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Determination of thermodynamic and transport properties of a polystyrene-*co*-acrylonitrile copolymer by infinite and finite concentration IGC

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ABSTRACT

The capillary column inverse gas chromatography technique was used to determine diffusivity and solubility data for several solutes in a poly(styrene-*co*-acrylonitrile) random copolymer (SAN). Both infinite dilution and finite concentration experiments were conducted using an IGC-mass spectrometer (IGC-MS) technique that combines the performance of the gas chromatography technique with the resolution of the mass spectrometer detector. Thirteen solutes were studied to obtain thermodynamic and diffusion coefficients at infinite dilution. Finite concentration experiments were conducted with toluene up to 10 wt.% concentration. Pseudo-binary experiments were also conducted in which a trace amount of hexane was injected in a mixture of toluene and SAN.

1. Introduction

Inverse gas chromatography (IGC) is one of the most versatile techniques to measure both solubility and diffusivity in polymer systems. It was originally developed to measure these properties at infinite dilution of the solute. Early experiments conducted in packed columns did not possess enough accuracy for the estimation of the diffusion coefficients because of the lack of uniformity of the polymer coating. By using a capillary column, where the polymer was deposited more uniformly on the capillary's walls, Pawlisch et al. [1,2] proposed a more accurate way of measuring diffusion coefficients. Tihminlioglu et al. [3] extended this method to finite concentration IGC experiments and showed good agreement with diffusivity taken with other sorption techniques. More recently the IGC technique has been applied to the study of solubility and diffusivity of solvents at high pressures by Zielinski et al. [4] and its application to measure diffusion coefficients in multicomponent systems is possible using a mass spectrometer detector as suggested by Galdámez et al. [5].

Diffusivity in polymer systems has been traditionally measured by gravimetric sorption methods where the mass pick up of a polymer sample is related to the displacement of a quartz spring in a conventional gravimetric balance or the torque exerted on a magnetic suspension balance. This method usually requires long times to conduct the experiments, cannot be easily applied to low-solvent concentration systems, and needs fairly expensive equipment. Conversely, inverse gas chromatography is an inexpensive technique (whose major component, a gas chromatograph, if often available in any laboratory) and provides a faster method to obtain solubility and diffusivity information. Faridi et al. [6] has shown the validity of the IGC method by comparing it with other gravimetric sorption methods.

This work is an example where this technique can be used to obtain the information needed to develop a new product or process in a reasonable time frame which is often critical in industrial applications. Polystyrene (PS) is a brittle, clear solid material at room temperature but has an extraordinary processability at higher temperatures. Its original properties can be adjusted to meet the desired specifications for many applications by selecting an appropriate comonomer or composition. For example, to improve the chemical resistance it can be polymerized together with acrylonitrile. Changing the composition of the resulting polymer also changes the thermodynamic and transport properties which may lead to modification of the physical properties and manufacturing process. A fast method to calculate those properties for new polymers, such as the IGC method is of great value. In this work, the effect of the acrylonitrile groups in polystyrene on the diffusion and solubility of several solvents is studied at infinite dilution and finite concentrations using the IGC technique.

2. Theory

The capillary column inverse gas chromatography method has been proven to accurately measure solubility and diffusivity in polymer–solvent systems [3,6]. The procedure to analyze the response from a capillary column for an infinitely dilute input pulse

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Nomenclature

C	solute concentration in the gas phase (mol/m^3)
C'	solute concentration in the polymer phase (mol/m^3)
D_p	diffusion coefficient of the solute in the stationary phase (m^2/s)
D_g	diffusion coefficient of the solute in the gas phase (m^2/s)
j	pressure-drop correction factor
K	partition coefficient
L	column length (m)
m_2	mass of polymer (g)
M_1	molecular weight
q	solute concentration in the polymer phase (mol/g polymer)
R	radius of the gas-polymer interface (m)
s	Laplace variable
T	temperature (K)
U	carrier gas velocity (m^2/s)
V_1	specific volume (m^3/g)
V_N	net retention volume (m^3)
V_S	volume of the stationary liquid phase (m^3)
w_i	weight fraction
y	mole fraction of solute in the gas phase
$Y(1,s)$	dimensionless concentration of solute in the gas phase in the Laplace domain

