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EVALUATION OF POLYMETHACRYLIC ACID FOR FOOD PACKAGING BY EXAMINING INTERACTIONS USING HPLC

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ABSTRACT

Interaction study of polymethacrylic acid with food components like ascorbic acid, niacin, phenylalanine and caffeine was conducted by immobilizing the same on silica support and using food based solvent like water as a mobile phase. The mechanism of interactions was determined from thermodynamic parameter such as enthalpy of sorption data. The Gibb's free energy and activity coefficient data were used to determine magnitude and kind (weak or strong) of interactions. From these thermodynamic data, it was possible to study migration and suitability of the polymer to be used as a packaging material.

INTRODUCTION

Many kinds of polymeric packaging materials are used for food and drugs. The residual substances from packaging matrix can migrate into container contents. On the other hand, the container content like food can also lose nutrients by migration into

packaging matrix. The loss of orange flavor from orange juice stored in a plastic bottle is a common consumer complaint. It has, therefore, become important to study interaction and evaluate packaging materials. Inverse gas chromatography has been applied to investigate interaction of volatile food components with packaging materials (1-2). In case of nonvolatiles, HPLC has been applied to investigate interaction of polymeric oligomers from polyvinyl alcohol with food and polyvinyl alcohol packaging matrix (3). Thermodynamic parameter such as enthalpy of adsorption, was used to conduct such study. In the present investigation, thermodynamic parameters like Gibb's free energy and activity coefficient along with enthalpy of adsorption were used to study magnitude, kind (weaker or stronger) and mechanism of interaction of nonvolatile food components with polymethacrylic acid. Suitability of the polymethacrylic acid for food packaging was determined from these thermodynamic parameters.

HPLC was performed on polymeric stationary phase of polymethacrylic acid monomer on vinyl bonded silica phase. In the previous investigation (3), polyvinyl alcohol was immobilized by reacting the same with glycidoxy bound silica support.

EXPERIMENTAL

Materials

Methacrylic acid, caffeine, niacin, phenyl alanine, phenol, ascorbic acid, and sodium peroxide were purchased from Aldrich Chemical Co. (Milwaukee, WI). The vinyl bonded silica gel was obtained from Whatman Specialty Products, Inc. (Fairfield, NJ).

Preparation of Packing Material

Polymethacrylic acid was immobilized by reacting 18 g of methacrylic acid with 25 g of vinyl bonded silica in acetonitrile using 0.6 g of sodium peroxide as catalyst. The unattached free polymer was extracted from immobilized polymer with chloroform in Soxhlet apparatus.

The column was packed by slurring 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 μ l 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 to provide an unretained peak.

The enthalpy changes were derived from the slope of the plots of $\ln K'$ vs $1/T$ by using the equation 1 (4-8)

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

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 ϕ , the activity coefficient (9-10).

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

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

RESULTS AND DISCUSSION

The nature and mechanism of interactions, i.e. hydrogen bonding and hydrophobic etc. can be determined from ΔH° values (1-2). The negative ΔH° values indicate an exothermic process or retention by hydrogen bond formation through polar groups. On the other hand, the positive ΔH° values is an indication of an endothermic adsorption process or hydrophobic interactions (1-2). The

magnitude or extent of interactions can be realized from ΔG or Gibb's free energy values and γ , or the activity coefficient can determine the kind (weaker or stronger) of interactions (9). The higher γ values, i.e. 1 or more than 1 will indicate the weaker interactions, and the lower γ values such as 0.9 or less than 0.9, determine the existence of stronger surface interactions (9).

Figure 1 shows the $\ln K'$ against temperature plots of various probes on polymethacrylic acid immobilized silica column. Enthalpy of sorption as determined from the slopes of these plots are exhibited in Table 1.

Enthalpy values are negative in the case of ascorbic acid, niacin and phenylalanine which indicate an exothermic adsorption process. It indicates that these components are retained on the surface due to hydrogen bond formation. The positive value in case of caffeine exhibit and endothermic adsorption process which indicates interaction due to hydrophobic forces. A possible interaction of these probes is projected in Figures 2 and 3. In case of ascorbic acid, niacin and phenylalanine, the polar groups

Table I. Enthalpy of sorption of ascorbic acid, niacin, phenylalanine and caffeine as derived from the plots of $\ln K'$ against $1/T$. Column: Polymethacrylic acid immobilized silica.

