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THERMOANALYTICAL BEHAVIOR OF BORIC ACID–POLYOXAALKANOL BINARY SYSTEMS

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Abstract

Binary mixtures of orthoboric acid with selected ethoxylated derivatives of methanol, ethanol or butanol (polyoxaalkanols) were investigated thermoanalytically. Both TG and DSC measurements indicated a three-step reaction course in general, which was explained by the evaporation in turn of esterification water, polyoxaalkanol and ester. A relationship was established between the TG-determined and the assumed ester content.

Keywords: boric acid esters, brake fluid analysis, DSC, ethoxylated alcohols, TG

Introduction

There is currently increasing interest worldwide in high-quality brake fluids (of DOT-4, DOT-4-super and DOT-5 type) which contain polyoxaalkyl esters of boric acid. Addition of boric acid esters to the 'traditional compositions of polyoxaalkanol-based brake fluids (DOT-3 type) improves many of their operating properties and their resistance to atmospheric moisture.

Although the manufacturing of polyoxaalkyl boric acid esters is well advanced, quantitative methods of esterification product analysis have not been developed on a satisfactory level. Esterification mixtures used in brake fluid manufacturing are usually characterized on the basis of the results of virtual water content determination by the Karl Fischer method and the results of titrimetric determination of the total boron content [1–4]. Characterization according to the above methods (particularly useful for material balance of esterification process computation) can not provide enough information about the ester content and its composition.

A thermogravimetric method for analysis of the fractional content of esterificates was recently presented [5]. The method was developed as a result of examinations of model solutions composed of boric acid and 3,6,9-trioxadecan-1-ol, the main component of the polyoxaalkanol technical mixture applied in polyoxaalkanol borate ester synthesis.

The purpose of the present work was to investigate the thermoanalytical properties of mixtures of boric acid and selected homologous polyoxaalkanols,

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so as to establish the basis for a thermoanalytical method to characterize esterificates made from polyoxaalkanols with various fractional contents.

Experimental

Materials

Orthoboric acid, analytical grade (POCh); 3-oxabutan-1-ol (reference code: M1), anal. grade (Aldrich); 3,6-dioxaheptane (M2), anal. grade (Aldrich); 3,6,9-trioxadecan-1-ol (M3), pure (Fluka); 3-oxapentan-1-ol (E1) anal. grade (Aldrich); 3,6-dioxaoctan-1-ol (E2), anal. grade (Aldrich); 3,6,9-trioxaundecan-1-ol (E3), pure (Fluka); 3-oxaheptan-1-ol (B1), anal. grade (Aldrich); 3,6-dioxadecan-1-ol (B2), anal. grade (Aldrich); and 3,6,9-trioxatridecan-1-ol (B3), pure (Fluka).

Preparation of model systems

The model solutions were prepared by heating a suspension of othoboric acid in the respective polyoxaalkanol in sealed high-pressure glass ampoules at 100°C. An alcohol to H_3BO_3 molar ratio of 4:1 was used for each solution. As soon as a clear solution had been obtained, heating was stopped.

Thermoanalytical measurements

The DSC30 differential scanning calorimeter and TG50 thermobalance, both of the Mettler TA4000 system were used with a TC11 processor. About 10 mg samples were heated in the range 20–450°C (DSC) or from room temperature to 450°C (TG). TG and DSC cells were purged with argon at flow rates of 100 $ml\cdot min^{-1}$ for DSC and 200 $ml\cdot min^{-1}$ for TG. A sealed platinum crucible with a holed (3×Ø 0.5 mm) lid was applied for TG treatment and an aluminium sealed one with a hole (1×Ø 0.5 mm) for DSC.

Results and discussion

The TG/DTG and DSC curves shown in Figs 1 and 2 were obtained from the measurements.

The TG curves exhibited a multistep course. In the case of curves 1c–i, three steps of mass loss occurred, which was explained on the basis of our later experience as the evaporation of esterification water up to ~120°C, followed by polyoxaalkanol evaporation and then by the evaporation and partial decomposition of the borate ester formed *in situ*.

Curves 1a,b, with different shapes, show that the mixtures H_3BO_3–M1 and H_3BO_3 – E1 behaved differently, since two steps of mass loss were observed.

