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Synthesis and Thermo gravimetric Studies of Polyaniline/Cobalt Chloride Composites

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Abstract: Chemical oxidative polymerization of aniline hydrochloride has been done by adding various weight% of $CoCl_2.6H_2O$ using ammonium peroxidisulphate as an oxidant to synthesize PANI and PANI/cobalt chloride composites. Both pure PANI and the composites were characterized by Thermo gravimetric Analysis (TGA). Various kinetic parameters like activation energy, frequency factor, entropy of activation and free energy change of decomposition have been calculated. The results indicate that the thermal stability of PANI is more in composite form. First, it increases with increase in cobalt chloride content up to 20 weights% and thereafter it starts decreasing.

Keywords: thermo gravimetric analysis, activation energy, entropy of activation, frequency factor, free energy change of decomposition.

Subject Classification: 81.70. Pg.

1. Introduction

Conducting polymers have obtained a wide attention in the last few decades after their discovery as they possess both characteristics of polymers and also their conductivity is high i.e. in metallic or semiconducting range after doping[1, 2]. Due to these unique properties of conducting polymers these polymers can used for various applications like

electrochromic display devices[3], sensors[4, 5], electromagnetic interference shielding[6] and rechargeable batteries[7] etc. Polyaniline is preferred over other conducting polymers due to its ease of synthesis, high environment and chemical stability and low cost[8, 9]. Till now a number of researchers have focused on studies related to polyaniline and its composites and study on their thermal properties[9-13]. But the evaluation of dynamic parameters by TG Analysis is still rarely available in literature.

In this paper we deal with the synthesis of PANI and PANI/$CoCl_2.6H_2O$ composites using chemical oxidative polymerization method using ammonium peroxidisulphate as an oxidant and using different weight% of cobalt chloride. The dynamic parameters i.e. entropy of activation, activation energy, frequency factor and free energy of change of decomposition were calculated using thermogravimetric analysis of these samples.

2. Experimental Details

2.1. Synthesis of PANI

Conducting polymer PANI was synthesized by oxidizing 0.2 M aniline hydrochloride (Aldrich) and 0.25 M ammonium peroxidisulphate (Aldrich) in aqueous medium[9, 11, 14 and 23]. Then both solutions were kept in refrigerator for cooling. After that these solutions were mixed in a beaker with constant stirring maintaining the temperature between 0-4 ^{0}C using an ice bath and left for polymerization in refrigerator at rest. PANI precipitate was collected on a filter paper and then washed with HCl and acetone[9, 11, 14 and 23]. Polyaniline (emeraldine) hydrochloride powder thus synthesized was put in air and then in vacuum keeping the temperature at 45^{0}C for proper dryness of the sample[9, 11, 14 and 23]. Polyaniline thus synthesized was referred as standard sample[9, 11, 14 and 23].

2.2. Synthesis of PANI/Cobalt chloride composites

5, 10, 20 and 40 percent by weight of 0.1 M $CoCl_2.6H_2O$ solution were added to 0.2 M aniline hydrochloride (Aldrich) solution in distilled with vigorous stirring for 1 hour for proper mixing for synthesizing the samples of PANI and cobalt chloride composites and by the procedure same as above, four different polyaniline and cobalt chloride composites with different weight% of cobalt chloride (5, 10, 20 and 40) were prepared and named as CoCl5, CoCl10, CoCl20 and CoCl40 respectively.

3. Results and Discussion

3.1. Thermogravimetric Analysis (TGA)

PANI and PANI/$CoCl_2.6H_2O$ composites were analyzed using TGA in nitrogen atmosphere and results are presented in figure 1. The TGA thermo grams of PANI/$CoCl_2.6H_2O$ composites show similar behaviour as shown by the pure PANI.

