Inverse gas chromatographic studies of styrene diffusion in polystyrene and monomer/polymer interaction

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The diffusion coefficients of styrene in polystyrene were studied using inverse gas chromatography (i.g.c.). Values between 4.3×10^{-10} and 5.5×10^{-9} cm^2 s^{-1} were found in the temperature range from 110°C to 140°C respectively. An Arrhenius type dependence of the diffusion coefficient on temperature was found in this narrow temperature range with an activation energy of 13.5 kcal mol^{-1}. The i.g.c. method was found to be fast and accurate for diffusion coefficient determination of vapours in molten polymers.

(Keywords: diffusion; interaction; styrene; polystyrene; monomer; polymer)

INTRODUCTION

Styrene polymers and copolymers are widely used in the packaging of foods. These polymers, however, contain different levels of residual styrene monomer, which may and in fact do migrate from the package into the contained food.

Migration of low molecular weight compounds, including residual monomers, from polymeric packaging materials into packaged foods and drugs has been the object of growing interest and concern in recent years, primarily due to the discovery that some of the monomers like vinyl chloride monomer (VCM) and acrylonitrile (AN) involve health hazards up to and including carcinogenicity. As a result, many studies on the migration of different additives and residues from poly(vinyl chloride) (PVC) and poly(acrylonitrile) (PAN) and its copolymers were reported[1-7]. Styrene monomer is not considered at present to be a carcinogen, although different studies have shown[8-13] that in a metabolic process styrene is transferred to styrene oxide which is known to be a carcinogen. However, styrene has a very strong and repellent smell and its migration from the packaging material into the contents imparts a highly disagreeable off-flavour. Several studies have dealt with styrene migration from polystyrene (PS)[14,15]. Miltz *et al.*[16] have shown that styrene migration is significant even at residual monomer concentrations much below the values allowed by the FDA (0.5% and 1% residual styrene in polystyrene for fatty and water based products packages, respectively).

In order to avoid possible off flavours in packaged foods, many polystyrene manufacturers started to reduce the residual styrene in their food grade polymers below the FDA allowed level.

Migration of residual monomers from a package into the contained food is in principle a diffusional process[17,18]. The rate and extent of migration depends on the diffusion coefficient of styrene in PS, on the monomer/polymer interaction, on the nature of the contacting phase and, of course, on the temperature. The reduction of the styrene level in PS is usually carried out by a stripping process from the melt which again depends among others on the diffusion coefficient, on the monomer/polymer interaction and on temperature. Therefore, the evaluation of the diffusion coefficient as well as the quantification of the polymer/monomer interactions are of great importance. Diffusion coefficients of monomers in molten polymers are not easy to determine by conventional methods. Inverse gas chromatography (i.g.c.) has been shown to be a simple and powerful tool for such studies[19,20].

Van Deemter *et al.*[21] related peak broadening in a gas chromatographic column to column properties through the following relation:

$$H = A + B/u + Cu \tag{1}$$

where H is the theoretical plate height, u is the linear velocity of the carrier gas and A, B and C are constants independent of u. Whereas A and B are related to instrument performance and gas phase spreading, C depends among others on the diffusion coefficient of the probe molecule in the stationary phase and is given by the relation:

$$C = (8/\pi^2)(d/D_p)(K/(1+K)^2)) \tag{2}$$

where d is the thickness of the stationary phase, D_p is the diffusion coefficient of the probe molecule and K is the partition ratio given by:

$$K = (t_r - t_n)/t_n \tag{3}$$

where t_r and t_n are the retention times to peak maximum of the probe molecule and a non-interacting material used as a marker respectively. The determination of D_p involves the measurement of H at several relatively high flow rates, where the term B/u is negligible. The slope obtained in a

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plot of H *versus* u enables one to calculate D_p, as K is known in these experiments. The plate height, H, is determined from the eluted peaks displayed on a chart recorder by the relation:

$$H=(L/5.54)(W_{1/2}/t_r)^2 \tag{4}$$

where L is the column length, $W_{1/2}$ the peak width at half the peak height and t_r the retention time from injection to peak maximum, as before. Braun *et al.*[19] used these equations to calculate the diffusion coefficients of several materials in low density polyethylene. Millen and Hawkes[20] following Giddings[22], claimed that a value of 2/3 should be used as the constant in equation (2) instead of $8/\pi^2$.

