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Benzalkoniumchloride Ionic Liquids as Novel Corrosion Inhibitors for Carbon Steel in Formation Water

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Abstract

New benzalkoniumchloride derivatives ionic liquids (ILs) were synthesized in ≥ 97% yield and their inhibiting properties for the corrosion of carbon steel in formation water had been evaluated using chemical methods. The structures of the ILs compounds were investigated by elemental analysis, FT-IR spectrophotometer and ^{1}H-NMR spectroscopy. The designed molecular structure of ILs, with N atoms, makes it good corrosion inhibitor via the adsorption of ILs on the carbon steel surface to suppress both anodic and cathodic processes. The inhibition efficiency increases with increased ILs concentration.

Keywords**:** carbon steel; ionic liquids; formation water; corrosion inhibitor

1- Introduction

Carbon steel is a well-known constructional material used in various industries and highly susceptible to corrosion in petroleum fields [1-2]. Formation water is highly corrosive saline water in the petroleum production [3-4]. The main problem of applying steel pipelines is its dissolution in formation water [5]. This causes huge economic losses [6-7]. One of the most important methods in corrosion control is to use corrosion inhibitors [8-10]. Numerous researchers have reported many classes of organic compounds that can be used as corrosion inhibitors for steel in corrosive solutions [11-13]. Protection efficiency of organic compounds is attributed mainly to the presence of a polar group acting as an active center for adsorption [14-15]. Unfortunately, many organic compounds are health hazards. Therefore, there is still an increased attention directed towards the development of environmentally compatible, nonpolluting corrosion inhibitors.

As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study investigates the inhibiting effect of new benzalkoniumchloride derivatives ionic liquids (ILs) in formation water.

2- Experimental

2.1. Materials and chemicals

The experiments were carried out using carbon steel disk with following composition (wt.%): C = 0.25%, Mn = 0.43%, Si = 0.33%, S = 0.12%, P = 0.06%, and Fe (balance). The working surfaces of the electrode were cleaned before using according to previous work [16]. Where the working electrode and coupons were abraded before each test with a series of emery papers ranging from 400 to 2500 grades, degreased with acetone, washed with distilled water and dried by a filter paper

The formation water was obtained from Bani- Sweif petroleum wells (Egypt). Its chemical analysis was shown in Table 1.

Table (1): chemical analysis of formation water analysis

Total Dissolved Solids (T.D.S.)	200154.2 mg/l
Salinity (as NaCl)	202451.1 mg/l
pH @ 25 ºC	5.429
Chloride concentration	122697.64 mg/l

All reagents used were analytical fine grade. They were used as received without further purification.

2.2. Preparation of ionic liquids (ILs).

The Fig. 1 summa rized the process of preparation of new benzalkoniumchloride derivatives ionic liquids (ILs). The structures of the ILs compounds were investigated by:

1- Elemental analysis (Elementary Viro El Microanalysis).

2- FTIR spectra (FT-IR spectrophotometer - Model 960 Mooog, ATI Mattson Infinity Series, USA)

3- 1H NMR spectroscopy (Jeol-EX- 270 MHz spectrometer).

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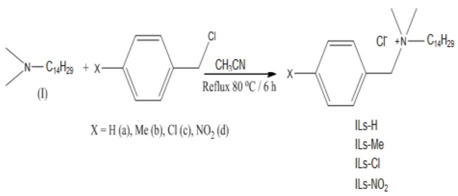

Fig (1): Preparation of new benzalkoniumchloride derivatives ionic liquids (ILs).

2.3. Corrosion rate measurements

The corrosion rate (W_{corr}) and the percentage protection efficiency (P_w %) for carbon steel in formation water containing benzalkoniumchloride derivatives ionic liquids (ILs) are calculated from the following relations [17].

$$W_{corr} = \frac{W_1 - W_2}{S \times t} \quad (1)$$

$$P_w \% = \frac{W^0_{corr} - W_{corr}}{W^0_{corr}} \times 100 \quad (2)$$

Here, W_1 and W_2 are the mass loss before and after immersion, respectively. W^0_{corr} and W_{corr} represent the corrosion rate for blank and solution containing ILs, respectively.

3. Results and discussion

3.1. Confirmation of chemical structures of ILs

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Table 2: Elemental analysis of ILs compounds.

