

## ISOLATION OF PURE TETRAETHYLDIALUMINOXANE

LESZEK SIERGIEJCZYK\* and LUDWIK SYNORADZKI

*Laboratory of Technological Processes, Faculty of Chemistry of Warsaw Technical University  
(Politechnika), Noakowskiego 3, 00-664 Warsaw (Poland)*

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### Summary

The reaction products of triethylaluminium with water at a molar ratio of 2/1 were studied. By means of gel permeation chromatography it was found that raw tetraethyldialuminoxane consists of ethyloligoaluminoxanes, a tetraethyldialuminoxane trimer and triethylaluminium. The isolated pure tetraethyldialuminoxane trimer did not undergo further separation and was stable at room temperature for several weeks.

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Although the chemistry of tetraethyldialuminoxane has been the subject of numerous reports in the literature, the structure of this compound has not been determined definitely until now.

Most of the authors [1–7] suggested that tetraethyldialuminoxane forms a trimeric associate,  $[(Et_2Al)_2O]_3$ . On the other hand, it was also suggested [8,9] that this trimer does not exist and the compound named tetraethyldialuminoxane consists only of a mixture of ethyloligoaluminoxanes and triethylaluminium.

We found that by using gel permeation chromatography it was possible to isolate the pure oligomeric associate from its mixture, together with ethyloligoaluminoxanes and triethylaluminium.

The raw tetraethyldialuminoxane obtained in the reaction of  $Et_3Al$  with  $H_2O$  at a molar ratio of 2/1 can be separated into three phases (Fig. 1) by gel permeation chromatography, using polystyrene cross-linked with divinylbenzene gel and toluene as eluant. Within the range characteristic of  $>Al-O-Al<$  moieties, the IR spectra of the first and second phases comprised one absorption band of high intensity at  $800\text{ cm}^{-1}$ . The band at  $980\text{ cm}^{-1}$ , characteristic of the C–C vibrations of ethyl groups, was of high intensity in the spectrum of the third phase and weak in the spectra of the first and second phases. The mass ratio of phases I/II/III was 15/65/20.

The first phase consisted of a mixture of ethyloligoaluminoxanes of average molecular weight ca. 1670. The molecular weight of the second phase corresponded to that of trimeric tetraethyldialuminoxane (found: 562;  $Et_4Al_2O$  calcd.: 186). The

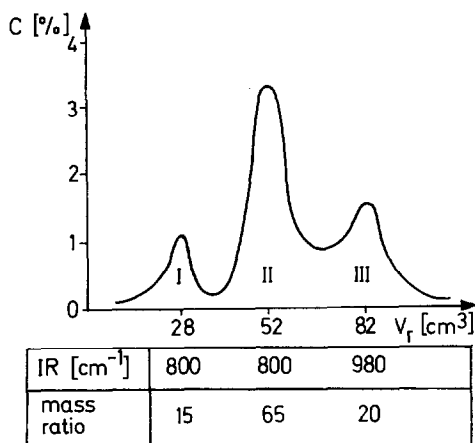


Fig. 1. Gel permeation chromatography of raw tetraethylaluminum oxide.

third phase was triethylaluminum, molecular weight 232. The cryoscopically determined molecular weights of the first and second phases were consistent with the molecular weights calculated from the calibration curve of the column (eq. 1):

$$\log(\text{mol. wt.}) = 3.68 - 0.0163V_r \quad (1)$$

where  $V_r$  is the retention volume.

The raw product of triethylaluminum hydrolysis could be expected to comprise an equilibrium mixture of ethyloligoaluminum oxanes, tetraethylaluminum oxide and triethylaluminum (eq. 2):



At room temperature a shift in the position of equilibrium was kinetically inhibited; that is the reason why we could isolate pure tetraethylaluminum oxide. In addition, almost all the amount of triethylaluminum could be distilled from the raw tetraethylaluminum oxide at room temperature and no change in the position of equilibrium was observed (Fig. 2). Further separation of the previously isolated pure tetraethylaluminum oxide (phase II) was not observed.

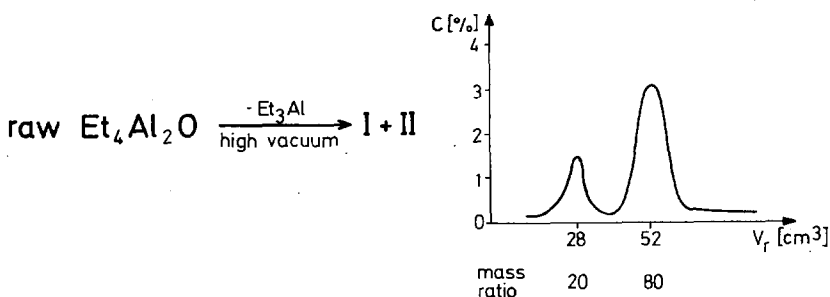


Fig. 2. Distillation of triethylaluminum from raw tetraethylaluminum oxide.

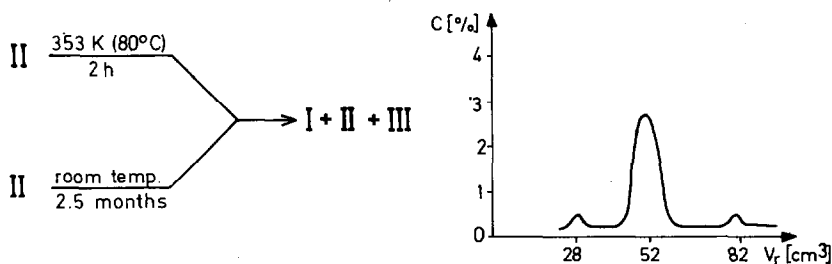


Fig. 3. Influence of the storage temperature and time of the pure tetraethylaluminumoxane on the equilibrium position of the condensation reaction.

However, after heating pure tetraethylaluminumoxane up to 353 K (80°C) for 2 h, phases I and III appeared (Fig. 3). Also after keeping pure phase II at room temperature for 2.5 months, phases I and III appeared (Fig. 3).

We hope that by further careful investigation of the transformation of tetraethylaluminumoxane its nature as well as the mechanism of triethylaluminum hydrolysis will be clarified.

### Experimental

Tetraethylaluminumoxane was prepared by a continuous method [10].

The polystyrene gel was obtained by suspension polymerization (3% divinylbenzene was added to the monomer).

The calibration curve of the column of polystyrene gel was determined using  $(Et_3Al)_2$ ,  $(Et_2AlOEt)_2$  and  $[(i-Bu)_2AlO(i-Bu)]_2$ .

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