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Received for review October 24, 1989. Accepted August 13, 1990.

Determination of Equilibrium Constants of a Trialkyl Borate Used in the Development of Brake Fluid Manufacturing

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For each of the three stages in the hydrolysis of tris(3,6,9-trioxadecyl) borate, the equilibrium constant is determined through aquametric analysis. It is shown that the amount of water in the equilibrium can be determined from the boiling points of mixtures made of known amounts of 3,6,9-trioxadecan-1-ol, water, and the borate ester. The equilibrium constants are then employed to calculate the composition ranges (characterized by the Karl Fischer water content and boron content) of automobile brake fluids based upon the borate ester, which obey the quality criteria set by the U. S. Department of Transportation (DOT criteria). They are also used to calculate the optimal temperature gradient in the reactor of the first industrial plant in operation producing tris(3,6,9-trioxadecyl) borate in a continuous process.

Introduction

Tris(3,6,9-trioxadecyl) borate (TMB; see nomenclature section for abbreviations), synthesized by esterification of boric acid and 3,6,9-trioxadecan-1-ol (TME) is the chief ingredient in a new type of long-life automobile brake fluid, which contributes to an increase in road safety. It does so because its hydrolysis fights water that inevitably penetrates from the atmosphere into brake systems. Brakes may not hold when water is present in the system. The specification of a brake fluid based on this principle requires the translation of the quality criteria set by the U. S. Department of Transportation (DOT criteria) into composition ranges to be expressed as the Karl Fischer water content and boron content. To do this efficiently, the equilibrium constants of the esterification/hydrolysis of TMB were determined. They also served to calculate the optimal temperature gradient in the reactor of the first industrial plant producing TMB in a continuous process, now on stream at Proviron Industries. The determination of the equilibrium constants is based on measurements of vapor pressures and boiling points. As such, it is experimentally simple and applicable to equilibria of other multistage processes in which one component is much more volatile than the others.

Hydrolysis of TMB includes the following fast equilibria

$$\mathrm{TMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{DMB} + \mathrm{TME}$$

$$\mathrm{DMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{MMB} + \mathrm{TME}$$

$$\mathrm{MMB} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3BO_3} + \mathrm{TME}$$

with equilibrium constants K_1, K_2, and K_3, defined as

$$K_1 = [\mathrm{H_3BO_3}][\mathrm{TME}]/[\mathrm{MMB}][\mathrm{H_2O}],\quad K_2 = [\mathrm{MMB}][\mathrm{TME}]/[\mathrm{DMB}][\mathrm{H_2O}],\quad K_3 = [\mathrm{DMB}][\mathrm{TME}]/[\mathrm{TMB}][\mathrm{H_2O}] \qquad (1)$$

In eq 1 [A] signifies the mole fraction of A in the equilibrium. Obviously, for each mol of H_2O reacting with TMB, 1 mol of TME is released, and thus

$$x^\circ(\mathrm{H_2O}) + x^\circ(\mathrm{TME}) = [\mathrm{H_2O}] + [\mathrm{TME}] \qquad (2)$$

where $x^\circ(\mathrm{A})$ signifies the mole fraction of component A before any reaction has occurred.

Further straightforward mathematical manipulation leads to

$$n = K_1K_2K_3(3 - n)B^3 + K_2K_3(2 - n)B^2 + K_3(1 - n)B \qquad (3)$$

with

$$n = \frac{x^\circ(\mathrm{H_2O}) - [\mathrm{H_2O}]}{x^\circ(\mathrm{TME})} \quad \text{and} \quad B = \frac{[\mathrm{H_2O}]}{[\mathrm{TME}]}$$

From eqs 2 and 3, it is clear that K_1, K_2, and K_3 follow from measurements of (at least) three values of $[\mathrm{H_2O}]$, starting from mixtures with known values of $x^\circ(\mathrm{H_2O})$, $x^\circ(\mathrm{TMB})$, and $x^\circ(\mathrm{TME})$.

