Influence of Anions on the Corrosion Inhibition Effect of Imidazolium Based Ionic Liquids for Copper in 3.5 % NaCl Solution

Hui Huang[1], Beiyao Li[1], Xingwen Zheng[1,2,], Jinlong Fan[2,3,*] and Min Gong[2,3]*

[1] School of Chemical and Environmental Engineering, Sichuan University of Science & Engineering, Zigong 643000, China
[2] Key Laboratory of Material Corrosion and Protection of Sichuan Province, Zigong 643000, China
[3] School of Materials Science and Engineering, Sichuan University of Science & Engineering, Zigong 643000, China
[*]E-mail: zxwasd@126.com, laban110@126.com

The corrosion inhibition of effect of 1-octyl-3-methylimidazolium L-tartrate ([OMIM]TA), 1-octyl-3-methylimidazolium L-lactate ([OMIM]LA) and 1-octyl-3-methylimidazolium acetate ([OMIM]Ac) on copper in 3.5 % NaCl solution was investigated by potentiodynamic polarization, electrochemical impedance analysis, and corrosion morphology analysis. Moreover, the effect of anions on the corrosion inhibition of copper performance of the tested ionic liquids was also investigated and analyzed. The results shown that the three ionic liquids are mixed inhibitors, and anions have a significant effect on their inhibition behavior. [OMIM]TA mainly inhibited the anodic reaction of copper in 3.5 % NaCl solution, while [OMIM]LA had a greater inhibition effect on the cathode. The inhibition efficiency of [OMIM]TA and [OMIM]LA increased with the increase of concentration, but that of [OMIM]Ac decreased. The inhibition efficiency of [OMIM]TA is higher than that of [OMIM]LA under the same conditions, its corrosion inhibition efficiency of copper could reach 86.3% at the concentration of 0.005 mol/L. The morphology analysis of the corrosion samples by SEM confirmed the electrochemical results. Meanwhile, it was found that the adsorption of [OMIM]TA and [OMIM]LA on the copper surface conforms to the Langmuir isotherm, and the adsorption parameters and kinetic parameters were obtained and discussed.

Keywords: ionic liquid, anion, copper, corrosion inhibitor, adsorption

1. INTRODUCTION

Copper and its alloys have been widely used in the industry due to their excellent corrosion resistance, high conductivity and thermal conductivity, and easy machinability [1]. However, copper and

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its alloys are easily corroded in the atmosphere and aqueous solution, especially in the presence of chloride ions [2,3]. It has been widely accepted that CuCl corrosion product film will be formed on the surface of copper and its alloy in the medium containing chloride ions, but due to the weak binding force between CuCl and matrix and its transformation to soluble coordination ions [CuCl$_2$]$^-$ and divalent copper salts, hence, the protective effect of the film on the corrosion of a copper substrate is very limited [4]. Therefore, the development of methods to prevent copper from corrosion has attracted much attention. The addition of organic corrosion inhibitor was found to be an effective and cheap method to inhibit the corrosion of copper and its alloys in liquid medium [5]. Organic compounds containing O, N, S atoms and/or heterocycles, such as benzotriazole and its derivatives [6-13], amino acid and its derivatives [14-20], and Schiff base [21,22] have been studied to use as the inhibitors of copper. However, many organic inhibitors are highly toxic and low biodegradable and are potentially harmful to the ecological environment [23]. Therefore, the development of environment-friendly corrosion inhibitors has become a hot research field.

Ionic liquid (IL) is a liquid substance at room temperature usually are composed of specific organic cations and inorganic or organic anions. Because of its good stability, low melting point, green and designable characteristics, ionic liquid meets the need for green corrosion inhibitor and has attracted the attention of researchers. Qiang and others [24] found that the inhibitors efficiency of allyl imidazolium ionic liquids on copper in sulfuric acid solution increased with the extension of substituent chain length and the increase of concentrations of ionic liquids. Deyab and others [25] synthesized four kinds of imidazolium-based ionic liquids, their results also confirmed that the longer the length of the fat chain, the higher the corrosion inhibition performance; and they noticed that the corrosion inhibition efficiency is also related to the number of branched chains on the imidazole ring, the more branched chains, the greater the inhibitive efficiency. Cao and co-workers [26] compared the corrosion inhibition of sulfonate/ carboxylate functionalized ionic liquids, they found that the corrosion inhibition efficiency of a sulfonate-type ionic liquid with a longer alkyl chain is higher than those of the carboxylate-type ionic liquids. Subasree and colleagues [27] evaluated the corrosion inhibition of 3-hexadecyl-1-methyl-1H-imidazol-3-ium bromide and 3-hexadecyl-1,2-dimethyl-1H-imidazol-3-ium bromide on carbon steel in hydrochloric acid solution.At present, the research on ionic liquid corrosion inhibitors mostly focuses on the influence of cations, but less on anions. However, Likhanova and others [28] had found that the anions affected the corrosion inhibition of ionic liquids on carbon steel in acidic solution. In this work, the inhibition of three imidazole based ionic liquids containing different organic anions on copper in 3.5 % NaCl solution was investigated by electrochemical measurements and corrosion morphology analysis, the adsorption behavior of ionic liquids and the effect of temperature are also discussed, and the effect of anions on its corrosion inhibition ability is tested and analyzed.

2. EXPERIMENTAL

2.1 Materials and reagents

The experimental samples were cut from pure copper with a thickness of 5 mm, the working electrode was a cylinder with a working area of 1 cm^2, and the non-working area was coated with epoxy

resin, while the size of the surface analysis sample is 15 mm × 10 mm. Before the experiment, the working electrode was polished to 1000# with metallographic emery paper, and then washed by deionized water, anhydrous ethanol and acetone in turn. [OMIM]TA, [OMIM]LA, and [OMIM]Ac were purchased from Shanghai Chengjie Chemical Co. Ltd., and their purity was 97%.

2.2 Experimental methods

2.2.1. Electrochemical experiments

The electrochemical test was carried out in a conventional three-electrode cell using the CHI 660E electrochemical workstation of Shanghai Chenhua Instrument Co., Ltd. The saturated calomel electrode (SCE) was used as reference electrode, and all potentials reported in this paper were relative to SCE, while the counter electrode was a platinum electrode. Firstly, the open circuit potential (OCP) of the electrode in the test solution was monitored until a stable potential was reached, in our experiments, the test time was set to 1800 s. And then the electrochemical impedance spectroscopy (EIS) was carried out under OCP with an amplitude of 5 mV in the frequency range from 10^{-2} Hz to 10^{5} Hz. Finally, the potentiodynamic polarization curve was tested in the potential range of ± 0.35 V vs. OCP with a scanning rate of 0.5 mV/s. The temperature of the solution was controlled by a constant temperature water bath.

