

Characterisation of mineral oil–polyester, mineral oil–poly- α -olefin mixtures by inverse gas chromatography

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Poly- α -olefins and polyesters are the base stocks for the production of synthetic oils, and after mixing with mineral oils for semi-synthetic oils. Their behaviour at the temperatures found in a car engine at work (around 140 °C) is very important. The authors propose the use of an inverse gas chromatography (IGC) technique for qualification of their mixing properties.

Information on the basic parameters for SN-200 oil (H-6), poly- α -olefin (PAO-6), ester (DB-51) and their mixtures H-6–PAO-6, H-6–DB-51 was obtained from standard, normalised methods.

All examined base oils and their mixtures were placed in gas chromatographic columns and act as liquid stationary phases in the chromatographic process. The Flory–Huggins parameter χ_{12}^{∞} was calculated from the retention data (IGC) for selected test solutes. For the mixtures H-6–PAO-6, H-6–DB-51 the values of Flory–Huggins parameter $\chi_{1(2,3)}^{\infty}$ were calculated.

The interactions between components of investigated mixtures were expressed by the Flory–Huggins interaction parameter χ_{23}^{∞} .

Introduction

Inverse gas chromatography is a good and reliable method for the physicochemical characterisation of typical stationary phases and also for the characterisation of other materials, which can be placed in a chromatographic column.^{1–3}

The authors have examined many different materials, *e.g.* polymers, polymer blends, filled polymers, oxyethylated fatty alcohols and hydroxyoxime extractants of copper and their mixtures and, of course oil mixtures.³

IGC is presented here as a method of characterisation of the interactions in mineral oil–polyester, mineral oil–poly- α -olefin systems.

The term *inverse* indicates that the examined material is placed in a chromatographic column and studied using test solutes. Carefully selected test solutes are injected into the flow of the carrier gas and transported over the surface of the examined material. The retention time of the test solute influenced by interactions between the solute and the stationary phase are used to estimate their interactions.

Base oils^{4–6}

Mineral oil is the established base stock for the production of automotive engine lubricants. PAO, being a hydrocarbon, is seen as a “sister” to mineral oil, but is more expensive. PAOs are closely related to mineral oil but the same is true for certain types of ester base fluids.

In those applications where mineral oils as well as synthetic or partly synthetic oils are used, *e.g.* in automotive engines, it is essential to make the right choice regarding the synthetic base fluids available and, for blends, to ensure that the ratios in which they are used are correct.

The difference between PAO's and ester base fluids' chemical structure is caused by the presence of one or more carboxylic groups in esters. So, the polarity of the base oils increases in the order: poly- α -olefin < mineral oil < diester.

Differences in polarity exist between mineral oil, PAO and ester base fluids which could influence their anti-wear performance as well as the response of anti-wear additives.

At the base of literature data we can study the relative performance of ester base fluids, mineral oils and poly- α -olefins.

The advantages of ester base fluid can be found in:
 properties at high temperatures (esters are superior over mineral oil regarding engine cleanliness and insolubles—sludge. However, esters and PAOs required the addition of anti-oxidants to control viscosity and acid value),
 properties at low temperatures,
 viscosity vs. temperature relationship,
 volatility (for the ester base fluids is far the lowest),
 lubricity,
 biodegradability (a strong point of esters is their good biodegradability),
 additive solubility,
 frictional properties.

The advantages of ester base fluids in comparison to mineral oils and poly- α -olefins are summarised in Table 1.

The tendency to swell elastomer materials is often mentioned as a disadvantage of diesters. In the latter case, these esters are

Table 1 Comparison of the useful properties of mineral oil, PAO-6 and diesters (DB-51)^a

	Mineral oil	PAO-6	Diesters
High temperature properties	++	+++	+++
Low temperature properties	+	++++	++++
Viscosity–temp. relationship	++	+++	+++++
Volatility	++	+++	+++
Biodegradability	++	+	++++
Lubricity	++	+	++++
Additive solubility	++++	++	+++++

^a+ poor, ++ sufficient, +++ good, ++++ very good, +++++ excellent.

necessary to overcome distinct deficiencies of PAO such as elastomer shrinkage and additive solubility. Ester base fluids and PAOs offer the lubricant industry possibilities to create lubricants with improved properties over mineral oil. Each synthetic component does have certain benefits and shortcomings but these can be minimised by making use of combinations of both components.

