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Synthesis and Properties of Poly(N-alkyliminoalanes) in Tetrahydrofuran

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A correspondence has been found between the conductimetric trends observed during the reaction of AlH_3 with different primary amines and the structure of the resulting poly(N-alkyliminoalanes) (PIA). The conductivity measurements proved also to be effective in showing the formation of PIA having the same structural features from different synthetic methods as well as the interaction of PIA with AlH_3.

Introduction

The reaction between $AlH_3 \cdot NMe_3$ and an equimolar amount of a primary amine in diethyl ether yields poly(N-alkyliminoalanes), PIA, whose structures strictly depend on the nature of the alkyl group bonded to nitrogen of the amine[1].

When carrying out the reaction of AlH_3 with lower amounts of isopropylamine or n-butylamine in tetrahydrofuran, it has been possible to isolate and characterise some of different N-alkyliminoalanes, owing to their higher stability in THF[2]. These compounds can be regarded as possible intermediates in PIA synthesis. The reaction has also been followed conductimetrically and a relationship between the conductivity changes and the composition of the intermediates was found[2].

These findings prompted us to extend our research to other primary amines, as well as to the properties of PIA obtained in THF solution.

Results and Discussion

The conductivity changes as a function of hydrogen evolution from the reaction between AlH_3 and different amines are reported in Figure 1 and Figure 2. The conductivity trends are different and depend on the nature of the amine.

In addition to results obtained with ethyl and n-butylamine[1] the use of n-propylamine confirmed that linear amines show a maximum of conductivity at H_2/Al = *ca.* 1.5, which can be associated with the formation of aluminum tris(N-alkyliminoalanes) [reaction (1)], as previously shown for n-butylamine[2].

$$4\,AlH_3 + 3\,RNH_2 \xrightarrow{THF} \underset{(I)}{Al(NR{-}AlH_2)_3} + 3\,H_2 \quad (1)$$

For amines having a nitrogen with secondary α or β carbon atoms (Figure 2), the conductivity curves show an inflection at H_2/Al = *ca.* 1, which we suggested to be related to the formation of N-alkyliminodialane species (II) on the basis of the evidence found in the case of isopropylamine[2] [reaction (2)].

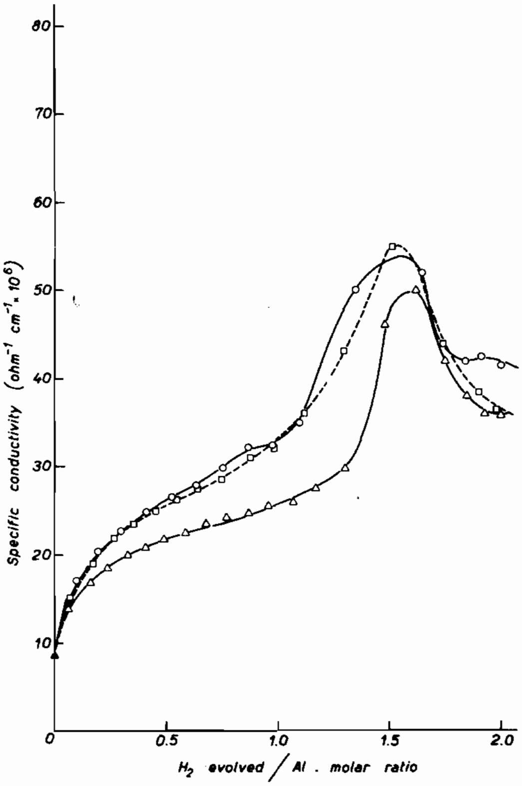


Figure 1. Plot of conductivity against hydrogen evolution observed during the addition of different amines to AlH_3 in THF solution. □ $C_2H_5NH_2$; ○ n-$C_3H_7NH_2$; △ n-$C_4H_9NH_2$. Reaction conditions: a 5*M* solution of the amine was added to an 0.06*M* solution of AlH_3 at 20° C; the rate of addition was 0.25 ml/10 min and after each addition the hydrogen evolution and the conductimetric change were measured.