Analytical methods that bind water chemically will shift the equilibria and thus cannot be used to measure $[\mathrm{H_2O}]$. Hence, physical methods are required. Despite the fact that the equilibrium mixture is complex, containing TMB, DMB, MMB, TME, H_3BO_3, and H_2O (henceforth abbreviated as the TMB/H_2O system), it proved possible to describe the system as an ideal mixture, following the simplified expression of Raoults's law:

$$p^{\mathrm{tot}} = p^\circ(\mathrm{H_2O})[\mathrm{H_2O}] + p^\circ(\mathrm{TME})[\mathrm{TME}] \qquad (4)$$

Determination of $[\mathrm{H_2O}]$ then reduces to measurements of pressures, p, at known temperatures or, alternatively, measurements of boiling points at known pressures.

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0021-9568/91/1736-0007$02.50/0

Table I. Boiling Points (°C at 1013 mbar) and Constants for TMB, TME, and Water in the Antoine Equation $\ln p° = A + B/(C + T)$

	bp[a]	A	B	C
H_2O	100	18.8	−3965	232.9
TME	248	17.3	−4296	166.0
TMB	455*	16.4	−4824	56.9

[a] Value marked with an asterisk is extrapolated; TMB decomposes at 220 °C.

Simplification of Raoults Law: Justification

The vapor pressure above a mixture, such as TMB/H_2O, is generally given by

$$p^{\text{tot}} = \sum_{i=1}^{n} \gamma(A_i)\, p°(A_i)[A_i] \qquad (5)$$

where $\gamma(A_i)$ signifies the activity coefficient of A_i and the summation is taken over all components. In this section, we will discuss the justification for the use of eq 4. We need to show that the omission of all boron-containing components from eq 5, as well as the assumption of $\gamma(H_2O) = \gamma(\text{TME}) = 1$ in eq 5, leads to insignificant errors in $[H_2O]$ for our practical purposes.

Boiling points of TMB and TME, measured at various pressures, resulted in the Antoine constants given in Table I. It follows that $p°(\text{TMB}) < 0.1$ mbar up to 200 °C. The vapor pressures of the highly viscous liquids DMB and MMB and the solid H_3BO_3 are still lower. We then define the difference, δ, between $[H_2O]$ calculated from the complete and $[H_2O]$ calculated from the simplified Raoult eq 4 as

$$\delta = [\sum_i \gamma(A_i)\, p°(A_i)[A_i]]/[(p°(H_2O) - p°(\text{TME})]$$

The summation is taken here over the boron-containing components. Taking $\gamma(A_i) = 1$ (vide infra) and $p°(A_i) = p°(\text{TMB})$, one contains $\delta_{\max}$ as

$$\delta_{\max} = x°(H_3BO_3)\, p°(\text{TMB})/[p°(H_2O) - p°(\text{TME})]$$

Substitution of appropriate values shows that under normal experimental conditions ($x°(H_3BO_3) < 0.19$; $p = 1013$ mbar; 125 °C $< T <$ 240 °C; $[H_2O] > 0.02$), the maximum relative error in $[H_2O]$ remains under 0.1%. Thus, the omission of all boron-containing components in eq 4 is justified.

The validity of $\gamma(H_2O) = \gamma(\text{TME}) = 1$ for the TMB/H_2O system cannot be checked directly, because at this point knowledge of the equilibrium concentrations is lacking. Although the final argument has to come a posteriori, some arguments can be inferred from the accessible, binary TME/H_2O system.

