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Abstract

This study describes the use of model compounds combined with gas chromatography analysis as a simple method to characterize complex adsorption systems and to obtain information on the adsorption mechanism. The possibility of using adsorbents for the selective removal of nitrogenous compounds from petroleum fractions is demonstrated. The adsorbent chosen in this study is ilmenite treated with bromide. The extent of removal is high for basic nitrogenous compounds but low for acidic/neutral nitrogenous compounds.

INTRODUCTION

Nitrogenous compounds in crude oils and petroleum products have been associated with several problems in recovery and processing operations. They contribute to the emulsion problem encountered in the hot water separation process of bitumen from tar sand, to catalyst deactivation during upgrading, and to gum formation in oils and fuels during storage (*1*, *2*).

For these reasons, nitrogen must be removed from the feedstock in the early stages of upgrading. This is done by severe hydrotreating at high pressures and temperatures which has several disadvantages: high capital cost investment, degradation of valuable material, and high operating cost due to hydrogen consumption.

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A method allowing the separation of nitrogenous compounds from the feestock would greatly reduce the cost of upgrading synthetic crudes, decrease capital cost requirements, improve process efficiency by avoiding degradation and excessive hydrogen/energy requirements, and permit optimum use of the nitrogenous compounds.

Several analytical procedures are known for the separation and characterization of nitrogenous compounds. Jewell and Snyder used complex formation on supported ferric chloride and ion-exchange resins to isolate the "nonbasic" nitrogenous compounds from petroleum (*3*). Ford et al. (*4*) employed alumina adsorption chromatography to separate the nitrogenous compound types while Guerin et al. (*5*) used acid-base extraction and Sephadex LH-20 column chromatography. Ben'Kovski and Olzseva removed nitrogen compounds from diesel fuel by complexation with titanium tetrachloride (*6*). These methods are complex and are not designed for industrial scale. More recently Audeh (*7*) developed a method for large-scale (gallons) removal of nitrogenous compounds from lubricating oils using anhydrous hydrochloric acid adsorbed on an alumina-silica catalyst.

Work at Energy Research Laboratories has shown that various waste minerals could be used as low cost adsorbents for the removal of nitrogenous compounds from synthetic crudes. This paper describes the treatment of ilmenite and its adsorptive properties.

EXPERIMENTAL

Treatment of Ilmenite

Ilmenite ore was crushed to about 74 μm. The ore was taken from a site about 2.4 km southwest of St-Urbain and about 11.2 km north of the village of Baie St-Paul, Québec, on the north shore of the St. Lawrence River. Its elemental composition is given in Table 1. In a 100-mL round bottom flash equipped with a reflux condenser containing 15 g crushed ilmenite, an excess of bromine (about 10 mL) was added. The mixture was heated at 58°C for 2 h, cooled, and the excess bromine washed with 50 mL pentane. The treated ilmenite was filtered and then washed again with pentane until the solvent became colorless. The treated ilmenite was then dried with a stream of nitrogen and used as adsorbent. The treatment was also conducted at room temperature for 70 h.

TABLE 1
Typical Analysis of Ilmenite Ore from St-Urbain Deposits, Québec

Constituent	wt%
TiO_2	38.70
Fe_2O_3	18.64
FeO	28.66
SiO_2	4.27
Al_2O_3	4.00
MgO	4.80
CaO	0.50
MnO_2	0.12
Na_2O	0.05
V_2O_5	0.16
Cr_2O_5	0.08
NiO	0.10
CuO	0.04
BaO	0.01

Removal of Nitrogenous Components

A coker kerosene was obtained from Great Canadian Oil Sands. Its properties are given in Table 2. A coker kerosene sample of ~120 mL was percolated through a column packed with 10 g brominated ore. Eight fractions of the eluate were collected (two 5-mL and six 10-mL fractions) and analyzed for total nitrogen using a Dohrmann micro-coulometer Model C-200B.

Model Compound Study

To understand the adsorption mechanism, a standard solution of 18 nitrogenous compounds in toluene was prepared. Its composition is given in Table 3.

