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INTERACTION BETWEEN LOW-MOLECULAR-WEIGHT COMPOUNDS AND NITRILE-BASED POLYMERS

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SUMMARY

The interaction of four low-molecular-weight, non-polar and five polar liquids with homopolymer polyacrylonitrile and two nitrile copolymers was studied using inverse gas chromatography. For the non-polar liquids, the interaction between the studied compounds and the three polymers was found to be independent of concentration. For the polar compounds, however, the interaction between these compounds and the three polymers was found to increase with decrease in sample concentration, suggesting that at some low but finite solute concentration no effective migration of the solute from the polymer can occur.

INTRODUCTION

Inverse gas chromatography (IGC), sometimes also referred in the literature as inverse phase gas chromatography (IPGC), has received general recognition as an effective and simple technique for rapid polymer-solvent interaction determinations. Guillet and co-workers[1–7] have shown that this technique can be applied to the study of glass transition temperatures (T_g) of polymers, melting points (T_m), interaction parameters (χ) and for the determination of different thermodynamic parameters. Other investigators[8,9] have also applied this technique to the study of polymer–solvent interactions. IGC was recently applied to the determination of diffusion coefficients in polymers[10,11]. According to the thermodynamic theory of gas–liquid chromatography (GLC), the relationship between the activity coefficient of the solute at infinite dilution, γ_1^∞, and the specific retention volume, V_g^0, is given by the equation

$$\ln \gamma_1^\infty = \ln \frac{273.2\ R}{V_g^0\ M_2 P_1^0} \tag{1}$$

where M_2 is the molecular weight (MW) of the stationary phase (solvent), P_1^0 is the

vapor pressure of the solute in the pure liquid phase and R is the universal gas constant. V_g^0, the specific retention volume, is calculated from the experimentally determined chromatogram[1]:

$$V_g^0 = uj \left(\frac{t_r - t_0}{W} \right) \frac{273}{T} \tag{2}$$

where

u = carrier gas flow-rate;

j = pressure drop correction factor;

t_r = retention time of solute;

t_0 = retention time of a non-interacting; low-molecular-weight material (such as air);

W = weight of stationary phase;

T = absolute temperature.

Eqn. 1 is applicable to low-MW stationary phases. However, when high-MW compounds, such as polymers, are used as the stationary phase, a difficulty arises in applying this equation. This difficulty stems from the fact that the experimentally measured activity coefficients become independent of the MW for high-MW stationary phases while eqn. 1 predicts that the activity coefficient will decrease with increase in MW, reaching a limit of $-\infty$ for very high MWs. This was the reason why Patterson et al.[4] suggested the use of the weight fraction activity coefficient, Ω_1, instead of the molar fraction activity coefficient, γ_1. In this case the weight fraction activity coefficient at infinite dilution, Ω_1^∞, is related to the specific retention volume by the equation

$$\ln \Omega_1^\infty = \ln \left(\frac{a_1}{W_1} \right)^\infty = \ln \left(\frac{273.2\,R}{V_g^0 M_1 P_1^0} \right) - \frac{P_1^0}{RT} (B_{11} - V_1) \tag{3}$$

where M_1 is the MW of the solute, B_{11} is the gas-state second virial coefficient and V_1 is the molar volume of the pure solute. Eqn. 3 is applicable to high polymers as the activity coefficient calculated from this equation is independent of the MW of the polymer.

The activity coefficient can be used to calculate different thermodynamic parameters. Brawn and Guillet[12] have shown that the heat of adsorption can be calculated from a plot of log V_g^0 as a function of $1/T$.

This study deals with the interaction of three nitrile-based polymers (above and below their glass transition temperatures) and a series of low-MW compounds, including acrylonitrile (AN) monomer. Because of the use of nitrile-based high barrier polymers in food packaging and because of their potential use as beverage containers in the future (although currently the latter use is banned), it is very important to investigate accurately the interaction of these polymers with low-MW compounds. IGC was utilized for this study and the results are reported here. A subsequent paper will deal with the thermodynamics of these systems.

EXPERIMENTAL

Apparatus

Retention times were measured using an F & M Model 810 gas chromatograph with a dual flame-ionization detector.

A DuPont 990 differential scanning calorimeter was used to determine the glass transition temperatures of the three polymers under investigation.

The composition of the polymers was established using a Perkin-Elmer Model 521 grating infrared spectrophotometer.

