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Effect of Some Tetrabutylammonium Salts on the Impedance Behavior of Indium in Acidic Media

Adbel-Rahman EL-SAYED,* Hossnia MOHRAN, and Farouk RASHWAN
Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt.

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The ac impedance of a planar indium electrode in both HCl and H_2SO_4 solution was measured at −20, 0.0, and 10 mV vs. the open circuit potentials. Various amounts of Bu_4NBF_4, Bu_4NPF_6, and Bu_4NClO_4 were gradually introduced to the electrolytic solution and the impedance of the electrode was remeasured. Subsequently, R_s, R_p, and C_{dl}, in the absence and presence of the additives, were computed and compared. It was found that Bu_4NBF_4 has an inhibitive action in both acids. On the other hand, acceleration of the electrochemical processes in the presence of Bu_4NPF_6 also in both acids, is observed. However, some retardation of the electrode reactions was obtained at the lowest concentration of the additive only in HCl. It is noteworthy that Bu_4NClO_4 has contradictory effects on the electrochemical processes, i. e. an inhibitive action in HCl solution, whereas in H_2SO_4 the electrode reactions are significantly enhanced.

Impedance spectroscopy (IS) has found wide application in the study of corrosion phenomena.[1]

The adsorption of tetrabutylammonium cation on an indium electrode has been studied by Korokov and Damaskin in sodium sulfate and potassium iodide solutions.[2]

There have been few systematic studies concerning the effects of additives on the electrochemical and corrosion behavior of indium in acid solutions using modern techniques. Therefore, this work presents the influence of some quaternary ammonium salts on IS parameters of indium in both HCl and H_2SO_4 solutions.

Experimental

Solutions of HCl and H_2SO_4 (both 0.25 M, 1 M = 1 mol dm^{-3}) were prepared from AR-grade samples by proper dilution with twice distilled water. Prior to each experimental measurement, the solution under investigation was made oxygen-free by passing through it prewashed pure nitrogen for a sufficient duration of time.

Reagent grade (Aldrich Chemical Company) tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) was used without further purification. Both tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) and tetrabutylammonium perchlorate (Bu_4NClO_4), which are Fluka production, were further purified by recrystallization from a 2 : 1 mixture of pure methanol and twice distilled water. The additive solutions were prepared by dissolving the appropriate amounts in 10 ml redistilled methanol. The desired volume was then added to the electrolyte (100 ml) by means of a graduated pipett.

The whole measurements were made on a planar indium-disk electrode (A = 0.196 cm^2) of specpure 99.999%, Gold Label Aldrich production. The electrode was prepared by cutting the rod and setting it in an Araldite holder. Prior to each measurement, the electrode was polished with No. 600 emery paper, and then degreased in pure ethanol, and finally washed in running twice distilled water, before being inserted in the polarization cell.

A conventional three-electrode cell was used with 1.0 cm^2 Pt sheet as counter electrode, which was separated from the main cell-compartment using a sintered glass tubing. The reference electrode was the saturated calomel to which all potential values were referred. The cell description has been given elsewhere.[3]

The impedance spectroscopic measurements were carried out in a frequency range of 0.1 to 0.005 Hz. Five data points were taken for each decade of frequency, or for each change in it by a power of ten. An amplitude of 10 mV peak-to-peak for ac signal was used for all IS experiments.

An EG&G Princeton Applied Research Potentiostat/Galvanostat, Model 273, coupled with EG&G Princeton Applied Research 5208, two phase lock-in Analyzer, were equipped with an IBM PC Model 30 computer. Model 378 ac impedance software, from EG&G Princeton Applied Research, was used for all IS measurements.

The cell temperature was kept constant, (25.0±1.0°C), using a Haake N3 ultrathermostat. Each experiment was repeated until reproducibility of results was satisfactory.

