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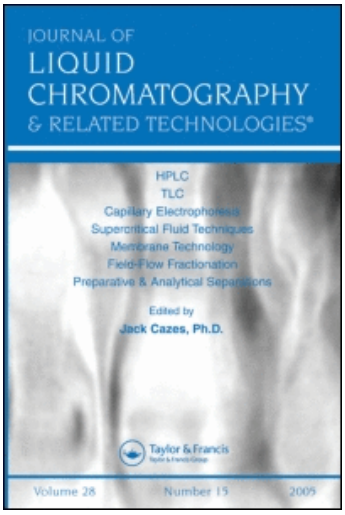

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EVALUATION OF POLYTRIPHENYLMETHYL METHACRYLATE FOR FOOD PACKAGING BY DETERMINING INTERACTIONS USING HPLC

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ABSTRACT

Polytriphenylmethyl methacrylate was evaluated for food packaging by determining interactions with food components such as ascorbic acid, niacin, phenylalanine and caffeine. The polymer was covalently bonded on silica surface by polymerizing monomer of the same with vinylic bonded silica gel. Food based solvent like water was used as a mobile phase. Enthalpy of sorption data were used to determine mechanism of interactions. Other thermodynamic parameters such as Gibb's free energy and activity coefficient were used to determine magnitude and kind (weak or strong) of interactions. Suitability of the polymer for packaging food system containing ingredients under investigation was determined from activity coefficient values.

INTRODUCTION

It is important to evaluate a packaging material as migration of residual substances from packaging into food or of the nutrients

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from food into the packaging matrix can cause problems. For example, the loss of orange flavor from orange juice stored in a plastic bottle is a common consumer complaint. The suitability of a polymeric material for packaging food and drugs can, therefore, be determined by studying its interaction with various food components. Inverse gas chromatography has been used to examine interaction of volatile food components with packaging materials (1-2). HPLC has been exploited to investigate interaction of nonvolatile polymers such as polyvinyl alcohol with food ingredients (3). Thermodynamic parameter such as enthalpy of adsorption, was used to conduct such study. During the present investigation, use of HPLC has been further extended to examine interaction of a polymeric material such as polytriphenylmethyl methacrylate and evaluate it for food packaging by using thermodynamic parameters such as enthalphy of adsorption, Gibb's free energy and activity coefficient. The polymer was immobilized on silica support by polymerizing the monomer of the same on vinyl bonded silica gel. In the previous studies (3), polyvinyl alcohol was immobilized by reacting the same with glycidoxy propyl bonded silica support.

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EXPERIMENTAL

Materials

Ascorbic acid, niacin, phenylalanine, caffeine, phenol, sodium peroxide, triphenylmethyl methacrylate and vinyl dimethylchlorosilane were purchased from Aldrich Chemical Co. (Milwaukee, WI). Spherical silica was obtained from Whatman Specialty Products, Inc. (Fairfield, NJ).

Preparation of Packing Material

Vinyl bonded silica (A) was obtained by reacting 40g of spherical silica with 11g of vinyldimethylchlorosilane in toluene at 70°C.

Polytriphenylmethyl methacrylate bonded phase was synthesized by reacting 2.5 g of triphenylmethyl methacrylate with 10 g of vinyl

bonded silica (A) in acetonitrile at 80°C using 0.6 g of sodium peroxide as a catalyst. The final product was extracted with chloroform in Soxhlet apparatus to remove excess of unattached polymer from silica surface. The product was further treated with trimethylchlorosilane at 80°C to cap residual silanols.

The column was packed by slurrying the bonded phase in methanol and applying 5000 psi pressure.

Sample Preparation

The solution of ascorbic acid, niacin, phenylalanine and caffeine were prepared by dissolving 20 mg of the same in 20 ml of water.

HPLC Analysis

HPLC analysis was performed by 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). The column was run by using water as a mobile phase. Phenol was used as a reference. The enthalpy changes were determined from the slope of the plot of lnK′ vs 1/T by using the equation 1 (4-8)

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

Here K′ = capacity factor, T = column absolute temperature, ΔH° = standard enthalpy change on transferring a solute from the stationary phase, ΔS = standard entropy change and ϕ is the phase ratio.

