The electrochemistry of coal and coal liquids. II. Cyclic voltammetry of H-coal liquids

LEONEL M. SANTOS, RICHARD P. BALDWIN

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA

The electrochemical behaviour of three H-coal liquids, ASO, ASB and VSO, has been characterized by cyclic voltammetry at glassy carbon electrodes. Voltammograms obtained for the three intact coal liquids in methanol/water solution showed a broad, irreversible anodic wave at $+0.5$ V versus saturated calomel electrode. In order to determine which components of the coal liquids were primarily responsible for the observed electrochemistry, two column chromatography procedures were employed to separate the ASO, ASB and VSO into several fractions on the basis of functional group content. Subsequent cyclic voltammograms recorded for the resulting chromatographic fractions exhibited substantial anodic current only for the fractions designated as containing predominantly aromatic, polar aromatic/N-heterocyclic, and monophenolic components. Of these, the phenolic fractions appeared to account largely for the $+0.5$ V wave observed for the intact coal liquids. Chromatographic fractions corresponding to other functional groups exhibited only slight electrochemical activity, or none at all, under the conditions employed.

1. Introduction

Electrochemical methodology has recently begun to draw increasing attention as a new and potentially useful approach to coal treatment and conversion. In this regard, Coughlin and Farooque [1–3] initially demonstrated that aqueous coal slurries could be oxidized electrolytically in a process which, coupled with hydrogen ion reduction, resulted in both coal gasification and hydrogen production. Subsequently, several investigations [4–9] have been conducted in other laboratories for the purpose of elucidating the mechanism of the coal oxidation and directing the process toward more practical applications. As a result, it has been clearly shown that the mechanism involved in this process does not entail the direct electrooxidation of the coal itself but rather depends on electrocatalytic oxidation via Fe^{2+}/Fe^{3+} extracted into solution from the solid coal sample. Beyond this, however, few facts have been substantiated concerning the mechanism of the coal oxidation, or even the nature of the oxidized groups, other than the observation that the process probably involves the gradual formation of surface oxides on the slurry particles [7–8].

In this work, we report the electrochemical behaviour of some coal-derived liquids at anodic potentials. Coal liquids were chosen for initial study because, unlike coal itself, they are available in relatively 'clean' form without significant amounts of inorganic ash material, and they can be readily dissolved in a variety of electrochemically compatible solvents. Previously, coal liquids have only rarely been the object of electrochemical study [10–12] and, in the few cases thus far reported, only reduction behaviour has been reasonably well characterized. Most notably, Given and Schola [10] employed dropping mercury electrode polarography to quantitate the quinone, carbonyl and polyaromatic content of coal extracts while, more recently, differential pulse voltammetric analysis of several polyaromatic compounds in anthracene oil and asphaltenes has also been described [11]. Coal liquids contain numerous components which might be expected to undergo electrochemical oxidation. These include hydroquinones, phenols, aromatic

amines, organosulphur compounds and poly-aromatic and heterocyclic species. The coal materials selected for study here were several liquids produced by the H-coal liquefaction process, and the primary electrochemical technique employed was cyclic voltammetry (CV). Since our primary goal was to identify the major electro-oxidizable components of the coal liquids, column chromatography separation on the basis of functional group and CV characterization of the resulting fractions was also used. For the H-coal liquids examined, most of the electrochemical activity was found to reside in the phenolic, N-heterocyclic, and polyaromatic fractions.

2. Experimental details

2.1. Materials

The coal-derived liquids used in this work were supplied by the Kentucky Institute for Mining and Minerals Research, Lexington, Kentucky. The samples were fractions from the H-coal liquefaction process using a $ZnCl_2$ catalyst in the 'syncrude mode,' a reaction temperature of $454°$ C, and an exit reactor partial pressure of $\simeq 15$ MPa. The fractions used in this study were the atmospheric still overhead (ASO), the atmospheric still bottom (ASB) and the vacuum still overhead (VSO). The approximate boiling ranges used for designating process outputs were: ASO, C_4–$200°$ C; ASB, 200–$350°$ C; and VSO, 350–$520°$ C. The aromaticity values, defined as the ratio of aromatic carbon to total carbon and determined by quantitative ^{13}C NMR, were: ASO, 0.27; ASB, 0.44; and VSO, 0.52. These ^{13}C NMR data, together with elemental analyses and vapour phase osmometry molecular weight determinations, allowed the prediction of an average molecular formula for each of the liquids as: ASO, $C_{21.0}H_{35.5}O_{0.6}$; ASB, $C_{24.1}H_{33.4}O_{0.6}$; and VSO, $C_{27.4}H_{33.5}O_{0.6}$ [13].

