Ion chromatographic determination of some anions and alkaline cations in liquid crystal materials after ultraviolet irradiation

Yongjian Liu, Shifen Mou*

Research Center for Eco-Environmental Sciences, The Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

Received 30 October 2002; received in revised form 10 March 2003; accepted 18 March 2003

Abstract

A method was developed for the quantitative determination of inorganic cations and anions present in liquid crystal materials pretreated with ultraviolet irradiation by ion chromatography. The samples were irradiated at less than $20 \pm 2^\circ\text{C}$ and then pretreated with OnGuard RP and P cartridges to remove the interferential organic compounds prior to ion chromatographic analysis for both cations and anions. With a high capacity and very hydrophilic anion exchange column, four anions (fluoride, chloride, bromide, iodide) were determined in 20 min with gradient of sodium hydroxide. By employing a cation exchange column, five cations (sodium, ammonium, potassium, magnesium, calcium) could be determined in 12 min. The spiked recoveries for the cations and anions were 84.0–108.1% and 86.1–108.2%, respectively.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Ion chromatography; Ultraviolet irradiation; Liquid crystal materials; Anions; Alkaline cations

1. Introduction

Since the first application of liquid crystal material in the early seventies, the commercial interest in this field of research has been steadily increasing. Nowadays they play an important role in industrial world, especially in the electronics industries, such as in the production of liquid crystal displays, etc.

The electroconductibility of the liquid crystal material as determined by its structure and align-

ment is one of the most important properties. However, it is affected by the inorganic anions and cations that are inevitably introduced in the material as impurities during the synthesis. In order to guarantee the quality of the material, it is necessary to detect and control the content of the inorganic anions and cations in it.

Ion chromatography (IC) is one of the simplest and most effective techniques to determine both anions and cations owing to its high sensitivity, rapidity and ease of operation. It is universally employed in the determination of anions as well as cations in a lot of matrices [1–3].

* Corresponding author. Tel./fax: +86-106-284-9239.

E-mail address: shifenm@mail.rcees.ac.cn (S. Mou).

The presence of inorganic ions in organic matrixes is widely investigated [4–6]. With regard to the whole procedure, the pretreatment of the sample is extremely important for accuracy. The typical methods used for the pretreatment of organic matrixes are dry ash [4], oxygen flask/bomb combustion [5] and Kjeldahl digestion [6], etc. However, all these methods are time consuming and impurities are easily introduced during the treatment and may interfere in the determination.

Oxidative UV-photolysis has been proven to be an attractive pretreatment method to decompose organic matrixes due to its simplicity, low interference and high recoveries [7]. Oxidative UV-photolysis-IC has got many applications in the pretreatment of complex organic matrixes [8–11]. Liquid crystal material is a kind of orderly arranged organic compounds whose states are between solid state and liquid state. The material is synthesized with many small molecular organic compounds and has a wide range of chemical structures, including rod-like molecules, disc-like molecules, etc. The small molecular organic compounds may cover various diphenacryle compounds, diphenylacetylene compounds and esters, etc. Because of the complexity of the material, there is little study of common anions and cations in it.

The present work deals with the application of ultraviolet irradiation-IC to the determination of sodium, ammonium, potassium, magnesium, cadmium, fluoride, chloride, bromide and iodide in one kind of liquid crystal materials whose main components are diphenacryle series and esters. The developed method has been successfully used for monitoring the content of these ions in the process of production of the liquid crystal materials.

2. Experimental

2.1. Reagents and samples

All chemicals were of analytical reagent grade and all reagents, eluents and standard solutions were prepared using 18.3 M Ω reagent water (EASY pure LF system, Barnstead). Fluoride, chloride, bromide, iodide, sodium, ammonium,

potassium, magnesium and calcium stock solutions (1000 mg l⁻¹) were prepared by dissolving the corresponding mass of the dried salts (Beijing Chemical Industrial Factory, China) in purified water to a final volume of 1000 ml. The stock solutions were stored in refrigerator at 4 °C and they were proved to be stable for at least 1 month. Standard solutions were prepared daily by serial dilution of the stock solution prior to use. The eluent used for the determination of cations was 20 mmol l⁻¹ methanesulphonic acid. The flow rate was 1.0 ml min⁻¹. For the analysis of anions, the eluents were 100 mmol l⁻¹ sodium hydroxide, 5 mmol l⁻¹ sodium hydroxide which were prepared with 50% (w/w) sodium hydroxide and deionized water. The flow rate was kept at 1.0 ml min⁻¹. All the determinations were performed in room temperature. Each sample was injected in triplicate. The liquid crystal materials were furnished by a native company.