Components	ΔH° (K Cal/mole)
Ascorbic acid	- 0.175
Niacin	- 0.127
Phenylalanine	- 2.400
Caffeine	+ 1.670

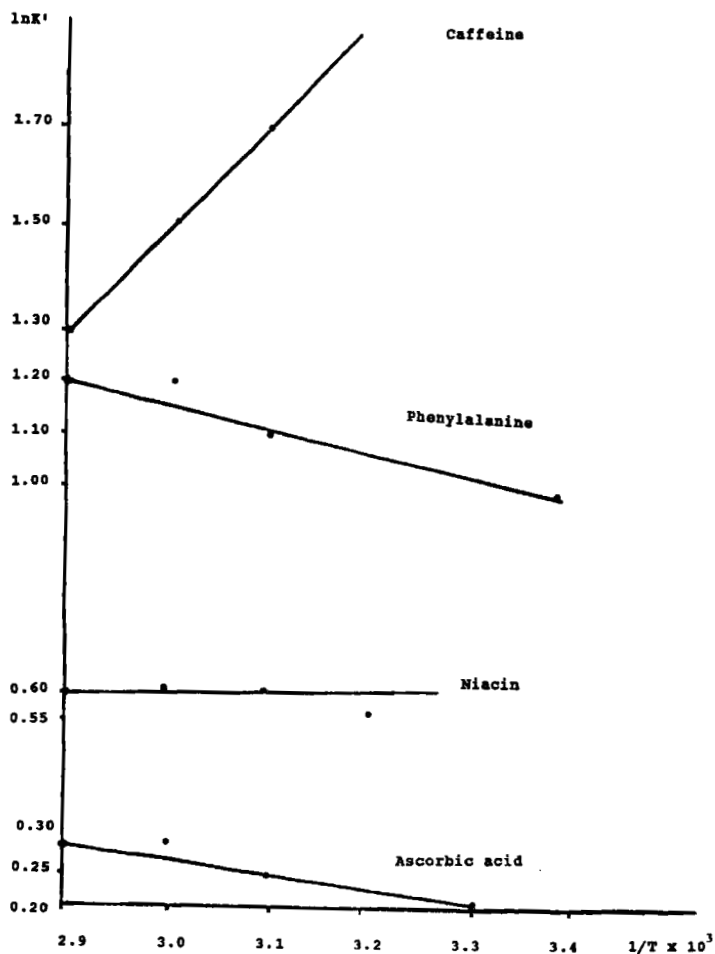


Fig. 1. Plots of $\ln K'$ or capacity factor against $1/T$ in case of ascorbic acid, niacin, phenylalanine and caffeine. Here T is the column absolute temperature. Column: polymethacrylic acid-PartiSphere 5 Silica (25 x 4.6 mm, I.D.). Mobile phase: water at 1 mL/min; λ_{\max} : 280 nm; sample size: 10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

