Studies in Kolbe electrosynthesis. I. Electrolysis of capric acid

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A study of the various parameters affecting the Kolbe electro-synthesis reaction with capric acid has shown that amongst the water–solvent systems studied, a mixture of 30 vol.% of 2-methoxy ethanol with water is superior. The necessary conductance could be readily maintained by using potassium carbonate. The desirable conditions under which capric acid could be converted to the expected reaction product, 'octadecane', have been established. Continuous electrolysis was possible and yields of the order of 90% were readily achieved.

1. Introduction

Kolbe electrosynthesis, and its modifications like the Brown–Walker synthesis and additive- and cross-condensations, have been reported in the literature as useful methods for the preparation of straight-chain hydrocarbons as well as their mono- and α-, ω-, bi-functional derivatives. Critical reviews [1–4] of the literature on these reactions have shown that the possibility of using the technique is dependent on a fuller knowledge of the electrochemical system and in particular the electrolytic medium. Earlier work [3, 5–7] on the synthesis of n-paraffins from lauric, myristic, palmitic, stearic and arichidic acids involved electrolysis of partially neutralized solutions of the acids in methanol or ethanol using a pair of platinum electrodes. The product was isolated by extraction with solvent ether. The operating cell voltage was not reported. The problems encountered during the processes were; loss of alcohol due to excessive heat evolution, frequent discontinuities in the electrolysis due to the coating of the anode by the product and precipitation of the soaps with slight lowering of the electrolysis temperature. These difficulties, as well as the absence of a convenient method for the product isolation, discouraged the development of a technologically viable method. Work was therefore undertaken to evaluate the factors that affect the extent of the reaction and ready isolation of the product.

Among the various fatty acids, capric acid could be considered as representative, as it has properties similar to water-soluble fatty acids with spheroidal carboxylate ions on the one hand and water-insoluble fatty acids with carboxylate ions having rope-like structures with charge located at one end. In view of the inherent limitations of water as the solvent medium, in this case because of the low solubility and surface active characteristics of the caprate ion, it becomes necessary to choose a more appropriate medium among which aqueous solutions of organic liquids appear to be the most convenient. The organic solvent should not only enhance the solubility of capric acid and/or its alkali metal salt, but along with water should enhance the dissociation of the solute into free caprate ions, of fairly high mobility. Also its mixture with water should facilitate the isolation of the product. The conductance of the electrolyte could be enhanced by adding the minimum quantity of electrochemically non-reactive salts.

2. Experimental

Capric acid used in the present work has the following composition: 4% caprylic acid, 91% capric acid and 5% lauric acid, acid number 323–326.

Table 1. Influence of H_2O–MeOH medium composition on the yields of the Kolbe product obtained from capric acid sodium soap. Current 2·0 A (0·202 A cm^{-2}); Q/Q_T 2·99; temperature 35–45° C

| No. | H_2O–solvent volume composition | | Soap Composition 0·05 M/100 ml | | Soap Composition 0·1 M/l)) ML | |
	MeOH (ml)	H_2O (ml)	Conversion (%)	Yield (%)	Conversion (%)	Yield (%)
1	100	–	28·4	23·8	36·8	36·1
2	90	10	25·1	25·0	37·3	36·9
3	80	20	25·8	26·6	44·8	45·7
4	70	30	57·8	57·3	98·0	97·3
5	60	40	83·7	83·4	98·2	97·3
6	50	50	88·9	89·9	98·7	99·8
7	40	60	88·5	88·0	99·3	98·6
8	30	70	89·0	89·8	99·1	99·5
9	20	80	78·1	–	–	–
10	10	90	No electrolysis was possible due to excessive			
11	0	100	frothing when the current was switched on			

Aqueous solutions of the following solvents, with varying volume compositions, were used as media for carrying out the electrolysis: methanol, ethanol, n-propanol, t-butanol, ethylene glycol, diethylene glycol, dioxane, dimethyl formamide and 2-methoxy- and 2-ethoxy-, ethanols. All the solvents were purified under appropriate conditions.

