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FRACTIONAL ANALYSIS OF TECHNICAL POLYOXAALKYL BORATES BY TG

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Abstract

Results of preliminary thermoanalytical investigations (DSC/TG) of polyoxaalkyl esters of boric acid are presented. One aim of these investigations was the development of a method of characterization of the technical esterificate. The optimum parameters of quantitative thermogravimetric analysis of boric acid esters and the excess of polyoxaalkanols were assumed. The precision and accuracy of the developed method are discussed.

Keywords: DSC/TG, boric acid estersfractional analysis

Introduction

Esters of boric acid form a numerous group of compounds of general formula $(BO_3)_nR_m$, wherein the group B–O–R_i is the characteristic structural element responsible for their being esters.

The variety of the types of alcohol radicals and the modes of bonding of these structural elements leads to the possibility of obtaining substances with interesting physical, chemical or physiological properties. This accounts for the growing interest in this particular group of compounds as polymer stabilizers [1–4], dehydrants for liquid fuels [5, 6], biocides [7–9], selective catalysts of hydrocarbon oxidation [10–16], impregnating agents [17] and mechanical energy transfer fluids [18, 19].

In the technology of mechanical energy transfer fluids, and especially in the compounding of brake fluids, polyoxaalkyl boric acid esters are applied as additives which improve certain operating properties of the final product, e.g. moisture resistance, boiling point, viscosity and others.

Even though the process for the production of polyoxaalkyl borates is quite well advanced and relatively simple [17, 18], few data are available on the chemical composition of the esterificate, and the parameters used to characterize the synthesis product (e.g. water and boron content) [20] do not provide direct information on the content of the resulting ester, its structure and the quantity of unconverted substrates.

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This paper reports results of preliminary thermoanalytical examinations the aims of which included development of a procedure for analytical characterization of a technical esterificate.

Experimental

Apparatus and materials

Thermoanalytical measurements were made with a TG 50 thermobalance and a DSC 30 differential scanning calorimeter operating in the Mettler TA 4000 System.

Examinations were performed on esterificates obtained by laboratory dehydration of 1:4 molar ratio mixtures of orthoboric acid (H_3BO_3) with pure 3,6,9-trioxadecan-1-ol or with Bikanol M3 (produced at the ICSO Chemical Production plant), a technical mixture of polyoxaalkanols $R(OCH_2CH_2)_nOH$ (where R = CH_3, C_2H_5 or C_4H_9), containing 68.34% by weight of 3,6,9-trioxadecan-1-ol and 19.85% of 3,6,9,12-tetraoxatridecan-1-ol as the main components.

Procedure

Thermoanalytical measurements of the products of boric acid esterification with the above alcohols were carried out by TG and DSC methods under a dynamic argon or air atmosphere (200 ml/min) at constant heating rate. Open platinum crucibles were used.

Discussion of results

Interpretation of TG curves

The shapes of the TG curves of the products of H_3BO_3 esterification with 3,6,9-trioxadecan-1-ol indicate a quasi-two-stage course of the process of mass loss in the run under argon, and a three-stage course in the case of air (Fig. 1).

The steps of mass loss can be explained as follows:

$\Delta m_{100-200}$ = evaporation of excess of 3,6,9-trioxadecan-1-ol,

$\Delta m_{200-260/320}$ = evaporation and/or thermal and/or thermooxidative decomposition of boric acid ester (200–260°C for air, 200–320°C for argon),

$\Delta m_{320-380}$ = thermal decomposition of carbonized products (?).

Such an interpretation is justified by the stoichiometric relationship between the respective mass losses and the calculated composition of the esterificate (assuming that esterification under superstoichiometric conditions produces a $B(OR)_3$–type ester).