Flory–Huggins parameters

The retention of the test solutes is expressed by specific retention volume V_g :

$$V_g = t_R' \times \frac{273.15 \times F}{w_L \times T} \times \frac{3}{2} \times \frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \quad (1)$$

where: F is the corrected flow rate of the carrier gas at column temperature T

$$F = F_a \left(\frac{T}{T_a}\right) \left(1 - \frac{P_w}{P_o}\right) \quad (2)$$

F_a is the gas flow rate measured at ambient temperature T_a , *i.e.* at the column outlet; P_w is the vapour pressure of water; w_L is the mass of the stationary phase; and P_i and P_o are the inlet and outlet pressures respectively.

To calculate the interactions parameter χ_{12}^∞ of oil–solute systems V_g from eqn. 1 is utilised as follows:

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

1 denotes the solute and 2 denotes examined material (oil, ester, poly- α -olefin), M_1 is the molecular weight of the solute, p_1^o is the saturated vapour pressure of the solute, B_{11} is the second virial coefficient of the solute, V_1^o is the molar volume, ρ_i is the density, R is the gas constant.^{1,7}

When a mixture of oils is used as a stationary phase in a chromatographic column, subscripts 2 and 3 are used to represent mineral oil and ester (poly- α -olefin), respectively.

$$\chi_{12}^\infty = \ln \left(\frac{273.15 \times R}{p_1^o \times V_g \times M_1} \right) - \frac{p_1^o}{R \times T} \times (B_{11} - V_1^o) + \ln \left(\frac{\rho_1}{\rho_m} \right) - \left(1 - \frac{V_1^o}{V_2^o} \right) \times \varphi_2 - \left(1 - \frac{V_1^o}{V_3^o} \right) \times \varphi_3 \quad (4)$$

where φ_2 and φ_3 are the volume fractions of mineral oil and its modifiers.²

The interactions expressed in term χ'_{23} are an indicator of miscibility of two components of the system.^{8,9} So, the χ parameter can be derived from:²

$$\chi'_{23} = \frac{1}{\varphi_2 \times \varphi_3} \times (\chi_{12(2)}^\infty \times \varphi_2 + \chi_{12(3)}^\infty \times \varphi_3 - \chi_{12(mix)}^\infty) \quad (5)$$

There are a number of laboratory distillation tests being routinely used to determine the boiling ranges of crude oils and their products.¹⁰ Simulating distillation is based on the fact that hydrocarbons are eluted from a non-polar column in boiling point order, and the column temperature is programmed until all the sample is eluted. Integration is done in fixed time slices not on individual peaks. Appropriate standards are examined under identical conditions to that of the sample. The analytical data may be presented as a chromatogram and/or in tables containing the percentage recovered at any temperature or *vice versa*.

Until now four methods for SIMulated DISTillation (SIMDIS) of crude oils and petroleum fractions (middle

distillates and lube oils; gasoline and gasoline fractions; heavy lube oils and residues) have become available.

SIMDIS is usually the method of choice for unknown samples, since it can run quickly and cheaply. However, the technique has not replaced other methods of physical distillation in specifications due to the lack of good data reproducibility. On the other hand the application of PTV injectors solve several problems with the range of available boiling points. Readers interested in the closer discussion on SIMDIS problems may refer to the excellent review of Abbot¹⁰ or earlier work of Butler.¹¹

The aim of our work is to present the applicability of inverse gas chromatography in the characterisation of base oils, their mixtures and the miscibility of mineral and synthetic base oils. The magnitude of mineral oil–polyester, mineral oil–poly- α -olefin interactions have been expressed by the Flory–Huggins (χ'_{23}) parameter.

Experimental

Materials

The examined materials used in this work as stationary phases in inverse gas chromatography and tested in the SIMDIS experiments were:

- mineral oil SN-200 from distillation of petroleum (H-6),
- poly- α -olefin as a base for production the semi-synthetic motor oils (PAO-6),
- diesters as a base for production semi-synthetic oils (DB-51), and their mixtures H-6–PAO-6, H-6–DB-51 in a weight ratio 7:3 (w/w).

Useful properties of mineral oil, poly- α -olefin and diesters are given in Table 1.

