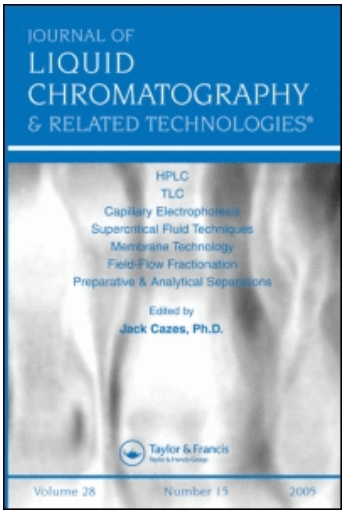

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Evaluation of Polyvinyl Acetate for Food Packaging by Studying Interactions Using HPLC

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To cite this Article Khurana, Amrik L. and Ho, Chi-Tang(1991) 'Evaluation of Polyvinyl Acetate for Food Packaging by Studying Interactions Using HPLC', Journal of Liquid Chromatography & Related Technologies, 14: 18, 3425 — 3437
To link to this Article: DOI: 10.1080/01483919108049400
URL: http://dx.doi.org/10.1080/01483919108049400

JOURNAL OF LIQUID CHROMATOGRAPHY, 14(18), 3425-3437 (1991)

EVALUATION OF POLYVINYL ACETATE FOR FOOD PACKAGING BY STUDYING INTERACTIONS USING HPLC

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ABSTRACT

Polyvinyl acetate was evaluated for food packaging by studying interactions with food nutrients like ascorbic acid, niacin, phenylalanine and caffeine. The polymer was immobilized on silica support and food based solvent like water used as a mobile phase. Thermodynamic parameters such as enthalpy of sorption, Gibb's free energy and activity coefficient data were used to determine mechanism, magnitude and kind (weak or strong) of interactions. Possibility of migration of the nutrients into the polymer and its suitability as a packaging matrix was concluded from the activity coefficient values.

INTRODUCTION

It is important to study interaction of polymeric materials with food nutrients as the migration of the residual components from packaging into food, or of the nutrients from food into

packaging matrix is of serious consumer concern. For example, the loss of orange flavor from orange juice packaged into polymeric plastic bottles is a common complaint by consumers. Therefore, it is possible to evaluate a polymeric material for food packaging by examining its interaction with container contents. Gas chromatography (1-2) is used to study interaction of volatile food components with packaging materials. HPLC has been used (3) to investigate interaction of nonvolatile food nutrients with polymer such as polyvinyl alcohol. Thermodynamic parameter such as enthalpy of sorption was used to conduct such study. During the present investigation, use of HPLC has been further extended to examine the interaction of polymeric materials such as polyvinyl acetate. Nonvolatile food ingredients such as ascorbic acid, niacin, phenylalanine and caffeine were used for this purpose. Thermodynamic parameters, such as enthalpy of sorption, Gibb's free energy and activity coefficient were used to pursue such studies. The monomer such as vinyl acetate was polymerized on silica gel to generate a covalently bonded polymeric stationary phase on silica-surface. In the previous publication (3), polyvinyl alcohol was immobilized by reacting the same with epoxy bonded silica support.

EXPERIMENTAL

Materials

Ascorbic acid, niacin, phenyl alanine, caffeine, phenol and vinyl acetate were purchased Aldrich Chemical Co. (Milwaukee, WI). Spherical silica gel (5 μm) was obtained from Whatman Speciality Products, Inc. (Fairfield, NJ).

Preparation of Packing Material

The vinyl bonded silica (A), used for synthesizing low carbon load polymer, was prepared by reacting 40 g of spherical silica gel at 70° C with 3 g of vinyldimethylchlorosilane in toluene. In case of vinyl bonded silica used to synthesize heavy carbon load

polymer, 40 g of the spherical silica was reacted at 70° C with 11 g of vinyldimethylchlorosilane in toluene (B).

The low carbon load polyvinyl acetate was synthesized by reacting 6 g of vinyl acetate monomer with 15 g of vinyl bonded silica (A) in acetonitrile at 80° C by using 0.6 g of sodium peroxide as catalyst. The heavy carbon loaded polyvinyl acetate was synthesized under the similar conditions by reacting 18 g of monomer with 15 g of vinyl bonded silica (B).