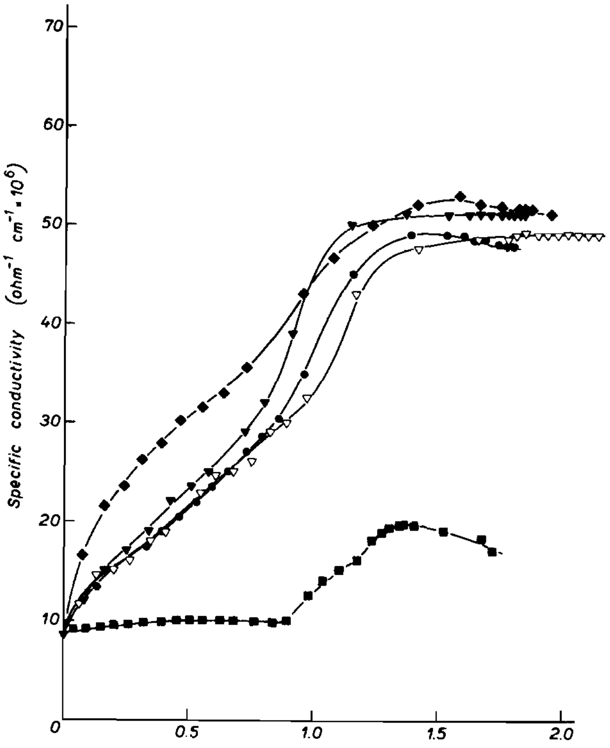


Figure 2. Plot of conductivity against hydrogen evolution observed during the addition of different amines to AlH_3 in THF solution. ▼ iso-$C_3H_7NH_2$; ◆ iso-$C_4H_9NH_2$; ▽ *sec*-$C_4H_9NH_2$; ● $C_6H_{11}NH_2$; ■ *tert*-$C_4H_9NH_2$. For the reaction conditions see Figure 1.

$$2\ AlH_3 + RNH_2 \xrightarrow{THF} \underset{(II)}{H_2Al\text{–}NR\text{–}AlH_2} + 2\ H_2 \qquad (2)$$

Tert-butylamine shows a different trend with lower conductivity values. In our experiments the AlH_3 was obtained by the method of Finholt *et al.*[3] and contains a small amount of complexed LiH, which as previously reported[2] has an enhanced effect on conductivity by its complexation with N-alkyliminoalane species. However the conductivity measurements proved to be a good tool in showing how the nature of the amine influences the course of the reaction with AlH_3 and finally the structure of PIA obtained according to the reaction (3).

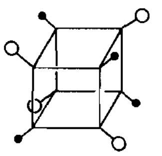
$$AlH_3 + RNH_2 \xrightarrow{THF} \underset{(III)}{\frac{1}{n}(HAlNR)_n} + 2\ H_2 \qquad (3)$$

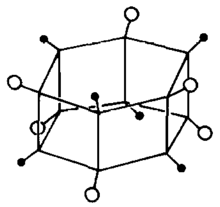
In fact, the dependence of the structure of (III) on the nature of the amine used has been found as follows: i) a mixture of oligomers $(HAlNR)_n$ with n ranging from 6 to 8 is formed from linear amines; ii) prevailingly hexamers $(HAlNR)_6$ from amines having a secondary carbon atom in an α or β position with respect to the nitrogen; iii) a tetramer $(HAlNR)_4$ from *tert*.-$C_4H_9NH_2$.

These data confirm our previous results obtained for reaction (3) carried out in diethyl ether starting from $AlH_3 \cdot NMe_3$[1]. Chemical and physico-chemical results are given in Table I.

The different oligomers were identified by mass spectrometry which showed the most important fragmentation at the C–C linkage adiacent to the nitrogen atom[2]. In the case of PIA prepared in THF, the presence also of oligomers complexed with solvent molecules has been shown in the vapour state together with the solvent-free oligomers, while PIA obtained from $AlH_3 \cdot NMe_3$ in diethyl ether retain some molecules of solvent only in the solid state or in solution[1]. For example poly(N-isopropyliminoalane) prepared in THF showed beside the ion at m/e 495 from hexamer $[(M\text{–}CH_3)^+]$, ions at m/e 567 $[(M\text{–}CH_3)^+ \cdot THF]$ (calculated mass for $Al_6N_6C_{21}H_{53}O$ = 567.3170; measured mass 567.3216) and at m/e 639 $[(M\text{–}CH_3)^+ \cdot 2THF]$.

