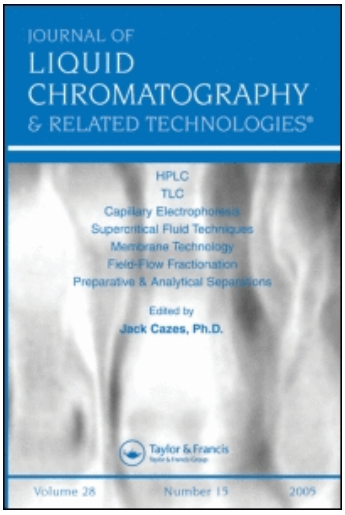

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DETERMINATION OF INTERACTION OF FOOD COMPONENTS WITH MODIFIED GUAR GUM BY HPLC

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ABSTRACT

Interaction of food components such as ascorbic acid, niacin, caffeine and phenylalanine with acrylamide derivatised and acetate modified guar gum was studied by immobilizing the same on silica support and using food based solvent like water as a mobile phase. The thermodynamic parameter such as enthalpy of sorption data were determined from the slopes of plots of lnK' against 1/T. An exothermic adsorption process was indicated for ascorbic acid, niacin and phenylalanine. An endothermic adsorption process for caffeine was observed.

INTRODUCTION

Guar gum, or guaran, is the endosperm polysaccharide of the seed of Cyamopsis tetragonoloba which belongs to Luguminosae family. The plant is cultivated for forage in India, Pakistan and the United States (Texas). Guar gum is a galactomannan which consists of a backbone of (1 → 4)-β-D-mannopyranosyl units with

every second unit bearing a (1 → 6)-α-D-galactopyranosyl unit (1). It is used as a thickening agent and a stabilizer in salad dressings amd ice creams. It promotes longer shelf life in baked goods and lessens absorption of water by sucrose in pastry icings. Guar gum is also used in meat products such as sausage to improve casing stuffing. In addition to its food applications, the guar gum is also used in paper sizing, as a binding and disintegrating agent in tablet formulations, in pharmaceutical jelly formulations, in suspensions, emulsions, lotions, creams and toothpastes. In derivatised form such as an acrylamide adduct, it is used for flocculating slimes (4) of bentonite and kaolin, in increasing dry strength of paper and also in textile print. The application of modified guar gum into food systems has not been reported, but its future usage in this regard can not be ignored. It is, therefore, very important to study its interaction in native or modified form with other food components. The present investigation involves the use of HPLC to study interaction of nonvolatile food components with modified guar gum in the acetylated form which is also derivatised at the sixth carbon atom of galactose side chain with acrylamide to immobilize on the silica support. Food simulating solvent such as water was used as a mobile phase. Changes in thermodynamic parameters such as enthalpy of adsorption was used to conduct such study.

EXPERIMENTAL

Materials

Guar gum, acrylamide, triethylamine, acetylcholine, toluene, caffeine, ascorbic acid, phenylalanine, niacin, trimethylbenzyl ammonium hydroxide and t-butyl alcohol were purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI). Epoxypropyl dimethyl silanized PartiSphere-5 material was obtained from Whatman Inc. (Clifton, NJ).

Packing Material

The packing material for chromatographic purposes was synthesized as follows:

(a) Acrylamide derivatised guar gum: A mixture of guar gum (25 g), acrylamide (25 g) and 40% trimethyl benzyl ammonium hydroxide (15 mL) in 200 mL t-butyl alcohol was stirred at 84°C for 8 hrs. The reaction mixture was cooled to room temperature, filtered and washed with methanol. The acrylamide derivatised product gave the following elemental analysis: C = 41%, H = 6% and N = 1.1%. The elemental analysis of guar gum before reaction was as follows: C = 39.79%, H = 5.9% and N = 0.4% (4).

(b) Immobilization of acrylamide derivatised guar gum on silica support: 2 g of the acrylamide derivatised guar gum was dissolved in 3000 mL water by dispersing the fine powder of the same and then stirring at room temperature overnight. 15 g of epoxypropylsilanized PartiSphere-5 was added to this solution and the reaction mixture was stirred at 90°C for 2 hrs., filtered, washed with hot water and rinsed with methanol. The dry material had the following elemental analysis: C = 2.9%, H = 0.52%, and N = 0.4%. The elemental analysis of the epoxypropylsilanized phase was as follows: C = 1.86%, H = 0.52% and N = 0.1%.

