Multicomponent Inverse Gas Chromatography for Analyses of Sorption in Polymers

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Removal of trace monomer and/or solvent from polymer (that is, devolatilization or DV) can be a difficult rate process due to the low diffusivity of volatiles and the encroachment of equilibrium solubility. Equipment designed to optimally stretch fluids, as well as application of high vacuum, is used to effect maximum residual removal with minimum polymer overheating and overworking. In the absence of limiting mass-transfer processes, however, the volatiles content of the finished polymer depends on chemical equilibrium, temperature, composition and pressure, not equipment residence time and/or mixedness. The solubility of trace volatiles in polymer can be decreased by (1) decreasing pressure, (2) increasing temperature, and (3) manipulating melt composition. The first two approaches are limited by thermal degradation, depolymerization, side reactions, and vacuum equipment limitations.

Manipulating melt composition by adding a "third" component to the system is an approach which is seldom explored. The effect is analogous to adding an azeotropic breaker in distillation. By adding additional thermodynamic pathways to an equilibrium-limited process, it becomes possible to enhance separation, using existing equipment without modification. A requisite for this approach is a single-phase system in which chemical species interact nonlinearly. The third component must be inert, benign, itself easily removed, and not be detrimental to product quality. It must be soluble in the polymer-monomer (a homogeneous system) and contribute to increasing residual volatile diffusivity and decreasing solubility.

One of the difficulties of using this approach is that evaluating multicomponent VLE of trace volatiles can be extremely difficult. Conventional equilibrium techniques require preparing a series of compositions and equilibrating them in sealed isothermal, isobaric vessels. This process can be long, tedious, and, for low solubilities, unreliable. Nevertheless, it is essential to understand the relationship between equilibrium solubility of the volatile component and variables in the system, such as temperature, pressure, and polymer phase composition. For instance, without knowledge of solubility, it is not clear if extending equipment residence time, or increasing shear rate or equipment dimensions will be effective in reducing the solute content. Trying to explore multicomponent interactions with batch equilibrations is clearly not feasible.

A useful and simple technique for measuring polymer-solvent VLE and transport is quantitative chromatography. Capillary column inverse gas chromatography (IGC) may be used for determining trace volatiles solubility and diffusivity in polymer films. A small quantity of solute is injected into a flowing carrier gas and passed over a thin layer of polymer coating the internal surface of a capillary tube. The resulting broadening and retention of the solute, characterized at the column outlet by the peak width and retention time, are used to evaluate its diffusivity and solubility in the polymer at column conditions. Even though it suffers a different column preparation and evaluation step, it is much more accurate than packed column GC due to the reduced contribution of gas-phase axial diffusion and is much simpler and faster than batch equilibrations.

Quantitative IGC has been used extensively (Pawlisch et al., 1987, 1988) with single permeants and single species detection in systems of high solute solubility and low diffusivity such that elution peak characteristics are determined solely by polymer-solute interactions. In DV applications (that is, high temperatures), IGC must be used for solutes having inherently very low solubility, in the presence of other coeluting components (such as solvents) and high mobility. Low solubility taxes the ability of IGC to reliably quantify sorption since saturation is a major problem. High mobility is an issue since unavoidable instrument dynamics become significant relative to weak solute-polymer interaction. Finally, many components (including inerts and solvents) eluting simultaneously cause peak overlap which makes it impossible to evaluate individual species peak widths and retention times.

Capillary column IGC, coupled with mass-selective detection, with an internal inert gas reference analysis, can overcome these limitations and allow fast, convenient, and reliable evaluation of interactive effects between many and assorted solutes under conditions similar to DV.

Theory

The diffusion coefficient and solubility of a trace permeant in a thin film are given by the solution to the system Eqs. 1-6 (Pawlisch et al., 1988), where c' is the solute concentration in the polymer phase, c the solute concentration in the gas phase, D_p the solute-polymer diffusivity, D_g the solute-gas diffusivity, v the average carrier velocity, τ the average coating thickness, and R the capillary inside diameter. The solubility, K, is based on a linear isotherm assumption across the solute partial pressure range within the column:

$$c'\,(t=0,\ \text{all}\ r)=0 \tag{1}$$

$$c'\,(r=R-\tau)=cK \tag{2}$$

$$\left.\frac{\partial c'}{\partial r}\right|_{r=R}=0 \tag{3}$$

$$c(z=0,t)=c_0(t) \tag{4}$$

$$\frac{\partial c'}{\partial t}=D_p\,\frac{\partial^2 c'}{\partial r^2} \tag{5}$$

$$D_g\,\frac{\partial^2 c}{\partial z^2}-v\,\frac{\partial c}{\partial z}+\left(\frac{2D_p}{R}\right)\left.\frac{\partial c'}{\partial r}\right|_{r=R-\tau}=\frac{\partial c}{\partial t} \tag{6}$$