This solution was pumped continuously at 0.5 mL/min into a 30-cm long × 0.4 cm i.d. column, packed with 20 g treated ilmenite. A fraction collector was used to collect 5-mL samples which were subsequently analyzed using a Varian 6000 gas chromatograph equipped with a 12.5-m long SE-30 capillary column.

TABLE 2
Typical Properties of Coker Kerosene

Boiling range (°C)	193-279
Specific gravity (60/60°F)	0.871
Sulfur (wt%)	2.32
Nitrogen (ppm)	430
Pour point (°F)	Below −60
Cloud point (°F)	Below −60
Flash point (°F)	116
Vanadium (ppm)	0.40
Nickel (ppm)	0.36
Iron (ppm)	0.50
Ramsbottom carbon residue (10% bottoms) (wt%)	0.29
Aromatics and olefins (vol%)	58
Saturates (vol%)	42

TABLE 3
Composition of Standard Solution

Compound	ppm N
Aniline	30.12
1,2,5-Trimethylpyrrole	28.20
Benzylamine	39.79
n-Octylamine	32.62
Quinoline	32.02
n-Decylamine	27.08
Indole	29.37
3-Methylindole	26.74
2,2′-Dipyridyl	55.58
2-Phenylpyridine	24.26
1-Phenethylpiperidine	22.88
Dibenzylamine	26.48
Tetrahydrocarbazole	27.70
Carbazole	25.24
2-Methylacridine	19.40
3,4-Benzacridine	7.85
2-Aminochrysene	13.90
Phenothiazine	29.60
Total N concentration	518.21

Calculation

The fraction of each compount in each sample of effluent was calculated by comparing the corresponding peak area of the gas chromatogram for a particular sample with the area of this peak for the original solution.

$$\text{Fraction species } i = \frac{\text{area of peak } i \text{ in sample}}{\text{area of peak in feed}}$$

$$\text{Fraction total nitrogen} = \frac{\Sigma \text{ area of peak } i \text{ in sample}}{\Sigma \text{ area of peak } i \text{ in feed}}$$

No error analysis was done on these results.

RESULTS AND DISCUSSION

Industrial separation methods are significantly different from those of analytical separation. Analytical separation methods use only a very small portion of the available sites of the adsorbent: under these conditions the distribution isotherm is linear and there is no competition between compounds. In large-scale separation methods the feed is pumped continuously to the adsorbent bed until saturation occurs. At or close to saturation, competition between compounds will take place. For large-scale separation it is, therefore, important to characterize the system under saturation. Such characterization is obtained by measuring the breakthrough curve. The breakthrough point is a measure of the capacity of the adsorbent.

The breakthrough curve was measured for the standard feed containing 18 nitrogenous compounds. Figure 1 gives the fraction nitrogenous compounds in the feed vs volume pumped into the column. Breakthrough (Curve 2, Fig. 1) occurs around 40–60 mL: below that volume most of the nitrogenous compounds are retained by the brominated ilmenite.

An x-ray photoelectron spectroscopy (XPS) study of the brominated ilmenite showed the presence of $TiBr_x$ and $FeBr_x$ on the surface. These salts are readily soluble in methanol, and methanol-washed ilmenite lost its adsorption capacity for nitrogenous compounds (Curve 1, Fig. 1). The methanol solution extracted most of the bromide salts as evidenced by the dark-brown color of the extract. These results suggest that the