The vinyl bonded silica products were treated with trimethylchlorosilane in toluene at 80° C to cap the residual silanols. The unreacted free polymers were removed from the polymeric bonded silica end products by extracting with chloroform in Soxhlet apparatus.

Columns for HPLC chromatography were packed by slurrying 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 columns were run by using water as a mobile phase. Phenol was used to provide a reference peak. The enthalpy changes were derived from the slope of the plots 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 ϕ, the activity coefficient (9-10).

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

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

RESULTS AND DISCUSSION

The mechanism of interactions, i.e. hydrogen bonding and hydrophobic etc. can be determined from ΔH° values. An exothermic process of retention of a solute by hydrogen bond formation through polar groups is indicated when ΔH° values are negative (1-2). On the other hand, the positive ΔH° values show an endothermic adsorption process which is generally an indication of hydrophobic interactions.

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

$\ln K'$ values at various absolute temperatures for ascorbic acid, niacin, caffeine and phenylalanine in case of low carbon load vinyl acetate silica-phase are shown in Table 1. The ΔH° values as derived from slopes of the plots of $\ln K'$ against $1/T$ are also shown in Table 1. The polymeric stationary phases can be of low or heavy carbon load if the monomer of the same is polymerized on silica gel having single (A) or multiple (B) vinyl chains on a silanol or -Si-OH group of the surface.

The positive ΔH° values exhibit an endothermic adsorption process which is an indication of the interaction of all these probes with the polymeric surface due to hydrophobic forces. A possible projection of these components are shown in the Figures 1

Table I. lnK' at various absolute temperatures and enthalpy of sorption of ascorbic acid, niacin, phenylalanine and caffeine on low carbon load polyvinyl acetate column.

Components	lnK'	$1/T \times 10^3$	ΔH° (K Cal/mole)
Ascorbic acid			+ 3.50
	0.20	2.90	
	0.55	3.00	
	0.76	3.05	
	0.90	3.10	
Niacin			+ 5.26
	0.90	3.00	
	1.23	3.05	
	1.66	3.10	
	1.90	3.20	
Phenylalanine			+ 4.50
	1.23	2.90	
	1.70	3.00	
	1.90	3.05	
	2.20	3.10	
Caffeine			+ 7.60
	1.90	2.90	
	2.53	3.00	
	3.37	3.10	
	3.80	3.15	

and 2. The polar groups like -OH, -COOH and $-NH_2$ in the case of ascorbic acid, niacin and phenylalanine, are not interacting with the surface to form hydrogen bonds.

Figure 3A and 3B exhibit resolution of ascorbic acid, niacin, phenylalanine and caffeine at 40°C and 70°C. Caffeine shows more change in retention time as compared to the other components. It shows that caffeine has more surface interaction than all other probes under investigation. The ΔG values at various temperatures (Table II) exhibit the similar trend. The order of interaction from γG values can be assigned as follows: caffeine > phenylalanine

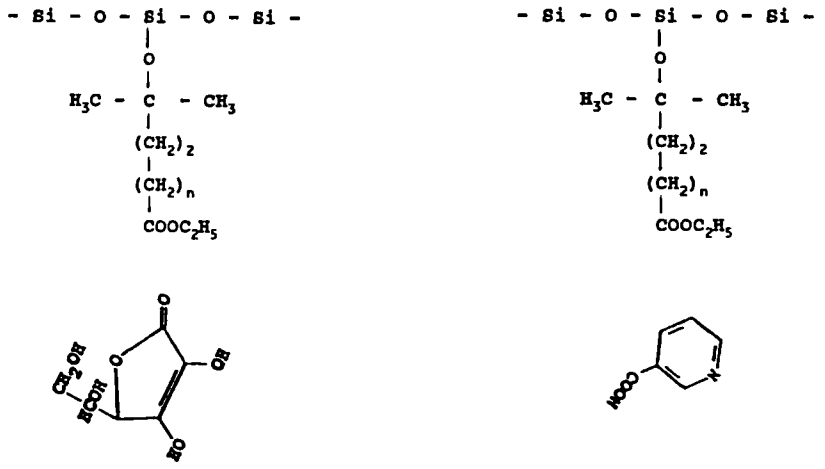

Fig. 1. Interaction of ascorbic acid and niacin with low carbon load polyvinyl acetate immobilized silica surface.