The solution to this set of equations in the Laplace domain yields the mean and variance of the elution peak from an assumed ideal impulse input [$c_0(t)$ is a Dirac function]:

$$\mu=\frac{L}{v}\left(1+\frac{2\tau}{R}\,K\right)$$

$$\frac{\sigma^2}{2\left(\dfrac{L}{v}\right)}=\frac{1}{3\pi}\,\frac{\tau}{R}\,K\left[\frac{\tau^2}{D_p}\right]+\left(\frac{2D_g}{v^2}\right)\left(1+\frac{2\tau}{R}\,K\right)^2 \tag{7}$$

For systems with low solubility,

$$\frac{\tau}{R}\,K<<1 \tag{8}$$

such that the solute retention time is very similar to that of an inert gas ($K=0$). In this case, reference of the solute elution peak to an inert gas coinjected with the solute(s) is necessary. The inert gas reference allows the significant instrument effects to be removed from the solute-polymer interaction. Correcting with an inert gas yields "relative" moments shown below:

$$\Delta\mu=\frac{\mu}{\mu_{\text{inert}}}=1+\frac{2\tau}{R}\,K \tag{9}$$

$$\frac{\Delta\sigma^2}{2(\mu_{\text{inert}})}=\frac{\sigma^2-\sigma^2_{\text{inert}}}{2(\mu_{\text{inert}})}=\frac{1}{3}\,(\Delta\mu-1)\frac{\tau^2}{D_p} \tag{10}$$

K is the ratio of molar concentrations of solute in the gas and polymer phases at equilibrium. Reversible or irreversible physical effects such as shrinkage/swelling, degradation, reaction, plasticization and saturation (concentration-dependent sorption) may occur during sorption, but are not incorporated in the model to avoid nonlinearity. These effects are considered negligible for a linear, infinite-dilution (solute to polymer) sorption experiment such as IGC. At high temperatures, applicable to DV applications, these effects can become significant. Under these severe conditions, stability of the thin-film coating is also tested; sagging (gravity) and flow-induced coalescence and rippling (axial pressure gradient and surface tension) can ruin a column, or at least generate sufficient coating thickness nonuniformity that reliable column behavior is lost (Pawlisch et al., 1988). The second moment or variance (diffusivity estimate) is particularly vulnerable to column degradation.

For reliable estimates of solubility and diffusivity, it is, at a minimum, required that:

$$[1+(2\tau/R)K]L/v>\tau^2/D_p>D_g/v^2,$$

such that solute exposure to the film is sufficient to satisfy the boundary conditions of the model and that solute broadening be mainly due to polymer diffusion and not axial gas-phase diffusion. For example, typical values of K and D_p for slightly soluble solutes might be 10 and 10^{-8} cm^2/s, respectively. For capillary columns, a typical design might be $L=15$ m, $2R=530$ micron, $\tau=2$ micron, $v=2$ cm/s and $D_g=0.1$ cm^2/s. This leads to solute retention ~900 s, $\tau^2/D_p\sim 4$ s, $D_g/v^2\sim 25$ ms. Obviously, exposure is sufficient, and gas-phase diffusion is negligible; an inert gas reference (other than to determine velocity) is unnecessary.

Other significant sources of retention and dispersion are injector backmixing (particularly with liquid injections), slow detector response, and dispersion. These also must be minimized relative to solute-polymer dynamics. Thin-layer (low τ) capillary column chromatography (high v) fulfills the above constraints for systems of high solubility, leading to precise and reliable characterization of sorption, relative to packed columns. For low-solubility solutes, at high temperatures (low $K\tau/R$ and high D_p), the above requisites can be severely tested. Low-solubility systems are characterized by low column retention and narrow peaks which are very unreliable to quantify, since broadening and retention depend more on instrument effects than sorption. Thin coatings and narrow capillaries are useful, but they are inconvenient ways of overcoming the diminished reliability of IGC. It is necessary to use a coinjected inert gas reference, fast and precise multicomponent detection, careful minimization of the amount of solute(s) injected, and a realistic appraisal of the significance of the results.