From Table I it follows that $p°(\text{TME}) < 0.1$ mbar for temperatures up to 50 °C. Hence, the influence of the term $\gamma(\text{TME})\, x(\text{TME})\, p°(\text{TME})$ upon the total pressure above a TME/H_2O mixture is smaller than the accuracy attainable in our pressure measurements. Furthermore, there is excellent agreement (see Figure 1) between the experimental boiling point–composition curve and the theoretical one, calculated assuming ideal behavior of TME/H_2O mixtures. These two facts show that negligible errors are introduced by taking $\gamma(\text{TME}) = 1$ at temperatures below 50 °C and above 100 °C. If in the inbetween temperature range $\gamma(\text{TME})$ would deviate from unity, then $\gamma < 1$ would be more likely than $\gamma > 1$, because negative deviations from Raoults' law frequently occur in alcohol–water mixtures as a result of ROH···H_2O complexation. We further note that if one wrongly assumes $\gamma(\text{TME}) = 1$ the relative error percentage on p is

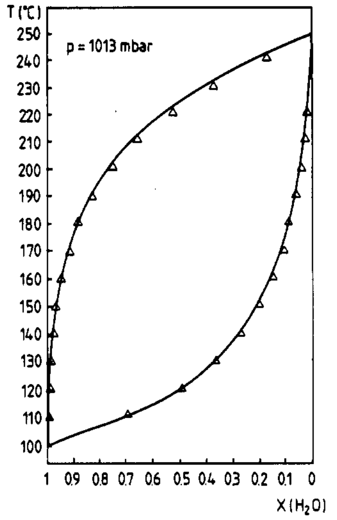

Figure 1. Boiling point–composition curve for TME/H_2O mixtures. Experimental points are represented by Δ; the drawn line represents the calculations.

$$[100\,(1 - \gamma(\text{TME})\, x(\text{TME})\, p°(\text{TME})]/p$$

Substitution of relevant numbers (at 75 °C, $p > 45.8$ mbar, $p°(\text{TME}) = 0.59$ mbar, $x(\text{TME}) > 0.5$) shows that the relative error on p will always be less than 1%.

Having established that the use of $\gamma(\text{TME}) = 1$ does not lead to serious errors, we determined $\gamma(H_2O)$ from vapor pressures of TME/H_2O mixtures at various temperatures. Table II shows the results. It follows that $\gamma(H_2O)$ rapidly approaches unity as the temperature is raised from 50 to 80 °C. In the TMB/H_2O system, the temperature region of interest is between 125 and 240 °C. Furthermore, the very weak electrolytes or nonelectrolytes H_3BO_3, MMB, DMB, and TMB present in the TMB/H_2O system can be expected to give as great a similarity in interactions (mainly H bonding) between the components as exists in the TME/H_2O system.

Actual Determination of $[H_2O]$ and Equilibrium Constants

A series of 89 equilibrium mixtures TMB/TME/H_2O with known starting compositions ($0.15 < x°(\text{TMB}) < 0.36$; $0.22 < x°(\text{TME}) < 0.54$; $x°(H_2O) < 0.62$) was made (Table III), and their boiling points were determined in an apparatus designed for mixtures containing small amounts of the volatile compo-

Table II. Activity Coefficients [$\gamma(H_2O)$] at Various Temperatures (T) in TME/H_2O Mixtures, Determined from Vapor Pressures

		T = 24.84 °C		T = 40.04 °C		T = 54.93 °C		T = 74.81 °C	
% H_2O	$x(H_2O)$	p, mbar	$\gamma(H_2O)$	p, mbar	$\gamma(H_2O)$	p, mbar	$\gamma(H_2O)$	p, mbar	$\gamma(H_2O)$
1	0.12	2.3	0.61	5.7	0.64	17.8	0.94	45.8	0.99
2	0.21	4.2	0.64	11.0	0.71	29.2	0.88	75.1	0.93
5	0.34	7.7	0.72	22.3	0.88	53.9	1.01	137.5	1.06
10	0.52	12.9	0.79	34.0	0.88	80.2	0.98	203.1	1.02
20	0.69	17.5	0.81	45.3	0.89	104.9	0.97	270.0	1.02
40	0.86	22.3	0.83	57.7	0.91	128.7	0.95	339.0	1.03
50	0.90	24.1	0.85	63.1	0.95	135.9	0.96		
60	0.93	25.6	0.88	65.3	0.95	141.7	0.97		
80	0.97	28.8	0.95	70.0	0.98	149.5	0.98		
90	0.99	28.1	0.90	70.5	0.96	151.0	0.97		