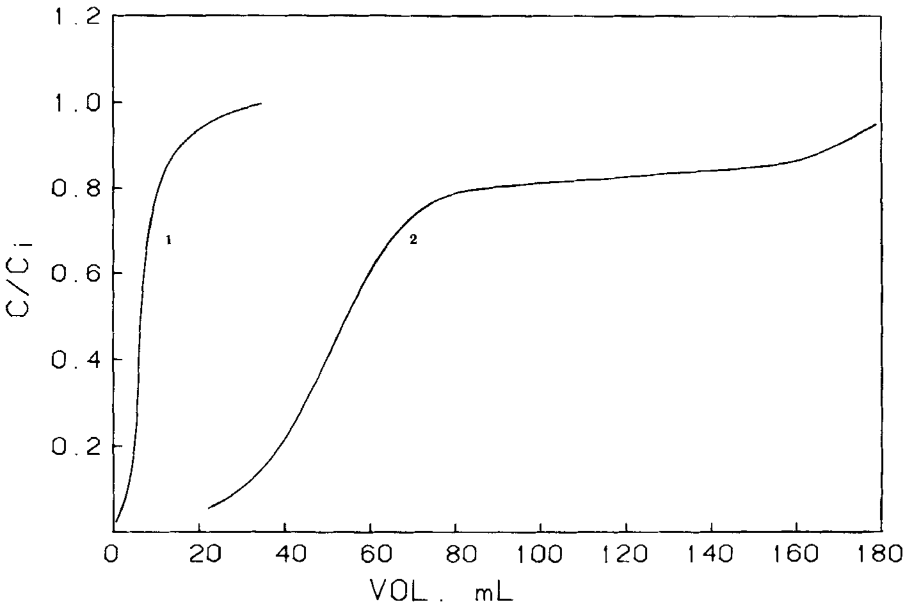

FIG. 1. Breakthrough curves for the adsorption of nitrogenous compounds on 1) brominated ilmenite washed with methanol; 2) brominated ilmenite.

bromide salts are responsible for the adsorption of the nitrogenous compounds.

To gain more insight into the mechanism of adsorption, the effluent was analyzed by gas chromatography (GC). This analysis showed that the 18 compounds have significantly different adsorption properties. Figure 2 shows the individual breakthrough curves. These results show that some compounds such as benzylamine and 2,2'-dipyridyl are extensively adsorbed by the treated ilmenite. These compounds are still completely retained by the ilmenite after 150 mL has been pumped into the column. Other compounds such as carbazole and indole are not extensively adsorbed and elution occurs after 40 mL. The amount of benzylamine adsorbed is at least 10 times that of carbazole. Table 4 shows the order of elution of the 18 compounds and the pK_a and proton affinity of the compound where possible. There seems to be a general correlation between the extent of adsorption and the basicity of the compound. Carbazole is acidic and elutes immediately while very basic compounds such as dibenzylamine and 2,2'-dipyridyl are still totally retained after 150 mL.

