Solubility parameter as polarity measure for high-boiling oil products

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HIGHLIGHTS

- Conventional, non-conventional base oils and solid hydrocarbons characterized by physicochemical methods.
- IGC in examination of oil products.
- Solubility parameter reflect the material composition and structure – it works as polarity measure.

ARTICLE INFO

ABSTRACT

The use of solubility parameter determined by means of inverse gas chromatography, as a polarity measure of polarity for oil products from refinery and petrochemical processes is presented and discussed. The higher value of solubility parameter corresponds to higher polarity of examined materials. Higher polarity resulted from the higher content of polar components, i.e. aromatics hydrocarbons and resins.

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1. Introduction

Application of standard methods of gas chromatography in the examination of high-boiling oil products, i.e. having initial boiling point above 350 °C, is limited by their thermal stability and low volatility. The technique of inverse gas chromatography (IGC) is an alternative solution for examination of these products. IGC is most often used in physicochemical investigations. The basic difference between inverse and classical gas chromatography consists in the aim of investigation. The goal of investigation in IGC technique is the estimation of the magnitude of interactions between different test solutes (having various physicochemical properties) with non-volatile examined material (liquid or solid) placed in the chromatographic column [1].

The properties of the examined material might be deduced basing on the retention parameters of the carefully selected test solutes. Test solutes should represent the ability to various types of intermolecular interactions, i.e. dispersive, polar and hydrogen bonding. Test solutes are injected into the flow of the carrier gas and transported over the stationary phase. Values of retention parameters and peak profiles depend on the magnitude of molecular interactions between test solutes and stationary phase.

Davis et al. [2–6] and Boduszyński and Szkuta-Pochopien [7] were the first applying IGC technique in the examination of heavy oil products – road asphalts. They introduced the new term – coefficient of interactions I_x calculated from the retention volumes of test solute and hypothetical *n*-paraffin. Values of I_x coefficient were further correlated with oils' resistance to oxidation, shear strength or accelerated weathering durability. Authors of two papers [5,6] replaced coefficient of interactions by the specific coefficient of interactions I_g calculated from the specific retention volume (instead of retention volume) of standard test solutes.

De Anadrade Brauning [8] and Burg et al. [9] applied this chromatographic technique in classification of lubricating oils. In both cited papers classification was based on the polarity of oils expressed by McReynolds constants [8]. These values were calculated from the relations presented by Abraham et al. [10].

Hildebrand and Scatchard [11] defined solubility parameter as the square root of the cohesive energy density according to the following relation:

$$\delta_i = \left(\frac{E_i^{koh}}{V_i^*}\right)^{1/2} \tag{1}$$

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Value of this parameter depends on chemical structure and group composition of examined oil materials. Solubility parameter characterizes only the examined material. Therefore, it might be treated as a polarity measure for oil products from different refinery processes – very often having close values of boiling point. Higher value of solubility parameter corresponds to more polar character of the examined oil material.

Solubility parameter is expressed in: $(cal/cm^3)^{1/2}$, $(J/m^3)^{1/2}$, $MPa^{1/2}$ or $(atm)^{1/2}$ units.

Crucial point in the history of IGC was the introduction by Guillet et al. [12,13] the procedure of the estimation of Flory–Huggins interaction parameter χ_{12}^∞ and further Hildebrand solubility parameter δ_2:

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

where "i" denotes the consecutive test solute; δ_1, solubility parameter of test solute; χ_{12}^∞, Flory–Huggins interaction parameter at infinite dilution; δ_2, solubility parameter of the examined non-volatile material; χ_s^∞, entropic component of solubility parameter; V_1^0, molar volume of test solute.

Plot of left hand side of this equation versus δ_i yields δ_2 from the slope.

Funk [14] has used IGC technique in the examination of asphalts and asphaltenes. He first characterized the physicochemical properties of heavy oil products with the use of Flory–Huggins interaction parameter.

Hansen introduced three dimensional solubility parameter or Hansen solubility parameters (HSP) [11]. According to the Hansen theory, the cohesive energy can be considered as a sum of contributions from dispersive (E_d), polar (E_p) and hydrogen bonding (E_h) interactions:

$$-E_{coh} = -E_d - E_p - E_h \quad (3)$$

and the total solubility parameter (δ_T) is expressed as

$$\delta_T^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

where δ_p, δ_p, δ_h denotes dispersive, polar and hydrogen bonding contribution, respectively.