Table III. Boiling Points (T, °C) at 1013-mbar Pressure of TMB/TME Mixtures (Boron Content 1.45%), To Which Various Amounts of Water Are Added (Mass Percentage Measured According to Karl Fischer, H(KF))[a]

H(KF)	T, °C	$x°$(TMB)	$x°$(TME)	$x°$(H_2O)	[H_2O]
0.706	232	0.358	0.537	0.105	0.020
0.883	229	0.349	0.523	0.129	0.023
0.997	230	0.344	0.516	0.140	0.021
1.028	224	0.341	0.512	0.147	0.027
1.133	225	0.336	0.504	0.159	0.025
1.173	220	0.334	0.501	0.164	0.030
1.189	218	0.334	0.500	0.166	0.032
1.317	218	0.328	0.491	0.181	0.032
1.444	214	0.322	0.484	0.195	0.036
1.461	210	0.321	0.482	0.197	0.040
1.599	212	0.315	0.473	0.212	0.038
1.605	208	0.315	0.472	0.213	0.043
1.749	205	0.309	0.463	0.228	0.047
1.908	202	0.303	0.454	0.244	0.051
2.054	199	0.297	0.445	0.258	0.055
2.177	191	0.292	0.438	0.269	0.068
2.252	189	0.290	0.434	0.276	0.072
2.320	189	0.287	0.431	0.282	0.072
2.369	190	0.285	0.428	0.287	0.070
2.462	186	0.282	0.423	0.295	0.078
2.603	187	0.277	0.416	0.307	0.076
2.674	178	0.275	0.412	0.313	0.097
2.745	182	0.273	0.409	0.318	0.086
2.826	174	0.270	0.405	0.325	0.107
2.978	180	0.265	0.398	0.337	0.091
3.026	171	0.264	0.395	0.341	0.117
3.130	175	0.261	0.391	0.349	0.105
3.281	171	0.256	0.384	0.360	0.116
3.431	170	0.252	0.378	0.370	0.119
3.582	168	0.248	0.371	0.381	0.126
3.586	162	0.248	0.371	0.381	0.148
3.725	160	0.244	0.366	0.391	0.157
3.732	164	0.244	0.365	0.391	0.140
3.864	162	0.240	0.360	0.400	0.148
3.881	165	0.240	0.359	0.401	0.137
4.003	160	0.237	0.355	0.408	0.156
4.031	159	0.236	0.354	0.410	0.161
4.141	158	0.233	0.350	0.417	0.165
4.180	159	0.232	0.348	0.419	0.160
4.279	158	0.230	0.345	0.425	0.165
4.328	160	0.229	0.343	0.428	0.156
4.417	160	0.227	0.340	0.433	0.156
4.477	160	0.225	0.338	0.437	0.156
4.554	154	0.224	0.335	0.441	0.184
4.625	155	0.222	0.333	0.445	0.179
4.691	152	0.220	0.330	0.449	0.195
4.772	155	0.219	0.328	0.453	0.197
4.828	150	0.217	0.326	0.457	0.207
4.919	149	0.216	0.323	0.461	0.207
4.965	150	0.215	0.322	0.464	0.204
5.066	154	0.212	0.318	0.469	0.184
5.101	150	0.212	0.317	0.471	0.207
5.213	151	0.209	0.314	0.477	0.201
5.237	149	0.209	0.313	0.478	0.213
5.359	151	0.207	0.310	0.484	0.201
5.372	148	0.206	0.309	0.485	0.219
5.505	151	0.204	0.305	0.491	0.201
5.508	148	0.204	0.305	0.491	0.218
5.643	144	0.201	0.301	0.498	0.245
5.650	148	0.201	0.301	0.498	0.219
5.777	144	0.199	0.298	0.504	0.245
5.940	145	0.196	0.293	0.511	0.238
6.085	145	0.193	0.289	0.518	0.238
6.229	144	0.191	0.286	0.524	0.235
6.313	140	0.189	0.283	0.527	0.275
6.373	144	0.188	0.282	0.530	0.245
6.516	138	0.186	0.278	0.536	0.292
6.580	142	0.185	0.277	0.538	0.249
6.633	139	0.184	0.276	0.541	0.284
6.659	142	0.183	0.275	0.542	0.260
6.712	140	0.183	0.274	0.544	0.275
6.802	141	0.181	0.272	0.547	0.267
6.845	140	0.181	0.271	0.549	0.275
6.977	140	0.178	0.268	0.554	0.275
7.109	136	0.177	0.265	0.559	0.310
7.370	138	0.173	0.259	0.568	0.291
7.370	135	0.173	0.259	0.586	0.319
7.511	138	0.171	0.256	0.574	0.292
7.652	138	0.169	0.253	0.578	0.291
7.764	132	0.167	0.251	0.582	0.349
7.793	132	0.167	0.250	0.583	0.349
7.894	132	0.165	0.248	0.587	0.350
7.933	132	0.165	0.247	0.588	0.349
8.154	132	0.162	0.243	0.595	0.349
8.212	131	0.161	0.242	0.597	0.350
8.430	130	0.159	0.238	0.604	0.371
8.541	131	0.157	0.236	0.607	0.360
8.789	131	0.154	0.231	0.615	0.360
8.926	128	0.153	0.229	0.619	0.395