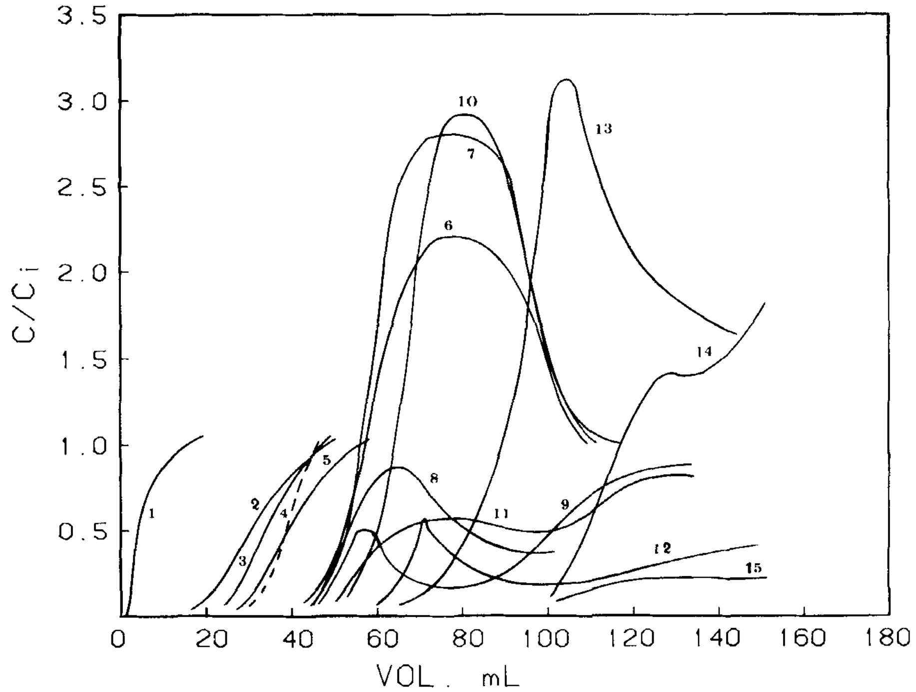

FIG. 2. Breakthrough curves of individual compounds 1) carbazole; 2) 3-methylindole; 3) phenothiazine; 4) indole; 5) tetrahydrocarbazole; 6) aniline; 7) 2-phenylpyridine; 8) 2-aminochrysene; 9) 1,2,5-trimethylpyrrole; 10) 3,4-benzacridine; 11) *n*-octylamine; 12) *n*-decylamine; 13) quinoline; 14) 2-methylacridine; 15) benzylamine. Not broken through: dibenzylamine; 1-phenetylpiperidine; 2,2′-dipyridyl.

Another important feature observed in Fig. 2 is that some compounds are irreversibly adsorbed while others are reversibly adsorbed. Compounds such as 3-methylindole, indole, and tetrahydrocarbazole are irreversibly adsorbed; in other words, these compounds have saturated the sites that were available to them and were not subsequently desorbed. Conversely, compounds such as aniline, 2-phenylpyridine, and 3,4-benzacridine are reversibly adsorbed. Their behavior is typical of displacement chromatography where a compound is desorbed by another, thus giving rise to a concentrated front that eventually elutes in the effluent. Figure 2 shows that these compounds elute in the effluent at a concentration of about three times that of the original feed. A rough mass balance indicates that these compounds are quantitatively desorbed

TABLE 4
Order of Breakthrough for Model Compounds

Curve from Fig. 2	Compound	Volume at which 10% is reached (mL)	PK_a (*11*)	Proton affinity (*12*)
1	Carbazole	1		
2	3-Methylindole	20		
3	Phenothiazine	25		
4	Indole	31		
5	Tetrahydrocarbazole	30		
6	Aniline	45	4.63	213.5
7	2-Phenylpyridine	45		
8	2-Aminochrysene	45		
9	1,2,5-Trimethylpyrrole	48		
10	3,4-Benzacridine	51		
11	*n*-Octylamine	55	10.65	
12	*n*-Decylamine	60	10.63	
13	Quinoline	65	4.90	228.4
14	2-Methylacridine	100		
15	Benzylamine	100	9.33	
16	1-Phenethylpiperidine	—		
17	2,2′-Dipyridyl	—		
18	Dibenzylamine	—		

and practially none is left on the column after the concentrated front has eluted. For this study, compounds were subdivided into four classes according to their adsorption behavior (Table 5).

Class 1 is composed of carbazole, tetrahydrocarbazole, indole, 3-methylindole, and phenothiazine. These compounds are not extensively retained (first five breakthrough curves in Fig. 2) and were irreversibly adsorbed. There is a striking similarity between these compounds; they are all acidic/neutral, and they have a pyrrole ring (except phenothiazine) and a proton on the nitrogen atom. This similarity is used to explain their adsorption mechanism.

It is well known that titanium halides will react with primary and secondary amines to form a complex (*8*). Nitrogenous compounds with an active hydrogen can displace halides to give complexes $X_2Ti(NHR)_2$ or $X_3Ti(NR_2)$. Similar reactions probably occur at the surface of the treated ilmenite for titanium and iron salts.