2.2.2. Surface analysis

The copper samples were immersed in 3.5% NaCl solution with and without the addition of 0.005 M the investigated ionic liquid for 4 days, and it was taken out and cleaned with a hydrochloric acid solution to remove the corrosion products on the copper surface, after that the samples were washed with deionized water and dried with cold air, and then the surface morphology of the sample was tested using Tescan Vega3 scanning electron microscope (SEM) instrument at high vacuum.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization curves

The potentiodynamic polarization curves for copper electrodes in 3.5% NaCl solution containing different ionic liquids are shown in Fig. 1. It can be found from Fig. 1 that different ionic liquids have different effects on the polarization curve of copper electrodes in 3.5% NaCl solution, which reflects the influence of anions on the corrosion inhibition behavior of ionic liquids. Fig. 1(a) shows that the addition of [OMIM]TA makes the corrosion potential shift positively, and the anode polarization curve and cathode polarization curve moves in the direction of low current density, but the anode current density decreases more significantly. Therefore, [OMIM]TA is a mixed type inhibitor mainly inhibiting the anodic reaction for copper in 3.5% NaCl solution. It can also be found the increase of polarization

potential from the anodic polarization curve, the current density increases and reaches a peak, and then decreases rapidly, resulting in a minimum, which is caused by the formation of insoluble CuCl, then the current density increases again with the further increase of polarization potential, due to the transformation of CuCl to soluble $CuCl_2^-$ complex ions [29,30]. Moreover, the anode current density is significantly reduced because of the sorption of [OMIM]TA on the surface of the copper electrode, but when the anodic polarization potential reaches a certain value, the anodic current density increases significantly with the increase of polarization potential due to the desorption of corrosion inhibitor, at about 0 V, all anodic polarization curves almost overlap, indicating that the corrosion inhibitor has been completely desorbed at this potential. Similar phenomena also appear in Fig. 1(b) and Fig. 1(c). Conversely, [OMIM]LA makes the corrosion potential move negatively, and its effect on the cathodic polarization curve is more significant than that of the anode, as shown in Fig. 1(b). Considering that the addition of [OMIM]LA reduces both anode current density and cathode current density, and the negative shift of corrosion potential is not significant, [OMIM]LA is a mixed type inhibitor.
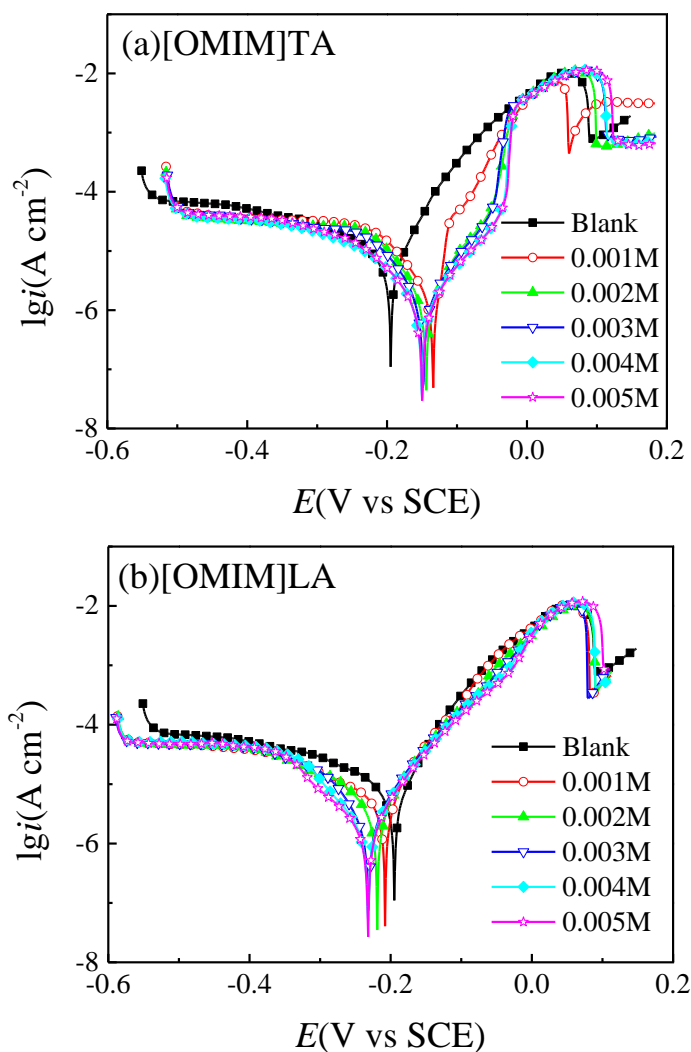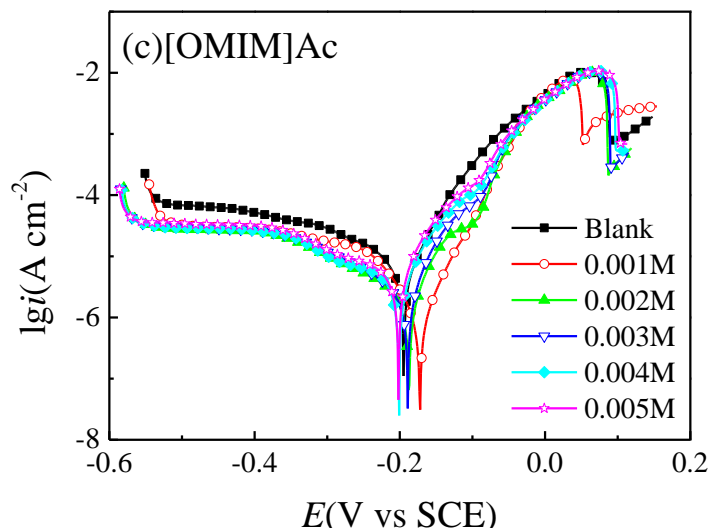
Figure 1. Polarization curves of copper in 3.5% NaCl solution without and with various concentrations of ILs at 30 °C, (a) [OMIM]TA, (b) [OMIM]LA and (c) [OMIM]Ac

It is worth noting that Fig. 1(c) shows that the polarization curve moves towards high current density with the increase of [OMIM]Ac concentration, but it is still lower than that in the blank solution, which means that [OMIM]Ac has corrosion inhibition effect on copper in sodium chloride solution, but the corrosion inhibition effect with the increase of concentration in the experimental concentration range, that is significantly different from the other two ionic liquids investigated. Fig. 1(c) also illustrates that [OMIM]Ac is a mixed type inhibitor.

