

# Behaviour of benzylidene acetone during zinc electrodeposition in weakly acid solution containing a nonionic surfactant and/or carboxylic acid

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The transformation products of benzylidene acetone formed during zinc electrodeposition in solutions containing a nonionic surfactant and/or carboxylic acid were determined by IR and  $^1\text{H}$  NMR-spectra after extraction and chromatographic separation. 1-Phenylbutanone-3, 1-phenylbutanol-3 and 1-phenylbutane were cathodic reaction products. Benzaldehyde, acetone, benzyl alcohol and benzoic acid were chemical reaction products in the cathodic layer. The nonionic surfactant increased the solubility of benzylidene acetone and carboxylic acid. This effect is probably caused by hydrophobic interaction and formation of associates. The associates cover a larger area of the cathodic surface than unsaturated ketone and/or carboxylic acid alone. It is supposed that a synergistic effect of additive mixtures on zinc electrodeposition may be caused by the formation of associates.

## 1. Introduction

Bright electrodeposits are formed in electrolytes containing benzylidene acetone (BDA) together with nonionic surfactants (NS) and carboxylic acids [1–3]. NS increases the brightening power of electrolytes containing BDA [4, 5]. Carboxylic acids improve the solubility of anodes, buffer the cathodic layer, and some of them have brightening properties [4–10]. It has been shown [4] that cinnamic acid at low  $i_c$  (cathodic current density) and nicotinic acid at high  $i_c$  widen the range where bright electrodeposits can be obtained from electrolytes containing NS and BDA. The range of bright electrodeposition widens when the latter two compounds are present together with mono- and dicarboxylic acids in the solution [5, 11].

Investigations of carbon inclusions into coatings show that the amount of carbon included from BDA is an order of magnitude higher than that included from benzoic acid [5, 12]. Nearly all carbon atoms are included from BDA at  $c$  (concentration) 3.5 mM, only up to  $i_c \approx 1.8 \text{ mA cm}^{-2}$ . If nonylphenylpolyethylene glycol is used as a NS, it is included in a nondecomposed form [13].

A double bond may be hydrogenated in the BDA molecule at the cathode during zinc electrodeposition, and a carbonyl group is reduced to either a hydroxyl or a methylene group [14–17]. It should be noted that some substances separated by chromatography have been incorrectly characterized using only UV spectroscopy (UVS) [17].

Some investigations [6, 18–22] consider the role of the NS during electrodeposition of metals. It is supposed that NS form a noncontinuous film at the cathode surface and effect the processes occurring during electrodeposition of zinc [18–20, 22].

No analysis of the part each component of the mixture of organic additives plays when a synergistic effect is observed during zinc electrodeposition is available in the literature.

This work investigates the behaviour of benzylidene acetone in a mixture of additives.

## 2. Experimental details

The behaviour of BDA was investigated in electrolyte containing ( $\text{g dm}^{-3}$ ):  $\text{ZnCl}_2$  100,  $\text{KCl}$  200,  $\text{H}_3\text{BO}_3$  30. Additives investigated were BDA (m.p. 41–42 °C), benzoic acid, adipic acid, laprol 2402Ts (LP) (polyoxyethylated-polyoxypropylated alcohol), and sintanol DS-10 (ST) (polyoxyethylated alcohol). Inorganic salts,  $\text{H}_3\text{BO}_3$ , benzoic and adipic acids were of analytically pure grade. Zinc plates of purissimus grade served as anodes and brass plates as cathodes.

The experiments for qualitative analysis of mixtures of BDA transformation products were conducted in 1.5 L glass vessels at pH 4.5, 20 °C,  $i_c = 20 - 40 \text{ mA cm}^{-2}$ . Transformation products in the form of vapours were collected in closed vessels (traps). The traps were cooled using ice and a mixture of ice and acetone (–15 °C). Transformation products were extracted from the electrolytes and traps using chloroform and ethyl ether. The extracted compounds were separated by thin layer chromatography ( $\text{Al}_2\text{O}_3$ , eluent: benzene + ethyl ether in the ratio 5:1) [15]. The compounds were identified using

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u.v. (Specord UV-VIS), i.r. (UR-20) and  $^1\text{H}$  NMR-spectra (R-20).

