the net retention volume of probe molecules into surface and bulk retention components.

An interesting overview on the determination of glass transition temperature of polymers was recently published by Nastasovic and Onija [16]. Advantages and drawbacks of the IGC over traditionally used methods for glass transition temperature determination were discussed. Authors discussed the parameters influencing precision and accuracy of $T_g$ determination. These are (i) inert support type, (ii) coating thickness, (iii) sorbate type and (iv) flow rate. This paper and references should be carefully studied by all investigators using IGC method in the examination of polymer properties both below and above $T_g$.

According to the definition of the gas hold-up time (dead-time) this parameter should be measured for the non-retained marker (methane and air). Dead-time was also calculated from retention time of $n$-alkanes by using, e.g. Grobler–Balizs procedure [17–21]. The use of $n$-pentane as non-interacting marker is not justified and might be the source of significant error [22]. Whether alkanes such as pentane are suitable as tracer depends on the measurement temperature and on the adsorption potential of the examined surface.

Thielmann in his review [6] indicated that the use of commercial gas chromatograph without some kind of technical sophistication usually does not deliver the required accuracy and reproducibility. The modification should include the column oven temperature stability, the control of carrier gas flow rate, and reproducibility of injection system. However, it should be stressed that the appropriate high standard of IGC measurements could be also achieved by using non-commercial equipment.

Columns from different materials were used in inverse gas chromatographic experiments. These were stainless steel, copper, glass, polymeric and others. Anyway, the material of the inner wall of the column should be as inert as possible to reduce undesirable adsorption of the test solutes. Chapel and Williams [23] corrected the retention data for the adsorption effect on the column walls by the subtraction of retention volume with the use of empty column from apparent data in IGC experiment. The size of the column depends on properties of examined material. The length varies from 10 cm [3] to approximately 400 cm [4]. Column inner diameter varied from 2 to 7 mm. The column diameter should be as small as possible to minimize the gas-phase diffusion effects [6]. Wider diameters of the column are beneficial when loading material of small particle sizes.

It is worth to note Saito et al. discuss the properties of the so-called packed-capillary column with the high temperature fibers as stationary phases [24,25]. Although separation ability and not physicochemical properties of these fibers was examined these papers might be good opening of the new field of inverse gas chromatography.

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 and (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.

Authors of this chapter like to cite the crucial statements of Bel-gacem and Gandini [4] concerning the validity of IGC method at infinite dilution. These are as follows: (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 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 to cover the solid’s surface. This mode allows the determination of adsorption isotherms [26]. Readers interested in IGC at finite concentration (FC-IGC) could find the required information in several extended reviews including those of Papirer and Balard [3,27], Thiellmann et al. [28] as well as Charmas and Leboda [29]. The interesting possibility of FC-IGC is the assessment of the surface heterogeneity through the distribution functions of adsorption energy of the probe. Such opportunity 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 preliminary the 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. Therefore, it is no surprise that this technique was applied many times commercially available. There-fore, it is no surprise that this technique was applied many times commercially available gas chromatographs could be used. There-fore, it is no surprise that this technique was applied many times commercially available gas chromatographs could be used. There-fore, it is no surprise that this technique was applied many times commercially available gas chromatographs could be used. Therefore, it is no surprise that this technique was applied many times commercially available gas chromatographs could be used.

Inverse gas chromatography is one of the few techniques which could be used for the determination of transport properties of volatile compounds through a polymer matrix [44]. In several papers the effect of the temperature above \( T_0 \) of the material was examined in capillary column IGC [45,46], on packed column filled with coated glass beads [47,48] or small polymer particles [49]. All these works were carried out at very low volatile concentrations, i.e. at infinite dilution. Danner et al. [50,51] extended the concentration range where examination of transport properties is carried out to finite concentration of the test solutes. Results of IGC investigations could be used for the estimation of, e.g. which polymeric composition will have the best barrier properties or which surface properties are necessary [52–54]. Relationships used during the examination of kinetic effects and the transfer of retention data into physicochemical parameters were presented in the above cited papers, i.e. in Refs. [44–54].

2. Surface characterization of solids

Surface of solids is characterized by their activity, acid-based properties, surface area and porosity. Almost all of these properties can be measured by means of IGC [2]. The other techniques used for studying surface properties of solids, e.g. oxides, silica, are infrared spectrophotometry (IR) and wetting method [55–58].

To determine the parameters of surface free energy by contact angle measurement, the three-liquid method is often used [59]. Well-known Young’s equation

\[
\gamma_S = \gamma_L \cos \theta + \gamma_{SL}
\]

where \( \gamma_S \), \( \gamma_L \), and \( \gamma_{SL} \) denote the surface free energy of the solid, the surface tension of the liquid and interfacial energy between solid and liquid, respectively, is rearranged into:

\[
y_1(1 + \cos \theta) = 2[(\gamma_{SL}^{lw})^{1/2} + (\gamma_L^{lw})^{1/2} + (\gamma_S^{lw})^{1/2}]
\]

where upper indices \( LW \), \( + \), and \( - \) denote Liskitz–van der Waals component, electron acceptor and electron donor parameters, respectively.

It is possible to determine the \( \gamma_S^{lw} \), \( \gamma_L^{lw} \) and \( \gamma_{SL}^{lw} \) components of the surface free energy of examined material from contact angle measurements using three liquids of known properties \( (\gamma_1^{lw}, \gamma_2^{lw}, \text{ and } \gamma_3^{lw}) \).

However, inverse gas chromatography reveals several advantages as independent of sample morphology, it does not require an elaborated apparatus and accurate measurements are possible over a wide range of temperatures [4–6]. The applicability of van Oss concept to IGC was deeply presented and discussed by Goss [60].

Surface of solids is described by both dispersive and specific properties. The energy of solids surface, \( \gamma_S \), is expressed by the sum of dispersive, \( \gamma_S^{dp} \), and specific components, \( \gamma_S^{sp} \):

\[
\gamma_S = \gamma_S^{dp} + \gamma_S^{sp}
\]

Dispersive properties are characterized by the dispersive component of the free surface energy, \( \gamma_S^{dp} \). Specific properties of the solid surface can be described by IGC derived \( K_L \) and \( K_D \) parameters characterizing surface ability to acid (acceptor of electrons) and basic (donor of electrons) interactions, accordingly.

2.1. Dispersive properties of the solid surface

The dispersive properties of the examined material are calculated from retention data of test solutes determined at infinite dilution (or zero surface coverage) in the Henry’s law region [4,61]. It is also assumed that interactions between the adsorbed molecules are negligible. Net retention volume \( V_N \) is related to molar free energy of adsorption:

\[
\Delta G_A = RT \ln V_N + C
\]

where \( R \) is the gas constant, \( T \) the absolute temperature and \( C \) is the constant.

For non-polar probes (test solutes) only dispersive (Lisfhitz–van der Waals) interactions occur with the solid surface. The work of adhesion could be described as

\[
W_a = W^{lw} = 2(\gamma_S^{lw} \gamma_L^{lw})^{1/2}
\]

The free energy of adsorption is related to the work of adhesion by the following equation:

\[
\Delta G_A = aW_a
\]

Combination of Eqs. (5)–(7) leads to:

\[
RT \ln V_N = 2N((\gamma_S^{lw})^{1/2} + (\gamma_L^{lw})^{1/2}) + C
\]

Most often in IGC literature this relation is presented in the form introduced by Schultz et al. [62,63]:

\[
RT \ln V_N = 2N a_p \sqrt{\gamma_S^{dp} \gamma_L^{dp}} + C
\]

where symbol \( \gamma_S^{dp} \) is used instead of \( \gamma_S^{lw} \) denoting the dispersive component of surface free energy of the solid; symbol \( \gamma_L^{dp} \) is used instead of \( \gamma_L^{lw} \) denoting the dispersive component of surface free energy of the test solute; symbol \( \gamma_{ap} \) is used instead of \( a \) denoting the area occupied by adsorbing molecule.

\( \gamma_S^{dp} \) is calculated from the slope of the straight line as presented in Fig. 1.
The most popular way of determination of the dispersive component of the surface free energy, \( \gamma^D \), is Dorris and Gray method. Here, \( \gamma^D \) is calculated according to the equation:

\[
\gamma^D = \frac{-RT^2}{4N^2a_{CH2}^2} \left[ \frac{1}{N} \left( \frac{V_{CH2}}{V_{CH2}^{(CH2)}} + \frac{V_{CH4}}{V_{CH4}^{(CH2)}} \right) \right]^2
\]

(10)

where \( a_{CH2} \) is the surface area of a methylene group. The value of this parameter is assumed to be equal to 6 Å² but sometimes is taken as 5.2 or 5.5 Å²; variation of these quantities is even higher, e.g. 3.1 Å² was calculated from spherical model [64] while values up to 7.7 Å² have been observed by scanning tunneling microscopy (STM) [65]. \( N \) is the Avogadro’s number (6.023 \times 10^{23} /mol); \( V_{CH2}^{(CH2)} \) is the net retention volume of alkane \( C_{n+1}H_{2n+2} \); \( V_{CH4}^{(CH2)} \) is the net retention volume of alkane \( C_nH_{2n+2} \); \( \gamma_{CH2} \) is the surface energy of the polyethylene-type polymers with a finite molecular weight (nm²/m²). The value \( \gamma_{CH2} \) is calculated according to the following equation:

\[
\gamma_{CH2} = 34.0 - 0.058t
\]

(11)

or

\[
\gamma_{CH2} = 35.6 + 0.058(293 - T)
\]

(12)

where \( t \) is the temperature (°C) and \( T \) is the temperature (K).