Table 1. Electrochemical parameters of copper in 3.5% NaCl solution without and with various concentrations of ILs at 30 °C

ILs	c(mol/L)	E_{corr}(V vs SCE)	i_{corr}(µA/cm^2)	$-\beta_c$(mV/dec)	β_a(mV/dec)	η(%)
[OMIM]TA	blank	-0.195	9.69	197	65	\
	0.001	-0.134	2.41	72	46	75.1
	0.002	-0.144	1.78	72	64	81.7
	0.003	-0.149	1.76	81	68	81.8
	0.004	-0.150	1.47	90	75	84.8
	0.005	-0.150	1.32	83	75	86.3
[OMIM]LA	0.001	-0.208	5.95	166	61	38.7
	0.002	-0.219	4.29	112	69	55.7
	0.003	-0.232	3.80	229	72	60.8
	0.004	-0.232	2.26	79	77	76.7
	0.005	-0.232	2.04	83	74	78.9
[OMIM]Ac	0.001	-0.185	1.75	193	62	82.0
	0.002	-0.188	2.16	174	43	77.7
	0.003	-0.189	5.01	187	94	48.4
	0.004	-0.201	5.97	151	83	38.4
	0.005	-0.202	8.11	173	79	16.3

The electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel slopes of cathode and anode (β_c and β_a), are obtained by using Tafel curve extrapolation method and listed in Table 1. The corrosion inhibition efficiency (η) was counted follow:

$$\eta = (1 - i_{corr,inh}/i_{corr,0}) \times 100\% \tag{1}$$

where, $i_{corr,0}$ and $i_{corr,inh}$ represent the corrosion current without inhibitor and with inhibitor, respectively.

It is obvious from Table 1 that with the increase of addition concentration, [OMIM]TA increases the values of E_{corr}, while [OMIM]LA and [OMIM]Ac make E_{corr} shift negatively, moreover, [OMIM]TA and [OMIM]LA reduce the values of i_{corr}, and their corrosion inhibition efficiency increase, the maximum inhibition efficiency of [OMIM]TA reaches 86.3% and that of [OMIM]LA is 78.9%. However, with the increase of [OMIM]Ac concentration, the values of i_{corr} increase, resulting in the decrease of corrosion inhibition efficiency, but it still exhibits a certain corrosion inhibition in the investigated concentration range. The change of Tafel slope reflects the influence of corrosion inhibitors on the corrosion reaction mechanism. The data in Table 1 show that compared with the anode Tafel slope (β_a), the three investigated ionic liquids make the change of cathode Tafel slope (β_c) greater, indicating that they have a more significant impact on the cathode reaction mechanism, while the difference of the effect of different ionic liquids on β_c reflects the difference of their corrosion inhibition.

3.2. EIS

Fig. 2 shows the EIS of copper electrodes in 3.5% NaCl solutions containing different concentrations of ionic liquids, it is clear that the shapes of EIS of copper electrodes in solutions containing different ionic liquids are different, which reflects the differences of in their corrosion inhibition behavior. As shown in Fig. 2(b), the Bode plot of copper electrode in blank solution shows that there is an obvious peak in the high frequency region, which is usually attributed to the capacitive response [31-33]; the weak peak or flat zone in the middle frequency region corresponds to another relaxation process; in the low frequency region, the phase angle increases further, and the value of impedance modulus ($|Z|$) does not reach a stable value, which means the existence of diffusion and/or adsorption/desorption processes [31,32], and the diffusion phenomenon is also confirmed by Fig. 2(a). It can be seen from Fig. 2(a) and Fig. 2(b), with the addition of [OMIM]TA, the diameter of capacitive loop and the value of $|Z|$ increase significantly in the medium and high frequency region, and obviously, the two capacitive arcs in the high frequency region and the medium frequency region overlap partially, which may be due to their close time constants [34], however, in the low frequency region, the value of the imaginary part of impedance ($-Z_{im}$) does not increase greatly, and no horizontal impedance modulus is observed, suggesting that the diffusion process still exists. A similar phenomenon is also observed in the impedance spectrum of copper electrode in the solution with 0.005 mol/L [OMIM]Ac. The shapes of the Nyquist and Bode plots do not change significantly in the solution added with [OMIM]LA and [OMIM]Ac, compared with that in the blank solution. As described above, the EIS data are fitted by using the equivalent circuit shown in Fig. 3, the simulating examples are given in Fig. 2(g) and Fig. 2(h), and the fitting results are listed in Table 2.

In the selected equivalent circuit, R_s is the solution resistance, C_1 and R_1 correspond to the film capacitance and film resistance of the corrosion product film on the surface of the copper electrode, CPE_2 and R_2 are related to double-layer capacitance and charge transfer resistance, CPE_3 and R_3 represent the adsorption of electro-active species on the copper/solution interface, W is Warburg impedance corresponding to the diffusion process on the electrode surface. *CPE* is usually used to replace pure capacitance due to the inhomogeneous nature of electrode surface, the impedance of CPE can be described as follows [31,32]:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \tag{2}$$

where Q is the magnitude of *CPE*, n is the phase shift, j represents the imaginary unit, and ω is the angular frequency, respectively.

The data in Table 2 show that the value of Q_2 corresponding to the electric double-layer capacitance decreases with the increase of [OMIM]TA concentration, which is caused by the adsorption of corrosion inhibitor, and the value of R_2 increases accordingly. The values of C_1 are greater than that in the blank solution, indicating that the thickness of the corrosion product film decreases because of the adsorption of the corrosion inhibitor, however, with the increase of the concentration of [OMIM]TA, the value of C_1 decreases, indicating that the thickness or compactness of the corrosion inhibitor adsorption film is increasing [31,32], and the value of R_1 is also increasing. Similar results are also observed in the solution containing 0.001 mol/L [OMIM]Ac. Except for 0.005 mol/L [OMIM]Ac solution, the value of R_3 is higher than that in the blank solution, which may reflect that the addition of ionic liquids enhances the adsorption due to the increase of the number of electro-active species on the copper/solution interface. In the solution with [OMIM]LA, the general trend is that the R_2 value increases and the value of Q_2 decreases with the increase of inhibitor concentration. However, the regularity of the data is not obvious due to the obvious diffusion phenomenon and only 1/4 arcs in the impedance spectrum in the solutions containing [OMIM]LA and [OMIM]Ac.

