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TEMPERATURE PROGRAMMED HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

APPLICATION TO THE ANALYSIS OF STRETFORD PROCESS SOLUTIONS AND ANTHRAQUINONE DISULFONIC ACID DYE LOTS

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SUMMARY

A high-performance liquid chromatographic method capable of assaying both commercial dye lots of anthraquinone disulfonic acid (ADA) salts and Stretford process solutions for total ADA content and for isomer distribution has been developed. The method relies on a thermal gradient to elute the various ADA structural isomers. Analytical precision is 2% R.S.D. for total ADA content.

INTRODUCTION

The Stretford process[1–6] has found wide application within the petroleum industry for direct desulfurization of hydrocarbon fuel gas streams, purification of tail gases, desulfurization of amine regenerator offgases, and desulfurization of low heat value gas streams from coking operations. The chemistry of the process revolves about the oxidation of hydrogen sulfide to sulfur using vanadium(V) as the oxidant. The reduced vanadium(IV) is then oxidized by air blowing in the presence of the sodium salts of anthraquinone disulfonic acid (ADA). Commercial dye lots are used as a source of ADA for the Stretford process and a reliable, accurate, and rapid analysis for the total ADA content of a given lot is needed to optimize process efficiency. Additionally, since the various isomers of ADA show different reactivity in the Stretford process[4], the most useful information is the percentage that each isomer contributes to the total ADA content of the dye lot. Finally, the method should also be applicable to analysis of Stretford process solutions after only minimal clean up, allowing rapid evaluation of isomer distribution and concentration of the more active ADA isomers in a Stretford process solution. A number of techniques (ref. 7 and references contained within) have been applied to the analysis of sulfonic acids. The most successful of these has been the use of inorganic salts (typically sodium sulfate) both with and without organic mobile phase modifiers[8–10]. Three of the six isomers of interest in this work have been successfully separated from each other using this approach. However, insufficient resolution was encountered when

this approach was extended to the analysis of samples containing all six possible isomers, as well as Stretford process solutions. This work presents an alternate separation technique, thermal gradient elution, to accomplish the resolution of the compounds of interest.

EXPERIMENTAL

Equipment

A Spectra-Physics SP-8000 liquid chromatograph was used for all studies. Detection was accomplished using a Shoeffel Model 770 variable-wavelength detector tuned to 254 nm. The detector output was fed to a Nelson Analytical chromatographic data system. The data system consisted of a Nelson Analytical Model 761 interface box, Nelson Analytical 364/366 (Revision 2.1) chromatographic software, a Hewlett-Packard 87XM computer, a Hewlett-Packard 82901M dual 5-1/4 in. disk drive, and a Hewlett-Packard 2671G thermal graphics printer. All separations were carried out using a Microsorb C_{18} column (3 μm, 100 $\times$ 4.6 mm, Rainin Instrument). All gradients were run using the constant rotation pump mode.

Full wavelength UV–VIS spectra of eluting peaks were obtained with a Hewlett-Packard Model 1040A photodiode array detector. Spectral analysis was done on a Hewlett-Packard 85 microcomputer using the Infometrix MCR2 software package, an upgraded version of the original operating program.

Static UV analysis was performed with a Perkin-Elmer Lambda 3 UV–VIS spectrophotometer.

Reagents

Water was obtained from a Millipore water purification system. All other solvents were obtained from Burdick and Jackson and used as received. Samples of 1,5-, 1,8-, 2,6-, and 2,7-ADA salts were obtained from commercial sources (Aldrich, Pfaltz and Bauer). Samples of the 1,6- and 1,7-ADA isomers were donated by Brandeis Intsel Company and purified by British Gas Corporation.

Commercial ADA powders were obtained from several suppliers (M Chemical Company, Brandeis Intsel Company), and actual Stretford process solutions were obtained from various working refineries and gas plants. All other reagents employed in the study were analytical grade or better.

