

A new route towards deep desulfurization: selective charge transfer complex formation¹

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An alternative to the classical hydrodesulfurization process is proposed, based on the formation and subsequent removal of insoluble charge-transfer complexes between suitable π -acceptors and alkylated dibenzothiophenes.

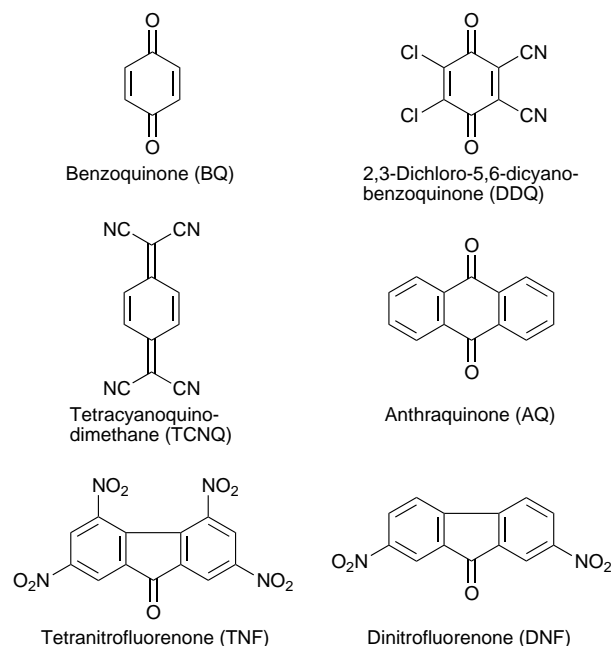
Due to more stringent environmental regulations to protect urban areas and new legislation in Europe, the sulfur level in diesel fuel is now limited to 0.05 wt%, and will certainly be lowered in the near future. However, present refinery diesel hydrodesulfurization (HDS) processes can only be achieved under severe conditions, leading to shorter catalyst life. It is now well established that the achievement of deep HDS is prevented by one type of sulfur compound, namely alkyl-dibenzothiophenes.^{2,3} These molecules have been subject of numerous studies as models to improve the properties of HDS catalysts.^{4–6} Recently, a new method has been proposed⁷ where the hydrodesulfurized stream is treated with a solid material (activated carbon, alumina, zeolite *etc.*) capable of adsorbing substituted dibenzothiophenes (DBT) by 'form selectivity' and steric hindrance. However, this interesting method presents some limitations because the capacity of the described (weight percent DBT on adsorbent) does not exceed 12% and furthermore, the selectivity factor α [eqn. (1)] toward aromatic system models (1-methylnaphthalene, MN) is just 7.

$$\alpha = \frac{\text{DBT}_{\text{adsorbed}} \cdot \text{MN}_{\text{solution}}}{\text{DBT}_{\text{solution}} \cdot \text{MN}_{\text{adsorbed}}} \quad (1)$$

Considering the electron-rich structure of alkylated DBT, we have studied its ability to form charge-transfer complexes with π -acceptors in order to describe a new method for their specific removal from gas oil.

Electron donor–acceptor complexes are easily detected *via* UV–VIS spectroscopy because their formation is generally accompanied by the appearance of a new absorption band (Benesi–Hildebrand band). Following the method of Foster–Hammick–Wardley,⁸ this phenomenon allows the calculation of the association constant (and hence the free enthalpy) characterizing the new complex.

DDQ was tested as a π -acceptor due to its easy availability and its known ability to form charge-transfer complexes. Indeed, a mixture of 4,6-dimethyldibenzothiophene (DMDBT)⁹ and DDQ in CHCl₃ gave rise to a new absorption wave (λ_{max} 633 nm) corresponding to a ΔG of 15 kJ mol⁻¹ (see Fig. 1). 1-Methylnaphthalene was chosen as a model to represent the aromatic compounds contained in the gas oil which are capable of complexing DDQ competitively with DMDBT to form charge-transfer complexes. Using the same procedure as for DMDBT, DDQ and MN formed a charge-transfer complex showing a maximum absorption at 654 nm ($\Delta G = 7.3$ kJ mol⁻¹) (see Fig. 2). This result indicates stronger complexation of DDQ with the sulfur compound than with the aromatic one. Complexation thus appears to be selective toward alkyl-DBT species, although the π -acceptor's chosen structure had not been optimized.



Having demonstrated the possibility of forming selectively a charge-transfer complex between DMDBT and DDQ, we have tested several other π -acceptors. The properties required are a high selectivity factor α for DMDBT toward the aromatics, and complete insolubility in alkanes in order to easily remove the complex formed from the gas oil.