Any insoluble particulate material was removed by filtration prior to analysis. All chemicals were obtained as chromatographic or reagent grade and were used as received without any further purification.

2.2. Apparatus

Voltammetric experiments were performed using a Model 364 polarographic analyser (Princeton Applied Research, Princeton, New Jersey) or a Model CV-1B cyclic voltammetry controller (Bioanalytical Systems, West Lafayette, Indiana). A three-electrode cell configuration was employed with a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). In the voltammetric experiments, all potentials were reported with respect to the SCE. The H-coal liquids and their oxidation products were found to adsorb strongly onto glassy carbon and consequently caused the electrode response to decrease gradually unless some cleaning procedures were regularly followed. In this work, reproducible currents were obtained by routinely polishing the working electrode surface with alumina and then rinsing it in an ultrasonic bath first with acetone and then with water. All samples were run in methanol/water solution with 0.1 M sodium acetate and adjusted to pH 5.0 with acetic acid. This solvent system was selected for study because of its suitability for use in the mobile phase/electrolyte in anticipated reverse-phase liquid chromatography applications employing amperometric detection.

Infrared spectra were recorded on a Nicolet Model 7199C Fourier-transform spectrometer using a 0.2 mm NaCl liquid cell. Before spectra were recorded for the fractions collected from silica and alumina column chromatography, eluting solvents were removed by rotary evaporation, and further drying was achieved by vacuum-pumping the residue overnight at $30°$ C. Spectra were obtained after redissolving the dried residue in chloroform. The spectra shown all represent the average of 32 scans. All were background-corrected for the chloroform solvent.

2.3. Column chromatography

Two different column chromatography procedures were applied in order to separate the H-coal liquids into fractions of components containing roughly the same types of functional groups. The first approach consisted of the

*Table 1. Solvent sequence employed for SESC fractionation**

Fraction	Eluent	Major components
1S	Hexane	Saturates
2S	15% benzene in hexane	Aromatics
3S	Chloroform	Polar aromatics; nonbasic N,O,S-heterocyclics
4S	Chloroform/4% diethyl ether	Monophenols
5S	Diethyl ether/3% ethanol	Basic nitrogen heterocyclics
6S	Methanol	Highly functional molecules (> 10 wt % heteroatoms)
7S	Chloroform/3% ethanol	Polyphenols
8S	Tetrahydrofuran/3% ethanol	Increasing O content and N basicity
9S	Pyridine/3% ethanol	Increasing O content and N basicity
10S	Non-eluted	Unidentified

* This solvent sequence is identical to that used by Farcasiu [14]. For further information concerning the rationale for this sequence or concerning the functional content of the eluting fractions, consult this reference.

sequential elution of fractions from a silica gel column by a succession of increasingly polar solvents. The solvent sequence employed was the same as that developed initially by Farcasiu [14] and is summarized in Table 1. The column contained 50 g of silica gel, and the H-coal sample size was 2 ml. Aliquots (200 ml) of each of the nine solvents were used for each elution; samples were collected and stored in 30 ml portions. The assignment of the collected eluent into Farcasiu's nine functional-group fractions was made primarily on the basis of eluent volume, with 200 ml allotted for each fraction. However, physical observation of the eluting bands indicated that the fractions sometimes eluted slightly earlier or later than the simple volume-based assignments predicted. Thus, final assignment of fractions was made taking both elution volume and visual appearance of the eluent into consideration. The second column chromatography procedure was adapted from the alumina fractionation sequence developed by Schiller and Mathiason [15]. In this approach, a coal liquid sample of approximately 0.1 ml was dissolved in chloroform and adsorbed onto 2–3 g of neutral alumina (activity I). After removal of the chloroform, the alumina/sample mixture was placed at the top of a column containing an additional 6 g of alumina. Five different fractions were eluted using the solvent sequence shown in Table 2. Assignment of the collected eluent into the five fractions identified by Schiller and Mathiason [15] was made directly on the basis of eluent volume.