The main difficulty in this method is connected with the estimation of the correct values of constants \( a_{CH2} \) and \( \gamma_{CH2} \). The way of determination of \( a_{CH2} \) value is discussed in some papers [66,67]. Similar problem appears with estimation of \( \gamma_{CH2} \) [4]. Belgacem and Gandini suggested the use of Eq. (12) as leading to the most accurate values of \( \gamma_{CH2} \) [4]. Moreover, the variation of the \( \gamma^D \) values calculated from the ratio of the net retention volume of two consecutive homologous alkanes is very often significant. Therefore, it should be suggested to use the average from the \( \gamma^D \) values for, e.g. three pairs of \( n \)-alkanes. Park and Brendle [66] interpreted their results using \( \gamma_{CH2} \) for expression of \( \gamma^D \). Authors indicated that the use of \( \gamma_{CH2} \) provides more detailed and precise information on the state of relatively low BET specific area solids (\( \leq 1 \text{ m}^2/\text{g} \)).

Brendle and Papier [68] indicated several limitations for the application of Schultz and Lavielle procedure. These were due to the problems in the determination of proper \( a_p(\gamma^D)^{1/2} \) values, i.e. correctness of IGC measurements [69]. Factors influencing the \( \gamma^D \) value may be as follows: (i) reference state applied in the procedure; (ii) contribution of “bulk retention” is possible for porous polymers, when the range of temperature of the experiment is too close to \( T_g \) of polymer, and when used test solute is a solvent or solubilizer for the examined polymer. To overcome these difficulties it is advised to (i) check if the porosity of examined polymer influences retention parameter of test solute; (ii) work in the “safe” distance from \( T_g \). The error of the determination of dispersive component of surface free energy may depend on accuracy of the determination of slope value of Eq. (9). Relatively low slope values are multiplied by a “constant” which is higher by three orders. The error of 10% in slope determination results in a 20% error in the value of \( \gamma^D \) [69]. Experimental values of \( V_g \) (±5%) and \( T_g \) (±0.1 °C) may be estimated relatively accurately. \( \gamma^D \) data are taken from literature or are determined experimentally. The most problematic value is \( a_p \) and may be determined with large error depending on adsorbent properties, temperature and reference substance. The assumption that \( a_p \) is constant is most comfortable. However, under IGC conditions the most realistic seems to be the assumption that the test solute behaves like ideal gas [69].

Schultz and Lavielle proved that the values of \( \gamma^D \) parameter determined according to their method are similar to the values of \( \gamma^D \) parameter determined according to Dorris and Gray method. Voelkel et al. also showed similarity of the values of \( \gamma^D \) parameter determined according to these two methods [70].

IGC method is the better method to determine the energetic properties of, e.g. fibers than wetting technique [71]. Generally, IGC gives \( \gamma^D \) values similar but usually higher than these from contact angle measurements [72]. Mukhopadhyay and Schreiber indicated that it can be the effect of the adsorption of extremely diluted test solutes’ molecules preferably on high-energy sites within the solid’s site energy distribution [15].

\( \gamma^D \) parameter can be used for evaluating the activity of the surface of solids. The value of \( \gamma^D \) parameter for non-active material, e.g. inert glass wool used for closing chromatographic columns is close to 20 mJ/m². Very active materials such as, e.g. alumina oxide or pyrogenic silica are characterized by the values of \( \gamma^D \) parameter close to 100 mJ/m² [73,74], up to 400 mJ/m² for carbon blacks [3] or even 500 mJ/m² for carbonaceous materials [4]. However, it should be noted that the high surface energy values are often compromised by microporosity. Relatively often, the experiment is carried out at too low temperature what leads to distorted peaks and results.

IGC was also presented as a useful tool in the examination of the surface properties (activity) of nanomaterials [75]. The monitoring of surfaces of nanomaterials modified by surfactants allowed the determination of Hamaker constant value for particles interacting in real environment. Values of Hamaker constant (\( A \)) were estimated from dispersive component of the surface free energy \( \gamma^D \) according to Eq. (13):

\[
A \approx 12.064a_m^2 \sigma_m^2 \times 10^{-21}[J]
\]

(13)

where \( \sigma_m \) is the mean weighted diameter of surface atom.

Changes of Hamaker constants follow the changes of \( \gamma^D \) caused by the modification of the surface by surfactant during mixing process. Authors indicated that the use of the constant value of Hamaker parameter in simulation procedures for dispersed systems cannot be advised.

### 2.2. Ability of the solid surface to specific interactions

Examination of the ability of the given surface to specific interactions was the obvious task of inverse gas chromatography from early years of its existence. Such possibility exists – it simply requires the injection of the polar probes of known characteristics and collection of the appearing peaks. However, its application is much more difficult than in the case of parameters describing the surface activity through dispersive forces. The reasons were
presented by Papirer and Balard [3]: (i) a polar test solute will interact with a polar surface through both dispersive and specific interactions; (ii) the investigator collects only one chromatographic peak and its parameters result from both types of interactions. One has to separate and evaluate both contributions. The term-specific interactions denote all type of interactions except London ones, i.e. bipolar, H-bond type, acid–base, metallic, magnetic and hydrophobic. Such intermolecular forces are known to dominate over dispersion and dipole–dipole interactions [76]. In the absence of electrostatic, magnetic or metallic interactions acid–base ones prevail over the dispersive ones. Therefore, the special attention was focused on the evaluation of procedures enabling the determination of the acid–base characteristics of the examined surfaces. The scales of acidity–basicity were already discussed by, e.g. Mukhopadhyay and Schreiber [77] or the reader could refer to original papers of Fowkes and Mostafa [78], Pearson [79], Drago and Wayland [80], Gutmann [81] and Kamlet and Taft [82], Schreiber et al. [83] proposed another definition of acceptor and donor number not related to Gutmann’s scale defined as follows:

\[ AN_{\text{Sch}} = \frac{V_{\text{NIF}}}{V_{\text{Ref}}} \]  
\[ DN_{\text{Sch}} = \frac{V_{\text{NClC}}}{V_{\text{Ref}}} \]  

where \( V_{\text{NIF}} \), \( V_{\text{NClC}} \), \( V_{\text{Ref}} \) denote the net retention volume of tetrahydrofurane, chloroform and hypothetical \( n \)-alkane having the same vapor pressure as the polar test solute, respectively. Acceptor and donor numbers defined by Eqs. (14) and (15) are directly related to the specific component of free energy of adsorption.

Using IGC method acidity and basicity of solid surface is concluded from behavior of polar compounds being injected onto the chromatographic column filled with studied material [1,5,84–86]. The ability of the solid surface to interact as base or acid is expressed in different ways. However, the Gutmann’s scale seems to be most often used in IGC procedures. One should note \( AN' \) and \( DN' \) numbers of the test solutes express their ability to act as electron acceptor and electron donor, respectively. Therefore, the final result should be discussed in term of Lewis acid–base interactions.

Ability of the examined surface to specific interactions is determined by the procedure consisting of the determination of the specific component of adsorption energy \( \Delta G^S \) then the specific component of the enthalpy of adsorption \( \Delta H^S \) followed by the solution of the relationship between \( \Delta H^S \) and parameters characterizing the examined material.

\[ \Delta G^S = \Delta G_{\text{polar}} - \Delta G_{\text{ref}} \]  

where

\[ \Delta G_{\text{polar}} = -RT \ln V_{\text{polar}} + C \]  and \[ \Delta G_{\text{ref}} = -RT \ln V_{\text{Ref}} + C \]

Chehimi and Pigois-Landureau [91] compared six methods of evaluating \( \Delta G^S \) where \( RT \ln V_n \) were related to the abscissa coordinates labeled as follows: I, \( \Delta H_{\text{vap}}^p \) (dispersive component of enthalpy of evaporation); II, \( \Delta H_{\text{vap}}^\eta \) (enthalpy of evaporation); III, \( T_b \) (boiling point); IV, \( \log P^o \) (saturated vapor pressure); V, \( q_{\eta}^{T^o} (\text{area occupied by adsorbing molecule and the dispersive component of the liquid solute surface tension, respectively}) \); VI, \( (h\mu)^{1/2} \) (molecular polarizability). They suggested the use of \( \Delta H_{\text{vap}}^\eta \) parameter for the description of the reference state as demonstrating the self-association character of polar test solutes what was earlier postulated by Fowkes [92]. However, this approach was seldom used in IGC practice.

\[ \Delta H^S \] is calculated from \( \Delta G^S \) dependence on temperature:

\[ \Delta G^S = \Delta H^S - T \Delta S^S \]  

where \( \Delta G^S \) is the specific component of the free adsorption energy and \( \Delta S^S \) is the specific component of the free adsorption entropy of polar compound onto the surface of investigated solid.