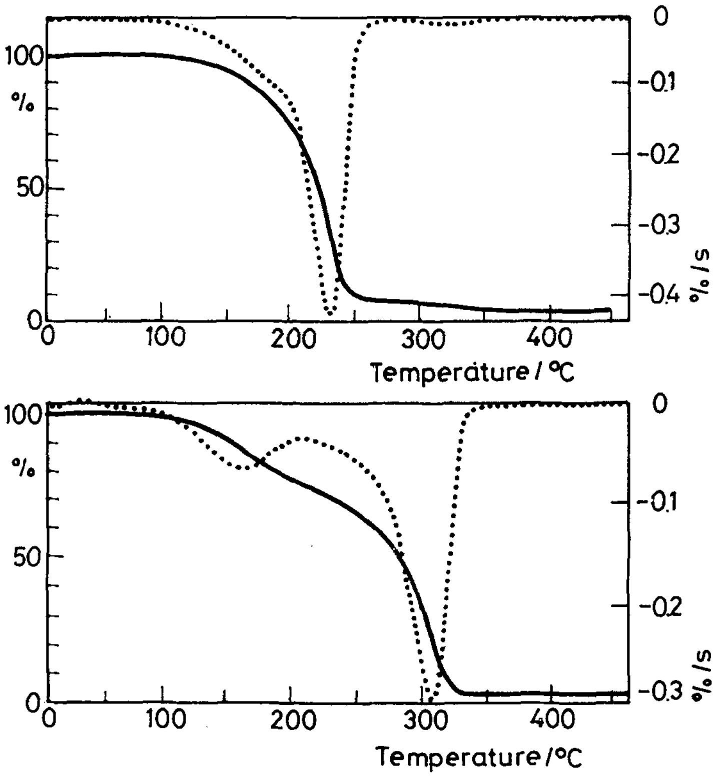

Fig. 1 TG/DTG curves of products of boric acid esterification with 3,6,9-trioxadecan-1-ol under a purge gas atmosphere of (a) air, (b) argon

Examinations were also carried out on the products of boric acid esterification with the mixture of polyoxaalkanols; the same types of TG/DTG curves were obtained (Fig. 2).

With the assumption that the molecular weight of the polyoxaalkanol employed in the esterification was equal to the weighted average molecular weight of the mixture, the relationships obtained between the mass losses and the calculated composition of the esterificate were similar to those for the esterificate obtained from pure 3,6,9-trioxadecan-1-ol.

Boric acid ester content (w_E/% wt) was evaluated via the formula:

$$w_E = 100 - w_A$$

where w_A was the content of polyoxaalcanols determined directly from the TG curve as the first mass loss in the range between the start temperature and the temperature corresponding to the minimum in the DTG curve.

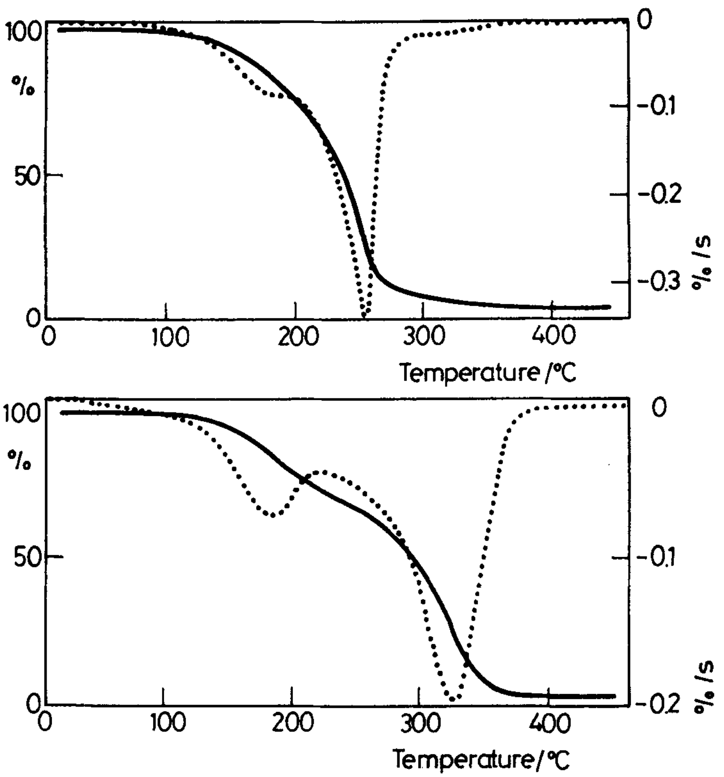

Fig. 2 TG/DTG curves of products of boric acid esterification with mixture of polyoxaalkanols (BIKANOL M3) under a purge gas atmosphere of (a) air, (b) argon

