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Paired electro-oxidation. I. Production of benzaldehyde

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Oxidation of toluene to benzaldehyde by Mn^{3+} and $^{\cdot}OH$ free radicals, generated in the anodic and cathodic reactions respectively, was carried out simultaneously in the cathodic and anodic compartments of a cell. The selectivity of benzaldehyde was very high in both the anodic and cathodic reactions. The maximum total current efficiency for benzaldehyde production in the paired electro-oxidation was 171%.

1. Introduction

Anodic oxidation methods for producing benzaldehyde have been studied by several investigators [1–6]. Ionic oxidants such as Mn^{3+}, Co^{3+}, and Ce^{4+}, etc. have been generated at the surface of anodes and used as redox mediators in the oxidation of toluene to benzaldehyde. Comninellis and co-workers have recently published a series of papers on the electrochemical production of ionic oxidants including Mn^{3+}, Co^{3+} and Ce^{4+} [7–9]. According to their results Mn^{3+} is an oxidant which can be obtained with higher current efficiency than other metal ions in high concentrations of aqueous H_2SO_4 solution. Kramer *et al.* (1980) [1] suggested a process consisting of an electrolyser and a homogeneous chemical reactor for producing benzaldehyde. The oxidant or mediator is introduced to the chemical reactor to oxidize toluene and then recycled to the electrolyser for regeneration. This type of process was found to be on the fringe of commercial feasibility. Wendt and Schneider (1986) [5] studied the oxidation of toluene using Mn^{3+} and Co^{3+} as mediators and pointed out that a separate chemical reactor is necessary because the high content of organic compounds in the anolyte reduces the oxygen overpotential and hence decreases the current efficiency for oxidant regeneration.

Beside the anodic oxidation method, oxidation of toluene by the cathodically generated $^{\cdot}OH$ free radicals has been studied recently [10–12]. It is well known that Fenton's reagent [13–15], a solution of H_2O_2 and ferrous ions, generates $^{\cdot}OH$ free radicals which can be used as an oxidant to oxidize toluene to benzaldehyde. Fenton's reagent can be prepared by the simultaneous cathodic reduction of molecular oxygen and Fe^{3+}. Osa and co-workers [10] have studied the oxidation of toluene by cathodically generated $^{\cdot}OH$ free radicals at 0° C and -0.6 V (vs SCE). They found that the products were benzaldehyde and cresol, and that the current efficiency for benzaldehyde production was small. Tomat and Rigo [12] studied the oxidation of toluene by cathodically generated $^{\cdot}OH$ free radicals at 50° C and -0.2 V (vs SCE) in various electrolyte solutions. The optimum concentrations of H_2SO_4 and Fe^{3+} for obtaining high current efficiency were about 0.5 M and 3×10^{-3} M, respectively. V^{5+}/V^{4+} and Cu^{2+}/Cu^{+} were also used as redox couples, and very high selectivity and current efficiencies for benzaldehyde production were obtained [12].

The economic advantages of paired electrochemical syntheses of organic compounds in a single cell, i.e. synthesis methods using both anode and cathode as working electrodes, have been outlined [16, 19, 21]. Several paired

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electrochemical syntheses of organic compounds have been proposed and investigated recently [16–22]. Pintauro *et al.* (1984) [20] have studied the paired electrolysis of glucose to yield gluconic acid and sorbitol. Baizer and co-workers [18] have investigated the paired electrolysis of ethyl acrylate and diethyl malonate to yield diethyl adipate and bimalonate. Wille *et al.* (1981) [19] have studied the paired electrosynthesis of sulphones by cathodic reduction of sulphur dioxide coupled with the anodic oxidation of bromide to bromine. Paired electrolysis is especially interesting when the anodic and cathodic reactions produce the same product from the same reactant.

The reactions in the paired electrochemical oxidation of toluene to benzaldehyde may be expressed as the following.

