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DETERMINATION OF THE ACIDITY INDEX OF ASPHALTS BY MEANS OF THERMOMETRIC TITRATIONS. COMPARISON WITH OTHER METHODS

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ABSTRACT

Different direct and back titration methods have been applied to determine the acidity index of asphalts. Thermometric titration presents not only the standard acidity, but also a supplementary value corresponding to weak acid compounds, which can be used to characterize different kinds of asphalts. Basicity index determination by thermometric techniques has also been considered.

A substantial advantage of the thermometric techniques is that it is not necessary to regenerate the transducer, which can be handled without any special care.

INTRODUCTION

Asphaltic emulsions are an example of cold application of asphalts in pavement, as they are usually an ambient-temperature asphalt supply.

These emulsions are a two-phase mixture: asphalt and water. They can be prepared in two different ways, one in which the asphalt base is dispersed in water (external phase), the other in which water is dispersed in asphalt (external phase), named o/w and w/o, respectively. A third component, named emulsifier or dispersant agent, is also added.

The acid components, like naphthenic acid, present in the asphalts in variable amounts, are beneficial for achieving o/w emulsions. Due to these reasons, asphalts coming from Venezuelan and Sicilian crudes are easily emulsifiable, due to their high acidity index.

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The acidity index is a measure of the acid content of asphalts, and is therefore used to detect their capacity to be emulsified. Asphalts that are easily emulsified present acidity indexes higher than 1.0, those moderately emulsifiable between 0.5 and 0.9, and those that are difficult or not emulsifiable show acidity indexes less than 0.6 [1]. In order to emulsify this last kind of asphalt, it is necessary to add acid compounds (above all, naphthalenic acids) to increase their acidity index to values higher than 1.0.

On the other hand, acidity indexes are a measure of the tendency of a metal to corrode when in contact with asphalts [2].

It is also convenient to point out the existence of several nitrogenated bases in asphalts. In the literature, several studies about organic acids and nitrogenated bases in asphalts can be found [1].

At present, the determinating acidity indexes of asphalts is usually carried out by direct potentiometry with hydroalcoholic KOH (ASTM D-664 [3] and IP 177 [4] methods), or by means of back titrations, after KOH addition and using HCl as titrant (IP-213/82 method [5]).

In the present paper we have performed a comparative study of the results obtained by means of the official methods [3–5], with those obtained by thermometric titrations.

The results obtained using tetra-*n*-butylammonium hydroxide as titrant are also presented.

An attempt to determine the asphalt basicity has also been performed.

This work is a continuation of previous thermometric titration applications to determine the acidity index of petroleum derivatives [6].

EXPERIMENTAL

To perform this work we have chosen several asphalts coming from different origins, listed in Table 1.

First we have studied different methods of determining the acidity index by direct titration: potentiometric titration with KOH [3,4] (method A), potentiometric titration with TBA (method B), and thermometric titration with KOH (method C).

With respect to back titrations, we have compared the official method with indicator (IP 213/82, [5] method D), a back potentiometric titration (method E), and a back thermometric titration (method F).

Reagents and apparatus

Method A: direct potentiometric titration with KOH [3,4]

The titrant was a hydroalcoholic solution (isopropanol/water, 80 : 20, v/v) of 0.1 M KOH, using a (50 : 49.5 : 0.5 (v/v)) toluene/isopropanol/water mixture as titration medium. For each titration, 125 ml of the last mixture was used.

TABLE 1

Selected asphalts

Sample	Asphalt crude procedure [a]	Penetration at 25°C (ASTM D-5)
1	Lagune (Venezuelan)	51
2	MCV-Mx	64
3	MCMx	50
4	Boscan (Venezuelan)	55
5	MC	62
6	MC	46
7	MC	89
8	MC	173
9	MC	229
10	MCEg-I	53

[a] MCV-Mx = Venezuelan and Mexican crude mixture; MCMx = mainly Mexican crude mixture; MC = mainly Venezuelan crude mixture; MCEg-I = Egyptian and Italian crude mixture. All asphalts are of the "straight-run" type, that is, obtained from direct distillation of the crude.

Potentiometric measurements were performed with a Crison 74 potentiometer using a Metrohm AG 9100 Herisau combined glass electrode.

Method B: direct potentiometric titration with TBA

In this case 0.1 M tetra-*n*-butylammonium hydroxide was used as titrant, prepared in a propanol/methanol mixture (2 : 1). As solvent medium a 50 : 40 : 30 (v/v) toluene/MIK/isopropyl alcohol mixture was used.