This is a general feature of the PIA obtained in THF from different amines, except poly(N-*tert*-butyliminoalane) which exhibits only one ion at m/e 381 $[(M\text{–}CH_3)^+$ from tetramer (IV)]. Finally the X-ray powder pattern confirmed the formation of a hexamer from iso-$C_3H_7NH_2$ which has the previously characterised cage structure (V).


(IV)


(V)

The fraction iPrPIA-C of Table I consists entirely of this structure. In a previous paper on this subject, we proposed[5] a different route for the synthesis of PIA, *i.e.* starting from aluminum amides and AlH_3 [reaction (4)].

$$Al(NHR)_3 + 2\ AlH_3 \rightarrow \frac{3}{n}(HAlNR)_n + 3\ H_2 \qquad (4)$$

It now seemed interesting to follow this reaction by means of conductivity. Limiting our investigations to n-butylamine and isopropylamine, $Al(NHR)_3$ was prepared *in situ* by addition of an AlH_3 solution to an excess of the amine, followed by further addition of AlH_3 until the ratio AlH_3/RNH_2 = 1 was obtained, that is, corresponding to the formation of PIA. This procedure corresponds to a reverse addition of the

TABLE I. Results Obtained for the Synthesis of Poly(N-alkyliminoalanes) by Addition of Primary Amines to AlH_3 in Tetrahydrofuran Solution

Compound	Amine	Fraction			Chemical composition[c] Found (Calcd.)			Mol. wt.[d]	n in $(HAlNR)_n$	Mass spectra data suggest
		Sample[a]	%	X-ray analysis[b]	Al (%)	N (%)	$H_{act.}$			
n-PrPIA	n-$C_3H_7NH_2$	n-PrPIA-C	45	XX	31.27 (31.71)	16.35 (16.46)	12.80 (11.75)[e]	471	5.5	mainly hexamer
		n-PrPIA-R	55	XX	28.92 (27.78)	14.82 (14.42)	10.28 (10.30)[f]	618	6.4	mainly hexamer, heptamer, octamer and their complexes with THF
i-PrPIA	iso-$C_3H_7NH_2$	i-PrPIA-C	10	XX	31.70 (31.71)	16.28 (16.46)	11.98 (11.75)[e]	–	–	hexamer
		i-PrPIA-R	90	XX	27.55 (27.78)	14.15 (14.42)	10.25 (10.30)[f]	544	5.6	hexamer with and without complexed THF
n-BuPIA	n-$C_4H_9NH_2$	n-BuPIA-U	100	A	24.21 (24.28)	12.38 (12.60)	8.58 (9.00)[f]	1115	10.0	hexamer and heptamer, their complexes with THF and higher m.w. compounds
i-BuPIA	iso-$C_4H_9NH_2$	i-BuPIA-C	35	XX	26.82	13.76	10.24	550	5.6	hexamer
		i-BuPIA-R	65	XX	26.81 (27.22)	13.15 (14.13)	10.15 (10.09)[e]	618	5.6	mainly hexamer
t-BuPIA	*tert*-$C_4H_9NH_2$	t-BuPIA-C	30	XX	26.72	14.01	12.35	382	3.8	tetramer
		t-BuPIA-R	70	XX	26.25 (27.08)	13.30 (14.06)	12.71 (12.55)[g]	380	3.8	tetramer
c-HexPIA	$C_6H_{11}NH_2$	c-HexPIA-U	100	XX	16.22 (16.74)	8.36 (8.69)	6.01 (6.20)[h]	795	4.9	hexamer with and without complexed THF

[a] C = fraction precipitated at −10° C from the THF solution; R = residue after the separation of C; U = unrefined product from the evaporation to dryness of the reaction solution. [b] As indicated by the X-ray powder pattern; XX = crystalline; A = amorphous. [c] H_{active} = hydridic hydrogen content indicated as meq/g. [d] By ebulliometry in diethylether. [e] Calcd. values for $(HAlNR)_n$. [f] Calcd. values for $1/n(HAlNR)_n \cdot 1/6$ THF. [g] Calcd. values for $[(HAlNR)_3(H_2AlNHR)]$. [h] Calcd. values for $1/n(HAlNR)_n \cdot 1/2$ THF.