Anodic reaction:

$$M^{n+} \xrightarrow{k_1} M^{(n+1)+} + e \qquad (1)$$

Chemical reaction in anodic compartment:

$$C_6H_5CH_3 + 4M^{(n+1)+} + H_2O \xrightarrow{k_2} C_6H_5CHO + 4M^{n+} + 4H^+ \qquad (2)$$

Cathodic reactions:

$$R^{n+} + e \xrightarrow{k_3} R^{(n-1)+} \qquad (3)$$

$$O_2 + 2H_2O + 2e \xrightarrow{k_4} H_2O_2 + 2OH^- \qquad (4)$$

Chemical reactions in cathodic compartment:

$$R^{(n-1)+} + H_2O_2 \xrightarrow{k_5} R^{n+} + OH^- + {}^{\cdot}OH \qquad (5)$$

$$C_6H_5CH_3 + {}^{\cdot}OH + O_2 \xrightarrow{k_6} C_6H_5CHO + \text{others} \qquad (6)$$

In this work the paired electro-oxidation of toluene to benzaldehyde, using Mn^{2+}/Mn^{3+} and V^{5+}/V^{4+} as anodic and cathodic mediators respectively, has been studied and factors affecting the current efficiency have been explored.

2. Experimental details

Electrolysis was carried out in a divided cell with anodic and cathodic chambers separated by a 4 × 4 cm anion exchange membrane. Both anode and cathode were platinum plates. The anodic and cathodic overpotentials were measured against two SCE electrodes, respectively, and recorded with a two-pen recorder. The temperature of the cell was controlled within ±0.1°C. The d.c. current was supplied by a galvanostat (Chungyu CYE-D3022). The total electricity passed during a run was measured by means of a coulometer (HOKUTO HF-201). The anolyte and catholyte were agitated by magnetic stirrers. Oxygen was introduced to the cathodic chamber through a hollow global glass disperser under the cathode. A reflux condenser cooled with water at 0° C was used to reflux the products which were carried out in the oxygen stream.

After electrolysis the anolyte containing Mn^{3+} ion was reacted with toluene. A 250 ml sample of Mn^{3+} solution together with 50 ml toluene were poured into a glass reactor. The solution in the reactor was agitated with a magnetic stirrer. The concentration of Mn^{3+} was sampled with a 5 cm^3 glass syringe and analysed by titration with standard ferrous ion solution. The organic products in the glass reactor, as well as those in the cathodic chamber, were analysed using a gas chromatograph (Shimadzu GC-8A) with a flame ionization detector and a 3 m column packed with 3 wt % Apiezon-L and 1.5 wt % QF-1 on chromosorb W80/100.

3. Results

3.1. *Organic products*

The results of gas chromatograph analysis revealed that the only detectable product was benzaldehyde in the reaction of toluene with Mn^{3+}. Other possible oxidation products, such as benzyl alcohol and benzoic acid, were not found. The yields of benzaldehyde basing on Mn^{3+} were very high as shown in Tables 1 and 2.

The selectivity of benzaldehyde in the cathodic chamber was also very high and the possible by-product, cresol, was not found. The results were consistent with the work of Tomat and Rigo [11].

Table 1. Production of benzaldehyde by paired electro-oxidation at a cathode to anode surface area ratio of 6.33

	Run 1	*Run 2*	*Run 3*	*Run 4*
Current density at cathode (mA cm^{-2})	2.78	4.44	8.33	11.1
Current density at anode (mA cm^{-2})	17.6	28.1	52.7	70.2
Concentration of V_2O_5 in the catholyte (M × 10^{-3})	3	3	3	3
Products				
Anodic reaction:				
Current efficiency of Mn^{3+} in anolyte (%)	84.2	82.5	72.9	65.2
Yield of benzaldehyde based on Mn^{3+} (%)	98	95	95	97
Current efficiency of benzaldehyde (%)	84	80	68	64
Cathodic reaction:				
Current efficiency of benzaldehyde (%)[a]	51	18	5.4	4.5
Total current efficiency of benzaldehyde (%)	135	98	73.4	68.5

Temperature, 50° C; charge passed, 150 C; concentration of H_2SO_4, anolyte 6 M, catholyte 0.25 M; vol % of toluene in the catholyte, 25%; concentration of Mn^{2+} in the anolyte, 0.1 M.

[a] Based on one ˙OH free radical oxidizing one toluene molecule to one benzaldehyde molecule.

3.2. *Current efficiency for benzaldehyde production in the paired electro-oxidation*

The desired current densities at the anode and cathode were adjusted by changing the surface area of the electrodes. Two sets of platinum electrodes were used as working electrodes. The surface area ratios of cathode to anode were 6.33 and 12.2, respectively.

