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Short communication

Direct determination of 4-nitrobenzoyl chloride by high-performance liquid chromatography based on silanophilic interaction

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Abstract

A high-performance liquid chromatographic method without prederivatization was investigated for the direct determination of 4-nitrobenzoyl chloride and 4-nitrobenzoic acid. The separation was carried out on C_3, C_8 and C_{18} alkyl-bonded silica columns with cyclohexane–tetrahydrofuran as the eluent. The retention behaviour observed was obviously caused by the silanophilic interaction between the solute and stationary phase. Optimum separation of 4-nitrobenzoyl chloride and 4-nitrobenzoic acid was obtained on the C_3 column and the calibration graph showed a significant linear relationship. The method was found to be quantitative, reproducible and rapid.

1. Introduction

The most widely employed methods for the determination of acid chlorides are titrimetric [1,2]. Hasegawa et al. [3], Colgan and Krull [4] and Bissinger et al. [5] reported RP-HPLC methods for the determination of acid chlorides using their ester and amide derivatives. Acid chlorides cannot be determined directly by RP-HPLC with an aqueous–organic eluent as they can react with water, so a non-aqueous solvent system must be adopted.

The aim of this work was to develop an HPLC method without prederivatization for the simultaneous determination of 4-nitrobenzoyl chloride and 4-nitrobenzoic acid. Conventional liquid–solid chromatography (LSC) with a silica column is assumed to be suitable for the separation of these compounds because, based on their molecular structures, 4-nitrobenzoic acid and 4-nitrobenzoyl chloride have different abilities to forming hydrogen bonds with silanol groups on the silica surface. However, these polar compounds interact very strongly with the adsorbent surface and result in peaks of poor symmetry and poor efficiency.

A non-polar alkyl-bonded silica stationary phase is usually used in the RP-HPLC mode with the use of a polar mobile phase. The use of an alkylsilica column with a pure non-polar organic eluent or a non-polar solvent-rich organic eluent would be classified as LSC owing to the polar residual silanol groups on the surface of the alkyl-bonded silica phase. We indeed found in

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this work that LSC could be carried out by using an alkylsilica gel as the stationary phase. The weaker interaction between the solutes and the residual silanol groups on the surface of the alkylsilica gel results in peaks with good symmetry and high efficiency.

Optimum analytical conditions were determined to ensure complete separation, quantification and reproducibility. The applicability of this method to the determination of 4-nitrobenzoyl chloride which was synthesized from 4-nitrobenzoic acid with PCl_3 as a chlorinating agent was demonstrated. It is also suggested that this method can be extended to the determination of other acid chlorides.

2. Experimental

2.1. Chemicals and equipment

Cyclohexane, tetrahydrofuran (THF) and 4-nitrobenzoic acid of analytical-reagent grade were obtained from Shanghai Chemical Supply (Shanghai, China). THF was redistilled before use. 4-Nitrobenzoyl chloride (purity 99.8%) was obtained from Professor Y.-B. Lin (Department of Chemistry, Xiangtan University, China). Chromatography was performed on a Shimadzu LC-6A chromatgraph equipped with an SPD-6AV variable-wavelength detector (190–900 nm) and a CR-3A data processor. The columns used were Shim-Pack CLC-C_3, CLC-C_8 and CLC-C_{18} (150 × 4.6 mm I.D.).

2.2. Procedures

Cyclohexane–THF was used as the eluent on the C_3, C_8, C_{18} columns at a flow-rate of 1.0 ml/min. The detector wavelength setting was 300 nm and the sensitivity was 0.04 AUFS. Capacity factors (k') were evaluated from the retention times of the test substances and that of an unretarded component, tetrachloroethylene (detection wavelength 254 nm). The eluent compositions were varied and the k' values of these compounds in each system were determined. The amount of 4-nitrobenzoyl chloride was calculated by a five-point external standard method under optimized conditions. The standards for analysis were prepared by dissolution of known amounts of 4-nitrobenzoyl chloride in cyclohexane–THF (70:30, v/v) solvent; the theoretical concentration of the solute was in the range 45.36–226.8 μg/ml. Aliquots (5 μl) of the standard solutions were injected on to the chromatographic column. Sample analyses were carried out under the same conditions. The amount of acid chloride was calculated by comparing the peak area in the reference chromatogram with that of the appropriate component in the sample chromatogram.

