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Synthesis of Cellulose Tris (4-Methylbenzoate) as Gas Chromatographic Stationary Phase and its Characterization

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Abstract: The cellulose tris (4-methylbenzoate) has been synthesised by the catalytic method and was supported at Gas Chrom Q. The absorption capability of cellulose tris (4-methylbenzoate) used as a gas chromatographic stationary phase was characterized by chromatographic method and the Clausius-Clapeyron equation. However, *n*-alcohols (C_1-C_8) were successfully separated on the column packed with Gas Chrom Q coated with cellullose tris (4-methylbenzoate).

Keywords: Cellulose tris(4-methylbenzoate), chromatographic stationary phase, absorption heat, alcohol.

Cellulose (MC) is the most accessible optically active polymer. Its benzoate and phenylcarbamate derivatives exhibit a high chiral recognition ability for a variety of racemic compounds as chiral stationary phases (CSPs) for high performance liquid chromatography[1-3]. However, the application of cellulose derivatives in gas chromatography has seldom been reported except that Zou reported cellulose tribenzoate (CTB) which was used as a stationary phase for gas chromatography [4].

Cellulose and its derivatives have high thermal and chemical stability and can be manufactured easily and inexpensively. In addition, these derivatives have a variety of organic functional group such as phenyl and ester carbonyl groups. While these derivatives were used as a stationary phase in gas chromatography, special interaction forces and effective separation of some compounds can be expected.

In this work, the chromatographic experiments were performed on 1102 gas chromatography equipped with FID (Shanghai Analytical Instrument Plant) and CDMC-1EX chromatographic data processor (Shanghai Institute of Calculate technology).

Cellulose tris (4-methylbenzoate) (CTMB) has been prepared by the reaction of microcrystalline cellulose with an excess of 4-toluoyl chloride in mixture solution of pyridine and triethylamine at 110°C in the presence of 4-dimethylaminopyridine and isolated as the ethanol-insoluble fraction. The synthesis yield was 87%. Its melting point was 269-272°C. Elemental analysis and IR spectrum (**Table 1**) indicated that all-hydroxy groups of cellulose were almost converted into carbonyl moieties. The degree of substitution (SD) equals 99%.

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Table 1 Elemental analysis and IR spectrum data of cellulose tris (4-methylbenzoate)

Compounds	n_{OH}, cm^{-1}	$n_{C=O}$, cm^{-1}	$n_{C=C}$, cm^{-1}	$d_{C=C-H}$, cm^{-1}	C (%)	H (%)
MC	3300	/	/	/	/	/
CTMB	/	1735	1610, 1490	840, 750	69.71 (69.76)*	5.46 (5.46)*

* Calculated values of elemental analyses are shown in parenthes.

Cellulose tris (4-methylbenzoate) (about 16% Gas Chrom Q) was dissolved in dichloromethane. The above solution was added to Gas Chrom Q (60-80 mesh). Then, the wet Gas Chrom Q was dried under vacuum. The packing material thus obtained was packed in a glass column (2 m×3 mm I.D.) by a vaccum-packing technique and conditioned at 220°C for 8 h.

The chromatographic behavior of cellulose tris (4-methylbenzoate) as a stationary phase for gas chromatography has been characterized by calculating the adsorption enthalpy ($-\Delta H_a$) between the probe molecules and stationary phase. The heat of adsorption of various substances has been determined using the Clausius-Clapeyron equation and a chromatographic method[5,6]. The experimental results showed that the retention time of probe molecule on Gas Chrom Q was close to the dead time for methane. However, the heat of adsorption ($-\Delta H_a$) of some probe molecules, their boiling points and relative molecular masses (RMM, $g.mol^{-1}$) are summarized in **Table 2**.

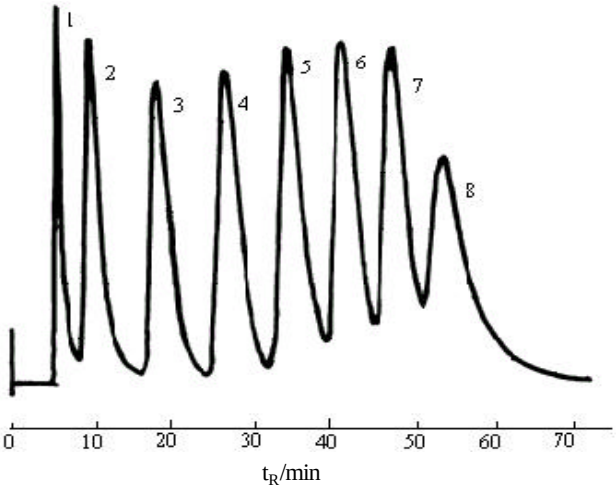
As shown in **Table 2**, the chromatographic retention characteristies of a variety of probe molecules on column packed with Gas Chrom Q coated with cellulose tris (4-metjylbenzoate) were from a variety of interaction forces between probe molecules and stationary phase. These interaction forces were consist of π-π interaction, hydrogen-bonding interaction, dipole-dipole interaction and so on. It indicated that a variety of the organic functional groups on the cellulose tris (4-methylbenzoate) as gas chromatographic stationary phase have important role in the chromatographic separation process. However, values of the heat of adsorption ($-\Delta H_a$) indicated that the interaction between probe molecules and stationary phase lies between physical adsorption and chemical adsorption.

Table 2 Results of determination of heat of adsorption ($-\Delta H_a$) of probe molecules on CTMB

Probe molecule	b. p. (°C)	RMM ($g.mol^{-1}$)	k'^{*}	$-\Delta H_a^{**}$ ($KJ.mol^{1)}$)
Benzene	80.1	78	0.67	37.80
Toluene	110.6	92	1.49	44.16
Chlorobenzene	132	112.6	3.06	37.77
2-Butanone	80.0	72	0.81	46.30
Ethanol	78.0	46	0.36	42.58
1-Butanol	117 .7	74	1.08	46.71
Cyclohexane	80.7	84	0.218	25.46
Hexane	69.0	86	0.103	37.49
1-Heptane	98	100	0.18	48.75
Nitromethane	101.2	61	1.37	41.11
Pyridine	115	79	3.11	40.81

* k' determined at 403K. ** $-\Delta H_a$ determined in range: 363-423K.

Figure 1 Chromatogram of *n*-aliphatic alcohols (C_1-C_8) on glass column packed with Gas Chrom coated with cellulose tris (4-methylbenzoate)



Peaks: 1. methanol, 2. ethanol, 3. 1-propanol, 4. 1-butanol, 5. amyl alcohol, 6. 1-hexanol, 7. 1-heptanol, 8. 1-octanol
Temperature: 65°C, 5 min; 65-150°C, 1°C·min^{-1}, Flow rate of the carrier gas: 20 mL.min^{-1}

The experimental results showed that the heat of absorption on cellulose tris (4-metjylbenzoate) chromatographic stationary phase for cyclohexane was less than that for hexane, but the retention time for cyclohexane was larger than that for hexane. It was shown that the chair or boat-like strucure of cyclohexane matched the structure of cellulose tris (4-methylbenzoate), so that it was easy to insert into the cavity of the spired construction of cellulose tris (4-methylbenzoate). It is indicated that the cavity of the spired construction of cellulos tris (4-methylbenzoate) also plays an important role in the separation process.

The separation of *n*-aliphatic alcohols was successfully carried out on a packed column of Gas Chrom Q coated with cellulose tris (4-methylbenzoate) by temperature programmed gas chromatography (**Figure 1**).

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