IGC experiments

The materials to be examined were coated (20% w/w) onto Chromosorb P (80–100 mesh). The IGC conditions are as follows: Hewlett Packard 5730A gas chromatograph with FID; 2 m \times 2 mm i.d. stainless-steel columns; column temperatures were: 100, 120, 140 °C; sampler temperature was 300 °C; detector temperature—350 °C; carrier gas—argon at the flow rate 20 ml min⁻¹; conditioning at 160 °C, overnight; injection volume—0.1 μ L.

The following compounds were used as the test solutes: C5–C10 *n*-alkanes, toluene, xylene, ethanol, nitromethane, chloroform and ethyl ether.

Saturated vapour pressures were taken from earlier works.^{1,3,7,12} The values of second virial coefficient B_{11} were calculated according to ref. 13. See also refs. 12, 14.

IGC parameters were calculated from eqn. (1)–(5).

SIMDIS experiments

The conditions from the Standard Test Method for Boiling Range Distribution of Petroleum Distillates in Boiling Range from 174 to 750 °C by Gas Chromatography (on the base of ASTM D6352) were: i) column — capillary, aluminium clad fused silica 5 m \times 0.53 mm i.d., film thickness 0.1 μ m of a 100% dimethylpolysiloxane stationary phase; ii) flow conditions — helium at 18 ml min⁻¹; iii) injection temperature — oven track mode; iv) detector FID, air 400 ml min⁻¹, hydrogen 32 ml min⁻¹, make-up gas, helium at 24 ml min⁻¹, temperature: 450 °C; v) oven program — initial oven temperature 50 °C, initial hold 0 min, program rate 10 °C min⁻¹, final oven temperature 400 °C, final hold 6 min, equilibration time 5 min; vi) sample dilution 1% (w/w) in carbon disulfide; vii) instrument — analyser SIMDIS HT-750 (A.C. Analytical Controls INC. USA) is the modified gas chromatograph equipped with temperature programmable vaporising injector; the chromatographic column may be heated to 430 °C.

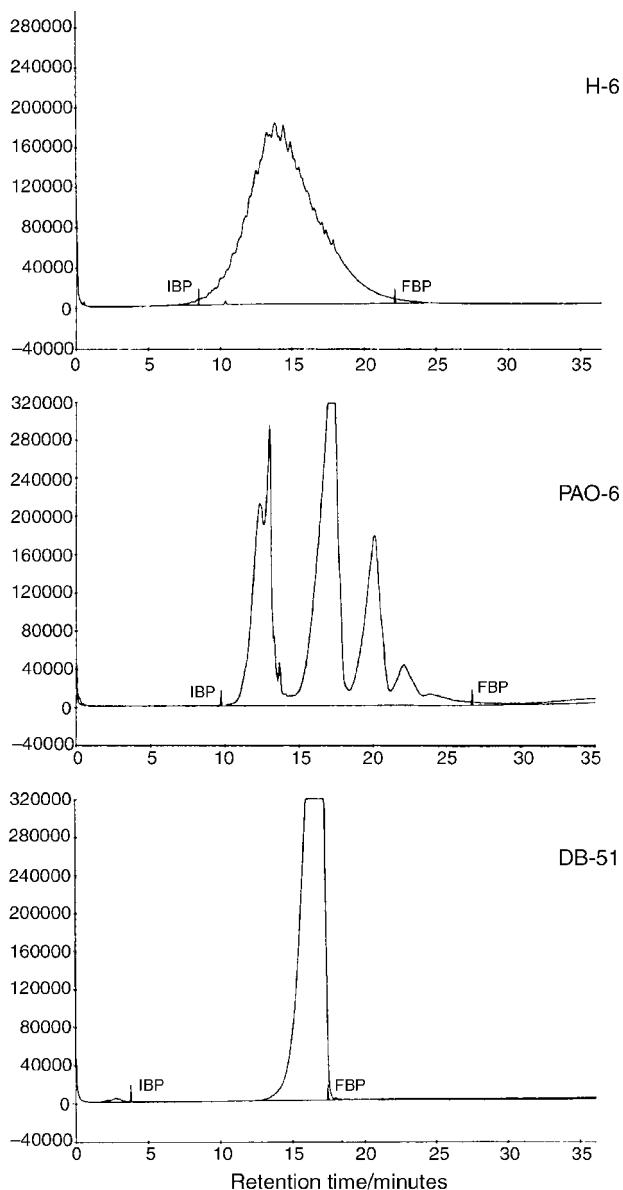


Fig. 1 SIMDIS chromatograms for the examined base oils.