Materials

Three polymers were used, a homopolymer of acrylonitrile, an acrylonitrile–methyl acrylate copolymer and an acrylonitrile–methyl acrylate–butadiene terpolymer. The polymers were provided by Standard Oil Company (Cleveland, OH, U.S.A.). The number-average molecular weights of these polymers were provided by the supplier and are listed in Table I. Nine low-MW compounds were used as solutes or probe molecules (four non-polar and five polar), as listed in Table II.

TABLE I

POLYMERS USED IN THE STUDY

Code No.	Polymer	Composition			Molecular weight	T_g (°C)
		Acrylonitrile	Methyl acrylate	Butadiene		
1	Polyacrylo-nitrile	100	—	—	109,000	85
2	Barex 200	69	20–30	—	150,000	80
3	Barex 210	72.5	22.1	5.3	90,000	85

TABLE II

LOW-MOLECULAR-WEIGHT COMPOUNDS USED IN THE STUDY

Compound	Molecular weight	Boiling point (°C)	Structure	Functional group	Expected interaction
Butadiene	54.09	−4.41	$CH_2 = CH–CH = CH_2$	Double bond	Dispersion
Hexane	86.18	68.95	$CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$	Alkane	Dispersion
Benzene	78.12	80.1	C_6H_6	Aromatic	Dispersion
Toluene	92.15	110.6	$C_6H_5–CH_3$	Aromatic	Dispersion
Ethyl acetate	88.12	77.06	$CH_3–\overset{\overset{\text{O}}{\|\|}}{C}–O–CH_2–CH_3$	Ester	Dispersion and polar
Methyl ethyl ketone	72.12	79.6	$CH_3–\overset{\overset{\text{O}}{\|\|}}{C}–CH_2–CH_3$	Carbonyl	Dispersion and polar
Ethanol	46.07	78.5	$CH_3–CH_2–OH$	Hydroxyl	Hydrogen bonding and polar
Acrylonitrile	53.06	77.5	$CH_2 = CH–CN$	Nitrile	Polar
Methyl acrylate	86.09	79.0	$CH_2 = CH–COOCH_3$	Ester	Dispersion and polar

TABLE III

COLUMNS USED IN THE STUDY

Column No.	Stationary phase	Column length (ft.)	Stationary phase content (g)	Solute injected
I	Uncoated support	10	0	
II	PAN	10	1.07	All compounds except ethanol and acrylonitrile
III	PAN	6	0.171	Ethanol, acrylonitrile
IV	Barex 200	6	0.840	All compounds
V	Barex 210	6	0.800	All compounds

Procedure

The experimental temperatures ranged from 30 to 120°C. Several headspace dilutions were prepared and preliminary experiments were conducted to ensure operation in the infinite dilution region (*i.e.*, Henry's law region of solute concentration). The lowest possible dilution detection for the nine compounds investigated varied from an injection of 40 nmol for hexane to 75 nmol for acrylonitrile.

Retention times were monitored by the use of a stop-watch with an accuracy of ± 0.1 sec. The stop-watch was started on sample injection and stopped on the appearance of the front profile of the elution peak. Air was used as an non-sorbed indicator and retention times of injected air were obtained at each temperature prior to the sample injection. A 5% copolymer loading on the inert support in the column was appropriate for most of the injected compounds, except for ethanol and acrylonitrile with PAN as the stationary phase, where a 1% loading had to be used. The columns used are listed in Table III.