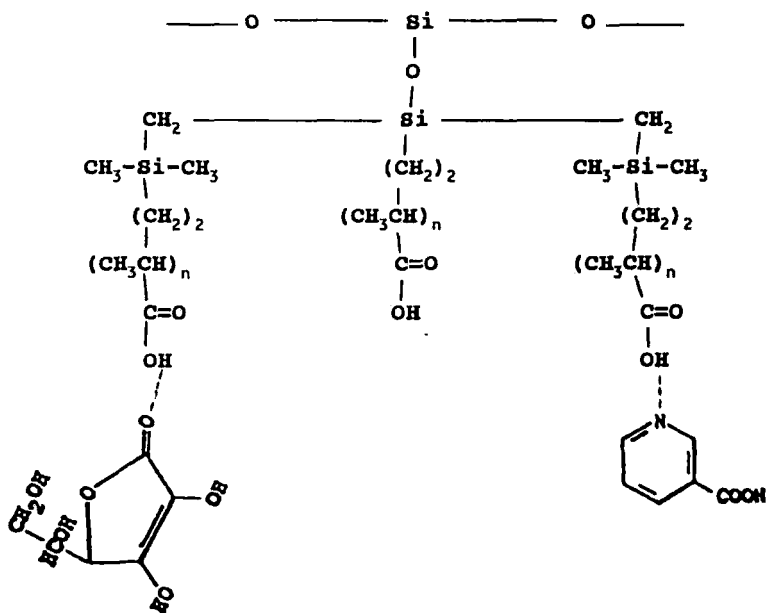


Fig. 2. Interaction of ascorbic acid and niacin with polymethacrylic acid on Partisphere 5 Silica.

such as $-C=O$, $=N-$ and $-NH_2$ are involved in forming hydrogen bond with $-COOH$ groups of the surface.

Figure 4 exhibits resolution of probe molecules on polymethacrylic immobilized silica column at 40°C and 70°C . The caffeine has more surface interaction as compared to other components which may due to its higher retention times. A small change in retention time of the other three components shows that their interaction does not change much as the temperature is increased. In case of caffeine, more change in interaction with the change in temperature is observed due its wide range in retention times at different temperatures. The higher surface interaction of caffeine can be further verified from ΔG or Gibb's free energy values at different temperatures. The higher ΔG (Fig.

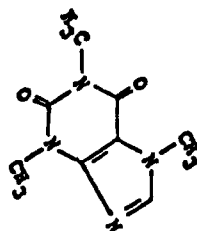
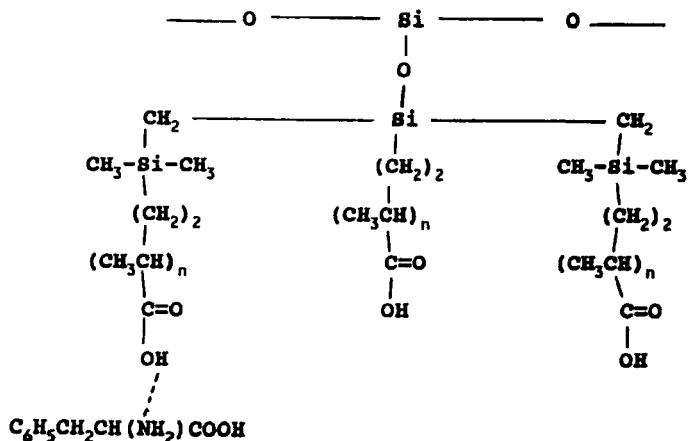


Fig. 3. Interaction of phenylalanine and caffeine with polymethacrylic acid on PartisSphere 5 Silica.

5) values of caffeine confirm the fact that it has more surface interaction than the other probes.

Figure 6 represents the plots of activity coefficient γ against temperature in case of ascorbic acid, niacin, phenylalanine and caffeine. The activity coefficient values of caffeine change rapidly with the increase of temperature whereas it shows a small change in case of other probes. Overall, the γ values of all these components are less than 0.9 which indicates stronger interaction of these probes with the polymeric surface of methacrylic acid. It is possible that all these nutrients will migrate from food into

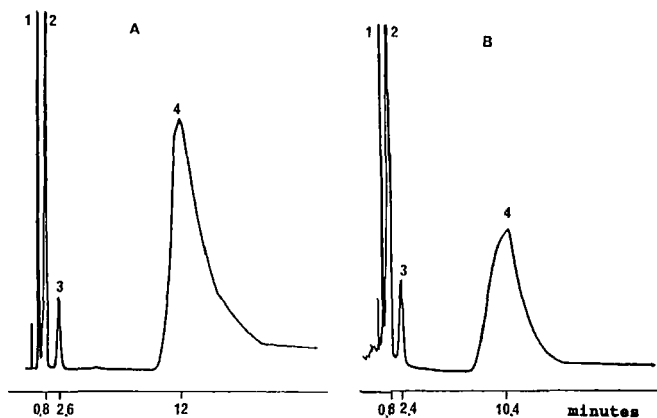


Fig. 4. Resolution on polymethacrylic acid-PartiSphere 5 Silica column (25 x 4.6 mm, I.D.) at 40° C (A) and 70° C (B); Mobile phase: water at 1 ml/min; λ_{max} : 280 nm. 1. ascorbic acid, 2. niacin, 3. phenylalanine, 4. caffeine.