Calculations

Values of χ_{12}^{∞} for mineral oil H-6, PAO-6 and DB-51 were calculated from eqn. (3), while for the mixtures H-6-PAO-6 and H-6-DB-51 from eqn. (4).

The values of the χ_{23} parameter were calculated from eqn. (5).

Results and discussion

SIMDIS results

SIMDIS is a useful method in the examination of oil products, at the temperature range from 36 to 750 °C. One of the most important applications is the simulated distillation of the raw petroleum.

The sample is injected directly into the evaporator with programmed temperature (PTV). The injector temperature is always above the oven analysis temperature.

The results are given as tables or as chromatograms.

The characteristic points are:

IBP, Initial Boiling Point — boiling temperature of 0.5% of probe weight,

FBP, Final Boiling Point — boiling temperature of 99.5% of probe weight.

The SIMDIS chromatograms are presented in Fig. 1. The

Table 2 IBP and FBP values for examined base oils

	H-6	PAO-6	DB-51
IBP [°C]	342	410	179
FBP [°C]	580	570	480

differences in the sources of these base oils are easily visible. It is worth noting also the changes of the values of IBP and FBP (Table 2). These are caused by the chemical composition of the respective base oil. H-6 is the product of the vacuum distillation of crude oil. The temperature of the process, accompanied by the refining, dewaxing and hydrogen processes, is the main factor influencing H-6 chemical composition. The base oil is then a mixture of organic chemical species having consecutively increasing boiling points in a given temperature range. PAO-6 is produced during a carefully controlled process leading to a mixture of oligomers having a restricted range of boiling points. PAO-6 contains trimer (the highest peak), tetramer, pentamer, hexamer and heptamer (the last one — the smallest peak) of α -olefin. Therefore, the relatively sharp and resolved peaks corresponding to the respective oligomers are present in the SIMDIS chromatogram of PAO-6. Polyesters, e.g. DB-51 are produced in an esterification process. It leads to a mixture of esters with a boiling point range corresponding to that of mineral oil and its appropriate physicochemical properties.

Flory-Huggins parameter χ_{12}^{∞}

The Flory-Huggins interaction parameter χ_{12}^{∞} is a measure of the free energy of the interaction between the probe and the examined material (oil or oil mixture). The influence of the type of test solute is presented in Figs. 2-4.

Very low values of χ_{12}^{∞} ($\chi_{12}^{\infty} < 0$) indicate strong intermolecular interactions between the solute and the liquid stationary phase while high, positive values characterise systems with weak interactions. Therefore, we may conclude that alcohols and nitro compounds do not interact with the various examined oils. Negative values of χ_{12}^{∞} are found, in all cases, for the *n*-alkane probes, for aromatic hydrocarbons and for halogen hydrocarbons on oil stationary phases. It means that the investigated materials exhibit highly non-polar character. Values of χ_{12}^{∞} , most often decrease with increasing temperature of IGC experiment.

We can observe very high similarity of the interactions between examined base oils and selected test solutes. This could lead to the conclusion that all these oils would probably exhibit complete mutual miscibility.

This statement may be verified (see below) by the examination of the values of χ_{23} Flory-Huggins interaction parameters.

The comparison of the interactions in the test solute-individual base oil systems (Figs. 2-4) and test solutes-base oil mixtures (Figs. 5, 6) indicates that these are influenced by the presence of a higher amount of mineral oil. Let's compare the

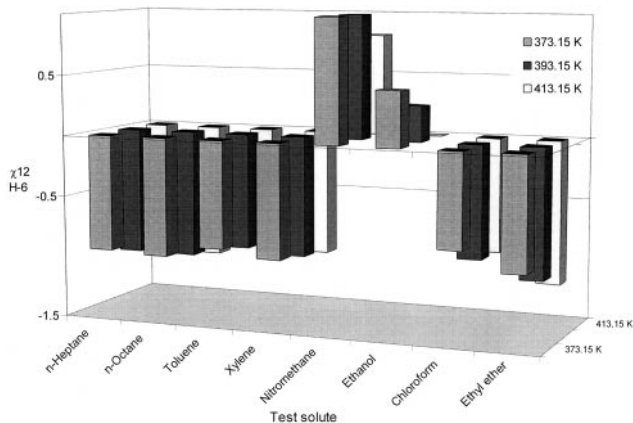


Fig. 2 Flory-Huggins parameter χ_{12}^{∞} for the mineral oil (H-6).