3. Results

3.1. Cyclic voltammetry

CV results obtained for ASO, ASB and VSO in aqueous/alcoholic solution are shown in Fig. 1. With the exception of a small amount of particulate matter which had to be removed from the VSO by filtration, all three H-coal liquids were completely soluble in the aqueous/methanol solvents employed or could be dissolved initially in a small volume of acetonitrile and then diluted with methanol. The voltammograms all exhibited the same principal feature, i.e. a broad, irreversible anodic wave extending from approximately $+0.3$ V to $+0.8$ V versus SCE. The current level observed for the ASO was two or three times that observed for the other coal liquids but, in each case, the peak potential of

*Table 2. Solvent sequence employed for alumina fractionation**

Fraction	Eluent	Major components
1A	Hexane	Saturates
2A	Toluene	Aromatics
3A	Chloroform	Ethers
4A	Chloroform	Nitrogen compounds
5A	90% tetrahydrofuran/ 10% ethanol	Hydroxyl compounds

* This solvent sequence is identical to that used by Schiller and Mathiason [15]. For further information concerning the rationale for this sequence or concerning the functional group content of the eluting fractions, consult this reference.
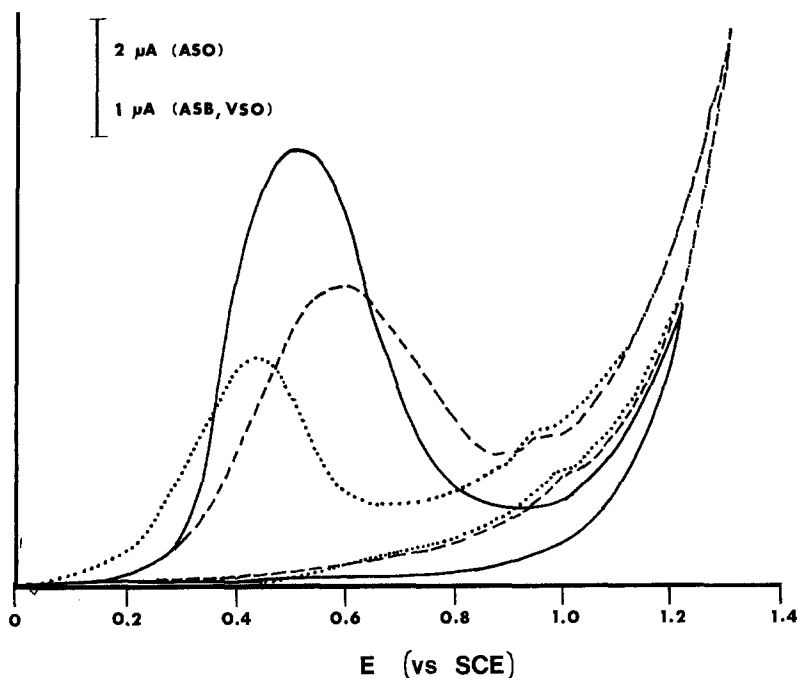
Fig. 1. Cyclic voltammograms of H-coal liquids: ASO (——); ASB (– – –); VSO (·······). Concentration, 0.16% (by volume) of each coal liquid in 4:1 methanol/water. Electrolyte, 0.1 M sodium acetate/acetic acid. Voltage scan rate, $5\,mV\,s^{-1}$.

this wave occurred at roughly $+0.4$ to $+0.6\,V$ versus SCE. In the cases of ASB and VSO a second, much smaller oxidation wave was also observed at higher potentials. The large anodic wave which occurred at $+1.3\,V$ versus SCE was due to the oxidation of the aqueous solvent and prevented the acquisition of electrochemical information at higher potentials. In general, the current levels observed for these waves were directly dependent on the coal liquid concentration. Unlike most of the previous work, these CV results were obtained at a glassy carbon working electrode rather than at platinum, although little difference was observed in the cases where the latter electrode material was employed.

All of these oxidations were observed only on the initial anodic scan. Subsequent scans in either the anodic or the cathodic direction exhibited no significant redox waves. Apparently, the initial oxidation was accompanied by fouling of the electrode surface, and cleaning of the glassy carbon surface was required to restore the initially observed electrochemical behaviour. Decreasing the concentration of the H-coal liquid in the electrolysis mixture reduced the rate of electrode fouling and resulted in the observation of plateau-shaped rather than peak-shaped

currents. The occurrence of similar electrode deactivation processes at moderate positive potentials has also been reported in one previous study involving the oxidation of coal liquids at glassy carbon electrodes [12].