Plotting \( \Delta G^S / T \) against \( 1/T \) yields a straight line with the slope of \( \Delta H^S \). \( \Delta H^S \) should be determined for, at least, four test compounds, and \( \Delta S \) should be determined at, at least, three temperatures. However, the calculation of \( K_A \) and \( K_D \) parameters from \( \Delta H \) is time consuming. The estimation of \( \Delta H \) from Eq. (17) might be the source of the largest error in determination of the specific characteristics of the examined material.

Specific component of enthalpy of adsorption of polar compound, \( \Delta H^S \) is related to acceptor and donor numbers describing the electron acceptor (\( AN' \)) and electron donor (\( DN' \)) properties of
the test compound:
\[ \Delta H^S = DN K_A + AN^* K_D \]  

(iii) the reproducibility of the amount injected on the column test with static method and found them being in good agreement.

Plotting \( \Delta H^F/\Delta AN^* \) against \( DN/AN^* \):

\[ \frac{\Delta H^F}{AN^*} = \frac{DN}{AN^*} K_A + K_D \]  

One obtains the straight line with the slope of \( K_A \). As the estimation of \( K_D \) from the intercept of Eq. (19) may lead to the significant error one should determine this value as the slope of the following relationship:

\[ \frac{\Delta H^F}{DN} = \frac{AN^*}{DN} K_A + K_D \]  

Parameters \( K_A \) and \( K_D \) were also calculated by using \( \Delta G^3 \) [8,87,88,93] instead of \( \Delta H^F \). This way of determination of \( K_A \) and \( K_D \) leads to the temperature-dependent values containing also entropic factor [5,93]. These values should not be compared to those calculated from \( \Delta H^F \). Fekete et al. [93] examined also the reliability of the various approaches of determination of acid–base characteristics and acid–base parameters used in current practice [93].

Hamieh et al. [94] proved that the relationship (18) is, in general, not verified in the case of some metallic oxides. They suggested the use of corrected version:

\[ \Delta H^F = K_A DN^* + K_D AN^* - K(K_A, K_D)AN^* DN^* = w(K_A DN^* + K_D AN^*) \]  

where \( w \) is a parameter expressing a weighing factor for the interactions between adsorbed molecules and solid substrate (0 ≤ \( w \) ≤ 1).

In the literature there are not many information about errors committed during determination enthalpy and entropy of adsorption by means of IGC [26]. The accuracy of the determination of enthalpy and entropy of adsorption by the IGC method is not completely reliable as the reproducibility of the primary chromatographic data [26], e.g. retention times, is influenced by many factors:

(i) variations of the flow of carrier gas and the accuracy of measurement of the carrier gas flow;

(ii) variations of purity of carrier gas;

(iii) the reproducibility of the amount injected on the column test compounds;

(iv) the temperature gradient in the column oven and the accuracy of temperature measurement; the increase of the temperature might cause the increase of retention time.

It was also shown that peak symmetry is not a sufficient evidence for thermodynamic equilibrium having been attained in the IGC tests [26]. Grajek described adsorption of several hydrocarbons on graphitized carbon black and zeolite. Differences between the values of the thermodynamic parameter determined by means of IGC and static method were reported even if the symmetric peaks were obtained from IGC measurements. To be sure that equilibrium adsorbate–adsorbent is achieved two columns with the same studied materials should be prepared and examined. Boucher and Everett [95] followed this idea and estimated enthalpy of adsorption of inert gas on two different columns filled with activated coconut shell carbon. They compared results from IGC experiment with static method and found them being in good agreement.

The problem is also the values of \( AN^* \) and \( DN \) [93]. Fekete et al. [93] calculated the values of \( K_A \) and \( K_D \) parameters and they affirmed that these should be derived from the corrected acceptor number of Riddle and Fowkes [86], and donor number of Gutmann [81].

IGC determined Lewis acid–base parameters for polymers and additives used in polymeric systems were applied in quantification of the acid–base interactions at interfaces and interphases between a polymer matrix and the additive [77] according to different relationships:

\[ I_{p1} = (K_A)(K_D) + 2(K_A)(1)(K_D) \]  

\[ I_{p2} = [(K_A)(K_D) + (K_A)(1)(K_D)]^{1/2} \]  

\[ I_{p3} = (K_A)(K_D) + (K_A)(1)(K_D) - (K_A)(1)(K_D) - (K_D)(1)(K_D) \]

where indices 1 and 2 denote the interacting species in polymeric system.

Mukhopadhyay and Schreiber [77] reported the existence of useful correlation between interaction parameters defined by Eqs. (22)–(24) and adhesion phenomena and other properties influenced by the strength of Lewis electron acceptor–donor intermolecular forces. Santos et al. [76] critically discussed these parameters and indicated that parameter considered to be suitable for multicomponent polymeric systems should take into account the following factors: (i) Lewis acid–base (properly electron acceptor–donor) parameters, (ii) the accessibility of the Lewis acidic and Lewis basic active sites in each species, (iii) the larger contribution of acid–base attraction forces for the overall interaction and (iv) the composition of the system.

Values of \( K_A \) and \( K_D \) as well as interaction parameters were most often used in the examination of various materials or systems. \( \gamma^{12}_A \), \( K_A \) and \( K_D \) parameters are useful for estimate modification of the solids surface [72,96]. The knowledge of \( \gamma^{12}_A \) is crucial to emulsion and suspension production [97]. \( \gamma^{12}_A \) parameter can be used for calculation adhesion [98–102]. Surface properties of various dental materials and their changes caused by, e.g. water sorption or influence of artificial saliva were determined by means of IGC [103–105]. Regrettfully, it is practically impossible to cite all valuable papers in which results collected by means of IGC were reported. Therefore, we have to advise the research in internet resources and follow the new ideas connected with IGC method.

It is worth to note that also other parameters were used to express the ability of the examined surfaces to specific interactions. Papier et al. [89] characterized the series of aluminas with the use of \( \Omega \) parameter defined as the ratio of net retention volumes of two test solutes: ethyl ether and methylene chloride:

\[ \Omega = \frac{V_{methylether}}{V_{methylene \ chloride}} \]  

Authors suggested the use of this parameter as offering more global information on acid/base properties of the examined samples in comparison to, e.g. \( K_A \).

Other \( \Omega \) was introduced by Osmont and Schreiber [106] during the examination of glass fibers. n-Butanol and butylamine were used as test solutes. For acidic surface the specific retention volume of the base exceeds that for acidic alcohol:

\[ \Omega = 1 - \frac{(V_{g,b})}{(V_{g,a})} < 0 \]  

where \( (V_{g,b}) \) and \( (V_{g,a}) \) denote the specific retention volume of base and acid test solute, respectively.
For the materials of basic character the specific retention volume of n-butanol exceeds that of butylamine and
\[ \Omega = \left( \frac{V_{k, a}}{V_{k, b}} \right)_T - 1 > 0 \quad (27) \]

Schreiber et al. [83] introduced the K index of acid–base properties as the difference of the \( AN_{Scb} \) and \( DN_{Scb} \) numbers (see Eqs. (14) and (15)). \( K > 0 \) for basic surfaces, \( K < 0 \) for acidic ones while \( K \approx 0 \) indicates neutral and amphoteric surface.

Chehimi et al. [107] introduced also another index of acidity:
\[ \Omega_A = \frac{V_N^{AB}(base)}{V_N^{AB}(acid)} \quad (28) \]
and the new index of basicity:
\[ \Omega_B = \frac{1}{\Omega_A} = \frac{V_N^{AB}(acid)}{V_N^{AB}(base)} \quad (29) \]
where \( V_N^{AB} \) denotes the acid–base contribution to the net retention volume of the polar probe.

They proposed also two dimensionless hard (H) and soft (S) indices of basicity:
\[ \Omega_{IHB} = \frac{V_N^{AB}(CHCl_3)}{V_N^{AB}(DXN)} \quad (30) \]
\[ \Omega_{ISB} = \frac{V_N^{AB}(t-BuOH)}{V_N^{AB}(THF)} \quad (31) \]
where CHCl_3, DXN, t-BuOH and THF refer to chloroform, 1,4-dioxane, tert-butanol and tetrahydrofuran, respectively.

Parameters defined by Eqs. (25)–(31), expressing the acid–base properties of the solid material, were seldom used in the IGC literature and these are mentioned for rather completion of presentation of the different approaches to difficult problem of surface characteristic. It should be indicated that \( \Omega \) concept is thermodynamically vague or even meaningless as \( \Omega \) values are probe molecule dependent.

