



# Application of inverse gas chromatography to the examination of annealing processes of semi-synthetic base oils<sup>☆</sup>

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## Abstract

The Flory–Huggins  $\chi_{1,2}^{\infty}$  parameter and solubility parameter  $\delta_2$  determined by means of inverse gas chromatography (IGC) were successfully used in the physicochemical characterisation of oxidation products of mineral oil–poly- $\alpha$ -olefin mixtures. Application of IGC parameters allows one to examine the changes occurring during three different oxidation procedures: classical oxidation in a stainless steel reactor, in a GC column and separate oxidation of the mixture's components. Changes in  $\chi_{1,2}^{\infty}$  values reflect the changing affinity of mixtures to different types (dispersive, polar, hydrogen bonding) of intermolecular interactions and their potential miscibility and solubility.

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## 1. Introduction

Base oils used for the manufacturing of final petrochemical products may be separated into two groups. The first group contains the so-called conventional base oils with viscosity index values no higher than 105. All the other base oils are classified in the second group. These latter oils are often called non-conventional oils. Conventional oils are obtained in the classical three-step process from vacuum distillate: selective raffination, deparaffination and hydrogenation. The first two steps are most often

carried out by solvent procedures but the catalytic processes come into importance. Final conventional oils may be further divided into two subgroups. Oils belonging to the first subgroup contain components having paraffinic character while those from the second subgroup are mainly compounds of naphthenic structure. Repartition is based on viscosity index and pour point values [1–3]. Base naphthenic oils have lower viscosity index and pour point values than base paraffinic oils. Lubrication products are most often produced with the use of the following base oils: solvent neutral oil (SNO), naphthenic pale oil (NPO), bright stocks (BS), cylinder oil (CO) speciality oils (Table 1).

(1) Solvent neutral oils: Oils from this class are produced by vacuum distillation of paraffinic fractions with additional raffination of distillates (increasing of the viscosity index value). Raffinates are

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Table 1  
Comparison of physicochemical parameters of mineral base oils from different stages of crude oil processing

	SNO-100	SNO-320	NPO-100	BS-150	Cylinder oil
API gravity	32.4	29.3	28.8	26.5	20.4
Pour point (°F)	0	10	–20	10	20
Viscosity index	95	95	95	95	70
Sulfur (% w/w)	0.17	0.31	0.02	0.52	0.70
Aromatics (% w/w)	16.1	25.4	24	32.5	36.6

further deparaffinated which results in the decrease of pour point temperature. The last step—hydrogenation—increases the stability of the final product.

(2) Naphthenic pale oils: These oils are produced from vacuum distillates of naphthenic character in the raffination process. Due to the low content of paraffinic hydrocarbons, a deparaffination process is not required.

(3) Bright stocks and cylinder oils: These mineral oils are obtained from vacuum residue. In their production, raffination and deparaffination steps are preceded by a deasphaltisation process. It is carried out most often with the use of *n*-propane and leads to deasphaltisate.

Differences in the chemical composition of vacuum distillates cause the differentiation of physicochemical properties of the final base oils.

Non-conventional oils are produced in the following chemical processes: polymerisation, polycondensation, chemical synthesis or catalytic hydrocracking. Due to this they have defined and designed composition and physicochemical properties. These oils are also called base synthetic oils. Physicochemical properties of mineral base oil and synthetic oils are, of course different [4].

Mixtures of mineral and synthetic oils in ratios not higher than 7:3 are called base semi-synthetic oils.

The variety of chemical processes being involved in the preparation of the base oil leads to the products from different groups having significantly different properties, and further, their fields of application. The most important physicochemical characteristics of the base oil as the raw material in the production of final oil (engine, hydraulic, gear, transformer, etc.) as well as grease are: viscosity index, kinematic viscosity, volatility at 250 °C (NOACK, % loss), density, sulfur content, content of aromatic hydrocarbons, resistance to oxidation. The

miscibility and solubility of synthetic, semisynthetic and mineral oils, is also important.

The differences in the chemical composition of the examined materials cause the different behaviours during the oxidation process. In this work two parameters determined by means of inverse gas chromatography (IGC) have been used in the characterisation of petroleum products before and after the annealing process.