$$MX_x + n(NH_2R) \rightarrow X_{x-n}M(NHR)_n + nHBr \qquad (1)$$

TABLE 5
Classes of Compounds Based on Adsorption Behavior

Compound	Class	Basicity	Adsorption capacity	Reversibility
1. Carbazole	1	Acidic	Low	Irreversible
2. 3-Methylindole	1	Acidic	Low	Irreversible
3. Phenothiazine	1	Acidic/neutral	Low	Irreversible
4. Indole	1	Acidic/neutral	Low	Irreversible
5. Tetrahydrocarbazole	1	Acidic/neutral	Low	Irreversible
6. Aniline	2	Weak	Medium	Reversible
7. 2-Phenylpyridine	2	Weak	Medium	Reversible
10. 3,4-Benzacridine	2	Weak	Medium	Reversible
13. Quinoline	2	Weak	Medium	Reversible
14. 2-Methylacridine	2	Weak	Medium/high	Reversible
8. 2-Aminochrysene	3	Strong	High	—
9. 1,2,5-Trimethylpyrrole	3	Weak	Medium/high	—
11. *n*-Octylamine	3	Weak	Medium/high	—
12. *n*-Decylamine	3	Strong	Medium/high	—
15. Benzylamine	3	Strong	Very high	—
16. 1-Phenetylpiperidine	4	Strong	Very high	—
17. 2,2′-Dipyridyl	4	Strong	Very high	—
18. Dibenzylamine	4	Strong	Very high	—

or

$$MX_x + n(NHR_2) \rightarrow X_{x-n}M(NR_2)_n + nHBr \qquad (2)$$

where M = Ti or Fe
X = halide
n = 1 or 2 depending on the nature of the amine
R = alkyl group

In this case, adsorption is really a surface complexation. For the purposes of this paper, the term "adsorption" is used.

Class 3 is composed of trimethylpyrrole, *n*-octylamine, *n*-decylamine, and 2-aminochrysene. Every compound in this class except (trimethylpyrrole) is a primary amine and a strong base. These compounds are more quantitatively adsorbed than those of Classes 1 and 2. They probably react with the surface according to Eq. (1) and are likely to be in competition with the compounds of Class 1. Note that compounds in Class 1 were irreversibly adsorbed, which indicates that the following reaction did *not* take place:

$$X_{x-n}M(NR_2)_n + nNH_2R \rightarrow X_{x-n}M(NHR)_n + nNHR_2 \qquad (3)$$

The more basic primary amines did not displace the compounds of Class 1.

The difference in adsorption capacity between the various classes can be explained in terms of their relative basicity. The surface is made of sites of various activity. The site distribution is expected to resemble a Boltzmann distribution where the highly active sites represent only a small fraction of the sites. The extent of adsorption of the nitrogenous compounds with the surface Lewis acids will depend on the availability of the lone pair of electrons on the nitrogen atom. Compounds of Class 1 are not basic and will react only with the highly active sites. These active sites represent only a small percentage of the total sites, which explains the low level of adsorption of Class 1 compounds. Compounds of Classes 3 and 4 are much more basic and will react with a much broader range of sites than those of Class 1 and have a higher level of adsorption. Steric hindrance could also possibly play a role.

Contrary to Class 1, Class 2 compounds were reversibly adsorbed. These compounds are characterized by a weak basicity: all except aniline have a pyridine ring, are highly aromatic, and do not have an active hydrogen on the nitrogen atom. One possible mechanism of adsorption is through the donation of the electron pair of the nitrogen to the Lewis centers. (Physical forces interactions of the pi electrons with the surface and hydrogen bond formation are neglected.) The reaction can be illustrated as follows:

$$X_xM + :NR_3 \rightarrow X_xM:NR_3 \qquad (4)$$

Delocalization of the one pair of electrons over the ring decreases its availability for bonding, and these compounds will form only weak bonds with the surface. This reaction is found to be reversible. The more basic compounds of Classes 3 and 4 probably displace compounds of Class 2 according to the reaction

$$X_xM:NR_3 + nNH_2R \rightarrow X_{x-n}M(NHR)_n + :NR_3 + nHBr \qquad (5)$$

Class 4 compounds have the highest adsorption affinity for the surface. These compounds are basic and will react with a greater portion of the sites. 2,2′-Dipyridyl is particularly interesting. It does not have an active hydrogen, but is known to be a strong ligand (9). It gives stronger complexes than such ligands as primary and secondary amines. It probably reacts with the surface in a way similar to that described by Eq. (4).