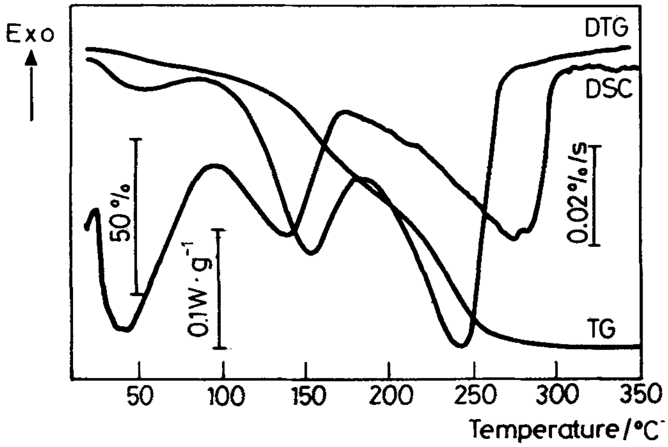

Fig. 3 TG/DTG curves for a boric acid: 3,6,9-trioxadecan-1-ol 1:4 (mol/mol) mixture

TG and DSC analyses of the reaction mixture of boric acid with 3,6,9-trioxadecan-1-ol showed (Fig. 3) the occurrence of an additional step of mass loss at temperatures up to 120°C. This was explained as water evaporation which, when associated with the existence of the 'ester' step in the TG curve and the compatibility of the mass loss for that particular step with the calculated stoichiometric ester quantity, signifies that the mixture underwent complete esterification during TG analysis. Thus, the quantitative information obtained on analysis of the mixture containing unconverted boric acid relates to the hypothetical, completely dehydrated mixture.

Optimum measurement conditions

In order to estimate the influence of the thermoanalytical measurement parameters on the TG curve shape, measurements were made with variation of the following parameters:

a) pan type (aluminium, sealed, with a 0.05 mm hole in the lid; aluminium, open; or platinum, open),

b) heating rate (from 3 to 30 deg·min^{-1}),

c) purge gas (Ar or air).

The mass of sample taken (about 10 mg) and the purge gas flow (200 ml/min) were not varied.

Analysis of the TG/DTG curves of the esterificates revealed, that at a heating rate of 12 deg·min^{-1} the steps of mass loss were better separated under argon than under air; further, the processes responsible for the mass loss were endothermic in the former (Fig. 4) and exothermic, due to the 'ester' step, in the latter case.

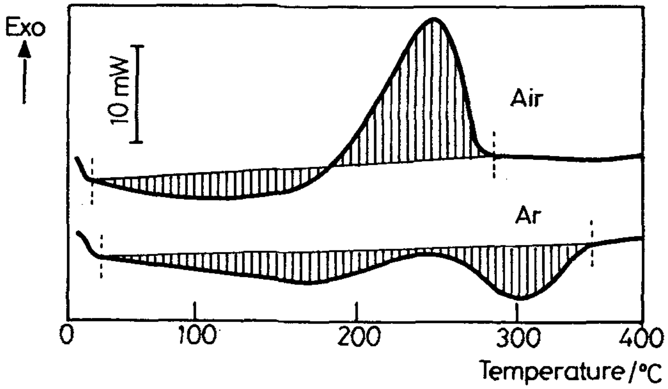

Fig. 4 Comparison of DSC curves of a post-esterification (H_3BO_3 : 3,6,9-trioxadecan-1-ol) mixture under an air or argon atmosphere

Observation of the influence of the heating rate and pan type on the ad hoc defined separation coefficient demonstrated the optimum range of the heating rate and the best pan type for measurements. However, the separation coefficient was found not to be influenced by the heating rate above 12 deg·min^{-1}. Measurements were not made at higher heating rates because of the shift of the mass loss steps into the higher temperature range and subsequent decomposition processes.