In the corrosion system with multiple time constants, polarization resistance (R_p) is usually used to evaluate the corrosion resistance of materials, a high R_p value means a strong corrosion resistance of metal. For the used equivalent circuit, the polarization resistance can be calculated as $R_p = R_1 + R_2 + R_3$. Table 2 shows that the addition of ionic liquids increases the value of R_p, indicating that the corrosion of copper electrode in 3.5% NaCl solution is inhibited. However, with the increase of [OMIM]TA or [OMIM]LA concentration, the value of R_p increases, especially [OMIM]TA, meaning [OMIM]TA has stronger corrosion inhibition. While with the increase of [OMIM]Ac concentration, the value of R_p decreases. It can also be found that the variation trend of corrosion inhibition efficiency calculated by R_p is consistent with the test results of polarization curve.

$$\eta = (1 - R_{p,0}/R_{p,inh}) \times 100\% \tag{3}$$

where $R_{p,0}$ and $R_{p,inh}$ represent the polarization resistance without inhibitor and with inhibitor, respectively.
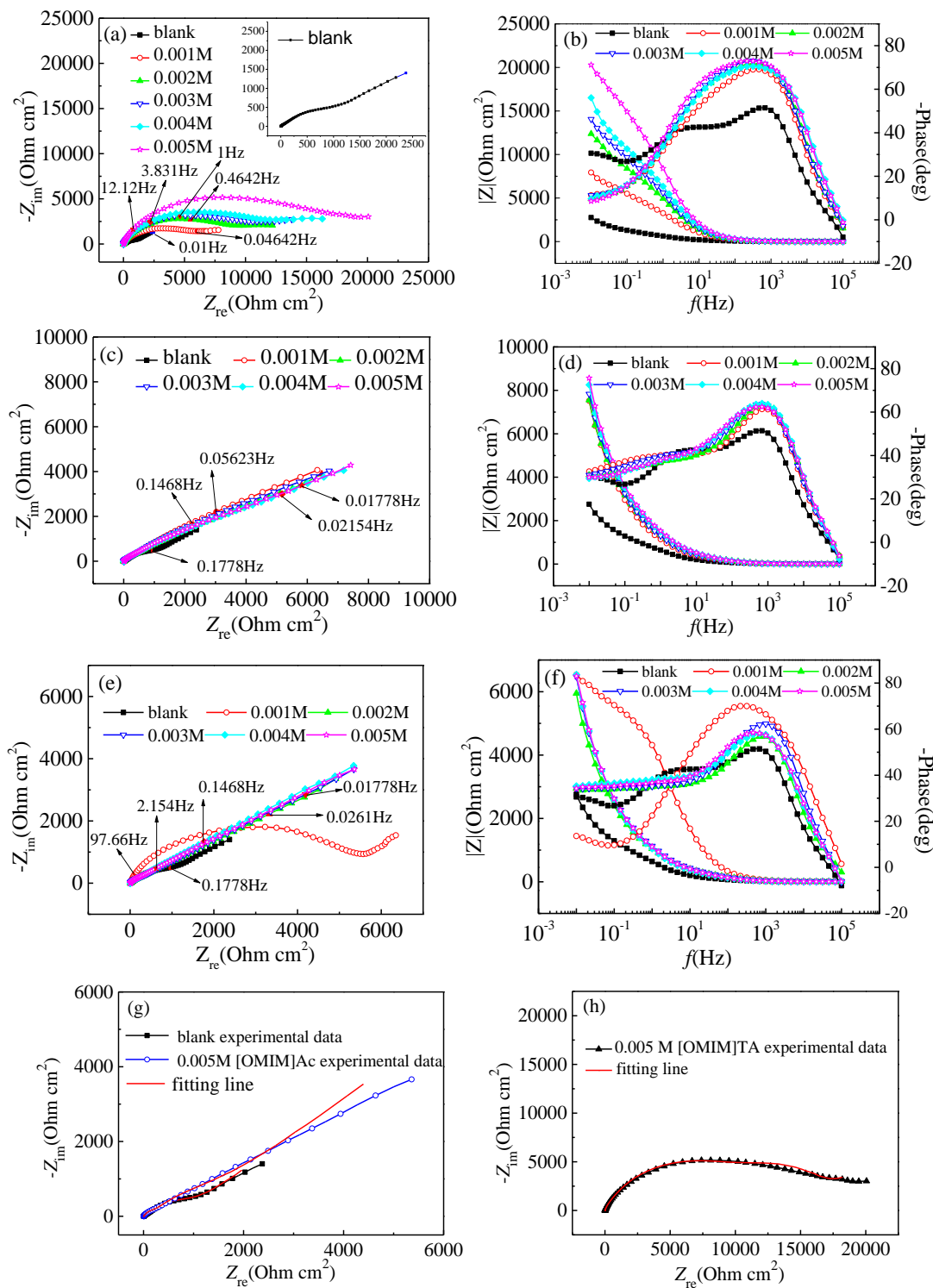
Figure2. Nyquist and Bode plots of copper in 3.5% NaCl solution without and with various concentrations of ILs at 30 ℃: (a) and (b) for [OMIM]TA, (c) and (d) for [OMIM]LA, (e) and (f) for [OMIM]Ac, (g) and (h) of the simulating examples
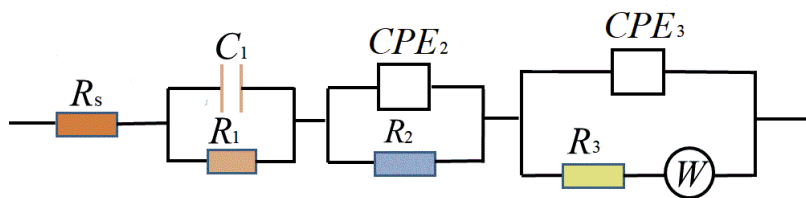
Figure 3. Equivalent circuit diagram used to simulate EIS

Table 2. Electrochemical impedance parameters of copper in 3.5% NaCl solution without and with various concentrations of ILs at 30 °C