Finally, the treated ilmenite was tested for its ability to remove the nitrogenous compounds from a coker kerosene. As expected from the model compound study, some nitrogenous compounds broke through immediately: after 10 mL the nitrogen concentration in the effluent increased to 40 ppm (Fig. 3). Treated ilmenite was much more effective in removing nitrogenous compounds than natural ilmenite. The nitrogenous compounds of the kerosene that are not being removed are probably the acidic/neutral types.

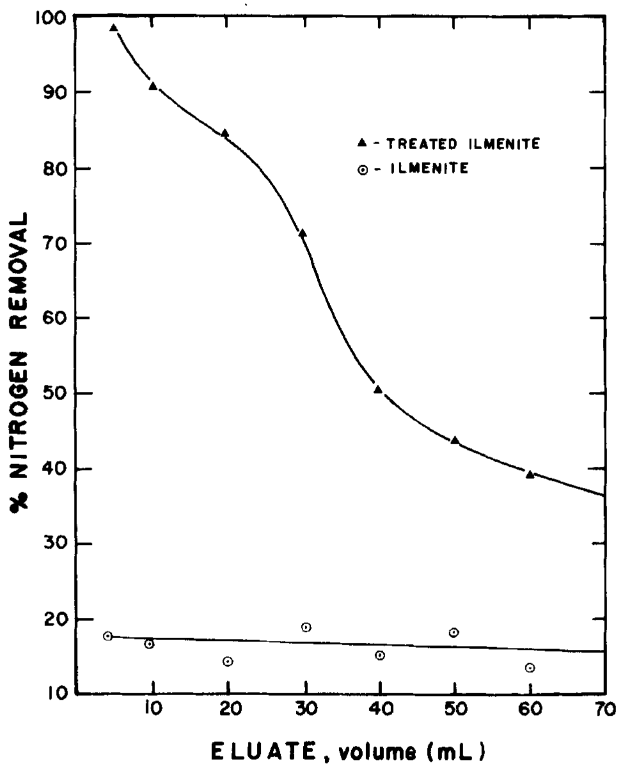

FIG. 3. Comparison of ilmenite with treated ilmenite for removing nitrogen from coker kerosene.

It was noted during our experiments that some of the complexes formed between the salts and the nitrogenous compounds were entrained in the effluent. Although in small concentrations, titanium and iron salts were found in the effluent. Stability is also affected by the presence of any trace of moisture which would hydrolyze the metal-bromide bond and destroy the active sites while liberating toxic HBr.

CONCLUSIONS

The aim of this study was to design a simple experiment that would yield information on the adsorption mechanism. The use of model compounds combined with gas chromatography analysis allow us to follow the fate of individual compounds present in a complex mixture.

The broad nature of the nitrogenous compounds contained in petroleum fractions makes it very difficult to remove them selectively. These compounds cover a broad range of polarity, structure, degree of substitution, basicity, boiling point, etc. Their selective removal, indiscriminately, implies equal attraction to the adsorbent regardless of their nature.

Treated ilmenite did not remove all nitrogenous compounds equally. The extent of adsorption was high for basic compounds but low for acidic/neutral compounds. The degree of adsorption of the nitrogenous compounds in the case of treated ilmenite depends on their ability to form complexes with the Lewis acid centers. This ability is a function of the nature of the compounds. Nonetheless, this study shows that some classes of compounds can be selectively removed. For instance, all Class 3 compounds can be removed using treated ilmenite.

This study points out the difficulty of finding one adsorbent that can remove widely different compounds. To be effective, such an adsorbent must capitalize on a characteristic common to all nitrogenous compounds. A classic example is the separation of straight chain paraffins from branched paraffins using zeolites. There may not be such a common characteristic for nitrogenous compounds. It may be possible to use a combination of adsorbents that complement each other. For instance, an adsorbent showing high selectivity for Class 1 compounds could be combined with treated ilmenite.

Work is presently in progress in our laboratories to identify other adsorbents where the adsorption mechanism is not based on acid/base character alone. The effort is directed at improving the selectivity for acidic/neutral nitrogenous compounds and also at improving the adsorption capacity.

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