Sodium caprate was prepared by neutralizing a methanolic solution of the capric acid with methanolic sodium hydroxide, water and methanol being subsequently removed by distillation with benzene.

The electrolytic cell employed in this work was made of glass. It had the shape of a sulphonating flask and was provided with a reflux condenser in order to minimize solvent losses. Platinum foil of size 25 × 20 × 1·0 mm and fused in a glass holder, served as an anode with working area 966 mm^2 (both sides). The platinum anode was flanked on both sides by two graphite cathodes of size 30 × 25 × 5 mm, with an inter-electrode spacing of 7–8 mm. The cell contents were agitated by a magnetic stirrer. The electrolyte was maintained at the required temperature by placing the cell in a water bath through which water at the required temperature could be circulated.

In the first set of experiments, the required amount of the preformed sodium caprate was dissolved in 100 ml of the water–methanol media with 0·005–0·01 mol of sodium perchlorate to enhance the conductance. The solution was then electrolysed under specified conditions such as temperature, anodic current density and duration of electrolysis. With media having more than 30 vol.% of water, the product separated out as the top layer and could be readily isolated using a separating funnel. The product still remaining in solution was extracted by n-hexane. The earlier separated product and the extract were mixed together and washed free of the soap, first by 50 ml of 90% ethanol and then by 150–200 ml of water. From the dried organic phase n-hexane was distilled off, and the weight of the product determined. The residual electrolyte and washings together were acidified by hydrochloric acid and the free capric acid was extracted with solvent ether. The ether extract was washed free of the mineral acid with water. After the removal of solvent ether the residue was titrated with standard sodium hydroxide solution using phenolphthalein indicator to determine the extent of conversion of the fatty acid. The product was further purified by fractional distillation under vacuum. I.r. spectra and the refractive index were determined. Microanalysis of the product was found to be C 85·1% and H 14·89% (for $C_{18}H_{38}$, C 85·05% and H 14·95% are the calculated values).

The influence of the process parameters such as volume composition of the water–methanol media, concentration of sodium caprate, pH of the electrolyte, concentration of sodium perchlorate,
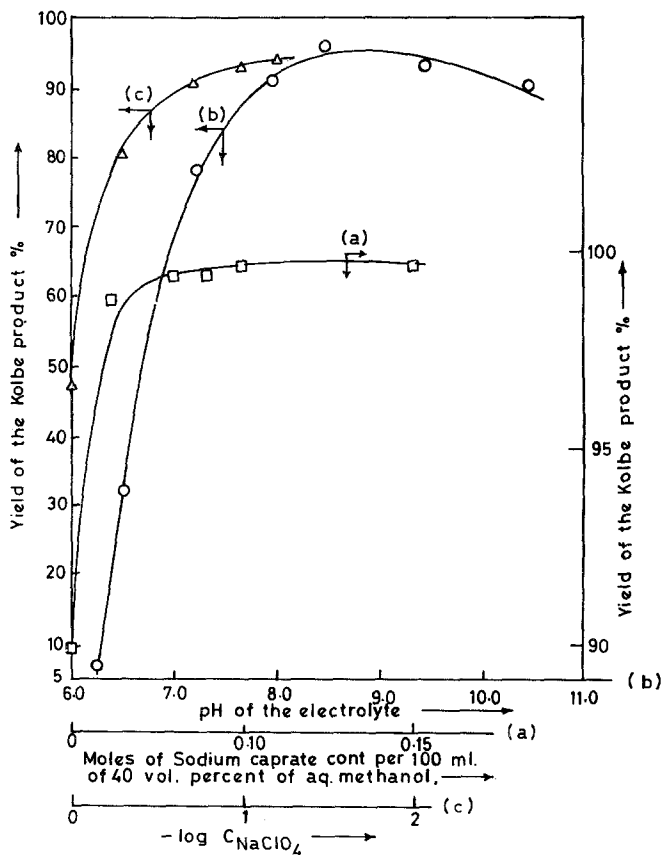
Fig. 1. Influence on the yield of Kolbe product of (a) sodium caprate content, (b) pH, and (c) log C_{NaClO_4}. Medium, 40 vol.% methanol–water; current 2·0 A; (0·202 A cm^{-2}); Q/Q_T 1·493; and temperature 45° C. For (a) and (b) C_{NaClO_4} = 0·006 mol and for (b) and (c) sodium caprate 1·0 mol l^{-1}.

