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Preparative Fractionation of Petroleum Heavy Ends by Ion Exchange Chromatography

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Different separation methods are currently used to evaluate the composition of heavy ends. They are based either on separation into asphaltenes and maltenes by using heptane precipitation of asphaltenes followed by fractionation of maltenes on alumina into saturates, aromatics, and resins using solvents with increasing elution strength (1) or else on selective removal of acids and bases followed by the separation of neutrals. According to the American Petroleum Institute API 60 procedure, this separation is achieved by using anion and cation exchange resins and alumina (2). According to Amat et al. (3) and Schmitter et al. (4), the selective extraction of bases and acids is performed by using, respectively, silica modified with hydrochloric or polyphosphoric acid and potassium hydroxide.

These methods are time-consuming, and faster procedures devoted to the separation of saturates, aromatics, resins, and asphaltenes (S.A.R.A.) have been developed (5, 6).

This paper discusses the initial experiments made to improve, in terms of time and solvent consumption, the separation scheme of heavy ends into fractions of acids, bases, and neutral compounds. This method is derived from the API 60 procedure (2) and like it can be applied to whole crude oils as well as to the maltenes, resins, and asphaltenes fraction.

EXPERIMENTAL SECTION

Apparatus. The experimental chromatography assembly (Figure 1) is a modular component system consisting of a Haskell Model MCP 110 pneumatic pump (Haskell Engineering and Supply Co., Burbank, CA), a pulse dampener (Touzart et Matignon, Vitry/Seine, France), a splitter (Waters Associates, Inc., Milford, MA), a Waters Associates Model 401 differential refractometer (Waters Associates, Inc., Milford, MA), a Rheodyne injection valve (Rheodyne, Inc., Cotati, CA), equipped with a 10-mL sample loop, a heat exchanger made from a 1.65 mm i.d. \times 2.5 m length of stainless steel tubing shaped in a spiral and fitted in a heating jacket, and three three-way valves (Hoke, Inc., Cresskill, NJ) allowing the columns either to be set on line or to be bypassed. The different parts are connected with 4.7 mm i.d. stainless steel tubing (Touzart et Matignon, Ivry/Seine, France), except for the splitter-detector connection where a 0.25 mm i.d. stainless steel tubing is used. The two columns utilized are two 2 cm i.d. \times 30 cm length sections of stainless tubing dry packed respectively with 16-50 mesh Amberlite IRA 904 and 16-50 mesh Amberlyst A 15 (Rohm and Haas Co., Philadelphia, PA).

In order to exhibit maximum effectiveness for petroleum applications according to Jewell (7), the resin must be converted to hydroxide form (IRA 904) and hydrogen form (A 15). This is performed by stirring with 10% potassium hydroxide in methanol (IRA 904) and by stirring with 10% aqueous HCl in methanol (A 15). Both of these activations are followed by exhaustive washings with methanol, benzene, and finally *n*-heptane.

Reagents. Cyclohexane, benzene, and methanol (RP Normapur quality) were obtained from Prolabo and purified by distillation; diethylamine (reagent grade, Fluka) was used as received.

Samples. The residues (bp > 350 °C) used to test the proposed method come from the Safanyia oil field (Saudi Arabia) and Boscan oil field (Venezuela). The residues are, respectively, a viscous liquid and semisolid tar. Moreover we have studied the maltene fraction (viscous liquid) and the asphaltene fraction (hard

solid) of these two residues. In this study we only present data from Safanyia.

Procedure. Through control of valves V_a and V_b , the pneumatic pump drives the circulating fluid through either both columns (I and II) or only one of them (I or II). An on-line detector is used to monitor, and then to optimize, the elution through the system. The eluate is preheated to speed up solvent evaporation. The solvent is removed from the fraction by distillation and then recycled. All of the concentrated fractions are recovered. During the equilibrium setup of the chromatographic system, the concentration device is bypassed by using the three-way valve V_c .

Column I is packed with anion exchange resin, and column II is packed with cation exchange resin.

The sample (3-3.5 g) was dissolved in a minimum of cyclohexane (a benzene-cyclohexane (40/60) mixture was used as solvent for asphaltenes) and the solution was fed into the sample loop injector. During the injection procedure and the elution of the neutral fraction, the flow rate was set at 400 mL/h and then the pump was regulated to maintain a flow rate of 3 L/h. Under such conditions, pressure was 40-50 atm. The eluting sequence was the one used by Mc Kay (8): cyclohexane was used to wash out the neutral fraction (columns I and II on-line), the benzene was used to eluate the weak acids fraction (column I on-line) and the weak bases fraction (column II on-line). The benzene-methanol (60/40) azeotropic mixture was used to recover the moderate acid fraction (column I on-line) and the moderate base fraction (column II on-line). CO_2 saturated benzene-methanol (60/40) was used to elute the strong acid fraction (column I on-line), and benzene-methanol (60/40) containing 10% diethylamine was used to wash out the strong base fraction (column II on-line). The used criteria for changing solvents is a lack of response of the detector set at high sensitivity. When the mobile phase is changed, the system can easily be emptied by using a purge valve in the lower part of the assembly.