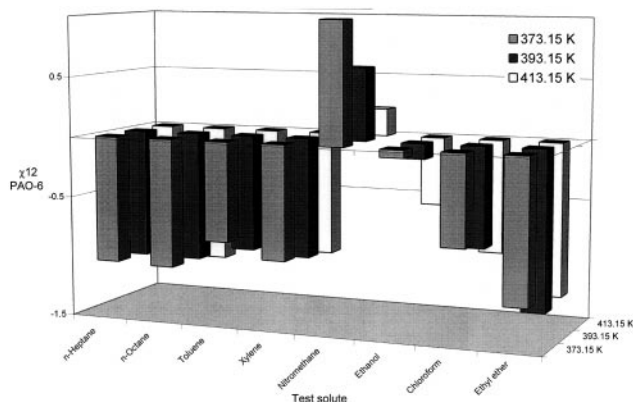


Fig. 3 Flory-Huggins parameter χ_{12}^{∞} for poly- α -olefin (PAO-6).

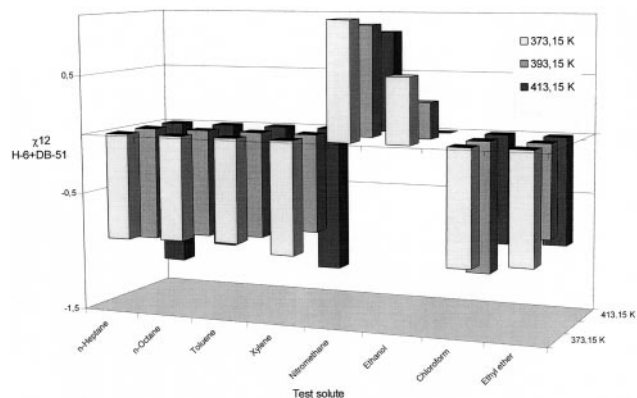


Fig. 6 Flory-Huggins parameter χ_{12}^{∞} for mineral oil (H-6)-ester (DB-51).

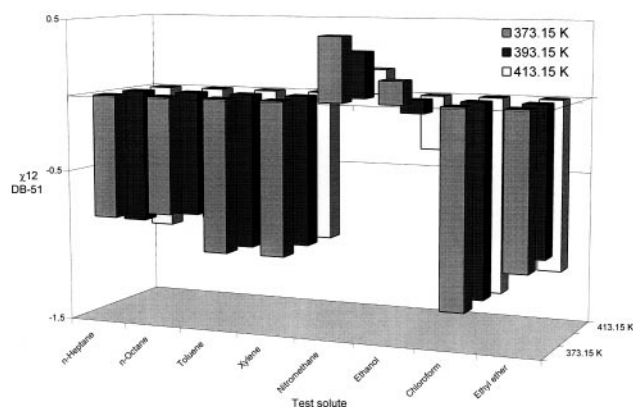


Fig. 4 Flory-Huggins parameter χ_{12}^{∞} for ester (DB-51).

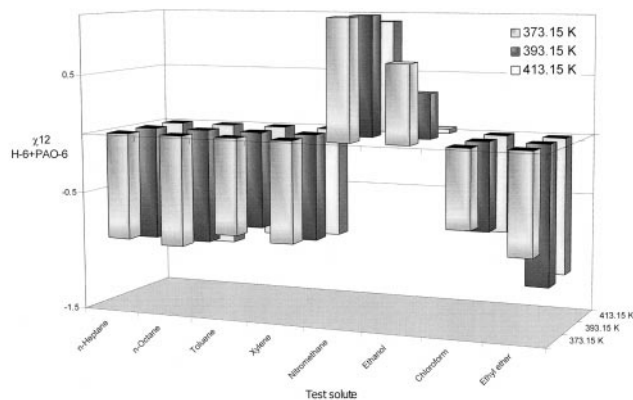


Fig. 5 Flory-Huggins parameter χ_{12}^{∞} for mineral oil (H-6)-poly- α -olefin (PAO-6).

χ_{12}^{∞} values for a polar test solute, *e.g.* ethanol. χ_{12}^{∞} values for the H-6-ethanol system are positive despite the experiment temperature. The corresponding values for PAO-6-ethanol and DB-51-ethanol systems are highly negative (one exception – positive value for DB-51-ethanol at 373.15 K). The mixing of base oils (mineral oil:synthetic oil 7:3) causes the change of the mixture's ability for interactions with this polar test solute. The respective χ_{12}^{∞} values are positive (Figs. 5, 6), rather similar to those found for H-6 oil (Fig. 2) than for two synthetic bases (Figs. 3, 4).