Greek letters

α	thermodynamic dimensionless group
β	polymer phase diffusion dimensionless group
Γ	axial dispersion dimensionless group
τ	polymer coating thickness (m)

was introduced by Pawlisch et al. [1,2]. It involves fitting an experimental elution profile with a theoretical one obtained by solving the continuity equation for the solute in the polymer and gas phase throughout the column. Eq. (1) shows the expression for the theoretical response peak in the Laplace domain at the exit of the column at infinite dilution.

$$Y(1,s) = \exp\left(\frac{1}{2\Gamma} - \sqrt{\frac{1}{4\Gamma^2} + \frac{s}{\Gamma} + \frac{2\sqrt{s}}{\alpha\beta\Gamma}\tanh(\beta\sqrt{s})}\right) \tag{1}$$

Here, Y is the dimensionless concentration in the gas phase, s is the Laplace domain variable and α, β, Γ are the three dimensionless parameters which contain the transport and thermodynamic information. α is related to the thermodynamics of the system, β and Γ to the polymer and gas phase transport properties, respectively. They are defined as follows:

$$\alpha = \frac{R_c}{K\tau} \quad \beta = \sqrt{\frac{U\tau^2}{LD_p}} \quad \Gamma = \frac{D_g}{UL} \tag{2}$$

Here L is the length, τ is the thickness of polymer coating, and R_c is the void cross-section radius of the capillary column. D_g is the diffusion coefficient of solute in the carrier gas, U is the velocity of carrier gas, D_p is the mutual diffusion coefficient in the polymer, and K is a dimensionless quantity defined as the concentration in the polymer phase divided by that in the vapor phase. Although Eq. (1) requires three dimensional parameters, Γ has little effect on the peaks' shape and its value can be calculated independently. A non-linear least square regression was used to find the values of α and β that best fit the experimental curve. A typical example of the fit of the model using Eq. (1) to the experimental elution profile is shown in Fig. 1.

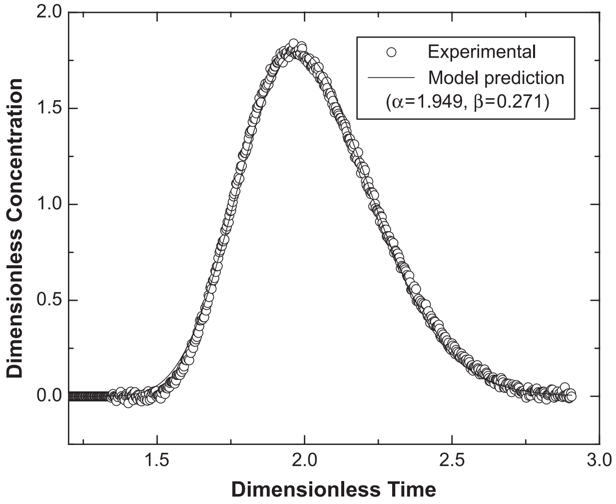

Fig. 1. Comparison of experimental data and model fit of elution profile for toluene–poly(styrene-*co*-acrylonitrile) system at 150 °C.

Tihminlioglu and Danner [7] developed a model for finite concentration, based on Pawlisch et al. work, that allows one to estimate diffusivity and solubility from the elution profiles obtained at finite concentration of the solute. A similar expression to Eq. (1) was obtained in that work to predict the theoretical elution profiles. The only difference is in the definition of the thermodynamic parameter α which is defined as:

$$\alpha = \frac{R}{(1-y)(\mathrm{d}C'/\mathrm{d}C)\tau} \tag{3}$$

Here y is the true mole fraction of the solute in the gas phase and the $(1-y)$ term accounts for the change in velocity with concentration, i.e., the *sorption effect* (Conder and Young [8]). α, at finite concentrations, is inversely related to the slope of the sorption isotherm $\mathrm{d}C'/\mathrm{d}C$ where C' and C are the solute concentrations in the polymer and vapor phases, respectively. At infinite dilution, the isotherm slope is equal to the partition coefficient K defined previously and the original expression for α is recovered.