The electrodeposition of zinc for quantitative analysis of BDA transformation products was carried out in a two-chamber cell containing a diaphragm of porous glass (the catholyte had volume of  $0.1\text{ dm}^3$ ) at pH 4.5, and  $20^\circ\text{C}$ . The catholytes containing BDA or BDA + organic acid and its transformation products were extracted using chloroform. BDA and its transformation products from catholytes with LP or ST were driven off by water vapour and concentrated by extraction with chloroform upon saturating the solution with NaCl. The extracts were analysed by means of gas-liquid chromatography (LKM-8MD, flame ionization detector). Separation of the mixture was carried out in a column ( $100 \times 0.3\text{ cm}$ ) filled with chromosorb WAW + 10% PEGA using 5,5-dimethylcyclohexanedion-1,3 as an internal standard.

### 3. Results and discussion

The BDA dissolved in  $\text{CHCl}_3$  (as shown by i.r. and  $^1\text{H}$  NMR-spectra) is mainly in the form of *s-trans* (Fig. 1(a)). When kept in the zinc electrolyte for 10 days, about 25% of unsaturated ketone transform into *s-cis* form (Fig. 1(b)). Similar phenomena taking place in solutions of other composition have been described in the literature [23, 24]. After storing the electrolyte in the presence of metallic zinc for 10 days, traces of 1-phenylbutanone and 1-phenylbutanole-3 are found (Fig. 1(c)). The same quantity of the above compounds is accumulated within several minutes during zinc electrodeposition.

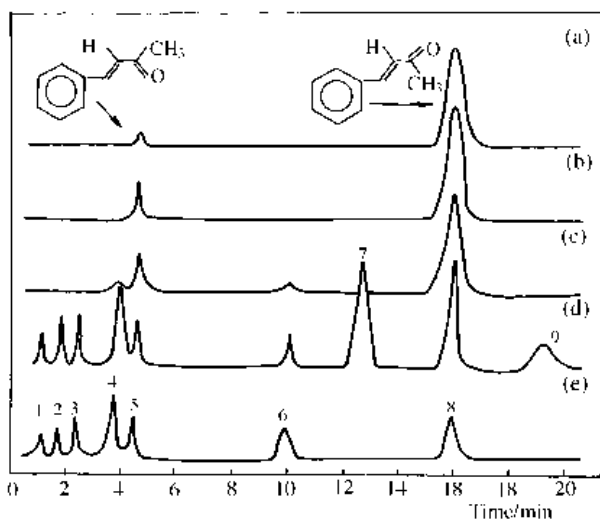


Fig. 1. Gas-liquid chromatograms of benzylidene acetone dissolved in  $\text{CHCl}_3$  (a), extracted from zinc solution stored for ten days without (b) and with metallic zinc (c), extracted mixture of organic compounds formed from benzylidene acetone during zinc electrodeposition at pH 4.5,  $20^\circ\text{C}$ ,  $i_c = 20\text{ mA cm}^{-2}$  (d) and vapour (e). Components of mixture: (1) 1-phenylbutane, (2) benzaldehyde, (3) benzyl alcohol, (4) 1-phenylbutanone-3, (5) *s-cis*-benzylidene acetone, (6) 1-phenylbutanol-3, (7) internal standard (5,5-dimethylcyclohexanedion-1,3), (8) *s-trans*-benzylidene acetone, (9) unidentified compound.

In addition to 1-phenylbutanone-3 and 1-phenylbutanole-3, 1-phenylbutane, benzaldehyde, benzyl alcohol, benzoic acid and unidentified compounds are synthesized in electrolytes during Zn electroplating (Fig. 1(d)). 1-Phenylbutanole-3 may be formed at the cathode from BDA and 1-phenylbutanone-3. The content of benzyl alcohol, benzaldehyde and benzoic acid increases with increase in concentration of BDA and  $i_c$ . It has been shown [7], that the cathodic layer pH increases markedly at  $c = 2.8\text{ mm}$  and  $i_c$  ranging from 20 to  $40\text{ mA cm}^{-2}$ . The pH exceeds 7 near the cathode at  $i_c \approx 30\text{ mA cm}^{-2}$ . Benzaldehyde and acetone are formed during BDA hydrolysis in the electrolyte under investigation. It is known that the hydrolysis of unsaturated ketones and aldehydes takes place during electrohydrogenation [25, 26]. According to the Cannizzaro, reaction, two benzaldehyde molecules may form benzoic acid and benzyl alcohol in the cathodic layer. Benzaldehyde may also be reduced to benzyl alcohol on the zinc cathode. The data on chemical reactions of BDA obtained in the cathodic layer (Fig. 1(d) and (e)) explain published results [12], where it has been shown that not all carbon atoms present in a side BDA chain are included in electrodeposits. Possibly, a mixture of benzaldehyde and BDA are included.