The equation 2 and 3 were used to determine thermodynamic parameters such as ΔG or Gibb's free energy and γ, the activity coefficient (9-10).

$$\Delta G = \Delta H^\circ - T\Delta S \qquad \text{(Eq. 2)}$$

$$\Delta G = - RT \ln\gamma \qquad \text{(Eq. 3)}$$

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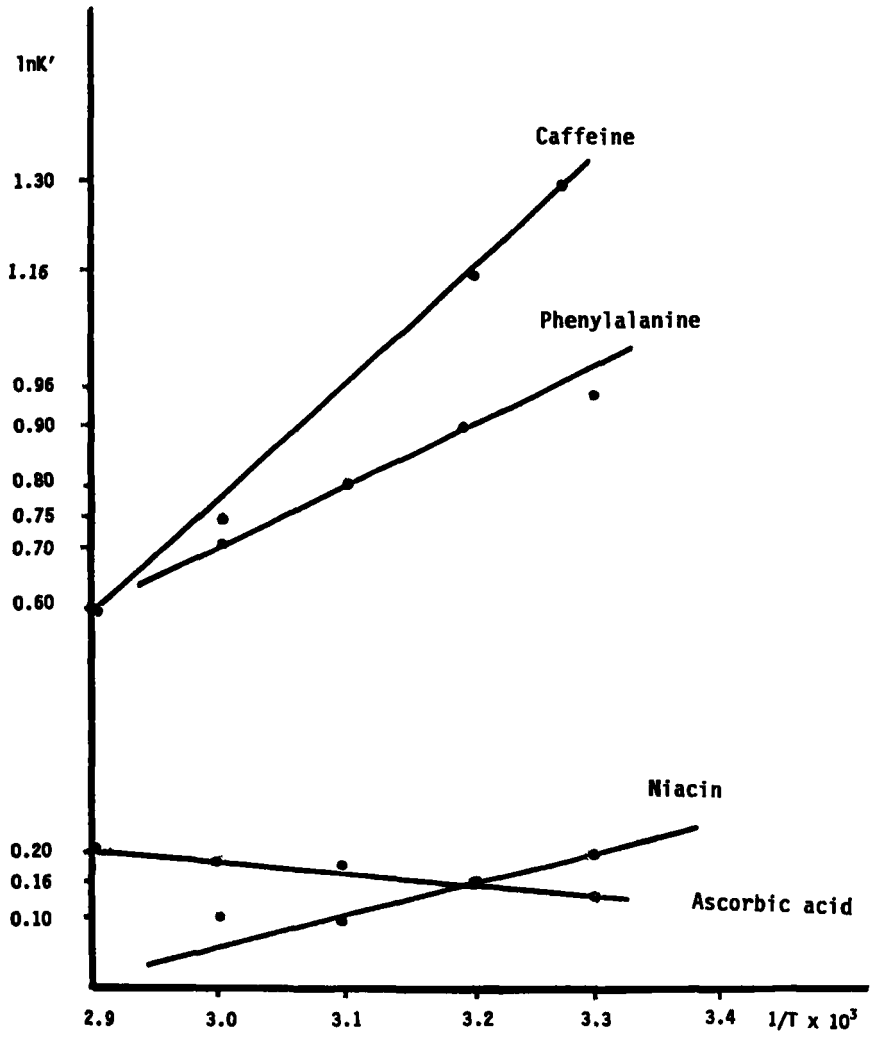

Fig. 1. Plots of lnK' or capacity factor against 1/T in case of ascorbic acid, niacin, phenylalanine and caffeine. Here T is the column absolute temperature. Column: polytriphenylmethyl methacrylate-PartiSphere 5 Silica (25 x 4.6 mm, I.D.). Mobile phase: water at 1 mL/min; λ_{max}: 280 nm; sample size: 10 uL.

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Table I. Enthalpy of sorption of ascorbic acid, niacin, phenylalanine and caffeine as derived from the plots of lnK' against 1/T. Column: Polytriphenylmethyl methacrylate immobilized silica.