We have used the Flory–Huggins interaction parameter:

$$\chi_{1,2}^{\infty} = \ln\left(\frac{273.15R}{p_1^0 V_g M_1}\right) - \frac{p_1^0}{RT} \cdot (B_{11} - V_1^0) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^0}{V_2^0}\right) \quad (1)$$

where 1 denotes the solute and 2 denotes the examined material (oil, ester, poly- $\alpha$ -olefin),  $M_1$  is the molecular mass of the solute,  $p_1^0$  is the saturated vapour pressure of the solute,  $B_{11}$  is the second virial coefficient of the solute,  $V_i^0$  is the molar volume,  $\rho_i$  is the density, and  $R$  is the gas constant.

Having the set of  $\chi_{(1,2)i}^{\infty}$  and  $\delta_{1i}$  values for the respective test solutes one may calculate the slope of linear relationship: left-hand-side (LHS<sub>*i*</sub> versus  $\delta_{1i}$ ) [5]:

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(1,2)i}^{\infty}}{V_1^0} = \frac{2\delta_2}{RT} \delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^{\infty}}{V_1^0}\right) \quad (2)$$

The slope is proportional to the solubility parameter of the examined material, i.e.,  $\delta_2$ .

Similar values of interaction parameters for different oils and test solutes (describing the same type of intermolecular interactions) may indicate the mutual miscibility of the compared oils. Differences in values of the solubility parameter, lower then approx.

2 (MJ/m<sup>3</sup>) indicate mutual solubility of oils. These parameters may be used in the description of the changes during the oxidation process of the oils. Resistance to oxidation is the crucial parameter characterising oil quality. According to IP 48 [6] resistance to oxidation is determined by the changes in: increase of kinematic viscosity at 40 °C and the increase in the coke content (% w/w) produced during oxidation process. These parameters do not always satisfactorily describe the resistance to oxidation of the examined materials. Therefore, the new control procedures have been elaborated where two additional parameters (volatility of the oil and infrared absorbance: C–O bond) are used.

The examination of both IGC parameters will help to indicate which groups of hydrocarbons are present in the oils and their ratio of oxidation. The examined base oils were produced from the distillates with different ranges of boiling points (mineral oils) and the products of different chemical processes (polymerisation and catalytic hydrocracking).

The aim of this paper was the examination of the oxidation processes of selected mineral oil–poly- $\alpha$ -olefin mixtures with the use of inverse gas chromatographic parameters.

## 2. Experimental

### 2.1. Materials

We have examined mixtures (7:3, w/w) of mineral and synthetic oils. Mineral oils were produced from vacuum distillates having different ranges of boiling points (200SN and 400SN) and bright stock oil from the vacuum residue (HBS). Poly- $\alpha$ -olefins (PAO-6, PAO-8 and PAO-40) are characterised by similar viscosity index values as the respective mineral oils. The mixtures 200SN/PAO-6, 400SN/PAO-8 and HBS/PAO-40 may be considered as semi-synthetic base oils.

We have examined the initial 7:3 mixtures of mineral oils and poly- $\alpha$ -olefins as well as “the oxidised oils”. The influence of the oxidation on the properties of the mixtures was examined with the use of the following products:

(1) (Base oil + poly- $\alpha$ -olefin) mixture oxidised in the traditional way (in stainless steel reactor).

(2) (Base oil + poly- $\alpha$ -olefin) mixture oxidised in the chromatographic column; base oil and poly- $\alpha$ -olefin oxidised separately as in (1); products of the oxidation were mixed in the ratio 7:3.

(3) The annealing of the oils was carried out under the following conditions: temperature, 200 °C; oxidation time, 24 h; oxidising agent, air (0.9 l/min). These oxidation conditions were used during both classical and chromatographic annealing of the oil.

### 2.2. IGC experiments

All examined materials were coated (20%, w/w) on chromatographic support Chromosorb P DMCS (80–100 mesh) (Johns-Manville, USA). Other IGC conditions were as follows: Hewlett-Packard 5730A gas chromatograph with a flame ionization detection (FID) system; stainless steel column of 2 m  $\times$  2 mm I.D.; column temperature: 80, 100, 120, 140 and 160 °C; sampler temperature: 200 °C; detector temperature: 250 °C; carrier gas: argon at a flow-rate of 20 ml/min; conditioning at 160 °C (ASTM D-5480), conditioning time: 12 h; injection volume: 0.1  $\mu$ l.