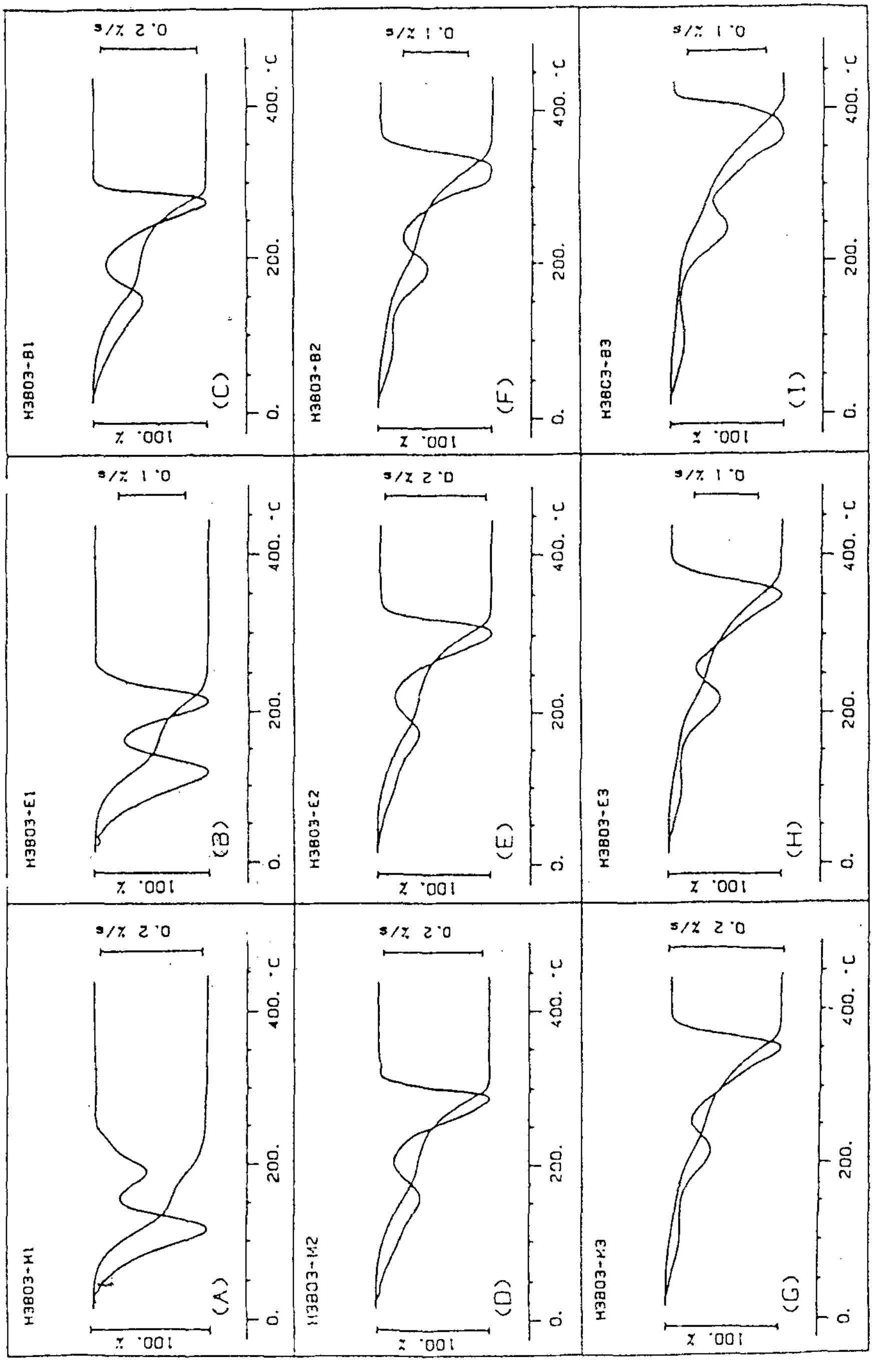

Fig. 1 TG and DTG curves of H_3BO_3 – polyoxaalkanol systems

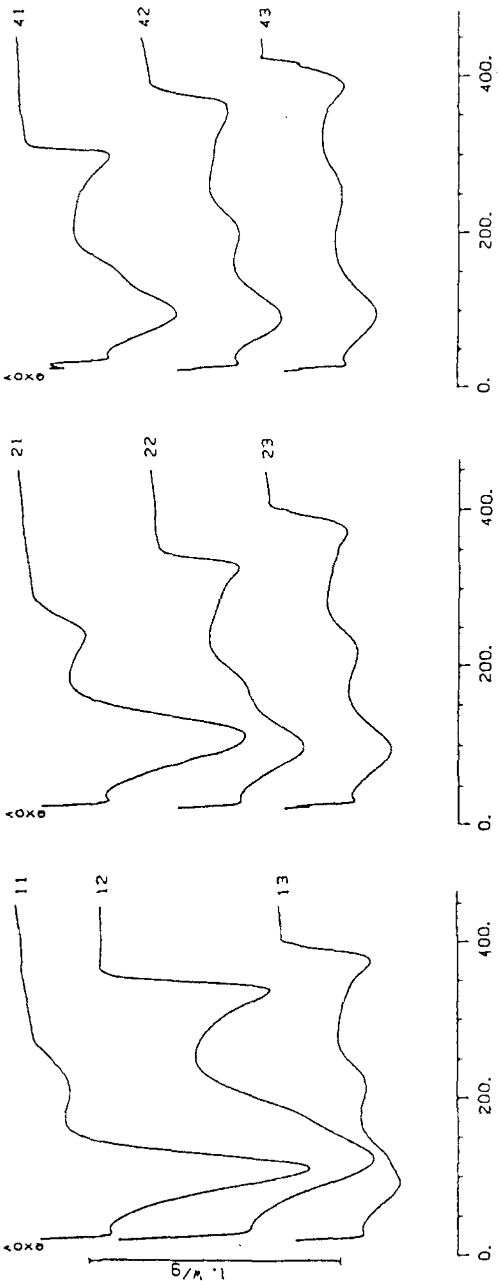

Fig. 2 DSC curves of H_3BO_3 –polyoxaalkanol systems (Meaning of the curve numbers is explained in Table 1)