RESULTS AND DISCUSSION

Figs. 1 and 2 are representative plots of the specific retention volume in a polyacrylonitrile (PAN)-coated column as a function of the amount of liquid injected. Fig. 1 is representative of a non-polar, non-interacting solute and Fig. 2 represents the behavior of a polar liquid. It can be seen that with AN–PAN, V_g^0 is independent of the sample size at temperatures above 80°C. Below this temperature V_g^0 starts to be concentration dependent. At lower temperatures a much greater increase in the retention volume with decrease in sample size was observed. This sharp increase in the retention volume for AN with decrease in sample size is similar to the sharp increase in K_p (partition coefficient) of vinyl chloride monomer (VCM) in a PVC–oil system previously observed in this laboratory[13]. The change in the partition coefficient as a function of the initial monomer concentration of this system is shown in Fig. 3. At low monomer concentrations, the affinity of the VCM towards the PVC is much greater than that towards the oil. The steep increase in K_p (for VCM) and V_g^0 (for AN) at low monomer concentrations reinforces our "effective zero" concept[14], suggesting that at some low but finite concentration of an active solute in a polymer, the interaction between the two may become so great that no effective migration of this solute from the polymer can occur.
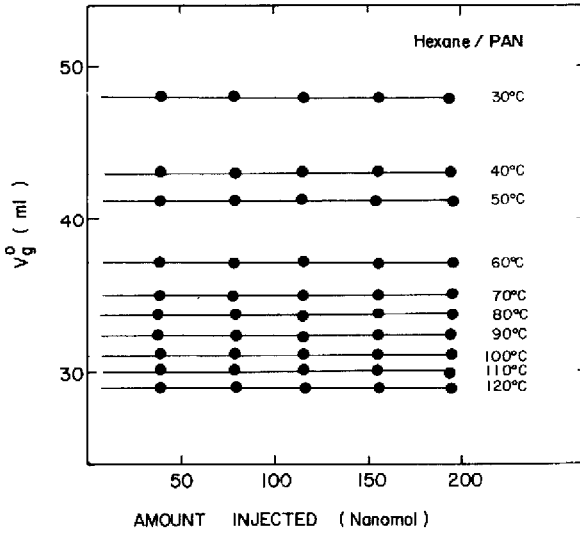
Fig. 1. Relationship between the specific retention volume and the solute concentration at different temperatures for a non-polar, non-interacting compound.
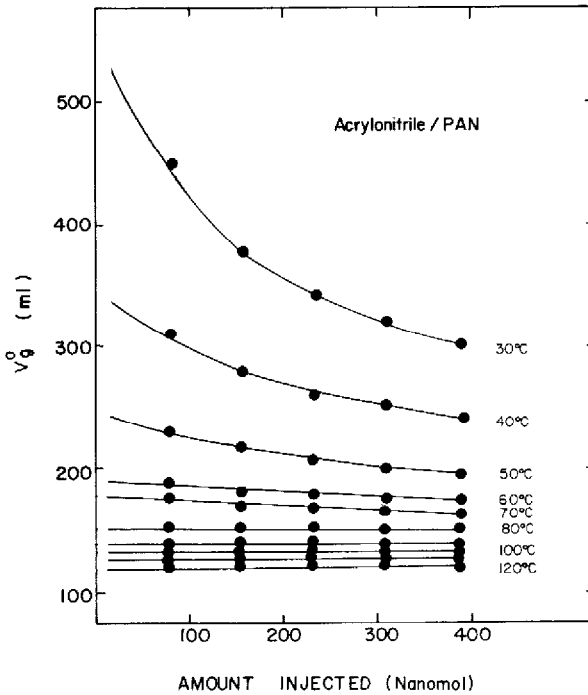

Fig. 2. Relationship between the specific retention volume and the solute concentration at different temperatures for a polar, interacting compound.
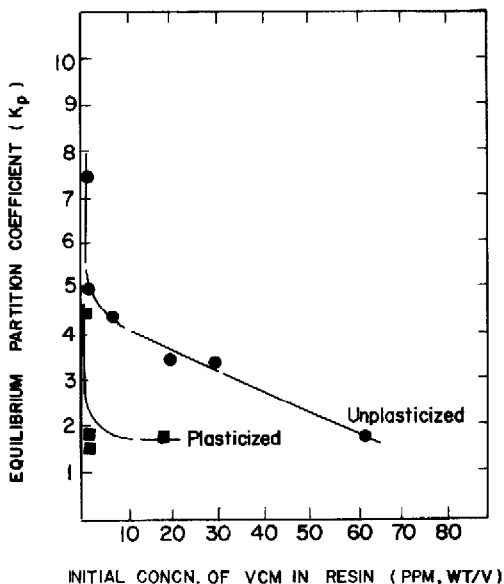
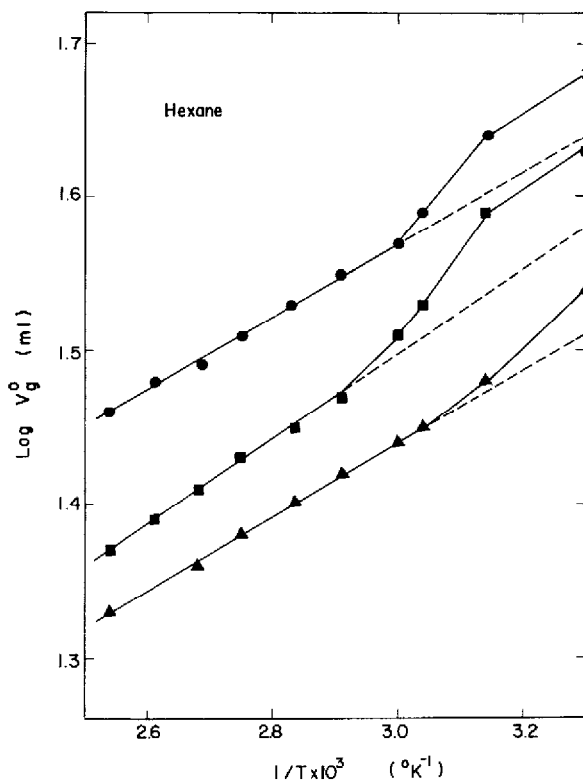Fig. 3. Relationship between K_p and monomer concentration for a VCM–PVC oil system.