Sidqi et al. [108] defined the specific interaction parameter by using the retention data (net retention volume) of n-alkane/n-alkene pair having the same number of carbon atoms in the molecule:
\[ \varepsilon_{\pi} = \Delta G_{alkane} - \Delta G_{alkene} = RT \ln \left( \frac{V_{alkene}}{V_{alkane}} \right) \quad (32) \]
This quantity is predominantly affected by the changes in the electron acceptor ability of the adsorbent [109]. Specific interaction parameter \( \varepsilon_{\pi} \) was used for the description of the surface properties of activated carbons [109], smectite [110] as well as pure and composite oxides [111].

Processes in which a solute is transferred from one phase to another respond to changes in solute properties caused, e.g. by changing environment. The number of types of solute–solvent interaction controlling such transfer is limited. Set of descriptors evaluated by Laffort et al., Weckwerth et al. and Abraham [112] consists of no more than five descriptor encoding similar information. The model proposed by Abraham is most widely used also in gas–liquid chromatography in form [112–117]:
\[ \log k = c + e + \kappa + s + aA + bB + IL \quad (33) \]
where \( \log k \) is the retention factor while the capital letters relate to solute descriptors: \( E \) the contribution from electron lone pair interactions, \( S \) the dipolarity/polarizability interactions, \( A \) the hydrogen bond acid (proton donor), \( B \) the hydrogen bond basic (proton acceptor) interactions and \( L \) the descriptor of solute size (contribution of cavity formation and dispersive interactions). The lower italic letters are the system constants defining the capability of the stationary phase to participate in the same interaction. In this sense this parameters could be called inverse gas chromatographic physicochemical parameters.

2.3. Influence of measurement conditions

The influence of water on the retention times of organic probes on clays examined by IGC was investigated by Balard et al. [118]. The \( \gamma_{CHCl_3} \) remained constant when dry carrier gas was used in IGC experiment. However, \( \gamma_{CHCl_3} \) values decreased significantly in wet carrier gas. Authors attributed this effect to the increase of clay hydration ratio. Adsorption of water molecules reduced the access of the alkane probes to the high-energy interactions sites.

Newell et al. observed the effect of relative humidity on \( \gamma_{CHCl_3} \) value of amorphous lactose [119]. The dispersive component of the free surface energy, decrease with the increase of carrier gas humidity. Authors indicated that the change in surface energy was reversible only in limited range of relative humidity (RH) up to 20%. The exposure to higher RH values and the following drying did not result in return to the initial \( \gamma_{CHCl_3} \) value of the amorphous form. The observed changes were the result of recrystallization at RH > 30%. Buckton and Gill [120] indicated that the observed effect is due to water increasing mobility. \( \gamma_{CHCl_3} \) for milled sample exhibits a similar behavior to the amorphous sample, the surface energy decreases with humidity.

Fekete et al. [93] showed the effect of the measurement time, conditioning and measurements magnitudes on the \( \gamma_{CHCl_3} \). Conditioning at high temperature leads to the desorption of water from high-energy sites of the filler surface. Further measurements at low temperature result in the adsorption of the water traces and/or other contaminations from the probe and carrier gas. This leads to the decrease of \( \gamma_{CHCl_3} \) at longer time. While conditioning was carried out at low temperature and measurements at high temperature the water molecules were not removed during the initial step and continuous desorption during experiment occurred. It resulted in the increase of the surface energy parameter. Fekete et al. [93] concluded that different types of fillers could be compared only under standard conditions.

Surface properties of powder materials and interactions of their surfaces with water were reported also in several other papers [121,122].

Cava et al. [44] reported that the sorption of water by the examined material increased the partition and diffusion coefficients (determined by means of IGC).

Anyway, the advantage of IGC is the possibility of controlling the temperature and relative humidity. However, Buckton and Gill [120] indicated that interpretation of the data collected from IGC experiment with the carrier gas saturated to the desired RH becomes difficult. The difficulties result from the possibility of various ways of the probe (test solute) interactions: (i) with water vapor adsorbed to the material surface, (ii) with unblocked (by water) active sites, (iii) displacement of water molecules from the surface by test solute and its interactions with the solid.

Papirer et al. [123] found that the grinding process of the mica filler significantly influenced the surface characteristic of the examined surface. They reported the increase of the “base-like” properties of muscovite but without the explanation of the observed effect. The activity of the final material depends also on the conditions of the grinding, i.e. the type of the additive and/or grinding duration [123,124].

York et al. [125] showed that powder milling leads to the domination of faces having the small attachment energy. Therefore, surface energy of the material is dictated by the exposure groups at the surface. During milling the particle size decreases so the
surfaces of the powder become more energetic. Groups on the surfaces are the same, just new surfaces are exposed and the dispersive component of the surface free energy increases. However, this observation is only true for propanol which fractures along the weakest plane.

Newell showed that milled sample of the crystalline α-lactose monohydrate has similar \( y_0^2 \) value to that observed for amorphous lactose. It indicates that the surface of milled was amorphous [119]. However, the behavior of milled and amorphous samples was different. No physical collapse (mentioned above) associated with the amorphous sample was observed. The bulk of the milled material (lactose) remains in the crystalline form and does not undergo a physical collapse. The changes occurring in the thin layer of amorphous do not significantly influence the behavior of the sample. Differences between the samples of salbutamol sulphate were attributed to differences in surface crystallinity [126]. The spray-dried sample collapses as it is 100% amorphous while the properties of the milled sample changed to lower extend since mild milling increases amorphous content to very limited amount. Buckton postulated the further efforts to define the detection sensitivity limit [127].

It is worth to note very recent paper of Balard et al. [34]. Authors showed the usefulness of IGC as a powerful and convenient method in studying the evolution of physicochemical surface properties of the series of milled graphites. The milling of graphites induced the formation of high energetic sites and an increase of nanoroughness surface characteristics of lateral surfaces of solids. The number of the active sites increased with the increase of milling time. The characteristic change observed after 2 and 3 h of milling was attributed to change of surface oxidation degree.

The opportunity to follow the changes of the surface energetic caused by the structure changes in the examined material resulting from the milling, grinding and/or water adsorption/sorption is the positive advantage of the IGC method.

### 3. Bulk properties

Many of the properties and processing characteristics of mixtures (i.e. polymer blends, compositions and modified fillers) depend on whether they are miscible or not. Theory operates with parameters relating to the pure components. However, mixture parameters that characterize polymer–polymer, polymer–filler interactions are generally required as well [128].

#### 3.1. Flory–Huggins interaction parameter

Flory–Huggins interaction parameter \( (\chi) \) as an important factor of miscibility of polymer blends and solutions has been determined by a number of methods (e.g. SANS, DSC, IGC) and reported in different papers. It reflects the 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 interaction parameter \( \chi \) can be divided into enthalpy \( \chi_H \) and entropy \( \chi_S \) components [129]:

\[
\chi = \chi_H + \chi_S
\]  

(34)

It was found that \( \chi_S \) is positive and usually should be between 0.2 and 0.6. This term, sometimes, is also related to the reciprocal of the coordination number in polymer solution. It has been assumed that in some cases it is between 0.3 and 0.4 limit [130]. For complete miscibility between polymer and solvent interaction parameter \( \chi \) should be less than 0.5. Also entropy term is about 0.3, therefore enthalpy term \( \chi_H \) to that must be very small to complete miscibility's criterion has been met [129].

Deshpande et al. [131] were first to suggest the use of IGC for studying the polymer blends. Starting from Flory–Huggins expression for the change of free enthalpy of mixing \( \Delta G_{mix} \) extended to three-component systems, they proposed a method of elaboration of IGC data collected with the use of polymer blend leading to the polymer–polymer interaction coefficient.

The values directly measured by IGC were the retention times of solutes, \( t_k \), the mass of the stationary phase, \( m_w \), the temperature of column, \( T \) and the flow rate, \( F \). Then the specific retention volume, \( V_k \), can be computed from [132]:

\[
V_k = \frac{3}{2} \frac{t_k F/273.15}{m_w T} \tag{35}
\]

where \( t_k' = t_k - t_M \), \( t_M \) is the gas hold-up time and \( j \) is the James–Martin coefficient [133].

At infinite dilution of the probe and for high molecular weight of the stationary phase the Flory–Huggins interaction parameter can be determined from Refs. [134–137]:

\[
\chi^c_{12} = \ln \left( \frac{273.15R}{p} \frac{B_{11} - V_o^2}{M_1 V_g^2} \right) - \frac{6}{p} \left( \frac{B_{11} - V_o^2}{V_g^2} + \ln \left( \frac{p_1}{p_2} \right) - \left( 1 - \frac{V_o^2}{V_g^2} \right) \right) \tag{36}
\]

1 denotes the solute and 2 denotes examined material, \( M_1 \) is the molecular weight of the solute, \( p^o_2 \) is the saturated vapor pressure of the solute, \( B_{11} \) is the second virial coefficient of the solute, \( V_o^2 \) is the molar volume of the polymer.