Procedure

Samples of commercial ADA dye lots were prepared by dissolving the powder in 0.03 *M* sodium sulfate. Samples of Stretford process solutions were prepared by diluting the process solution with 0.03 *M* sodium sulfate at 1:10 or 1:20, depending on the concentration of the sample. Injections of 25 μl were made into the 0.03 *M* sodium sulfate mobile phase at a flow-rate of 1.0 ml/min. The column compartment was initially cooled to 15°C with dry ice and a dynamic thermal equilibrium established between dry ice cooling and electrical heating. The sample was then injected. After three to five minutes (depending on sample complexity), the oven temperature set point was changed to 80°C, the dry ice removed from the oven compartment, and the gradient established as the column compartment warmed to the set point. After the last peak of interest eluted, the column was flushed with water for 3 min, then

methanol for 4 min, water for 3 min, and finally reequilibrated with the 0.03 *M* sodium sulfate mobile phase. Using dry ice to cool, the column compartment was again equilibrated at 15°C prior to the next injection.

RESULTS AND DISCUSSION

Thermal gradient elution

Several workers[11–14] have addressed the theoretical and practical aspects of temperature programming as a potential solution of the general elution problem in liquid chromatography. However, the technique has only occasionally been employed[15–19] as a substitute for the more common mobile phase gradient approach to altering component retention. Wider application of thermal gradient elution has not occurred for several reasons, including lengthy reequilibration times for normal phase separations, poor separation efficiencies generated by axial temperature gradients within the column, and the obvious success of solvent programming at solving the general elution problem. While excessive solvent viscosity at lower temperatures can impose some potential practical limitations (particularly with 3-μm packed columns), the use of elevated temperatures even beyond the normal boiling point of the mobile phase has shown[18,19] the capability for generating highly efficient separations.

Temperature programming was used to carry out the separation of the various ADA isomers under study because of several features unique to this separation. Low column temperatures could successfully resolve the 1,5-ADA isomer from contaminating impurities, but analysis times for the remaining isomers were unreasonably long because of the very different capacity factors of the isomers. This situation required some form of gradient elution to produce a complete analysis in a timely manner. Addition of organic mobile-phase modifiers in gradients that were steep enough to match the elution performance of the thermal gradient resulted in loss of

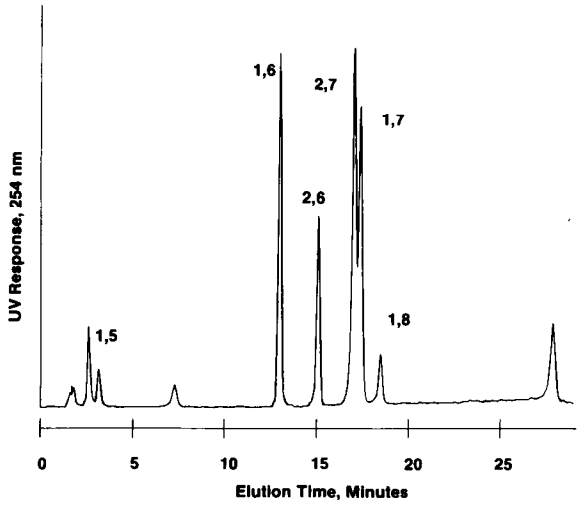

Fig. 1. Separation of ADA isomers using a methanol–water gradient at 15°C. Conditions: sample, 25 μl of ADA solution (0.0197 g powder dissolved in 114.23 g of 0.03 *M* sodium sulfate; mobile phase, A = 0.03 *M* sodium sulfate, B = methanol; gradient, 0% B for 2 min, then 0% to 40% B in 16 min (linear); column, Microsorb C_{18}, 10 × 0.46 cm I.D.; flow-rate, 1.0 ml/min; UV detector, 254 nm; range 0.16 A.U.