Fig. 4. Relationship between log V_g^0 and $1/T$ for hexane in GC columns coated with nitrile-based polymers. ●, PAN; ▲, Barex 200; ■, Barex 210.

Guillet and Gallin[5] have studied the structure of PAN by IGC using acetonitrile. They found two transition temperatures as detected by a change in the slope of a plot of ln V_g^0 versus $1/T$, viz., 80 and 110°C. They mentioned that the latter is the glass transition temperature, T_g, while the lower transition temperature was designated T_p. As will be shown later, we were not able to detect a transition temperature around 110°C from a similar plot to that used by Guillet and Gallin[5].

We were able, however, to detect changes in the interaction between PAN and AN below 80°C. One of these changes is represented by the change in V_g^0 versus sample size correlation as shown in Fig. 2 and explained previously. Another change will be discussed later. Moreover, we have found that the glass transition temperature of our polymer is 85°C, as determined by differential scanning calorimetry (see Table I). Although differences in molecular weights and in the morphology of the polymers may have caused the discrepancy between our findings and those of Guillet and Gallin, the exact reason for this discrepancy is not yet clear.

Figs. 4 and 5 are plots of log V_g^0 as a against $1/T$ for the three nitrile-based polymers with hexane and AN, respectively, used as the probe molecules. No transitions were detected for the three polymers at temperatures above 80°C using AN or above 72°C using hexane. The transition range for the polar compounds was found to be between 60 and 80°C and for the non-polar ones compounds between 45 and 72°C. No significant differences between the three polymers were found as far as transitions are concerned. This was also confirmed by calorimetric studies (see Table I). From these figures, no conclusion can be drawn about the existence of two distinct
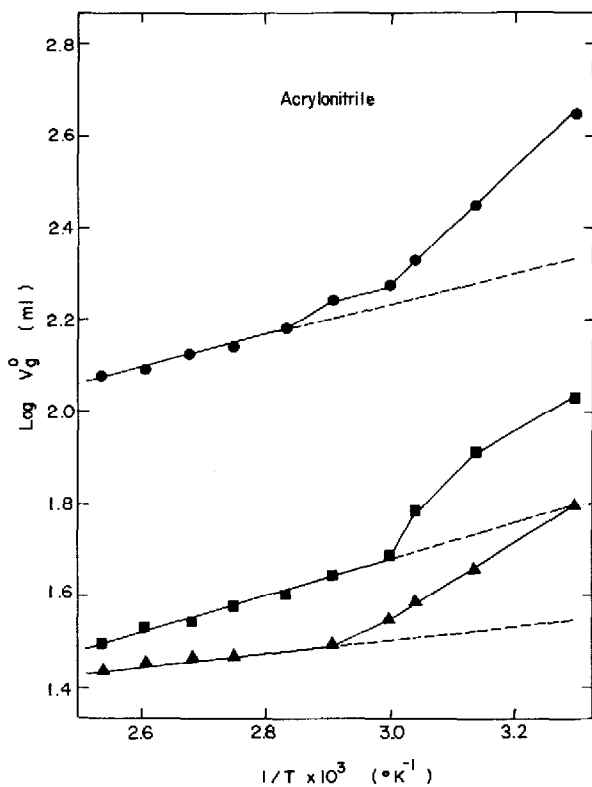
Fig. 5. Relationship between log V_g^0 and $1/T$ for acrylonitrile in GC columns coated with nitrile-based polymers. Symbols as in Fig. 4.

transition temperatures, T_p and T_g, as reported by Guillet and Gallin[5]. There is no doubt, however, about the existence of at least one transition temperature around 80°C. It can also be seen that the nature of the interaction between AN and the nitrile-based polymers starts to change about 30°C below the transition temperature. This change is represented by the deviation from the linear relationship reported to prevail[2,15,16] between log V_g^0 and $1/T$ below the glass transition temperature.

From Figs. 4 and 5, it can be seen that the retention volume changes with temperature in a different manner above and below the glass transition temperature. This difference in behavior can be explained in view of the fact that above T_g the polymer (the stationary phase) is in principle a liquid (although of very high viscosity) while below this temperature the polymer is a solid glass.