In systems of low solubility, a fat injection can ruin the experiment before solute even hits the column. This problem is easily diagnosed when the relative variance ($\Delta\sigma^2$) becomes statistically zero. Systems with high heat of vaporization or chemically dissimilar components being injected can be broadened even further. Systems of low solubility are easily saturated by solute. Saturation is usually evident by a split (usually square topped) elution peak comprising a nonretained (coincident with the inert reference) and retained fraction. The only way to overcome this problem is to reduce the amount injected or sacrifice the diffusivity observation by intentionally broadening the elution peak. Weakly retained solutes tend to escape the column without broadening. Their rapid arrival can overwhelm a slow detector, yielding spiked elution peaks. Finally, the sensitivity of the detector can become taxed as the amount of solute is minimized. Ultimately, achieving control of liquid volumes less than 0.05 mL can be challenging.

Multicomponent activity coefficients by chromatography

Equation 11 describes the equilibrium residual content, x_1, below an ideal vapor. Reductions in vacuum, use of a sweep gas, and increases in temperature to raise monomer vapor pressure are obvious methods of reducing volatiles content. In practice, these variables can become rapidly constrained; the remaining variable that can be used to reduce x_1 is the polymer phase activity coefficient, which must be increased. One way to increase the trace volatile activity coefficient is to add another component to the system.

$$\gamma_{1,2} x_1 P_1^0 = y_1 P_{\text{vac}} \tag{11}$$

A multicomponent IGC model is complex, since Eqs. 1-6 must be applied to each component. Each system is coupled in the boundary conditions through multicomponent activity coefficients, and in the body of the equations through multicomponent diffusivities. Analysis of individual elution peaks in a multicomponent system using the single-component model will yield values of "apparent" D_p, and K which will differ from their single-component values only if there is significant interaction within the polymer phase. These apparent parameters will be used as an indication of positive or negative interactions, that is, enhanced or decreased solute solubility and/or mobility.

The equilibrium solubility, K, is assumed to be independent of concentration using the infinite dilution assumption, solute relative to polymer. K for a binary system, where 1 refers to solute 1 (monomer) and 2 refers to polymer, is:

$$K = \frac{c'_1}{c_1} \tag{12}$$

$$c_1 = \frac{y_1 P_{\text{tot}}}{RT}, \quad c'_1 = \frac{x_1}{x_1 \dfrac{M_1}{\rho_1} + x_2 \dfrac{M_2}{\rho_2}} \approx x_1 \left(\frac{\rho_{\text{av}}}{M_{\text{av}}} \right) \tag{13}$$

The activity coefficient is defined as:

$$\gamma_{1,2} = \frac{y_1 P_{\text{tot}}}{x_1 P_1^0} \tag{14}$$

Substituting in the K expression reveals the activity coefficient, where an average, concentration-independent density is assumed (polymer swelling is negligible):

$$K = \frac{1}{\gamma_{1,2}} \left[\left(\frac{\rho_{\text{av}}}{M_{\text{av}}} \right) \left(\frac{RT}{P_1^0} \right) \right] \tag{15}$$

Adding a third component to the system leads to two solubilities derived from two simultaneously eluting peaks. Once again, density variations are assumed to be negligible:

$$K_1 = \frac{1}{\gamma_{1,2\text{-}3}} \left[\left(\frac{\rho_{\text{av}}}{M_{\text{av}}} \right) \left(\frac{RT}{P_1^0} \right) \right]$$
$$K_3 = \frac{1}{\gamma_{3,1\text{-}2}} \left[\left(\frac{\rho_{\text{av}}}{M_{\text{av}}} \right) \left(\frac{RT}{P_3^0} \right) \right] \tag{16}$$

Ratioing these expressions and reverting to chromatographically observable moments yields an equation connecting multicomponent chromatography to activity:

$$\frac{\Delta\mu_1 - 1}{\Delta\mu_3 - 1} = \frac{\gamma_{3,1\text{-}2} P_3^0}{\gamma_{1,2\text{-}3} P_1^0} \tag{17}$$

The volatile components must have similar vapor pressures to see differences in relative retention due to interactions in the polymer phase. Any chemical interactions that may occur in the polymer phase may be overwhelmed by relative volatility. The activity coefficient ratio should be concentration-dependent, since components 1-2 and 3-2 are dilute (solute to polymer), while 1-3 (solute-solute) may not be. The relative retention time ratio will depend on the concentration and interaction of each component within the polymer phase.