Many authors use simplified form of Eq. (36) [35,138,139]:

\[
\chi^c_{12} = \ln \left( \frac{273.15Rv_2}{p^o_2} \frac{B_{11} - V_o^2}{V_g^2} \right) - \frac{6}{p} \left( \frac{B_{11} - V_o^2}{V_g^2} + \ln \left( \frac{p_1}{p_2} \right) - \left( 1 - \frac{V_o^2}{V_g^2} \right) \right) \tag{37}
\]

where \( v_2 \) is the specific volume of the polymer.

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

\[
\chi^c_{1m} = \ln \left( \frac{273.15Rv_2}{p^o_2} \frac{B_{11} - V_o^2}{V_g^2} \right) - \frac{6}{p} \left( \frac{B_{11} - V_o^2}{V_g^2} + \ln \left( \frac{p_1}{p_m} \right) - \left( 1 - \frac{V_o^2}{V_g^2} \right) \right) \tag{38}
\]

where \( \psi_2 \) and \( \psi_3 \) are the volume fractions of components [129].

Voelkel and Fall [138] have shown that the significant variation in second virial coefficient data possibly collected from different sources may affect the final result, i.e. the value of physicochemical parameter which is used for the discussion of practical application of polymer and petroleum systems. Conder and Young [1] indicated that “there are no really satisfactory results for predicting second virial coefficient of polar substances although it is possible to extend the principle of corresponding states to substances with small dipole moments with limited success”. They have also stated that permissible uncertainty in estimation of second virial coefficient of solute should be 10% (at 20–50 °C).

Second virial coefficient \( B_{11} \) could be determined by using various methods. Guggenheim and McGlashan [140] suggested the use of the following relationship:

\[
B_{11} \frac{V_c}{V^c} = 0.461 - 1.158 \left( \frac{T^c}{T} \right) - 0.503 \left( \frac{T^c}{T} \right)^3 \tag{39}
\]

where \( B_{11} \) is expressed in cm³/mol, \( V^c \) in ml/g, and \( T \) and \( T^c \) in K (it is valid for Eqs. (39)–(44)).
McGlashan and Wormald [141] corrected Eq. (39) by introducing an extra term:

$$B_{11}^{\text{Vc}} = 0.430 - 0.886 \left( \frac{T^c}{T} \right) - 0.694 \left( \frac{T^c}{T} \right)^2 - 0.0375(n-1) \left( \frac{T^c}{T} \right)^{4.5}$$

(40)

where $n$ is the number of carbon atoms in hydrocarbons.

Guggenheim and Wormald [142] applied another version of Eq. (39):

$$B_{11}^{\text{Vc}} = 0.500 - 1.144 \left( \frac{T^c}{T} \right) - 0.480 \left( \frac{T^c}{T} \right)^2 - 0.042 \left( \frac{T^c}{T} \right)^3$$

(41)

while for paraffinic hydrocarbons having 1–8 carbon atoms they proposed to calculate $B_{11}$ from

$$B_{11}^{\text{Vc}} = 0.0375(n-1) \left( \frac{T^c}{T} \right)^{4.5}$$

(42)

Blu et al. [143] and Nesterov and Lipatov [144] predicted $B_{11}$ values from

$$B_{11} = \frac{9RT^c}{128p^c} \left\{ 1 - 6 \left( \frac{T^c}{T} \right)^2 \right\}$$

(43)

or

$$B_{11} = V^{\text{c}} \left[ 0.25 - 1.5 \left( \frac{T^c}{T} \right) \right]$$

(44)

in the case when $0.6 < T/T^c < 1.0$.

Pitzer and Curl [145] and O’Connell and Prausnitz [146] introduced theacentric factor ($\omega_1$) – a measure of deviations from the properties of a simple, inert gas. They predicted $B_{11}$ values from

$$p^c B_{11}^{\text{RT}} = f_B^{(0)}(T_R) + \omega_1 f_B^{(1)}(T_R)$$

(45)

where $p^c$ and $T^c$ denote critical pressure and temperature, respectively; $T_R$ is reduced temperature equal to the ratio $T/T^c$; $\omega_1$ is defined as

$$\omega_1 = -\log \left( \frac{p^c}{T^c} \right) - 1.000$$

(46)

where $p^c$ is the saturated vapor pressure when $T/T^c = 0.7$; factors $f_B^{(0)}(T_R)$ and $f_B^{(1)}(T_R)$ are calculated from the following equations:

$$f_B^{(0)}(T_R) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3}$$

(47)

$$f_B^{(1)}(T_R) = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^4}$$

(48)

Critical pressure may also be calculated from the general relationship [147] valid for all molecules

$$p^c = \frac{20.87^c}{V^c - 8}$$

(49)

and the error of prediction does not exceed 11% ($V^c$ expressed in ml/mol, $F^c$ in K and $p^c$ in atm).

Condor and Young [1] presented the rules for the calculation of $V^c_{1,2}$ and $T^c_{1,2}$. The second virial coefficient was also tabulated for limited group of compounds in few handbooks, e.g. Ref. [148].

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%.

While applying the Flory–Huggins equation of polymer solutions to a ternary system with two polymers and one probe, the interaction parameter $x_{1m}^\infty$ can be related to the probe–polymer interaction parameters and the polymer–polymer interaction parameter by the following Eq. [149]:

$$x_{1m}^\infty = \psi_2 x_{12}^\infty + \psi_3 x_{13}^\infty - \psi_2 \psi_3 x_{23}$$

(50)

where $\psi_2$ and $\psi_3$ are the volume fractions of the polymers.

When $x_{12}^\infty$ is lower than 0.5 (critical value) the probe liquid is generally characterized as a good solvent for the polymer, while a value higher than 0.5 designates a poor solvent and may lead to phase separation.

Al-Ghamdi et al. [150] investigated systems containing amylopectin – environmentally friendly polymer, and they calculated interaction parameters $x_{12}^\infty$ for alkanes. Values obtained in that system are negative and decrease with temperature. Authors concluded that IGC is a good method for measuring interaction parameters for polymer systems.

In the study [139], IGC method at infinite dilution was applied to determine the thermodynamic interactions of water-soluble DMA and MEMA homopolymers and their diblock copolymer, DMA–MEMA and the Flory–Huggins interaction parameters and the solubility parameters for hydrocarbons and polymers were calculated. The other goal of this study was to demonstrate that the IGC provides a convenient way to evaluate thermodynamic interactions of water-soluble (co)polymers. The values of $x_{12}^\infty$ showed that benzene is a good solvent and toluene is a moderate solvent, but n-alkanes and cycloalkanes are nonsolvents for DMA–MEMA diblock copolymer while all investigated sorbates for both DMA and MEMA homopolymers are nonsolvent in the temperature range of 110–140 °C.

With the growing interest in polymer composition a variety of methods was used to determine material compatibility. The techniques involved in the study of such polymer blends include thermal analysis [differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), thermogravimetric analysis (TGA)], microscopy [scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy (OM)], spectroscopy (FTIR), or other techniques such as NMR, density measurements, melting temperature depression and the measurement of contact angles [76]. Interaction parameter for the components of polymer blends may be also determined with the use of small angle X-ray scattering (SAXS) [151–153], thermal induced phase separation (TIPS) [154] and small angle neutron scattering (SANS) [155–159].

In recent years, the Flory–Huggins interaction parameter was determined using the melting point depression method for crystal-containing polymers by DSC [160]. A single glass transition temperature observed for the blends suggests the miscibility of the components. Measurement of the melting temperature ($T_m$) depression for the blends allowed determination of the Flory–Huggins interaction parameter ($x_{12}^\infty$) of the two polymers in the melt using the Nishi–Wang equation.

3.2. Polymer–polymer interaction parameter

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

If the parameters $x_{12}^\infty$ and $x_{23}^\infty$ are known (from IGC experiment with appropriate component “2” or “3”) the interaction parameter...
$X'_{23}$ may be calculated from equation [161,162]:

$$X'_{23} = \frac{X'_{23}V_g}{V_2} = \frac{1}{\varphi_2\varphi_3} \left( \frac{\ln V_{g,m}}{W_2V_2 + W_3V_3 - \varphi_2 \ln V_{g,2} - \varphi_3 \ln V_{g,3}} \right)$$

(51)

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

$$X'_{23} = \frac{1}{\varphi_2\varphi_3}(X'_{2,1}\varphi_2 + X'_{3,1}\varphi_3 - X'_{1,1m})$$

(52)

Values of Flory–Huggins $X'_{23}$ parameter depend on chemical structure of the solute and it is a common phenomenon [163]. It has been interpreted as arising for preferential interaction with one of two types of components. This phenomenon for polymer blends was described by Fernandez-Sanchez et al. [163].

Faroque and Deshpande [164] were the first ones suggesting the use of IGC for studying polymer blends. They observed probe dependence of polymer–polymer interaction and tried to develop a method to evaluate probe-independent interaction.