3. Results and discussion

3.1. Dependence of retention on composition of mobile phase

As illustrated in Table 1, changes in the capacity factors of 4-nitrobenzoyl chloride and 4-nitrobenzoic acid with the volume fraction of THF in binary cyclohexane–THF eluent were obtained on the C_3, C_8, C_{18} columns. The retention behaviours shown by 4-nitrobenzoyl chloride and 4-nitrobenzoic acid could be interpreted in terms of the LSC mode; the active adsorption sites were the residual silanol groups on the surface of the alkyl-bonded phase and the separation was carried out based on the silanophilic interaction between solutes and active sites. 4-Nitrobenzoic acid has a greater ability than 4-nitrobenzoyl chloride to form hydrogen bonds with silanols, which should result in a greater retention, and this was borne out by the experimental results.

Fig. 1 show the plots of k' versus eluent composition on the three columns. A common feature is an increase in retention with decrease in THF concentration, which is consistent with the interpretation that the retention was due to silanophilic interactions at low THF concentration whereas THF masked the silanol sites at higher concentration.

Table 1
Experimental values of k' for 4-nitrobenzoic acid (k'_1) and 4-nitrobenzoyl chloride (k'_2) with cyclohexane–THF from 40:60 to 98:2 (v/v)

Column	k'	Volume fraction of THF (v/v)													
		0.6	0.5	0.45	0.40	0.35	0.30	0.25	0.20	0.15	0.10	0.08	0.06	0.04	0.02
C_3	k'_1	0.103	0.162	0.201	0.260	0.331	0.414	0.534	0.738	1.100	1.992	–	–	–	–
	k'_2	0.027	0.046	0.056	0.070	0.090	0.111	0.137	0.177	0.243	0.337	–	–	–	–
C_8	k'_1	–	–	–	–	–	0.007	0.013	0.026	0.056	0.124	0.180	0.275	0.469	0.998
	k'_2	–	–	–	–	–	0.002	0.005	0.009	0.018	0.033	0.043	0.054	0.067	0.079
C_{18}	k'_1	–	–	0.048	0.055	0.064	0.067	–	0.108	–	0.202	0.253	0.326	0.571	1.358
	k'_2	–	–	0.065	0.067	0.071	0.081	–	0.105	–	0.139	0.147	0.163	0.186	0.212

Columns, Shim-Pack CLC-C_3, CLC-C_8 and CLC-C_{18} (150 × 4.6 mm I.D.); eluent, cyclohexane–THF; flow-rate, 1.0 ml/min.

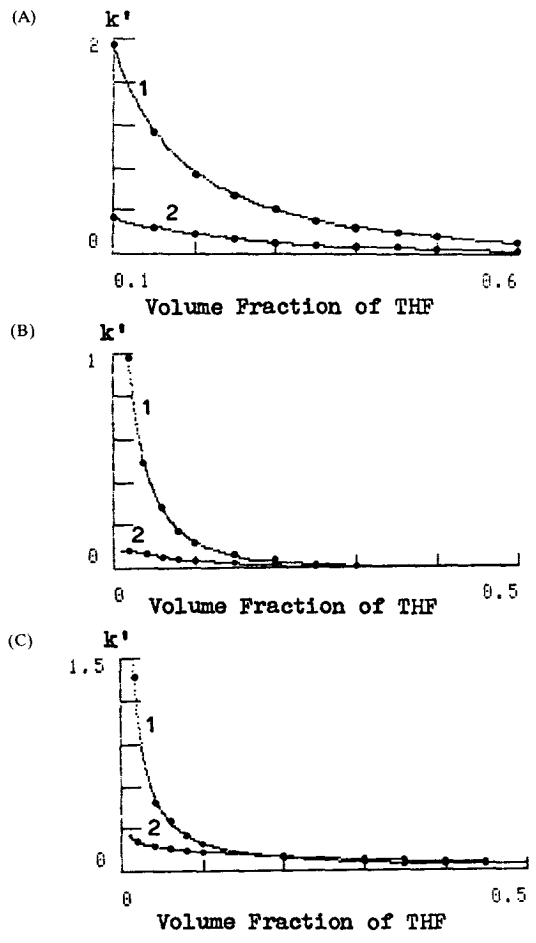

Fig. 1. Change in capacity factors of 4-nitrobenzoic acid (1) and 4-nitrobenzoyl chloride (2) with variation of the volume fraction of THF in eluent of the three Shim-Pack CLC columns: (a) C_3; (b) C_8; (c) C_{18}.