ILs	c mol/L	R_s Ω/cm^2	C_1 $\mu F/cm^2$	R_1 Ω/cm^2	Q_2 $\mu S/cm^2 \cdot s^n$	n_2	R_2 $\Omega \cdot cm^2$	Q_3 $\mu S/cm^2 \cdot s^n$	n_3	R_3 $\Omega \cdot cm^2$	W $\mu S/cm^2 \cdot s^{0.5}$	R_p $\Omega \cdot cm^2$	η %
	blank	5.9	113	27	444	0.73	734	17.5	0.98	24	1954	784	\
	0.001	6.3	415	1878	38	0.86	3086	24.5	0.89	327	1520	5291	85.2
[OMIM] TA	0.002	5.8	317	2892	25	0.87	5120	24.0	0.90	371	1075	8383	90.6
	0.003	6.2	308	3217	23	0.88	5849	23.8	0.89	529	932	9595	91.8
	0.004	6.0	328	3326	21	0.85	6914	26.1	0.86	571	863	10811	92.7
	0.005	6.1	229	4997	17	0.87	10050	28.2	0.87	572	863	15619	95.0
	0.001	5.9	71	530	1079	0.89	683	22.0	0.87	120	593	1332	41.1
	0.002	5.9	86	138	394	0.73	1457	10.9	0.94	128	663	1723	54.5
[OMIM] LA	0.003	5.1	261	760	1619	0.79	939	18.8	0.91	169	647	1868	58.0
	0.004	5.1	52	159	309	0.73	1686	11.4	0.96	77	619	1922	59.2
	0.005	5.3	48	151	300	0.71	1758	10.6	0.98	52	593	1961	60.0
	0.001	6.2	547	637	18	0.81	2162	33.8	1.00	2261	1675	5060	84.5
	0.002	8.4	12	44	57	0.84	204	206.0	0.75	1458	737	1706	54.0
[OMIM] Ac	0.003	5.3	15	23	493	0.71	805	18.8	0.93	211	692	1039	24.6
	0.004	6.0	21	12	600	0.68	819	22.1	0.92	152	674	983	20.2
	0.005	5.9	38	96	455	0.68	839	8.0	1.00	22	669	956	18.0

3.3. Adsorption isotherm

Adsorption isothermal curves are widely used to analyze the adsorption mechanism of corrosion inhibitors. The main adsorption models include: Langmuir, Freundlich, Temkin and Bockris-Swinkel [35]. In order to further study the adsorption mode of the studied ionic liquids on copper superficies, the data shown in Table 1 and Table 2 are used to fit various adsorption isothermal equations. It is found that the data meet the Langmuir isothermal equation [36], and the fitting results are shown in Fig. 4. Moreover, the adsorption equilibrium constant (K_{ads}) can and the adsorption free energy (ΔG_{ads}) are calculated by following formula [37-39]:

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \tag{4}$$

$$\theta = \frac{\eta}{100} \tag{5}$$

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \tag{6}$$

where θ is the surface coverage, η is the inhibition efficiency, R is the gas constant, T is the thermodynamic temperature.

According to Fig. 4 and the fitting parameters in Table 3, the adsorption of [OMIM]TA and [OMIM]LA on copper superficies conforms to Langmuir adsorption isotherm. The values of ΔG_{ads} are negative, implying that the adsorption of [OMIM]TA/[OMIM]LA on copper surface is a spontaneous adsorption process, however, compared with [OMIM]LA, [OMIM]TA shows a more negative ΔG_{ads} value and a larger K_{ads} value, which means that [OMIM]TA has stronger adsorption capacity than [OMIM]LA, which corresponds to the greater corrosion inhibition efficiency of [OMIM]TA at the same concentration.
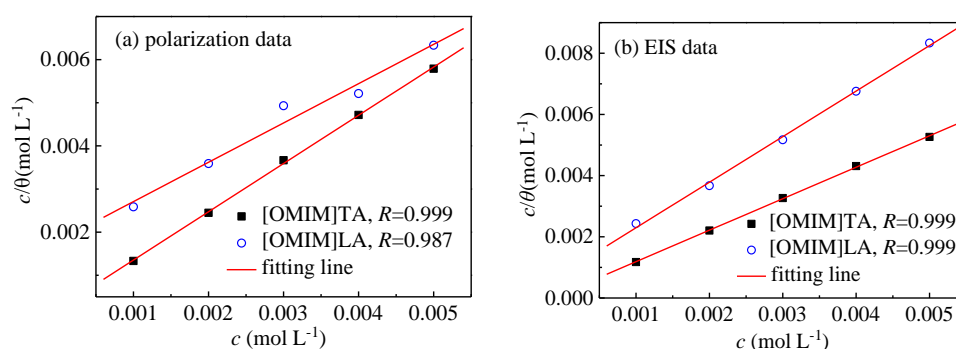
Figure 4. Langmuir adsorption isotherm fitting diagrams of [OMIM]TA and [OMIM]LA on the copper surface in 3.5% NaCl solution

Table 3. The adsorption parameters of [OMIM]TA and [OMIM]LA on copper surface in 3.5% NaCl solution

ILs	Polarization data		EIS data	
	K_{ads}(L/mol)	ΔG_{ads}(kJ/mol)	K_{ads}(L/mol)	ΔG_{ads}(kJ/mol)
[OMIM]TA	4270	-31.19	6297	-44.96
[OMIM]LA	556	-26.05	1240	-28.08

3.4. Effect of temperature

Temperature is an important factor affecting the performance of corrosion inhibitors. The polarization curves of copper electrode in 3.5% NaCl solution containing 0.005mol/L ionic liquids at different temperatures are given in Fig. 5, and based on Tafel extrapolation, the corresponding electrochemical parameters are listed in Table 4. It is can be seen that the corrosion current density in all test solutions increase with the increase of temperature, however, compared with that in the blank