Su et al. [165] measured the interaction parameter of PVC and dioctyl phthalate as plasticizer to study their compatibility. Later, this method was also utilized to measure the compatibility of polymer blends. However, many studies showed that the polymer–polymer interaction parameter determined by this depends on the probes used and blend compositions. Hsu and Prausnitz [166] and Su et al. [165] suggested that the compatibility of polymeric components should reflect not only the interaction between the components themselves, i.e. $X'_{23}$, but also the difference in strength of the polymer–probes interactions, i.e. $\Delta X = X'_{2} - X'_{3}$. They called it the $\Delta X$ effect, and a large $\Delta X$ in addition to a high $X'_{23}$ value leads to immiscibility. Su and Patterson [167] suggested that the probe dependency of $X'_{23}$ arises from the difference between $X'_{2,1}$ and $X'_{3,1}$. Accordingly, one must select probes that give $X'_{2,1} = X'_{3,1}$ for studying the blend.

Olabi [162] applied that procedure to poly(vinylchloride) (PVC), poly(e-caprolactone) (PCL), and their blends. A polyblend can be described as microheterogeneous, the size of the different phases and their interpenetration being limited by a host of factors among which are the extent of mixing, compatibility, molecular weight, clustering behavior of each polymer, rheological, and surface and interfacial properties. The variation of $X'_{23}$ with probe can be justified on the basis of the above argument which, in essence, states that the total polymer–probe interactions may not be correctly accounted for by the theory. $X'_{23}$ data obtained from IGC measurements are affected by a considerable error due to the weak contribution of the $X'_{23}$ term in the equation from which it is calculated (see for instance Eqs. (51) and (52)).

Faroque and Deshpande [164] proposed to rearrange Eq. (50) to the following form:

$$\frac{X'_{23}(22) - X'_{13}}{V_1} = \varphi_2 ~ \frac{X'_{23}}{V_2} - \varphi_2 \varphi_3 \frac{X'_{23}}{V_2}$$

(53)

By plotting the left-hand side vs. $\varphi_2((X'_{2,1} - X'_{3,1})/V_1)$ the interaction parameter can be obtained from the intercept. This method was used by Etxeberria et al. [168,169] and Lezcano et al. [170], and straight lines were obtained. Although this method gives reliable $X'_{23}$ values, they are affected by large errors. To reduce the uncertainty in the $X'_{23}$ values, a possible alternative is an approximate selection of the probes to use. However, the slopes deviated from their theoretical values.

In recent papers Huang [149,171] proposed to rearrange Eq. (53) into the following form:

$$\frac{X'_{23}(22)}{V_1} = \varphi_2 \frac{X'_{23}}{V_1} + \varphi_3 \frac{X'_{23}}{V_2} - \varphi_2 \varphi_3 \frac{X'_{23}}{V_2}$$

(54)

A linear plot can be obtained from the left-hand side vs. $(\varphi_2 X'_{2,1} + \varphi_3 X'_{3,1})/V_1$. The polymer–polymer interaction term can be determined from the intercept at $(\varphi_2 X'_{2,1} + \varphi_3 X'_{3,1})/V_1 = 0$. A physical meaning of this procedure is that when $(\varphi_2 X'_{2,1} + \varphi_3 X'_{3,1})/V_1 = 0$ the probe is experiencing a similar environment in the blend as compared to the probe liquid. The disturbance of liquid polymer structure is expected to be the minimum.

Tan and Vancso [172] tried to characterize the non-random partitioning of probes in a mixture by applying KBZ cluster integrals. They derived thermodynamic relationships between the preferential salvation of probes at their infinite dilution in a binary mixture and the correlation structure factor of the mixture, which can be directly determined from IGC experiments. In that paper the non-random partitioning is defined as follows. A molecule, when it is dissolved in a polymer blend, does not probe the average composition in the mixture. It “feels” a local composition of the different components. The local composition depends on the fluctuation of both the particle density and the chemical composition of the blend, as well as on the interactions of the probe with the different components.

Feraz et al. [173] used IGC ($X'_{23}$ 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-co-4-vinyl pyridine) or poly(isobutyl methacrylate-co-4-vinyl pyridine).

SAA/PIBMA was found to be immiscible as confirmed from the observation of two glass transition temperatures and the positive $X'_{23}$ values. SAA/PME, SAA/EM4VP, SAA/EM4VP and SAA/IBM4VP were miscible as evidenced from the negative $X'_{23}$ values and single composition-dependent glass transition temperature.

Benadeghli et al. [174] studied the miscibility behavior of blends of poly(styrene-co-methacrylic acid) (PSMA-12) containing 12% methacrylic acid with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) at five different compositions by IGC.

They proposed to rearrange Eq. (53) using only experimental measured magnitudes, such as specific volumes and specific retention volumes by

$$\frac{1}{V_1} \ln \left( \frac{V_{g,m}}{V_1} \right) = \left[ \frac{1}{V_1} \left( \varphi_2 \ln \left( \frac{V_{g,2}}{V_2} \right) + \varphi_3 \ln \left( \frac{V_{g,3}}{V_3} \right) \right) \right]$$

$$+ \varphi_2 \varphi_3 \frac{X'_{23}}{V_2}$$

(55)

Therefore, a plot of the left-side term as a function of the expression between brackets of the right-side term of Eq. (55) allows us to calculate from the intercept the true $X'_{23}/V_2$.

Authors concluded that $X'_{23}$ values obtained for investigated systems are in good agreement with DSC measurement parameter ($T_g$). The results show that IGC can be considered as a reliable method in order to calculate the true polymer–polymer interaction parameter.

Zhao and Choi [175] used non-random partitioning solutes in binary polyolefin blends to test whether that solutes may cause solute dependence of Flory–Huggins parameter $X'_{23}$ observed in IGC experiments. They concluded that the non-random partitioning behavior of solutes is not the real reason to probe the dependence problem. This is mainly attributed to the improper use of the reference volume in calculations of the solute–stationary phase interaction parameters ($X'_{1,1}$). Authors suggested to use single common reference volume ($V_o$) instead of individual molar volumes of the solutes used in IGC experiments for the calculations of the $X'_{1,1}$ parameter. As the reference volume Zhao and Choi proposed to use molar volume of repeated unit of polymer at the experimental
temperature \([175,176]\):

\[
\chi_1 = \frac{V_0}{V_1} \left( \ln \frac{273.15 W_2 + W_3}{M_2 p_2} \right) - 1 + \frac{V_1}{M_2 p_2} + \frac{V_1}{M_3 p_3} - \frac{B_1}{RT} + \frac{P_1}{p_1^i} \right) \right) 
\]

(56)

Milczewska and Voelkel \([177,178]\) used IGC method to investigate another compositions – polymers filled with modified inorganic materials. Authors expressed the magnitude of interaction between polymer and filler by using Flory–Huggins parameters. They calculated interaction parameter \(\chi_{12}\) by classical way from Eqs. (36) and (38) and polymer–filler interaction equation from Eq. (50). Later \([176,179]\) they used procedures proposed by Farooque and Deshpande, Zhao and Choi, and Huang to calculate values of \(\chi_{12}\) parameters independent from solute type. The results (values of \(\chi_{12}\)) obtained from procedures showed minimizing \(\Delta\chi\) effect. For the system PU-N2 (system containing polymer-urethane filled with carbonate-silicate filler modified with octylsilane and stearic acid) they obtained low, negative values meaning strong interactions between the polymer and N2 filler \([176]\).

3.3. Cohesive energy – Hildebrand and Hansen solubility parameter (HSP)

In condensed phases (liquids, solutions and solid materials) exist strong interactions between molecules resulting in considerable (negative) potential energy of each molecule. This energy is called the molar cohesive energy \((-E) [180]\).

It has been assumed that there are three types of interactions between molecules which describe energetic characterization of liquid state:

(i) dispersive interactions, which arise from fluctuation of the atomic dipoles; this type of interaction is present in all molecules;

(ii) polar interactions: dipole–dipole and dipole-induced dipole interactions;

(iii) specific interactions especially hydrogen bonding interactions.

The molar cohesive energy can be expressed as a sum of two factors:

(i) the molar evaporation energy \(\Delta_f^f U\), required to convert the mole of liquid to its saturated vapor;

(ii) energy, required to separate molecules – energy which is necessary to expand saturated vapor to finite volume in the isothermal conditions \([129]\):

\[
-E = \Delta_f^f U + \int_{V_0}^{V_\infty} \left( \frac{\partial u}{\partial V} \right)_T dV
\]

(57)

Cohesive energy related to a molar volume is called cohesive energy density \(\zeta\):

\[
\zeta = \frac{-E}{V}
\]

(58)

and the square root of cohesive energy density is called solubility parameter \(\delta\). This term proposed by Hildebrand for non-polar systems, used as a measure of intermolecular forces of different solvents is related to the enthalpy of an evaporation \(\Delta H_v\):

\[
\delta = \sqrt{\zeta} = \sqrt{\frac{E_{coh}}{V}} = \sqrt{\left( \frac{\Delta H_v - RT}{V} \right)}
\]

(59)

where \(\delta\) is the solubility parameter, \(E_{coh}\) is the cohesive energy, \(V\) the molar volume of a pure liquid, \(R\) the gas constant and \(T\) the temperature. Solubility parameter expressed by relation (61) is called Hildebrand solubility parameter. Different units of solubility parameter, were presented in literature: \((\text{cal/(cm}^3)\)\(^{1/2}\), \((\text{J/m}^3)\)\(^{1/2}\), \((\text{MPa})\)\(^{1/2}\) \([180]\). The most convenient unit is \((\text{MPa})\)\(^{1/2}\).

