Study of the influence of the soluble organic fraction of an exhaust diesel soot by a linear solvation energy relationship approach

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Abstract

Two samples of soot are studied in the present work. The results obtained on a virgin diesel soot (VDS) are compared to those obtained on the corresponding material after removal of its soluble organic fraction (SOF). The adsorption properties of both materials towards organic compounds are investigated by gas chromatography (GC) using the linear solvation energy relationship (LSER) equation of Abraham [Chem Soc Rev 1993;22:73–83]. This approach allows each material to be characterized in terms of five quantitative molecular interaction parameters. The results show the large influence of the SOF in the adsorption process of gaseous organic compounds. This study reveals that the extracted diesel soot (EDS) can interact through molecular interactions similar to those obtained on fullerenes or graphite.
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1. Introduction

The elimination of exhaust diesel soots is important because of the toxicity of their emissions in atmosphere. One major objective of vehicle constructors is thus their destruction. In this goal, processes are studied to reduce and eliminate their emissions by filtration and catalytic combustion. It is commonly assumed that soots are constituted by carbonaceous units with adhering soluble organic fraction (SOF) and inorganic material (sulphates) [1]. The SOF and the other species are adsorbed by soots in the exhaust pipe of the engine and result from both lubricating oil and unburned fuel [2]. For these reasons, in several studies, the virgin diesel soots are often modelised as carbon blacks covered with engine oil and diesel oil [3]. Moreover, the carbon black is often used as a reference material [4]. As presented by Stanmore et al. [1] in a recent review, the amount of SOF is a function of engine operating conditions. Their quantities can vary from 5 to 60%. Thus, their influence is not negligible concerning the chemical composition of soots and the processes of elimination. In the aim to improve the understanding of the contribution of SOF in the adsorptive behaviour of soots, a linear solvation energy relationship study is undertaken. This type of study was already described in the literature to characterize carbonaceous materials in term of quantitative molecular interaction coefficients which can be used to predict their adsorptive properties towards volatile organic compounds [5].

This strategy was applied to compare the behaviour towards hydrocarbons of a virgin diesel soot with the corresponding SOF extracted material. In this aim, the materials under study are placed in a gas chromatographic column and they are characterized by injecting different organic compounds. The collected retention data are treated by the LSER approach of Abraham [6] using the classical equation:

$$\log_{10}(SP) = c + rR_2 + s\pi_2^{\mathrm{H}} + a\Sigma\alpha_2^{\mathrm{H}} + b\Sigma\beta_2^{\mathrm{H}} + l\log_{10}L^{16}$$

(1)

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where *SP* is a series of known properties of the injected solutes (probe molecules) on a given sorbent. In this work, *SP* is the gas–solid partition coefficient at infinite dilution (K_c) of a solute on the studied soots at a given temperature.

K_c is calculated from the adsorption isotherm, this latter being determined by the elution characteristic point (ECP) method [7]. The $\log_{10}(K_c)$ values are free energy parameters which can be separated in five free energy contributions as presented in Eq. (1). Each contribution or molecular interaction term holds one parameter (solute descriptor) characterizing the injected probe and the other is the expected parameter characterizing the material under study.

The parameters R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$ and L^{16} refer to the probe characteristics which are the excess molar refraction [8], the dipolarity/polarisability [9], the hydrogen bond acidity [6], the hydrogen bond basicity [6] and the gas–liquid partition coefficient of the probe on *n*-hexadecane [10], respectively. All these parameters result from physicochemical and thermodynamical measurements (at 298 K except R_2 determined at 293 K) which constitute a data bank containing about 3000 compounds [11]. The LSER approach makes the assumption that these descriptor values are invariant with the temperature i.e. as a reference state. Fixing these values, it is possible to obtain *r*-, *s*-, *a*-, *b*- and *l*-coefficients in whatever the temperature considering that these coefficients depend only of the material properties.

For a number of *n* injected solutes, *n* LSER equations are established for a given adsorbent at a given temperature. Then, the *r*-, *s*-, *a*-, *b*- and *l*-coefficients characterizing the adsorbent under study are extracted from the series of *n* equations by multiple linear regression analysis (MLRA). *r* is the ability of the soot to interact through π- and n-electrons, *s* is a measure of dipolarity/polarisability of the soot, *a* is its hydrogen bond basicity, *b* its hydrogen bond acidity and *l* its dispersive character. In a gas–solid transfer all the coefficients must be positive because the interactions in the gas phase are negligible and they cannot exceed those encountered in a condensed phase. An exception exists concerning the *r*-coefficient that can be sometimes negative when lone pair-lone pair repulsive interactions occur. This fact is observed in the characterization of fluorinated sorbents [12,13] or of carbonaceous materials [14–16]. *c* is the constant of the regression that is not a property of the studied material.