The following compounds were used as the test solutes: *n*-alkanes (C<sub>6</sub>–C<sub>11</sub>) (PolyScience, USA), aromatic hydrocarbons (benzene, toluene, *m*-xylene, *n*-propylbenzene) (Riedel-de Haen, Germany), *n*-alkanols (methanol–*n*-hexanol-1) and *tert*-butanol (Unichem, UK), acetone (POCh, Poland), butanone-2 (Fluka, Switzerland), nitromethane (POCh), chloroform, methylene chloride, 1,2-dichloroethane (Fluka), 1,4-dioxane, oxolane, cyclohexane (POCh) and pyridine (Fluka).

Saturated vapour pressures were calculated from Antoine's equation using data published in Refs. [7–9]. Values of second virial coefficient  $B_{11}$  were calculated according to procedures presented in Refs. [10,11].

IGC parameters  $\chi_{1,2}^{\infty}$  and  $\delta_2$  were calculated from Eqs. (1) and (2), respectively. The method way of calculation for one or both parameters was used earlier in several works [5,12–15].

### 2.3. Results and discussion

Physicochemical characteristics of examined mixtures are presented in Table 2. Physicochemical parameters for the 200SN/PAO-6 and 400SN/PAO-8

Table 2  
Physicochemical characteristics of examined mineral oil–poly- $\alpha$ -olefin mixtures

Parameter	Method	200SN*/PAO-6	400SN*/PAO-8	HBS**/PAO-40
Viscosity at 40 °C (cSt)	ASTM D-445	37.33±0.02	65.08±0.04	564.82±0.31
Viscosity at 100 °C (cSt)	ASTM D-445	6.19±0.01	8.74±0.01	37.63±0.02
Viscosity index	ASTM D-2270	113	106	104
Density at 20 °C (g/cm <sup>3</sup> )	ASTM D-4052	0.8567±0.0001	0.8661±0.0001	0.8920±0.0001
Refractive index at 20 °C	ASTM D-1218	1.4675±0.0001	1.4720±0.0001	1.4875±0.0001
Average molecular mass	ASTM D-2503	446±9	525±10	899±18
Coke content (% w/w)	EN/ISO 10370	0.02±0.005	0.04±0.005	0.92±0.03
Group composition (% w/w)	ASTM D-4124			
Saturates		83.81	80.41	47.50
Naphthenic aromatics		13.89	15.78	39.64
Polar aromatics		2.30	3.81	12.86

\*—Mineral base oil.

\*\*—Bright stock oil.

mixtures are similar while those for HBS/PAO-40 are significantly different. The components of this last mixture, both mineral oil and PAO consist of long-chain hydrocarbons. Moreover, the HBS/PAO-40 mixture contains a higher amount of polar components—naphthenic aromatics and polar aromatics. Differences in the chemical nature and composition are exhibited in the Flory–Huggins parameter values  $\chi_{1,2}^{\infty}$  presented in Table 3. Values of  $\chi_{1,2}^{\infty}$  for examined mixtures and test solutes representing the same type of intermolecular interactions

decrease in the following order: 200SN/PAO-6→400SN/PAO-8→HBS/PAO-40. These changes are especially significant when alcohols, i.e., test solutes representing hydrogen bonding ability were used. The same direction of changes in  $\chi_{1,2}^{\infty}$  values is also observed for the other group of test solutes representing dispersive and polar interaction abilities.

Oxidising of examined mixtures in a classical way significantly changes their properties. Values of  $\chi_{1,2}^{\infty}$  for 400SN/PAO-8 and HBS/PAO-40 increased for the applied test solutes (Table 4). It means that the

Table 3  
Values of Flory–Huggins parameter ( $\chi_{1,2}^{\infty}$ ) at 120 °C for different examined mixture–test solute pairs

Test solute	Examined mixture		
	200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
<i>n</i> -Hexane	−0.8053	−1.0087	−1.5753
<i>n</i> -Heptane	−0.9230	−1.0978	−1.6651
<i>n</i> -Octane	−0.9283	−1.1147	−1.6468
<i>n</i> -Decane	−0.9704	−1.1424	−1.6543
Benzene	−0.7584	−0.9441	−1.5651
Toluene	−0.7886	−0.9899	−1.5882
<i>m</i> -Xylene	−0.8670	−1.0148	−1.6243
Methylene chloride	−0.6980	−0.7381	−1.4579
Chloroform	−0.7191	−0.9179	−1.5821
1,2-Dichloroethane	−0.3379	−0.5259	−1.1704
Methanol	0.6900	0.1637	−0.6600
Ethanol	0.3905	0.0663	−0.6700
Propanol-1	0.1996	−0.0747	−0.6956
<i>tert.</i> -Butanol	−0.1188	−0.4421	−0.9090