The solubility parameter \([\text{Eq. (59)}]\) reflects 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 \([181–183]\):

\[
E = E_d + E_p + E_h
\]

(60)

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.

Division of the energy by a molar volume leads to

\[
\frac{E}{V} = \frac{E_d}{V} + \frac{E_p}{V} + \frac{E_h}{V}
\]

(61)

The total solubility parameter (Hildebrand solubility parameter) also known as corrected solubility parameter \(\delta_1\) is therefore defined as follows:

\[
\delta_1^2 = \delta_d^2 + \delta_p^2 + \delta_h^2
\]

(62)

where \(\delta_d\), \(\delta_p\), and \(\delta_h\) denote dispersive, polar and hydrogen bonding contribution, respectively.

It is also known as three-dimensional solubility parameters or HSP. According to Hansen interpretation of solubility parameter, estimation of interactions between different materials appears to be more precise.

Understanding quantitative expression of interactions between components of different systems seems to be very important for the estimation of the utility of materials for complex applications. One of the potential solutions is the calculation of cohesive energy of materials, or precisely, solubility parameter value, which can be used for the estimation of the magnitude of intermolecular interactions in material. Therefore, solubility parameter and Hansen solubility parameters are physicochemical parameters which enable the estimation of type and interactions’ force, responsible for compatibility between materials. 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 \([130,184–192]\).

There are a number of methods which can be used for the calculation of solubility parameter value. For simple, volatile solvents solubility parameter may be calculated by using the enthalpy of an evaporation data \([193,194]\). However, for more complex systems, e.g. non-volatile polymer materials such methods could not be used. Therefore, it was necessary to elaborate some methods or procedures, enabling estimation of the solubility parameter different materials, in order for their more precise physicochemical characterization \([195–200]\).

Fundamental review on the solubility parameter and its applications was published by Barton \([129]\) and Hansen \([201]\).

Smidsrod and Guillet \([12]\) applied inverse chromatography method for the examination of interactions between solvent and polymer, used as a stationary phase. Proposed method is based on rule, that Flory–Huggins interaction parameter \(\chi_{12}\), calculated from retention data, can be related to solubility parameter by rela-
tation:
\[ \chi^\infty = \left( \frac{V_1}{RT} \right) \left( \delta_1 - \delta_2 \right)^2 \]
(63)
where \( \delta_1 \) and \( \delta_2 \) are the solubility parameter solvent and polymer, respectively and \( V_1 \) is the solvent molar volume.

Guillet and co-workers [202,203] have proposed IGC method for estimating of Flory–Huggins interaction parameter and solubility parameter for polymers by the modification of Eq. (63):
\[ \frac{\delta_1^2}{RT} - \frac{\chi_1^\infty}{V_1} = 2\delta_2 \frac{RT}{V_1} \delta_1 - \left( \frac{\delta_2^2}{RT} \right) \]
(64)

It is a straight line equation. The left-hand side contains the values of Flory–Huggins interaction parameter the test solute (see Eq. (36), solubility parameter of test solute (\( \delta_1 \)) and its molar volume. Plotting the left-hand side of such equation vs. solubility parameter of test solute (\( \delta_1 \)) one obtains the slope (\( a = 2\delta_2/RT \)) enabling the calculation of the solubility parameter of the examined material. This value should be equal to that found from the intercept and positive. However, in practice, it is not always fulfilled. Moreover, the important entropic contribution to Flory–Huggins interaction parameter \( \chi_1^\infty \) is omitted above. The Flory–Huggins interaction parameter can be expressed as
\[ \chi_{12}^\infty = \chi_{11}^\infty + \chi_2^\infty \]
(65)
and taking for \( \chi_2^\infty = 0.2, 0.3 \) or 0.4 [120,204], it is possible to calculate a value of \( \chi_{11}^\infty \). Then Eq. (64) should be rewritten as
\[ \frac{\delta_1^2}{RT} - \frac{\chi_1^\infty}{V_1} = 2\delta_2 \frac{RT}{V_1} \delta_1 - \left( \frac{\delta_2^2}{RT} + \chi_2^\infty \right) \]
(66)
Therefore a plot of left-hand side of this equation vs. \( \delta_1 \) yields \( \delta_2 \) from the slope and the intercept. Such relationship has already been used in several papers discussing the application of IGC. However, \( \chi_{12}^\infty \) values have been used instead of \( \chi_{11}^\infty \) values [205–208] what is theoretically not justified and leads to significant error in \( \delta_2 \) determination.

By introducing the entropic factor into Eqs. (63) and (64) one obtains, accordingly
\[ \chi^\infty = \left( \frac{V_1}{RT} \right) \left( \delta_1 - \delta_2 \right)^2 + \chi_2^\infty \]
(67)
and
\[ \frac{\delta_1^2}{RT} - \frac{\chi_1^\infty}{V_1} = 2\delta_2 \frac{RT}{V_1} \delta_1 - \left( \frac{\delta_2^2}{RT} + \chi_2^\infty \right) \]
(68)
where “I” denotes the consecutive test solute.

In this case, for the estimation of \( \delta_2 \) value from intercept, the value of entropic factor and molar volume should be known.

In case of estimation the molar volume, Zhao and Choi [209] have introduced reference volume, according to Flory–Huggins lattice theory. For polymer–solvent system, where different number of test solvents is used (as above), the reference volume is the smallest among the molar volume in examined system.

It has been stated that contribution of \( \chi_2^\infty /V_1 \) factor to intercept value is about 3%, therefore solubility parameter data \( \delta_2 \) obtained for examined material, calculated from the slope and the intercept can be similar. However, \( \delta_2 \) value, calculated from the slope should be taken as more proper. Moreover, the assumption that \( \chi_2^\infty \) varies between 0.2 and 0.4 is also not always justified [210].

3.3.1. Estimation of the components of solubility parameter

Procedure proposed by Guillet and co-worker [211], has been applied by Price [212] for the estimation of the low-molecular-weight compounds’ solubility parameter – non-polar, long-chain alkanes – hexadecane and squalane, two compounds with polar groups – N-methylpyrrolidone and dibutyl-2-ethylhexamide, and also alkyl phthalates, used as plasticizers – dinonyl and di-n-octyl phthalate.

Price reported that the experimental relation between the left-hand side of Eq. (68) and solubility parameters of test solutes is different from the linear relationship. The significant curvature of left-hand side of Eq. (68) vs. \( \delta_1 \) relation was observed. It was found the downward curvature for alkanes and upward curvature for other compounds. Therefore, the tendency for alkanes leads to underestimation of \( \delta_2 \) while tendency for polar compounds may cause the overestimation value of \( \delta_2 \).

According to three-component solubility parameter theory of Hansen, Price assumed that different types of intermolecular interactions between examined material and test solute will influence the value of solubility parameter. Price proposed to estimate the solubility parameter as sum of two terms:
\[ \delta_2^2 = \delta_d^2 + \delta_h^2 \]
(69)
resulting form dispersive and polar intermolecular interactions 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 [213]. They have extended a group of test solutes used in IGC experiments, by the addition of solutes, representing hydrogen bonding interactions.

Values of each component of the total solubility parameter are calculated from the slope of straight line by using the following relationships:
\[ \delta_d = \frac{m_{n-alkanes}RT}{2} \]
(70a)
\[ \delta_p = \frac{(m_1 - m_{n-alkanes})RT}{2} \]
(70b)
\[ \delta_h = \frac{(m_2 - m_{n-alkanes})RT}{2} \]
(70c)
where \( m_{n-alkanes} \) is the value of the slope for n-alkanes, \( m_1 \) the value of the slope for aromatic hydrocarbons, ketones, 1-nitropropane, acetonitrile, 1,2-dichloroethane and \( m_2 \) is the value of the slope for alcohols, 1,2-dioxane and pyridine.

Components of solubility parameter can be calculated by the modification of Eq. (68) and Hansen concept of solubility parameter presented by relation (62):
\[ \chi_{12}^\infty = \left( \frac{V_1}{RT} \right) \left[ \left( \delta_{1,d} - \delta_{2,d} \right)^2 + \left( \delta_{1,p} - \delta_{2,p} \right)^2 + \left( \delta_{1,h} - \delta_{2,h} \right)^2 \right] + \chi_2^\infty \]
(71)
Above equation can be modified as [214]:
\[ \left( \frac{\delta_1^2}{RT} - \frac{\chi_{12}^\infty}{V_1} \right) = \left( \frac{2\delta_{2,d}^2}{RT} \right) \delta_{1,d} + \left( \frac{2\delta_{2,p}^2}{RT} \delta_{1,p} + \left( \frac{2\delta_{2,h}^2}{RT} \right) \delta_{1,h} \right) \]
(72)
where \( \delta_{1,d}, \delta_{1,p}, \delta_{1,h} \) are the dispersive, polar and hydrogen bonding solubility parameter of the test solvents. By using such equation components of solubility parameter \( \delta_{2,d}, \delta_{2,p}, \delta_{2,h} \) for research material can be obtained by multiple regression of Eq. (72). The total solubility parameter \( \delta_2 \) is then calculated from Eq. (62).