resolution between the 2,7- and 1,7-ADA isomers, as demonstrated in Fig. 1. Resolution of the 2,7- and 1,7-ADA isomers was lost upon substitution of a methanol gradient with elution strength equivalent to the thermal gradient. Combinations of salt content (0.02–0.2 *M* sodium sulfate), methanol content (up to 40%, v/v), and gradient shape (linear and exponentials) were studied, but none could achieve the resolution and speed of the thermal gradient. Lack of resolution between the 2,7-ADA isomer and the 1,7-ADA isomer was the problem in most cases, with the 1,7-ADA retention behavior showing the most sensitivity toward separation conditions. The higher methanol concentrations also produced significant backpressures at low temperatures (15°C), limiting the choice of flow-rates. The presence of even small amounts of methanol (2%, v/v) in the mobile phase eliminated resolution of the 1,5-ADA isomer from UV-active impurities achievable with aqueous sodium sulfate, as did separations performed at initial temperatures above 25°C. Organic modifiers from several other solvent selectivity groups[20] (acetonitrile, Group VIb; tetrahydrofuran, Group III; ethanol, Group II) were studied as methanol replacements in an attempt to improve separation selectivity for the 2,7- and 1,7-ADA isomers. None were successful in achieving a separation equivalent to that generated by the thermal gradient on the same time scale. Last, the addition of significant amounts of organic modifier was not compatible with the aqueous salt solution used for the bulk of the mobile phase, as well as the high salt content of untreated Stretford process solutions.

Thermal gradient generation

As described in the Experimental section, the initial oven temperature was established by a dynamic thermal balance between dry ice and electrical heating. Fig. 2 shows a plot of observed oven temperature against run time for several analyses. The actual column temperature almost certainly lagged well behind the observed

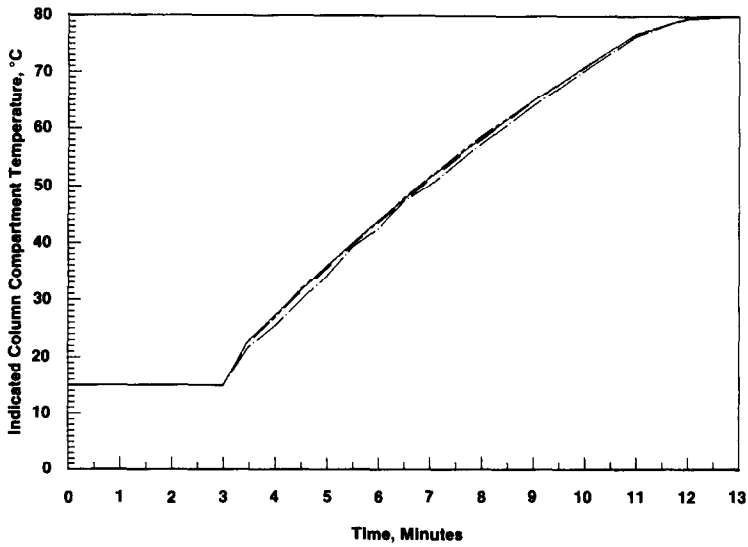

Fig. 2. Indicated heating curve for SP-8000 column oven. Run 1 (———); Run 2 (— —); Run 3 (— · — ·); Run 4 (– – –).