The influence of the chemical composition of the base oil on χ_{12}^{∞} values for different test solutes is presented in Fig. 7. The observed changes significantly depend on the chemical nature of the test solute. *n*-Octane miscibility decreases (increasing χ_{12}^{∞}) with increasing polarity of solvent (mixed solvent). However, the term "polarity" is very general. It is clearly shown when

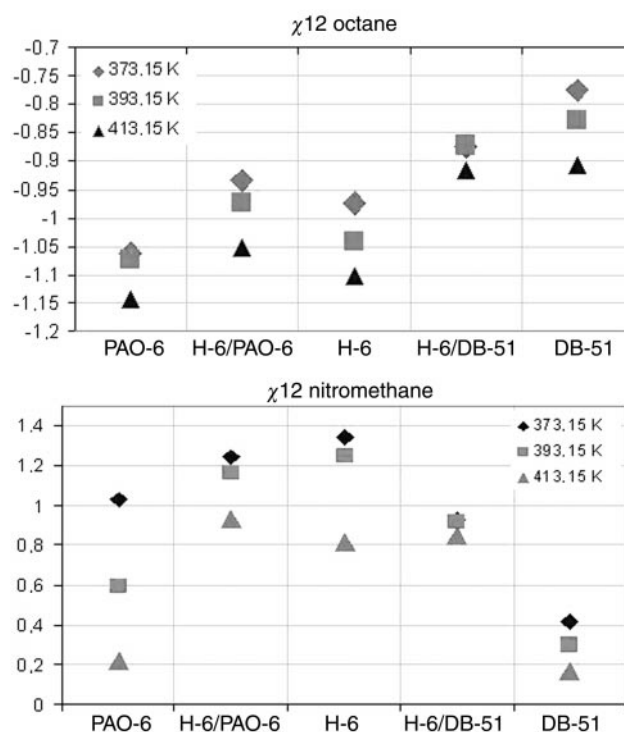


Fig. 7 The influence of the solvent composition on χ_{12}^{∞} values for selected test solutes.

values of χ_{12}^{∞} for nitromethane are taken into account. The highest χ_{12}^{∞} values (the lowest miscibility) are found for H-6 oil. As nitromethane acts as electron acceptor it means that one may expect the presence of electron acceptor active centres in H-6 oil. This means an increase of the forces excluding nitromethane molecules from the solvent. Addition of DB-51 to H-6 mineral oil introduces the ester groups which can act as electron donor centres. Hence, the increasing solute-solvent interactions increase the miscibility of the solute and the solvent. It is evidenced by decreasing χ_{12}^{∞} values in the order: H-6→H-6-DB-51→DB-51.

Flory-Huggins interaction parameter χ'_{23}

The values of the interaction parameter χ'_{23} for H-6-PAO-6 and H-6-DB-51 mixtures indicate the mutual components' miscibility. Values above zero indicate poor miscibility, while values below zero indicate good miscibility of components (Fig. 8, 9).

Most often χ'_{23} values are negative for both examined base oil mixtures. In a few cases the value of χ'_{23} is near zero. It happened when ethyl ether was used as the test solute and the temperature of IGC experiments was equal to 393.15 K

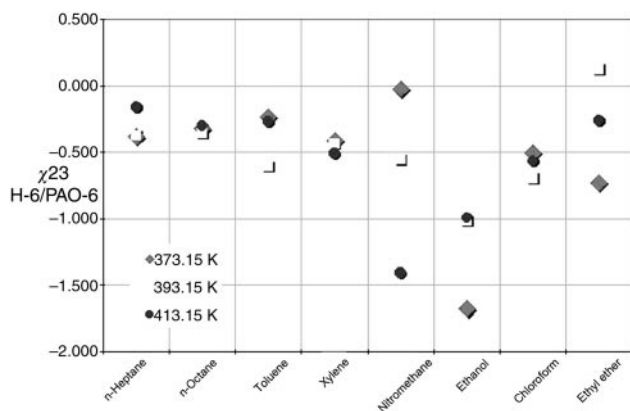


Fig. 8 Flory–Huggins interaction parameter χ'_{23} for H-6–PAO-6 mixture.