solution, the corrosion current decreases in the solution containing [OMIM]TA and [OMIM]LA, indicating that [OMIM]TA and [OMIM]LA inhibit the corrosion inhibition of copper in 3.5% NaCl solution, and the inhibitory effect of [OMIM]TA is stronger than that of [OMIM]LA except at 60 °C, but with the increase of temperature, the corrosion inhibition efficiency for copper decreases, which is the difficulty of corrosion inhibitor adsorption due to the intensification of molecular thermal movement, and the increase of corrosion reaction rate also leads to the acceleration of desorption of corrosion inhibitor molecules. While [OMIM]Ac only has a weak inhibitory effect on copper in 3.5% NaCl solution at 30 °C and accelerates the corrosion of copper at higher temperatures.
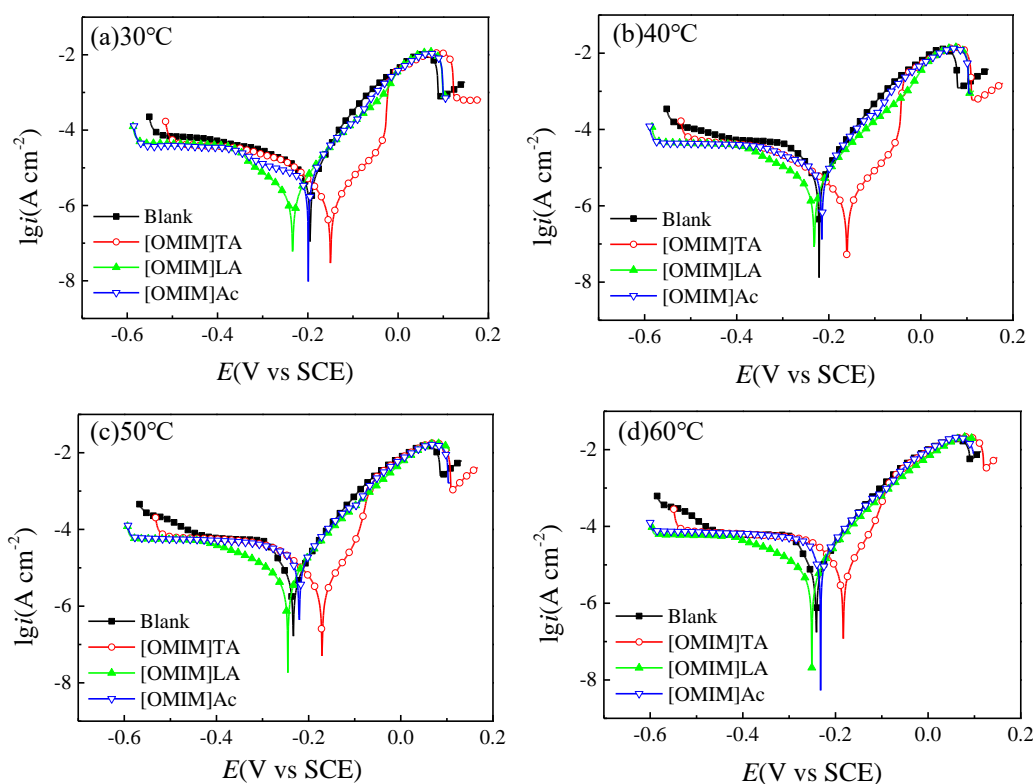
Figure 5. Polarization curves of copper in 3.5% NaCl solution without and with 0.005mol/L ILs at different temperatures

Moreover, based on the data in Table 4, the relationship between corrosion current density and temperature was investigated according to the Arrhenius equation [40], and the fitting results are shown in Fig. 6.

$$\ln(i_{\text{corr}}) = -\frac{E_a}{RT} + \ln A \tag{7}$$

where A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant and T is the thermodynamic temperature.

Fig. 6 shows that the experimental data basically accord with the Arrhenius equation, and the kinetic parameters are obtained by linear fitting and listed in Table 5. In the solution containing ionic liquids, the value of E_a is greater, indicating that the addition of ionic liquids increases the energy barrier of corrosion electrochemical reaction and inhibits the reaction. Moreover, in the system with

[OMIM]TA, the E_a value is the largest, which corresponds to the highest inhibition efficiency of [OMIM]TA. However, considering the value of *A*, it can be found that E_a is not the only factor affecting corrosion electrochemical reaction.

Table 4. Electrochemical parameters of copper in 3.5% NaCl solution without and with 0.005mol/L ILs at different temperatures

T(°C)	ILs	I_{corr}($\mu A/cm^{2)}$	E_{corr}(V vs SCE)	η(%)
30	blank	9.69	-0.195	\
	[OMIM]TA	1.32	-0.150	86.3
	[OMIM]LA	2.04	-0.232	78.9
	[OMIM]Ac	8.11	-0.202	16.3
40	blank	11.37	-0.221	\
	[OMIM]TA	1.90	-0.160	83.3
	[OMIM]LA	4.60	-0.232	59.6
	[OMIM]Ac	15.23	-0.216	\
50	blank	12.12	-0.233	\
	[OMIM]TA	3.50	-0.171	71.1
	[OMIM]LA	6.30	-0.245	48.0
	[OMIM]Ac	30.10	-0.222	\
60	blank	15.86	-0.241	\
	[OMIM]TA	9.76	-0.183	38.5
	[OMIM]LA	8.59	-0.251	45.8
	[OMIM]Ac	36.88	-0.227	\
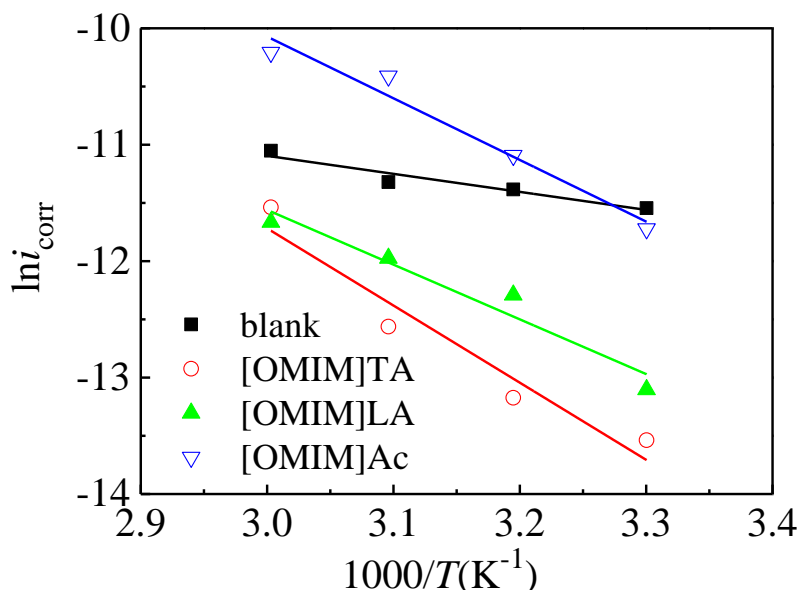
**Figure 6.** Arrhenius equation fitting curves of copper in 3.5% NaCl solution without and with 0.005mol/L ILs

Table 5. Kinetic parameters of copper in 3.5% NaCl solution without and with 0.005mol/L ILs

ILs	E_a (kJ/mol)	A
blank	12.88	1.58×10^3
[OMIM]TA	55.15	3.54×10^9
[OMIM]LA	39.10	1.27×10^7
[OMIM]Ac	44.07	3.38×10^8

3.5. Effect of anions on corrosion inhibition of ionic liquids

Polarization curves and EIS show that the corrosion inhibition behaviors on copper of the three ionic liquids are different. The three ionic liquids have the same imidazolium cation, therefore, their different corrosion inhibition behavior is obviously affected by anions. In order to further reveal the influence of anions on the corrosion behavior on copper of ionic liquids, the polarization curves of copper electrodes in 3.5 % NaCl solutions containing 1-octyl-3-methylimidazolium chloride ([OMIM]Cl) and sodium salts of three anions (i.e. NaHTA, NaLA and NaAc) were tested respectively to evaluate the corrosion inhibition of cations and anions on copper. The results are shown in Fig. 7 and the fitted electrochemical parameters are shown in Table 6.