Table 1 shows the results of the paired electro-oxidation of toluene at various current densities with a surface area ratio of cathode to anode of 6.33. The anodic current efficiency for benzaldehyde production decreased from 84 to 64% as the anodic current density increased from 17.6 to 70.2 mA cm^{-2}. The current efficiency for benzaldehyde production in the cathodic chamber decreased from 51 to 4.5% as the cathodic current density increased from 2.78 to 11.1 mA cm^{-2}. The total current efficiency for benzaldehyde production in run 1 was 135%.

Table 2 shows the results of the paired electro-oxidation of toluene at various current densities with a surface area ratio of cathode to anode of 12.2. The anodic current efficiency for

Table 2. Production of benzaldehyde by paired electro-oxidation at a cathode to anode surface area ratio of 12.2

	Run 1	*Run 2*	*Run 3*	*Run 4*
Current density at cathode (mA cm^{-2})	1.0	2.78	3.56	5.56
Current density at anode (mA cm^{-2})	12.2	33.9	43.4	67.8
Concentration of V_2O_5 in the electrolyte (M × 10^{-3})	1	1	5	5
Products				
Anodic reaction				
Current efficiency of Mn^{3+} in anolyte (%)	87.2	84.1	76.8	69.5
Yield of benzaldehyde based on Mn^{3+} (%)	96	97	95	95
Current efficiency of benzaldehyde (%)	84	82	73	66
Cathodic reaction:				
Current yield of benzaldehyde (%)[a]	87	51	10	3.3
Total current yield of benzaldehyde (%)	171	133	83	69.3

Temperature, 50° C; charge passed, 150 C; concentration of H_2SO_4, anolyte 6 M, catholyte 0.15 M; vol % of toluene in the catholyte, 25%; concentration of Mn^{2+} in the anolyte, 0.1 M.

[a] Based on one ˙OH free radical oxidizing one toluene molecule to one benzaldehyde molecule.

benzaldehyde production decreased from 84 to 66% as the anodic current density increased from 12.2 to 67.8 mA cm^{-2}. The current efficiency for benzaldehyde in the cathodic chamber decreased from 87 to 3.3% as the current density increased from 1.0 to 5.56 mA cm^{-2}. The current efficiencies in the cathodic chamber in runs 3 and 4 of Table 2 were relatively small compared with those of run 2 of Table 1 and runs 1 and 2 of Table 2. This indicated that increasing the concentration of V_2O_5 decreased the current efficiency. The total current efficiency for benzaldehyde production in run 1 of Table 2 was 171%. This was much more than the value obtained in electrochemical oxidation methods with only the anode or cathode as working electrode.

4. Discussion

4.1. *Current efficiency for benzaldehyde production in the cathodic chamber*

The total current efficiencies for benzaldehyde production in run 1 of Table 1 and runs 1 and 2 of Table 2 were much higher than 100%. At high current density or high concentration of V_2O_5, i.e. runs 3 and 4 in both Table 1 and Table 2, the current efficiency for benzaldehyde in the cathodic chamber was relatively small. Toluene was oxidized to benzaldehyde in the cathodic chamber by the $^{\cdot}$OH free radicals generated from the reactions of hydrogen peroxide and reduced metal ions, $R^{(n-1)+}$. The $^{\cdot}$OH free radicals may be consumed according to

$$^{\cdot}OH + R^{(n-1)+} \xrightarrow{k_7} R^{n+} + OH^- \qquad (7)$$

The above reaction has been demonstrated in studies on Fenton's reagent [10, 14, 15, 23, 24]. The rate constant for Reaction 7 (k_7 = 2.3–3 × $10^8\,M\,s^{-1}$) [10, 14, 23] is much larger than the rate constant for the generation of $^{\cdot}$OH free radicals, i.e. Reaction 5 (k_5 = 10–200 M s^{-1}) [15, 23]. The experimental results indicated that increasing the concentration of V_2O_5 in the catholyte decreased the current efficiency for benzaldehyde production.