Components	ΔH° (K Cal/mole)
Ascorbic acid	- 0.20
Niacin	+ 0.40
Phenylalanine	+ 0.87
Caffeine	+ 0.18

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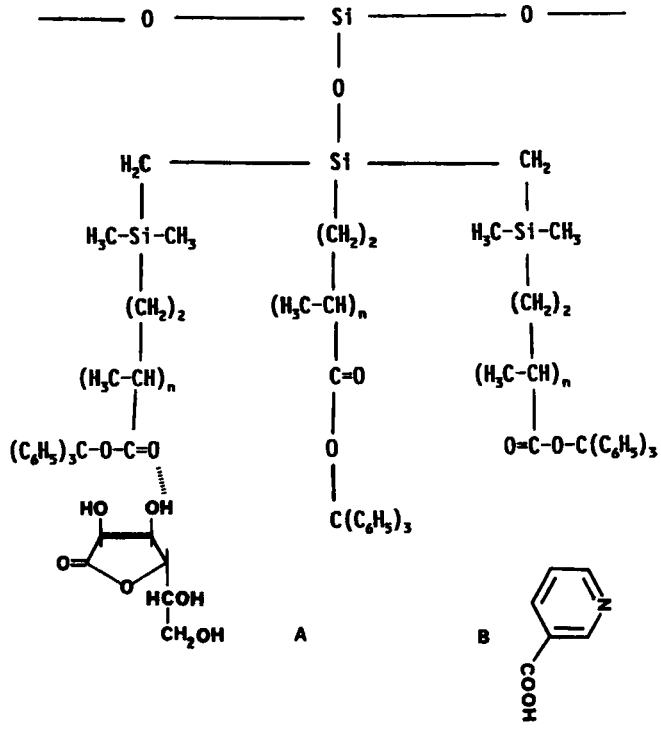

Fig. 2. Interaction of ascorbic acid and niacin with polytriphenylmethyl methacrylate surface.

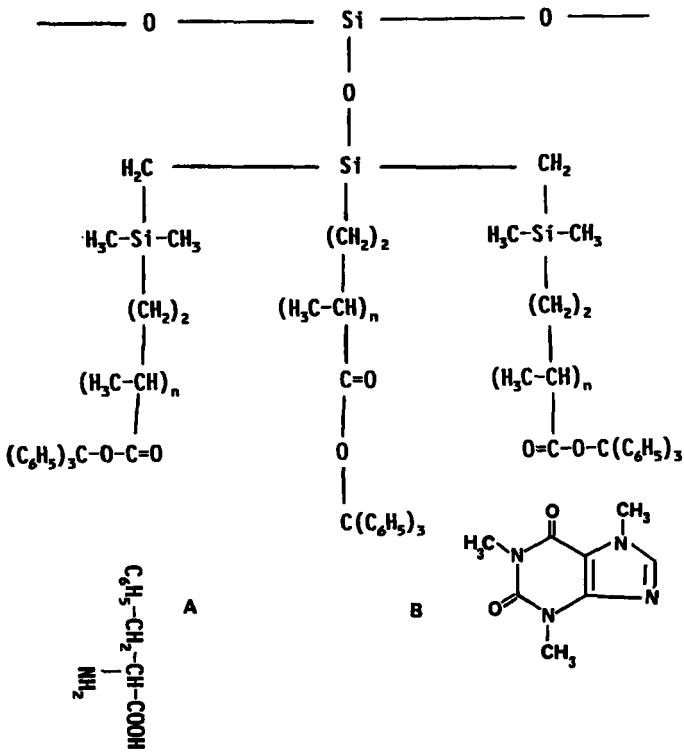

Fig. 3. Interaction of phenylalanine and caffeine with polytriphenylmethyl methacrylate surface.

RESULTS AND DISCUSSION

It is possible to determine the nature or mechanism of interactions, i.e. hydrogen bonding and hydrophobic etc. from ΔH° values (1-2). An exothermic adsorption process or retention by hydrogen bonding is indicated from negative ΔH° values, In case of positive ΔH° values, an endothermic adsorption process or hydrophobic interactions is indicated (1-2).