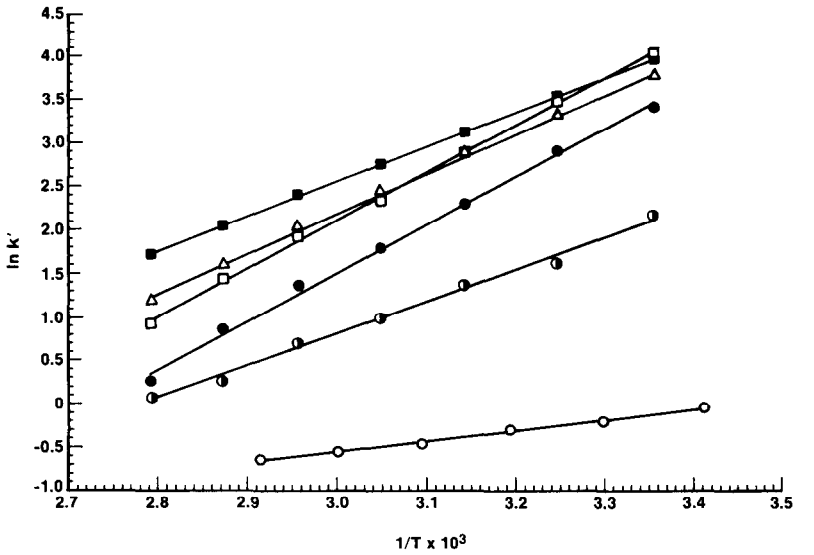

Fig. 3. Van 't Hoff plot of ADA isomers: 1,5 (○); 1,6 (◑); 2,6 (●); 2,7 (□); 1,7 (△); 1,8 (■).

oven temperature. No effort was made to determine the lag time since the temperature gradient produced in this crude manner was reasonably repeatable and produced a suitable separation. No attempt to study more complex temperature gradients was made.

Temperature-capacity factor relationships

Fig. 3 shows the relationship between the reciprocal of the isothermal column

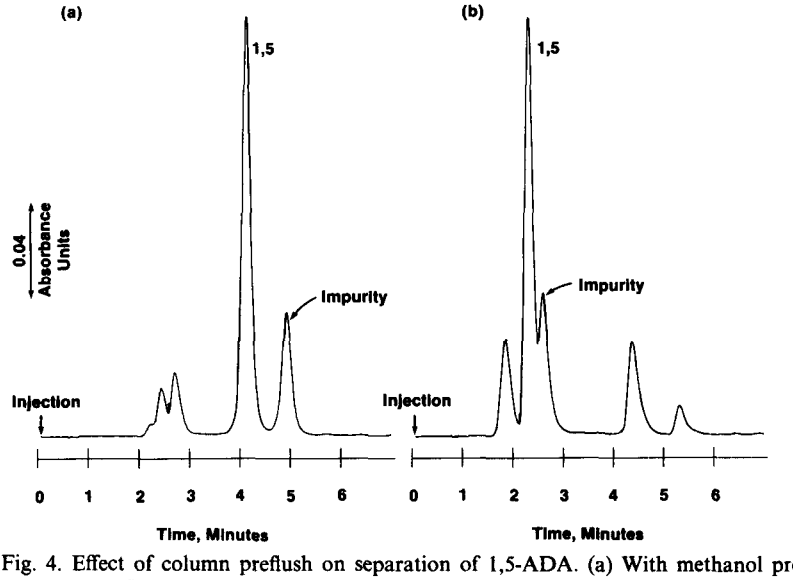

Fig. 4. Effect of column preflush on separation of 1,5-ADA. (a) With methanol preflush; (b) without methanol preflush.

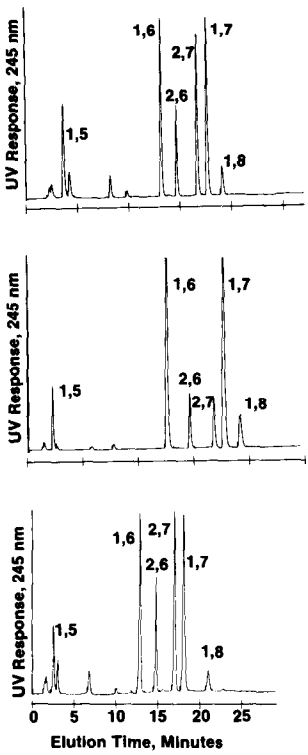

Fig. 5. Chromatograms of various ADA batches.

temperature and ln k' for the various ADA isomers. The 1,5-isomer has a much different retention behavior than any of the other isomers. It is not strongly retained at lower temperatures, and little temperature dependence is observed. The figure also shows several changes in elution order with temperature for the other isomers.

