CHAPTER (4)

RESULTS AND DISCUSSION

4.1. Identification of Adducts:

In the present work adducts of polyalkyarylamines with stannous chloride, (I-IV), were obtained from the reaction of di - or polychloroalkanes with aromatic diamines in the presence of hydrochloric acid and stoichiometric amounts of stannous chloride as illustrated in scheme 1 [16]:

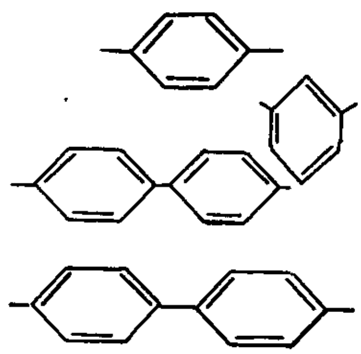
$$NH_2\text{-}Ar\text{-}NH_2 + Cl\text{-}R\text{-}Cl + SnCl_2 + H^+ \overset{K}{\rightleftharpoons}$$

$$H{+}HN\text{-}Ar\text{-}\overset{+}{N}H_2\,HR{+}Cl\ [SnCl_3^-] \xrightarrow{Kp}$$

$$H{+}HN\,Ar\,\overset{+}{N}H_2\,R{+}_n Cl + n\,SnCl_2 + n\,HCl$$

Polymer	R
I	$-(CH_2)-$
II	$-(CH_2)-$
III	$-(CH_2)-$
IV	$-CH(Cl)-$

Ar



Scheme 1

X-ray diffractometry, tables (1-4), indicates that aromatic diamines with di-or polychloroalkanes in the presence of $SnCl_2$ in methanol give additive products, which contain $SnCl_2$ chemically bounded with polyalkylarylamine hydrochloricles. Figures (2-5) illustrates the x-ray diffraction patteon of adducts (I-IV). These results are in agreement with those reported by Studnicki [17].

Table (5) represents the analytical data of adducts of polyamines (I - IV). Infrared spectra of these adducts shows $\nu_{\overset{+}{N}H_3}$ at 2850 cm^{-1}, $\nu_{\overset{+}{N}H_2}$ at 2575 cm^{-1}, $\delta_{\overset{+}{N}H_3}$ at 1500 cm^{-1} and $\delta_{\overset{+}{N}H_2}$ at 1600 cm^{-1}. Figure (6) illustrates the IR spectrum of adduct (II) as an example.

Table (6) shows the thermal analysis data of adducts (I-III) of polyalkylarylamines with $SnCl_2$. Decomposition of adduct (I) began at 145 °C,(lowest value), but adduct (III) decomposed at 300°C (the highest value). It seems that the thermal stability of these products is adequate to examine these adducts as additives to polyvinyl chloride in order to increase the thermal stability. Figures (7 - 9) illustrates the TG, DTG and DTA curves of adducts (I - III).

Table (7) represents the structures and analytical data of the products of the reaction of adducts of polyalkylarylamines and $SnCl_2$ with aqueous solution of ammonium carbonate. Products of the reaction are polyalkylarylamine hydrochlorides. These products are examined as polyelectrolytes in water treatment.

IR spectra of polyalkylarylamine hydrochlorides (V - VIII) show $\nu_{\overset{+}{N}H_3}$ and $\nu_{\overset{+}{N}H_2}$ at 2400-3600 cm^{-1} (broad), $\delta_{\overset{+}{N}H_3}$ at 1500 cm^{-1}, $\delta_{\overset{+}{N}H_2}$ at 1610 cm^{-1} and $\nu_{C-\overset{+}{N}}$ at 1400 cm^{-1} (strong) [64] Figures (10-13) shows the IR spectra of adducts (V - VIII).