Experimental Studies

As an example of how IGC can work for low-solubility, multicomponent systems, three systems were chosen: dichloromethane/water, methanol/water, and phenol/diphenylcarbonate (DPC), all over polycarbonate (PC). A 15-m, 2-micron-thick film, 530-micron-ID ($R/\tau = 133$) fused silica polycarbonate column was used. Liquid and vapor injections of varying volumes were used with a split injector (20:1 flow). Argon (10-μL gas) was used as the inert tracer and was injected with the solutes to provide the internal reference and injected alone to monitor instrument drift. The column was prepared by heating at 250°C overnight in carrier.

Column velocity was fixed at an argon retention of ~50 s (solute retention ~60-400 s). Argon peak width was 5-8 s (solute width 6-60 s). The selection of a single flow rate is not a limitation in the analysis. Lower flow rates would increase retention, but *not* relative retention, which is the significant variable in the model. Lower flow rates do increase the contribution of dispersion from injection and gas-phase diffusion. Thus, there is no advantage to altering the flow rate for a particular system other than to ensure model applicability and linearity.

A Hewlett-Packard 5971A MS detector (MSD) was used. It is a multispecies detector with extremely good sensitivity (10^{-9} g). The MSD was used to monitor characteristic and unique ions of the solute(s), for example, argon at 40 amu, water at 18, dichloromethane at 84, phenol at 94, DPC at 214, with time and recover single species elution peaks regardless of overlap. The selected ion mode of the MSD was used to speed detector response and increase sensitivity. Peak integration was done with instrument supplied software. Reported concentrations are based on integrated ion abundances and were not corrected nor calibrated. This eliminated the need to carefully measure and control solute composition at the injector. Quantitative comparison of these results with other IGC systems may be unreliable due to the method of calculating moments and using the inert-gas reference IGC model.

One difficulty with the MSD is slow response. In normal IGC, an analog detector (such as FID) is used, and the peak is sampled with fast A/D. MS detection works by scanning. Even though perhaps only two ions are sampled, reset and recycle time can be 0.1-1 s. Occasionally, MSD response was sufficiently slow that very weakly retained solutes overwhelm

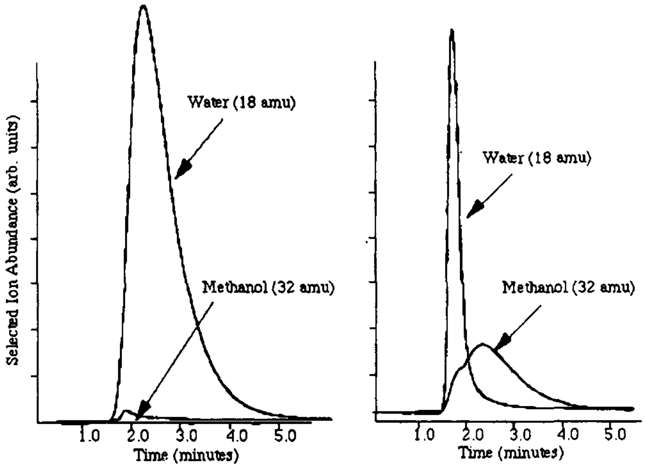

Figure 1. Elution peaks of dichloromethane and water over PC at 75°C at two compositions.

the detector, resulting in jagged and split peaks, not due to column or detector saturation (not influenced by amount injected). Another difficulty of MSD is coincidence of the cracking patterns of certain eluting solutes (such as series of hydrocarbons or alcohols). Instrument software does not perform deconvolution prior to peak analysis, and this limits the selection of solute combinations.