Accordingly, the following measurement conditions were assumed as optimum for analyses aimed at application of a TG method for determination of the composition of the esterificate:

- 10 mg samples in an open platinum crucible,
- heating from 20 to 450°C at a rate of 12 deg·min^{-1},
- a dynamic argon atmosphere (200 ml/min).

Preliminary assessment of the precision and accuracy of the TG method for determination of the composition of the esterificate

Under the optimum measurement conditions, TG curves of seven laboratory samples with known compositions were recorded. The samples were made from tris-(3,6,9-trioxadecyl) borate or from a mixture of polyoxaalkyl borates with the addition of a certain quantity of 3,6,9-trioxadecan-1-ol to dilute them. The 'true' content of boric acid ester was calculated from the known quantity of boric acid used to synthesize the ester. The contents of the esters and polyoxaalkanols were determined by the tested TG method.

Table 1 Results of thermogravimetric determination of boric acid esters and polyoxaalkyl alcohols in compounded samples

No. of	w_E/ % wt		w_A/ % wt	
sample	'True'	Determined	'True'	Determined
1	74.01	67.99	25.99	32.01
2	72.62	68.46	27.38	31.54
3	70.77	66.60	29.23	33.40
4	75.39	70.31	24.61	29.69
5	15.08	14.34	84.92	85.66
6	37.28	33.77	62.72	66.23
7	36.54	32.84	63.46	67.16
Linear regression parameters ($w_{det} = A + B * w_{true}$)				
Slope	0.9414		0.9414	
Intercept	−0.7159		6.5764	
Correl. coef.	0.9994		0.9994	
Std. est. err.	0.8829		0.8829	

Results of determination of the boric acid esters and polyoxaalkanols in the compounded samples are presented in Table 1. The parameters of the linear regression of two data vectors (content determined and 'true' content) are given under the Table.

Analysis of the relationships between the compositions found by TG and the 'true' compositions of the samples revealed, that the TG method for determination of the quantity of esters and the 'excess' of polyoxaalkanols has only a small, variable systematic error. The error can be simply corrected by a correction factor.

The standard estimation error (Table 1) is proposed as a preliminary assessment of the precision of the method of boric acid ester determination.

Final remarks

1. In the thermogravimetric measurement, under an inert gas, of samples of esterificates obtained by dehydration of mixtures of boric acid with a superstoichiometric quantity of polyoxaalkanols, mass loss steps are observed in association with:

a) evaporation of unconverted alcohols,

b) evaporation (with partial decomposition) of the ester.

The individual mass loss steps correspond to endothermic effects in the DSC curve.

2. The mass losses correspond to the stoichiometric quantity of the components of the mixture (assuming that esters of the type $B(OR)_3$ are formed on esterification with analytically pure ethoxylated alcohol and with a technical mixture of ethoxylated alcohols).

3. The 'thermoanalytical behaviour' of polyoxaalkyl borates and polyoxaalkanols permits accurate and precise determination of the contents of the two main components of the dehydrated post-esterification mixture, i.e. the esters and polyoxaalkanols. If the reaction mixture is not completely dehydrated (or if it becomes wet secondarily), the determined ester content relates to the state of the product that can be obtained after renewed dehydration.

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Zusammenfassung — Es werden die Resultate von thermoanalytischen Untersuchungen (DSC/TG) von Polyoxoalkylestern von Borsäure dargelegt. Ein Ziel dieser Untersuchungen bestand in der Entwicklung einer Methode zur Charakterisierung der technischen Veresterung. Die optimalen Parameter der quantitativen thermogravimetrischen Analyse von Borsäureestern und der Überschuß von Polyoxoalkanolen wurde vorausgesetzt. Präzision und Genauigkeit der Methode werden diskutiert.