As described by Conder and Young [8], retention volumes, V_N, can be used to calculate the sorption isotherms and other thermodynamic properties at finite concentration. Retention volumes are calculated from IGC experiments as follows.

$$V_N = V_s(1-y)\frac{\mathrm{d}C'}{\mathrm{d}C} \tag{4}$$

Here V_s is the volume of the stationary phase. Tihminlioglu and Danner [7] have shown how the group $(1-y)\mathrm{d}C'/\mathrm{d}C$ in Eq. (3) can be obtained from the capillary column IGC experiment. The solubility isotherm q, defined as the moles of solute sorbed per gram of dry polymer, is obtained by integrating Eq. (4).

$$Q = \frac{j}{m_2}\int_0^C \frac{V_N}{1-y}\mathrm{d}C \tag{5}$$

Here j is the pressure-drop correction factor [8], which is generally close to the unity for capillary columns, and m_2 is the mass of the polymer in the GC column. The concentration in the gas phase, C, was calculated using the second virial coefficient to correct for the non-ideality as follows

$$C = \frac{1}{j}\frac{yP_{\text{column}}}{RT + P_{\text{column}}y^2B_{11}} \tag{6}$$

The integral in Eq. (5) was evaluated by fitting the data to a second or third order polynomial function prior to integration. The weight fraction of solute in the polymer follows directly from Eq. (7), where M_1 denotes the solute molecular weight

$$w_1 = \frac{qM_1}{1+qM_1} \tag{7}$$

2.1. Weight-fraction activity coefficient and interaction parameters at infinite dilution

At infinite dilution of the solute, the relation between chromatographic data and the solute weight fraction activity coefficient is (1 = solute, 2 = polymer) is as follows:

$$\Omega^\infty = \frac{273.2R}{V_g^0 P_1^s M_1}\exp\left(-\frac{P_1^s(B_{11}-V_1)}{RT}\right) \tag{8}$$

The standard state in Eq. (8) is pure liquid solute at the system temperature and zero pressure. The exponential term in this equation corrects for the gas phase non-ideality of the solute. The specific retention volume is given by

$$V_g^0 = \frac{273.2K}{T\rho_2} \tag{9}$$

Here, T is the temperature, K is the partition coefficient, and ρ_2 is the polymer density. At infinite dilution the interaction parameter is related to the weight fraction activity coefficient through the following relationship.

$$\chi^\infty = \ln \Omega_1^\infty - \left(1-\frac{1}{r}\right) + \ln\frac{\rho_1}{\rho_2} \tag{10}$$

2.2. Estimation of the polymer solubility parameter

The solubility parameters were calculated using a combination of the Flory theory [9] with the Hildebrand–Scatchard equation [10,11], as found through the following equation.

$$\left[\frac{\delta_1^2}{RT} - \frac{\chi^\infty}{V1}\right] = \frac{2\delta_2^\infty}{RT}\delta_1 - \left[\frac{\delta_2^{\infty 2}}{RT} + \frac{\chi_s}{V_1}\right] \tag{11}$$

Here δ_2^∞ is the polymer solubility parameter at infinite dilution of the solute and δ_1 is the solubility parameter of the solute given by

$$\delta_1 = \left[\frac{\Delta H_v - RT}{V_1}\right]^{1/2} \tag{12}$$

Here ΔH_v is the heat of vaporization of the solute. Since χ, V_1, and δ_1 are known, the solubility parameter of the polymer, δ_2^∞ can be determined from the slope of $(\delta_1^2/RT - \chi/V_1)$ vs δ_1.