Results

Dichloromethane/water

This system is important in the removal of trace solvent from solution-polymerized PC by steam contacting. Steam performs heating as well as a chemical interaction with sorbed dichloromethane. Dichloromethane is insoluble in water but is completely soluble in PC; water has limited solubility in PC. The vapor pressure ratio is P_1^0 (dichloromethane)/ P_3^0(water) = 1,150 torr/92 torr = 12.5 at 50°C, 9.28 at 75°C, and 7.35 at 100°C.

The total amount of solute injected was 0.05 μL liquid at 100°C and 0.1 μL at 75°C, and had to be carefully controlled to eliminate saturation and split peaks. Figure 1 shows examples of ion chromatograms for dichloromethane and water at two extremes of composition. The change in the character of the dichloromethane peak confirms a significant interaction in the sorbed phase. Figure 2 shows the variation in dichloromethane and water solubility vs. water content at 40 and 100°C. Relative retention ratio is defined as:

$$\text{Relative Retention Ratio} = \Delta\mu - 1 = \frac{\mu}{\mu_{\text{inert}}} - 1$$

such that if it is multiplied by $R/2\tau = 62$, one recovers solubility. For instance, the solubility of pure dichloromethane at 100°C from Figure 3 is $K = 0.25(62) = 17$. Baltus (1991) measured $K = 697$ at 50°C and 1,500 at 37°C with a different PC column.

During DV, the system will move from left to right (low water to high water content) in Figure 2 as dichloromethane is removed. With only trace water present, PC may be considered swollen with dichloromethane. The influence of water infiltration is minimal, and solubilities are relatively invariant. However, as polymer free volume collapses due to displacement of dichloromethane with water, solubility of dichloromethane falls. With trace dichloromethane, solubility is a very sensitive and decreasing function of water content; in fact, the solubility of water and dichloromethane become similar. The effect is more pronounced at lower temperature (40°C), when physical phenomena are minimized relative to chemical interactions and species solubilities are higher. In contrast, water solubility is unaffected by the presence of dichloromethane and the state of swelling of the polymer. This implies that water sorption is a chemical effect, due perhaps to association with PC rather than solubility, and not influenced by polymer swelling due to sorption.

As water content rises, Figure 2, dichloromethane activity relative to water increases. It is this effect which can be ex-

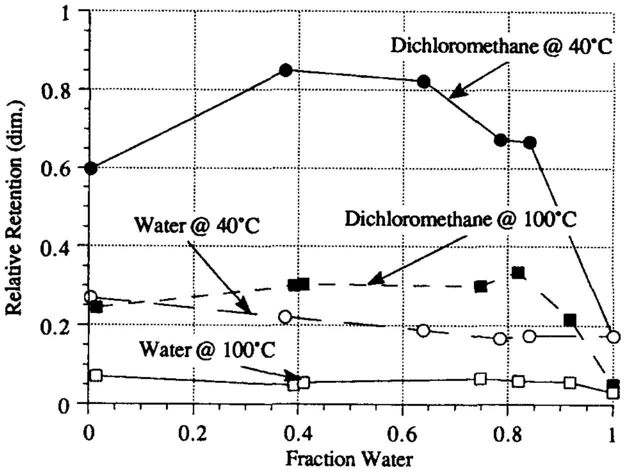

Figure 2. Solubility (relative retention ratio) of dichloromethane and water at varying water content and temperature.

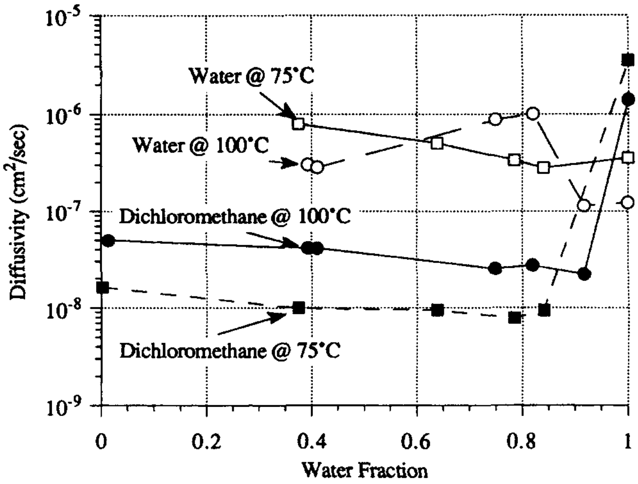

Figure 3. Diffusivity of dichloromethane and water in polycarbonate at varying water content and temperature.

ploited during DV of dichloromethane by steam contacting. The observed fourfold increase in dichloromethane activity is equivalent to removing ~20°C of DV temperature. The effect is due to solute-solute chemical interaction in the polymer phase and is maximized when the polymer is a minimum free volume glass.