Orr *et al.*[6] have shown that from the chromatograms obtained in inverse gas chromatographic (i.g.c.) experiments the Gibbs free energy for the process can be calculated from the following equations:

$$\Delta\bar{G}^\circ_T = -RT\ln K_p \tag{5}$$

where $\Delta\bar{G}^\circ_T$ is the Gibbs molar free energy, and K_p is the partition coefficient (the ratio between the probe molecule concentration in the polymer to that in the moving gas). K_p can be calculated from:

$$K_p = V_g^\circ \frac{\rho T_c}{273} \tag{6}$$

where V_g° is the specific volume, ρ is the density of the polymer and T_c is the column temperature. The partition coefficient and Gibbs free energy are related to the probe molecule/polymer interaction. Thus, higher values of K_p and $-\Delta\bar{G}^\circ_T$ indicate a stronger interaction between the stationary phase polymer and the injected probe molecules.

The present publication deals with diffusion coefficients of styrene in polystyrene and monomer/polymer interaction.

EXPERIMENTAL

Materials

A food grade polystyrene (PS), used to manufacture yogurt cups, was applied for coating the gas chromatographic columns used in the present study. The styrene used in the diffusion studies was of 99% purity manufactured by Merck.

An analytical grade methylene chloride made by Frutarom Ltd., Israel, was used as a solvent.

Methods

A Varian 3700 Gas Chromatograph equipped with a dual flame ionization detector was used. The copper column 6′ × $\frac{1}{4}$″ was filled with Chromosorb P AW/DMCS 60/80 mesh coated with 7.85% polystyrene. The PS coating was obtained by dissolving a predetermined amount of PS in methylene chloride, adding a predetermined amount of support (Chromosorb) and slowly evaporating the solvent while mixing in a rotary evaporator. The final removal of the solvent was accomplished in a vacuum oven heated to 100°C overnight. The exact per cent coating was determined by Soxlet extraction.

From the specific surface area of the support (4.0 m^2/g) and the weights of the support and PS in the column (14.79 and 1.26 g, respectively) the average thickness of 2.1×10^{-6} cm of the PS coating was calculated. Different amounts of styrene were injected into 100 cm^3 vials closed with Teflon faced septa and aluminium crimps. The vials were preheated to 130°C in an oil bath for at least one hour. Samples withdrawn from these vials with gas tight syringes were then injected into the gas chromatograph (g.c.). This method was found to give reproducible results if not more than 8 samples were taken from one vial during a period of two hours. Varying amounts of styrene were injected into the g.c. at different temperatures and carrier gas flow rates. The peaks obtained were recorded on a Linear Model recorder and the area measured with a Varian CDS 111 C integrator. Triplicate samples were usually used.

RESULTS AND DISCUSSION

In *Figure 1* the change in specific volume with temperature is shown. Three distinct regions can be clearly seen. In the lower temperature range a straight line is obtained when log V_g° is plotted *versus* $1/T$. In this low temperature range the polymer is in its glassy state and monomer–polymer interaction takes place primarily via surface adsorption. In this region the partition coefficient, K_p, and the Gibbs free energy, $-\Delta\bar{G}^\circ_T$, as calculated from equations (5) and (6) and tabulated in *Table 1*, decrease with the increase in temperature. The decrease in these values points towards a decreasing styrene/polystyrene interaction and can be explained by the increase in thermal energy and motion of the styrene molecules enabling them to escape more easily from the polymer surface.