3. Experimental

3.1. Materials

A random polystyrene-*co*-acrylonitrile copolymer was studied in this work at infinite dilution with 13 different solutes and at finite concentration of toluene. The copolymer was obtained from Dow Chemicals Inc. (Midland, MI) with an average molecular weight of 111,000 and a M_w/M_n ratio of 2.17. The PS/AN composition weight ratio of the copolymer was 85:15, the T_g was approximately 105 °C and with a specific density at 25 °C of 1.035. Thirteen solutes were studied at infinite dilution at temperatures ranging from 120 °C to 170 °C. The solutes can be classified as aromatic compounds (benzene, toluene, and *meta*-, *para*-, and *ortho*-xylene), ring compounds (cyclopentane, cyclohexane, 1-cyclohexene, and methylcyclohexane), and three linear hydrocarbons (pentane, hexane and 1-hexene). All of them were of chemical reagent grade, purchased from Sigma–Aldrich (Milwaukee, WI.), and were used without further purification. Ultra high purity helium was used as the carrier gas.

3.2. Column preparation

An empty, 0.053-mm inner diameter fused-silica capillary column was supplied by Supelco (Bellefonte, PA). The column was coated using a static method similar to the one described by Grob [12]. A methylene chloride solution with the desired amount of the copolymer was prepared and degassed by sonication for about 1 h. The degassed solution was put into a 15-m fused-silica capillary column. The column was filled using a syringe pump that contained the polymer solution. Several millilitres were flushed out of the column to guarantee a constant concentration after the filling procedure. Then, one end was sealed using an UV curing epoxy resin (Dymax Corp., Torrington, CT) and vacuum was applied through the other end at constant temperature (35 °C). The solvent was slowly evaporated to form a uniform 5 μm coating as the polymer was deposited on the walls. The column was conditioned in a gas chromatograph to eliminate residual solvent by flowing helium through it while increasing the temperature at a rate of 1 °C per minute until the maximum experimental working temperature was reached. The columns' thicknesses were determined from the polymer concentration in the original solution as described by Grob [12] and corroborated by SEM images.

3.3. Experimental setup and procedures

An HP 5890 Series II gas chromatograph unit equipped with an HP 5971 mass spectrometer detector was used in this work. An extensive study of the use of a mass spectrometer detector, instead of the traditional thermal conductivity or flame ionization detectors, for measuring diffusivity and solubility of solute in polymeric systems has been presented in a previous publication [5].

UHP helium was used as the carrier gas with an average flow rate of approximately 1–2 mL/min through the column. Argon was used as the marker gas to calculate the linear velocity of the carrier gas. Linear velocities between 4 and 8 cm/s were used in most cases. A 0.03-μL solute injection was done for each analysis and three replicas were conducted for each solute and temperature. For mixed carrier gas streams, helium was allowed to flow through a saturator in which the solute is kept under gentle agitation provided by a mechanical stirrer and at constant temperature maintained by a combination of an immersion heater and a cooling plate. The total pressure in the saturator was monitored by means of an Omega PX303 (Stanford, CT) pressure transducer and it was slightly above atmospheric pressure at all times. To ensure that there were no condensation of the solute between the saturator and the injector port, the connecting tubing and the saturator lid were wrapped in heating tape and maintained at temperatures well above those in the saturator and in the column.

4. Results and discussion

4.1. Infinite dilution results

Inverse gas chromatography experiments were conducted with the solutes listed previously. Experiments were done at temperature from 120 to 170 °C in 10-degree intervals. Typically three repeat runs were made except at 120 °C. At this temperature, there were only two because of the longer time needed for the complete elution of the peak due to their low diffusivity.