Taking into consideration the above data on electrochemical and chemical BDA reactions, quantitative investigations were carried out in electrolytes which contained  $1.4\text{ mM}$  BDA together with other additives.

Dicarboxylic adipic acid competes far less with BDA during adsorption at the cathode surface than benzoic acid (Fig. 2(a)). The adipic acid quantity, 15 times as high as that of BDA, diminishes the consumption rate ( $V_c$ ) of the latter compound by  $\sim 15\%$  (curve 1). The same quantity of benzoic acid diminishes  $V_c$  of BDA by  $\sim 40\%$  (curve 2).

The main changes in BDA behaviour occur when adding the first  $3\text{ g dm}^{-3}$  of both benzoic acid and/or NS (Fig. 2, curves 2, 4, 5). The LP decreases the accumulation rate ( $V_a$ ) of 1-phenylbutanone-3 negligibly and increases  $V_a$  of 1-phenylbutanole-3 more than ST. The latter compound noticeably decreases the  $V_c$  of BDA in comparison with LP. It is possible that a higher competitiveness during adsorption at the cathode is caused by a greater number of etheric oxygen atoms relative to the number of carbon atoms in ST than in LP.

The competition of organic additives at the cathode may be judged not only by  $V_c$  of BDA (Figs 2 and 3), but also by data on carbon inclusion in the coatings [14]. A two hundred times smaller BDA amount  $\sim 0.35\text{ mM}$  ( $0.05\text{ g dm}^{-3}$ ) decreases the total carbon quantity from 0.71 to 0.29% in electrodeposits obtained from the electrolyte containing  $10\text{ g dm}^{-3}$  ST. With  $0.7\text{ mM}$  BDA in this electrolyte, 0.37% of carbon is found; and with  $1.4\text{ mM}$  BDA, 0.57% of carbon is included. The carbon content increases in electrodeposits with increase in  $c$  of BDA; whereas with increase in  $c$  of benzoic acid from

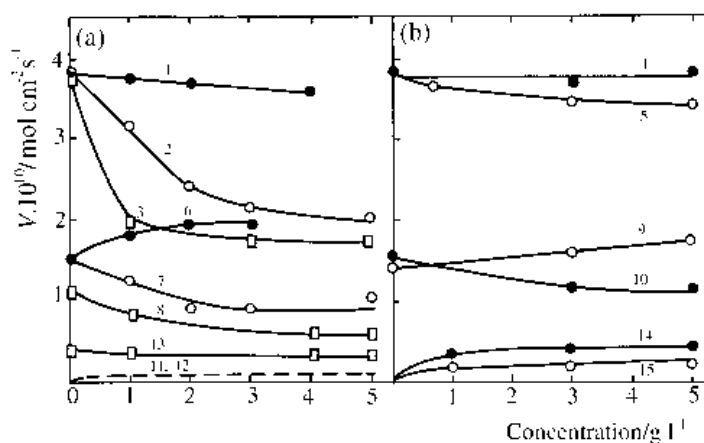


Fig. 2. Dependence of consumption rate ( $V_c$ ) of benzylidene acetone (1, 2, 3, 4, 5) and accumulation rates ( $V_a$ ) of 1-phenylbutanone (6, 7, 8, 9, 10) and 1-phenylbutanol-3 (11, 12, 13, 14, 15) on concentration of carboxylic acid (a) and surfactant (b) during zinc electrodeposition at  $i_c = 20 \text{ mA cm}^{-2}$ , pH 4.5,  $20^\circ\text{C}$  in weakly acid solutions, which contain  $0.2 \text{ g dm}^{-3}$  ( $\sim 1.4 \text{ mM}$ ) benzylidene acetone and: adipic acid (curves: 1, 6, 11); benzoic acid (curves: 2, 7, 12); benzoic acid +  $10 \text{ g dm}^{-3}$  (4 mM) laprol 2402Ts (curves: 3, 8, 13); laprol (curves: 4, 9, 14); sintanol DS-10 (curves: 5, 10, 15).

1 to  $5 \text{ g dm}^{-3}$  (8–40 mM) in the electrolyte containing  $10 \text{ g dm}^{-3}$  ST a gradual decrease in the total carbon quantity from 0.71% to 0.47% is observed.