The solutes used should be sufficient in number and variety to establish the statistical and chemical validity of the model [17]. Moreover, a large number of solute is required to avoid the influence of the removal of some probes because of the impossibility to determine $\log_{10}(K_c)$ in the case of irreversible adsorption for example. In these conditions the LSER coefficients of different materials established at a given temperature can be compared even if they are not obtained with exactly the same set of solutes. In the present work, more than 20 solutes were injected in

a classical gas chromatograph. They are selected for their chemical diversity and their high volatility as presented in Table 1, to cover a wide range of molecular interactions, and to minimize inter-correlations between solute descriptors so as to thoroughly test each type of interactions.

2. Experimental

2.1. GC measurements

All the GC measurements were performed on a Shimadzu GC14 gas chromatograph equipped with a thermal conductivity detector (TCD). The carrier gas was helium (purity of 99.995%) with a flow-rate of 20 cm^3 min^{-1}. The temperature of the injector, detector and column were fixed at 250, 250, and 50 °C, respectively. The gas-flow rate was measured using a bubble-soap flow-meter. This measure was corrected by the James–Martin correcting factor (*J*) [7] which takes into account the pressure drop of the column. Moreover, the gas flow-rate was also corrected for the vapor pressure of the water existing in the flow-meter [7]. Consequently, the corrected gas-flow rate is obtained multiplying the measured gas-flow rate by both correcting factors. The chromatographic columns were made of Teflon® and were 20 cm long. Soots are powdery materials and, so, to avoid blocking columns, these were filled with soots diluted in acid washed and silanised glass beads of 250 μm diameter furnished by Supelco. To verify the inert character of the glass beads, all the molecular probes were injected in a column containing the beads without soot. All these solutes were eluted at the same time than air, with non or moderate peak tailing. Thus, the adsorption generated by the glass beads can be considered as negligible.

2.2. Computational

The chromatogram data acquisitions were performed using a Diamir software (Borwin) and an acquisition station Hercule 2000. The LSER equations were established using Minitab software (Minitab). During the MLRA, all the parameters (*c*, *r*, *s*, *a*, *b* and *l*) having Student's *t*-values inferior to 95% were removed and the LSER equations were recalculated.

2.3. Molecular probes

All the injected solutes were supplied by Sigma-Aldrich and are up to 99% purity. Two matrices of correlation were calculated from the values of the solute descriptors used to establish every LSER equation. The results are presented in Table 2. It can be noticed that all the coefficients of correlation are low with a maximal absolute value of 0.616 that is the guarantee that there is no inter-correlation between the various descriptors. Each solute is injected

Table 1
Solute descriptors values

Solutes	B_p	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\log_{10} L^{16}$
n-Pentane	36	0.000	0.00	0.00	0.00	2.162
n-Hexane	69	0.000	0.00	0.00	0.00	2.668
n-Heptane	98	0.000	0.00	0.00	0.00	3.173
n-Octane	126	0.000	0.00	0.00	0.00	3.667
n-Nonane	151	0.000	0.00	0.00	0.00	4.182
n-Decane	174	0.000	0.00	0.00	0.00	4.686
c-Hexane	80.7	0.305	0.10	0.00	0.00	2.964
Hex-1-ene	64	0.078	0.08	0.00	0.07	2.572
Benzene	80	0.610	0.52	0.00	0.14	2.768
Toluene	111	0.601	0.52	0.00	0.14	3.325
Thiophene	84	0.687	0.57	0.00	0.15	2.819
Propan-1-ol	97	0.236	0.42	0.37	0.48	2.031
Butan-1-ol	117	0.224	0.42	0.37	0.48	2.601
Butan-2-ol	98	0.217	0.36	0.33	0.56	2.338
HFIP	59	−0.240	0.55	0.77	0.10	1.392
TFE	77–80	0.015	0.60	0.57	0.25	1.224
Propanone	56	0.179	0.70	0.04	0.49	1.696
Pentan-2-one	80	0.143	0.68	0.00	0.51	2.755
Dipropylether	68–69	0.008	0.25	0.00	0.45	2.954
1,4-Dioxane	101	0.329	0.75	0.00	0.64	3.892
Ethylacetate	77	0.106	0.62	0.00	0.45	2.314
Triethylamine	88.8	0.101	0.15	0.00	0.79	3.040
Pyridine	115	0.631	0.84	0.00	0.52	3.022
Nitroethane	114–115	0.270	0.95	0.02	0.33	2.414
1-Nitropropane	131–132	0.242	0.95	0.00	0.31	2.894
Chloroform	61	0.425	0.49	0.15	0.02	2.480

