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CALORIMETRIC, EMF AND CONDUCTOMETRIC STUDIES OF ENGINE OILS *

ZENON PAWLAK **, ELZBIETA GIERSZ and GIZELA URBANCZYK
Technology Department of Industrial Production, University of Gdansk, 81-824 Sopot (Poland)

REED M. IZATT and JOHN L. OSCARSON
Departments of Chemistry and Chemical Engineering, Brigham Young University, Provo, UT 84602 (U.S.A.)

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ABSTRACT

Conductometric, calorimetric and potentiometric (ASTM D-2986) techniques were applied to the determination of the basicity index and the acidity index of engine oils. The values of basicity index obtained using various titration techniques agreed fairly well. The advantages of conductometric and calorimetric methods are rapidity, good reproducibility, and avoidance of poisoning of detectors by organic substances. The conductometric method gave a sharp break in the titration curve for used and new oils.

INTRODUCTION

The acid–base determination of petroleum products in media of low polarity with micellar properties has not been an easy analytical problem to solve [1]. Many lubricants for internal combustion engines contain highly overbased additives, ashless dispersants and nitrogenous polymeric compounds. Metal carbonates remain in these media in colloidal form [2–4].

Analysis of overbased barium (calcium) phosphonate, sulfonate or phenolate using the ASTM D-664 method has shown approximately 10–40% less base content than is obtained using the ASTM D-2986 method [3–7]. Determination of colloidal calcium, barium and magnesium carbonates in mixtures of chlorobenzene and glacial acetic acid with perchloric acid as a titrant has been successful [4,8–10]. The neutralization number (the basicity

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* Dedicated to Professor James J. Christensen in memory of his contribution to innovation in calorimetry.

** Author to whom correspondence should be directed at the present address of Department of Chemistry, Brigham Young University, Provo, UT 84602, U.S.A.

index and the acidity index) is being used as a criterion of the remaining service life in used oils. While a modern additive-type oil may have both acid and base numbers, it is recognized that there is no valid correlation between these numbers and the corrosiveness of the oil in service [11,12].

In petroleum oils, no ionization of acids, bases or salts takes place. Thus the pH concept is useless and cannot be used directly [13]. However, the properties of base and acid mixtures in low-polar media have been studied extensively [14–31]. Information gained from these studies has been used to overcome the difficulties inherent in analyzing petroleum products. Many laboratories have modified the procedure by dissolving the petroleum product in alcohol [14] or in mixtures of the following solvents: isoamyl alcohol–benzene–CCl_4 [15–18], isopropyl alcohol–benzene–H_2O [19], dimethyl sulfoxide–chlorobenzene [20,21], isopropyl alcohol–toluene–H_2O [16,17], chlorobenzene–glacial acetic acid [3,4], toluene–glacial acetic acid [5–7] and benzene–pyridine [28]. A potentiometric [14–21], conductometric [22,23], high-frequency [27] calorimetric [24–26] or chemical indicator [18,19,30] method is used to detect the end point.

The following standard analytical methods for determination of the basicity index and the acidity index are now in general use: ASTM D-664 (IP-177) (potentiometric) [29], ASTM D-974 (IP-139) (color-indicator) [30] and ASTM D-2896 (IP-276) (potentiometric) [31]. The latter method only covers the determination of basic constituents in petroleum products.

The aim of this study was to apply conductometric and thermometric techniques to the determination of the basicity and acidity indices of a series of used and new engine oils and to compare the results with those obtained using the standard ASTM D-2986 potentiometric method.

EXPERIMENTAL

The basicity index was determined by direct potentiometric, conductometric and calorimetric back titration. In the potentiometric technique (ASTM D-2986), 0.1 M $HClO_4$ in glacial acetic acid was used as titrant and chlorobenzene–glacial acetic acid (2 : 1 (v/v)) was used as titration medium (method A) [31]. In the conductometric technique, 0.1 M HCl in isopropanol was used as titrant and toluene–isopropanol–H_2O (50 : 49.5 : 0.5 (v/v)) was used as the titration medium (method B) [22]. In the calorimetric back titration (method C), the sample of engine oil was dissolved in a mixture of toluene–isopropanol–H_2O (50 : 49.5 : 0.5 (v/v)) and 0.25 M $HClO_4$ in isopropanol–toluene (1 : 1) was used as titrant; the excess acid was titrated by 1.0 M $(CH_3)_4NOH$ in isopropanol.

The determination of the acidity index was performed by direct calorimetric titration (method D). $(CH_3)_4NOH$ (1.0 M) in isopropanol was used as titrant and a toluene–isopropanol–H_2O mixture (50 : 49.5 : 0.5 (v/v)) was used as titration solvent.

Calorimetric titration was carried out with a Tronac 450 titration calorimeter at 298.15 K. The reaction vessel contained 10–15 cm^3 of a mixture of solvents and $(CH_3)_4NOH$ titrant was added from a syringe buret of 2.00 cm^3 capacity with a delivery rate of 0.001756 cm^3 s^{-1}. Potentiometric measurements were performed using the Precision Potentiometer E353 (Metrohm Herisan), and conductometric studies were performed with the Radelkis Conductometer (Hungary) (type OK-102/1) with OK-902 electrodes.