Column equilibration

As demonstrated in Fig. 4a and b, achieving consistent separation of the 1,5-ADA isomer from other early-eluting UV-active peaks requires flushing the column with methanol prior to beginning a separation, then reequilibrating the column with 0.03 M sodium sulfate. The resolution of the other isomers is not affected by the methanol flush; however, all of the isomers are less strongly retained by the column without a methanol flush. It is assumed that residual methanol remains behind on the column during the reequilibration step, providing a slightly modified surface upon which the separation actually occurs. The thermal gradient apparently removes the methanol residue, which necessitates flushing the column prior to performing the next analysis.

Analysis of commercial ADA dye lots

Fig. 5a–c show typical chromatograms obtained for different commercial dye lots of ADA (as the disodium salts) using the thermal elution gradient protocol. The

TABLE I

NORMALIZED ISOMER RESPONSE FACTORS

RF 1,5 = RF 2,7
RF 1,6 = RF 1,7 = 1.445 × (RF 2,7)
RF 1,8 = 1.380 × (RF 2,7)
RF 2,6 = 0.851 × (RF 2,7)

chromatograms were collected over a three-month span using several different columns. The changes in retention behavior are due to column variations, as replicate analyses of a sample on a single column over an 8-h period show retention time variations of less than 2%. The initial 3-min period of the chromatogram, run isothermally at 15°C, resolves the 1,5-isomer from an impurity peak eluting immediately after it and ensures suitable separation between the 2,6- and 1,6-isomers. Raising the column compartment temperature to 80°C elutes the remaining isomers in a timely fashion. Each isomer is base line resolved from the others, as well as from other UV-active impurities in the sample. These three samples were selected to demonstrate the diversity of isomer distribution encountered in commercial dye lots of ADA. Normally, the distribution of ADA isomers is a function of the manufacturing process[3]. The use of a mercury catalyst for sulfonation produces predominately the 1,5- and 1,8-isomers, while the 2,6- and 2,7-isomers are generated without a catalyst. Since the latter isomers are much more reactive toward sulfide[3], dye lots with smaller amounts of 1,5- and 1,8-ADA isomers are preferred for preparing the Stretford process solution.

The weight percentage of each isomer in a dye lot was determined in the following manner. A 2,7-ADA standard was chromatographed to obtain a response factor (RF 2,7). The response factor of each of the other isomers was then obtained by the set of normalized relationships shown in Table I[21].

Multiplying the peak area and the appropriate response factor gave the mass of each isomer (when corrected for dilution factors), and ratioing the isomer mass to the sample weight produced the appropriate weight percentage.

Since the analysis is heavily dependent on the appropriate value for the 2,7-ADA isomer response, special attention was paid to the analysis precision for that isomer. Table II shows the results obtained for replicate analyses of a 2,7-ADA standard solution (59.2 ppm 2,7-ADA dissolved in 0.03 *M* sodium sulfate).

During the span of the analysis program, the solution was protected from light but not oxygen. Within the precision limits of the analytical data, no decomposition

TABLE II

REPLICATE ANALYSIS OF 2,7-ADA STANDARD SOLUTION

Hours	*Preparation*	*Average response, (μV)*	*R.S.D.*
0	4 Analyses	49 704	0.4
24	4 Analyses	49 872	0.8
48	3 Analyses	50 000	0.5
72	4 Analyses	49 905	1.6

TABLE III

ADA ASSAY PRECISION STUDY

Response factors (RF) used in calculation:
RF (1,5) = RF (2,7) = $1.194 \cdot 10^{-9}$
RF (1,6) = RF (1,7) = $1.725 \cdot 10^{-9}$
RF (1,8) = $1.648 \cdot 10^{-9}$
RF (2,6) = $1.016 \cdot 10^{-9}$