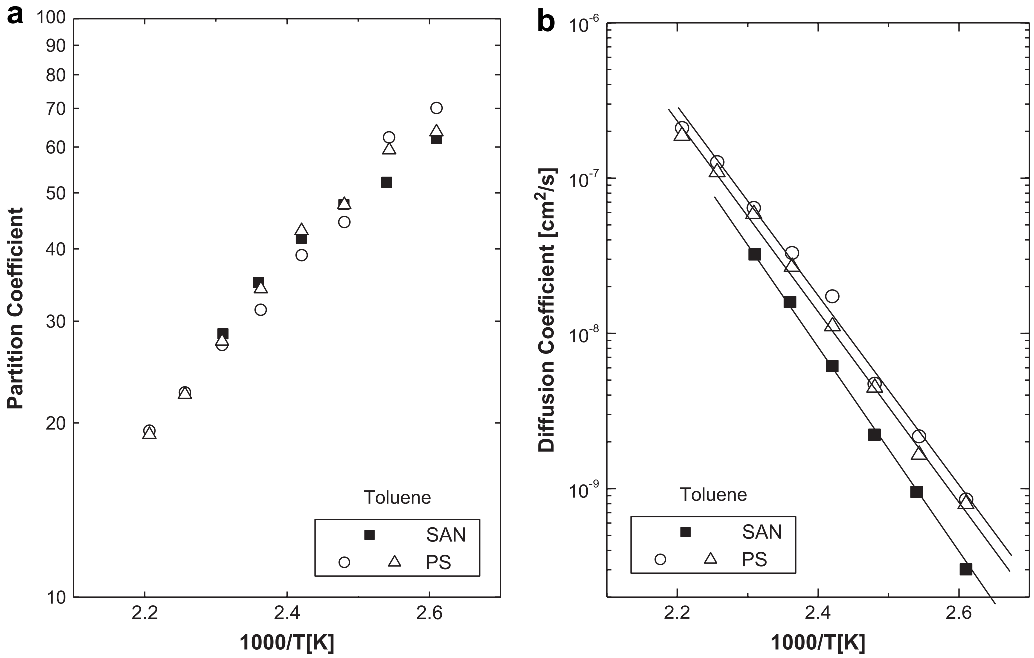

Fig. 2. Comparison of the (a) partition coefficient and (b) diffusion coefficient for SAN (this work) with those obtained for PS from the literature: Tihminlioglu and Danner [14] (○) and Becker (△) [15].

One of the goals of this work was to compare the properties of the copolymer with those from the neat PS to understand the effect of the addition of the acrylonitrile groups. Previous work [13] done for PS and the poly(styrene-*co*-acrylonitrile) copolymer with some gases (CO_2, N_2, O_2) at room temperature using a pressure decay technique has shown that acrylonitrile has little effect on the solubility of these gases. All gases showed similar solubility in the neat PS as in the copolymer. On the other hand, acrylonitrile did affect diffusivity of these gases, decreasing by a factor between two and four times relative to the values obtained in PS. A similar conclusion can be drawn from the IGC studies as shown for toluene in Fig. 2. PS has been extensively studied, and it was easy to find some literature values [14,15] for the toluene–PS system for comparison with the data taken in this work. Fig. 2a shows that, within experimental error, there are no significant changes in the partition coefficient for poly(styrene-*co*-acrylonitrile) with respect to PS, whereas Fig. 2b shows a decrease in the diffusion coefficient of toluene in poly(styrene-*co*-acrylonitrile) as compared with PS. An Arrhenius dependence of the diffusion coefficient with respect to temperature was observed in both cases. The average values of the experimental diffusion and partition coefficients are presented in Tables 1 and 2.

In general, the linear hydrocarbons show the lowest solubilities of all solutes studied as inferred from their weight fraction activity coefficients (Ω^∞) shown in Table 2. Eqs. (8) and (9) were used to calculate Ω^∞ from the experimental partition coefficients. Despite their small solubility the resulting elution profiles provided meaningful diffusion coefficients, as long as the experiments were conducted at relatively low carrier gas velocities to assure equilibrium with the stationary phase.

On the other hand, aromatic solutes showed the best affinity with poly(styrene-*co*-acrylonitrile) due to the high percentage of styrene groups in the chain's backbone. Consequently, the lowest values of the interaction parameters were obtained for those solutes. Fig. 3 shows the relationship between the solute structures and the partition coefficients and for several aromatic and non-aromatic rings. There is a significant decrease in the partition coefficient as the ring loses its aromatic property and becomes saturated.