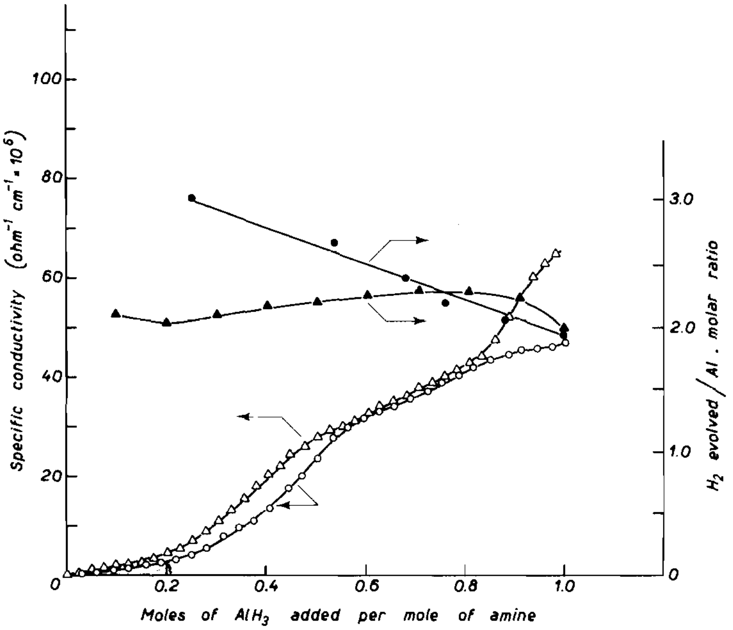


Figure 3. Plot of conductivity against hydrogen evolution observed during the addition of AlH_3 to primary amines in THF solution. ▲△ iso-$C_3H_7NH_2$; ●○ n-$C_4H_9NH_2$. Reaction conditions: a 1.7*M* solution of AlH_3 was added to an 0.06*M* solution of amine at 20° C; the rate of addition was 0.25 ml/2 min.

reactants, with respect to the method followed in reaction (3).

Both hydrogen evolution and conductivity changes were followed during the reaction (Figure 3). In the case of n-butylamine, the initial evolution of three moles of hydrogen per mole of AlH_3 agrees well with the formation of aluminum tris(n-butylamide) [reaction (5)]:

$$3\ n\text{-}C_4H_9NH_2 + AlH_3 \rightarrow Al(NH\text{-}n\text{-}C_4H_9)_3 + 3\ H_2 \quad (5)$$

On the other hand, when using isopropylamine the value of the H_2/Al molar ratio (H_2 again indicates evolved hydrogen) is near 2 during the entire course of the reaction. This agrees with the substitution of only two hydridic hydrogens by the amino groups to form bis(isopropylamino)alane [reaction (6)]:

$$2\ iso\text{-}C_3H_7NH_2 + AlH_3 \rightarrow HAl(NH\text{–}iso\text{-}C_3H_7)_2 + 2\ H_2 \quad (6)$$

This result was unexpected, because Al(NH–iso-$C_3H_7)_3$ was easily obtained by a different method as previously reported^6. Evidently our reaction conditions enhance the effect of the steric hyndrance of the hydrocarbon radical of the amine.

By continuing the AlH_3 addition up to $AlH_3/RNH_2 = 1$, the total H_2 evolved per mole of AlH_3 is *ca.* 2 for both amines, as expected for the formation of PIA. The conductivity increases during the reaction and at $AlH_3/RNH_2 = 1$, the values are very similar to those found when using the normal order of addition of the reactants, *i.e.* when the amine is added to an equimolar amount of AlH_3 in THF and the reaction solution is allowed to stand for some hours in order to complete the hydrogen evolution according to reaction (3). In this case the final value of the conductivity was $43 \times 10^{-6} \Omega^{-1} cm^{-1}$ when starting from n-$C_4H_9NH_2$ and $60 \times 10^{-6} \Omega^{-1}\ cm^{-1}$ when starting from iso-$C_3H_7NH_2$. Therefore, conductivity measurements suggest that PIA having the same structure are obtained from the same amine regardless the synthesis method employed, *i.e.* reaction (3), (4) or (7).

$$HAl(NH\text{–}iso\text{-}C_3H_7)_2 + AlH_3 \rightarrow \frac{2}{n}(HAlN\text{–}iso\text{-}C_3H_7)_n + 2\ H_2 \quad (7)$$

This has been confirmed by the chemical and physico-chemical characterizations (mass spectrometry, X-ray powder patterns and NMR) which show similar properties for the fractions of PIA obtained by the different methods of additions of the reactants (*cf.* Table II and Table I).