Compound		ILs-H	ILs-Me	ILs -Cl	ILs-NO_2
C %	Calc.	75.06	75.45	68.64	66.90
	Obs.	75.03	75.52	68.58	66.87
H %	Calc.	11.50	11.61	10.27	10.01
	Obs.	11.58	11.59	10.25	10.05
N %	Calc.	3.81	3.67	3.48	6.78
	Obs.	3.76	3.64	3.49	6.75
Cl %	Calc.	9.63	9.28	17.62	8.58
	Obs.	9.71	9.25	17.67	8.56

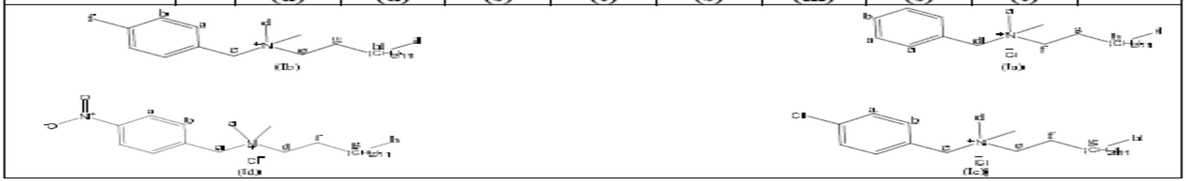
Table 3: Infra-Red bands for ILs compounds

Cpd.	ν cm^{-1}						
	CH--H_2O	$CH_{Aromatic}$	$CH_{Aliphatic}$	N-C	C=C	NO_2	C-Cl
ILs - H	3446-3381	3006	2923-2853	3087	1619	-	-
ILs - Me	3424	3011	2923-2853	3199	1618	-	-
ILs - Cl	3427	3008	2924-2953	3195	1625-1600	-	725
ILs – NO_2	3439	3010	2922-2852	3199	1625	1519-1470	-

^{1}H-NMR spectra of prepared BCIL ionic liquids were recorded in Table 4.

Table 4: ^{1}H-NMR spectroscopy of ILs compounds

		Chemical Shift (δ) ppm								
Type of proton		a	b	c	d	e	f	g	h	i
Compound	Ia	7.603 (t)	7.456 (t)	7.326 (t)	4.521 (s)	3.347 (s)	3.229 (t)	1.770 (m)	1.276 (s)	0.862 (t)
	Ib	7.449 (d)	7.325 (d)	4.530 (s)	3.364 (s)	3.242 (t)	2.954 (s)	1.769 (m)	1.246 (s)	0.859 (t)
	Ic	7.653 (d)	7.585 (d)	4.657 (s)	3.385 (s)	3.297 (t)	1.770 (m)	1.251 (m)	0.857 (t)	
	Id	8.366 (d)	7.890 (d)	4.745 (s)	3.019 (t)	3.031 (s)	1.787 (m)	1.238 (s)	0.862 (t)	



3.2 corrosion studies

The corrosion rate and the corresponding corrosion inhibition efficiency for carbon steel in formation water in the absence and presence of ILs at 298 K are presented in Table 5. Here, we will study the influence of the introduction of different groups substitution to benzyl- group (i.e. H, Me, Cl and NO_2) on the ILs protection efficiency.

Tables 5 reveal that the corrosion rates of carbon steel in formation water containing ILs decrease with increasing their concentration (up to critical values). This behaviour can be attributed to the increase in the number of ILs ionic liquids molecules adsorbed at metal/solution interface on increasing its concentration [18].

So, molecules of the BCIL constitute adsorption films on carbon steel surface which protects it against corrosive species [19]. The decrease in the corrosion rate of carbon steel in formation water in the presence of ILs ionic liquids confirms the adsorption of ILs ionic liquids molecules on carbon steel surface.

We noted that the different groups substitution to benzyl- group (i.e. H, Me, Cl and NO_2) led to different inhibition performance. Where the P_W% values have the following order: Me>H>NO_2>Cl.

Table 5: Mass loss parameters and the corresponding corrosion inhibition efficiency for carbon steel in formation water in the absence and presence of ILs at 298 K.