The intensity of the influence of NS and of that of benzoic acid on the BDA behaviour depends both on the relationship between BDA concentration and NS or organic acids concentration (Fig. 2) and on  $i_c$  of the electrode (Fig. 3) in electrolytes containing three organic additives. The  $V_c$  of BDA are nearly the same (Fig. 3, curve 6, 7) in both electrolytes investigated containing three additives, whichever NS is used.

Addition of NS and benzoic acid decreases  $V_c$  BDA approximately two fold within the  $i_c$  range from 20 to  $40 \text{ mA cm}^{-2}$  (Fig. 3). These data correlate with the data on carbon inclusion from BDA [5]. Addition of benzoic acid to the electrolyte containing BDA (labelled with  $^{14}\text{C}$ ) and ST decreases the carbon quantity in the deposits from BDA over two fold.

Apparently, the carbon quantity included from BDA depends not only on  $V_c$  of BDA, but also on the duration of the presence of molecules on the electrode surface during cathodic reactions. 1-Phenylbutanone-3 is formed only after adding two hydrogen atoms to BDA, while 1-phenylbutanol-3 and 1-phenylbutane are formed after adding four atoms. Probably, the duration of the contact with the cathode surface during synthesis of the two latter compounds is longer than that during 1-phenylbutanone-3 synthesis. About 50% of the BDA consumed is hydrogenated to 1-phenylbutanone-3 (Fig. 3, curves 6, 7 and 13, 14), and approximately 10–20% is transformed to 1-phenylbutanol-3 (Fig. 3, curves 6, 7 and 20, 21). The remaining 30–40% of the additive may be consumed in several ways, namely, electrosynthesis of 1-phenylbutane, chemical reactions (benzaldehyde, benzyl alcohol, benzoic acid) and evaporation (Fig. 1, curve (e)). The pathways for BDA consumption depend on both electrolysis conditions and concentrations of other additives (Figs 2 and 3). There is no correlation between  $V_c$  of BDA (Figs 2 and 3), the carbon included and the cathodic

potential shift [5, 14]. Probably these processes are independent. It is possible that the carbon content included, which changes analogously to  $V_c$  of BDA, is controlled by molecules coming in contact with a cathode during electrodeposition (Figs 4 and 5).

According to classification of organic additives given in other work [27], BDA should be classified as a reactive additive. As has been shown experimentally, benzoic acid and NS are unaffected during zinc

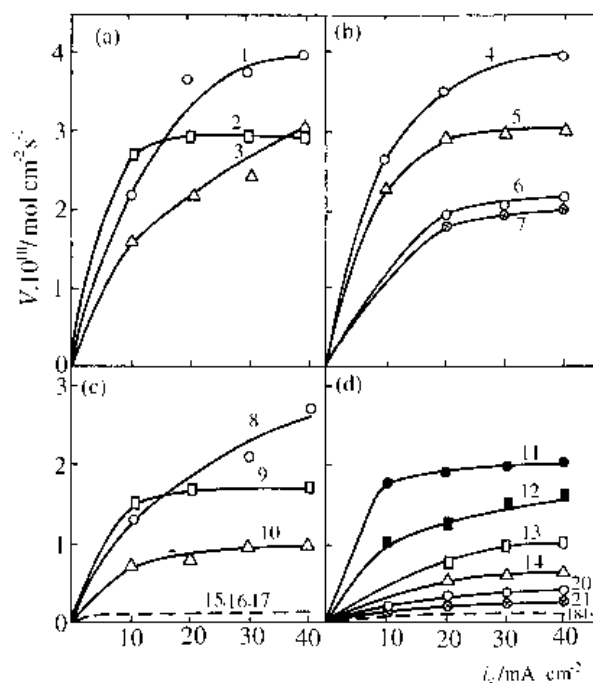


Fig. 3. Dependence of consumption rate ( $V_c$ ) of benzylidene acetone (1, 2, 3, 4, 5, 6, 7) and accumulation rates ( $V_a$ ) of 1-phenylbutanone (8, 9, 10, 11, 12, 13, 14) and 1-phenylbutanol-3 (15, 16, 17, 18, 19, 20, 21) on  $i_c$  during zinc electrodeposition at pH 4.5,  $20^\circ\text{C}$  in weakly acid solutions, which contain  $0.2 \text{ g dm}^{-3}$  ( $\sim 1.4 \text{ mM}$ ) (1, 8, 15) benzylidene acetone and:  $3 \text{ g dm}^{-3}$  adipic acid (curves: 2, 9, 16);  $3 \text{ g dm}^{-3}$  benzoic acid (curves: 3, 10, 17);  $5 \text{ g dm}^{-3}$  laprol 2402Ts (curves: 4, 11, 18);  $5 \text{ g dm}^{-3}$  sintanol DS-10 (curves: 5, 12, 19);  $5 \text{ g dm}^{-3}$  laprol 2402 ts +  $3 \text{ g dm}^{-3}$  benzoic acid (curves: 6, 13, 20);  $5 \text{ g dm}^{-3}$  sintanol DS-10 +  $3 \text{ g dm}^{-3}$  benzoic acid (curves: 7, 14, 21).