2.2. Instrumentation

Ultraviolet irradiation is carried out in NDC photochemical reactor (Nanjing Changning radio factory, China) equipped with a 300 W medium pressure mercury lamp with inner water-cooling. The medium pressure mercury lamp used has a wide radiation spectrum ranged from 250 to 580 nm. Ultraviolet source is shielded as per safety equipments. All ultraviolet irradiations were performed in quartz beakers.

A Dionex model DX-500 IC (Sunnyvale, CA, USA) equipped with a GP40 gradient pump, a Dionex Ionpac AS16 analytical column (4 × 250 mm), an Ionpac AG16 guard column (4 × 50 mm), a Dionex ED40 conductivity detector and a Dionex ASRS-ULTRA (4 mm) suppressor were used for the analysis of anions. Injections of 150 μ l of sample were performed.

For the determination of cations, a Dionex DX-300 IC equipped with GPM gradient pump, conductivity detector, a Dionex CSRS-I (4 mm) micromembrane suppressor and 50 μ l sample loop was used. A Dionex IonPac CG12A (4 × 50 mm) guard column and an IonPac CS12A (4 × 250 mm) analytical column were used. Both instruments control and data collection were performed with

Dionex PeakNet 5.11 chromatography workstation.

After ultraviolet irradiation, Dionex OnGuard RP and P cartridges connected in series were used to remove the interferential organic compounds still present in the samples. Samples were filtrated through a 0.45 μm filter (Autoscience, Tianjin China) before injection. All tubing in the chromatography path (from the outlet of the pump to the exit of the suppressor) was made of PEEK [0.005 in (0.125 mm) I.D.].

2.3. Sample pretreatment

The liquid crystal materials are hardly soluble in water. They can be dissolved in acetonitrile that is selected due to its volatility and compatibility with IonPac CG12A and CS12A chromatographic columns.

50.0 mg of the liquid crystal material is weighed in a 50 ml quartz beaker. It is completely dissolved in 4.0 ml of acetonitrile. The sample is irradiated not overcoming 20 ± 2 °C to prevent the volatilization of the solvent and of the volatile species. After irradiation, the sample is quantitatively transferred into a lighttight volumetric flask that is used to prevent the irradiation of sunlight and diluted to 10.0 ml with deionized water. The solution becomes a suspension that can not be directly injected into the system.

Treated with the tandem OnGuard RP and P cartridges, the residual organic compounds that are not degraded nor destructuralized by irradiation can be removed, the suspension becomes clear and can be directly injected. During the analysis, blank samples are done in parallel with the real ones. Peak areas are obtained using the PeakNet software to quantitate anions and cations. Background subtraction is applied wherever necessary.

3. Results and discussion

3.1. Identification of ultraviolet irradiation condition for anions

Before the liquid crystal material was irradiated, a preliminary investigation was done to study the

species and content of anions existed as free form by dissolving and determining the sample. The results showed that no anion was found in the solution, which indicated that no anion was present as impurities in the sample.

From Fig. 1, it was found that fluoride, chloride and bromide could be detected in the solution after the dissolved sample was irradiated for 2 h, although the peak of fluoride suffered serious interference of a big unknown peak. Since no free anion exists in the sample, it can be concluded that in the liquid crystal materials, the detected halogen atoms may connect with the liquid crystal molecules by covalent bond. Under the irradiation of the lamp, the bonds between fluorine, chlorine, bromine and the molecules were destructuralized by the ultraviolet radiation energy. The halogen atoms were split off from the molecules and present in acetonitrile as fluoride, chloride and bromide.

Hydrogen peroxide is a strong oxidizing agent no matter in acidic or alkaline conditions. It is widely used to degrade organic compounds and release inorganic halogen atoms via hydroxyl radical in photolysis process [12–14]. In liquid crystal material, the halogen atoms are tightly bonded to the organics. It is difficult to cut them down from the compounds only with ultraviolet irradiation. In order to accurately determine the content of the atoms in the liquid crystal materials, hydrogen peroxide can be used to completely degrade the organics and release the atoms.