Results and Discussion

Since the adsorbability on an electrode surface depends on its charge, it is necessary to compute the potential ϕ, which is the difference between the steady-state potential (ϕ_{st}) of the electrode, and the zero-charge potential ($\phi_{z.ch}$),[4] according to Eq. 1.

$$\phi = \phi_{st} - \phi_{z.ch} \tag{1}$$

Under the experimental conditions of this work, the value of ϕ-potential of indium (In-ϕ) in acidic solutions was found to be +0.24, indicating that the indium surface is positively charged at the stationary potential. Accordingly, an additive which exhibits a positive charge in acidic solution will not be readily adsorbed on the indium surface.

A) Behavior in 0.25 M HCl Solution.

Figures 1A, 1B, and 1C represent the diagrams of the complex-plane impedance of indium electrode in 0.25 M HCl, in the absence and presence of various concentrations of Bu_4NBF_4 at −20, 0.0, and 10 mV, vs. the open circuit potential (O.C.). As the Fig.1 shows, the IS behavior at the cathodic region is nearly an ideal semicircle. At both the O.C. and anodic to it, the spectrum is distorted at low frequencies by the appearance of

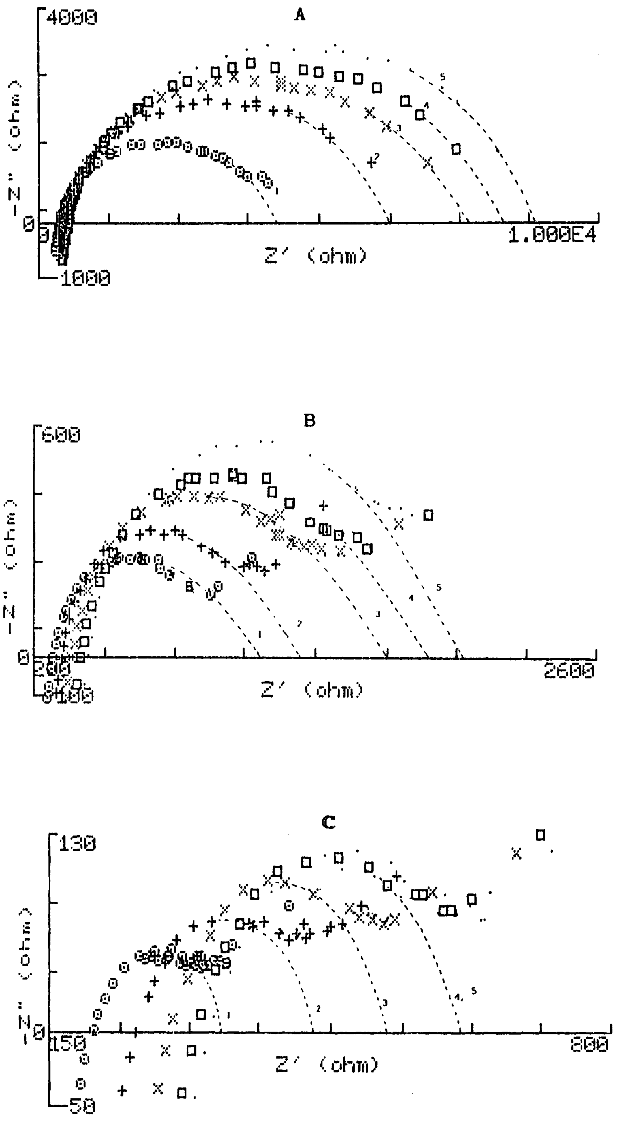

Fig. 1. Complex plane impedance of indium electrode in 0.25 M HCl at different potentials; (A) −20 mV, (B) 0.0 mV, (C) +10.0 mV vs. O.C. in the presence of Bu_4NBF_4; (1) 0.0 M, (2) 2.5×10^{-6} M, (3) 1.0×10^{-5} M, (4) 5.0×10^{-5} M, (5) 2.0×10^{-4} M.

Warburg behavior. Addition of Bu_4NBF_4 within the concentration range 2.5×10^{-6}—2.0×10^{-4} M demonstrates a marked influence on the IS diagram at all the examined potential points. From Table 1, it is clear that by increasing the additive concentration, the solution resistance (R_s), and the polarization resistance (R_p), are increased, while the double-layer capacitance (C_{dl}) is significantly decreased. The inhibition efficiency of the additive at the anodic potential is relatively small, (30%), and gradually increases as the potential becomes cathodic (37% at O.C. and 56% at −20 mV). This view is reinforced by comparing the values of both R_p and C_{dl} as shown in Table 1.