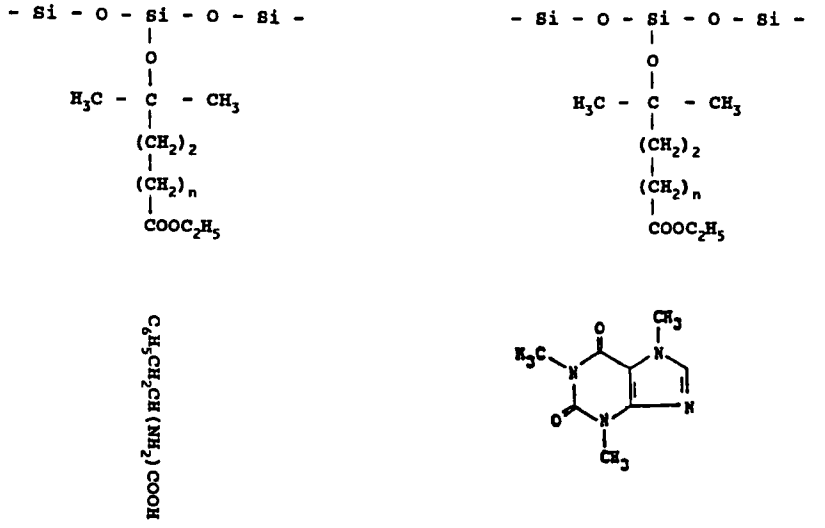

Fig. 2. Interaction of phenylalanine and caffeine with low carbon load polyvinyl acetate immobilized silica surface.

Table II. ΔG values and the coefficient of activity or γ values at various temperatures in case of ascorbic acid, niacin, phenylalanine and caffeine on low carbon load polyvinyl acetate column.

Component	ΔG	γ	t (°C)
Ascorbic acid	0.667	0.410	50
	0.564	0.460	55
	0.364	0.570	60
	0.137	0.800	72
Niacin	1.238	0.150	40
	1.158	0.170	45
	0.891	0.290	55
		0.410	72
Phenylalanine		0.136	50
	1.238	0.150	55
	1.158	0.170	60
	0.891	0.220	72
caffeine		0.022	45
	2.163	0.034	50
	1.674	0.054	60
	1.303	0.136	72

> niacin > ascorbic acid. The activity coefficient or γ values are less than 0.9 which indicates that all these probes have stronger surface interactions. These interactions become weaker as the temperature is increased. The stronger surface affinity of these components indicates that their migration from food is a good possibility. The low carbon load polyvinyl acetate, therefore, can not be used as a packaging material for the food systems containing any of the food ingredients under instigation.

Table III shows the capacity factor or $\ln K'$ and ΔH° values at various temperatures for ascorbic acid, niacin, phenylalanine and