RESULTS AND DISCUSSION

Seven fractions were generated by using this separation scheme: one containing the neutral compounds, three containing the most acidic compounds, and three containing the most basic compounds. The neutral fraction elutes within approximately 3 h, and the other fractions elute within less than 30 min each. The whole separation procedure requires less than 6 h. This is a major improvement compared to the 8 days required by the standard API 60 procedure. The recycling procedure keeps the mobile-phase consumption to a decent level of 0.5 L for each eluted fraction.

Tables I and II exhibit results gained from fractionation of maltenes and asphaltenes. Balance is good; moreover the amount of each fraction and its structural parameters, according to spectrometric analysis (NMR, IR) and ultracentrifugation data (9), closely match those produced by the standard API 60 procedure.

This procedure is perfectly suited for crude oils, maltenes, and resins; but problems arise when dealing with asphaltenes. Since asphaltenes have low solubility in cyclohexane, the first eluent for the elution sequence, a precipitation phenomenon occurs at the column head, adding a selective dissolution situation to the ion exchange chromatography. In order to investigate to what extent this overlapping phenomenon interferes in the asphaltene case, we carried out a separation

Table I. Comparison of Open Column and Fast Preparative API 60 Data for Maltenes (Safanya)

fraction	API 60 procedure: open column		API 60 derived procedure: fast preparative API 60			
	M1 wt %	elution time, h	M2 wt %	M3 wt %	av wt % ^a	elution time, h
neutrals	79	66 (42 + 24)	78	80	79 ± 1	3
weak acids	13	12	12	12	12 ± 1	0.5
moderate acids	2	12	4	2	3 ± 1	0.5
strong acids	0	8	0	0	0	0.5
total acids	15	32	16	14	15 ± 1	1.5
weak bases	1	12	1	1	1 ± 0.5	0.5
moderate bases	2	12	3	2	2.5 ± 0.5	0.5
strong bases	2	8	2	2	2 ± 0.5	0.5
total bases	5	32	6	5	5.5 ± 0.5	1.5
balance	99	130	100	99		6

^a Quoted precision is based on the maximum average error obtained for each specific kind of fraction.

Table II. Comparison of Open Column and Fast Preparative API 60 Data for Asphaltenes (Safanya)

fraction	API 60 procedure: open column			API 60 derived procedure: fast preparative API 60			
	A1 wt %	A2 wt %	av wt % ^a	A3 wt %	A4 wt %	A5 wt %	av wt % ^a
neutrals	26	30	28 ± 2	26	32	31	29.5 ± 3.5
weak acids	48	46	47 ± 1.5	49	45	46	47 ± 2
moderate acids	9	8	8.5 ± 1	10	7	8	8.5 ± 2.5
strong acids	2	2	2 ± 0.5	2	2	2	2 ± 0.5
total acids	59	56	57.5 ± 2	61	54	56	57.5 ± 3.5
weak bases	3	5	4 ± 1	5	7	8	6.5 ± 1.5
moderate bases	5	4	4.5 ± 1	4	3	2	3 ± 1
strong bases	2	2	2 ± 0.5	2	2	2	2 ± 0.5
total bases	10	11	10.5 ± 1	11	12	13	12 ± 2
balance	95	97		98	98	99	

^a Quoted precision is based on the maximum average error obtained for each procedure and for each specific kind of fraction.

Table III. Fractionation of Asphaltenes (Safanya) with a Benzene-Cyclohexane (60/40) Mixture as First Eluents, Influence of the Equilibration Time

fraction	equilibration time allowed after the elution of the neutral fraction					
	without equilibration			overnight equilibration		
	A1 wt %	A2 wt %	av wt % ^a	A3 wt %	A4 wt %	av wt % ^a
neutrals	52	50	51 ± 3.5	55	48	51 ± 3.5
weak acids	29	26	27.5 ± 2	8	5	6.5 ± 2
moderate acids	4	3	3.5 ± 2.5	18	23	20.5 ± 2.5
strong acids	1	1	1 ± 0.5	2	3	2.5 ± 0.5
total acids	34	30	32 ± 2	28	31	29.5 ± 2
weak bases	5	7	6 ± 1.5	0.5	0.5	0.5 ± 1.5
moderate bases	4	6	5 ± 1	13	12	12.5 ± 1
strong bases	2	2	2 ± 0.5	1.5	2	1.75 ± 0.5
total bases	11	15	13 ± 2	15	14.5	14.75 ± 2
balance	97	95		98	93.5	

^a Quoted precision is based on the maximum average error obtained for each procedure and for each specific kind of fraction.

run using benzene-cyclohexane as the first eluent. The results are shown in Table III. As a matter of fact, when Table II and Table III are compared, it can be pointed out that the relative proportion of neutral and acid compounds was altered, with the former increasing and the latter decreasing. This behavior might have been expected. More surprising is the observation that the base fractions are not affected.