[a] $x°$(TMB), $x°$(TME), and $x°$(H_2O) are the mole fractions of TMB, TME, and H_2O, respectively, before hydrolysis. [H_2O] is the mole fraction of water after equilibrium has been reached.

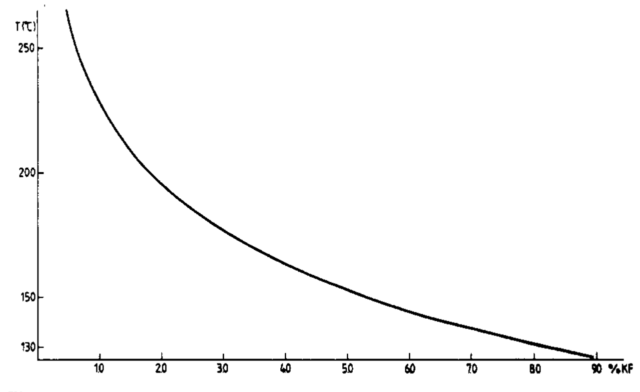

Figure 2. Boiling points of equilibrium TMB/TME/H_2O mixtures as a function of KF (the percentage of water determined by the Karl Fischer method).

nent. Exploratory kinetic measurements had proved that even at room temperature equilibrium is reached within seconds. Thus, the time needed to mix the components suffices to attain equilibrium.

The very strong variation of the boiling points at low values of $x°(H_2O)$ and the very weak variation at high $x°(H_2O)$ values result in a mathematically ill-balanced data set. At the usual measuring accuracy of boiling points and concentrations, classic least-squares procedures can easily fail, which indeed occurred here. Two steps were taken to alleviate the problems. First, the experimental boiling points were fitted to a smooth function (Figure 2)

$$T = a \ln (b\mathrm{KF})$$

with $a = -46.729$ and $b = 7.575 \times 10^{-3}$, where KF signifies the apparent water percentage, determined by the Karl Fischer method (see Experimental Section). The function reproduces the observed boiling points for $T < 240$ °C with an average deviation of 2.7 °C.