The impedance parameters evaluated in the absence and presence of increasing Bu_4NPF_6 concentration, demonstrate that the additive has two opposite effects. At the lowest concentration, namely at 2.5×10^{-6} M, inhibition of the electrode processes takes place. On the other hand, acceleration of the electrode reactions with further increase of the alkylammonium salt is observed. The latter finding is indicated by an increase in C_{dl} and a decrease in R_p values. It is noteworthy to observe that the additive has its maximum acceleration effect at the open circuit rather than at the cathodic or anodic potentials.

The introduction of different concentrations of Bu_4NClO_4 to the In/HCl system produces a significant increase in the R_p values, whereas the C_{dl} of the electrode is gradually decreased. The data reveals that retardation of the electrochemical processes in the presence of Bu_4NClO_4 takes place at all the examined potential points. Within the used concentration range of the additive (2.5×10^{-6}—2.0×10^{-4} M), a gradual increase in the inhibiting action of the additive is observed. As the IS results demonstrate, (Table 1), maximum retardation of the electrode reactions is reached at the cathodic potential (−20 mV vs. O.C.). The inhibition efficiency of Bu_4NClO_4 within the used concentration range, is computed from the capacitance values, and is found to be 37, 26, and 23.9% at −20, 0.0, and 10 mV, respectively.

As Table 1 shows, the IS results obtained in 0.25 M HCl in the presence of Bu_4NBF_4 and Bu_4NPF_6 indicate opposite influences, i. e. inhibition and acceleration of the electrode processes, respectively. Since both additives have the same cation part, (Bu_4N^+), one may conclude that the anion part of both additives, (BF_4^- and PF_6^-), plays the important role in the electrochemical behavior. We suggest that BF_4^- anion may be chelate with indium, forming the less soluble complex $[In(BF_4)_3]$ on the electrode surface. While, the chelation of PF_6^- anion with indium is the more soluble complex $[In(PF_6)_3]$. Accordingly, inhibition of the electrochemical processes in the presence of Bu_4NBF_4, and enhancement in the presence of Bu_4NPF_6, must be expected. The conclusion concerning the concept that soluble complexes accelerate corrosion reactions, was frequently suggested.[5] In HCl solution, the adsorption of chloride ions on the surface of In will alter its charge so that the adsorption of Bu_4N^+ cation becomes possible.[6] This interpretation can be applied to the observed inhibitive action of Bu_4NPF_6 at very low concentration (2.5×10^{-6} M). Under these conditions, the effects due to the formation of a soluble complex, suggested above, can be negligible. However, as the additive concentration is further increased, the influences due to the soluble-complex formation predominate, and hence acceleration of the electrode reactions takes place.

The data included in Table 1 concerning the inhibitive effect of both Bu_4NBF_4 and Bu_4NClO_4, demonstrates that the inhibiting efficiency of the former additive exceeds that of the latter one by about 10—

Table 1. Effect of Some Tetrabutylammonium Salts on the Impedance Parameters of Indium Electrode in 0.25 M HCL Solution at Cathodic, Open Circuit, and Anodic Potentials

Additive	Concn	at −20 mV			at O.C.P.			at 10 mV		
	$M\times10^6$	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}
		Ω	Ω	μF	Ω	Ω	μF	Ω	Ω	μF
Bu_4NBF_4	0.0	330	3920	34	313	965	130	205	159	870
	2.5	396	5970	20	336	1050	105	261	225	698
	10.0	462	7560	18	358	1420	95	292	283	668
	50.0	528	8110	16	381	1560	88	322	289	638
	200.0	660	8770	15	426	1620	82	335	290	610
Bu_4NPF_6	0.0	415	3650	43	388	990	125	275	208	812
	2.5	452	3830	35	398	1023	109	292	225	707
	10.0	490	2900	46	404	858	145	292	158	954
	50.0	528	2770	52	319	660	263	265	145	1071
	200.0	566	2760	55	338	670	267	248	142	1080
Bu_4NClO_4	0.0	576	3510	35	173	996	138	251	168	900
	2.5	580	4180	32	207	1100	125	248	171	756
	10.0	585	4180	28	225	1110	120	225	161	721
	50.0	588	4320	26	225	1120	109	275	175	702
	200.0	590	4780	22	225	1130	102	295	192	685