Adamska et al. [15] proposed to use Lindvig et al. [16] relationship correlating experimentally determined values of Flory–Huggins interaction parameter and the differences between HSPs values of the examined material and respective test solutes:

$$\chi_{12}^\infty = \alpha\frac{V_1}{RT}((\delta_{1,d} - \delta_{2,d})^2 + 0.25(\delta_{1,p} - \delta_{2,p})^2 + 0.25(\delta_{1,hb} - \delta_{2,hb})^2) \quad (5)$$

where R – gas constant; T – temperature of experiment; 1 and 2 – test solute and examined substance, respectively; α – Lindvig's coefficient ($\alpha = 0,\ldots,1$).

Adamska et al. used χ_{12}^∞ experimental data for series of test solutes, to calculate HSPs parameters of the examined material from Eq. (4). Solution was achieved by the finding of minimum of function:

$$G^2 = \frac{4\chi_{12}^\infty RT}{\alpha V_1}((\varepsilon_{1,d} - \varepsilon_{2,d})^2 + (\delta_{1,p} - \delta_{2,p})^2 + (\delta_{1,p} - \delta_{2,p})^2) \quad (6)$$

where $\varepsilon_{1,d} = 2\delta_{1,d}$.

The aim of this paper was the characteristics of selected petrochemical products by standard parameters and presentation of the possibility to express polarity of oils and waxes by the use of solubility parameter δ_2 and Hansen solubility parameters (HSPs).

2. Experimental

2.1. Examined materials

Products from different refinery and petrochemical processes were the subject of the present investigation:

- Conventional mineral oils (100SN, 200SN, HBS – bright stock oil) – from solvent extraction processes.
- Non-conventional mineral oils and synthetic oils (Shell XHVI 5, BP HC-6) - catalytic hydrocracking processes, poly-α-olefins (PAO-4, PAO-6, PAO-40) – oligomerization processes, diesters DB-51- esterification processes.
- Semi-synthetic base oils obtained by mixing of conventional oils with non-conventional mineral oils, poly-α-olefins, diesters having similar value of kinematic viscosity at 100 °C (100SN/PAO-4, 200SN/PAO-6, HBS/PAO-40, 200SN/DB-51).
- Solid hydrocarbons from solvent deparaffinization with the Di–Me mixture: vacuum raffinate (paraffinic slack wax SAE-30) and raffinate from vacuum residue (heavy slack wax).
- Heptane fraction (Hp), paraffinic slack waxes (raw and refined) from elaborated laboratory procedure for determination of the group composition of vacuum residue as described in [17–20].

Physicochemical characteristic of examined oil and petrochemical products is given in Tables 1–4. The following standard methods have been used: group composition (ASTM D2007), viscosity index (ASTM D2270), density at 20 °C (ASTM D4052), refractive index at 20 °C (ASTM D1218), oil content (ASTM D721), content of n-paraffinic hydrocarbons (ASTM D5442), content of aromatic hydrocarbons and resins (IP 469), congealing point (ASTM D938). Full characteristic of these oil products have been presented in earlier papers [17,18,21–27].

2.2. Inverse gas chromatography

Retention data necessary for calculation of solubility parameter were determined by means of IGC experiments. Examined oil products were deposited onto the inert chromatographic Chromosorb P AW DMCS, 80/100 mesh. The content of the oil material in column filling was equal to 20% (w/w). 1.8 m (6 feet) long, 2.0 mm I.D. stainless steel columns were applied. Columns were conditioned overnight as described in ASTM D5480.

Test solutes: (a) n-paraffinic hydrocarbons (from hexane to undecane) – characterizing dispersive interactions, (b) aromatic hydrocarbons (toluene, ethylbenzene, m-xylene, n-propylbenzene), halogene derivatives (dichloromethane, chloroform, 1,2-dichloroethane), butanone-2, THF, nitromethane, cyclohexane, alkenes (from hexen-1 to decene-1) and diethyl ether – characterizing polar interactions, (c) alcohols: from methanol to hexanol-1, 2-methyl-2-pentanol and pyridine – characterizing the ability of hydrogen bonding interactions. Volume of injection of test solute was equal to 0.1 µl.

Temperatures: injector 300 °C, detector 350 °C, chromatographic column isothermally at 120 °C. All examined materials were liquids at the column temperature – the retention occurs in gas–liquid system. Methane was used as marker for the hold-up time (t_M) determination.

Argon at flow rate 20 cm^3/min. was used as carrier gas. Values of solubility parameter were calculated according to the following procedure:

(i) Values of retention times t_R collected for all test solutes were used to calculate the values of specific retention volume V_g