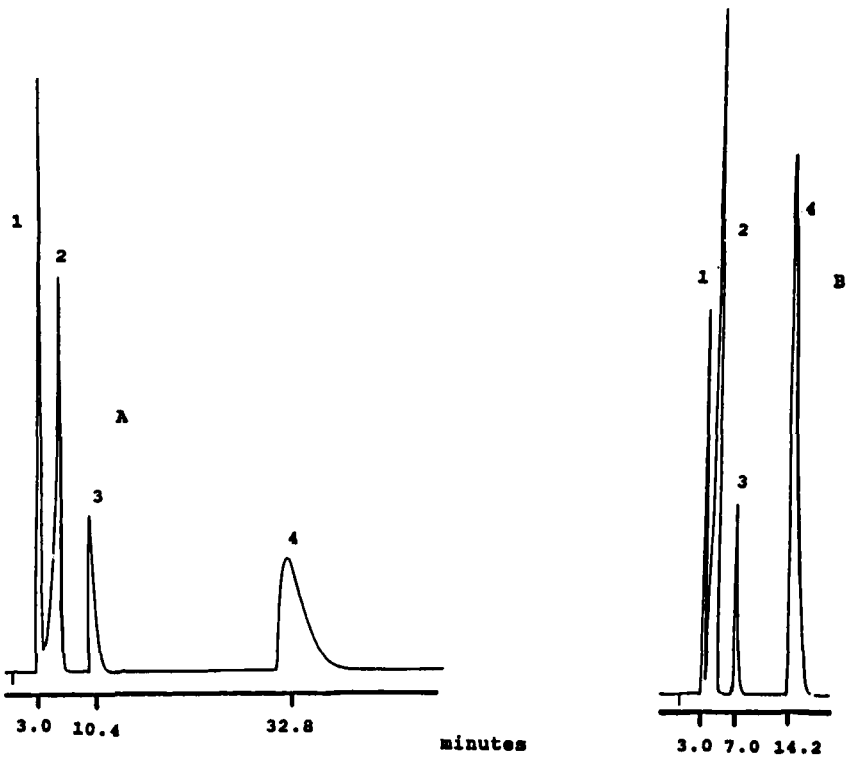

Fig. 3. Resolution on Polyvinyl acetate (low carbon load) PartiSphere-5 column (25 cm x 4.6 mm, I.D.) at 40° C (A) and 70° C (B); Mobile phase: water at 0.5 ml/min; λ_{max}: 280 nm. 1. ascorbic acid, 2. niacin, 3. phenylalanine, 4. caffeine.

caffeine on heavy carbon load vinyl acetate immobilized silica column.

The enthalpy of sorption shows negative values in the case of ascorbic acid and niacin which indicates exothermic adsorption process. The positive ΔH° values for phenylalanine and caffeine indicate an endothermic adsorption processes in these two cases. A possible interaction of these probes with the surface is shown in Figures 4 and 5. The polar groups such as -OH and -COOH are

Table III. lnK′ at various absolute temperatures and enthalpy of sorption of ascorbic acid, niacin, phenylalanine and caffeine on heavy carbon load polyvinyl acetate column.

Components	lnK′	$1/T \times 10^3$	ΔH° (K Cal/mole)
Ascorbic acid			- 0.45
	0.73	3.00	
	0.67	3.10	
	0.60	3.30	
	0.55	3.40	
Niacin			- 0.25
	0.60	3.10	
	0.55	3.30	
	0.50	3.40	
Phenylalanine			+ 3.30
	0.80	3.20	
	1.10	3.30	
	1.40	3.40	
Caffeine			+ 0.25
	0.73	3.00	
	0.80	3.10	
	0.92	3.20	

involved in forming hydrogen bonds with the surface in case of ascorbic acid and niacin.

Figures 6A and 6B show the resolution of ascorbic acid, niacin, phenylalanine and caffeine at 40°C and 70°C on a heavy carbon load polyvinyl acetate column. Higher retention time of caffeine indicates more surface interaction for this probe at various temperatures than the rest of the components. This fact is further confirmed from ΔG or Gibb's free energy values at various temperatures (Table IV). The activity of coefficient or r values at different temperatures (Table IV) shows that all these probes have values less than 0.9 which indicates their stronger surface

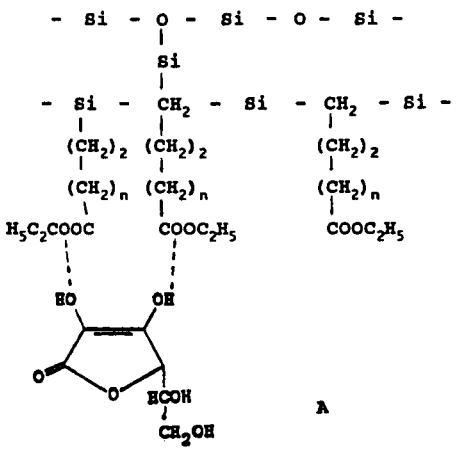

Fig. 4. Interaction of ascorbic acid and niacin with heavy carbon load polyvinyl acetate immobilized silica surface.