Titrations were carried out with a Metrohm E-536 potentiometer, a Metrohm E-535 autoburette, a Metrohm E-427 reference electrode with a salt bridge filled with absolute alcohol saturated with LiCl, and an EA-109 glass electrode. Titrant addition speed was 0.1 ml min^{-1}.

Method C: direct thermometric titration with KOH

An isopropanol 0.5 M KOH solution was used as titrant. A toluene/isopropanol mixture (3 : 1, v/v) was chosen as solvent medium. Due to the volume capacity of the cell, 70 ml of this mixture was used for each titration.

Apparatus for thermometric titration has been described elsewhere [6] consisting of a nyon cell, a 100 kΩ thermistor (thermometer type), an ABU 12 Radiometer autoburette, a Konik KNK 801-949 register and a conventional voltage source.

Method D: back titration with indicator [5]

The base added in sufficient excess to displace the equilibrium was 0.1 M KOH, whereas 0.1 M HCl was used as titrant, both in aqueous medium. Alkali blue 6B (2% in ethanol) was used as indicator.

As medium we have chosen a 60 : 136 : 24 : 20 (v/v) toluene/isopropyl alcohol/water/indicator mixture.

Method E: back potentiometric titration

TBA (0.1 M) in isopropanol/methanol (2 : 1) was used as base, the excess being determined by hydroalcoholic 0.1 M HCl.

The solvent was a 50 : 20 (v/v) toluene/isopropyl alcohol mixture. The solvent used in methods A and D brought on the precipitation of asphaltenes, and hence the glass electrode was soiled, producing erroneous potential readings. The selected medium prevented the use of KOH as base, since in this medium KCl is insoluble, causing problems in potential measurements. Due to these reasons we have chosen 0.1 M TBA in alcoholic medium as base. Potential measurements were carried out with the apparatus described in method A.

Method F: back thermometric titration

The sample was dissolved in a 50 : 20 : 10 (v/v) toluene/isopropyl alcohol/TBA 0.1 N in alcohol mixture. HCl (0.5 M) in isopropanol was used as titrant.

Method G: direct thermometric titration with HCl

HCl (0.5 M) in isopropanol was used as titrant, and a 50 : 20 (v/v) toluene/isopropanol mixture as titration solvent.

PROCEDURE AND RESULTS

While in potentiometric titrations about 5 g of asphalt were used, in thermometric titrations from 10 to 15 g of sample were needed.

First, the asphalt was dissolved (with slight heating) in toluene and then the remaining products were added to reach the medium composition described for each kind of titration.

The acidity index has been expressed in mg KOH/g of sample. Results obtained by the different methods are shown in Table 2.

As it can be observed, acidity index values obtained by methods A and B (potentiometric titrations with KOH and TBA, respectively) are coincident, whereas those resulting from thermometric titrations are higher.

Except for asphalts No. 1 and 3 that present only one slope in the titration curve, the others give titration curves with two clearly different zones, as we can appreciate in Fig. 1 and Table 2. The first interval, which can be assigned to acid compounds of the same strength as carboxylic acids, agrees with the acidity indexes obtained with methods A and B. The second interval corresponds to weaker acids, which cannot be titrated by Gibbs methods (KOH and TBA).

TABLE 2

Acidity index determination by direct titrations (mg KOH/g sample)

Sample	Pot. titrat. with KOH, method A [a]	Pot. titrat. with TBA, method B [b]	Thermomet. titrat. with KOH, method C [a]		
			1st stage	2nd stage	Total
1	2.81 ± 0.09	2.93 ± 0.08	3.23 ± 0.04	–	3.23 ± 0.04
2	1.07 ± 0.08	1.06 ± 0.01	0.98 ± 0.04	0.45 ± 0.04	1.43 ± 0.04
3	0.30 ± 0.05	0.40 ± 0.06	0.70 ± 0.05	–	0.70 ± 0.05
4	1.27 ± 0.07	1.20 ± 0.08	1.24 ± 0.03	0.72 ± 0.02	1.93 ± 0.04
5	1.43 ± 0.06	1.50 ± 0.05	1.36 ± 0.09	0.51 ± 0.06	1.87 ± 0.10
6	1.56 ± 0.07	1.61 ± 0.05	1.50 ± 0.08	0.58 ± 0.02	2.08 ± 0.06
7	1.03 ± 0.09	1.08 ± 0.03	1.15 ± 0.10	0.81 ± 0.08	2.06 ± 0.09
8	1.35 ± 0.08	1.30 ± 0.07	1.19 ± 0.02	0.61 ± 0.02	1.80 ± 0.02
9	1.95 ± 0.10	2.07 ± 0.03	1.90 ± 0.09	0.48 ± 0.04	2.38 ± 0.07
10	0.54 ± 0.04	0.60 ± 0.05	0.51 ± 0.02	0.73 ± 0.09	1.25 ± 0.07

[a] Results from two determinations.