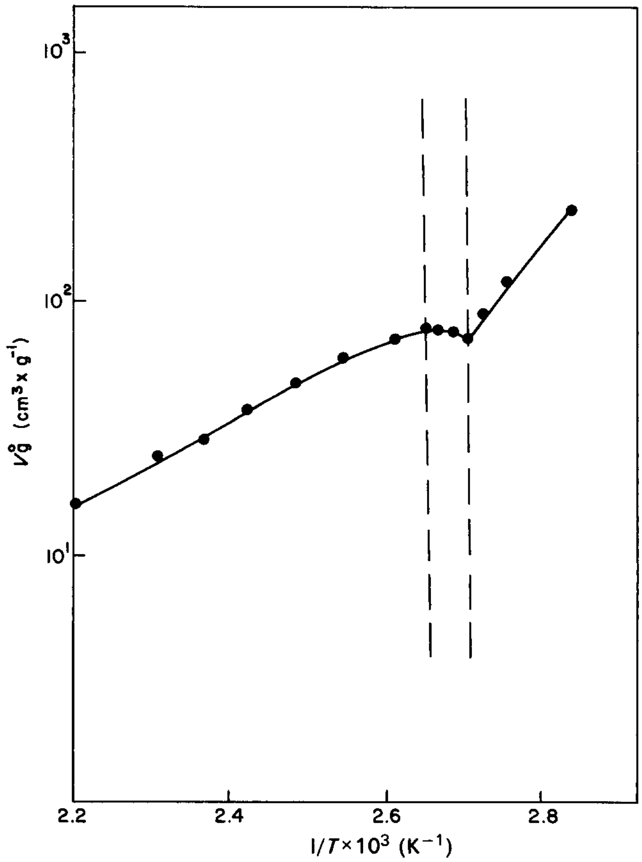

Figure 1 Change in specific retention volume with temperature

A deviation from the straight line is observed at 97°C. This temperature is identified as the glass transition temperature (T_g) of the polymer. Differential scanning calorimetry (d.s.c.) has shown a T_g of 98°C, in close agreement with the value obtained by the i.g.c. method.

In the second region, extending from 97°C to 110°C, a range of instability (as far as equilibrium is concerned) is observed where the monomer is inhibited in the g.c. column via surface adsorption and partial bulk absorption in the polymer. From *Table 1* it can be seen that when entering into this region, the K_p as well as the $-\Delta\bar{G}^\circ_T$ values do not continue to decrease with the increase in temperature. As was pointed out earlier, in the transition region (between 97°C and 110°C) both modes of interaction (surface adsorption and bulk absorption) take place, causing stronger monomer/polymer interaction as represented by the higher K_p and $-\Delta\bar{G}^\circ_T$ values.

In the third region, extending above 110°C, again a straight line is obtained. In this range styrene/polystyrene interaction takes place via bulk absorption only. This interaction steadily decreases with the increase in temperature as represented by the decreasing values of K_p and $-\Delta\bar{G}^\circ_T$ in *Table 1*. Since K_p is proportional to V°_g (see eq. (6)), the values of the specific retention volume can be used as a measure for monomer/polymer interaction, the higher this value, the stronger the interaction. In *Figure 2* the change in V°_g with the amount of styrene injected at three temperatures is shown. It is clear that the lower the temperature the higher the specific retention volume. From this figure however, it can also be seen that at the two lower temperatures the retention volume increases with the decrease in the amount of styrene injected. This reflects increased interaction at decreasing monomer concentrations and strengthens our claim[5–7,18] that at low enough temperatures and monomer levels migration of residual monomers from polymeric packaging materials may become ineffective because of very strong monomer/polymer interaction.

Table 1 Partition coefficient and Gibbs free energy as determined from gas chromatographic data

T (K)	K_p	$-\Delta\bar{G}^\circ_T$ (kcal mol^{-1})
353	347.1	4.13
363	179.8	3.77
368	133.9	3.60
370	109.4	3.47
373	118.5	3.56
376	117.6	3.58
378	123.6	3.64
383	115.4	3.64
393	99.8	3.62
403	77.3	3.50
413	64.6	3.44
423	50.1	3.31
433	44.1	3.28

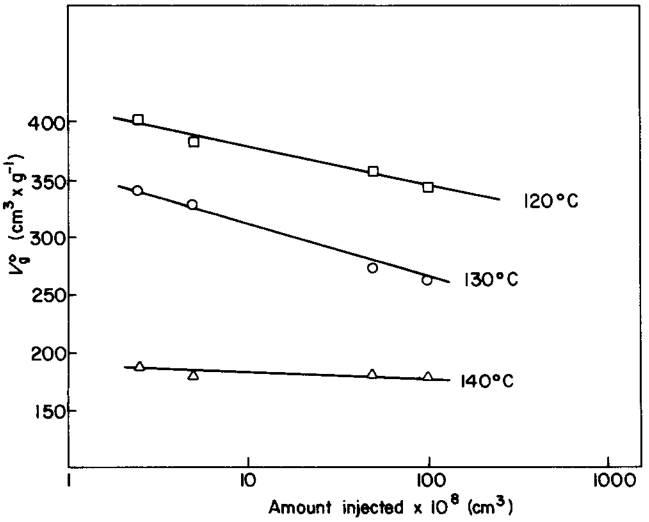

Figure 2 Effect of the amount of injected styrene on the specific retention volume