Analysis data run number	*Isomer concentration (wt. %)*						*Total ADA (%)*
	1,5	*1,6*	*2,6*	*2,7*	*1,7*	*1,8*	
Day 1 (6 analyses)							
Mean	4.95	22.5	8.72	13.8	25.9	4.01	79.9
R.S.D.	3.0	2.2	1.5	0.7	1.5	1.3	1.1
Day 2 (5 analyses)							
Mean	4.84	22.6	8.71	14.2	26.1	4.01	80.5
R.S.D.	0.6	0.6	2.4	4.9	0.6	1.0	1.6
Day 3 (6 analyses)							
Mean	5.02	22.9	8.62	14.2	26.2	4.05	80.9
R.S.D.	1.8	0.9	1.5	6.3	1.2	2.5	2.1
Day 4 (5 analyses)							
Mean	5.02	23.2	8.73	13.9	26.6	4.01	81.5
R.S.D.	1.8	1.3	1.3	2.9	1.1	2.0	1.6

of the standard solution was observed during the time of the experiment. However, close examination of the chromatograms showed small UV-active peaks eluting close to the 2,7-ADA peak. No effort was made to characterize the molecular structure of these new peaks, but they may be decomposition products of the 2,7-ADA isomer. Assuming these new peaks do represent the appearance of decomposition products and that the response factors for these products are the same as the response factor

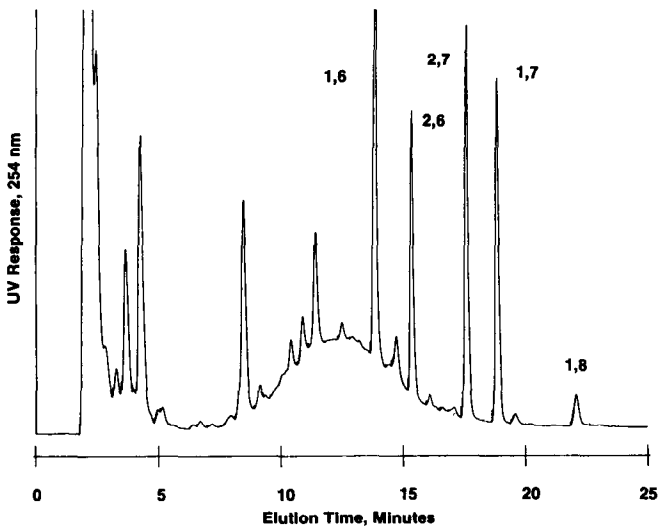

Fig. 6. Chromatogram of Stretford process solution.

for 2,7-ADA, after 72 h less than 1% of the 2,7-ADA had decomposed. No stability studies were carried out with the other isomers, but for the purposes of this study all analyses of dissolved samples were carried out within 24 h of preparation.

Each isomer was examined to determine the linearity of detector response over a range of concentrations. Up to 600 ng of each isomer could be injected and still produce a linear detector response at 254 nm. Beyond this level, deviations from linearity became evident.

Table III shows the results of replicate analyses of an ADA dye lot sample obtained from a commercial source. From these results, solutions of commercial dye lot ADA powders appear to be stable in solution for at least 72 h. In addition, analysis for total ADA content is repeatable to within 2% R.S.D. over the entire four-day period.

Analysis of Stretford process solutions for ADA content

Stretford process solutions can be sampled and analyzed directly for ADA content using the same procedure employed for analysis of commercial lots of ADA powders. Typically, a dilution of 1:15 or 1:20 will generate suitable chromatograms.

Fig. 6 shows a typical chromatogram of a Stretford process solution obtained from an operating plant. Because of the complex nature of the sample, the 1,5-ADA isomer is difficult (and in some cases impossible) to resolve from other constituents. To ensure that no contaminant peaks coelute with the ADA isomers in such a complex mixture, the UV spectrum of each isomer peak was captured by a photodiode array detector as it eluted. The spectrum of the leading edge and trailing edge of each peak was then compared to the spectrum obtained for that isomer by static measurements. No impurity was detected for the major isomers.

Slightly poorer precision was obtained for replicate analyses of Stretford plant solutions compared to the analysis of ADA powders. Typical analyses showed 3–5% R.S.D. for the major isomers (1,7; 1,6; 2,7; 2,6; 1,8).

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