B_p = boiling point of the solutes expressed in °C. HFIP = 1,1,1,3,3,3-hexafluoroisopropanol; TFE = 2,2,2-trifluoroethanol.

several times to verify the superposition of the peak tailing and thus verify the equilibrium state between the gas and the solid phases.

2.4. Materials

The VDS was supplied by Renault. It is a soot without catalyst obtained from the exhaust pipe of a test bench equipped with a F9Q diesel engine of 1900 cm³ running at

Table 2
Matrices of correlation of the solute descriptors used to characterize the soots

	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$
VDS				
π_2^H	0.434			
$\Sigma\alpha_2^H$	−0.297	0.209		
$\Sigma\beta_2^H$	0.138	0.444	0.133	
$\log_{10} L^{16}$	0.070	−0.486	−0.616	−0.328
EDS				
π_2^H	0.592			
$\Sigma\alpha_2^H$	−0.119	0.169		
$\Sigma\beta_2^H$	0.236	0.594	0.109	
$\log_{10} L^{16}$	−0.086	−0.352	−0.520	−0.146

VDS = virgin diesel soot; EDS = extracted diesel soot.

2000 rpm. Moreover, this material has a low specific area of 75 m² g⁻¹ determined by adsorption of benzene. The SOF is extracted from VDS by a sequential Sohxlet extraction using dichloromethane (24 h) and then toluene (24 h) [18,19] providing the extracted diesel soot (EDS). The amount of SOF is 8%. The elemental analysis for VDS gives (wt%) C, 86.50; H, 0.88; O, 10.59; N, 0.46; S, 0.20 and for EDS C, 84.76; H, 0.88; O, 13.9 (by difference); N, 0.41; S, <0.10. VDS contains near 3% ash and it is free of catalyst.

3. Results and discussion

For both studied soots, the established LSER equations are the following:
For the unextracted soot (VDS):

$$\log_{10}(K_c) = -1.61 - 0.52R_2 + 0.43\pi_2^H + 1.02\Sigma\alpha_2^H$$
$$+ 0.38\Sigma\beta_2^H + 0.717\log_{10} L^{16} \qquad (2)$$

S.D. = 0.162 ρ = 0.948 F = 28.3 n = 22

For the extracted soot (EDS):

$$\log_{10}(K_c) = 0.37\pi_2^H + 0.81\Sigma\alpha_2^H + 0.358\log_{10} L^{16} \qquad (3)$$

S.D. $= 0.102$ $\rho = 0.915$ $F = 995$ $n = 20$

where S.D. is the standard deviation, ρ is the coefficient of correlation between observed and calculated $\log_{10}(K_c)$ values, F is the Fisher-statistic and n the number of injected solutes.

First, it can be noticed that the models are satisfactory from a statistical point of view, with correlation coefficients between observed and calculated $\log_{10}(K_c)$ values of more than 0.900 for around 20 injected solutes. The results are presented in Figs. 1 and 2.

Eq. (2) reveals that the VDS can interact through different types of molecular interactions. Principally, it is a basic material ($a = 1.02$) which can interact with organic compounds through dispersive ($l = 0.717$) and dipolarity/polarisability ($s = 0.43$) interactions. It also has a weak acidic character ($b = 0.38$). The negative r-coefficient value ($r = -0.52$) signifies that some lone pair-lone pair repulsive interactions occur between a compound in gas phase and the solid material. Thus VDS possesses a polar character.