(c) Acetylation of guar gum silanized phase: 5 g of silanized guar gum was acetylated with 5 mL acetyl chloride in presence of 12 mL triethylamine as catalyst and 500 mL toluene as solvent. The reaction was performed at 60°C. The end product had the following elemental analysis: C = 4.5%, H = 0.8% and N = 0.4%. The columns were packed by slurrying in methanol under 6000 psi pressure.

Sample Preparation

Solutions of caffeine, niacin, ascorbic acid, phenol and phenylalanine were prepared by dissolving 50 mg of each in 5 mL water.

HPLC Analysis

HPLC was performed using a variable wavelength UV detector, Spectroflow monitor SF-770 (Kratos Analytical, Ramsey, NJ); a programmable solvent delivery system, Series 3B (Perkin-Elmer Corp., Norwalk, Conn.); a manual injection valve, with 50 μl loop (Valco Instruments Co., Houston, TX) and a chart recorder (Laboratory Data Control, Riviera Beach, FL).

Water was used as a mobile phase. A flow rate of 1 mL/min was maintained during the run. All the samples were analyzed at various temperatures i.e. from 20°C to 70°C by phenol as reference sample to provide the unretained peak. The enthalpy changes were determined from the slope of the plots of ln K′ against 1/T using the equation 1 (2, 3, 5, 6).

$$\ln K' = \Delta H^0/RT - \Delta S^0/R + \ln\phi \qquad \text{(Equation 1)}$$

RESULTS AND DISCUSSION

The guar gum is derivatised with acrylamide at the sixth carbon atom of α-D-galactopyranosyl side unit which is attached by (1 → 6) linkages to linear chains of (1 → 4)-β-D-mannopyranosyl units. This derivatised gum is immobilized as hydroxylamine when reacted with epoxypropyl silanized silica gel. The remaining hydroxyl groups are esterified after reacting with acetyl chloride.

The equation 1 shows the relationship between capacity factor K′ and the column absolute temperature T (2, 3, 5, 6). Here ΔH^0 represents standard enthalpy change on transferring a solute from stationary phase to a mobile phase, ΔS^0 is the standard entropy change and ϕ is the phase ratio of the column. The magnitude of ΔH^0 value can decide the nature of interaction of solute molecule with the stationary phase.

Figures 1-4 represent the plot of ln k′ or capacity factor against 1/T for ascorbic acid, niacin, phenylalanine and

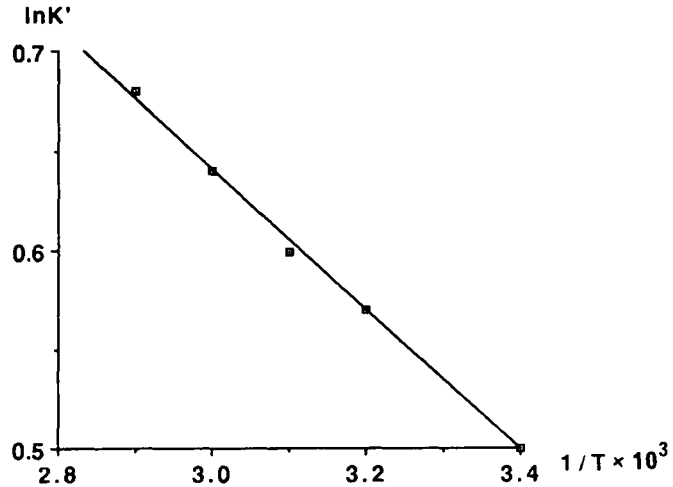

Fig. 1. Plot of lnK' against 1/T in case of ascorbic acid as analyzed on modified guar gum column.

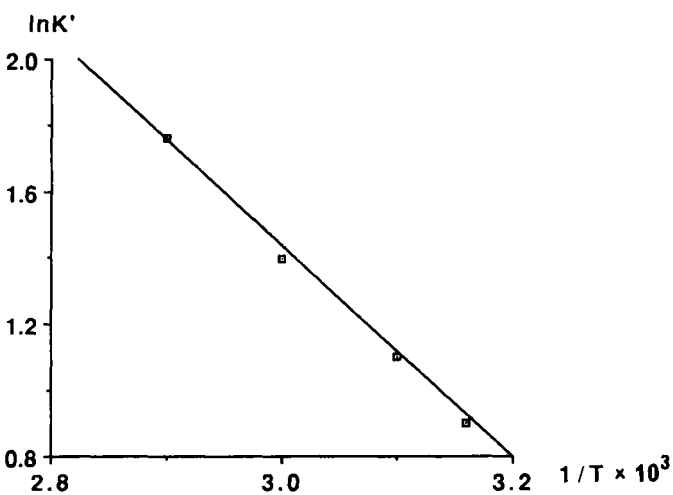

Fig. 2. Plot of lnK' against 1/T in case of niacin as analyzed on modified guar gum column.