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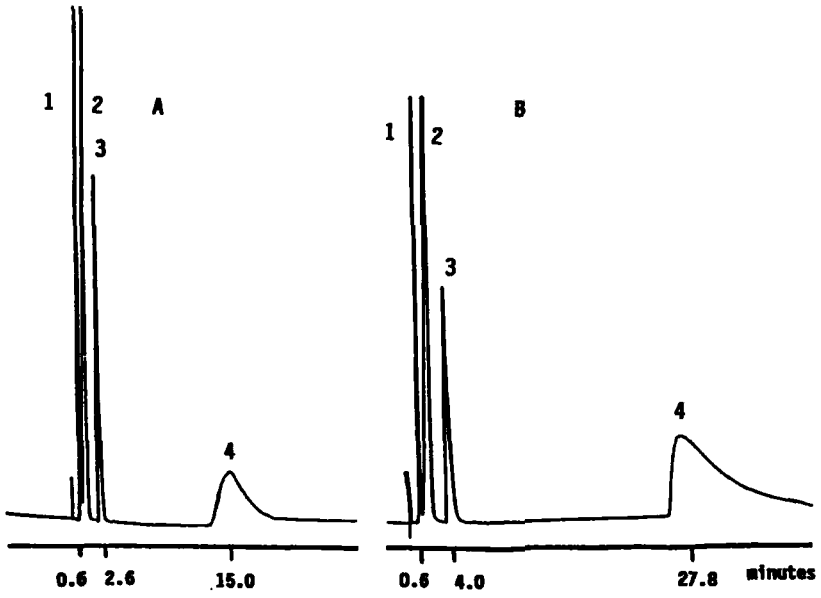

Fig. 4. Resolution on polytriphenylmethyl methacrylate-Parti-Sphere 5 Silica column (25 x 4.6 mm, I.D.) at 40° C (A) and 70° C (B); Mobile phase: water at 1 ml/min; λ_{max}: 280 nm. 1. ascorbic acid, 2. niacin, 3. phenylalanine, 4. caffeine.

The magnitude or kind (weaker or stronger) of interactions can be determined from activity coefficient values. The higher γ values, i.e. 1 or more than 1 will indicate the weaker interactions while the lower γ values such as 0.9 or less than 0.9, determine the existence of stronger surface interactions (9-10).

Figure 1 shows the $\ln K'$ against temperature plots of the probes and ΔH° values derived from the slopes of these plots are shown in Table I.

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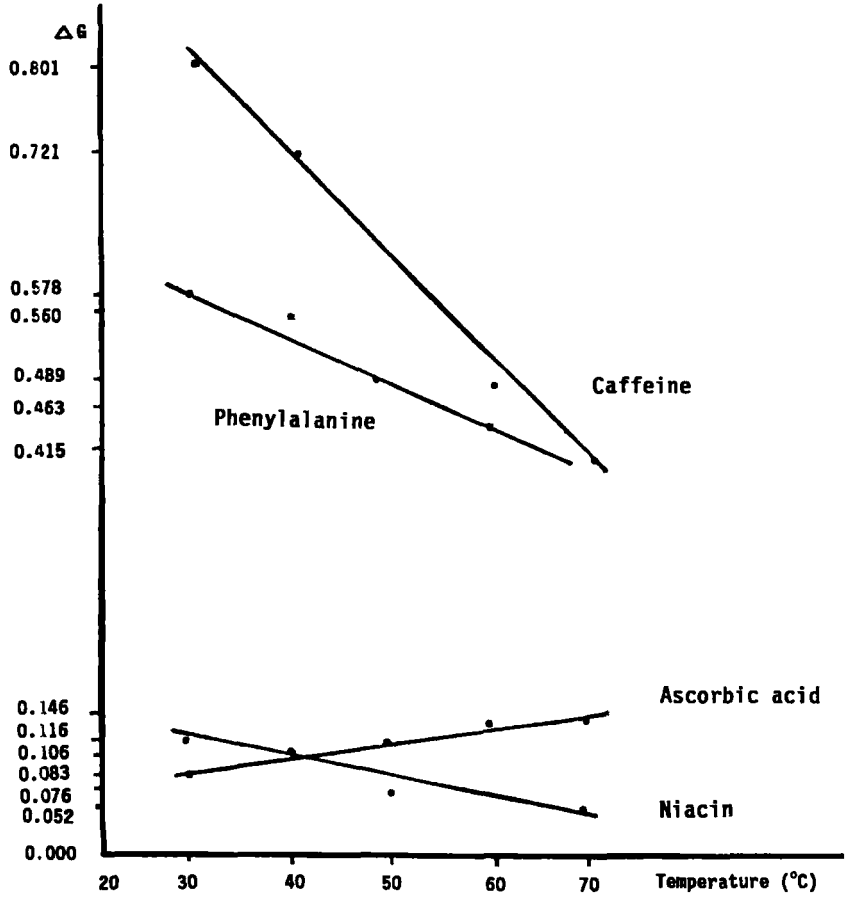

Fig. 5. Plot of ΔG's against temperature in case of ascorbic acid, niacin, phenylalanine and caffeine. Column: polytriphenylmethyl methacrylate-PartiSphere 5 Silica column (25 x 4.6 mm, I.D.).