We were also concerned by problems dealing with interactions with the solid phase because of the high mass transfer times which can be expected from the mesh size of the ion exchange resins used. Therefore, we considered the dependence of the separation as a function of the time, that the first eluent (either neat cyclohexane or 60/40 benzene/cyclohexane) remained in the system after recovering the neutral fraction.

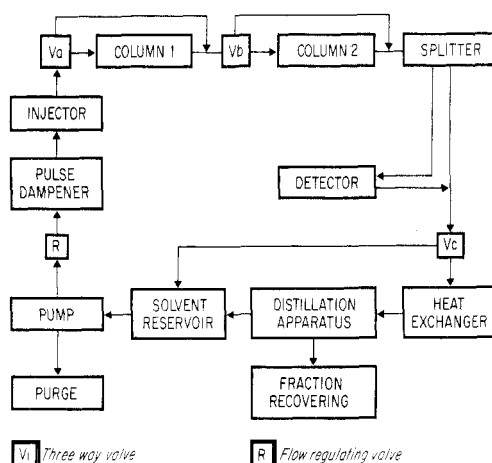


Figure 1. The experimental chromatography assembly.

It can be noted on Table III that a difference appears in the proportion of weak acids and weak bases related to moderate acids and moderate bases which is modified, with the distribution of strong acids and strong bases remaining basically the same. In spite of these differences, the balance and reproducibility remain acceptable.

So the separation scheme described here can be used as a preparative method which is well suited for crude oils, heavy ends, maltenes, and resins.

However, we have outlined the limitations of the standard eluting sequence when dealing with asphaltenes. To overcome the interference effect of the low solubility of asphaltenes in cyclohexane, we have suggested using a cyclohexane-benzene (60/40) mixture as the first eluent. But we must be aware that such a change obviously modified the meaning of the neutral, acid, and basic fractions recovered which no longer match the corresponding API 60 fractions.

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Determination of Ethylenediaminetetraacetic Acid in Boiler Water by Liquid Chromatography

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Tetrasodium ethylenediaminetetraacetate (Na_4EDTA) is an active ingredient in boiler treatment formulations, and it has been used for metal oxide solubilization and for maintenance of metal ions in a sequestered state in solution (1, 2). At high temperatures (200 °C), EDTA may decompose forming iminodiacetate (IDA) and other degradation products (1-3). It is therefore imperative that a procedure be devised that would allow a determination of total EDTA in boiler water.

The ASTM method for determination of EDTA is based on a spectrophotometric determination of the reduction of color intensity in a solution containing zirconium and xylenol orange indicator (4). The method is susceptible to interference from other chelating agents and phosphate which can be present in boiler water up to the range 10-25 mg/L (2).

A variety of chromatographic methods have been developed for the analysis of EDTA. Gas chromatography has been used for the simultaneous determination of EDTA, IDA, and *N*-(2-hydroxyethyl)iminodiacetate, HEIDA (5). The method however involves a preliminary derivitization step which is time-consuming. An ion chromatography method is available, but the method may be susceptible to interference from phosphate ion, and it has a limited linear range (6). Two methods utilizing ion pair high-performance liquid chroma-

tography (HPLC) have been reported; however, the methods are based on the formation of a stable $\text{Cu}(\text{EDTA})^{2-}$ complex (7, 8). These methods are not applicable to boiler water samples which contain large amounts of iron and nickel which compete effectively with copper for the EDTA.

In order to circumvent most of the limitations in the current procedures, we have devised an HPLC procedure which can determine total EDTA in the presence of Fe^{3+} , Cu^{2+} , Ni^{2+} , phosphate, Ca^{2+} , and Mg^{2+} . The method is based on the chromatographic determination of $\text{Fe}(\text{EDTA})^-$ using octadecylsilane (ODS) bonded phase as the stationary phase and tetrabutylammonium bromide (TBABr) in acetate buffer as the mobile phase.

EXPERIMENTAL SECTION

Apparatus. The liquid chromatography was performed with a Varian 8500 pump equipped with an Aerograph high-pressure septumless injector. A Whatman guard column adapted with a Varian inlet fitting and filled with CO: Pell ODS 30-38 μ packing material was prepositioned prior to the analytical column (Ultrasphere ODS-5 μ , 4.6 mm i.d., 25 cm long). An Aerograph 254-nm UV detector and a Heath Schlumberger dual pen chart recorder were also used. Helium was used as the solvent pressurizing gas.

An SMI IIIA direct current argon plasma emission spectrometer (Spectrametrics, Inc., Andover, MA) was used for the element analyses.

Reagents and Chemicals. Water was obtained from a Millipore Water Purification System. Methanol was obtained from

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