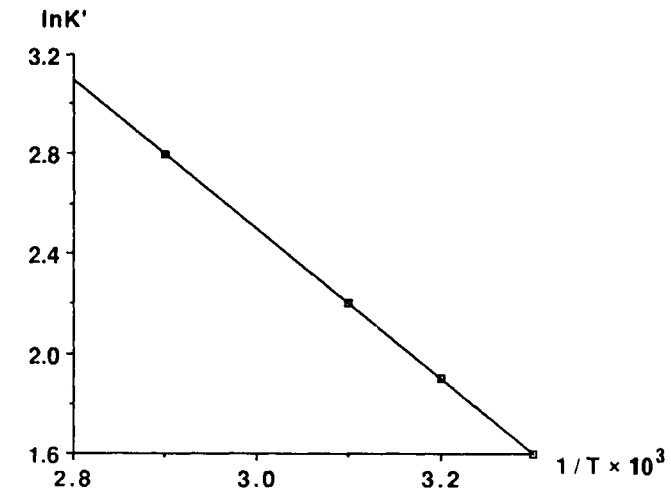

Fig. 3. Plot of lnK' against 1/T in case of phenylalanine as analyzed on modified guar gum column.

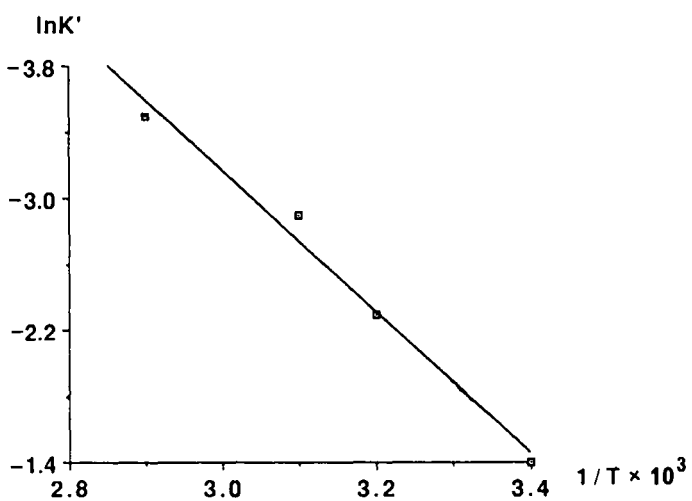

Fig. 4. Plot of lnK' against 1/T in case of caffeine as analyzed on modified guar gum column.

Table 1. Enthalpy of sorption of ascorbic acid, niacin, caffeine and phenylalanine as determined from Figures 1-4.

Components	Δ H (K cal/mol)
Ascorbic	- 0.3
Niacin	- 3.3
Caffeine	+ 4.2
Phenylalanine	- 3.0

caffeine. The values of ΔH^0 as determined from the slopes of the graphs are shown in the Table 1.

Enthalpy of sorption showed negative values for ascorbic acid, niacin and phenylalanine. The negative values indicated an exothermic adsorption process. It showed that there is interaction of all these probes with the carbohydrate or hydrocolloid surface due to O--H or N--H bond formation.

Enthalpy of sorption showed positive value in case of caffeine which indicated an endothermic adsorption process. It showed that caffeine interacts with the surface due to mechanism other than hydrogen bonding. Such interaction may involve hydrophobic and or electrostatic forces.

The interaction of ascorbic acid, niacin, phenylalanine and caffeine with the silica bound guar gum acetate can be depicted as shown in the Figures 5 and 6. Ascorbic, niacin and phenylalanine seem to be approaching the surface in such a manner as can facilitate their retention through hydrogen bonding between -OH, $-NH_2$ or -COOH of the guar gum. In the case of caffeine, it is associating with surface in a manner which does not allow the formation of any kind of hydrogen bonding.