Table 4  
Values of Flory–Huggins parameter ( $\chi_{1,2}^\infty$ ) at 120 °C for examined oxidised mixtures oxidised in a classical way

Test solute	Examined mixture		
	200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
<i>n</i> -Hexane	−0.9450	−0.7873	−1.2313
<i>n</i> -Heptane	−1.0064	−0.8407	−1.0805
<i>n</i> -Octane	−1.0774	−0.8460	−1.0261
<i>n</i> -Decane	−1.1271	−0.7697	−1.0072
Benzene	−0.9201	−0.7198	−1.1596
Toluene	−0.9850	−0.7157	−1.1342
<i>m</i> -Xylene	−1.0282	−0.7013	−1.0403
Methylene chloride	−0.7229	−0.6408	−1.0420
Chloroform	−0.9014	−0.7145	−1.0767
1,2-Dichloroethane	−0.5026	−0.3087	−0.7760
Methanol	0.5518	0.6404	0.3260
Ethanol	0.4646	0.4751	−0.1968
Propanol-1	0.3584	0.4610	−0.1822
<i>tert.</i> -Butanol	−0.1440	−0.0892	−0.4287

miscibility of test solutes and these two mixtures decreased after oxidation due to the presence of products of oxidation. Different changes may be observed for the 200SN/PAO-6 mixture.  $\chi_{1,2}^\infty$  values for test solutes representing dispersive and polar interaction abilities decreased indicating increasing ability of the examined mixture to respective interactions.  $\chi_{1,2}^\infty$  values for *n*-alkanols increased. All these changes are caused by changes in the chemical composition of mixtures (Table 5). Increase of the content of polar fraction corresponding to polar aromatics is the result of the thermal degradation and oxidation of naphthenic aromatics and the presence of products of oxidation and thermal degradation of saturates.

Oxidation of examined mixtures in the chromatographic column caused significant and large changes in  $\chi_{1,2}^\infty$  values for all test solutes (Table 6). Values of  $\chi_{1,2}^\infty$  generally increased indicating decrease of mis-

cibility of test solutes and examined mineral oil–poly- $\alpha$ -olefin mixtures. Most significant changes were found for *n*-alkanols.

Comparison of changes in values of  $\chi_{1,2}^\infty$  after oxidation in the classical way and in the chromatographic column is presented in Fig. 1. The magnitude of  $\chi_{1,2}^\infty$  changes was much higher when probes were oxidised in the gas chromatograph. Oxidation in the classical way proceeds in the bulk of the probe while in the chromatographic column it occurs in the thin layer of the mixture coated onto the chromatographic support. In the second case oxidation is much deeper than in the classical way. However, direction of changes in values of  $\chi_{1,2}^\infty$  is the same in both processes.

Separate oxidation of components of examined mineral oil–poly- $\alpha$ -olefin mixtures lead to similar results (Table 7). Values of  $\chi_{1,2}^\infty$  are different than in the two previous cases but the direction of changes is

Table 5  
Content of different groups of hydrocarbons and coke content in examined mixtures after their oxidation in a classical way

Parameter	Method	Mixture		
		200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
Group composition (% w/w)	ASTM D-4124			
Saturates		78.89	69.87	44.05
Naphtheno aromatics		9.71	15.92	29.11
Polar aromatics		11.40	14.21	26.84
Coke content (% w/w)	EN/ISO 10370	0.26±0.02	0.45±0.02	2.23±0.07

Table 6

Values of Flory–Huggins parameter ( $\chi_{1,2}^\infty$ ) at 120 °C for examined oxidised mixtures (oxidised by chromatographic method)