Q/Q_T ratio, anodic current density and temperature, on the extent of conversion and the product yield was investigated and the results recorded in Table 1, Figs. 1 and 2 and Table 2 respectively.

After confirming that results with preformed and regenerated *in situ* sodium caprate are the same, further work was carried out with *in situ* generated caprate by using carbonates as alkali. As sodium carbonate and bicarbonate tend to deposit on the anode, because of their low solubility in the water–methanol media, potassium carbonate was used. Excess of potassium carbonate was added to the system to enhance electrical conductance as potassium perchlorate has limited solubility in the medium.

Although satisfactory conversions were obtained with the water–methanol media, methanol losses were excessive despite the reflux condenser attached to the cell and continuous working was rather difficult. Work was therefore extended to other water–solvent media by carrying

out electrolysis under the optimum conditions obtained for the 40 vol.% of methanol–water. As viscosity, specific conductance and dielectric constant of an electrochemical system influence the performance under identical conditions of electrolysis, these properties were determined for all the media in order to ascertain their influence on the product yield.

Table 2. Influence of temperature on the yield of the Kolbe product. Anodic current density 0·404 A cm^{-2}, and Q/Q_T 1·493

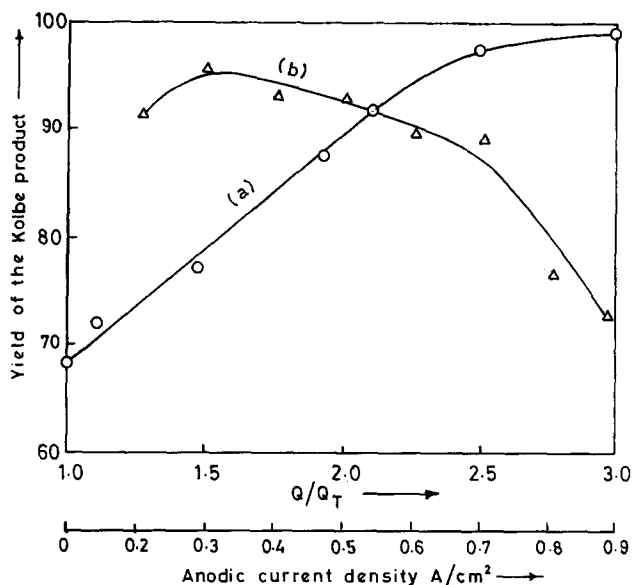| Medium	Temperature				
	25	35	45	55	65
40 vol.% of methanol–water	77·0	84·4	86·3	–	–
30 vol.% of 2-methoxy ethanol–water	–	82·0	89·4	81·5	78·0

Fig. 2. Influence on the yield of the Kolbe product of (a) the ratio Q/Q_T and (b) anodic current density. Medium, 40 vol.% methanol–water; sodium caprate 1·0 M; Q/Q_T 1·493; $C_{NaClO_4} = 0·006$ M; temperature 45° C; and current 2·0 A (0·202 A cm^{-2}).