Other procedure, which allows to calculate the HSP data can be a model proposed by Lindvig et al. [215], combining experimental...
data of Flory–Huggins interaction parameter $\chi_{12}^e$ with components of solubility parameter for material 

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

(73)

where $\alpha, V_1, R, T$ are a corrective coefficient, molar volume of the test solute, gas constant and temperature of measurement, respectively. In this relation known, 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 the estimation of Flory–Huggins interaction parameter. For the purpose of IGC, experimentally obtained $\chi_{12}^e$ values can be used for the determination of the HSP for examined material by applying the above relation (Eq. (73)) [216].

Experimentally obtained values of $\chi_{12}^e$ parameter and solubility parameters ($\delta_{1,d}, \delta_{1,p}, \delta_{1,h}$) data of test solutes can be used for the calculation of values of the solubility parameter’s components. According to Flory–Huggins theory a critical value of interaction parameter can be estimated by using the following relationship:

$$X = X_{crit}$$

The components of the solubility parameter of the examined material are then calculated as the average of the respective values for all selected solutes. Therefore, all data for “disqualified” test solutes are omitted and not taken into consideration.

This Flory–Huggins assumption has been applied by Choi et al. [217] for the estimation of Hansen solubility parameters for selected group of surfactants.

3.3. Guillet procedure

In procedure, proposed by Guillet solubility parameter for material is calculated from the slope and the intercept of a straight line, according to Eq. (68). Therefore, solubility parameters’ data for the series of test solutes should be known. These data can be taken from literature, but the variation of the data in different sources is observed. Most often these differences are small, but in several cases the considerable variability is found. The same observation is valid also for Hansen solubility parameters. As a consequence the calculation of components of the solubility parameter (HSP) for material can be burdened with significant error.

During the determination of solubility parameter, especially in the 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 the 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 definite type of intermolecular interaction should be taken into consideration.

The proper selection of test solutes representing polar or hydrogen bonding interactions seems to be a crucial point of procedure proposed by Price and later by Voelkel and Janas. The ability of test solutes to different types of intermolecular interactions (expressed, e.g. by the HSP values) might be used as a criterion for their classification. It should be noted that presented in literature criteria of test solute selection are not always clear especially for solutes representing polar or hydrogen bonding type of interaction. Besides n-alkanes representative for dispersive interactions other potential test solutes exhibit most often the ability to different types of intermolecular interactions. The test solute might be classified to the group representing given type of interaction by using the following parameters: (i) $\delta_p/\delta_h > 1$ indicates the test solute representing ability to polar interactions; (ii) $\delta_h/\delta_p > 1$ represents test solute, classified to group, representing hydrogen bonding interactions. The high value of $\delta_p/\delta_h$ and $\delta_h/\delta_p$ means higher ability to polar and to hydrogen bonding interactions, respectively. However, even such defined criterion might be misleading.

Tables 1 and 2 contain values of polar and hydrogen bonding components of solubility parameter for selected test solutes taken from literature. Both Data 1 and Data 2 have been taken from Ref. [129] (Data 1 from Table 2, p. 94, while Data 2 from Table 5, p. 153).

It may cause the significant error while moving 1,2-dichloroethane (Table 1) and calculated value of Chloroform 13.7 3.1 6.3 5.7 0.46 1.84
1,4-Dioxane 10.1 1.8 7 7.4 0.69 4.11
1-Butanol 10.0 5.7 15.4 15.8 1.54 2.77
1-Propanol 10.5 6.8 17.7 17.4 1.68 2.56
Ethanol 11.2 8.8 20 19.4 1.78 2.20
2-Butanone 9.5 9 9.5 5.1 1.0 1.76
Acetonitrile 11.1 18 19.6 6.1 0.57 1.23

Table 2
An example of polar and hydrogen bonding solubility parameter values and δp/δh ratio for different test solutes (from Ref. [128]).

<table>
<thead>
<tr>
<th>Test solute</th>
<th>δp (MPa)1/2</th>
<th>δh (MPa)1/2</th>
<th>δp/δh</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data 1</td>
<td>Data 2</td>
<td>Data 1</td>
<td>Data 2</td>
</tr>
<tr>
<td>Ethanol</td>
<td>11.2</td>
<td>8.8</td>
<td>20</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>10.5</td>
<td>6.8</td>
<td>17.7</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>10.0</td>
<td>5.7</td>
<td>15.4</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>10.1</td>
<td>1.8</td>
<td>7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>13.7</td>
<td>3.1</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Considerable differences between Data 1 and Data 2 for one, selected test solute are evident. Therefore, estimated values of δp/δh and/or δp/δh ratios also differ. In extreme case it can lead to incorrect classification of given test solute. For example, taking 1,2-dichloroethane (Table 1) and calculated value of δp/δh ratio, according to Data 1, one can find that this test solute characterizes little share in polar interactions. However, the value of δp/δh ratio calculated according to Data 2 shows that this test solute should be classified for group of solutes which are capable, in higher degree, of polar interactions. Therefore, one should remember that selection of values of polar and/or hydrogen bonding solubility parameter component, will significantly influence the results of test solute classification procedure.

3.4. Solubility parameter for solids

The above discussion concerns the determination of solubility parameter value for material being liquid or quasi-liquid at the temperature of IGC experiment. However, engineers often require the data for “room” temperature or e.g. 25 °C. Extrapolation of the values of δ2 or HSP determined above Tg is possible, but is a dangerous operation. It may cause the significant error while moving from the liquid material to solid one. Therefore, some efforts have been done to work out the appropriate methods and procedures. The importance of measurement temperature should be stressed as only at elevated temperature solids with high Tc can be studied with respect to bulk absorption. Determination of HSP for solids is much more complicated. 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 solution Martin’s model. Another possibility is the calculation of solubility parameter from group contribution method [8]. Determination of the magnitude of the interactions between solid material and test solute could be carried out visually and/or by absorption measurements. The compatibility region solid material/test solute can be considered as a sphere of radius R with the centre located at the point with coordinates: dispersive (δd), polar (δp) and hydrogen bonding (δh) components. These coordinates are defined as the three-dimensional solubility parameters of the examined solid material [219].

Determination of 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 value of adsorption energy (EΔ) determined from temperature dependence of specific retention volume:

\[
\ln V_g = \left( \frac{E_A}{RT} \right) + \text{const} \tag{76}
\]

for the respective test solutes [220–222].

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

\[
-\Delta E_A = V_i (\delta_{p,i}^2 + \delta_{h,i}^2) + V_j (\delta_{p,j}^2 + \delta_{h,j}^2) \tag{77}
\]

(ΔEΔ) for series of test solutes of (δp) and Vj values. Hansen solubility parameters (δp, δh, δd) of the solid stationary phase are calculated (β values) by multilinear regression using the set of N equations for N test solutes:

\[
-\Delta E_A = \beta_i V_i \delta_{p,i} \delta_{d,i} + \beta_p V_i \delta_{p,i} + \beta_h V_i \delta_{h,i} + \epsilon_1

-\Delta E_h = \beta_i V_j \delta_{p,i} \delta_{d,j} + \beta_h V_j \delta_{h,j} + \epsilon_n

-\Delta E_d = \beta_i V_j \delta_{p,i} \delta_{d,j} + \beta_p V_j \delta_{p,j} + \epsilon_h \tag{78}
\]

4. Summary

IGC is still a developing technique due to its theoretical potential and wide application. To date, IGC could be called milestone in testing physicochemical properties of liquid and solid materials. IGC offers its applicability where it is difficult and even impossible to characterize the surface of some forms of solids (powders and grains) by means of other popular techniques as wetting method or FTIR. Actually, the solids and liquids in every form can be easily studied by means of IGC. This method was most often used to study the activity of the surface of solids by the estimation of Kp, Kf parameters leading further to the deduction of adhesion ability. Both surface and bulk properties and the polymeric systems were characterized by γD parameter and/or solubility parameter(s). Nowadays, new applications of this method are presented every year. Let us mention here the examination of the surface character of the series of conducting polymers [223–227]. Data obtained from IGC measurements were also used in the prediction of mechanical properties of some clay/polymer nanocomposites [228,229]. Besides some disadvantages (like imprecise physicochemical data) IGC will be still developed and used due to its huge practical meaning and simplicity. Authors do hope that this review will help all IGC users and encourage all young, potential newcomers to creative exploitation of this fascinating method.

References