Table 2. Effect of Some Tetrabutylammonium Salts on the Impedanc Paramteers of Indium Electorode in 0.25 M H_2SO_4 Solution at Cathodic, Open Circuit, and Anodic Potentials

Additive	Concn	at −20 mV			at O.C.P.			at 10 mV		
	$M\times10^6$	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}	R_s	R_p	C_{dl}
		Ω	Ω	μF	Ω	Ω	μF	Ω	Ω	μF
Bu_4NBF_4	0.0	490	2153	40	283	706	80	158	196	230
	2.5	490	2165	33	283	1009	65	173	265	190
	10.0	490	5159	30	283	2379	56	231	848	150
	50.0	490	5250	26	283	2408	50	218	900	135
	200.0	490	5552	22	283	2495	48	231	928	130
Bu_4NPF_6	0.0	528	2180	38	340	720	72	212	205	209
	2.5	528	2020	46	340	360	158	212	110	426
	10.0	528	1600	66	340	342	180	192	80	600
	50.0	528	1100	76	340	292	281	219	42	1479
	200.0	340	1105	76	245	290	280	265	41	1479
Bu_4NClO_4	0.0	707	2160	35	434	715	93	286	202	239
	2.5	707	2120	43	434	760	80	304	252	163
	10.0	707	1800	59	434	550	138	298	190	250
	50.0	707	1150	76	434	400	195	298	110	588
	200.0	707	930	100	434	370	185	309	105	585

19%. However, retardation of the electrode reactions in the presence of both additives in HCl solution, can be ascribed to adsorption of the cation form (Bu_4N^+) of both additives on the electrode surface, as mentioned above. It was suggested that the chloride ions in solution enhance such adsorption process.[6] Now the reason that Bu_4NBF_4 is more effective as an inhibitor than Bu_4NClO_4 can be attributed to the concept that BF_4^- could form a less soluble complex[5] on the indium surface, whereas the ClO_4^- ion has a very low tendency to undergo such chelation processes.[7] The solution-resistance values, (listed in Table 1), are increasing in the presence of Bu_4NBF_4, while these values are almost constant in the presence of Bu_4NClO_4 when increasing the concentration of the additive in both cases. These observations are in agreement with the above conclusion.

B) Behavior in 0.25 M H_2SO_4 Solution. Figures 2A, 2B, and 2C display the complex plane impedance plots for a planar indium electrode in 0.25 M H_2SO_4 solution, in the absence and presence of various concentrations of Bu_4NBF_4at −20, 0.0, and 10 mV