Test solute	Mixture		
	200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
<i>n</i> -Hexane	−0.2964	0.1310	−0.3594
<i>n</i> -Heptane	−0.0268	0.0614	−0.4284
<i>n</i> -Octane	0.2031	−0.0287	−0.3762
<i>n</i> -Decane	0.5055	0.1458	−0.3373
Benzene	−0.2898	−0.3960	−0.5228
Toluene	−0.0727	−0.3530	−0.5383
<i>m</i> -Xylene	0.0604	−0.2772	−0.5387
Methylene chloride	−0.6768	−0.4429	−0.5173
Chloroform	−0.5857	−0.4857	−0.5930
1,2-Dichloroethane	−0.1709	−0.1612	−0.2641
Methanol	0.3574	0.4848	0.6956
Ethanol	0.0919	0.2895	0.4722
Propanol-1	0.1428	0.2320	0.3741
<i>tert.</i> -Butanol	−0.2540	−0.1318	−0.0843

generally the same. Oxidation process always caused significant changes in chemical composition (Tables 2, 5 and 8) of the mixture what was reflected by changing values of  $\chi_{1,2}^\infty$ .

Discussion of properties of the examined mixture with the use of the  $\chi_{1,2}^\infty$  parameter is somewhat difficult as this parameter reflects the interactions between the material and test solute. We may compare different mixtures bearing in mind specific properties of the test solute. The value of  $\chi_{1,2}^\infty$  exhibits the magnitude of interactions for a given material–test solute pair. Much more convenient is the comparison of values of solubility parameter  $\delta_2$ .

Values of  $\delta_2$  for examined mixtures are given in Table 9. Differences in  $\delta_2$  values are significant and may indicate limited mutual solubility of HBS/PAO-40 with the other two mixtures.

Oxidation in the chromatographic column caused a large change (increase) in  $\delta_2$  for the 200SN/PAO-6 mixture (Table 10). Separate oxidation of mineral 200SN oil and PAO-6 lead to small increase of  $\delta_2$  values. However, oxidation in the classical way caused a decrease in solubility parameter for the above mixture. Other changes were found for the 400SN/PAO-8 mixture. Oxidising in the chromatographic column caused a small increase in  $\delta_2$  while

Table 7

Values of Flory–Huggins parameter ( $\chi_{1,2}^\infty$ ) at 120 °C for mixtures of oxidised components (each component oxidised separately)

Test solute	Mixture		
	200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
<i>n</i> -Hexane	−1.1845	−0.7082	−0.7311
<i>n</i> -Heptane	−1.2056	−0.7901	−0.8118
<i>n</i> -Octane	−1.1376	−0.7266	−0.8413
<i>n</i> -Decane	−1.0761	−0.6944	−0.7535
Benzene	−1.1176	−0.6892	−0.6960
Toluene	−1.0855	−0.6831	−0.7726
<i>m</i> -Xylene	−1.0446	−0.6864	−0.7997
Methylene chloride	−0.9388	−0.6833	−0.5618
Chloroform	−1.1619	−0.8009	−0.7485
1,2-Dichloroethane	−0.7917	−0.3808	−0.3895
Methanol	0.4974	0.6377	0.6477
Ethanol	0.0003	0.2625	0.4786
Propanol-1	−0.0288	0.3148	0.3824
<i>tert.</i> -Butanol	−0.5652	−0.2299	−0.0956