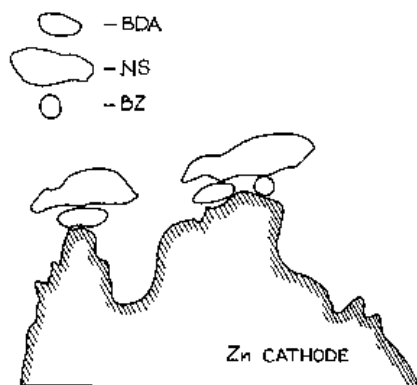


Fig. 4. Schematic representation of adsorption of assumed associates (BDA: benzylidene acetone, NS: nonionic surfactant, BZ: benzoic acid).

electrodeposition. The NS increases the solubility of organic compounds and diminishes their evaporation. Possibly this is due to hydrophobic interactions, and formation of associates of different kinds (Fig. 4), namely,  $nNS \cdot kBDA$ ;  $nNS \cdot mBZ$ ;  $nNS \cdot kBDA \cdot mBZ$ , where BZ is benzoic acid and  $n, k, m = 0.1, 2, \dots$ . The associates are adsorbed at the cathode surface by BDA and benzoic acid molecules which are adsorptionally more active than NS. The associates cover a larger area at the cathode surface than BDA or benzoic acid and effect the metal deposition process more strongly. Their action depends on the duration of the interaction with the cathode surface during BDA cathodic reactions (Fig. 5) and on the lifetime of the associate entity. Apparently, the presence of associates capable of exerting a greater influence on zinc electrodeposition than separate additives is the main reason for the synergistic effect of the mixtures of organic additives under study. Possibly NS of the associates may take part in formation of various films at the cathode surface, data on this being available in the literature [18–20, 22].

#### 4. Conclusions

It has been shown that BDA is consumed in zinc electrodeposition in electrolytes containing NS

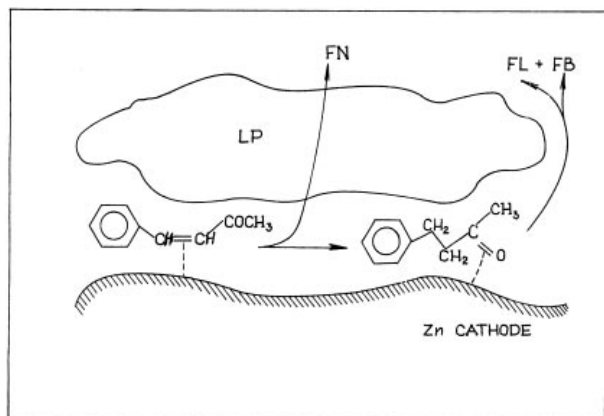


Fig. 5. Schematic representation of benzylidene acetone cathodic reactions in association with nonionic surfactant (NS). FN: 1-phenylbutanone-3, FL: 1-phenylbutanol-3, FB: 1-phenylbutane.

and/or benzoic acid mainly due to electrochemical reactions at the cathode and involving formation of 1-phenylbutanone-3, 1-phenylbutanol-3 and 1-phenylbutane. A small part of BDA and its transformation products evaporates. A noticeable part of BDA is hydrolysed in the cathodic layer with formation of acetone and benzaldehyde at BDA concentration  $> 2.5 \text{ mM}$  and  $i_c > 20 \text{ mA cm}^{-2}$ . According to the Cannizzaro reaction, two molecules of the latter compound transform into benzyl alcohol and benzoic acid. Benzaldehyde may also be reduced to benzyl alcohol at the cathode.

NS increases the solubility of BDA and BZ in the electrolyte due to their hydrophobic interaction and formation of associates. Apparently these are the reasons for a synergistic effect because they occupy a larger area on the cathode surface than separate additives such as BDA and/or benzoic acid do, and they have a greater effect on the electrodeposition of zinc.

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