

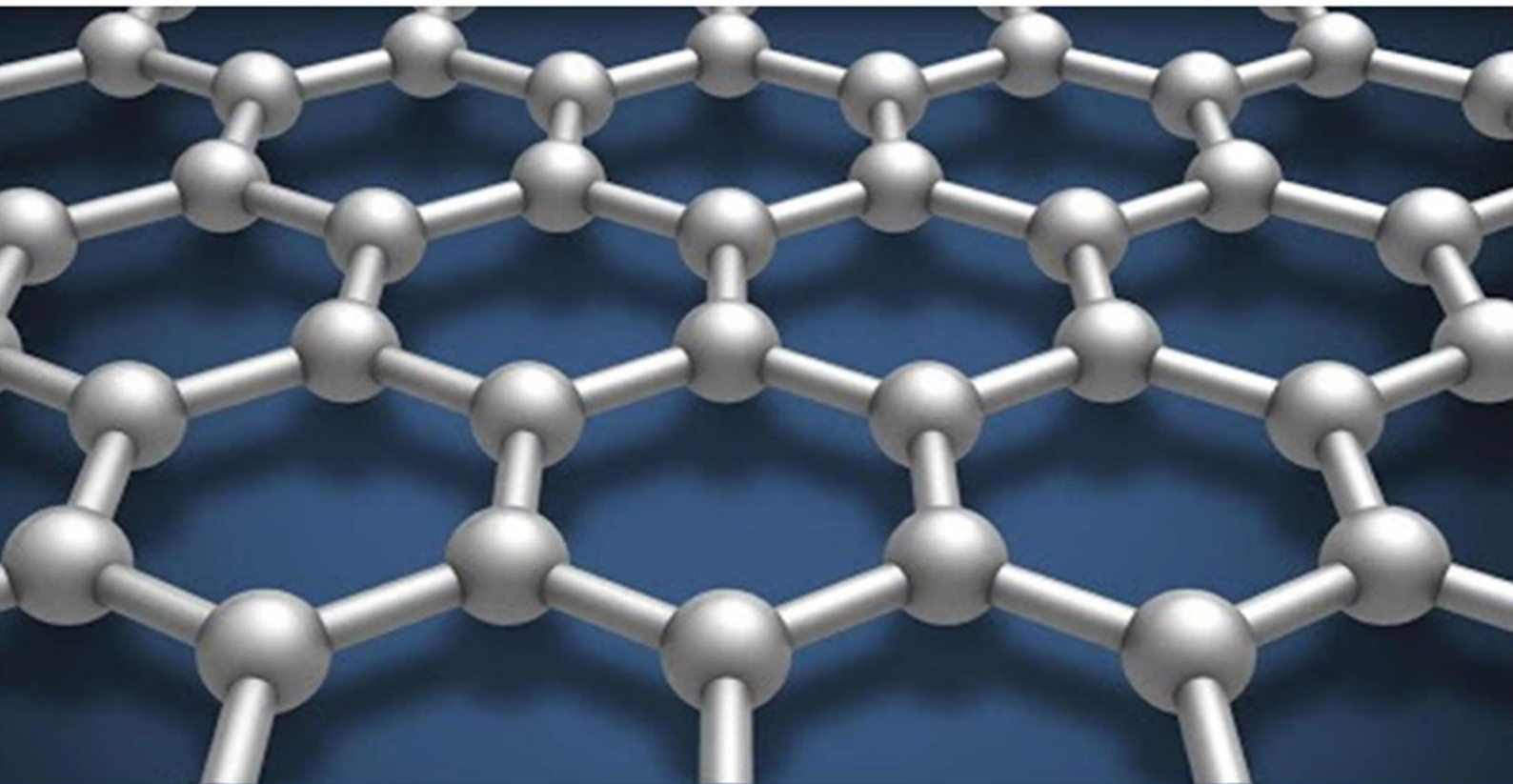
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Композиционные материалы

SYNTHESIS OF IONIC LIQUIDS BASED ON DIPHENYL AMINE AND PHOSPHORIC ACID

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Abstract. Ionic liquids have attracted the attention of researchers due to their properties such as high solubility and stability, high ionic conductivity and low toxicity. Ionic liquids are of great economic and technological importance due to their applications as solvents in chemical synthesis, for dissolving catalysts in catalysis, in electrochemistry in batteries and solar cells, in sensors for detecting gases and ions, as photocatalysis, as corrosion inhibitors and in many other fields such as solar cells. In this research work, ionic liquids were obtained by reacting diphenyl amine with phosphoric acid. The effects of pH, time and temperature on the synthesis of ionic liquids were studied. The gravimetric result of the ionic liquid based on diphenylamine and phosphoric acid was determined and their synthesis was analyzed in detail.

