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MEASUREMENT OF C_p OF SOME LUBRICATING OILS WITH A DIFFERENTIAL SCANNING CALORIMETER

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ABSTRACT

The specific heat at constant pressure (C_p) of various lubricating oils was determined at different temperatures using differential scanning calorimetric techniques. The values obtained correlated well with those calculated from empirical expressions.

INTRODUCTION

A knowledge of the specific heat at constant pressure, C_p, of lubricants is of importance in determining net heat fluxes in all heating and cooling problems [1]. It is also of considerable value in estimating the rise in temperature for a given set of heat transfer conditions, and the most common liquids used for such purposes are lubricating oils [2,3]. It is also used in the evaluation of the accuracy of liquid heat capacity correlations [4].

The specific heat of a liquid increases with temperature and in the case of mineral oils is a function of density or of average hydrocarbon type [5].

For oils, the specific heat at constant pressure, C_p, may be calculated fairly accurately from the following expression

$$C_p = (0.403 + 0.0008t)d^{-1/2} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1} \tag{1}$$

where t = temperature (°C) and d = density of oil at 20°C (g cm^{-3}).

Thermoanalytical techniques, such as differential scanning calorimetry, have been used extensively in recent years [6,7] for studying the thermal properties and degradation pattern of many types of lubricating oils.

When an oil is heated in a DSC cell and is not undergoing a physical or chemical change, the DSC curve is still usually offset from the theoretical baseline. This is primarily due to the difference in the heat capacities of the test and reference samples. The magnitude of the endothermic offset provides us with a means of estimating specific heats at constant pressure, C_p.

In this paper, the use of differential scanning calorimetry in determining C_p values of different types of lubricating oils is reported, and values obtained were compared with those derived from empirical expressions.

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EXPERIMENTAL

Apparatus

The DSC measurements were carried out using a Heraeus TA 500 thermal analyser. Oil samples weighing 5–8 mg were heated at a rate of 10°C min^{-1} in an aluminium crucible. The reference cell was left empty.

Materials

Additive-free lubricating oils of grade 40 base stock, grade 60 high viscosity index (HVI), grade 60 low viscosity index (LVI) and grade 150 base stock were all obtained from a local refinery. Specifications are given in Table 1. Pure benzoic acid and tin were used in calibrating the DSC apparatus.

Procedure

When measuring C_p for lubricating oils, the DSC instrument is first operated under standard conditions with no sample in either sample or reference pans. Any deviation of the DSC curve from the theoretical baseline will then be due to deficiencies in the apparatus, which are assumed to be constant. The sample is then placed in one pan, leaving the reference pan empty, and both are closed with a press and the lids are perforated with a fine needle. The experiment is then repeated under the same conditions. Because of the change in heat capacity resulting from the presence of sample, a new offset temperature will be obtained. The difference between the blank and experimental offset temperatures is used to calculate the specific heat at constant pressure, C_p.

All results obtained were the average of three determinations.

TABLE 1

Specifications of the lubricating oils

Specification	Grade 40	60HVI	60LVI	Grade 150
Density at 20°C	0.8660	0.8702	0.8860	0.8930
Refractive index at 20°C	1.4785	1.4855	1.4899	1.4958
Flash point, COC (°C)	175	248	245	295
Pour point (°C)	−10	−7	−7	−4
Viscosity sus at 98.9°C	39	62	57	162

RESULTS AND DISCUSSION

Figure 1 shows a typical DSC diagram obtained on determining the C_p values of the oils studied. The specific heat of the oil at any temperature is calculated using the following expression

$$C_p = \frac{U_{corr} \times 60}{EHRm} \text{ J g}^{-1} \text{ K}^{-1} \tag{2}$$

The equation for correction in the case of a weight difference of the aluminium pans is

$$C_p = \frac{U_{corr} \times 60}{EHRm} - C_{p(Al)} \frac{m_{TP} - m_{TR}}{m} \tag{3}$$

where U_{corr} = corrected potential difference between the baseline and the measuring curve at the chosen temperature; E = caloric sensitivity which is temperature dependent and supplied with the instrument; m = mass of sample (g); HR = heating rate (°C min^{-1}); $C_{p(Al)}$ = specific heat of aluminium (J g^{-1} K^{-1}); m_{TP} = mass of sample crucible (g); m_{TR} = mass of reference crucible (g).

Table 2 shows C_p values for the different lubricating oils at 50, 100 and 150°C obtained using the DSC apparatus. These values were used in modifying eqn. (1) for C_p calculation in order to improve its capabilities. The modified empirical equation arrived at in this work is given below.

$$C_p = (0.415 + 0.0008t)d^{-1/2} \times 4.19 \text{ J g}^{-1} \text{ K}^{-1} \tag{4}$$

where t = temperature (°C) at which C_p is measured and d = density at 20°C (g cm^{-3}). The calculated values of C_p obtained from eqn. (4) are also given in Table 2.

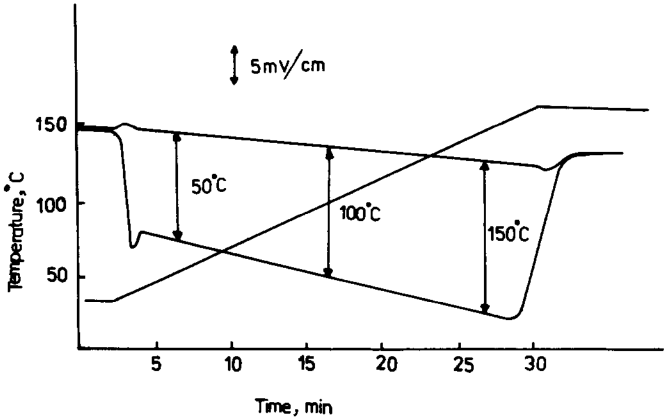

Fig. 1. A typical DSC diagram for the determination of the specific heat of lubricating oils at constant pressure.

TABLE 2

Specific heats, C_p, of lubricating oils

Type of oil	Temperature (°C)					
	50		100		150	
	meas.	calc.	meas.	calc.	meas.	calc.
Grade 40	2.12	2.05	2.34	2.23	2.45	2.41
60 HVI	2.07	2.04	2.29	2.22	2.38	2.40
60 LVI	1.98	2.03	2.26	2.20	2.35	2.38
Grade 150	1.93	2.02	2.15	2.19	2.32	2.37

$$\text{Percentage deviation} = \frac{C_{p(\text{calc})} - C_{p(\text{meas})}}{C_{p(\text{meas})}} \times 100.$$

The maximum percentage deviation of all values calculated was -4.7, while the absolute average percentage deviation is 2.5, and the average percentage deviation was -0.6. These calculations showed that eqn. (4) is satisfactory in calculating specific heat values at constant pressure for the lubricating oils in the temperature range given.

The DSC method possessed certain important advantages which can be summarized as follows:

(1) it provided experimental data over wide temperature ranges which are usually sparse in the literature;

(2) only very small samples are required;

(3) information is obtained quickly and reproducibly;

(4) equipment has multiple use rather than only being able to do one test.

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