Furthermore, the blue colour of V^{4+} ions in the catholyte was noted during electrolysis in runs 2 to 4 of Table 1. The blue colour became deep when the cathodic current density increased and the current efficiency for benzaldehyde in the catholyte decreased with increase of current density. The blue colour also appeared in the catholyte at high concentrations of V_2O_5 in runs 3 and 4 in Table 2. This further confirmed that the low current efficiency for benzaldehyde generation was due to the reaction of $^{\cdot}$OH free radicals with excess V^{4+} accumulated in the catholyte. The available $^{\cdot}$OH free radicals and V^{4+} were consumed according to Reaction 7.

4.2. *Reduction of oxygen to hydrogen peroxide*

The cathodic reduction of oxygen also affects the current efficiency for benzaldehyde generation. Several previous studies of the reduction of oxygen have been reported [25–32]. It has been pointed out that the reduction follows two pathways [25, 27, 28, 31]: a peroxide pathway, i.e. Reactions 8 and 9, and a direct four-electron pathway, i.e. Reaction 10.

$$O_2 + 2H^+ + 2e \xrightarrow{k_8} H_2O_2 \qquad (8)$$

$$H_2O_2 + H^+ + 2e \xrightarrow{k_9} H_2O + OH^- \qquad (9)$$

$$O_2 + 4H^+ + 4e \xrightarrow{k_{10}} 2H_2O \qquad (10)$$

The reduction of O_2 to hydrogen peroxide is strongly dependent on the electrocatalytic effects of the electrode materials and mass transfer conditions for oxygen [25, 28–34]. Yeager [25] concluded that the reduction of oxygen to hydrogen peroxide on a platinum electrode always follows the direct four-electron pathway to H_2O over the whole range of overpotential. Several investigators [25, 31, 32] have reported that the four-electron pathway is predominant and that the current efficiency for hydrogen peroxide is small in acid electrolytes. Therefore, the current efficiency for hydrogen peroxide decreased at high current density because of water formation, i.e. Reactions 9 and 10, whereas the generation rate of $R^{(n-1)+}$ ions increased with the cathodic current density. This also led to the accumulation of excess $R^{(n-1)+}$ metal ions in the catholyte and current loss resulted from the wastage of available $^{\cdot}$OH free radicals, i.e. Reaction 7.