Keywords: Diphenyl amine, phosphoric acid, N,N-diphenylammonium dehydrogen phosphate ionic liquid, physical sorption, chemical sorption, ionic liquid, gravimetric analysis.

Introduction: Ionic liquids generally have high thermal stability, low vapor pressure, non-flammability, moderate polarity, high ionic conductivity, and non-toxicity. There are the following types of ionic liquids: 2-methylbenzene ammonium dehydrogen phosphate, 1,2-diammoniumbenzene hydrogen phosphate, N,N-diphenylammonium dehydrogen phosphate, imidazole, triazole, thiazole, indole, pyrrolidine, ammonium, piperidine, and pyridine complex and basic ionic liquids. Ionic liquids are easily adsorbed and block corrosion processes occurring at the anode or cathode. Almost all ionic liquids have attracted many researchers due to their low toxicity and high efficiency. As a result of these studies, the properties and mechanisms of ionic liquids against steel corrosion in salt water have been studied. Ionic liquids, whose electrons are bound to the negative part of the anode sites, lead to chemisorption by transferring to the d-orbital of the steel. Physical sorption also occurs through electrostatic repulsion between the positive part of the cathode sites and N,N-diphenylammonium dehydrogen phosphate. Most of the studies conducted to date have focused on solid ionic liquids based on N,N-diphenylammonium dehydrogen phosphate ionic liquids, and the use of ionic liquids based on 1,2-diammonium benzene hydrophosphate and 2-methylbenzeneammonium dehydrogen phosphate is of great importance. Ionic liquids are a protective layer on the metal surface. Currently, most of the studies studied are inhibitors based on solid ionic liquids, and the use of N,N-diphenylammonium dehydrogen phosphate and 2-methylbenzolammonium dehydrogen phosphate ionic liquids and the application of their anti-corrosion activity are also of interest to scientists. The aim is to study the inhibitory effectiveness of these ionic liquids in other electrolytes. Our

research group synthesized an ionic liquid derived from a compound based on diphenylamine and phosphoric acid (ionic liquid), and then studied the anti-corrosion effect of the ionic liquid on a steel sample in a 0.5 M HCl medium using several experimental methods and computational methods. In this study, the ionic liquid inhibitor N,N-diphenylammonium dehydrophosphate showed excellent corrosion inhibitory properties on the corrosion of a steel sample in an acidic solution. It was found that the ionic liquid molecules physically adsorbed on the HCl solution interface on the steel, which was subject to the Frumkin adsorption isotherm. The corrosion inhibitory index increased with the concentration of the ionic liquid, reaching a maximum value of 96.6% at a concentration of 400 ppm of the ionic liquid inhibitor. Other corrosion inhibitor compounds based on N,N-diphenylammonium dehydrophosphate and 2-methylbenzeneammonium dehydrophosphate are used in corrosion solutions. Indole compounds are cationic bicyclic structures consisting of a five-membered pyrrole ring fused to a six-membered benzene ring. The effect of N,N-diphenylammonium dehydrophosphate and 2-methylbenzolammonium dehydrophosphate ionic liquids on the corrosion inhibitory properties of various metals or alloys in various aggressive media is studied.

Required reagents: Diphenyl amine, phosphoric acid, ethyl alcohol, dis. Water.

Synthesis: A 0.1 M solution of diphenyl amine in 50 ml of alcohol was mixed with a 0.1 M solution of phosphoric acid in a 1:1 ratio in a 500 ml volumetric flask. Both solutions were first stirred separately for 10 minutes, then the diphenyl amine solution in alcohol was slowly poured into the phosphoric acid solution. This mixture was connected to a reflux condenser and reacted with a

magnetic stirrer at 50°C (t=5 hours) and 700 rpm. After the formation of a homogeneous mixture, the resulting solution was cooled to room temperature. Then, the resulting ionic liquid was precipitated at 0°C for 12 hours. The resulting ionic liquid solution was filtered. The resulting ionic liquid was dried at 30°C for 2 hours and a dry ionic liquid was obtained.

The resulting ionic liquid based on diphenylamine and phosphoric acid was purified by recrystallization. To purify the product, it was dissolved in distilled water and alcohol, and the resulting solution was cooled in a refrigerator at 0°C and recrystallized. The above recrystallization procedure was repeated 3 times.

Analysis of results: Effect of N,N-diphenylammonium dihydrogen phosphate ionic

liquid concentration. Table 1 presents the corrosion rate (CR_{Grav.}) for Steel No. 20, the inhibition efficiency (η_{Grav.}), and surface coverage (θ_{Grav.}) for N,N-diphenylammonium dihydrogen phosphate inhibitor in 0.5 M HCl and 1 M HCl solution. It is evident that with increasing concentration, η_{Grav.} and θ_{Grav.} increase, while CR_{Grav.} decreases. This is due to the fact that as the inhibitor concentration increases, the metal surface becomes covered with a thin protective film.

