Thermochimica Acta, 98 (1986) 1–7
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DETERMINATION OF THE ACIDITY INDEX OF CRUDE OILS AND PETROLEUM DERIVATIVES BY MEANS OF THERMOMETRIC TITRATIONS. COMPARISON WITH OTHER METHODS

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(Received 4 June 1985)

ABSTRACT

Different methods have been applied to determine the acidity index of petroleum products. Thermometric titrations present not only the standard acidity, but also a supplementary value (corresponding to very weak acid compounds), which is characteristic for each kind of crude.

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

The acidity index (AI) is a measure of the inorganic and total acidity of petroleum derivatives. This parameter shows the tendency towards corrosion of metals in contact with these products [1].

The determination of AI of petroleum products is usually carried out titrimetrically with a strong base (KOH), using either potentiometric methods [2,3] or chemical indicators [4,5] to detect the end point.

As Quilty points out [6], the petroleum constituents with acid properties are: organic and inorganic acids, esters, phenolic compounds, lactones, resins, heavy metal salts, ammonium and other weak base salts, acid salts of polybasic acids and additives, as inhibitors and detergents. This great variety of possible acid constituents, with completely different acidity constants, implies that end points obtained by potentiometric titrations or with indicators do not always agree.

Titrations with indicator (1-naphtholbenzene) only allow the determination of acid compounds with dissociation constants in water greater than 10^{-9} [4,5]. Therefore, by this method, some compounds of petroleum

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0040-6031/86/$03.50

derivatives are not determined; it cannot be applied with highly coloured samples.

The potentiometric method, which is more versatile, has also proved to be non-problematic in the case of coloured compounds. On the other hand, it sometimes takes a long time to complete, and the glass electrode needs frequent reactivation; as the electrode is covered with a thin film of organic compounds, its life is considerably decreased.

Thermometric titrations have been used for a long time to detect end points of acids and bases [7–9]. Due to the advantages of thermometric end-point detection above other classical methods in weak acid titrations, we have used this technique to determine the acidity index of crude and petroleum derivatives.

In the present paper we have compared thermometric titrations with the official methods [2–5]. Results obtained using tetra-*n*-butyl ammonium hydroxide (TBA) are included for comparison.

EXPERIMENTAL

Reagents

All titrations with KOH (potentiometry, with indicator and thermometry) were performed in a 50:49.5:0.5 (v/v) mixture of toluene/isopropyl alcohol/water.

A mixture of 50:40:30 (w/w) toluene/methylisobutyl ketone/isopropyl alcohol was used when TBA was selected as titrant. Its concentration was 0.1 M in a propanol–methanol mixture (2:1).

As it is well known, thermometric titrations are favoured when the titrant reagent is more concentrated, due to a lighter jump and a greater linearity of the thermometric curves [10]. Thus, we used 0.5 M KOH in isopropanol as titrant base.

The remaining titrimetric determinations were carried out with 0.1 or 0.01 M KOH, according to sample acidity.

Apparatus

Potentiometric titrations [2,3]

These were performed with a Crison potentiometer (model digit 74) with a combined Metrohm AG 9100 Herisau electrode.

Titrations with TBA

Carried out with a Metrohm E-536 potentiometer, with a Metrohm E-535 autoburette, an EA-109 glass and EA-427 reference Metrohm electrodes (salt bridge of LiCl saturated in absolute ethyl alcohol). Titrand addition speed was 0.1 ml min^{-1}.

Thermometric titrations

The apparatus slightly differs from that used in previous papers [11]. Due to the use of non-aqueous media we selected nylon for the titration cell and teflon for all the other accessories (agitator, delivery tubes for titrant, thermistor support, etc.).

We selected a thermistor of the thermometer type, with 100 kΩ nominal resistance.

Titrant was added with a Radiometer ABU 12 autoburette, with a 25-ml cylinder. The reagent was added with a speed of 0.71 ml min^{-1}. Register speed was 5 cm min^{-1}. Sensitivity was 50 mV, which corresponded to 0.02°C cm^{-1}. Initial sample volume was 50 ml.

Procedure

Potentiometry and titrations with indicator

Samples of 0.5–5 g dissolved in the previously indicated mixture were titrated.

Acidities were calculated by means of the expression

$$\text{AI} = \frac{(V - V_0)N \times 56.1}{W}$$

where AI = acidity index (in mg KOH/g sample); V = titrant volume needed for the sample (ml); V_0 = titrant volume needed for a blank (ml); N = titrant concentration (eq l^{-1}); W = weight of sample (g).

Thermometric titrations

Samples of 5–20 g were used, depending on their acidities. All solutions were prepared as previously described.

Acidities were calculated by means of the expression

$$\text{AI} = \frac{D V_\text{b} N \times 56.1}{W V_\text{p}}$$

where D = distance until the equivalence point (cm); V_b = speed of burette (ml min^{-1}); V_p = register speed (cm min^{-1}).