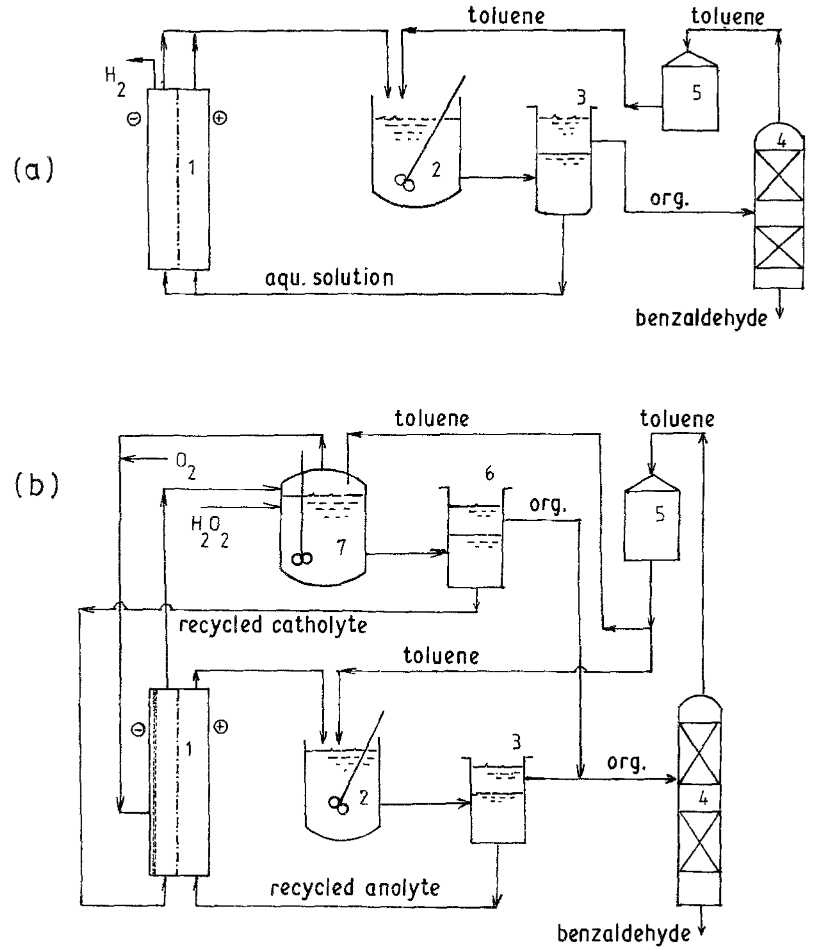

Fig. 1. Flow scheme for the electrochemical oxidation of toluene to benzaldehyde. (a) Conventional anodic oxidation process; (b) paired electro-oxidation process. 1, Electrolysis cell; 2, chemical reactor for the anodic reaction; 3, separation of anolyte and organics; 4, distillation tower; 5, toluene storage tank; 6, separation of catholyte and organics; 7, chemical reactor for the cathodic reactions.

4.3. *Paired electro-oxidation process*

In addition to the usual advantages of paired electrolysis, both the reactants and products of the anodic and cathodic branches are the same in this process and hence the separation and storage costs may be reduced. A divided electrolyser and a chemical reactor were used in this work. However, many variations of the process may be envisaged. The schematic flow diagram for the anodic reaction proposed by Ibl and co-workers [1] involved an electrolyser, a chemical reactor, a separation tank for separating the aqueous and organic phases and a distillation tower for the recovery of unreacted toluene. Because the degree of toluene conversion affects the selectivity very strongly, it is necessary to keep the benzaldehyde concentration below a critical value within the organic phase [5]. Wendt has suggested a similar flow scheme with two reactors in series [5]. The first reactor converts toluene partially to benzyl alcohol. The second reactor converts the dissolved benzyl alcohol to benzaldehyde and extracts the benzaldehyde into an inert organic phase not containing toluene. In this work, excess toluene was used as organic solvent as well as reactant to avoid the formation of benzoic acid.

The applied cathodic current density was relatively low. The cathodic current efficiency for benzaldehyde generation was small at high current density because the generation rate of $R^{(n-1)+}$ ions is faster than that of hydrogen peroxide, which results in the undesired Reaction 7 and consumes the available $^{\cdot}OH$ free radicals as mentioned above. In order to increase the current densities as well as the cathodic current efficiency for benzaldehyde, a separate chemical reactor may be used for the reaction of toluene with the $R^{(n-1)+}$ and hydrogen peroxide. Hydrogen peroxide may be fed continuously to the chemical reactor to make up the required amounts of hydrogen peroxide. Fig. 1b depicts a possible flow scheme for the paired electro-oxidation process and Fig. 1a shows the conventional anodic oxidation process. Instead of hydrogen evolution, oxidation of toluene to benzaldehyde occurs in the cathodic chamber. The mechanism for the reaction between $^{\cdot}OH$ free radicals and hydrocarbons in the presence of oxygen has been discussed in the literature [10, 35–40]. A mechanism involving a chain of reaction steps has been suggested by several authors [11, 35, 38]:

$$C_6H_5\text{–}CH_3 + {}^{\cdot}OH \xrightarrow{k_{11}} C_6H_5CH_2^{\cdot} + H_2O \tag{11}$$

$$C_6H_5CH_2^{\cdot} + O_2 \xrightarrow{k_{12}} C_6H_5CH_2OO^{\cdot} \tag{12}$$

$$C_6H_5CH_2OO^{\cdot} \xrightarrow{k_{13}} C_6H_5CHO + {}^{\cdot}OH \tag{13}$$

Thus, if the propagation of chain reactions in the cathodic compartment is established, a very high current efficiency for benzaldehyde production may be obtained. Although the current efficiency for oxygen reduction to hydrogen peroxide is, in general, small in acid solution, the oxidation of toluene to benzaldehyde by cathodically generated $^{\cdot}OH$ free radicals still has a very high current efficiency. Therefore, the cathodic branch of the paired electro-oxidation produces benzaldehyde effectively. The paired electro-oxidation process is attractive and may become a useful method for producing benzaldehyde.