Table 2 Diffusion coefficients of styrene in polystyrene

	Temperature (°C)			
	110	120	130	140
D_p (cm^2 s^{-1})	4.3×10^{-10}	9.2×10^{-10}	2.8×10^{-9}	5.5×10^{-9}

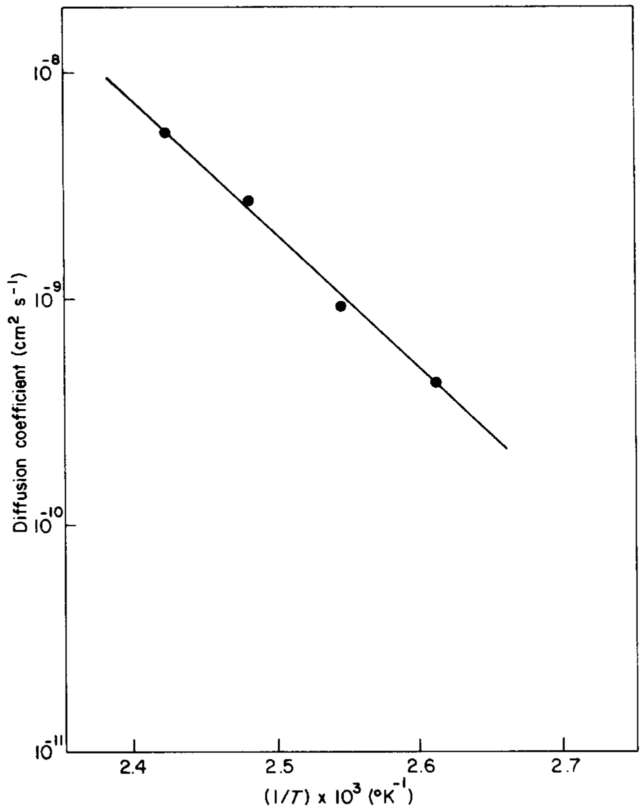

Figure 3 Change of the diffusion coefficient of styrene in polystyrene with temperature

The diffusion coefficients of styrene in polystyrene were studied in the third region mentioned above, namely at temperatures at and above 110°C. A plot of the theoretical plate height, H, as a function of linear velocity according to equation (1) gave straight lines (at the higher u values) at all temperatures. The slopes of these plots provided the C values from which the corresponding diffusion coefficients given in *Table 2* were calculated (using 2/3 instead of $8/\pi^2$ in equation (2)). The value of the diffusion coefficient obtained at 130°C is comparable to that obtained by Duda *et al.*[23] using a sorption technique. At 140°C, however, our value is approximately 40% lower (their data were extracted from a figure and therefore cannot be quoted very accurately). No data at 110°C and 120°C were reported and therefore no comparison can be made. However, whereas the sorption technique to determine the diffusion coefficient may take several days, in the i.g.c. method only several minutes or tens of minutes are required. Moreover, the latter technique seems to be more reliable for the determination of diffusion coefficients at very low monomer concentrations, a situation existing during stripping operations of residual styrene from food grade polystyrene. On the other hand, the i.g.c. method is applicable only for very low monomer concentrations, whereas the sorption techniques can be used for the whole range of monomer concentrations.

In the limited temperature range presently studied, the diffusion coefficient of styrene in PS changes with temperature accoding to an Arrhenius type equation as shown in *Figure 3*. The activation energy calculated from the slope of this plot was found to be -13.5 kcal mol^{-1}, somewhat higher than the values obtained by Braun *et al.*[19] for different systems but reasonable for a diffusional process.

To summarize, the i.g.c. method was shown, once again, to be a powerful tool for diffusion coefficients of vapours in polymers and for monomer/polymer interaction studies.

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