Also the ^1H NMR spectrum of neutralized product of polymer (VIII) by ammonium hydroxide to give the corresponding free polyalkylarylamine polymer (XII) [65] is given in Figure (14). From this figure it is obvious that the aromatic proton (8 H) of two pairs of symmetric signals around δ 7.2,6.6 ppm and around δ 7.05, 6.45 ppm corresponding to two $A\bar{A}$ $B\bar{B}$

spin system, which may most probably be assigned to proton of two para disubstituted benzene rings, the aliphatic proton (1 H) of multiplet broad peak at δ 4.9 ppm due to C-H and the amino protons (4 H) of multiplet peaks around δ 3.1,3.95 ppm corresponding to primary and secondary amino groups

4.2. Application of Adducts (V) , (VII) and (VIII) As a Coagulant Aid in Water Treatment:

Adducts (V), (VII) and (VIII) were used either alone or in combination with alum. A typical graph showing the relationship between the dose of the coagulant (on log scale) and residual turbidity ratio (on linear scale) are used for presenting the results. Results for adducts (V), (VII) and (VIII), polyacrylamide and alum individually at different pH values are shown in Fig(15). The critical dose and the respective residual turbidity ratio for each compound at different pH values are given in Table (8). From this table it is obvious that in acidic medium, (pH $\simeq$ 3), compound (V) gave the same results as polyacrylamide. They gave the least residual turbidity ratio with equal concentrations. Following these two compounds coming: compound (VII), compound (VIII), then alum. Alum gave the highest residual turbidity ratio at a critical dose of 5 mg/liter.

In neutral medium, (pH $\simeq$ 7), alum gave a residual turbidity ratio of about 0.06, which is very low, but with high critical dose of 35 mg/liter, compared with 0.5 mg/liter obtained from compounds (V) and (VII) which gave a residual turbidity ratio of 0.31 and 0.33 respectively. It seems that the three presented compounds, in neutral medium, gave better results than polyacrylamide, which, gave a residual turbidity ratio of 0.48 with a critical dose of 1 mg/liter.

In alkaline medium (pH $\simeq$ 10), alum gave a residual turbidity ratio of 0.06 at a critical dose of 120 mg/liter, whereas polyacrylamide and the other three compounds (V, VII and VIII) gave a residual turbidity ratio of 0.7, 0.69, 0.56 and 0.65 with a critical dose of 0.25 mg/liter for each respectively. In alkaline medium the hydrochloride derivatives of the polyalkylamine tend to give the free polymer which precipitates in solution, therefore, the efficiency of these polymers, as a coagulant aid, significantly decreased in alkaline medium.

Results obtained from alum are concordent with that given in literature [1]. Investigation through Fig.(15) indicates that the clarification effect of both polyacrylamide and adducts (V), (VII) and (VIII) is lower than alum, specifically in neutral medium. This may be attributed to their lower capacity for charge neutralization, as they are nonionic. Therefore, the use of these compounds alone will not offer a charge neutralization, and it is recommended to be used in combination with inorganic coagulant as alum.

Results obtained from polyacrylamide in combination with different alum doses are given in Fig.(16A), whereas the results obtained from the other threecompounds (V), (VII) and (VIII) are given in Fig(16B), Fig (17C and D) respectively. The critical dose and the respective residual turbidity ratio for each compound with different fixed alum doses are given in Table (9). Investigation through these results reveals the role of adducts (V) and (VII) with 5 mg/liter alum dose; they could decrease the residual turbidity ratio from 0.6 to o.34 and 0.39 with critical dose of 0.75 mg/liter for each respectively. Best clarification effect was obtained from adduct (VIII). It could decrease the turbidity ratio from 0.06-obtained by the use of 35 mg/liter alum dose-to 0.04 with a critical dose of o.75 mg/liter. It is worthy of notice that the final turbidity obtained by the system 35 mg/liter alum + 0.75 mg/liter of of adduct (VIII) reaches 1 NTU. The reduction of turbidity to such low value is necessary before chlorination to ensure complete inactivation of virus [30]. The typical polyelectrolyte behaviour displayed by adduct (VIII) may be attributed to the residual amine unit in the structure of this adduct [2].