At 303 K, Steel No. 20 exhibits an inhibition efficiency of 93.36% at 200 mg/L and 82.01% at 150 mg/L. However, even at low concentrations in 0.5 M HCl solution, N,N-diphenylammonium dihydrogen phosphate has proven to be an effective inhibitor for the corrosion of Steel No. 20.

Results of gravimetric determination of the effectiveness of the inhibitor N,N-diphenylammonium dihydrogenphosphate at different temperatures and concentrations

T, K	C _{inh} , mg/L/mM	CR _{Grav.} , mg/sm ² ·hour	η _{Grav.} , %	θ _{Grav.}
303	Fon	0,9864	-	-
	50	0,32234	67,32	0,6732
	100	0,283546	71,25	0,7125
	150	0,177418	82,01	0,8201
	200	0,065528	93,36	0,9336
313	Fon	1,21968	-	-
	50	0,445104	63,51	0,6351
	100	0,384912	68,44	0,6844
	150	0,299376	75,45	0,7545
	200	0,188496	84,55	0,8455
323	Fon	1,2512	-	-
	50	0,552816	55,82	0,5582
	100	0,494208	60,50	0,6050
	150	0,429264	65,69	0,6569
	200	0,337392	73,03	0,7303
333	Fon	1,4164	-	-
	50	0,742896	47,55	0,4755
	100	0,684288	51,69	0,5169
	150	0,619344	56,27	0,5627
	200	0,539898	61,88	0,6188

The inhibition efficiency of N,N-diphenylammonium dihydrogen phosphate is related to the molecular size of the inhibitor. This is because even at low concentrations, the inhibitor is able to cover a large portion of the metal surface. Experimental results show that the selected inhibitor is more effective at lower concentrations. This is associated with the parallel adsorption orientation of the adsorbed N,N-diphenylammonium dihydrogen phosphate molecules, allowing them to cover a larger surface area of the metal. The increase in concentration affects the adsorption configuration. Thus, N,N-diphenylammonium dihydrogen phosphate is considered an effective inhibitor even at low

concentrations. Unlike in the temperature range of 313–333 K, η_{Grav.} at 200 mg/L is 93.36% at 313 K and 61.88% at 333 K. Therefore, this ionic liquid of N,N-diphenylammonium dihydrogen phosphate is considered a good corrosion inhibitor at higher temperatures. In conclusion, N,N-diphenylammonium dihydrogen phosphate forms an effective protective film on the surface of Steel No. 20, effectively isolating the steel from the aggressive attack of Cl⁻ ions.

Effect of temperature: The effect of temperature was analyzed using various concentrations of N,N-diphenylammonium dihydrogen phosphate inhibitor in a 0.5 M HCl solution. The data observed in Table 1 indicate that

the corrosion rate increases with rising temperature. This implies that Steel No. 20 exhibits lower corrosion resistance at higher temperatures. The inhibitor efficiency decreases from 93.36% at 303 K to 61.88% at 333 K. This confirms that N,N-diphenylammonium dihydrogen phosphate effectively protects the surface of Steel No. 20 from aggressive chloride ion solutions in the temperature range of 303 to 333 K. It is important to note that corrosion protection is less effective at higher temperatures, as increased kinetic energy leads to the desorption of the inhibitor from the metal surface, thereby affecting its inhibition performance. Additionally, the electrostatic interaction between the inhibitor and the metal surface weakens at elevated temperatures. These factors contribute to the reduced inhibition efficiency at higher temperatures. The electrostatic interaction between the inhibitor and the metal surface is temperature-dependent. N,N-diphenylammonium dihydrogen phosphate adsorbs onto the metal surface through both chemical and physical adsorption mechanisms. Physical adsorption occurs via electrostatic interactions between the inhibitor and the metal surface. The

corrosion inhibitor interacts electrostatically through the positively charged nitrogen atoms with the negatively charged metal surface. Chloride and hydroxyl ions are adsorbed onto the metal surface, making it negatively charged. The corrosion inhibitor neutralizes the metal surface through electrostatic interaction. As the temperature increases, chloride and hydroxyl ions become more active, gradually weakening the electrostatic interaction force.

Conclusion: The synthesis of N,N-diphenylammonium dihydrogen phosphate ionic liquid was studied with respect to temperature and time. It was observed that the optimal and stable conditions were 50°C for 5 hours at 700 r/min. The reaction was carried out using diphenylamine and phosphoric acid, resulting in the synthesis of N,N-diphenylammonium dihydrogen phosphate ionic liquid. The efficiency of the N,N-diphenylammonium dihydrogen phosphate inhibitor at various temperatures and concentrations was determined using gravimetric methods. The obtained N,N-diphenylammonium dihydrogen phosphate ionic liquid is stable, inexpensive, non-toxic, and highly soluble in water.

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