Fig. 7 shows that the sodium salt of anion mainly inhibits the cathodic reaction of copper electrode in 3.5 % NaCl solution and shifts the corrosion potential negatively. Compared with NaLA and NaAc, the inhibitory effect of NaHTA on cathodic reaction of copper electrode is more obvious, which may be due to its two negative charges or more hydroxyl groups in its molecules. The data in Table 4 show that the inhibition efficiency of NaHTA, NaLA and NaAc decreases in turn. It can also be seen from Fig. 7 that [OMIM]Cl mainly inhibits the anodic reaction of copper electrodes and increases the corrosion potential. Fig. 7(a) shows that [OMIM]TA mainly inhibits the anodic reaction of copper electrode in 3.5 % NaCl solution, and the corrosion inhibition effect is stronger than that of [OMIM]Cl, but the corrosion inhibition effect on the cathodic reaction is much less than that of NaHTA. Therefore, it can be considered that the corrosion inhibition effect of [OMIM]TA is mainly affected by imidazolium cation, but TA anions promote the corrosion inhibition effect on the anodic reaction. As Fig. 7(b) indicated, the anodic inhibition of [OMIM]LA is weakened relative to [OMIM]Cl, but the inhibition of [OMIM]LA on the cathode is stronger than that of NaLA, and its inhibition on the anode is also stronger than that of NaLA. Therefore, the inhibition of [OMIM]LA is mainly affected by LA anion, but imidazolium cation also contributes to its inhibition. Fig. 7(c) clearly shows that the corrosion inhibition effect of [OMIM]Ac on the anode is weaker than that of [OMIM]Cl, and the corrosion inhibition effect on the cathode is weaker than that of NaAc, especially, the corrosion inhibition efficiency is also reduced. Combined with the results of polarization curves in Fig. 1, it can be found that Ac anion have a greater impact on the corrosion inhibition effect than imidazolium cation, resulting in the decrease of corrosion inhibition efficiency with the increase of concentration. The influence of anions on the corrosion inhibition behavior of ionic liquids may be related to the interaction between anions and the surface of copper electrode, the coordination ability with copper and cuprous ions, the influence on the acidity of solution and so on, which needs to be revealed by more in-depth research and more ingenious experimental design.
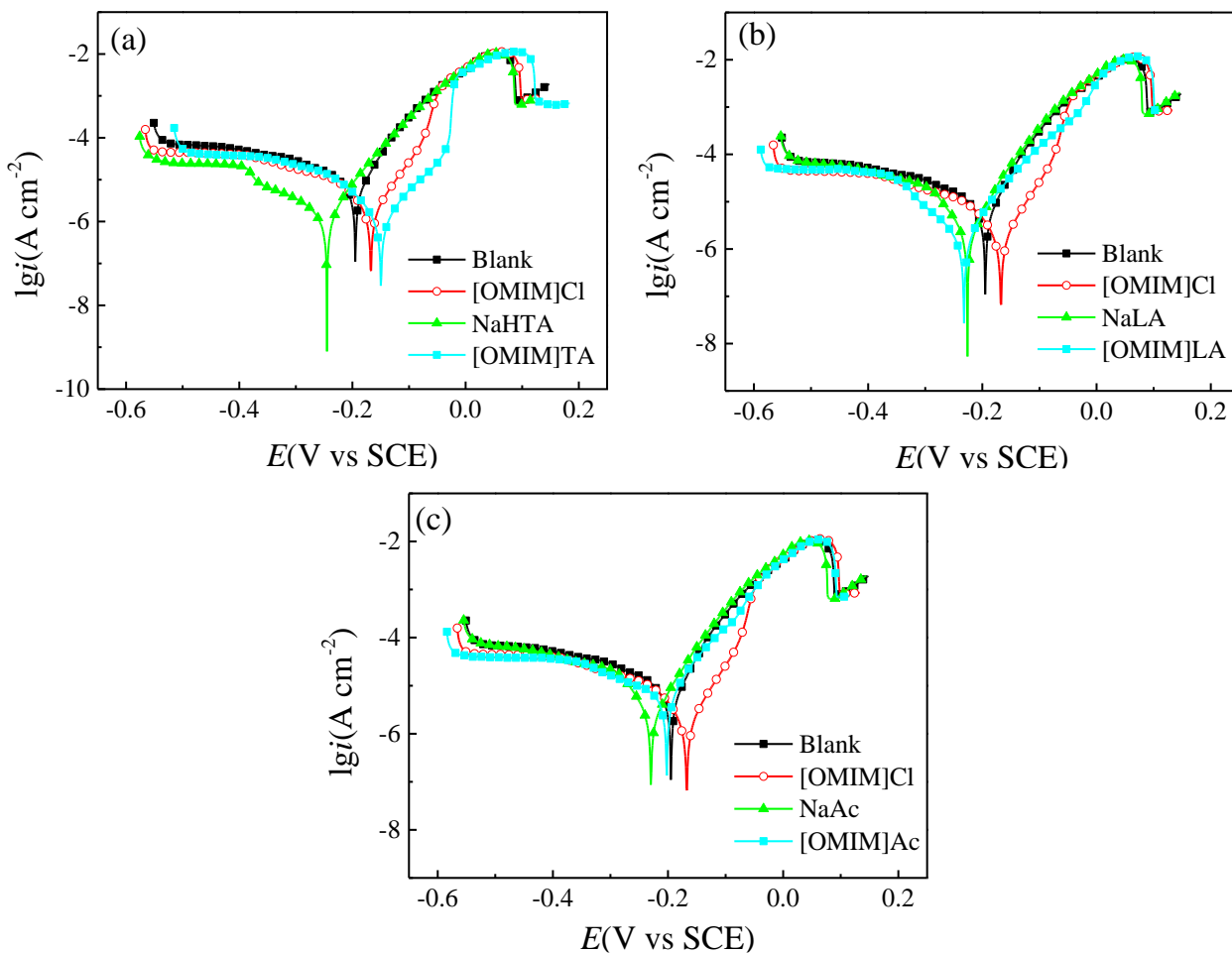
Figure 7. Polarization curves of copper in 3.5 % NaCl solutions with 0.005 mol/L different inhibitors at 30 °C