1.0 ml of 30% hydrogen peroxide was added in the sample solution and then the sample was irradiated and determined. The results indicated that besides fluoride, chloride and bromide, little iodide could also be found in the solution (Fig. 1 and Fig. 2). In addition, the big unidentified peak became much smaller than that in the sample treated only with ultraviolet. The responses of fluoride, chloride and bromide were 6.6, 1.3 and 1.2 times higher than those in the sample treated without hydrogen peroxide, respectively. It indicated that during the irradiation, the addition of hydrogen peroxide gave rise to the formation of hydroxyl radicals, which accelerated the degradation of the organic compounds. More fluorine, chlorine, bromine and iodine were to a great extent

Fig. 1. Chromatograms of anions in the liquid crystal material samples.

rapidly split off from the liquid crystal molecules, forming fluoride, chloride, bromide and iodide. Therefore, the peak responses of these anions were much increased. During the irradiation, the bonds between the halogen atoms and the molecules were also destructurized via ultraviolet radiation energy. However, due to the fact that the ultraviolet intensity of the lamp was not very high, the temperature was only about 20 °C, the ultraviolet

irradiation did not play an important role in the forming of the anions.

The determination of iodine bonded to organics suffers several serious problems, which were caused by the formation of iodine species or derived from the oxidative pretreatment and sublimation of iodine from the sample with the increase of temperature. Although ultraviolet irradiation is a widely used method to degrade

Fig. 2. Chromatograms of iodide after different pretreatments.

organic compounds and release the bonded atoms, during the irradiation, the released iodide will be oxidized to elementary iodine (I_2) owing to the strong oxidizing ability of hydroxyl radicals and the ultraviolet irradiation, which leads to analyte loss. Consequently, there has little application of determination of iodine bonded to organics with ultraviolet irradiation.

In alkali solution, Iodine (I_2) will be disproportionated to form IO_3^- and I^- (reaction 1). The standard electrode potentials (φ^θ) of $\varphi_{IO_3^-/I_2}^\theta$, $\varphi_{IO_3^-/IO^-}^\theta$, φ_{I_2/I^-}^θ are 0.445, 0.145 and 0.535 V, respectively. With Eq. (1), it can be calculated that the standard electrode potential (φ^θ) of $\varphi_{IO_3^-/I_2}^\theta$ is 0.205 V. The equilibrium constant (K) of reaction 1 can be calculated with Eq. (2) ($\varphi_1^\theta = \varphi_{IO_3^-/I_2}^\theta = 0.535$ V, $\varphi_2^\theta = \varphi_{IO_3^-/I_2}^\theta = 0.205$ V, where n is the electronic numbers transferred in reaction 1, $n = 5$). The result is $K = 10^{28}$ which indicates that the almost all the I_2 in the alkali solution can be converted to I^- and IO_3^- .

$$\varphi = \frac{n_1\varphi_1^\theta + n_2\varphi_2^\theta + \cdots + n_i\varphi_i^\theta}{n_1 + n_2 + \cdots + n_i} \quad (1)$$

$$\lg K = \frac{(\varphi_1^\theta - \varphi_2^\theta)n}{0.059} \quad (2)$$

It can be seen from Fig. 2 that in the unirradiated sample, no free iodide is detected. In the sample irradiated with hydrogen peroxide, little iodide can be detected. It indicates that with the help of hydroxyl radical, one part of organics with iodine is degraded, part of the bonds between iodine and the molecules are broken. Iodine can be split off from the molecules and forms iodide in the solution. Because of the low ultraviolet intensity and temperature, the number of iodide released by irradiation is small and the response of iodide is not high. From the figure it can also be seen that in the sample irradiated with hydrogen peroxide and sodium hydroxide, the response of iodide is greatly improved (7.6 times as high as that of the sample treated only with hydrogen peroxide). It suggests that during the process, most of the released iodide may be oxidized to iodine

(I_2). With the addition of sodium hydroxide, iodine (I_2) can be transformed to iodate and iodide, which greatly improved the response of iodide. For iodate, its concentration was too small to be detected. Therefore, the total amount of iodine released by sodium hydroxide should be the sum of iodide and iodate. The quantity of iodide in the sample treated with sodium hydroxide and hydrogen peroxide was 8.92 times as much as that in the sample treated only with hydrogen peroxide.

From Fig. 3, it can be seen that the response of iodide reaches the maximal level when the concentration of sodium hydroxide in the sample is 0.009 mol l^{-1} . Whereafter, following the increase of sodium hydroxide's concentration, the response of iodide begins to decline. Much differing from the variation of iodide, the responses of chloride and bromide decline with the addition of sodium hydroxide, which indicates that with the action of hydroxyl radicals and ultraviolet energy, chloride and bromide may be oxidized to chlorine (Cl_2) and bromine (Br_2). In the alkaline solution, chlorine (Cl_2) and bromine (Br_2) can be transformed to chloride and hypochlorite ($Cl^- + ClO^-$), bromide and hypobromite ($Br^- + BrO^-$), which lead to the losses of the compounds. Because of the very weak reductibility of fluoride, its response hardly changes during the whole process. In order to accurately determine the content of fluorine, chlorine, bromine and iodine in the liquid crystal materials, two parallel samples should be treated and determined simultaneously according to the corresponding methods. One is for the treatment of iodine. The other one is for fluorine, chlorine and bromine.