[b] Results from three determinations.

In a previous paper [6] we pointed out that the relationship between the two intervals or slopes obtained in the thermometric titrations, or the existence of only one interval, were characteristic for petroleum distillates coming from the same crude.

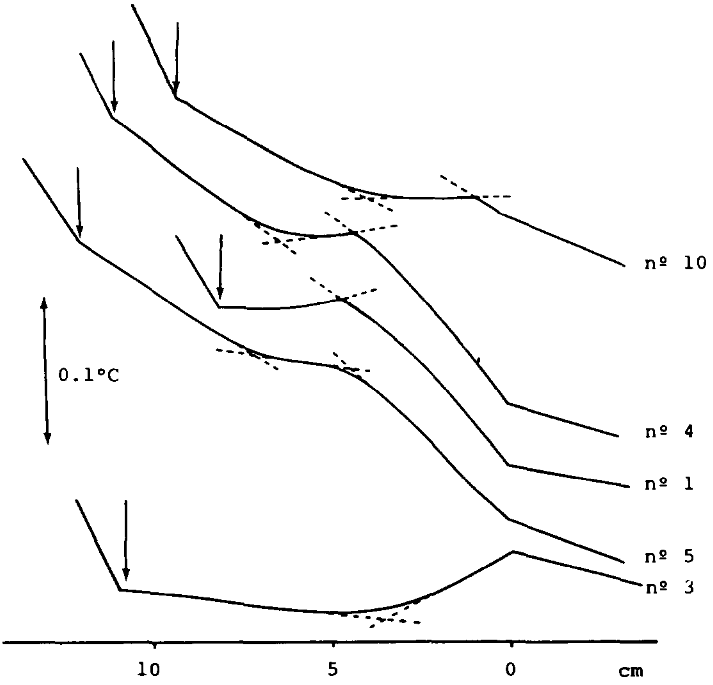

Fig. 1. Direct thermometric titrations of asphalts. The arrows indicate the end of the addition.

Thus, in distillates of the Lagune crude and in its asphalt, only one interval can be observed in the thermometric titration curve. From these results we can conclude that its acid components show the same strength as the carboxylic acids.

For Boscan crude and its derivatives (asphalt and distillates) there are two clearly different intervals, one which shows an acidity like that of the carboxylic acids (first interval), and another corresponding to much weaker acids (second interval), being the equivalent of the second zone a little lower than the first.

In asphalt No. 3, only a very rounded curve can be appreciated, which shows the existence of only very weak acids. These results differ from those obtained for the distillates of the same crude mixture, where two intervals (not well defined) can be observed, the second being substantially longer than the first.

The fact that the overall acidity found by thermometric titrations does not agree with the other methods has encouraged us to compare these results to those obtained from back titrations, also defined as standard methods [5].

Acidity indexes obtained by means of back titrations are shown in Table 3.

Although values obtained by potentiometric and thermometric techniques are similar, values resulting from the use of indicators are quite different, being much lower than expected. Results obtained by indicator titrations (method D) are similar to those obtained in direct titrations (methods A and B), some even lower.

Values resulting from methods E and F completely agree with those found from direct thermometric titrations (method C) when the sum of the two

TABLE 3

Acidity index determination by back titration (mg KOH/g sample)

Sample	Back titrat. with indicator, method D [a]	Back potent. titrat., method E [b]	Back thermom. titrat., method F [a]
1	2.67 ± 0.12	3.28 ± 0.07	3.35 ± 0.09
2	1.01 ± 0.09	1.32 ± 0.04	1.37 ± 0.05
3	0.32 ± 0.05	0.66 ± 0.03	0.70 ± 0.04
4	1.28 ± 0.11	1.95 ± 0.05	1.88 ± 0.07
5	1.45 ± 0.10	1.91 ± 0.08	1.98 ± 0.07
6	1.38 ± 0.09	2.07 ± 0.05	2.06 ± 0.09
7	1.06 ± 0.06	2.12 ± 0.09	2.05 ± 0.09
8	1.25 ± 0.11	1.70 ± 0.07	1.67 ± 0.08
9	1.84 ± 0.07	2.19 ± 0.02	2.31 ± 0.10
10	0.47 ± 0.08	1.10 ± 0.09	1.17 ± 0.10

[a] Results from two determinations.

[b] Results from three determinations.