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References

[1] K. Kramer, P. M. Robertson and N. Ibl., *J. Appl. Electrochem.* **10** (1980) 29.
[2] M. E. Kurz and T. R. Chen, *J. Org. Chem.* **43** (1978) 239.
[3] M. Okano and T. Aratani, *Bull. Chem. Soc. Jpn.* **49**(1976) 2811.
[4] J. H. Wagenknecht, *J. Appl. Electrochem.* **13** (1983) 535.
[5] H. Wendt and H. Schneider, *ibid.* **16** (1986) 134.
[6] Japanese Patent 48-28442, US Patent 4212710 and 4582942.
[7] Ch. Comninellis and E. Plattner, *J. Electrochem. Soc.* **129** (1982) 749.
[8] Ch. Comninellis, E. Plattner and Ph. Javet, *J. Appl. Electrochem.* **9** (1979) 595.
[9] Ch. Comninellis and E. Plattner, *ibid.* **13** (1983) 117.
[10] T. Matsue, M. Fujihira and T. Osa, *J. Electrochem. Soc.* **128** (1981) 2565.
[11] R. Tomat and A. Rigo, *J. Appl. Electrochem.* **6** (1976) 257.
[12] *Idem, ibid.* **14** (1984) 1.
[13] I. M. Kothoff and A. I. Medalia, *J. Amer. Chem. Soc.* **71** (1949) 3777.
[14] G. G. Jayson, B. J. Parsons and A. J. Swallow, *J. Chem. Soc. Faraday Trans. I* **68** (1972) 2053.
[15] I. M. Kolthoff and R. Woods, *J. Electroanal. Chem.* **12** (1966) 385.
[16] M. M. Baizer and R. C. Hallcher, *J. Electrochem. Soc.* **123** (1976) 809.
[17] K. Park, P. N. Pintauro, M. M. Baizer and K. Nobe, *ibid.* **132** (1985) 1850.
[18] M. M. Baizer, T. Nonaka, K. Park, Y. Saito and K. Nobe, *J. Appl. Electrochem.* **14** (1984) 197.
[19] H. J. Wille, D. Knittel, B. Kastening and J. Mergel, *ibid.* **10** (1980) 489.
[20] P. N. Pintauro, D. K. Johnson, K. Park, M. M. Baizer and K. Nobe, *ibid.* **14** (1984) 209.
[21] D. K. Johnson and R. E. W. Jansson, *J. Electrochem. Soc.* **128** (1981) 1885.
[22] M. M. Baizer, Proc. Electrochem. Soc. 1983, 83-6 (*Proc. Symp. Electrochem. Process Plant Des.* 1982) pp. 31–41.
[23] J. F. Skinner, A. Glasel, L. C. Hsu and B. L. Funt, *J. Electrochem. Soc.* **127** (1980) 315.
[24] W. G. Bars, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.* **47** (1951) 462.
[25] E. Yeager, *Electrochim. Acta* **29** (1984) 1527.
[26] J. P. Collman, M. Marrocco and P. Denisevich, *J. Electroanal. Chem.* **101** (1979) 117.
[27] R. C. M. Jakobs, L. J. Janssen and E. Barendrecht, *Electrochim. Acta* **30** (1985) 1433.
[28] I. Morcos and E. Yeager, *ibid.* **15** (1970) 953.
[29] G. Kokkinidis and D. Sazou, *J. Electroanal. Chem.* **199** (1986) 165.
[30] C. Oloman and A. P. Watkinson, *J. Appl. Electrochem.* **9** (1979) 117.
[31] P. Fischer and J. Heitbaum, *J. Electroanal. Chem.* **112** (1980) 231.
[32] J. C. Huang, R. K. Sen and E. Yeager, *J. Electrochem. Soc.* **126** (1979) 786.
[33] T. C. Chou, J. J. Jow and S. T. Yu, *Chem. Eng. Commun.* **42** (1986) 191.
[34] T. C. Chou and J. C. Chang, *Chem. Eng. Sci.* **35** (1980) 1581.

[35] R. Tomat and A. Rigo, *J. Appl. Electrochem.* **9** (1979) 301.
[36] J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.* (1963) 2897.
[37] G. A. Russell, *J. Amer. Chem. Soc.* **79** (1957) 3871.
[38] T. C. Chou and C. C. Lee, *I & EC Fundamentals* **24** (1985) 32.
[39] H. C. Christensen, K. Sehested and E. J. Hart, *J. Phys. Chem.* **177** (1973) 983.
[40] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.* (1964) 4857.