From Fig. 4, it can be seen that iodide gets maximal response after 1.5 h irradiation. For the other three anions, they get the highest responses after 2 h irradiation. It can be concluded that the bond between iodine and the molecule may be the weakest. Under the action of hydroxyl radicals and ultraviolet energy, iodine can be cut off from the molecule easily. For the strong bonds of the other three anions, it need more time to complete release the anions. The responses of chloride, bromide and iodide begin to decrease after the maximal level. It is because the anions may be oxidized to chlorine (Cl_2), bromine (Br_2) and

Fig. 3. The influences of the concentration of NaOH added in the samples on the responses of the anions.

iodine (I_2), which result in the decline of the responses of the anions. In order to prevent the formation and volatilization of the compounds and exactly determine the content of the elements in the material, the irradiation times should be strictly controlled. For fluoride, it can not be oxidized by hydroxyl radicals and irradiation due to the very weak reducibility. Its response hardly changed after reaching the peak value.

3.2. Selection of the chromatographic conditions

Iodide is a polarizable anion. It has strong retention on ion chromatographic solid phase. In order to elute it quickly, it needs to add solvent in eluent as modifier to lower the retention. However, extraneous interference may be introduced in. Moreover, the suppressor should be run in external water mode, which is inconvenient.

Fig. 4. The influence of irradiation time on the peak responses of the anions.

Table 1
Detection limits and linear ranges of the cations and anions

Analyte	Concentration (mg l ⁻¹) ^a	R.S.D. (% , n = 7)	Linear range (mg l ⁻¹)	Detection limit (mg l ⁻¹ , S/N = 3)
Na ⁺	2.0	2.1	0.1–50	0.03
NH ₄ ⁺	2.5	1.3	0.1–60	0.035
K ⁺	5.0	2.0	0.05–50	0.025
Mg ²⁺	2.5	1.7	0.08–70	0.028
Ca ²⁺	5.0	2.3	0.1–100	0.03
F ⁻	2	1.5	0.1–70	0.04
Cl ⁻	3	1.1	0.1–60	0.03
Br ⁻	10	1.4	0.1–80	0.05
I ⁻	20	1.7	0.3–80	0.1

^a Standard solution.

The IonPac AS16 column is a high capacity, hydroxide selective anion exchange column with very strong hydrophilicity. On the column, the four anions could be sufficiently separated from the interference compounds in a single run within 20 min by employing the eluent of sodium hydroxide in a linear gradient (Fig. 1). In addition, it did not need to add solvent in the eluent to lower the retention of iodide. The suppressor could also be run in autosuppression recycle mode, which facilitated the determination very much. For the high capacity of the column, a large volume loop could be used for the injection to enhance the sensitivity of the analytes.

3.3. Determination of anions in the liquid crystal materials

The detection limits, linear ranges for the four anions are summarized in Table 1. The results and

spiked recoveries of the anions in real sample are listed in Table 2.

From Fig. 1, it can be seen that after the sample pretreatment, most of the interferential compounds are removed; the four anions are hardly interfered and can be quantified with accuracy under the specific chromatographic condition.

3.4. Identification of ultraviolet irradiation conditions for cations

Preliminary investigations with similar procedure as that described for the anions was carried out to study the species and content of cations in the liquid crystal materials, too. The results indicated that five cations (sodium, ammonium, potassium, magnesium, calcium) were detected in the dissolved sample solution. It meant that the free cations are present in the samples. When the sample was irradiated for 2 h, the responses of the five cations were greatly improved. The concen-

Table 2
Concentrations and spiked recoveries of cations and anions in a real sample

Ions	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	F ⁻	Cl ⁻	Br ⁻	I ⁻
Concentration (mg l ⁻¹)	9.9	47.9	10.5	14.3	84.4	30.1	3.5	67.4	33.6
R.S.D. (% , n = 3)	6.6	3.4	2.1	2.6	2.8	5.9	4.5	3.2	4.7
Spiked (mg l ⁻¹)	5.0	20.0	5.0	8.0	40.0	15.0	2.0	30.0	15.0
Found (mg l ⁻¹)	4.33	16.8	5.41	7.57	40.8	12.92	1.76	32.5	13.49
Recovery (%) ^a	86.1	84.0	108.1	94.6	102.1	86.1	87.8	108.2	89.9
R.S.D. (% , n = 7)	6.4	5.5	4.7	4.2	6.7	5.8	8.7	4.0	5.1

^a Spiked recoveries were obtained by adding standard solution to the sample, and then irradiated and determined.