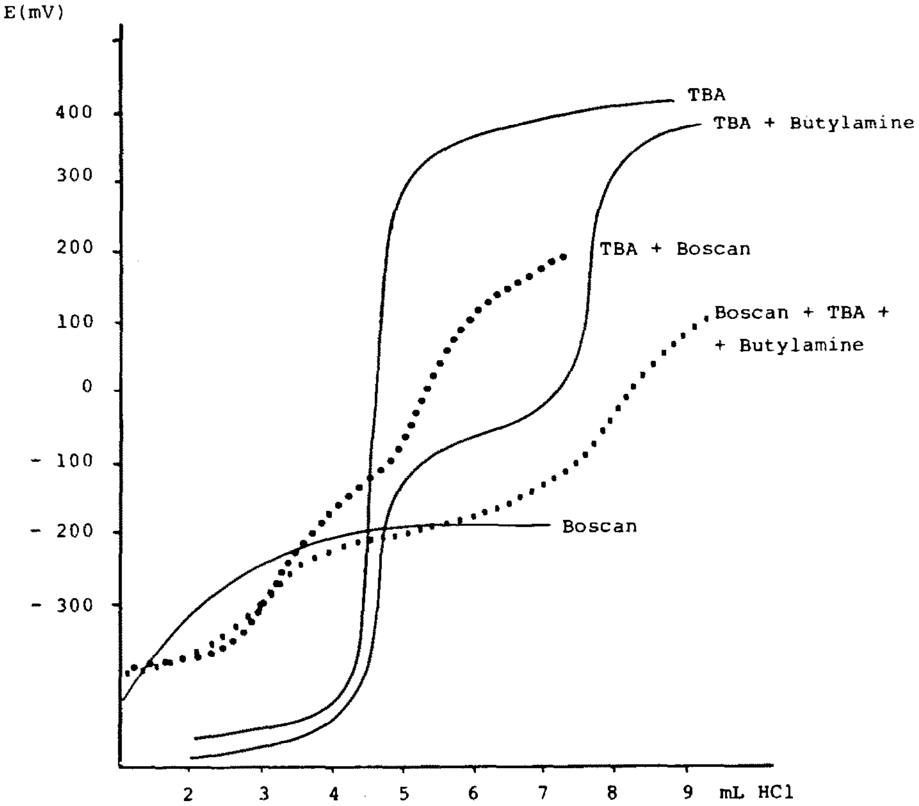

Fig. 2. Back potentiometric titrations of asphalts.

different acid intervals is considered (total acidity), which confirms the validity of thermometric titrations to determine the total acidity of asphalts.

In back potentiometric titration (method E), two stages can be observed, the first due to the titration of excess added base and the second due to the weak bases contained in the asphalts. Direct thermometric titration with HCl confirmed the existence of weak bases.

Addition of *n*-butylamine to the asphalt solution to be titrated, shifted the second stage (Fig. 2), which confirmed the presence of some bases in the asphalts of similar strength to *n*-butylamine.

Similar results were obtained when back thermometric titrations were performed (Fig. 3), where, after titration of excess base, a second, well-defined endothermic stage is observed (which indicates the presence of weak bases), sometimes a third exothermic stage appears, not well defined, which shows the presence of the other very weak bases, which are very difficult to determine.

The existence of this basicity in the asphalt has encouraged us to compare the results obtained by the different selected methods. These results can be observed in Table 4.

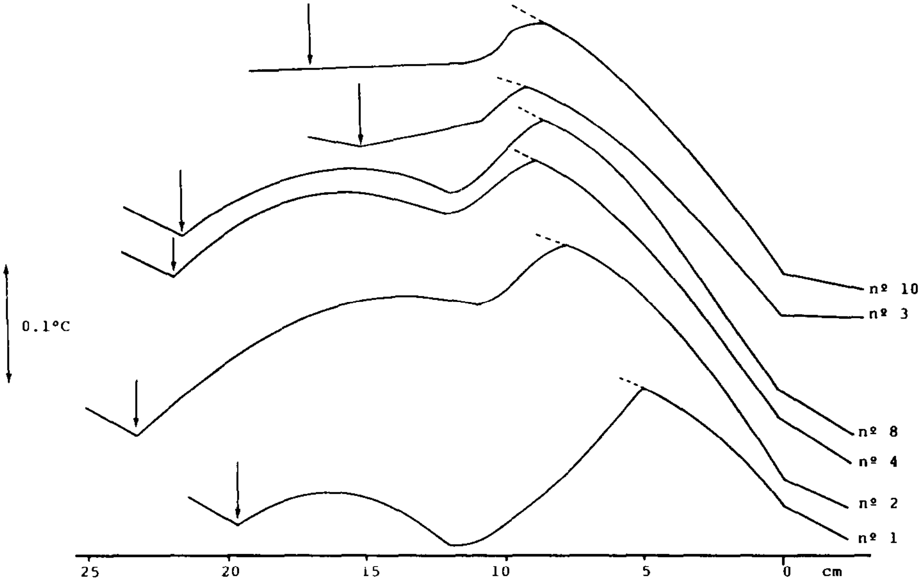

Fig. 3. Back thermometric titrations of asphalts.