The retention volumes in Figs. 4 and 5 are seen to decrease when the stationary phase is changed in the order PAN < Barex 210 < Barex 200. From Table I it can be seen that this is also the order of decrease in acrylonitrile concentration in the copolymer. This decrease in retention volume with decrease in AN concentration in nitrile-based copolymers suggests the possibility of an increased interaction between solutes and nitrile-based packaging materials with increase in the AN concentration in their structure. As a result, the propensity of residual monomers or solvents to migrate into the contained product is expected to decrease with increase in the AN level in such copolymers.

Fig. 6 is a plot of log V_g^0 against $1/T$ for three different constant volume samples of AN injected into the GC system. It can be seen that whereas above the transition region one curve is obtained for all three sample sizes, below this region
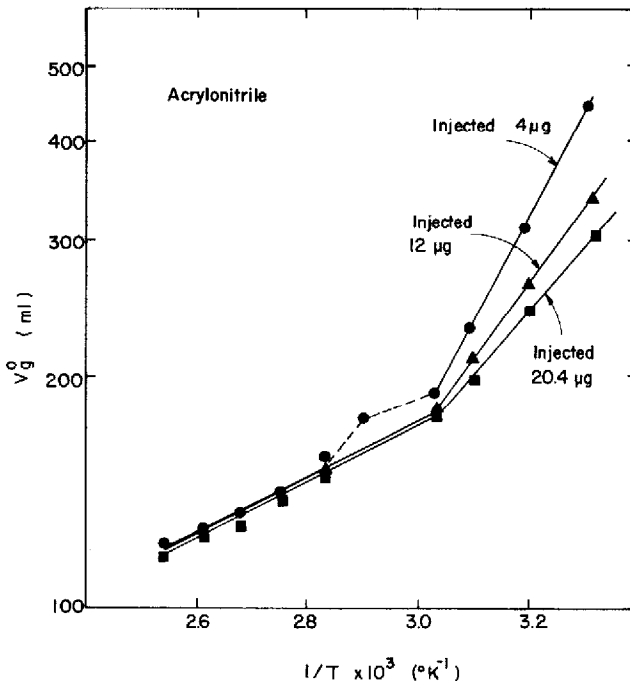
Fig. 6. Relationship between log V_g^0 and $1/T$ for acrylonitrile at three concentrations in a PAN-coated column.

each sample size gave a separate curve. The energies calculated from the slopes of the straight portions are 0.85 kcal/mol above the transition range and 5.87, 4.14 and 3.43 kcal/mol for the 4-, 12- and 20.4-μg samples, respectively. The increase in the energy with decrease in sample size is again indicative of the greater interaction between the polymer and the monomer at low monomer concentrations.

This result reinforces our proposal[14] that below some finite concentration of a solute in a polymer used as a packaging material, no effective migration of this solute into a food contacting phase will occur in terms of toxicologically significant amounts.

REFERENCES

1 O. Smidsrod and J. E. Guillet, *Macromolecules*, 2 (1969) 272.
2 A. Lavoie and J. E. Guillet, *Macromolecules*, 2 (1969) 443.
3 J. E. Guillet and A. N. Stein, *Macromolecules*, 3 (1970) 102.
4 D. Patterson, Y. B. Tewari, H. P. Schreiber and J. E. Guillet, *Macromolecules*, 4 (1971) 356.
5 J. E. Guillet and M. Gallin, *Polym. Lett.*, 11 (1973) 233.
6 J. M. Braun and J. E. Guillet, *J. Polym. Sci., Polym. Chem. Ed.*, 13 (1975) 1119.
7 J. M. Braun and J. E. Guillet, *Macromolecules*, 10 (1977) 101.
8 W. R. Summers, Y. B. Tewari and H. P. Schreiber, *Macromolecules*, 5 (1972) 12.
9 R. D. Newman and J. M. Prausnitz, *J. Phys. Chem.*, 76 (1972) 1492.
10 J. M. Braun, S. Poos and J. E. Guillet, *Polym. Lett.*, 14 (1976) 257.
11 W. Millen and S. J. Hawkes, *Polym. Lett.*, 15 (1977) 463.
12 J. M. Braun and J. E. Guillet, *Macromolecules*, 9 (1976) 617.
13 M. E. Kashtock, J. R. Giacin and S. G. Gilbert, *J. Food Sci.*, 45 (1980) 1008.
14 S. G. Gilbert, J. Miltz and J. R. Giacin, *J. Food Proc. Preserv.*, 4 (1980) 27.
15 J. M. Braun and J. E. Guillet, *Macromolecules*, 8 (1975) 882.
16 J. M. Braun and J. E. Guillet, *Macromolecules*, 9 (1976) 340.