The procedure used to test the different π -acceptors is as follows: an equimolar solution of DMDBT and MN in heptane (11 mmol l⁻¹) was stirred at room temperature in the presence of dodecane (1 equiv.) as the internal reference. The addition of the π -acceptor (1 equiv.) was followed by the immediate

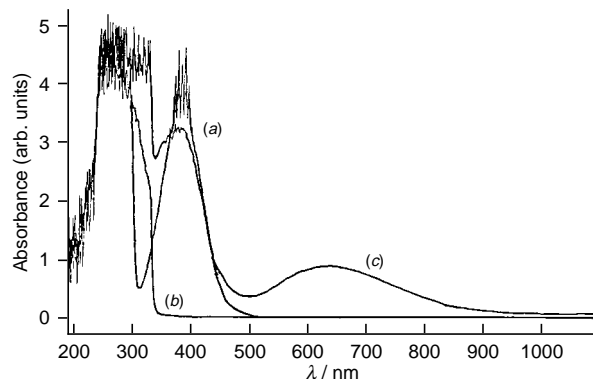


Fig. 1 UV–VIS spectrum from the donor–acceptor complex DMDBT–DDQ in CHCl₃; (a) DDQ, (b) 4,6-DMDBT and (c) complex

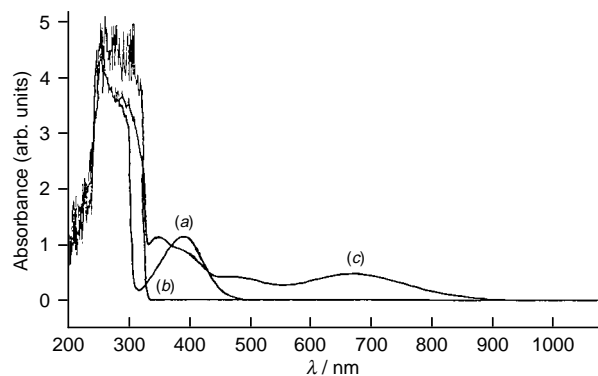


Fig. 2 UV-VIS spectrum from the donor-acceptor complex MN-DDQ in CHCl_3 ; (a) DDQ, (b) MN and (c) complex

formation of a coloured precipitate (except for *p*-benzoquinone). The samples were removed and the composition of the resulting solution analysed by gas chromatography to determine the amount of unreacted MN and DMDBT. The capacity value C [eqn. (2), where MW equals molecular weight] and the

$$C = \frac{MW_{\text{DBT}}}{(MW_{\text{DBT}} + MW_{\text{acceptor}})} \times 100 \quad (2)$$

separation factors α were calculated for each complexing material and are reported in Table 1 (for a direct comparison with results reported with solid materials as adsorbent, see ref. 7). Among all the π -acceptors tested, tetranitrofluorenone (TNF) seems to have the best characteristics, with a maximum factor of separation (rapidly reached) and a satisfactory capacity.

Fluorene was then used instead of MN to check the selectivity for DMDBT in the presence of a molecule rich in electrons with a similar geometry.¹⁰ In this case, the selectivity factor was only 80 after 60 h stirring. Even if this value is lower than the previous one with MN, the selectivity remains higher than that obtained with adsorbent materials by shape selectivity.⁷

Following the results of this preliminary study on model molecules, the possible selective complexation of substituted DBT from a gas oil, already hydrodesulfurized (960 ppm) by classical methods, was examined. Firstly, the gas oil was diluted in heptane (15 g in 200 ml) and analysed by X-ray fluorescence spectroscopy, which showed a sulfur level of 214 ppm. Taking into account that this value is representative of the quantity of alkyldibenzothiophenes (and more precisely 4,6-DMDBT) present as refractory molecules, an equimolar quantity of TNF was added and the heterogeneous mixture was stirred at room temperature. After 74 h, the sulfur level of the solution obtained after filtration was only 120 ppm.

A similar experiment was conducted with pure gas oil (1920 ppm sulfur, at least 50% being 4,6-DMDBT) and the same π -acceptor, leading to 840 ppm sulfur after 92 h stirring. In

Table 1 Capacity and selectivity factor values for DMDBT and MN for different complexing materials depending on the stirring time

π -Acceptors	α			C (%)
	4 h 30 min	29 h	96 h	
BQ	Soluble	—	—	—
DNF	—	—	—	—
AQ	—	—	3	50
DDQ	28	35	> 1000	48
TNF	137	> 1000	> 1000	37
TCNQ	10	132	191	51

these two examples, we have been able to remove 60 wt% of the initial sulfur containing compounds by formation of insoluble charge-transfer complexes. A detailed GC analysis would provide us with a precise distribution of the sulfur compounds contained in the residual gas oil. This work is in progress.

We have thus demonstrated that the sulfur compounds remaining in the gas oil after deep HDS (*i.e.* alkyldibenzothiophenes) are able to form stable electron donor-acceptor complexes with common π -acceptor compounds. These complexes are then easily separated from aliphatic/aromatic mixture by simple filtration. This behaviour is of major importance to the development of an analytical method for the determination of the exact composition and structure of the sulfur compounds contained in such mixtures. Work is in progress to create a polymer containing such a π -acceptor structure (and which is thus easily regenerated) and then a new process for limiting the sulfur level in the gas oil by formation and subsequent removal of charge-transfer complexes.

Notes and References

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