Sol.	ILs conc.	wt. loss	corrosion rate	P_W%
	ppm	g	g cm^{-2} min^{-1}	
blank		0.0074	8.92168E-08	
ILs - H	20	0.0042	4.05093E-08	54.586
	60	0.004	3.85802E-08	56.749
	300	0.0033	3.53652E-08	60.353
	500	0.0025	3.38423E-08	62.06
ILs - Me	20	0.0052	5.01543E-08	43.773
	40	0.0057	5.49769E-08	38.367
	60	0.005	4.82253E-08	45.936
	100	0.0046	4.43673E-08	50.261
	300	0.0029	3.10785E-08	65.159
	500	0.0037	3.96519E-08	55.547
ILs - Cl	20	0.0039	4.75146E-08	46.732
	40	0.0048	4.62963E-08	48.098
	60	0.0049	4.72608E-08	47.017
	200	0.0042	4.05093E-08	54.586
ILs – NO_2	100	0.004	3.85802E-08	56.749
	200	0.0037	3.56867E-08	59.992
	300	0.0034	3.27932E-08	63.236
	500	0.0032	3.89864E-08	56.293

3.3.Adsorption isotherms

The mechanism of corrosion inhibition can be explained on the basis of adsorption principle. The nature of the interaction between ILs ionic liquids and carbon steel surface can be understood using an adsorption isotherm [20].

Frumkin, Freundlich, Temkin, Flory–Huggins and Langmuir adsorption isotherms [21] have been attempted for fitting the adsorption of molecules of ILs ionic liquids on carbon steel surface in formation water. It was found that the Langmuir model have showed the best fitting where it had the highest values of regression factor (r^2). Langmuir isotherm is represented with a relation between θ (where θ = PW% x 10^{-2}) and ILs ionic liquids concentration (C_{inh}) according to equation (3) [22].

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \qquad (3)$$

where K_{ads} is the adsorption–desorption equilibrium constant.

Langmuir plot is drawn based on the data obtained mass loss method (Fig. 2) and the change in free energy of adsorption (ΔG^0_{ads}) is calculated according to the following equation [23]:

$$\Delta G^0_{ads} = -RT \ln (55.5\, K_{ads}) \qquad (4)$$

where R is the molar gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution expressed in molar .

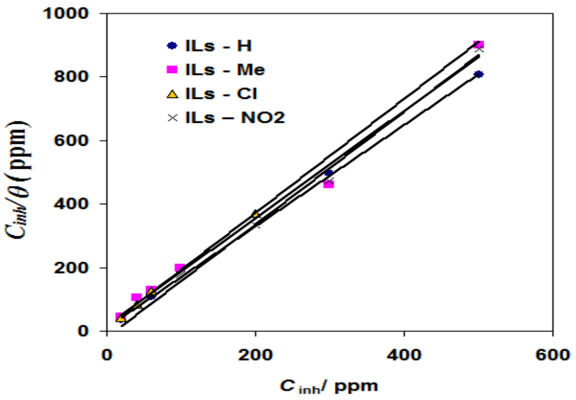


Fig. 2 Langmuir adsorption plots for carbon steel in formation water inhibited by benzalkoniumchloride derivatives ionic liquids (ILs).

ΔG^0_{ads} values are in the range (-24) - (-28) kJ mol^{-1}. The value of ΔG^0_{ads} determines the nature of adsorption process such that: (i) if ΔG^0_{ads} is less negative than -20 kJ mol^{-1} the adsorption will be physical (known as physisorption) which occurs via electrostatic interactions. (ii) If ΔG^0_{ads} is more negative than -40 kJ mol^{-1} the adsorption is chemical (known as chemisorption) where coordinate bonds are formed via electron transfer from inhibitor molecules to the metal surface. (iii) But, if the ΔG^0_{ads} is between -20 and -40 kJ mol^{-1} then both types of adsorption are involved [24-28]. For ILs ionic liquids, ΔG^0_{ads} value is around -28 kJ mol^{-1} which indicates the occurrence of both physisorption and chemisorption processes.

4. Conclusions

(1) New benzalkonium chloride derivatives ionic liquids (ILs) have been synthesized and acted as effective corrosion inhibitor for carbon steel in formation water.
(2) The weight loss studies showed that the ILs molecules acted as good corrosion inhibitors.
(3) The adsorption of ILs molecules on the steel surface was found to obey the Langmuir adsorption isotherm best. The values of free energy of adsorption indicates the occurrence both physisorption and chemisorption.

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