Second, the smoothed data points were given appropriate weights. This is not at all trivial. Fortunately, recent evolution in statistics has resulted in so-called "robust methods", such as the least-median-squares method (*1*). In comparison to the classic least-squares method, the least-median-squares procedure is less sensitive to outliers and not normally distributed errors in the data set. From the smoothed boiling points, values of [H_2O] were enumerated by using eq 5 and the Antoine relations (Table I). Then application of eq 3 and the method of least-median-squares (*1*) resulted in

$$K_1 = 1.0, \quad K_2 = 1.9, \quad K_3 = 11.2$$

Table IV. DOT Criteria for Automobile Brake Fluids

	DOT-3	DOT-4	DOT-5
dry boiling point (°C)	>205	>230	>260
wet boiling point (°C)	>140	>155	>180
viscosity (mm^2/s at -40 °C)	<1500	<1800	<900

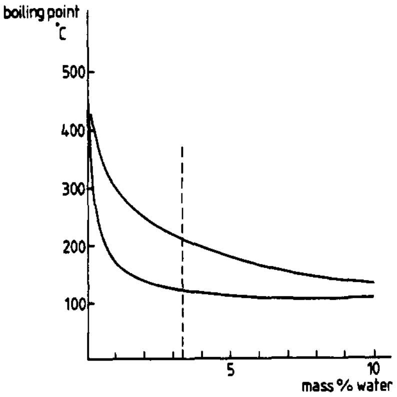

Figure 3. Boiling points (°C) of real TMB/H_2O mixtures (top) and hypothetical nonhydrolyzing TMB/H_2O mixtures (bottom). The intersection of the boiling point curve with the vertical line at 3.38 mass % water defines the wet boiling point.

with an estimated standard deviation of $\sigma = 0.3$. The equilibrium constants can be applied inter alia to calculate boiling points of $TMB/TME/H_2O$ mixtures of arbitrary beginning composition and hence to predict composition ranges of TMB/TME-based automobile brake fluids, which will obey quality criteria set by the U. S. Department of Transportation (DOT criteria). The accuracy of such predictions can be estimated from

$$Q = [\sum_{n}^{1} (T_{\text{exp}} - T_{\text{calc}})^2]^{1/2}$$

and is in the order of 4 °C or 0.1% in composition over all operational ranges of interest (pressures, temperatures, boron and water contents). We consider this as a posteriori justification for the use of eq 4.

DOT Criteria and Composition Ranges

DOT criteria (Table IV) concern the boiling point of the fresh, commercial product (dry bp), the boiling point after addition of 3.5 g of water to 100 g of fresh product (wet bp), and the viscosity at -40 °C.

The viscosity at -40 °C of pure TMB (1900 $mm^2\ s^{-1}$), exceeding all DOT limits, can be reduced in mixtures with TME, thus rendering the boron content an important parameter. The importance of the water content is connected with the (wet) boiling point criterion. Figure 3 depicts the calculated boiling point curve of TMB to which various amounts of water are added, together with the boiling point curve of the same mixtures in the hypothetical case that no hydrolysis would occur. It follows that a nonhydrolyzable TMB would have a wet boiling point of 130 °C and would not meet any of the DOT criteria. The occurrence of hydrolysis in real TMB/H_2O mixtures, however, raises the wet boiling point (about 200 °C) above the DOT-5 norm. In fact, the increase is so large that for high-quality brake fluids mixtures of TMB and the lower boiling TME can be used and that it is not necessary to remove all water of esterification, $H_3BO_3 + 3TME \rightarrow TMB + 3H_2O$.

A convenient way to look at TMB-based brake fluids is to see them as liquids in equilibrium, originating from a small amount of water (characterized by the Karl Fischer water content, KF) in a TMB/TME mixture (characterized by the boron content, BE). These two numbers, KF and BE, together with the equilibrium constants characterize the complete equilibrium mixture by providing values for $x°(TMB)$, $x°(TME)$, and $x°(H_2O)$. We now enumerate the boiling points for such mixtures at equilibrium. For example, the line DOT-3D in Figure 4a is the line connecting all combinations of KF, BE that lead to a boiling point of 205 °C. Thus, any TMB-based brake fluid with a combination of KF, BE to the right of the line obeys the dry boiling criterion for DOT-3 quality.