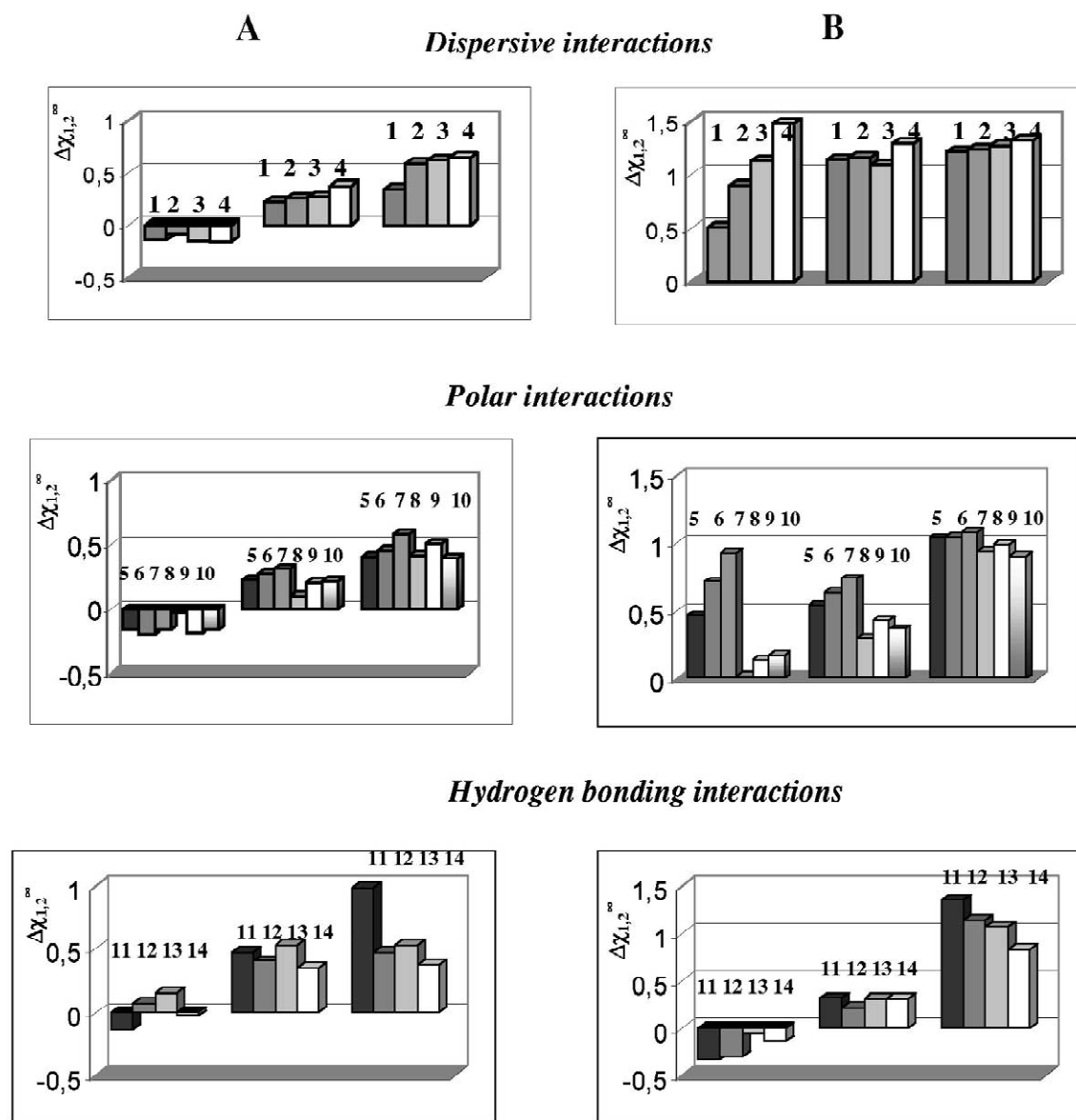


Fig. 1. Changes in values of Flory–Huggins parameter ( $\Delta\chi_{1,2}^{\infty}$  at 120 °C) caused by annealing of examined mixtures in different ways: (A) oxidising in classical way, (B) oxidising in chromatographic column; 1=*n*-hexane, 2=*n*-heptane, 3=*n*-octane, 4=*n*-decane, 5=benzene, 6=toluene, 7=methylene chloride, 9=chloroform, 10=1,2-dichloroethane, 11=methanol, 12=ethanol, 13=propanol-1, 14=*tert.*-butanol.

oxidation by the two other methods resulted in products having lower solubility parameter values in comparison to the initial mixture. Products of HBS/PAO-40 oxidation were always characterised by significantly lower values of solubility parameter. It is in agreement with earlier observations of changes of the  $\chi_{1,2}^{\infty}$  parameter.

#### 2.4. Conclusions

Parameters determined by IGC may be successfully used in the characterisation of mixtures of mineral and synthetic oils. Significant differences were observed between values of Flory–Huggins interaction parameter  $\chi_{1,2}^{\infty}$  found for 200SN/PAO-6, 400SN/

Table 8  
Group composition and coke content after mixing of oxidised mineral oils and PAOs

Parameter	Method	Mixture		
		200SN/PAO-6	400SN/PAO-8	HBS/PAO-40
Group composition (% w/w)	ASTM D-4124			
Saturates		59.95	55.13	34.75
Naphthenic aromatics		12.10	11.94	20.01
Polar aromatics		27.95	32.93	45.24
Coke content (% w/w)	EN/ISO 10370	2.14±0.06	2.24±0.06	2.89±0.08