Fig. 4 shows the diffusion coefficients for a series of aromatic rings at different temperatures. They follow the expected trend as the diffusion coefficient decreases as the volume of the molecule increases by adding methyl groups. Cyclohexane with a molecular weight just slightly greater than benzene shows a much impeded mobility in the polymer. Unlike aromatic rings, cyclohexane does not take the shape of a perfect hexagon, adopting instead a 3-D "chair conformation" which is bulkier than the planar structure associated with aromatic rings. Fig. 4 is another example that the

Table 1
Diffusion coefficients for SAN–solvent systems

Solvent	$D_p \times 10^9$ (cm²/s)				
	130 °C	140 °C	150 °C	160 °C	170 °C
Pentane	4.3	11	22	49	
Hexane	2.5	5.6	22	38	
1-Hexene	3.0	6.8	21	40	
Cyclopentane	1.7	4.6	16	31	
Cyclohexane	0.87	2.3	8.0	17	33
Cyclohexene	1.8	4.3	11	25	50
Methylcyclohexane	0.61	2.1	6.4	13	28
Benzene	3.5	8.8	19	42	
Toluene	2.2	6.1	16	32	
para-Xylene		4.4	13	32	73
meta-Xylene		3.6	10	25	58
ortho-Xylene	0.82	2.6	7.9	18	43

Table 2
Weight fraction activity coefficients for SAN–solvent systems

Solvent	Ω^∞				
	130 °C	140 °C	150 °C	160 °C	170 °C
Pentane	18.10	18.13	19.35	19.60	
Hexane	19.88	17.91	18.38	17.62	
1-Hexene	13.45	13.57	14.10	13.71	
Cyclopentane	8.08	8.15	8.18	8.20	
Cyclohexane	11.19	10.44	10.52	9.98	9.59
Cyclohexene	9.25	8.66	8.24	7.91	7.73
Methylcyclohexane	12.38	11.88	11.88	10.99	10.34
Benzene	4.49	4.11	4.08	3.98	
Toluene	4.91	4.60	4.39	4.30	
para-Xylene		5.62	5.55	5.49	5.47
meta-Xylene		5.66	5.53	5.50	5.43
ortho-Xylene	5.24	5.00	4.96	4.97	4.99

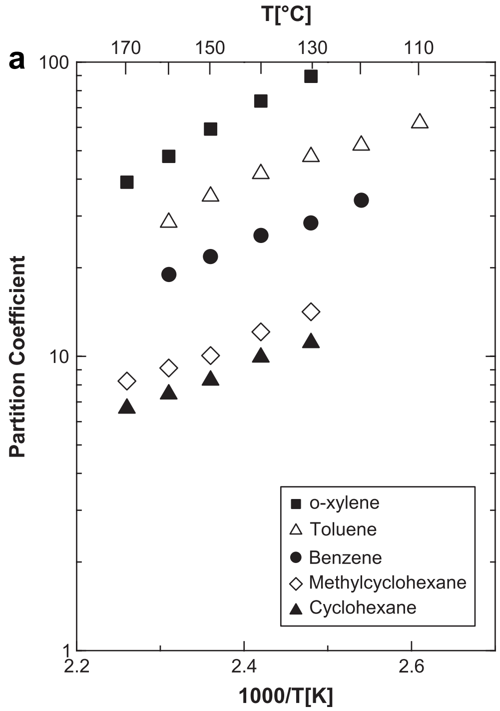

Fig. 3. Partition coefficients for several ring compounds in poly(styrene-*co*-acrylonitrile) as a function of temperature.

mobility of small molecules in polymers is strongly related to their molecular volumes.

The differences in the diffusion and partition coefficients measured at different temperatures for the xylene series are shown in Fig. 5. *Ortho*-, *meta*-, and *para*-xylene are molecules with the same chemical formula, which only differ in the relative location of the methyl groups around the aromatic ring. The effect of the location of these two methyl groups has a direct impact on the diffusion coefficient. Even though, according to the free-volume theory, these molecules diffuse as a single unit, their shape is not spherical. Therefore, they do not have an isotropic displacement: they show, instead, a preferential displacement along the smallest dimension. One can easily imagine that *para*-xylene has a preferential diffusion direction along its symmetry axes. Conversely, the two methyl groups on contiguous carbons present in the *ortho*-xylene have a bigger effect on the molecule's mobility since both groups contribute to the increase in size in one of the dimensions. The dependence of the partition coefficient on the structure of the three xylenes (Fig. 5b) is due to the chemical nature of the methyl groups. These groups are weakly electron donating and can share electrons with the aromatic ring. They would then be positively charged whereas the aromatic ring is charged negatively as it can delocalize the shared electrons along the π-orbital. The relative position of these donating groups can generate dipole moments in the molecule. It would vary from almost zero for the symmetric molecule of *para*-xylene to increasing values as the methyl groups get closer. Experimental values of the dipole moments of 0.06 and 0.45 Debye have been measured [16] for *para*- and *ortho*-xylene, respectively.