Figure 3 shows the diffusivity for dichloromethane and water at 100 and 75°C. Baltus (1991) measured a diffusivity of pure dichloromethane at 100°C of $1.81(10)^{-8}$ cm²/s, which agrees well with these results. Water has a diffusivity ~2 orders greater than dichloromethane. In fact, water diffusivity can be obtained only at high water content, when free volume is a minimum and water mobility is the lowest. With virtually any dichloromethane present, water diffusivity was too high to be significant (relative variance was zero). With increasing water content, dichloromethane diffusivity increases, as shown in Figure 1, and the dichloromethane peak shrinks in the presence of water. Thus, water displaces sorbed dichloromethane by raising its activity, but also increases its diffusivity in PC. Both of these effects encourage DV of the solute.

At 40°C dichloromethane is permanently retained within the column, and the equilibrium analysis is not applicable. At 125°C the solubilities of both species are too low to see interaction. The displacement effect occurs in a narrow temperature range, $75°C < T < 100°C$.

MeOH/water

The displacement effect observed with dichloromethane and water in PC is believed due to the incompatibility between the solutes. Two relatively similar molecules, methanol and water, should produce a diminished effect. At 100°C, split peaks with methanol and water were observed at >0.01 μL injection volume, due to very low solubility. Figure 4 shows the solubility of methanol and water coinjected over PC at 40°C. As expected, there is little interaction between the sorbed species. Methanol is approximately two times more soluble than water in PC, independent of water content. Compatible solutes demonstrate no sorbed phase interaction.

Phenol/diphenylcarbonate (DPC)

This system is important in high-conversion polymerization of PC. It is necessary to remove the monomer phenol to overcome reaction equilibrium by utilizing aggressive DV. At >200°C water in a phenol/water injection is retained only 4% relative to inert gas and can be considered insoluble in PC. In contrast, phenol is quite soluble in PC at 200°C and, not surprisingly, this solubility is independent of water content. The lack of interaction between water and PC is due to the large difference in volatility and allows phenol to be conveniently injected as the vapor above a water solution or as a solution without concern for interaction.

At >200°C, with liquid injections of phenol/water, saturation due to low phenol retention occurred. Injections had to be made with 20 μL of phenol/water vapor (above an 88% water solution) at room temperature and pressure, with helium diluent and 1-μL argon gas added as an internal reference. As shown in Figure 5, this incredibly small amount of phenol (~10 ng into the column) is still well resolved by the MSD. Replicate injections were made days apart to test for drift in the column coating, which was not observed in the zeroth and first moments. As seen in Figure 5, peak broadening was insignificant relative to the inert reference, and phenol diffusivities cannot be reliably estimated by IGC at >200°C when $D_p > 10^{-6}$ cm²/s.

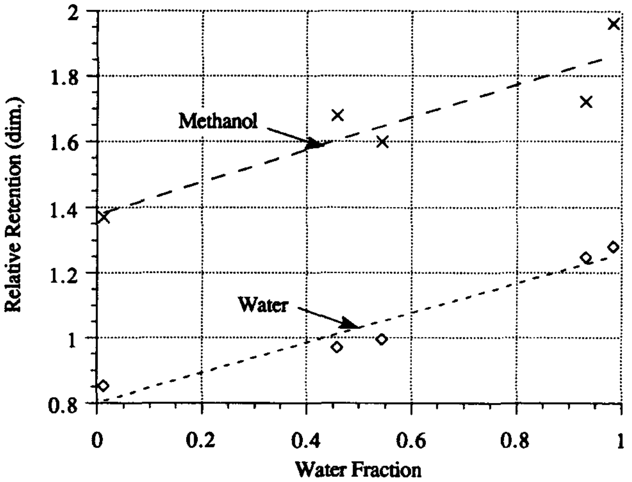

Figure 4. Solubility of methanol and water at 40°C in polycarbonate.