3.2. Electrochemistry of column chromatography fractions

In order to identify the specific components of the H-coal liquids primarily responsible for the observed electrochemistry, the liquids were partially fractionated by column chromatography, and the voltammetric behaviour exhibited by the collected fractions was then monitored. The first method of separation employed was based on the selective elution by specific solvents chromatography (SESC) method which was developed by Farcasiu [14] for use with solvent-refined coals, but which should be applicable in principle to other coal liquids as well. In this approach, a sequence of nine different solvents applied to a silica gel column is used to fractionate the coal liquid on the basis of functional groups. The solvent sequence used and the major components of the corresponding eluted fractions are given in Table 1. The procedural details required to adapt the approach outlined
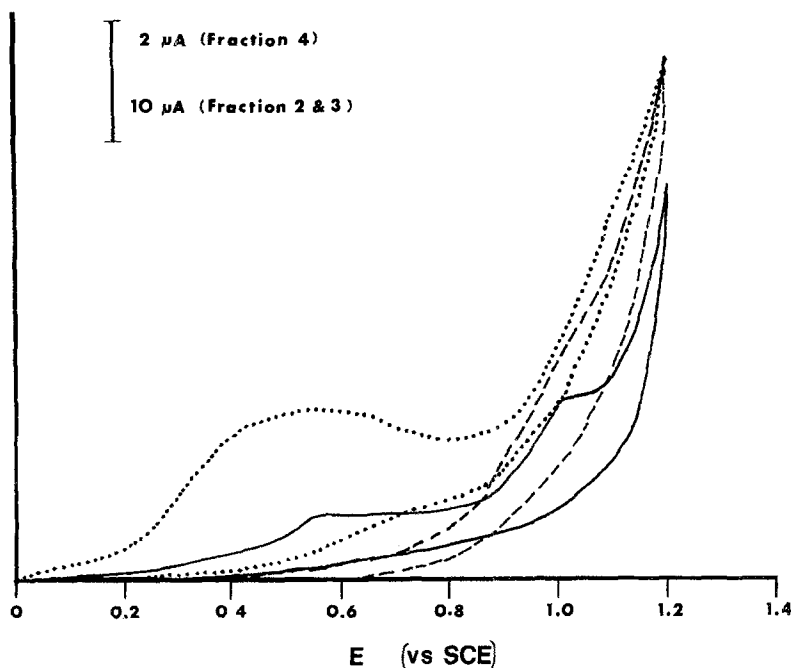
2 µA (Fraction 4)

10 µA (Fraction 2 & 3)

E   (vs SCE)

0   0.2   0 4   0.6   0.8   1.0   1.2   1.4

Fig. 2. Cyclic voltammograms of SESC fractions from VSO: fraction 2 (– – –); fraction 3 (———); fraction 4 (·······). Concentration, 4 ml of SESC fraction dissolved in 46 ml of 4:1 methanol/water. Electrolyte, 0.1 M sodium acetate/acetic acid. Scan rate, $10\,mV\,s^{-1}$.

by Farcasiu are described in the Experimental Section.

Cyclic voltammograms were obtained for the aqueous/methanol solutions of each of the roughly fifty 30 ml fractions that were collected during the SESC of each of the H-coal liquids. Although several of these fractions exhibited some anodic activity when examined by CV, by far the largest currents were observed for the samples which corresponded to the second 'aromatic-2S', third 'polar aromatic/nonbasic heterocyclic-3S' and fourth 'mono-phenolic-4S' SESC fractions. The voltammograms for these fractions are shown for VSO in Fig. 2; note the higher current scale required for the aromatic fractions. Except for the fact that the aromatic fraction for ASO showed no substantial electrochemical activity, the CV results obtained for fractions derived from ASO and ASB were qualitatively similar to those obtained for the VSO. The voltammograms for both the 'aromatic' and 'polar aromatic/nonbasic heterocyclic' fractions always exhibited plateau-shaped anodic waves which, though apparently irreversible in nature, did appear reproducibly not only on the first scan but on subsequent scans in the positive potential direction as well. However, the current observed on repeated scans for

the 'phenolic' fraction was greatly diminished compared to that for the first scan, suggesting electrode fouling by products of this oxidation process. In addition, some of the other chromatographic fractions also exhibited lesser amounts of current. The electrochemical activity of these fractions may be of some potential utility; however, no further studies of these fractions were performed in this work.

In view of the only approximate functional group resolution achieved by the SESC approach, a second independent fractionation procedure involving an alumina-based separation into five individual sub-classes was also examined. The solvents employed and the elution sequence achieved are summarized in Table 2. Of particular note is the reported capability of this approach to resolve separately the phenolic components (fraction 5A) from the nitrogen-containing species (fraction 4A). This represents a significant difference from the SESC approach wherein the monophenolic fraction has been reported to include significant pyrrolic content as well [14]. CV results obtained for the five alumina fractions showed anodic currents primarily in the aromatic, nitrogen-containing and hydroxyl fractions. Because of the lesser quantities of H-coal liquids employed in this chromatographic pro-

cedure, the resulting current levels were smaller in magnitude, but qualitatively, the CV results obtained for alumina fractions 2A, 4A and 5A closely resembled in shape and potential dependence the CV results previously described for SESC fractions 2S, 3S and 4S, respectively. Interestingly, only alumina fraction 5A showed severe electrode fouling such that second and subsequent CV scans showed no significant current unless the electrode surface was cleaned thoroughly between scans.