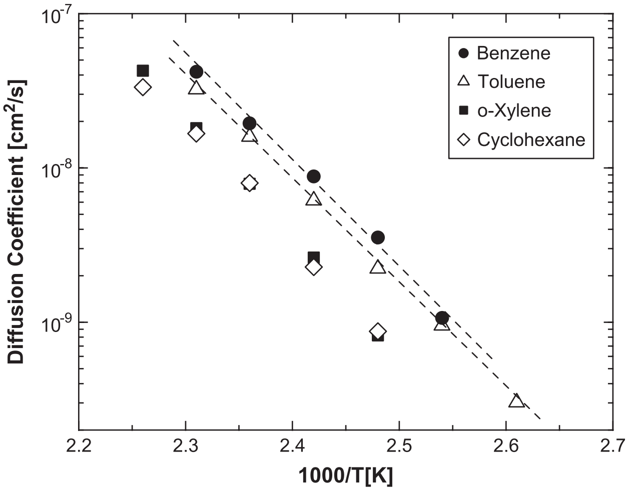

Fig. 4. Diffusion coefficients of some aromatic solutes in poly(styrene-*co*-acrylonitrile) as a function of temperature.

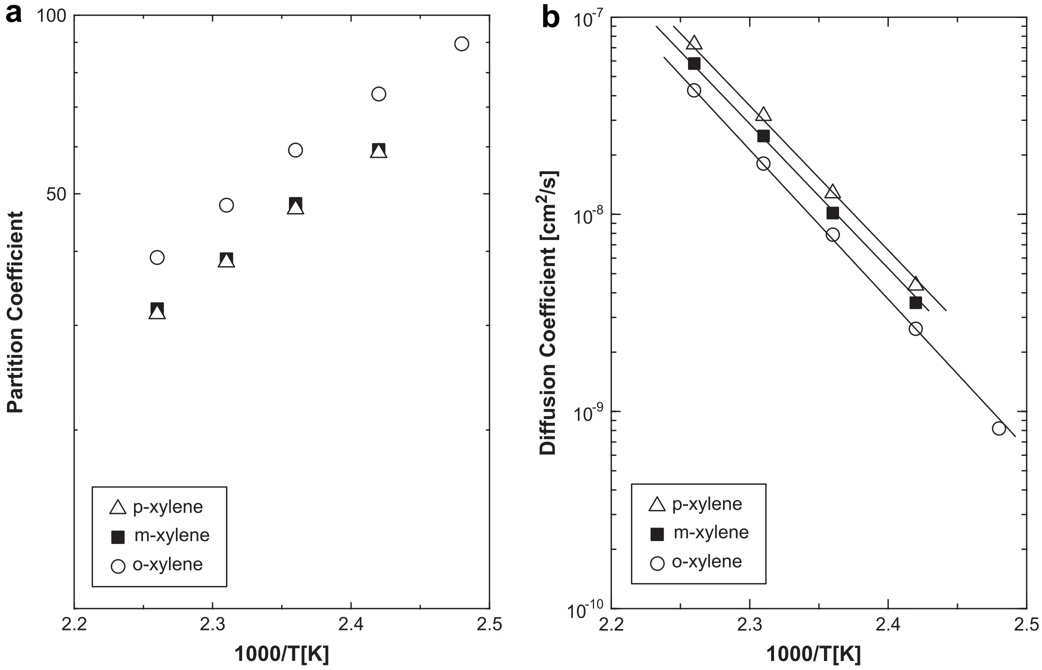

Fig. 5. Partition (a) and diffusion coefficients (b) for the xylene series in poly(styrene-*co*-acrylonitrile).