(Fig. 8). Generally H-6 mineral oil and poly- α -olefin PAO-6 as well as H-6 and DB-51 ester are miscible.

However, two significant problems should be raised here:

values of the χ'_{23} parameter depend on the test solute as was presented earlier in IGC literature,^{8,9} but cannot be explained on the basis of Flory–Huggins theory;

χ'_{23} values change with the change of temperature of IGC experiment. The increase of the temperature may cause both decrease (see χ'_{23} for nitromethane H-6–PAO-6, Fig. 8) or increase (ethyl ether for H-6–PAO-6, Fig. 8) of the value of χ'_{23} parameters.

The largest changes with temperature are noted for polar test solutes. A possible explanation may be that the two solvent components (here: oils H-6 and DB-51) have significantly different functionalities. H-6 is a non-polar solvent while DB-51 contains some polar (ester) groups. These ester groups may act as “active centres” interacting preferentially (in comparison to the co-solvent) with the polar test solutes (Fig. 8, 9).

As temperature increases, the relative strength of these interactions decreases in comparison to the non-polar forces between the solvent components so that the overall miscibility increases. It is also worth noting that the majority of non-polar test solutes exhibit the opposite behaviour. Limited miscibility (solute–mixed solvent) is indicated at lower temperatures and it becomes less miscible as temperature increases. The non-polar test solutes interact preferably with the H-6 component due to the predominant dispersive forces and interfering with the co-solvent interactions. The magnitude of these interactions would probably decrease with temperature but less rapidly than polar interactions. Flory–Huggins theory assumes that the solvent and co-solvent interactions are uniform. Such a situation does not exist in the case of two solvents possessing different properties (polar vs. non-polar). Probably, the same situation happened when Garcia-Dominguez *et al.*^{8,9} examined their polymers’ mixtures. However, these statements do not fully explain why the values of the χ'_{23} parameter describing interactions between two mixture components (not component–test solute!) are influenced by the magnitude of solute–co-solvent interactions!

The useful information could be obtained from IGC experiments for a broader range of oils’ mixtures. One may expect non-linear behaviour for Flory–Huggins parameters vs. mixture composition relationships. We can collect the data whose analysis could help us to explain the observed dependence of the χ'_{23} parameter. However, it is worth noting that from a technological point of view such examination is justified only within the range 20–30% (w/w) of the synthetic oil.

As the miscibility of the components may change with the

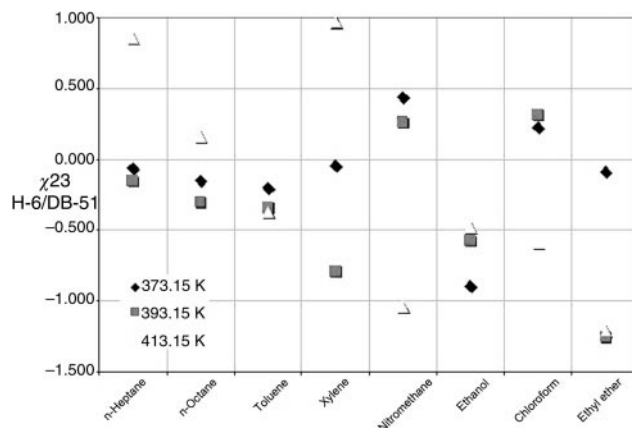


Fig. 9 Flory–Huggins interaction parameter χ'_{23} for H-6–DB-51 mixture.

temperature χ'_{23} is a useful tool for predicting the regions of potential limited miscibility. This could be crucial information for the production engineer and/or the user.

Conclusions

Chromatographic techniques (SIMDIS, IGC) are a useful tool in the examination of mineral and synthetic base oils.

The χ'_{12} parameter is the measure of the interactions between the test solutes (different types) and the examined oil. All examined materials are characterised by negative values of the χ'_{12} parameter (exceptions for: nitromethane and ethanol). It shows similar polarity of the tested base oils and their potential miscibility. The same effect can be observed for the oils’ mixtures (H-6–PAO-6 or H-6–DB-51).

Negative values of Flory–Huggins interaction parameter χ'_{23} are found for both examined mixtures, which indicate good miscibility of the used components. It has been found that χ'_{23} values depend on the test solute used in IGC experiments.

Temperature dependence of the χ'_{23} parameter could be used for the prediction of the areas of limited miscibility of the components.

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