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Vapour–liquid equilibrium of organoboron compounds

II *. Binary system: triethylboroxin–tetraethyldiboroxane

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Abstract

A temperature-composition diagram for the system triethylboroxin/tetraethyldiboroxane at 760.78 Torr has been determined by the ebulliometric method. The system is not azeotropic, and exhibits a negative deviation from ideality. The density–composition relationship and excess volume diagram have also been determined. The results have been approximated by Redlich–Kister (V^E) and NRTL (G^E) equations. The results do not indicate the formation of a mixed compound either in liquid or in the vapour phase.

Introduction

Oxygen-containing organoboron compounds such as triorganoboroxins $(RBO)_3$ or tetraorganodiboroxanes $(R_2B)_2O$, as well as their mixtures, have wide synthetic and analytical applications. With the help of boroxin/boroxane mixtures, carbohydrates can be transformed to *O*-substituted ethylboron derivatives. Köster and Idelmann described the synthesis of the 1:3 $(EtBO)_3/(Et_2B)_2O$ mixture and suggested distillation as a method by which to purify it [1]. The constant boiling point value reported for the 1:3 mixture, lying between the values of its pure components, shows that the system is not azeotropic, but rather suggests the occurrence of chemical interactions in the liquid phase. However, spectroscopic

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* For Part I see ref. 2.

measurements do not confirm the formation of a mixed compound. The aim of this work is to provide more detailed information on this binary system on the basis of a vapour–liquid equilibrium investigation.

Experimental

Materials

Triethylboroxin and tetraethyldiboroxane were obtained and purified as described previously [2].

Technique

The vapour–liquid equilibrium parameters were determined by a complete method, i.e. by the method of simultaneous determination of the composition of both the liquid and vapour phase, pressure and temperature. The pressure was stabilized and measured and the temperature was measured as described in Part I [2]. The construction of the ebulliometer was modified to enable the sampling of the liquid and the condensate by a syringe according to Rogalski and Malanowski [3].

Determination of liquid and vapour composition

The composition of the liquid and vapour was determined by density measurements. The accuracy of this method seems to be better than that of refractometry, because there is a substantial difference in densities between $(EtBO)_3$ and $(Et_2B)_2O$, whereas the refractive indices of both compounds are similar: 1.3965 and 1.4032, respectively [1]. The density was measured by a DMA 02C densimeter (Anton Paar K.G., Austria) at 25.0 ° C with an accuracy of 0.00001 $g \cdot cm^{-3}$. The instrument was previously calibrated according to a standard method.

Results

The densities of the mixtures of triethylboroxin with tetraethyldiboroxane are shown in Table 1.

Table 1

Density, molar volume and excess volume values for the system $(EtBO)_3/(Et_2B)_2O$ as a function of mole fraction of $(EtBO)_3$ (x_1)

x_1	ρ ($g \cdot cm^{-3}$)	V ($cm^3 \cdot mol^{-1}$)	V^E ($cm^3 \cdot mol^{-1}$)
0	0.74572	206.339	0
0.12985	0.76284	204.048	0.173
0.24201	0.77827	201.984	0.237
0.38213	0.79820	199.353	0.265
0.62732	0.83451	194.719	0.284
0.72149	0.84909	192.899	0.250
0.81773	0.86449	190.994	0.172
0.88683	0.87579	189.613	0.102
0.90408	0.87872	189.252	0.068
1	0.89461	187.364	0

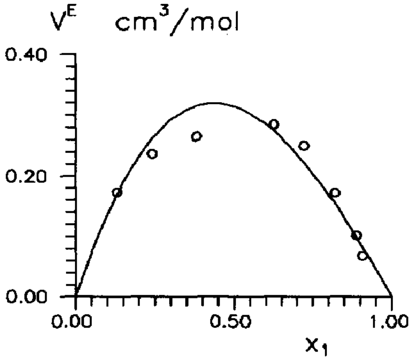

Fig. 1. Excess volume for the system $(EtBO)_3/(Et_2B)_2O$ at 25.0° C; ○ - experimental values, ——— - Redlich–Kister equation.

The density of the mixture is not a linear function of mole fraction. The appropriate relationship was approximated by a polynomial. Equation 1

$$\rho = 0.019432x_1^2 + 0.129389x_1 + 0.745759 \tag{1}$$

approximates the experimental data with a standard deviation of 0.000085 $g \cdot cm^{-3}$.

The molar volume and excess volume were calculated from Eq. 2 and 3:

$$V = \frac{x_1M_1 + x_2M_2}{\rho} \tag{2}$$

$$V^E = V - \left(x_1V_1^0 - x_2V_2^0\right) \tag{3}$$

where the index 1 corresponds to $(EtBO)_3$, the index 2 to $(Et_2B)_2O$, $V_1^0 = M_1/\rho_1$ and $V_2^0 = M_2/\rho_2$. The results are collected in Table 1.

Excess volume data have been correlated by the Redlich–Kister equation:

$$V^E = x_1(1 - x_1)[1.25418 + 0.336184(1 - 2x_1)] \tag{4}$$

with the standard deviation 0.02 $cm^3 \cdot mol^{-1}$. The experimental values and Redlich–Kister plot are shown in Fig. 1.