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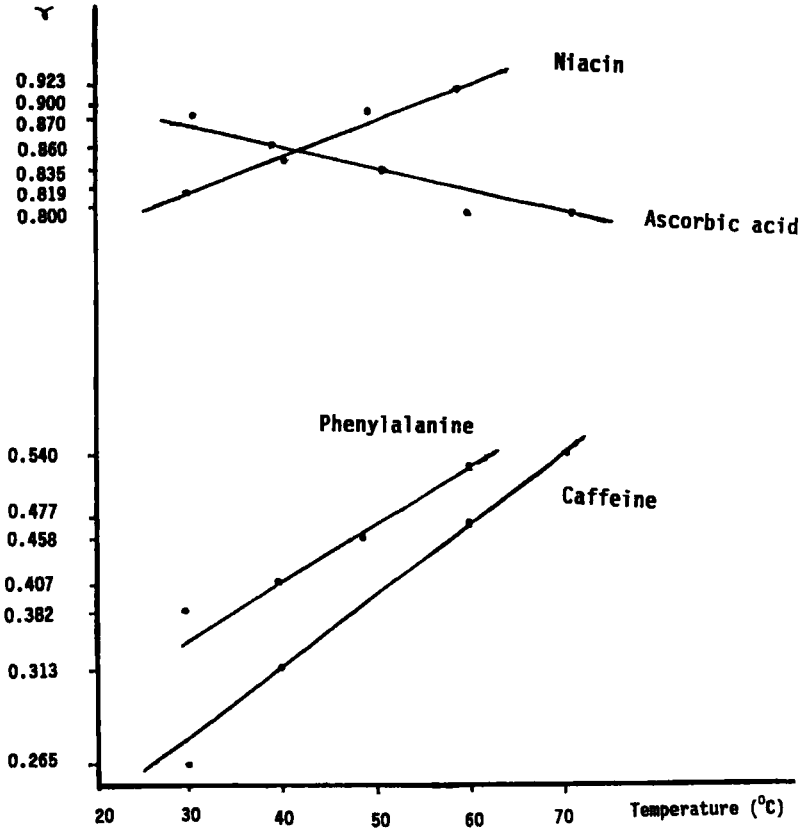

Fig. 6. Plot of activity coefficient γ against 1/T in case of ascorbic acid, niacin, phenylalanine and caffeine. Column: polytriphenylmethyl methacrylate-PartiSphere 5 Silica column (25 x 4.6 mm, I.D.).

The negative ΔH° value in case of ascorbic acid shows an exothermic adsorption process which indicates the involvement of polar group such as -OH etc. to form hydrogen bond with the surface. The positive value in case of rest of the components shows an endothermic adsorption process which indicates their retention due to hydrophobic mechanism. A possible projection of

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the interaction of these probes is shown in Figures 2 and 3. Ascorbic acid is retained through hydrogen bond formation between -OH and -C=O groups of ascorbic acid and surface respectively. The other components i.e. niacin, phenylalanine and caffeine are interacting through hydrophobic forces.

Figures 4A and 4B represent resolution of various probes on polytriphenylmethyl methacrylate bound silica column at 40°C and 70°C. Caffeine shows more change in retention time as compared to other components. The higher retention time of caffeine at various temperatures indicates that it has more surface interaction than the rest of components under investigation. The higher ΔG values (Fig. 5) of caffeine confirm the fact . The ΔG value decreases rapidly with the change of temperature which shows that interaction in case of caffeine is affected more with the change of temperature as compared to the other components.

Figure 6 shows the activity coefficient plots on polytriphenylmethyl methacrylate bound silica surface. All these components have values either 0.9 or less than 0.9 which indicate their stronger surface interactions. It is clear from γ values that change in interaction is more pronounced in case of caffeine and phenylalanine. The stronger interaction of all these components indicates that these ingredients will migrate from food into the packaging matrix of polytriphenylmethyl methacrylate, therefore, it is unsuitable to be used as a packaging material for food systems containing all or any of these ingredients under investigation.

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