Table 6. Electrochemical parameters of copper in 3.5 % NaCl solution with 0.005 mol/L different inhibitors at 30 °C

systems	E_{corr}(mV vs SCE)	I_{corr}(μA/cm^2)	$-\beta_c$（mV/dec)	β_a(mV/dec)	η(%)	S
blank	-0.195	9.69	197	65	/	/
[OMIM]Cl	-0.167	2.62	246	53	73.0	/
NaHTA	-0.245	1.89	188	64	80.5	/
[OMIM]TA	-0.150	1.32	83	75	86.3	0.38
blank	-0.195	9.69	197	65	/	/
[OMIM]Cl	-0.167	2.62	246	53	73.0	/
NaLA	-0.226	4.02	236	62	58.5	/
[OMIM]LA	-0.232	2.04	83	74	78.9	0.53
blank	-0.195	9.69	197	65	/	/
[OMIM]Cl	-0.167	2.62	246	53	73.0	/
NaAc	-0.230	5.00	335	60	48.4	/
[OMIM]Ac	-0.202	8.11	173	79	16.3	0.17

3.6. surface analysis

SEM was used to observe the surface of copper after immersion corrosion test, and the results are given in Fig. 8. It is clear that the surface of copper sample suffers obvious damage in 3.5% NaCl solution due to the occurrence of corrosion reaction. However, after adding the investigated ionic liquids, the corrosion of the copper sample surface is restrained and the damage is weakened, especially in the solution added with [OMIM]TA. It is found that there is more obvious pitting corrosion on the sample surface in the solution added with [OMIM]LA, but it cannot be ruled out that it is caused by the defects of the sample itself. In general, the corrosion inhibition of copper samples is more obvious in the solution added with [OMIM]Ac than in other solutions containing ionic liquids.
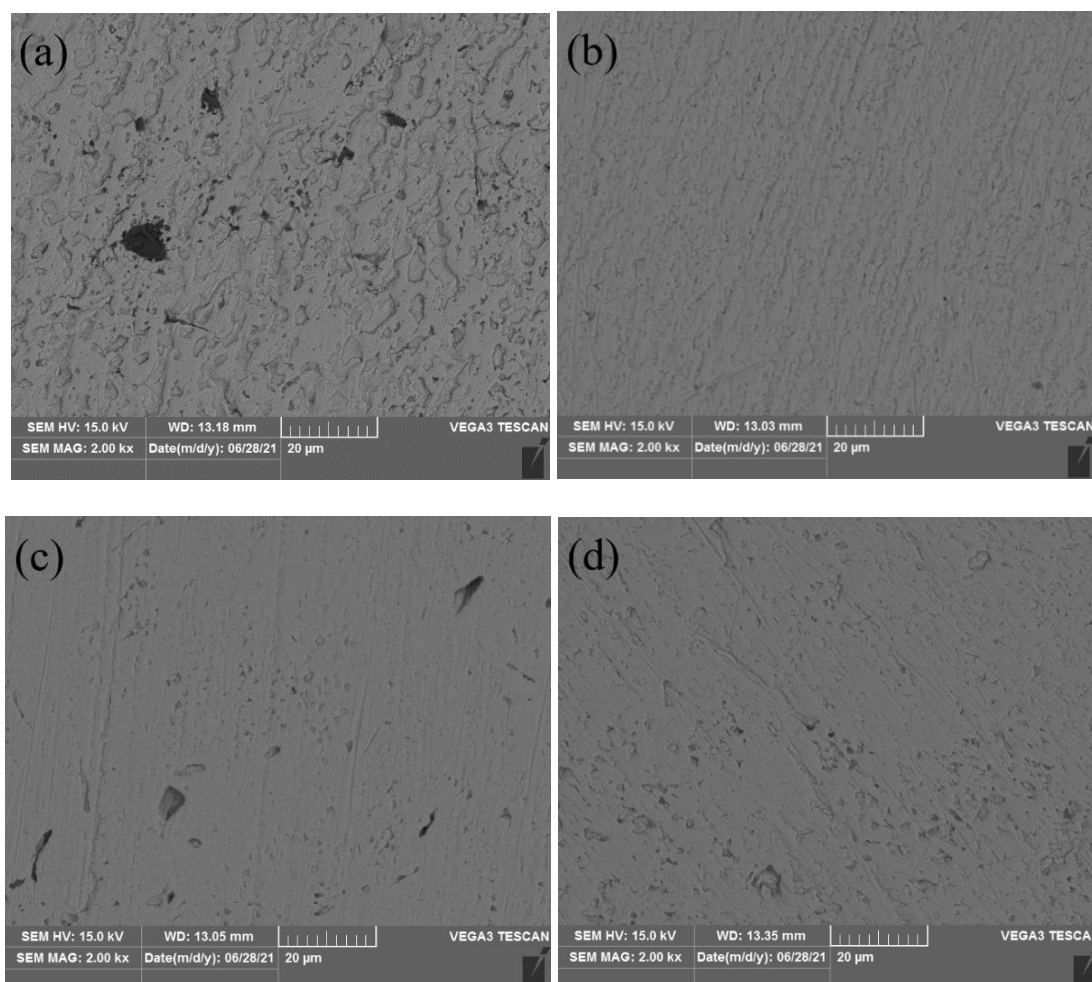
Figure 8. SEM diagrams of the copper sample immersed in 3.5% NaCl solution for 4 days: (a) without inhibitor, (b) with 0.005mol/L [OMIM]TA, (c) with 0.005mol/L [OMIM]LA, (d) with 0.005mol/L [OMIM]Ac.

4. CONCLUSIONS

The corrosion inhibition behavior for copper of three ionic liquids in 3.5 % NaCl solution is obviously different. [OMIM]TA is a mixed type inhibitor mainly inhibiting the anodic reaction, and its

inhibition efficiency is mainly affected by imidazolium cation. [OMIM]LA and [OMIM]Ac are mixed type inhibitors, however, their inhibitory on the cathode is stronger, and is mainly affected by anions. The corrosion inhibition of [OMIM]TA and [OMIM]LA increases with the increase of concentration, and the inhibition efficiency of [OMIM]TA was higher than that of [OMIM]LA, but the inhibition efficiency of [OMIM]Ac decreased with increasing concentration. [OMIM]TA and [OMIM]LA can spontaneously adsorb on the copper surface, and the adsorption conforms to the Langmuir isothermal equation. The increase of temperature accelerates the corrosion rate of copper in the test medium, and the corrosion inhibition efficiency of ionic liquid also decreases.

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