4. Discussion

Previous investigations of H-coal liquids have demonstrated that these liquids are relatively 'clean' materials consisting predominantly of mixed aliphatic and aromatic hydrocarbons. Small quantities of oxygen, present as phenols, ethers and furans, and nitrogen, present as amines, have also been reported [16]. On the basis of primarily ^{13}C NMR data, Joseph and Wong [13] suggested the following model compounds as average working structures for each of the H-coal liquids:
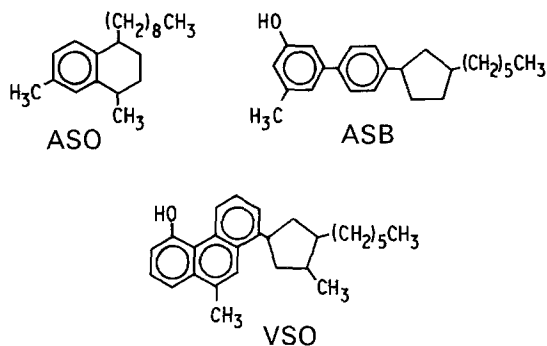
As can be readily inferred from these structures, the major differences between these fractions are the increasing molecular size and aromatic content from ASO to ASB to VSO. Substantial variations exist only in their aromatic character, with the ASB and VSO possessing increasing aromatic and polyaromatic content. Accordingly, it is not surprising that the three H-coal liquids display similar electrochemical properties.

The cyclic voltammograms obtained for the

intact H-coal liquids showed two roughly separate regions of electrochemical activity at the positive potentials used here: the first between $+0.3$ V and $+0.8$ V versus SCE and the second, which was observed only for ASB and VSO, at somewhat higher potentials shortly before the solvent oxidation was reached. Based on previous electrochemical studies not related directly to coal materials [17], numerous organic functional groups could be singled out which might be expected to undergo oxidation within these potential ranges. These include, at the lower potentials, hydroquinones, phenols, aromatic amines and organosulphur compounds while, at more positive potentials, aromatic hydrocarbons and heterocyclic compounds can also be considered. Of these possibilities, both phenolics and aromatics have to be given particular attention, considering both the likely functional composition of the H-coal liquids and the potential ranges ordinarily found for the oxidation of these functional groups. Phenols usually undergo oxidation throughout the range from $+0.4$ V to $+1.0$ V versus SCE and aromatic hydrocarbons require potentials greater than $+1.0$ V versus SCE [17]. In addition, the fact that, for both the SESC and alumina chromatographic procedures, the phenolic and aromatic/polyaromatic components exhibited substantial electrochemical activity provides strong supporting evidence that these functionalities, present in the native H-coal liquids, accounted largely for their anodic electrochemistry as well. This is not to discount completely the possible contributions of other groups to the observed current–voltage properties. For example, heterocyclic aromatics, which represent the principal content of the third SESC fraction (see Fig. 2), also represent likely electroactive constituents. These compounds, however, constitute a much more diverse group whose electrochemistry is somewhat more varied and consequently more difficult to categorize. The electro-oxidation of pyrroles [18], indoles [19] and carbazoles [20], for example, all require relatively high potentials ranging from $+1.0$ V to nearly $+2.0$ V versus SCE, depending on the nature of the substitution of the specific compound and the solution conditions in effe̊t. In addition, furans,
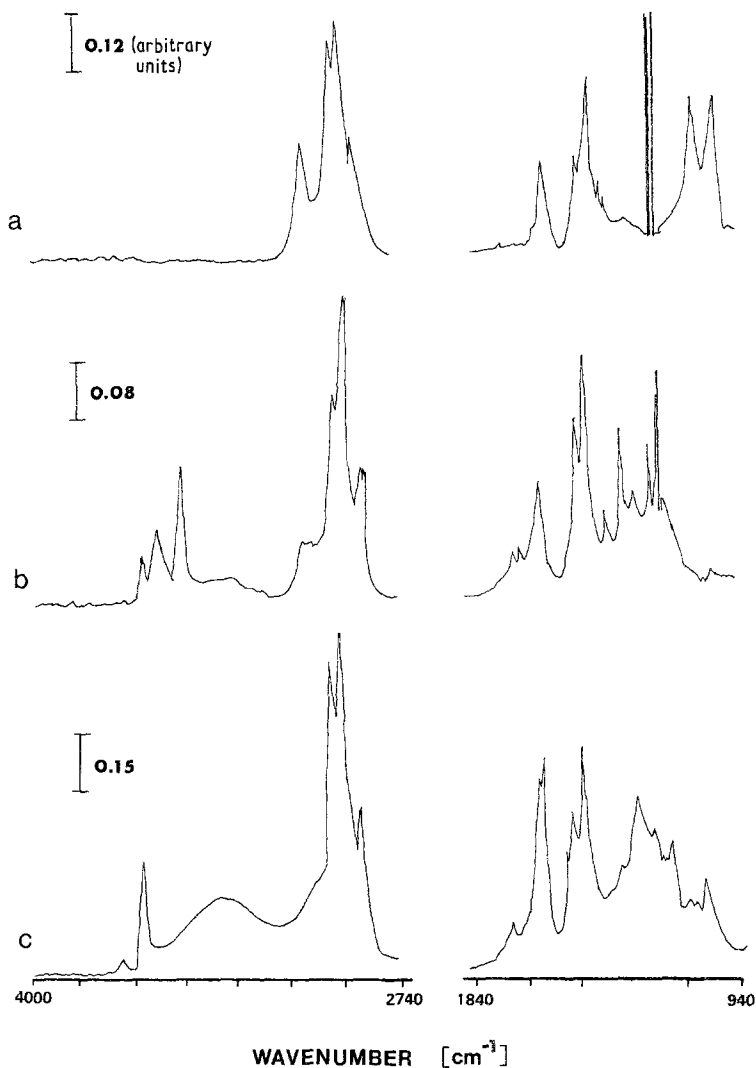
Fig. 3. FT–IR spectra of SESC fractions from VSO. (a) Fraction 2S; (b) fraction 3S; (c) fraction 4S.