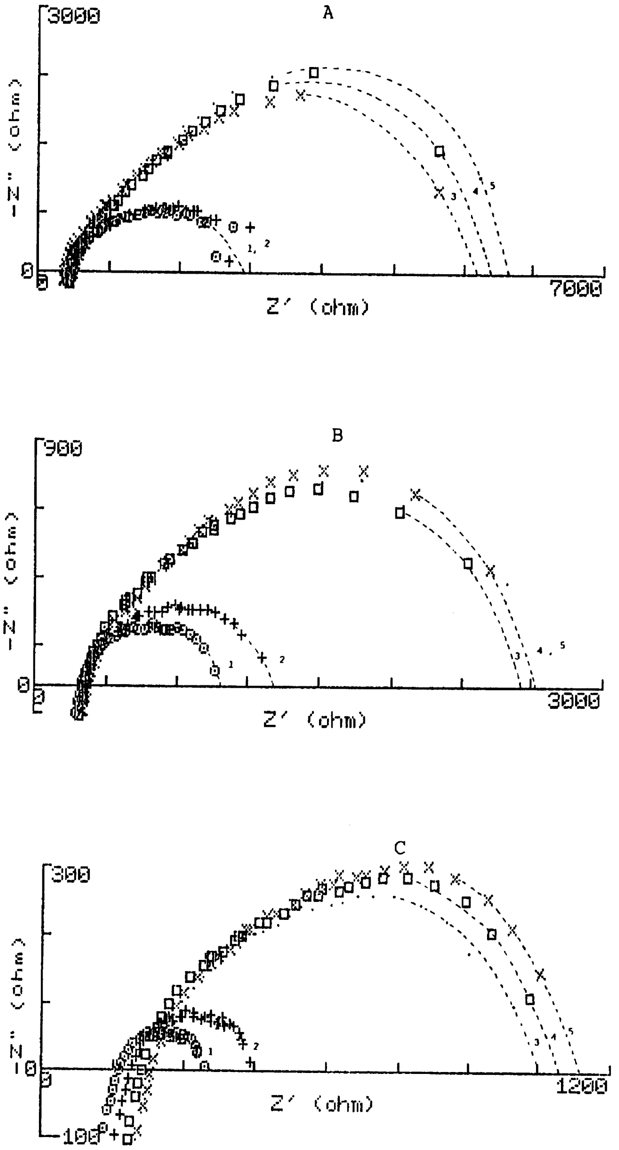

Fig. 2. Complex plane impedance of indium electrode in 0.25 M H_2SO_4 at different potentials; (A) -20 mV, (B) 0.0 mV, (C) $+10.0$ mV vs. O.C. in the presence of Bu_4NBF_4: (1) 0.0 M, (2) 2.5×10^{-6} M, (3) 1.0×10^{-5} M, (4) 5.0×10^{-5} M, (5) 2.0×10^{-4} M.

vs. the open circuit potential, respectively. When increasing the additive concentration from 2.5×10^{-6} to 2.0×10^{-4} M, and at all the three potential points under investigation, the computed IS data depicted in Table 2 shows a gradual increase in R_p values, whereas a systematic decrease in the values of C_{dl} is obtained. The results indicate retardation of the electrode processes due to the presence of Bu_4NBF_4. The inhibition efficiency values within the used concentration range, at both the O.C., and anodic to it, (10 mV), are comparable, (40 and 39%), and are a little bit lower than those calculated at cathodic potential, (45%).

IS results evaluated in the presence of gradual introduction of Bu_4NPF_6 (2.5×10^{-6}—2.0×10^{-4} M) to the In/H_2SO_4 system, show opposite influences to that obtained in case of Bu_4NBF_4, (Table 2). This means that the presence of Bu_4NPF_6 leads to increasing the corrosive action of the medium, as indicated by increasing the C_{dl}, and lowering the R_p values. It is observed that the additive enhancement of the electrochemical processes increases from cathodic to O.C. potential, and reaches its maximum acceleration at the anodic potential (10 mV).

A similar behavior to that of Bu_4NPF_6 is observed when introducing various concentrations of Bu_4NClO_4 (2.5×10^{-6}—2.0×10^{-4} M) to the In/H_2SO_4 system, as indicated by the IS data listed in Table 2.

In H_2SO_4 solution, inhibition and acceleration of the electrode reactions in the presence of Bu_4NBF_4 and Bu_4NPF_6, can also be ascribed to the foregoing suggested concept, i. e., less- and more-soluble complex formation on the electrode surface respectively. Since the chloride ions are absent, in case of sulfuric acid solutions, adsorption of the anions of the tetraalkylammonium salts on the electrode surface will be more favourable than their cations.[6] Therefore as expected, the anion parts of the additives must play the main role in the electrochemical processes. On the basis of the suggestion that adsorption of counter anions of the alkylammonium salt on the electrode surface, and/or at the metal-solution interface, will enhance the discharge of hydrogen ions,[8] acceleration of the electrode reactions in case of In/H_2SO_4 system, in the presence of Bu_4NClO_4, can be understood. This conclusion is in agreement with both previous studies,[9,10] and the computed IS data listed in Tables 1 and 2.

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