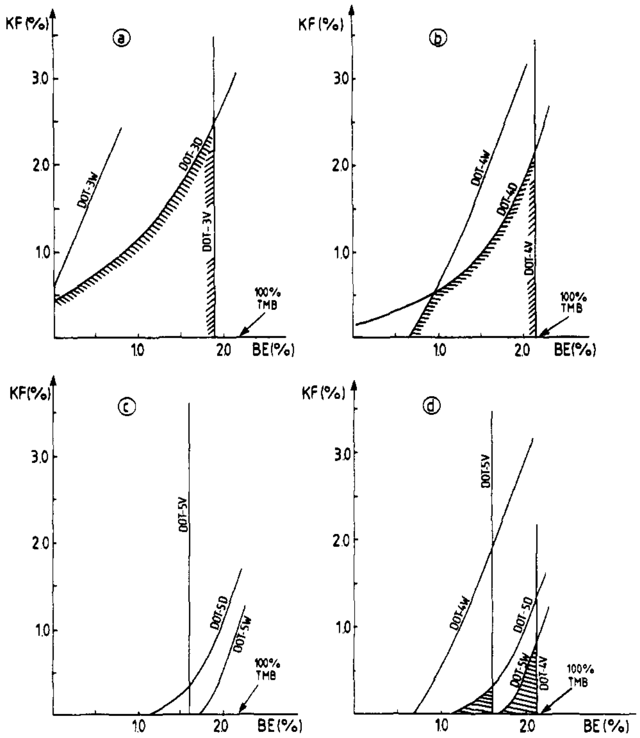

Figure 4. Composition ranges (mass %) obeying DOT quality criteria: (a) for DOT-3; (b) for DOT-4; (c) for DOT-5 (none possible); (d) for super DOT-4 (see text).

Similarly the line DOT-3W gives all combinations of KF, BE that, after addition of 3.5 g of water to 100 g of "dry" product, lead to a boiling point of 140 °C. Thus, compositions to the right of DOT-3W obey the wet boiling point criterion. Finally, products with a composition to the left of the line DOT-3V obey the DOT-3 viscosity criterion. Figure 4a shows that the composition range obeying DOT-3 criteria is dominated by the dry boiling point criterion. Figure 4b shows the composition range for DOT-4 quality. In this case, all three criteria play their role. Figure 4c reveals that no TMB/TME brake fluid of DOT-5 quality can be made. The two hatched regions of Figure 4d depict product ranges obeying all DOT-4 and two out of three DOT-5 criteria. The range near BE = 1.87%, KF = 0.10% only violates the DOT-5 viscosity criterion, while the range near BE = 1.45%, KF = 0.15% only violates the DOT-5 wet boiling point criterion. Giving equal weight to each criterion, both ranges represent different brake fluids of equivalent super DOT-4 quality. Nevertheless, production of the second type (BE = 1.45%, KF = 0.15%) is the better choice, because its boiling point will be about 30 °C lower than that of the first, and thus the required reactor temperature and concomitant production costs will be lower.

To produce this product in a continuous process, a mixture of 8% H_3BO_3 and 92% TME is fed into a long tubular reactor, and the water of esterification is evaporated at reduced pressure (60 mbar). Figure 5 depicts the boiling point of the reacting mixture as a function of its diminishing Karl Fischer water content. Hence, Figure 5 also represents the optimum temperature gradient in the reactor.

Experimental Section

TME was purchased from Aldrich (product number 31,729-2).