3. Discussion

The electrochemical system in the case of the higher fatty acids exhibits the following set of equilibria

$$2(R\ COOH)_n \rightleftarrows n(R\ COOH)_2$$

$$\rightleftarrows 2nR\ COO^- + 2nH^+.$$
$$\uparrow\downarrow$$
$$(R\ COO^-)_{2n}$$
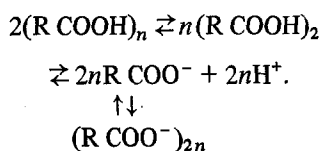
At any time the system, therefore, has fatty acid aggregates $(R\ COOH)_n$ and dimers $(R\ COOH)_2$, dissociated free carboxylate ions $R\ COO^-$ and its aggregates $(R\ COO^-)_n$ and hydrogen ions, all in equilibrium with one another. The behaviour of such a system is very much dependent on the pH of the system as well as on the solvolysis and dielectric characteristics of the medium.

It is evident from Table 1 that the yield of the product R–R (i.e. $C_{18}H_{38}$ in the case of capric acid) and the extent of conversion of capric acid are almost the same, indicating the absence of side reactions. The product yield is almost 100% for the media containing 40 or more vol.% water in methanol. As the role of methanol in the medium is to solubilize the caprate soap, a minimum of 20 vol.% of methanol is necessary to prevent excessive frothing. The work was therefore further carried out using 40 vol.% methanol–water. The product separated out as a top layer.

The influence of the process parameters (Figs. 1 and 2 and Table 2) such as concentration of sodium caprate, pH of the electrolyte, concentration of sodium perchlorate, the ratio Q/Q_T (where Q and Q_T are the quantities of electricity actually passed and theoretically required, respectively) and the anodic current density, on the product yield indicate the following optimum conditions for the maximum product yield: medium 40 vol.% methanol in water with sodium perchlorate concentration 0·1 mol l^{-1}, sodium caprate 1·0 mol l^{-1}, pH 8–8·5, temperature 45° C, Q/Q_T 1·493 and anodic current density 0·404 A cm^{-2}.

Experiments with other water–solvent media with varying compositions indicated their division into three distinct groups on the basis of maximum possible product yield for 20–30 vol.% composition of the solvent in water: (i) ethanol, 2-methoxy and 2-ethoxy ethanols, and dioxane with 85–89% yield; (ii) n-propanol, t-butanol and dimethyl formamide with 40–68% yield; (iii) ethylene glycol and diethylene glycol with 64–71% optimum yield at specific medium composition. No discernible relationship could be found between relative viscosity and specific conductivity of the electrolyte, and the product yield. However the maximum possible yield for a given water–solvent system would be found for the medium composition 20–30 vol.% of the

solvent corresponding to a dielectric constant of 50–70. The influence of dielectric constant on the product yield could be attributed to the enhancement of the dissociation of the solute into carboxylate ions. A similar observation was made in the case of acetic acid in methanol–water and ethanol–water media [8].

Amongst the investigated media, 30 vol.% of 2-methoxy ethanol in water appears to be more suitable for capric acid. As 2-methoxy ethanol has a boiling point of 124·5° C and a relatively low vapour pressure up to 85° C, the medium 30 vol.% of 2-methoxy ethanol in water appears to be a promising one for a technologically viable process.

Utilization of the system, water–2-methoxy ethanol for the Kolbe electrosynthesis using lauric, and higher fatty acids is in progress.

The construction of a larger cell, to work continuously, has also been undertaken.

4. Conclusion

Amongst the various water–solvent media investigated 30 vol.% 2-methoxy ethanol in water, appears to be the most convenient. The solvent losses are low in comparison with methanol. With the proposed water–2-methoxy ethanol system, the desirable conditions to get 85–90% yield of the product are, capric acid concentration $0·9–1·1$ mol l^{-1}, pH 8–8·5, 25% excess of required to neutralize the capric acid, Q/Q_T 1·5,

potassium carbonate over that stoichiometrically anodic current density $0·4$ A cm^{-2} and temperature 45–55° C. With continuous flow-type electrochemical reactors, higher anodic current densities and working temperatures could be tried.

Acknowledgement

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