thiophenes, etc. would each require separate consideration.

Of course, the functional group titles specified for each of the SESC and alumina fractions actually reflect only general and admittedly somewhat imperfect compositional assignments [14]. In fact, the named constituent is meant to represent only the predominant component eluted at a given stage in the separation procedure, but certainly not the only possible one. As a consequence, the mere occurrence of anodic current in the appropriate SESC and alumina fractions does not definitely prove the presence of polyaromatics, heterocyclics and phenols in the coal liquids. Accordingly, in order to confirm further the chemical nature of the

coal liquid components present and giving rise to the observed CV currents, FT–IR spectra were recorded for each of the principal electroactive SESC and alumina fractions. Such spectra obtained for the second, third and fourth SESC fractions derived from VSO are shown in Fig. 3. Detailed analyses of the IR spectra obtained for various coal liquids have been reported previously [21–23] and will not be recapitulated in detail here. However, in the light of the spectral assignments suggested previously, it is clear that spectra 2, 3 and 4 are consistent with the presence of aromatics, N-heterocyclics and phenols, respectively. In particular, the –OH stretch at 3330 and 3600 cm^{-1} and the aromatic C–C stretch at
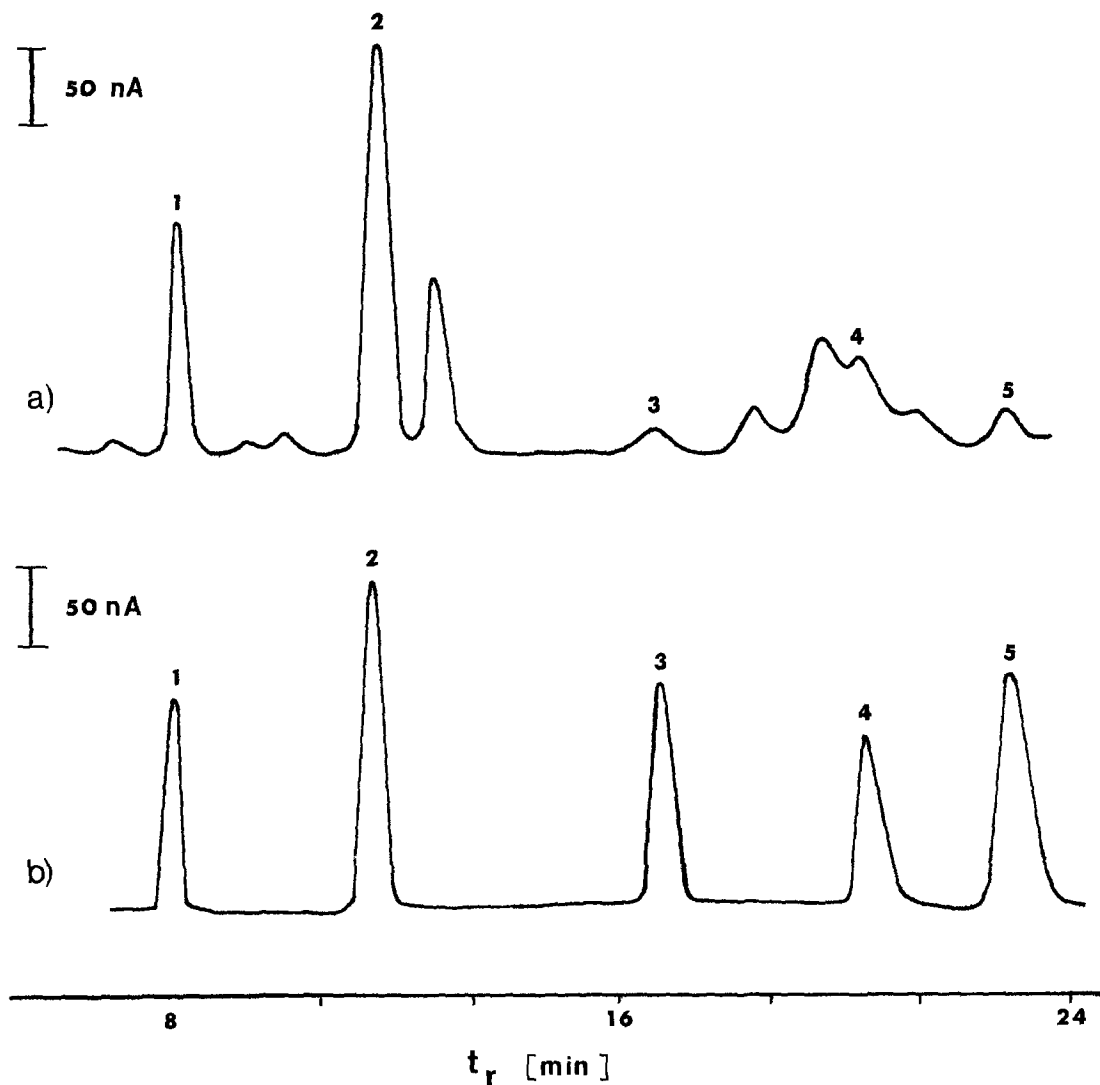
Fig. 4. Chromatograms of (a) 0.16% solution of ASO and (b) mixture of standard phenols (32 p.p.m) in 30% CH_3CN/70% pH 5 acetate buffer. The standards used were: (1) phenol; (2) *m*- and *p*-cresol; (b) 3,4-dimethylphenol; (4) 2,6-dimethylphenol; and (5) β-naphthol. The separations were performed on a 15 cm octadecylsilane column with 30% CH_3CN/70% pH 5 acetate buffer as mobile phase, a flow rate of 1 ml min^{-1} and an injection volume of 20 μl.