Diphenylcarbonate was dissolved ~20% in dichloromethane and injected at 200-300°C with argon. Once again, saturation was an issue and injections <0.04-μL liquid with 1 μL of argon gas were necessary. Figure 6 shows phenol, DPC, and water solubility in PC at 200-300°C. These data represent the limit of IGC analysis of weakly sorbed solutes. Assuming that the solubilities are pressure-independent, the ppm solute in PC can be estimated below, assuming ideal gas phase, no volume change upon sorption and a linear isotherm, with P as partial pressure in torr and T in K. For example, assuming no interactions, at 10-torr partial pressure and 300°C, phenol

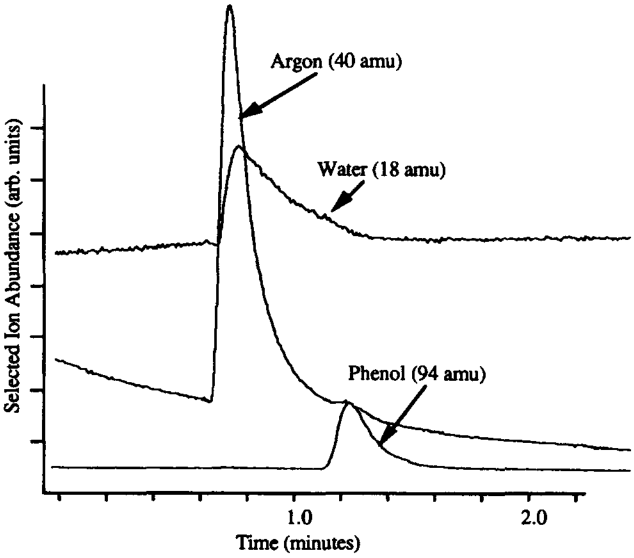

Figure 5. Elution of argon, water and phenol at 225°C over PC demonstrating peak overlap and lack of broadening due to low solubility/high diffusivity.

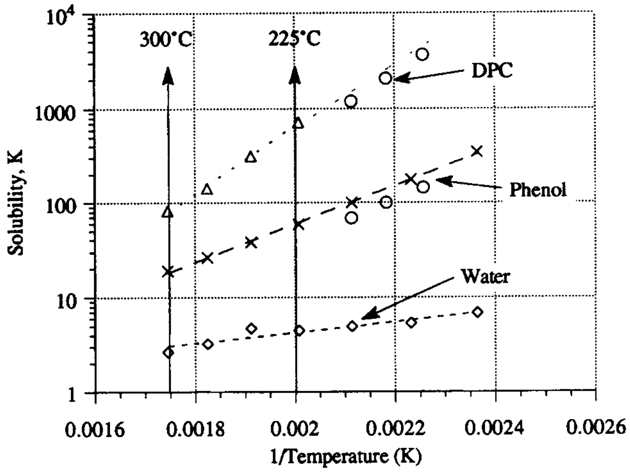

Figure 6. Solubilities of phenol, water and DPC in PC at temperatures >200°C by high-resolution inert-gas reference IGC vs. data (open circle) from R. Baltus.

solubility in polycarbonate is 390, DPC 4000, and water 12 ppm.

$$\text{ppm }(\phi-\text{OH})=6.2\,\frac{P}{T}\exp\left[\frac{4{,}694}{T}\right]$$

$$\text{ppm (DPC)}=0.1\,\frac{P}{T}\exp\left[\frac{8{,}364}{T}\right]$$

$$\text{ppm (water)}=72\,\frac{P}{T}\exp\left[\frac{1{,}322}{T}\right]$$

Conclusions

Capillary column IGC with an internal inert gas reference, injection of <10 ng, and a fast high-resolution multispecies detector is necessary to study multicomponent solute-polymer sorption of low-solubility solutes. Conventional capillary column IGC can resolve neither diffusivities $D_p > 10^{-6}$ cm^2/s nor solubilities $K<10$ due to unavoidable instrument dispersion and retention.

Multicomponent IGC can detect interactions between solutes in polymer sorption and permeation. The solutes must be mutually incompatible, and have roughly equal vapor pressures and solubilities in the polymer phase. Multicomponent interactions can be exploited in DV applications by displacing an undesirable sorbed species by another more benign component which is incompatible with it. Inversely, interactions may be exploited in stabilizing polymer blends by immobilizing a desirable solute by adding another molecule with which it is more thermodynamically compatible.

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