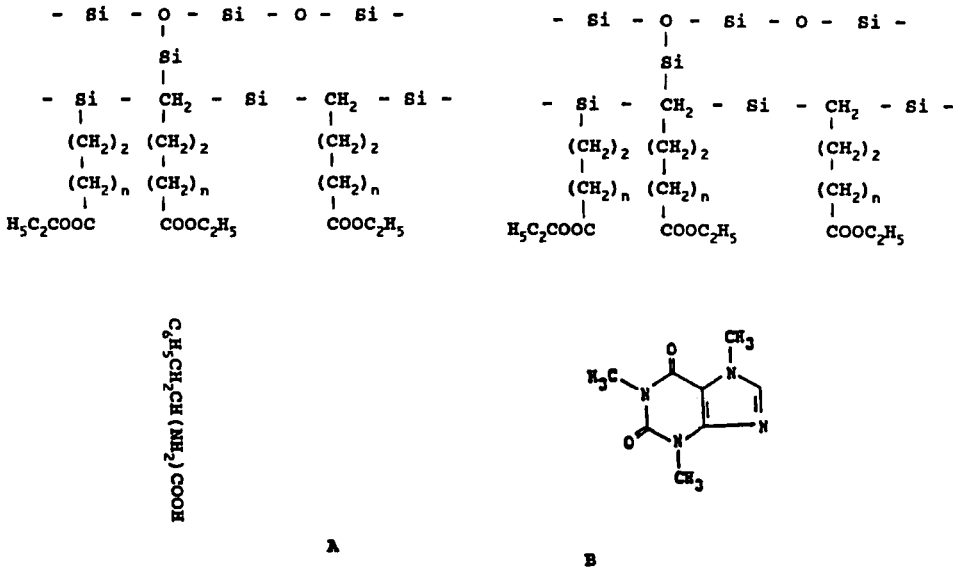

Fig. 5. Interaction of phenylalanine and caffeine with heavy carbon load polyvinyl acetate immobilized silica surface.

Table IV. ΔG values and the coefficient of activity or γ values at various temperatures in case of ascorbic acid, niacin, phenylalanine and caffeine on heavy carbon load polyvinyl acetate column.

Component	ΔG	γ	t (°C)
Ascorbic acid	0.362	0.570	20
	0.372	0.549	30
	0.392		50
		0.477	60
Niacin	0.321	0.589	30
	0.372	0.566	50
	0.397	0.549	60
Phenylalanine	0.815	0.247	20
	0.662		30
	0.490	0.450	40
	0.362	0.560	50
caffeine	0.662	0.332	20
	0.572	0.399	40
	0.539	0.432	50
	0.490	0.477	60

interactions (9). Therefore, vinyl acetate (heavy carbon load) is unsuitable to be used as packaging material for the food system containing any of these ingredients.

The present approach of synthesizing and covalently bonding a polymeric stationary phase to a silica support via silation technique allows us to investigate interaction of a polymer such as polyvinyl acetate with food components. This technique can be further extended to evaluate commercially available food and drug packaging.

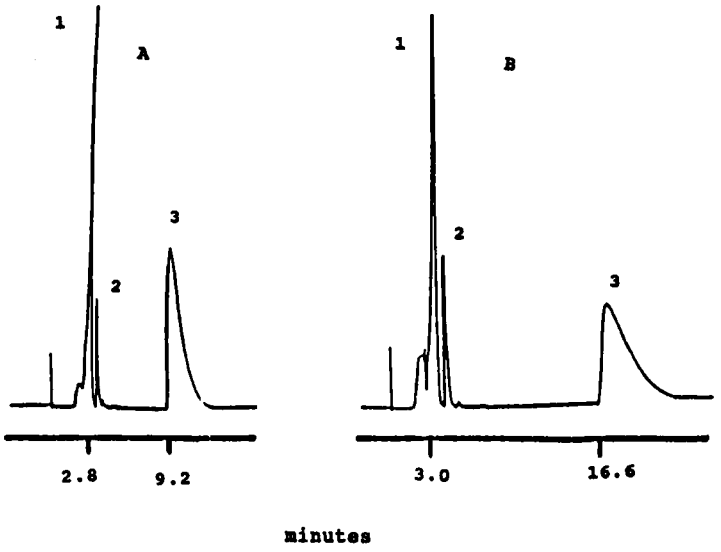

Fig. 6. Resolution on Polyvinyl acetate (heavy carbon load) PartiSphere-5 column (25 cm x 4.6 mm, I.D.) at 40° C (A) and 70° C (B); Mobile phase: water at 1 ml/min; λ_{max}: 280 nm. 1. ascorbic acid, 2. niacin, 3. phenylalanine, 4. caffeine.

ACKNOWLEDGEMENT

New Jersey Agricultural Experiment Station Publication No. D-10205-2-91 supported by State Funds.

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