RESULTS

To carry out the present study, we have chosen distilated products and crudes from Venezuela (Laguna, Mara and Boscan) and Mexico (mixture of crudes).

In Table 1 the results obtained in different experiments are shown.

Results of AI obtained using TBA as titrant are similar to those obtained with KOH, either using the potentiometric technique or indicators.

TABLE 1

Acidity index of the selected products

Derivative [a]	Titrations with indicators [b] [4,5]	Potentiometric titrations with KOH [b] [2,3]	Thermometric titrations [b]		Potentiometric titrations with TBA [c]
			1st zone	2nd zone	
Laguna DPw	– [d]	6.45	6.41±0.14	–	6.22
Laguna crude	– [d]	4.04	3.92±0.18	–	4.12
Laguna DLv	3.66±0.02	3.85	3.74±0.03	–	3.60
Laguna DMv	5.88±0.04	5.96	6.22±0.13	–	5.90
MCMex DMv	0.11±0.01	0.17	0.12±0.01	1.02±0.05	0.10
MCMex DLv	0.10±0.01	0.09	0.19±0.01	0.95±0.05	0.10
MCMex DAt	0.04±0.01	0.03	0.07±0.01	0.98±0.05	–
Mara DLv	2.86±0.01	2.81	2.90±0.05	0.60±0.07	2.82
Mara DAt	2.60±0.01	2.67	2.63±0.03	0.44±0.07	2.60
Boscan DMv	1.13±0.04	1.19	1.10±0.04	0.85±0.08	1.12
Boscan DLv	0.63±0.02	0.61	0.55±0.03	0.79±0.07	–
Boscan DPv	– [c]	1.56	1.51±0.03	0.82±0.07	–

[a] DPv, vacuum heavy distillate; DLv, vacuum light distillate; DMv, vacuum medium distillate; DAt, atmospheric distillate; MCMex, crude mixture from Mexico.

[b] Results of three determinations.

[c] Results of two determinations.

[d] Highly coloured samples that cannot be determined by this method.

In all thermometric titrations, except in the case of the Laguna crude and its distillates (where only one slope can be observed), a first, quite well-defined inflexion point, can be observed, whereas a second one is sometimes not so obvious. The end point is very clear due to the endothermic dilution heat of the titrant in the cell.

In Table 1 it is shown that the values obtained from the first zone of the thermometric curve agree with those of the potentiometric and indicator methods. The good linearity of the first zone of the thermometric curve is due to the higher acid strength, whereas the more curved second zone shows the presence of weaker acids (Fig. 1).

To confirm the presence of different kinds of acid compounds titrated in each of the zones of the thermometric curves, we added benzoic acid ($pK = 4.20$ in water), phenol ($pK = 10.0$ in water) and propyl propionate (Fig. 2) to a distillate derivative (Mara DAt). When benzoic acid is added we can observe an increment of the first zone of the curve, while the second remains unaltered. Therefore, this leads us to the conclusion that the acid compounds titrated in the first zone show the same acidity as carboxylic acids. Addition of phenol or the ester increases the second zone of the titration curve. Therefore, we suppose that the titrated acidity in this zone is similar to those of phenols or to the hydrolysis of an ester.

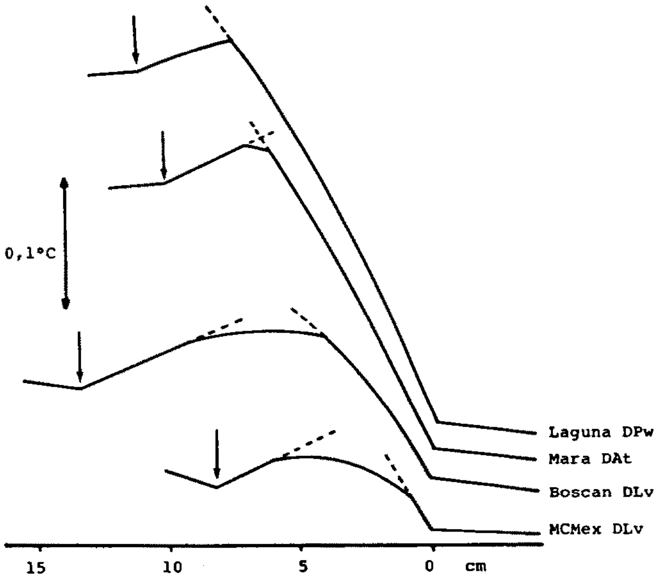

Fig. 1. Thermometric curves of several samples considered in the present study. The arrow indicates the end of the addition of 0.5 M KOH.

To find out what kind of acid constituents are determined with indicators, potentiometric or thermometric techniques, we prepared a synthetic mixture with benzoic acid (7.11 mM), phenol (7.14 mM) and propylpropionate (7.09 mM).