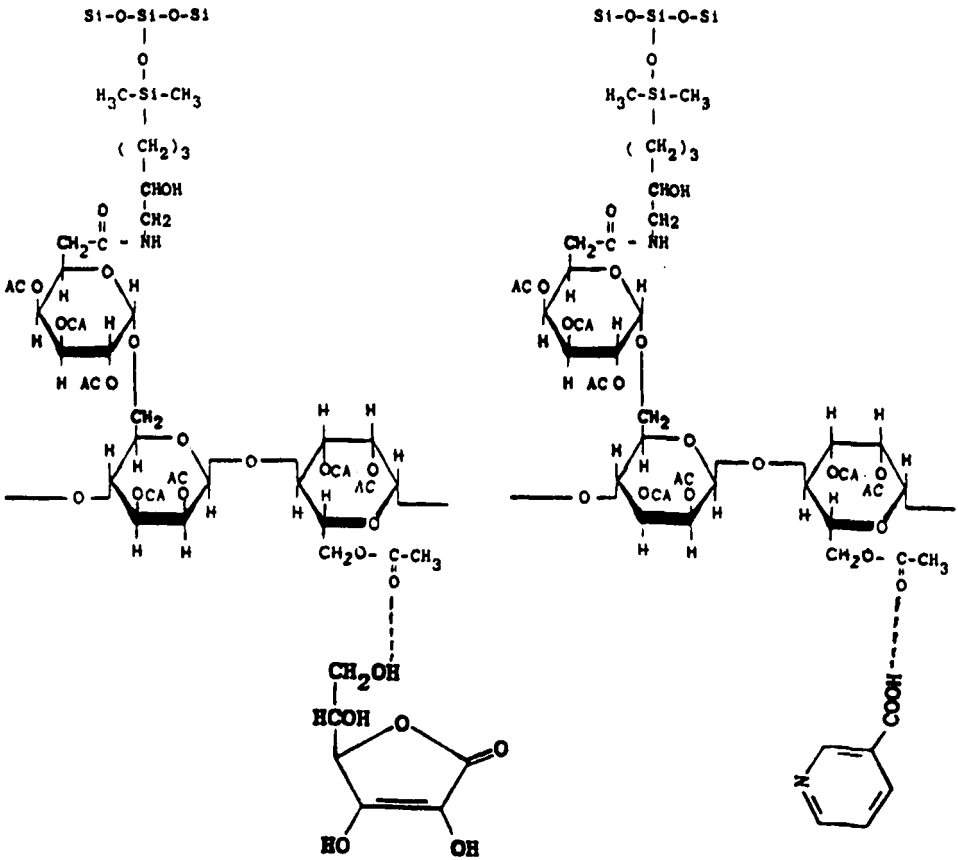

Fig. 5. Projected interaction of ascorbic acid and niacin with the modified guar gum silica support surface.

Figures 7A and 7B show the resolution of ascorbic acid, niacin, phenylalanine and caffeine at 20°C and 70°C. The caffeine shows more change in retention time at 70°C as compared to ascorbic acid, niacin and phenylalanine which exhibit very little or no change at all. It shows that caffeine has less surface interaction as compared to the rest of the components under investigation despite it is more retained on the surface.