This phenomenon is accounted for by the relatively high volatility of 3-oxabutan-1-ol and 3,6-dioxapentan-1-ol, which was the reason for their evaporation together with water in the first step of mass loss. Moreover, the glassy melt was observed as a residue because of excessive alcohol component loss and therefore incomplete conversion of H_3BO_3. It is also possible that the irregular shape of the right slope of the second DTG peak (Fig. 1a) is due to certain changes in unconverted residual boric acid.

The shape of the DSC curves (Fig. 2a–c) confirms the above explanations. The endothermic effects in the DSC curves correspond to the respective steps of mass losses in the TG/DTG curves.

In curves 11, 21 and 41, similarly as for the TG curves, two steps of an endothermic nature were detected. The significant values of their energetic effects are a result of evaporation of the water – alcohol system.

The above interpretation may be quantitatively confirmed by comparing the TG-determined contents of esters with the stoichiometric ester contents with the assumption that the simple ester $B(OR)_3$ is formed during esterification. Table 1 presents boric ester contents determined by TG, and the mass losses which would have been observed if the separation of the steps had been complete (w_e).

Boric acid ester content was evaluated according to the formula

$$w_2=100-w_1$$

where w_1 is the content of polyoxaalkanol and esterification water determined directly from the TG curve as the value of the mass loss step between the start and the temperature corresponding to the DTG minimum (between the alcohol and ester steps).

The relative deviations of the determined results, defined as

$$\delta=(w_2-w_e)/w_e$$

are also given in Table 1.

There is generally a quantitative relationship between the values determined and those assumed, with an accuracy limited by the deviation; this is probably caused by the systematic error of the method, as in the example presented in our preliminary investigations [5]. The value of the relative deviation increases, as the molar weight of alcohol decreases, which is explained by the separation conditions improving due to the increasing difference between the volatilities of the alcohol and the ester.

For mixtures of relatively highly volatile alcohols (3-oxabutan-1-ol and 3-oxapentan-1-ol), the determined values of w_2 differ significantly from the assumed ester contents, which confirms our expectations. Values of w_2 corrected for residual B_2O_3 are given in parentheses. A singularly high value of δ was observed for the mixture of 3-oxabutan-ol with boric acid, since the ester step in the curve involved a superposition of ester evaporation and unconverted boric acid degradation.

Table 1 Comparison of TG-determined and stoichiometric boric acid contents

System	DSC-curve no.	TG-curve	w_2/% (m/m)	w_c/% (m/m)	δ/% (m/m)
H_3BO_3–M1	11	(A)	34.80(71.49)	64.46	–46.01(+10.9)
H_3BO_3–M2	12	(D)	62.91	67.91	–7.4
H_3BO_3–M3	13	(G)	66.58	69.64	–4.4
H_3BO_3–E1	21	(B)	45.69(59.28)	65.87	–30.6(–10.0)
H_3BO_3–E2	22	(E)	63.72	68.56	–7.05
H_3BO_3–E3	23	(H)	65.75	70.03	–6.1
H_3BO_3–B1	41	(C)	59.57	67.80	–12.1
H_3BO_3–B2	42	(F)	65.45	69.59	–5.95
H_3BO_3–B3	43	(I)	67.88	70.66	–3.9

Final remarks

It follows from the experiments described above that mixtures of boric acid and polyoxaalkanols in general behave regularly during dynamic heating in an argon atmosphere.

The mass loss steps found in the TG curves are related to the evaporation of the esterification water and the alcohol and ester fractions, respectively. Moreover, the relationship found between the TG-determined and stoichiometric boric acid ester contents, depended on the volatility of the alcohol.

The above thermoanalytical behavior of the binary systems under study will form the basis of a method for quantitative analytical characterization of various polyoxaalkyl boric acid esters.

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Zusammenfassung — Binäre Gemische aus Orthoborsäure und ausgewählten ethoxylierten Derivaten von Methanol, Ethanol oder Butanol (Polyoxaalkanolen) wurden thermoanalytisch untersucht. Sowohl TG- als auch DSC-Messungen zeigten im allgemeinen auf eine Dreischritte-Reaktion hin, die anhand der Verdampfung in der Reihenfolge Veresterungswasser, Polyoxaalkanol und Ester erklärt wurde. Es wurde eine Beziehung zwischen dem mittels TG bestimmten und dem angenommenen Estergehalt hergestellt.