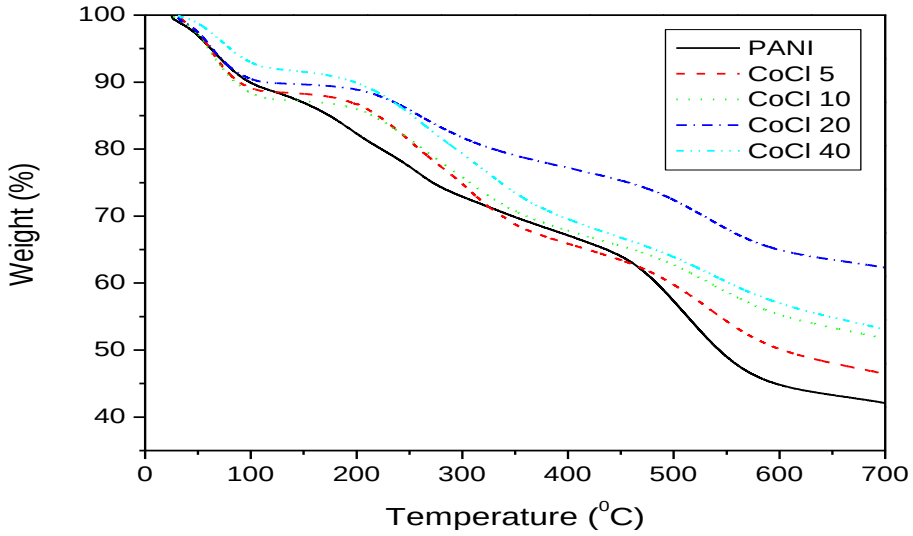

Figure 1: TGA thermo grams of PANI and PANI/$CoCl_2.6H_2O$ composites

The TGA analysis of PANI/$CoCl_2.6H_2O$ composites shows weight loss in four steps.

1. First step of weight loss begins at about 100^0C which is also known as initial dehydrating stage exists due to desorption of water absorbed at the surface of doped polymer[15].
2. Second step of weight loss at about 250^0C which is due to the removal of protonic acid component[15].
3. The subsequent stages (third at about 500^0C and fourth at about 600^0C) indicate breaking-up of the polymer chain which may lead to production of gases[16].

The various kinetic parameters for studying thermal properties have been determined and are discussed below:

3.1.1. Activation Energy (E_a)

The thermal activation energy E_a is calculated using equation (3.1) given as[9, 11 and 17-18]

$$\ln\left[\ln\left(\frac{w_0-w_f}{w-w_f}\right)\right]=\frac{E_a\theta}{RT_s^2} \quad (3.1)$$

where E_a is the activation energy, w_0 is the initial weight, w_f is the final weight, w is the remaining weight at temperature T, $\theta = T-T_s$ with T_s as the reference temperature corresponding to $\frac{w-w_f}{w_0-w_f}=\frac{1}{e}$ and R is gas constant.

By this equation, the thermal activation energy for Pure PANI and PANI/$CoCl_2.6H_2O$ composites is calculated from the slope of the fitted straight line of the plot between $\ln\left[\ln\left(\frac{w_0-w_f}{w-w_f}\right)\right]$ and θ, as described in figure 2.

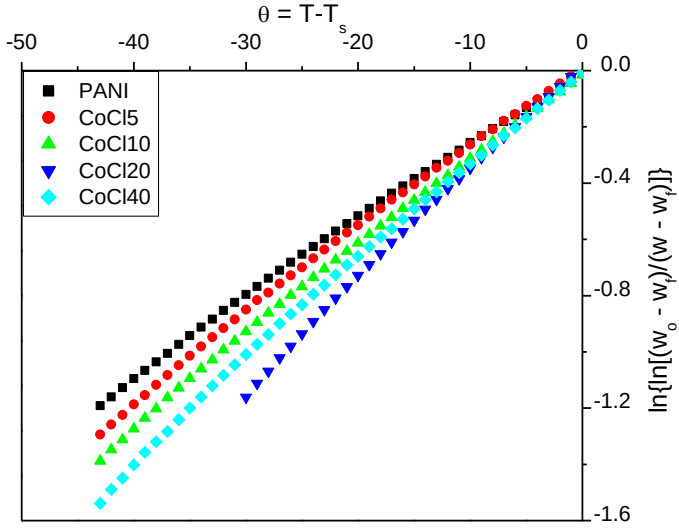

Figure 2: Plot of $\ln\left[\ln\left(\frac{w_0-w_f}{w-w_f}\right)\right]$ vs. θ for PANI and PANI/$CoCl_2.6H_2O$ composites.

The values of thermal activation energy thus calculated and are mentioned in Table I.