RESULTS AND DISCUSSION

Basicity index values of 11 samples of used and new oils of British production (obtained from M.F. Fox, School of Chemistry, Leicester Polytechnic, U.K.) were determined by us and other laboratories by potentiometry, thermometry or conductometry. The potentiometric ASTM D-2986 method was used by us as a standard technique and thermometry and conductometry were used as supporting methods.

A comparison of the basicity index values obtained by potentiometric, conductometric and thermometric methods is given in Table 1. The basicity index values obtained using our various titration methods show that the calorimetric back titration and conductometric methods give results which agree fairly well with potentiometric measurements (ASTM D-2986) in chlorobenzene–acetic acid mixtures. Our previous studies [8,22] have shown that conductometric methods give basicity index values which are 20–40% higher for most used oils than values obtained using the ASTM D-664 potentiometric method but correspond closely to results obtained with the ASTM D-2986 technique. The ASTM D-664 potentiometric method is not very satisfactory for carbonated high base calcium (barium) phenolates or sulfonates [3,4,31]. As shown by Labre and Briant [23], phenolates and sulfonates can be determined with much greater accuracy in a benzene–alcohol medium by conductometric than by potentiometric titration.

It has been shown [3,4] that results in a chlorobenzene–acetic acid medium are essentially identical with calculated values and correlate better with engine wear than those determined by the ASTM D-664 method. Titration with perchloric acid (ASTM D-2986 method) in a levelling mixture of glacial acetic acid–chlorobenzene (1 : 2 (v/v)) may determine not only phenolates and nitrogen-bases but also carbonates.

In the determination of basicity index by thermometric back titration, the basic titrant ($(CH_3)_4NOH$) neutralizes the unconsumed titration acid ($HClO_4$) and any non-volatilized acid present already or liberated from the basic additives. These acids are neutralized in order of decreasing strength.

TABLE 1

Basicity and acidity indices of lubricating oils (standard deviations given in parentheses)

Oil sample	Direct potentiometric (ASTM D-2986) (method A) [a]	Direct conductometric (method B) [a]	Back thermometric (method C) [b]	Direct thermometric (method D) [b]	
	Basicity index (mg KOH $(g\ oil)^{-1}$)	Basicity index (mg KOH $(g\ oil)^{-1}$)	Basicity index (mg KOH $(g\ oil)^{-1}$)	Acidity index (mg KOH $(g\ oil)^{-1}$)	ΔH (kJ mol^{-1})
1	5.63 (0.17)	5.62 (0.12)	5.75 (0.06)	1.02 (0.03)	−6.2
2	5.97 (0.16)	6.21 (0.14)	6.73 (0.07)	0.83 (0.03)	−3.7
3	6.05 (0.14)	6.60 (0.16)	6.82 (0.07)	0.94 (0.03)	−7.7
4	9.13 (0.12)	9.15 (0.12)	9.54 (0.10) [c]	2.52 (0.04)	−5.8
5	9.84 (0.22)	9.94 (0.20)	9.43 (0.14)	1.15 (0.04)	−10.5
6	8.92 (0.18)	8.93 (0.21)	9.12 (0.12)	2.46 (0.05)	−11.3
7	10.10 (0.18)	10.42 (0.25)	10.07 (0.15) [c]	2.82 (0.05)	−15.9
8	37.26 (0.45)	37.56 (0.40)	38.05 (0.37) [c]	4.63 (0.07)	−10.5
9	28.40 (0.30)	29.14 (0.30)	27.81 (0.40) [c]	4.44 (0.08)	−15.9
10	20.53 (0.27)	19.13 (0.26)	20.73 (0.36) [c]	1.76 (0.03)	−20.4
11	7.63 (0.16)	8.24 (0.14)	8.02 (0.16) [c]	1.91 (0.04)	−19.2

[a] Results of three determinations.

[b] Results of two determinations.

[c] Curve of two zones.

If the acidity strengths of these acids differ sufficiently from each other, they give separate and distinct inflexion zones on thermometric titration curves (except for samples 4 and 7–11 (Table 1) which give two zones (for $HClO_4$ and weak acid)). An estimation of the amounts of weak acid was made from direct titration on the samples (method D). Most oil samples have an acidity index of 1–2 units (mg KOH (g oil)$^{-1}$); however, samples 8 and 9 have an acidity index of around 4.5 units. Heats of neutralization of acidic products range from -3.7 to -20.4 ± 1.25 kJ mol^{-1} and indicate the presence of weak acids in engine oil samples. The precision of thermometric titration is comparable with conductometric and potentiometric methods. The advantages of thermometric and conductometric techniques are rapidity, good reproducibility and avoidance of poisoning of detectors by organic substances.

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