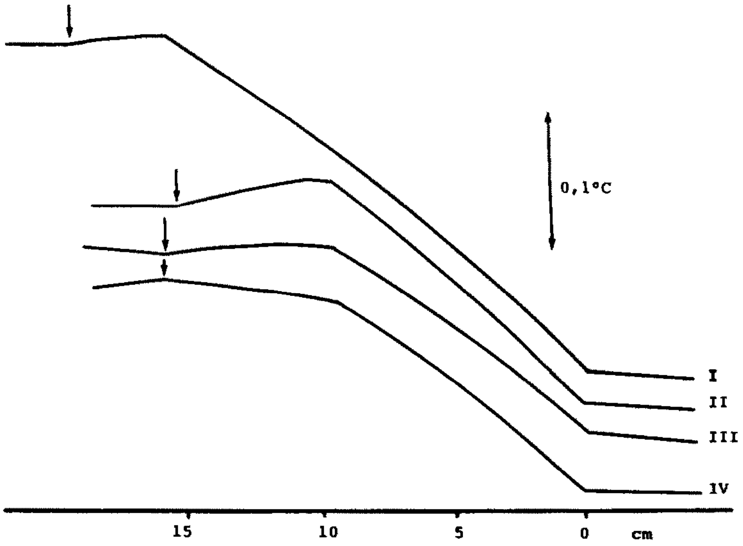

Fig. 2. Thermometric curves resulting in the titration of a solution of Mara DAt (II), to which benzoic acid (I), propyl propionate (III) and phenol (IV) were added. Titrant, 0.5 M KOH.

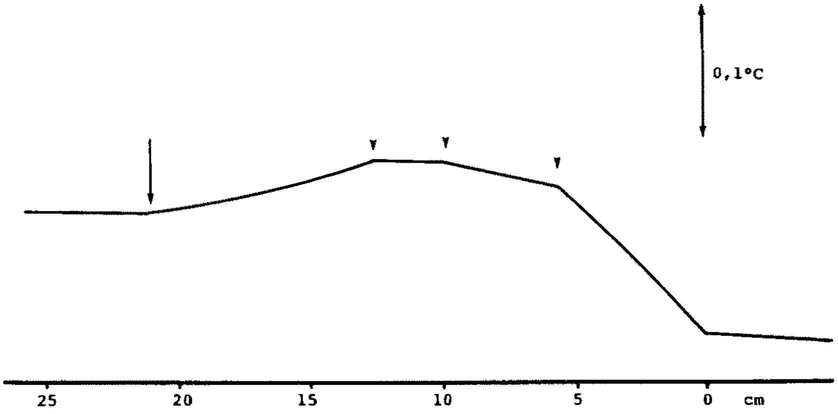

Fig. 3. Thermometric curve of a synthetic mixture constituting benzoic acid, phenol and propyl propionate. Titrant, 0.5 M KOH.

Results obtained by means of potentiometric techniques and with indicator show that 0.36 meq were determined, which exactly corresponds to the 0.35 meq of the benzoic acid added. In Fig. 3 we can see that results obtained by thermometric titrations are quite different. There are three different, well-defined zones, the first zone corresponding to benzoic acid (0.36 meq added), the second to phenol (0.30 meq found, 0.36 meq added), and the third to the hydrolytic titration of the ester (0.21 meq found, 0.35 meq added).

From these results we can deduce that, due to the different p*K* values of the components of the synthetic mixture, the potentiometric method and indicators allow determination of acid compounds with similar acidity to benzoic acid. Thermometric titrations, on the other hand, give more information, allowing titration of compounds with a similar acidity to phenol. Nevertheless, we can also observe that the titration error increases when the dissociation constant decreases.

Another interesting result which can be deduced from Table 1, is that the second interval of the thermometric titration curves is characteristic of a family or source. Thus, for the mixture of Mexican distilled crudes, the second interval is longer than the first, as opposed to distillates coming from Mara crudes, the stronger being greater than the weak acid. For Boscan crude distillates, carboxylic and weak acidities are similar. These results sometimes allow the determination of the purity degree of a crude or distillate.

Finally, we want to mention that thermometric titrations are perfectly valid for determining the acidity of petroleum distillates. They present, together with the standard acidity, a supplementary value (corresponding to very weak acid compounds) which is characteristic for each kind of crude.

The short time needed for each analysis, the precision, as well as independence from the distillate characteristics, make thermometric titrations very competitive with the standard methods. A substantial advantage of the thermometric techniques over the others is that the transducer is isolated from the sample solution by means of a glass sheath, which avoids its poisoning, inactivation, etc. Therefore, it is not necessary for it to be regenerated or for any other special care to be taken.

Due to these advantages, other thermometric techniques have also been used to determine organic compounds in non-aqueous media, such as catalytic titrations [12,13] and direct injection enthalpimetry [14].

ACKNOWLEDGEMENTS

We are grateful to ASESA (Asfaltos Españoles S.A.) Tarragona for reagents supplies and to Mr. Josep Ma. Gonzàles Escoda for helpful discussions.

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