Fig. 5. The influence of ultraviolet irradiation time on the peak responses of the cations.

trations of the five cations were 9.6, 9.5, 10.5, 12.7, and 45.6 times higher than those in the corresponding dissolved sample, respectively. It indicated that with the radiation of ultraviolet, more free cations could be released from the liquid crystal molecules.

A further investigation was done to study whether the pH value of the sample solution would affect the ultraviolet irradiation efficiency.

The results indicated that after 2 h irradiation, the five cations had almost the same responses no matter in neutral or acidic solution. The influence of hydrogen peroxide addition on the irradiation process was also studied. The results confirmed that the responses of the cations hardly changed along with the addition of hydrogen peroxide. It suggested that ultraviolet radiation was enough for the release of cations from the compounds.

Fig. 6. Chromatogram of five cations in the liquid crystal materials.

From Fig. 5, it can be seen that monovalent cations (sodium, ammonium, potassium) get the highest peak responses when the sample is irradiated for 1.5 h, which is because the linkage force between the monovalent cations and the liquid crystal materials is very weak, it can be cut off with ease. For the divalent cations (magnesium, calcium), because the bond force is much stronger than that of the monovalent cations, it needs more time (2 h) to get the maximal responses.

3.5. Determination of cations in the liquid crystal materials

The detection limits, linear ranges for the cations are summarized in Table 1. The results indicate that all the cations have high recoveries. Table 2 shows the concentrations and recoveries of the five cations in the liquid crystal material samples. The results manifest that after the sample pretreatment, the five cations are sufficiently separated, and there is not any interferential peak in the chromatogram (Fig. 6).

4. Conclusions

IC is applied to the determination of some anions and cations in liquid crystal materials after ultraviolet irradiation of the organic matrix and SPE filtration. No interference is found between the species usually present in these materials. Sodium, potassium, ammonium, magnesium, calcium, fluoride, chloride, bromide and iodide can

be well determined in the range of 3.5–84.4 mg l⁻¹ with precision of 4.0–8.7%. The method has been successfully applied to the monitoring of the described inorganic anions and cations in the liquid crystal materials production.

References

- [1] M. Arienzo, R. Capasso, *J. Agric. Food Chem.* 48 (2000) 1405.
- [2] T. Jauhiainen, J. Moore, P. Peramaki, J. Derome, K. Derome, *Anal. Chim. Acta* 389 (1999) 21.
- [3] N. Gros, B. Gorenc, *J. Chromatogr. A* 770 (1997) 119.
- [4] P.R. Haddad, S. Laksana, *J. Chromatogr. A* 671 (1994) 131.
- [5] Y.S. Fung, K.L. Dao, *Anal. Chim. Acta* 334 (1996) 51.
- [6] P.E. Jackson, J. Krol, A. Heckenberg, M. Mientjes, W. Staal, *J. Chromatogr.* 546 (1991) 405.
- [7] P.L. Buldini, D. Ferri, J.L. Sharma, *J. Chromatogr. A* 789 (1997) 549.
- [8] P.L. Buldini, J.L. Sharma, A. Mevoli, *J. Chromatogr. A* 654 (1993) 123.
- [9] P.L. Buldini, A. Mevoli, J.L. Sharma, *Analyst* 123 (1998) 1109.
- [10] P.L. Buldini, J.L. Sharma, S. Sharma, *J. Chromatogr. A* 654 (1993) 113.
- [11] C. Scheuer, B. Wimmer, H. Bischof, L. Nguyen, J. Maguhn, P. Spitzauer, A. Kettrup, D. Wabner, *J. Chromatogr. A* 706 (1995) 253.
- [12] W.C. Schumb, C.N. Satterfield, R.L. Wentworth, *Hydrogen Peroxide*, Reinhold, New York, NY, 1955.
- [13] R.P.S. Black, A.T. Hawkinson, *Symposium on Cleanness and Materials Processing for Electronic and Space Applications (ASTM STP, No. 342)*, America Society for Testing and Materials, Philadelphia, PA, 1962, pp. 87.
- [14] G. Pace, A. Berton, L. Calligaro, A. Mantovani, P. Uguagliati, *J. Chromatogr. A* 706 (1995) 345.