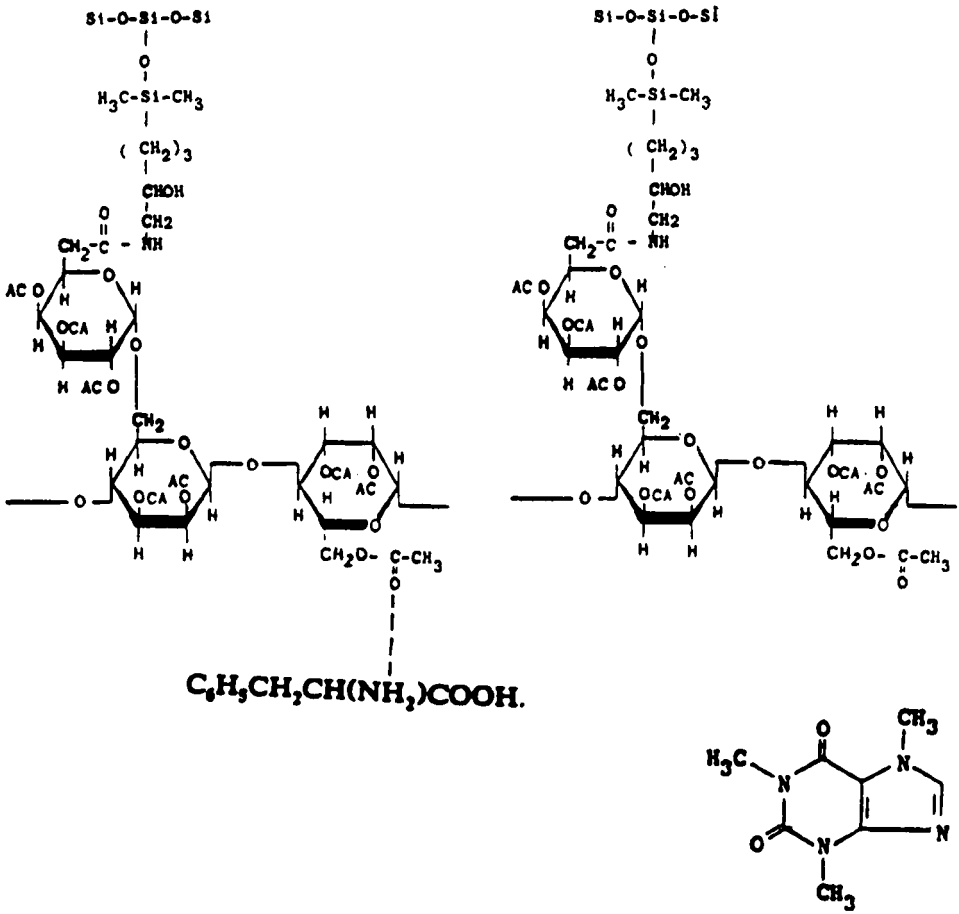

Fig. 6. Projected interaction of phenylalanine and caffeine with the modified guar gum silica support surface.

It is easier to study interaction of guar gum in the acetylated form as compared to its native form which has hydroxyl groups available in abundance to bind many fold of water molecules and thus making it less accessible to other food additives to conduct such investigations. The incorporation of

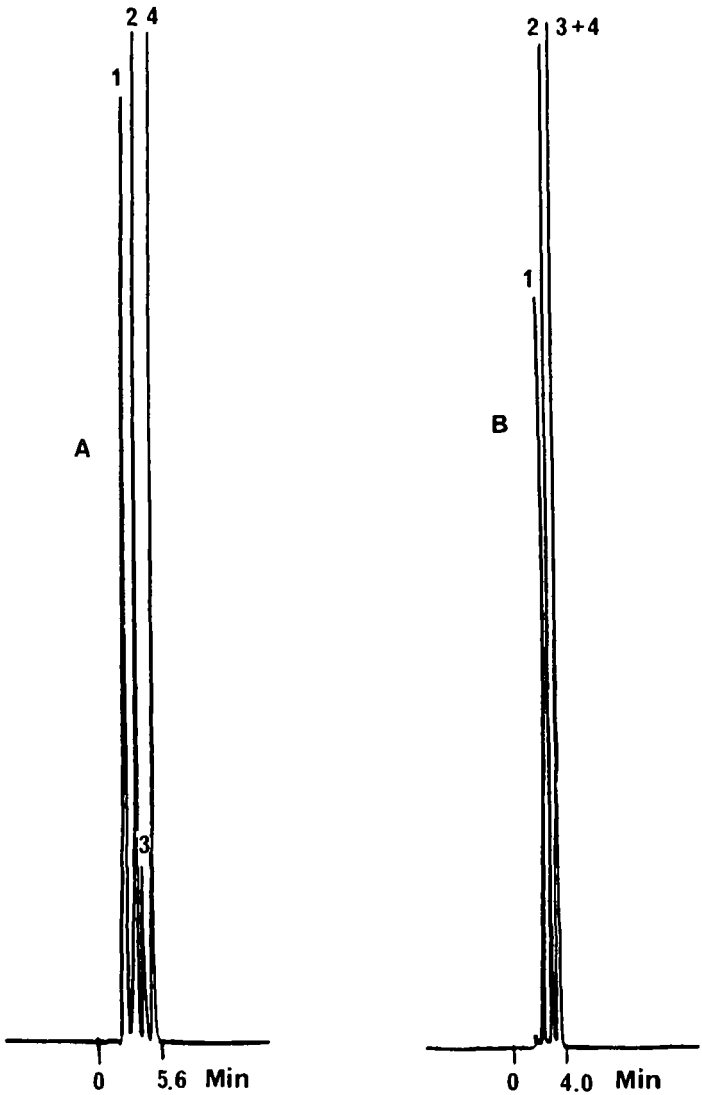

Fig. 7. Resolution of food components on modified guar gum-PartiSphere-5 column (20 cm x 4.6 mm, I.D.) at 20°C (Fig. 7A) and 70°C (Fig. 7B).
Mobile phase: water; Flow rate: 1 mL/min; λ_{max} = 254; Sample size = 10 µL.
1. Ascorbic acid, 2. Niacin, 3. Phenylalanine, 4. Caffeine.

ester groups in the guarn molecular skeleton makes it possible for the immobilized polysaccharide to compete with water and nonvolatile food components simultaneously.

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