These observations are in good agreement with the results obtained by Clague et al. [19] who characterized engine soots, exhaust soots and a carbon black using the gas chromatographic approach by inverse gas chromatography (IGC). They concluded that the unextracted diesel exhaust soots possess a relatively polar surface and are very different from carbon blacks. Concerning our study it can be noticed that Eqs. 2 and 3 are different. This means that both materials will behave differently towards gaseous organic compounds. Eq. (3) reveals that the EDS can interact through basic, dispersive and dipolarity/polarisability interactions and not through lone pair-lone pair repulsion and acidic interactions. In addition, the strength of the basic, dispersive and dipolarity/polarisability interactions are lower than those observed in Eq. (2). Thus, as already discussed in Ref. [19], the surface energy of the SOF extracted soot falls significantly in comparison with the surface energy of the unextracted material. It is obvious that the VDS and EDS are two different materials which exhibit different sorption properties. This demonstrates the influence of the SOF on the sorptive properties of soots. The extraction of the SOF modifies also the structure of
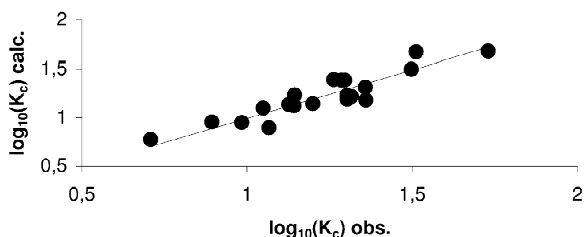

Fig. 2. Calculated $\log_{10}(K_c)$ values vs. observed $\log_{10}(K_c)$ values for EDS material.

the material and considering the low percentage of inorganic compounds and the lack of catalyst, the differences between both materials are mainly linked to the chemistry of the studied materials and certainly to structural factors (i.e. porosity). The LSER coefficients so obtained for both materials are thus dependent to the chemical composition and to the accessibility of the polar sites. Finally, these coefficients encode chemical and structural informations.

Then, as already described [13], the LSER approach enables materials used as stationary phases to be classified with the aim of comparing them in term of types and strengths of interactions and also to predict their behaviors. The efficiency of this method to characterize the different forms of carbon was demonstrated in the 1990s, by studying carbonaceous materials such as graphite [15], fullerenes [14], and graphitized carbon blacks (carbotrap) [20]. In each case LSER equations were established. For graphite and fullerenes at 25 °C, these studies showed significant s and a values, low values for l-coefficients and values near 0 for r-coefficients. It had been concluded that such materials were polarisable, basic and weakly lipophilic and that the fullerenes behave more as a giant closed-cage polyalkene than as a highly aromatic molecule [13,14]. For graphitized carbon black at 20 °C [20], the study showed that it is not a basic and a polarisable ($a = s = 0$) material but is a highly lipophilic material ($l = 2.65$) that can interact strongly through repulsive electron pair interactions ($r = -2.77$). Comparing these results and those obtained in this work, one can think that the studied soot and more particularly its extracted derivative—EDS—present some resemblances with fullerenes or
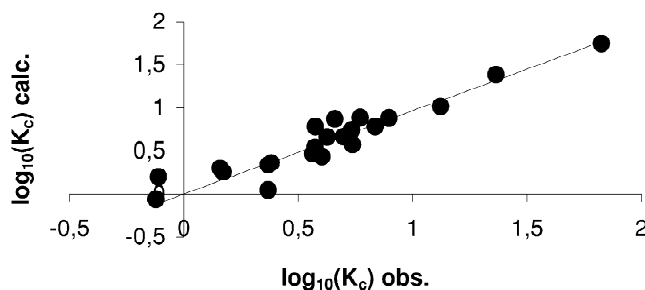

Fig. 1. Calculated $\log_{10}(K_c)$ values vs. observed $\log_{10}(K_c)$ values for VDS material.

graphite because of the similar type of the molecular interactions involved in the adsorption process of gaseous organic compounds. Conversely, the materials investigated in this study are not highly lipophilic and cannot interact through large repulsive electron pair interactions as a graphitized carbon black.

4. Conclusion

In conclusion, it is obvious that both studied materials are different in term of adsorptive properties towards hydrocarbons. The LSER method reveals that the SOF extracted soot (EDS) behaves as graphites or fullerenes and that it is different from a graphitized carbon black. The extraction of SOF greatly changes the adsorptive properties of a soot modifying molecular interactions involved between the soot material and gaseous hydrocarbons. This can be qualitatively and quantitatively followed by an LSER approach.

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