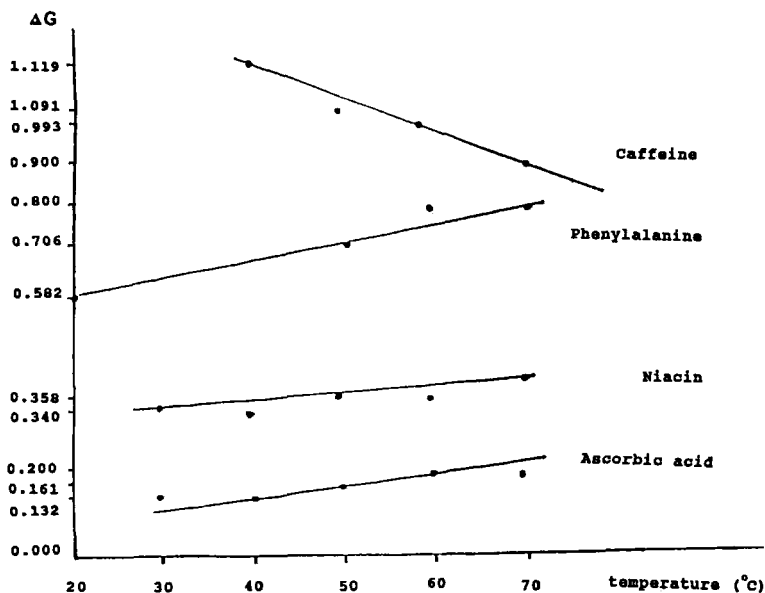


Fig. 5. Plot of ΔG 's against temperature in case of ascorbic acid, niacin, phenylalanine and caffeine. Column: polymethacrylic acid-PartiSphere 5 Silica column (25 x 4.6 mm, I.D.).

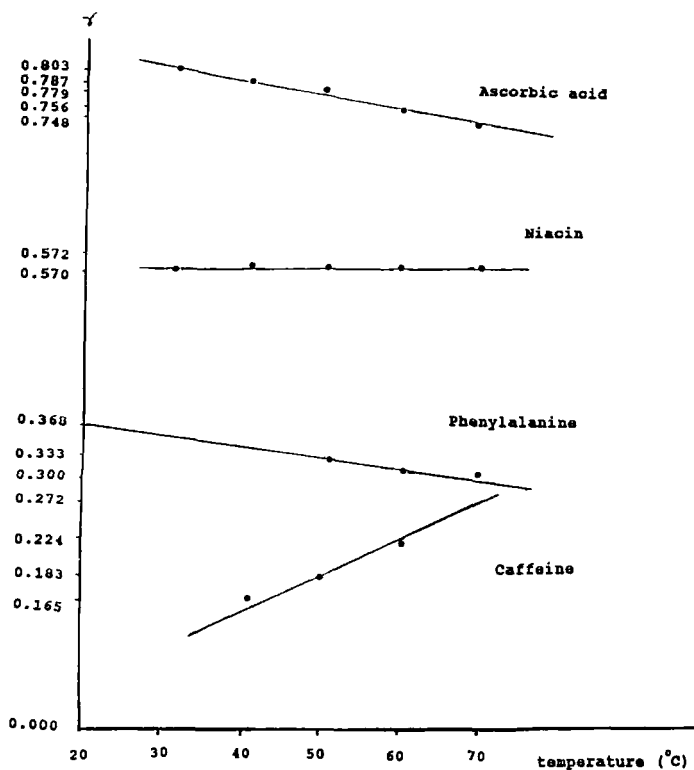


Fig. 6. Plot of activity coefficient γ against $1/T$ in case of ascorbic acid, niacin, phenylalanine and caffeine. Column: polymethacrylic acid-PartiSphere 5 Silica column (25 x 4.6 mm, I.D.).

polymeric matrix of methacrylic acid. Polymethacrylic acid, therefore, will be unsuitable to be used as a packaging food systems containing all or any of these components.

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