Finally we have observed that the addition of an AlH_3 solution to a solution of preformed PIA (from iso-$C_3H_7NH_2$ or n-$C_4H_9NH_2$) corresponds to an increase of conductivity. Provided that the aluminum concentration of the two solutions is the same, conductimetric curves, such as those of Figure 4, are observed which indicate an interaction between the PIA and the AlH_3. At least in the case of poly(N-isopropyliminoalane), this curve is quite different from

TABLE II. Results Obtained for the Synthesis of Poly(N-alkyliminoalanes) by Addition of AlH_3 to Primary Amines in THF Solution.

Compound	Amine	Fraction Sample[a]	%	X-ray analysis[b]	Chemical composition[c] Found (Calcd.) Al (%)	N (%)	$H_{act.}$	Mol. wt.[d]	n in $(HAlNR)_n$	Mass spectra data suggest
i-PrPIA	iso-$C_3H_7NH_2$	i-PrPIA-C	20	XX	30.54 (31.71)	15.49 (16.46)	11.92 (11.75)[e]	—	—	hexamer
		i-PrPIA-R	80	XX	26.31 (27.78)	13.29 (14.42)	10.71 (10.30)[f]	586	6.0	mainly hexamer with and without complexed THF
n-BuPIA	n-$C_4H_9NH_2$	n-BuPIA-U	100	A	24.01 (24.28)	12.20 (12.60)	7.95 (9.00)[f]	1238	11.1	mainly hexamer and heptamer with and without complexed THF and higher m.w. compounds

[a] C = fraction precipitated at −10° C from the THF solution; R = residue after separation of C; U = unrefined product from the evaporation to dryness of the reaction solution. [b] As evidenced by the X-ray powder pattern; XX = crystalline; A = amorphous. [c] H_{active} = hydridic hydrogen content indicated as meq/g. [d] By ebulliometry in diethylether. [e] Calcd. for $(HAlNR)_n$. [f] Calcd. for $1/n(HAlNR)_n \cdot 1/6$ THF.

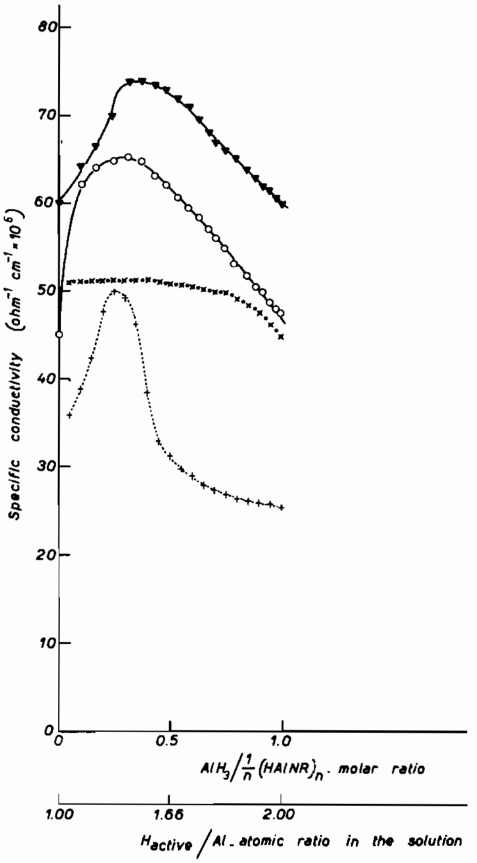
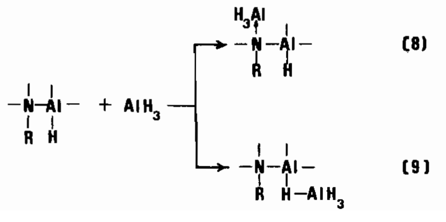