Table 9  
Values of solubility parameter  $\delta_2$  for examined mineral oil–poly- $\alpha$ -olefin mixtures [(MJ/m<sup>3</sup>)<sup>1/2</sup>]

Mixture	Temperature (°C)				
	80	100	120	140	160
200SN/PAO-6	16.33±0.14	16.19±0.10	16.20±0.06	15.94±0.07	15.76±0.05
400SN/PAO-8	17.23±0.18	17.14±0.13	16.64±0.09	17.07±0.07	17.46±0.06
HBS/PAO-40	17.70±0.15	18.26±0.14	18.51±0.11	18.89±0.16	19.61±0.11

Table 10  
Values of solubility parameter  $\delta_2$  [(MJ/m<sup>3</sup>)<sup>1/2</sup>] for examined mineral oil–poly- $\alpha$ -olefin mixtures after oxidation in different ways

Mixture	Method of oxidation	Temperature (°C)				
		80	100	120	140	160
200SN/PAO-6	Classical	15.54±0.09	15.59±0.07	16.03±0.07	16.43±0.07	16.65±0.17
200SN/PAO-6	Chromatographic	17.97±0.06	18.04±0.06	18.01±0.06	18.37±0.07	18.58±0.08
200SN/PAO-6	Each component separately	16.46±0.12	16.59±0.16	16.63±0.07	16.38±0.56	17.67±0.09
400SN/PAO-8	Classical	15.45±0.10	15.67±0.08	16.04±0.07	16.49±0.07	16.20±0.05
400SN/PAO-8	Chromatographic	17.72±0.03	17.43±0.04	17.41±0.05	17.71±0.05	18.25±0.07
400SN/PAO-8	Each component separately	16.09±0.16	16.10±0.08	16.48±0.06	16.77±0.07	16.10±0.05
HBS/PAO-40	Classical	16.45±0.11	16.92±0.08	17.00±0.07	17.18±0.11	17.00±0.07
HBS/PAO-40	Chromatographic	16.43±0.06	16.50±0.04	16.74±0.06	17.10±0.05	17.15±0.06
HBS/PAO-40	Each component separately	15.86±0.07	15.12±0.09	16.21±0.09	16.61±0.08	17.11±0.07

PAO-8 and HBS/PAO-40 mixtures. Values of  $\chi_{1,2}^\infty$  (the same test solutes) decrease in the order: 200SN/PAO-6→400SN/PAO-8→HBS/PAO-40. It means that the last mixture exhibits the highest activity in interactions with test solutes.

Annealing of the base oils most often caused the increase in the values of  $\chi_{1,2}^\infty$  indicating the decrease of the miscibility of the oil and test solute (Fig. 2). The decrease in  $\chi_{1,2}^\infty$  values was observed only for the 200SN/PAO-4 mixture. The method of the oxidation of all mixtures significantly affected the

range of the changes in values of Flory–Huggins interaction parameter. The highest changes were found when oils were oxidised in the chromatographic column. This is the result of the deep oxidation in the thin layer of the oil. It means that this procedure may be used in the examination of the thermal stability of different oils in a much shorter time than the classical way. Changes in the values of  $\chi_{1,2}^\infty$  and  $\delta_2$  parameters after oxidation in the chromatographic column may be also caused by the changes in the density and average molecular mass