3.2. Quantitative analysis

Fig. 1 also provided a visual approach to the optimization of the chromatographic conditions for quantitative analysis. The change in the k' of two components with the volume fraction of THF in the eluent (V_{THF}) on the three columns indicated that the C_3 column showed the widest variation in V_{THF} and the greatest difference between k'_1 and k'_2 for the complete separation of the two compounds, hence this column was selected as the optimum. Considering the solubility of the solutes in the eluent, the separation of the two components and the speed of analysis, the proportion of THF in the eluent was selected as at 30% (v/v), i.e., the optimum eluent was cyclohexane–THF (70:30, v/v). Under the optimized conditions, rapid ($k' < 1$) elution of the two components was obtained, as shown in Fig. 2. The first component eluted was 4-nitrobenzoyl chloride, followed by 4-nitrobenzoic acid.

The calibration graph for the determination of 4-nitrobenzoyl chloride was constructed by analysing a series of standards of known concentration. A significant linear relationship between peak area and solute concentration was found, as shown in Fig. 3; the correlation coefficient (r) was 0.9998.

The results obtained for sample analysis for 4-nitrobenzoyl chloride with six replicate determinations were 81.67, 81.51, 80.89, 81.34, 81.87 and 82.10%, mean 81.56, R.S.D. 0.52% and average recovery 99.1%. The relative standard

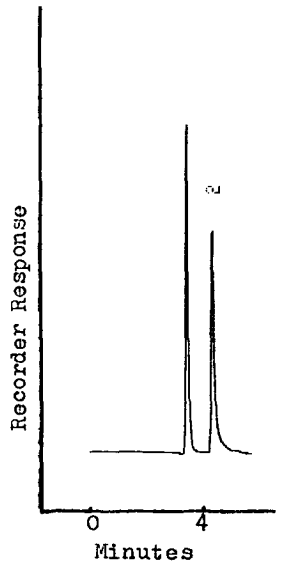

Fig. 2. Chromatogram of a mixture containing (1) 4-nitrobenzoyl chloride and (2) 4-nitrobenzoic acid. Column, Shim-Pack CLC-C_3 (150 × 4.6 mm I.D.); eluent, cyclohexane–THF (70/30, v/v); flow-rate, 1.0 ml/min; injection volume, 5 μl; detection, UV at 300 nm.

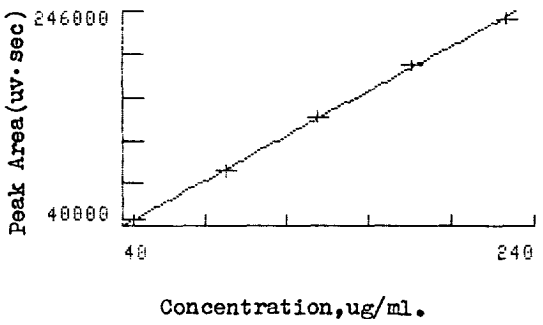

Fig. 3. Calibration graph for 4-nitrobenzoyl chloride. Column, Shim-Pack CLC-C_3 (150 × 4.6 mm I.D.); eluent, cyclohexane–THF (70/30, v/v); flow-rate, 1.0 ml/min; detection, UV at 300 nm.

deviation and average recovery were satisfactory.

4. Conclusion

The method described is very useful for the reproducible, rapid and easy determination of 4-nitrobenzoyl chloride. The separation is based on silanophilic interactions between the solutes and the residual silanol groups in the surface of the alkyl-bonded silica phase. This work also demonstrated that beyond its traditional use, a non-polar alkyl-bonded silica phase can be used in normal-phase HPLC for special separation purposes.

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