Figure 4. Conductivity curves observed during the addition of AlH_3 to different poly(N-alkyliminoalanes) in THF solution. ▼ iso-$C_3H_7NH_2$; ○ n-$C_4H_9NH_2$. Reaction conditions: an 0.067*M* solution of AlH_3 was added to an 0.067*M* solution of $1/n(HAlNR)_n$; the rate of addition was 10 ml/10 min. The dashed curves indicate the reverse of the conductivity trends observed for addition of iso-$C_3H_7NH_2$ (✖●✖●) or n-$C_4H_9NH_2$ (+—+—) to AlH_3.

the reverse of the curve reported in Figure 2, excluding the possibility that the interaction with AlH_3 occurs with the reformation of the intermediates of PIA synthesis. In our opinion an interaction occurring by complexation of AlH_3 by PIA under the reaction conditions used appears quite reasonable, either by the lone pair of the nitrogen atom [scheme (8)] or by the formation of hydrogen bridges [scheme (9)].



In fact a complex of hexamer poly(N-isopropyliminoalane) with one molecule of AlH_3 has been isolated by another method and fully characterized by X-ray diffraction on a single crystal[7]. Its molecular structure indicates that AlH_3 is retained both by N→Al and Al–H–Al linkages. In our case, the particular conductivity increase can be better explained by the occurrence of ionic $Al(AlH_4)$ groups and the maximum at AlH_3/PIA around 0.30–0.35 seems to indicate the complexation of two molecules of AlH_3 per one molecule of $(HAlN\text{–iso-}C_3H_7)_6$.

Experimental

Reagents and Solvents

$LiAlH_4$ and $(AlH_3)_x \cdot Et_2O$ were prepared from LiH (Degussa) and $AlCl_3$ (Kuhlmann) using the reactions of Finholt *et al.*[3].

In order to obtain THF solutions of AlH_3, $(AlH_3)_x \cdot Et_2O$ was dissolved in THF, and the solvent was removed under reduced pressure. This procedure was repeated several times. The amines were dried and purified by distillation from KOH. All solvents were purified and dried by the known methods and all operations were performed under an atmosphere of nitrogen.

Chemical Analyses and Physico-chemical Measurements

The same methods previously reported[1,2] were used for chemical analyses, conductivity measurements and mass spectra.

Synthesis of poly(N-alkyliminoalanes)

Two typical preparations were the following.

A soln. of isopropylamine (55 mmol) in THF (50 ml) was added dropwise to a stirred soln. of AlH_3 (55 mmol) in THF (100 ml) at room temp. Hydrogen evolution took place immediately. The reaction was stirred for *ca.* 10 hr, concentrated *in vacuo* to *ca.* 30% of the initial volume and left for 60 hr at –10° C. The precipitated crystals were separated by filtration, dried (10 hr, room temp., 10^{-3} mmHg) and analyzed. Found: Al, 31.70; N, 16.28; H_{active} 11.98 meq/g. Calcd. for $(HAlNC_3H_7)_n$: Al, 31.71; N, 16.46; H_{active} 11.75 meq/g).

The remaining soln. was evaporated *in vacuo* and the solid residue was dried under the above mentioned conditions and analyzed. Found: Al, 27.55; N, 14.15; H_{active} 10.25. Calcd. for $1/n(HAlNC_3H_7)_n \cdot 1/6$ THF: Al, 27.78; N, 14.43; H_{active} 10.30 meq/g).

Further data are reported in Table I.

A soln. of AlH_3 (55 mmol) in THF (50 ml) was added dropwise to iso-$C_3H_7NH_2$ (55 mmol) in THF (50 ml). Hydrogen evolution took place immediately. The reaction soln. was stirred for *ca.* 10 hr, concentrated *in vacuo* to *ca.* 30% of the initial volume and left 60 hr at –10° C. The precipitated crystals, were separated by filtration, dried (10 hr, room temp., 10^{-3} mmHg) and analyzed. Found: Al, 30.54; N 15.49; H_{active} 11.92 meq/g. Calcd. for $(HAlNC_3H_7)_n$: Al 31.71; N, 16.46; H_{active} 11.75 meq/g).

The remaining soln. was evaporated *in vacuo* and the solid residue was dried under the above mentioned conditions and analyzed. Found: Al, 26.31; N, 16.29; H_{active} 10.71 meq/g. Calcd. for $1/n(HAlNR)_n \cdot 1/6$ THF: Al, 27.78; N, 14.43; H_{active} 10.30 meq/g).

Further data are reported in Table II.

Acknowledgements

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