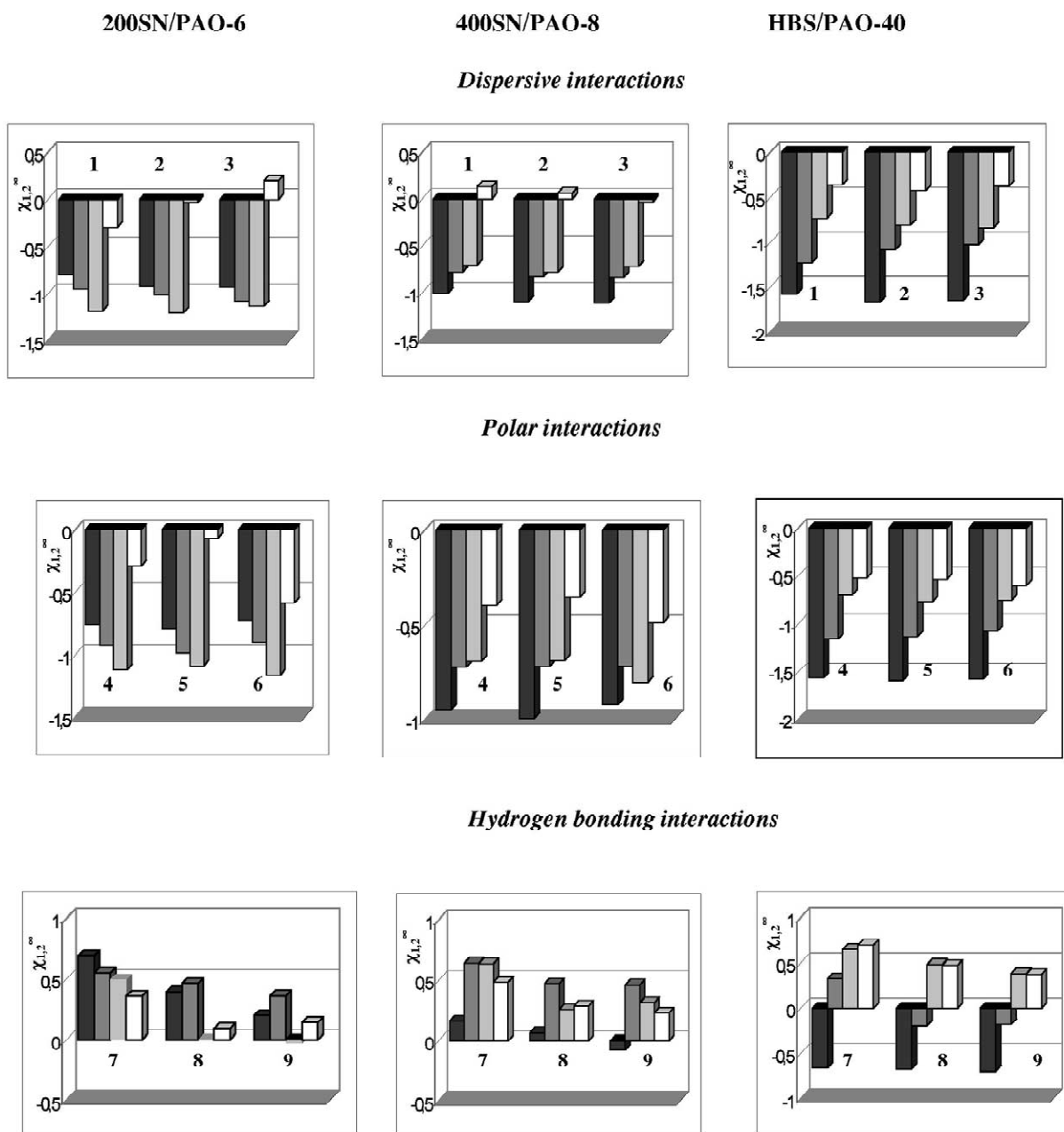


Fig. 2. Comparison of values of Flory–Huggins parameter ( $\chi_{1,2}^{\infty}$  at 120 °C) for examined mixtures and selected test solutes; 1=*n*-hexane, 2=*n*-heptane, 3=*n*-octane, 4=benzene, 5=toluene, 6=chloroform, 7=methanol, 8=ethanol, 9=propanol-1. Initial mixture, ■; components of the mixture oxidised separately, ■; mixture oxidised in traditional way, ■; mixture oxidised in chromatographic column, □.

of the examined stationary phase. Oxidation process significantly influenced the values of the solubility parameter of the examined base oils. The biggest

changes were found after oxidation in the chromatographic column (as for  $\chi_{1,2}^{\infty}$ ). The value of  $\delta_2$  significantly increased after oxidation of 200SN/

PAO-6, slightly increased for 400SN/PAO-8 and decreased for the HBS/PAO-40 mixture. The significant changes for the HBS/PAO-40 mixture are probably strengthened by the oxidation of the mineral oil.

All the above results prove that the examination of the oxidation process may be successfully carried out by means of IGC.

### 2.5. Nomenclature

$\chi_{1,2}^{\infty}$	Flory–Huggins interaction parameter
$\delta_2$	Solubility parameter
$M_1$	Molecular mass of the solute
$p_1^0$	Saturated vapour pressure of the solute
$B_{1,1}$	Second virial coefficient of the solute
$V_i^0$	Molar volume
$\rho_i$	Density
$R$	Gas constant

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