Experimental values of the composition of the liquid (x_1) and vapour (y_1) at 760.78 Torr (101429 Pa) as a function of temperature are collected in Table 2.

Table 2

Mole fraction of $(EtBO)_3$ in the liquid (x_1) and in the vapour (y_1) and excess Gibbs energy values for the system $(EtBO)_3/(Et_2B)_2O$ at 760.78 Torr

T (° C)	x_1	y_1	G^E ($J \cdot mol^{-1}$)
150.40	0.060	0.042	−10.2
151.15	0.227	0.197	−31.3
151.75	0.371	0.340	−41.1
152.10	0.506	0.479	−43.6
152.15	0.553	0.527	−42.9
152.35	0.658	0.634	−38.8
152.65	0.839	0.821	−23.0
152.85	0.866	0.850	−19.7

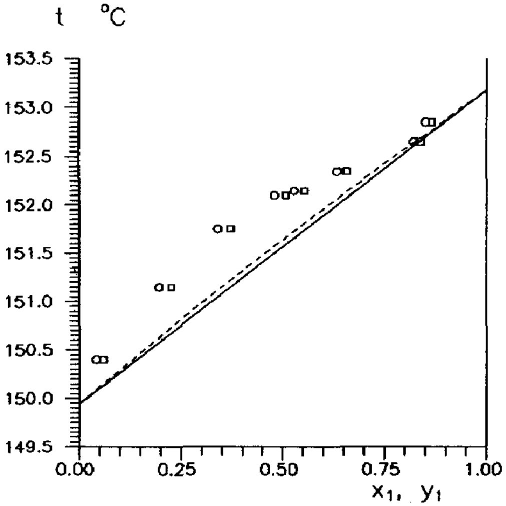

Fig. 2. t–x–y diagram for the system $(EtBO)_3/(Et_2B)_2O$ at 760.68 Torr ○ - vapour, □ - liquid composition (experimental data). - - - - - - vapour, ——— - liquid composition (calculated from Raoult's law).

The results have been correlated using the NRTL equation [4]. We assumed that three adjustable parameters (α, $C_{12} = g_{12} - g_{22}$ and $C_{21} = g_{21} - g_{11}$) are independent of temperature, the vapour phase is ideal and the molar volume of the liquid is negligible in comparison with the molar volume of the vapour. The following values for the parameters have been obtained:

$\alpha = 0.118$, $C_{12} = 2431.45\ \mathrm{J \cdot mol^{-1}}$, $C_{21} = -2410.87\ \mathrm{J \cdot mol^{-1}}$.

The NRTL equation with these parameters describes the data with a mean percentage error for pressure of 0.4% and for a mole fraction of component 1 in the vapour phase equal 0.009. A *t–x–y* diagram for the investigated system (experimental points and Raoult's law plots) is shown in Fig. 2. Excess Gibbs function values calculated from the NRTL equation are collected in Table 2 and shown in Fig. 3.

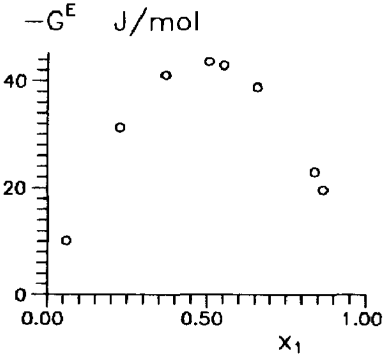

Fig. 3. Excess Gibbs function for the system $(EtBO)_3/(Et_2B)_2O$ at 760.68 Torr calculated from the NRTL equation.

Discussion

The reported results show that the $(EtBO)_3/(Et_2B)_2O$ system is not azeotropic, with very small negative deviations from ideality. Small differences in the boiling points of the pure components make their separation by distillation very difficult, and useless as a method of purification. The 1 : 3 $(EtBO)_3/(Et_2B)_2O$ mixture has an almost constant boiling point, which is caused by small differences in the vapour and liquid composition in equilibrium (differences in mole fraction of less than 0.03). A truly constant boiling point (but with an extremal value of temperature) could only be observed in an azeotropic system, which can be excluded on the basis of the results reported above for the investigated compounds. Another explanation could be the formation of a "mixed" compound (eq. 5):

$$(EtBO)_3 + 3(Et_2B)_2O \rightarrow 3Et_2BOB(Et)OBEt_2 \tag{5}$$

However, the values of the excess functions reported above exclude the formation of such a compound in the liquid phase, a result which is in agreement with spectroscopic measurements [1]. The formation of a "mixed" compound in the vapour phase only is not possible for thermodynamic reasons.

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References

1 R. Köster and P. Idelmann, Inorg. Synth., 24 (1986) 83.
2 A. Sporzyński and J. Gregorowicz, Main Group Met. Chem., 13 (1990) 1
3 M. Rogalski and S. Malanowski, Fluid Phase Equilibria, 5 (1980) 97.
4 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.