$1600 \, cm^{-1}$, characteristic of phenols, are in evidence in the fraction 4S spectrum; –NH stretches at $3470 \, cm^{-1}$ and $3550 \, cm^{-1}$, typical of pyrrolic systems, appear in the fraction 3S spectrum, as well as the $1600 \, cm^{-1}$ aromatic stretch. Fraction 2S, on the other hand, exhibited no significant absorptions above $3100 \, cm^{-1}$. Rather, its major absorptions included aliphatic/aromatic CH stretches between 2800 and $3100 \, cm^{-1}$ and the aromatic C–C stretch near $1600 \, cm^{-1}$. Spectra recorded for other SESC fractions displayed useful but invariably less-intense absorptions. Considering the relatively low heteroatom content of the H-coal liquids, the failure to find these 'highly functionalized' fractions present in the same proportions as the other fractions is not surprising. Infra-red spectra of the H-coal fractions resulting from application of the alumina column chromatography procedure likewise indicated the presence of aromatic, N-heterocyclic and phenolic components in the correspondingly designated alumina fractions.

Two additional features of the voltam-

mograms obtained for the SESC and alumina fractions are interesting to note. First, the aromatic fraction isolated from ASO failed to exhibit the large oxidation currents observed for its counterparts derived from ASB and VSO (see Fig. 2.) We do not believe that this should be interpreted to mean that ASO contains little or no aromatic character. Rather, as has previously been suggested [13], the aromatic species in ASO generally consist of single-ring systems whose oxidation requires more positive potentials than do polycyclic systems. For example, in acetonitrile solution, benzene and toluene are oxidized at $+2.08$ V and $+1.93$ V versus $Ag/0.1$ M Ag^+, respectively, while naphthalene can be electrolysed at $+1.31$ V and anthracene at $+0.84$ V under the same conditions [24]. Second, the electrode passivation which was observed following the initial CV scan for the intact H-coal liquids also occurred for each of their phenol-containing fractions. Phenol oxidations, which are notorious among electrochemists for the polymerization of the oxidation products and the formation of deactivating films on the electrode surface [25], could clearly account for the electrode passivation observed here and in another previous study [12].