Results obtained from back potentiometric titrations and back thermometric titrations are coincident, whereas those obtained by direct thermometry are, except for asphalt No. 1 (Laguna), much higher. This can be easily explained, since from back thermometric titrations (Fig. 3), a certain very weak, non-determinable basicity could be detected, a basicity which can be only determined by the direct method.

TABLE 4

Basicity indexes (mg KOH/g sample)

Sample	Back potent., method E [a]	Back therm., method F [b]	Direct therm. HCl, method G [b]
1	3.83 ± 0.10	3.69 ± 0.10	3.78 ± 0.08
2	1.64 ± 0.08	1.67 ± 0.10	3.43 ± 0.16
3	0.63 ± 0.07	0.70 ± 0.05	3.30 ± 0.12
4	2.24 ± 0.12	2.30 ± 0.07	3.33 ± 0.09
5	2.03 ± 0.09	2.16 ± 0.09	2.91 ± 0.08
6	2.07 ± 0.10	2.20 ± 0.08	4.12 ± 0.16
7	2.12 ± 0.09	2.15 ± 0.07	2.63 ± 0.10
8	1.74 ± 0.08	1.77 ± 0.09	2.76 ± 0.12
9	2.52 ± 0.13	2.61 ± 0.10	3.49 ± 0.14
10	1.11 ± 0.03	1.15 ± 0.10	4.23 ± 0.17

[a] Results from three determinations.

[b] Results from two determinations.

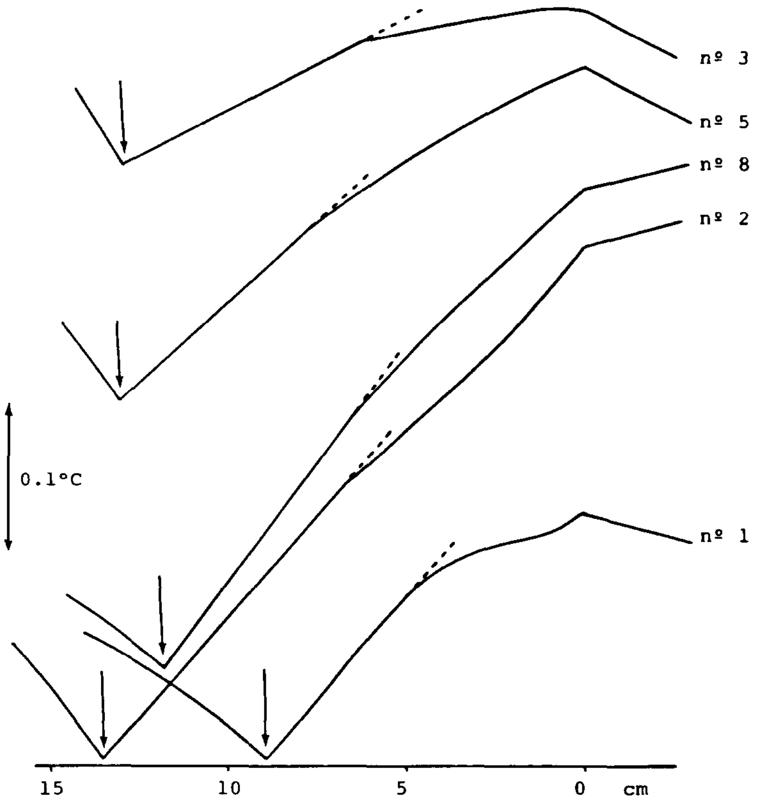

Fig. 4. Direct thermometric titrations of asphalts, with HCl.

As can be appreciated in Fig. 4, the thermometric curves are not well defined, giving poor end points. Nevertheless, the shape of the curves obtained are characteristic of each asphalt family.

From the results presented we can conclude that the thermometric end point of acid–base titrations constitutes a good method, due to their high sensibility, which allows strong and weak acid compounds to be distinguished and simultaneously determined. The short time and care needed for thermometric titrations, as well as the impossibility of poisoning the isolated transducer, make this technique very competitive with the official standard methods.

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