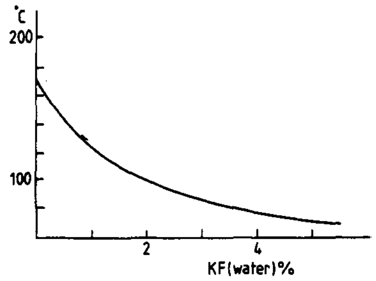

Figure 5. Boiling points (°C) of a reacting mixture of H_3BO_3/TME (starting from 8% H_3BO_3 and 92% TME) during evaporation of reactant water at 60 mbar, expressed as Karl Fischer water content (mass %).

TMB. A mixture of 493 g (3 mol) of TME and 62 g (1 mol) of boric acid was heated to 165 °C at 60-mbar pressure until 54 g (3 mol) of water had evaporated. The resulting product was used without further purification.

DMB. A mixture of 329 g (2 mol) of TME and 62 g (1 mol) of boric acid was treated as in TMB until 36 g (2 mol) of water had evaporated. The resulting liquid was considered to represent DMB.

MMB. A mixture of 164 g (1 mol) of TME and 62 g (1 mol) of boric acid was treated as in TMB until 18 g (1 mol) of water had evaporated. The resulting liquid was considered to represent MMB.

Boron was determined as boric acid. The boron-containing sample was hydrolyzed with excess water and after addition of a sufficient amount of mannitol titrated with sodium hydroxide by using phenolphtaleine as indicator (*2*). The water content according to Karl Fischer (*2*) was determined by using a 652-KF-Coulometer (Metzohn).

It should be realized that methanol present in the Karl Fischer reagent reacts with boric acid, DMB, and MMB. The Karl Fischer water content (KF, %) measures in these samples the amount of free water in addition to the amount of water still to be formed in esterifications:

$$\mathrm{KF} = \%\ \mathrm{water} + (\%\ \mathrm{boric\ acid})\frac{3 \times 18}{61.8} + (\%\ \mathrm{MMB})\frac{2 \times 18}{207.8} + (\%\ \mathrm{DMB})\frac{18}{353.8}$$

Thus KF is constant in equilibrium mixtures having a constant mass, and KF changes when water is removed (e.g. by distillation) or added (e.g. by weathering).

The boiling point–composition curve was determined as described in Vogel (*3*). Boiling points of mixtures containing only small amounts of the volatile component were measured in a vapor-lock apparatus manufactured by Castrol Ltd.

Static vapor pressure measurements were performed in an apparatus (*4*) built in the research laboratories of DSM (Geleen, The Netherlands). The sample temperature is kept constant to within 0.01 °C, while special care is taken to avoid condensation in the conduit pipes. After eight freeze–thaw degassing cycles (at −78 °C), an accuracy was achieved of 0.1 mbar in the tabulated pressures (Table II).

Acknowledgment

Dr. L. A. Kleintjens and Mr. T. Cuypers (DSM, Geleen, The Netherlands) are thanked for their help during the static pressure measurements.

Nomenclature

TMB = $(H_3COCH_2CH_2OCH_2CH_2OCH_2CH_2O)_3B$, tris(3,6,9-trioxadecyl) borate
DMB = $(H_3COCH_2CH_2OCH_2CH_2OCH_2CH_2O)_2B(OH)$, bis(3,6,9-trioxadecyl) hydrogen borate
MMB = $(H_3COCH_2CH_2OCH_2CH_2OCH_2CH_2O)B(OH)_2$, (3,6,9-trioxadecyl) dihydrogen borate
TME = $H_3COCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, 3,6,9-trioxadecan-1-ol
$p(\mathrm{i})$ = partial pressure of component i in the mixture
$y(\mathrm{i})$ = mole fraction of component i in the gas phase
$x(\mathrm{i})$ = mole fraction of component i in the liquid phase
$\gamma(\mathrm{i})$ = activity coefficient of component i
$p^\circ(\mathrm{i})$ = vapor pressure above the pure liquid i at a certain temperature
p = total pressure above the mixture

Registry No. TMB, 112-35-6; TME, 30989-05-0; water, 7732-18-5.

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Received for review November 27, 1989. Accepted August 28, 1990.