By comparing the values of the table, it is observed that up to 20 weight percent of cobalt chloride with increase in cobalt chloride content the value of thermal activation energy first increases and thereafter it (E_a) starts decreasing with further increase in concentration of cobalt chloride. The increase in thermal activation energy signifies the increase in thermal stability of the sample while its decrease shows the reverse trend[9, 11 and 18].

Table I: Values of various kinetic parameters for PANI and PANI/$CoCl_2.6H_2O$ composites

Sample	E_a(KJ/mol)	A (10^{10}) (s^{-1})	ΔS(J/mol/K)	ΔG(KJ/mol)
PANI	136.714	0.093	-187.568	286.393
CoCl5	149.333	0.237	-169.238	282.594
CoCl10	167.304	3.356	-118.706	261.438
CoCl20	202.329	1419.210	-9.274	204.360
CoCl40	185.006	30.004	-72.780	243.886

The activation energy first increases up to CoCl20 as expected may be due to increase in packing density and molecular reorganization etc. in the polymeric sample[9, 11 and 18-20] and the decrease in case of CoCl40 can be considered due to imperfections in lattice[20].

3.1.2. Frequency Factor (A)

The values of frequency factor (A) is calculated using equation (3.2) given as[9, 17 and 18]

$$A=\frac{\beta E_a}{RT_S^2}\exp\left(\frac{E_a}{RT_S}\right) \quad (3.2)$$

where E_a is activation energy, β is the constant rate of heating and A is the frequency factor[9]. The calculated values of frequency factor are listed in Table I. By comparing the values of frequency factor from the table it is observed that the value of frequency factor similar to activation energy, with increase in content of cobalt chloride up to 20 weight percent first increases and thereafter it starts decreasing[9]. The increase in the frequency factor shows an increase in the rate of reaction and its decrease shows the decrease in its value[9]. The increase in frequency factor with increase in cobalt

chloride concentration is expected to be due to the scissoring of the polymeric chains[9, 11, 18 and 20] and further decrease in value of frequency factor may be due to lattice defects.

3.1.3. Entropy of Activation (ΔS)

The values of entropy of activation can be calculated using equation (3.3) given as[9, 11, 17 and 18]

$$\Delta S = 2.303R\log\left(\frac{Ah}{kT_S}\right) \tag{3.3}$$

where h is Planck's constant and k is Boltzmann constant. The values of entropy of activation thus calculated by above mentioned equation are presented in Table I. By comparing the values of entropy of activation listed in Table I show that in the beginning with the increase in concentration of $CoCl_2.6H_2O$ up to 20 weight percent of cobalt chloride entropy of activation increases and after that it starts decreasing with further increase in its ($CoCl_2.6H_2O$) concentration[11, 21].

This increasing trend of entropy of activation in the beginning up to 20 weight% of $CoCl_2.6H_2O$ implies that the rate of reaction increases while its further decrease shows the reverse effect. Further, negative value of ΔS implies that the structure of products is more ordered as compared with that of the reactants[9, 11, 18 and 22].

3.1.4. Free Energy of Change of Decomposition (ΔG)

The values of free energy of change of decomposition can be calculated using equation (3.4) given as[9, 11, 17-18]

$$\Delta G = E_a - T_S\Delta S \tag{3.4}$$

The values of ΔG are now calculated and are listed in Table I. The values of ΔG come out to be positive in case of PANI/$CoCl_2.6H_2O$ composites which signify that the chemical reaction of degradation is non-spontaneous[21].

4. Conclusion

Chemical oxidative polymerization of aniline hydrochloride was done by added with various weight% of $CoCl_2.6H_2O$ using ammonium

peroxidisulphate as an oxidant to synthesize PANI and PANI/cobalt chloride composites. The thermo gravimetric analysis of PANI and PANI/ cobalt chloride composites shows that thermal stability of PANI increases in composite form. But among the composites the thermal stability increases up to 20 weights% of cobalt chloride after that its value decreases. Also, calculation of activation energy and frequency factor supports the same trend. Also, the kinetic parameter entropy of activation shows the similar trend which implies that the rate of reaction increases up to CoCl20 and decreases in case of CoCl40. The value of free energy of change of decomposition comes out to be positive in case PANI/$CoCl_2.6H_2O$ composites which signify that the chemical reaction of degradation is non-spontaneous.

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