5. Conclusion

The application of electrochemical methodology to the study of coal-derived materials is an area of investigation which is in a stage of relative infancy. In this survey we have attempted to introduce systematically the use of voltammetric techniques for the study of coal liquid oxidation and to identify some of the primary components of the coal liquid matrix giving rise to the observed anodic activity. In general, it appears that the observed current–voltage properties of coal materials can be directly related to the functional composition of the coal sample. For the H-coal liquids specifically examined here, the most readily oxidized constituents have been shown to include the phenolic, aromatic and N-heterocyclic species.

Numerous potential applications of electrochemical methodology with coal materials are readily envisioned in the area of coal treatment and analysis. One such application is shown in Fig. 4 where anodic electrochemical detection is employed for detection of phenolic H-coal components following high performance liquid chromatography. Chromatograms employing amperometric detection at $+0.9$ V versus Ag/AgCl for both ASO (curve A) and a standard mixture of phenols (curve B) clearly illustrates the capability of electrochemical techniques for this purpose. Preliminary observations indicate that this detection approach will provide a useful quantitation method which offers significant improvements in sensitivity and selectivity over the usual UV absorption methods. Extension of this work to coal materials other than the H-coal liquids and the application of electrochemically based approaches for the treatment and functional group analysis of coal samples are continuing in this laboratory.

Acknowledgements

References

[1] R. W. Coughlin and M. Farooque, *Nature* **279** (1979) 301.
[2] M. Farooque and R. W. Coughlin, *Fuel* **58** (1979) 705.
[3] R. W. Coughlin and M. Farooque, *Ind. Eng. Chem. Process Des. Dev.* **19** (1980) 211.
[4] R. P. Baldwin, K. F. Jones, J. T. Joseph and J. L. Wong, *Fuel* **60** (1981) 739.
[5] G. Okada, V. Guruswamy and J. O'M. Bockris, *J. Electrochem. Soc.* **128** (1981) 2097.
[6] P. M. Dhooge, D. E. Stilwell and S.-M. Park, *ibid.* **129** (1982) 1719.
[7] P. M. Dhooge and S.-M. Park, *J. Electrochem. Soc.* **130** (1983) 1029.
[8] *Idem, ibid.* **130** (1983) 1539.
[9] S. Lalvani, M. Pata and R. W. Coughlin, *Fuel* **62** (1983) 427.
[10] P. H. Given and J. M. Schola, *J. Chem. Soc.* (1958) 2680.
[11] K. D. Bartle, C. Gibson, D. Mills, M. J. Mulligan, N. Taylor, T. G. Martin and C. E. Snape, *Anal. Chem.* **54** (1982) 1730.
[12] J. B. Pierce, *ACS Symp. Ser.* **169** (1981) 331.
[13] J. T. Joseph and J. L. Wong, *Fuel* **59** (1980) 777.
[14] M. Farcasiu, *ibid.* **56** (1977) 9.
[15] J. E. Schiller and D. R. Mathiason, *Anal. Chem.* **49** (1977) 1225.

[16]   A. W. Fort,   C. T. Magura   and   T. T. Coburn,
       Abstract ‡78, 179th National Meeting of the
       American Chemical Society. American Chemical
       Society, Washington, D.C. (1980).
[17]   M. R. Rifi   and   F. H. Covitz, 'Introduction   to
       Organic Electrochemistry', Marcel Dekker, Inc.,
       New York (1974) p. 395.
[18]   A. Stanienda, Z. Naturforsch. 22b (1967) 1107.
[19]   C. J. Nielsen,   R. Stotz,   G. T. Cheek   and   R. F.
       Nelson, J. Electroanal. Chem. 90 (1978) 127.
[20]   J. F. Ambrose and R. F. Nelson, J. Electrochem.
       Soc. 115 (1968) 1159.

[21]   P. C. Painter and M. M. Coleman, Fuel 58 (1979)
       301.
[22]   R. S. Brown, D. W. Hausler, L. T. Taylor and R. C.
       Carter, Anal. Chem. 53 (1981) 197.
[23]   R. S. Brown and L. T. Taylor, ibid. 55 (1983) 723.
[24]   L. Eberson, in 'Organic Electrochemistry', (edited by
       M. Baizer), Marcel Dekker, Inc., New York
       (1973) p. 541.
[25]   R. N. Adams, 'Electrochemistry at Solid Electrodes',
       Marcel Dekker, Inc., New York (1969) p. 363.