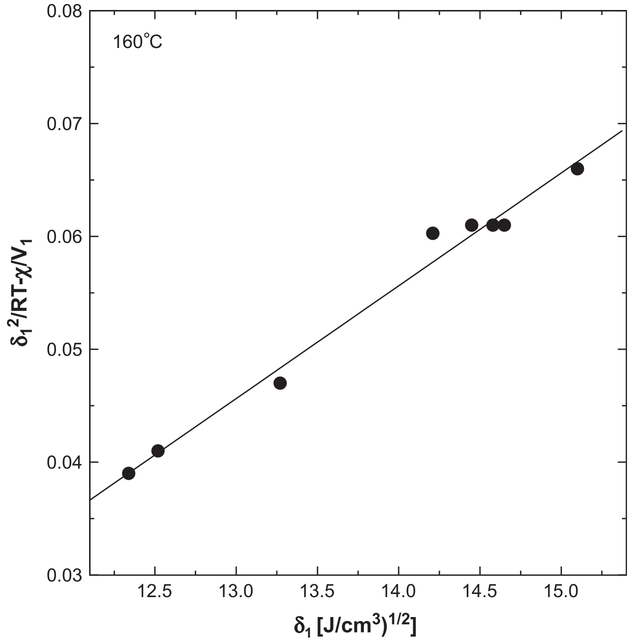

Fig. 6. Estimation of solubility parameter of PS-*co*-AN copolymer at 160 °C.

The higher the dipole moment the more interactions exist between the solute and polymer, increasing the solubility as observed in Fig. 5a. A similar behavior has been observed in other polar polymers such as PVAc by Arnould [17].

Solute solubility parameters were computed through Eq. (12). The latent heat of vaporization, ΔH_v, and the molar volume, V_1, were both obtained from Daubert and Danner [18] for each solute at the appropriate temperature. Using Eq. (11) and a least square analysis, δ_2^∞ values were determined. Fig. 6 is a plot of $(\delta_1^2/RT - \chi/V_1)$ versus δ_1, for various solutes in the polystyrene-*co*-acrylonitrile at 160 °C. The values of δ_2^∞ for poly(styrene-*co*-acrylonitrile) as a function of temperature are presented in Table 3. A range of 17.8–20.16 MPa$^{1/2}$ has been reported for PS at temperatures close to room temperature [19]. The data in this work were obtained at higher temperatures, where the solubility parameters are expected to be smaller. An extrapolation to room temperature, assuming a linear relationship of the solubility parameters with temperature, yields a value of 22.3 MPa$^{1/2}$. Nevertheless, it is not clear that the linearity would hold at temperatures below its T_g (105 °C), since the glassy state is not a true thermodynamic state. For this reason the indication that the cohesive energy is increased by the introduction of more polar acrylonitrile groups should not be considered as proven.

4.2. Finite concentration studies

Finite concentration experiments for the poly(styrene-*co*-acrylonitrile)–toluene systems were performed between 110 and 150 °C and up to 10 wt.% of toluene in the polymeric phase. Eq. (5) was used to calculate the experimental absorption isotherms for this system at three temperatures: 120, 130, and 150 °C. In Fig. 7a, the experimental sorption data are shown as points and the lines are second order polynomial correlations of these data, added as visual guides to observe the loss of the linearity of the isotherm as temperature is decreased or concentration of toluene is increased. These data were converted to activity and volume fractions to obtain the Flory–Huggins interaction parameters that describe the thermodynamics of the system (Fig. 7b). Solute and polymer density as a function of temperature were obtained from Refs. [20,21], respectively. Fig. 7b (inset) shows the equilibrium data for toluene at the temperatures studied. A constant value for the interaction parameter of 0.33 correlates all the temperatures well.

Table 3
Solubility parameters for SAN as a function of temperature

Temperature (°C)	δ_2 MPa$^{1/2}$
130	18.64
140	18.21
150	18.34
160	17.91
170	17.10

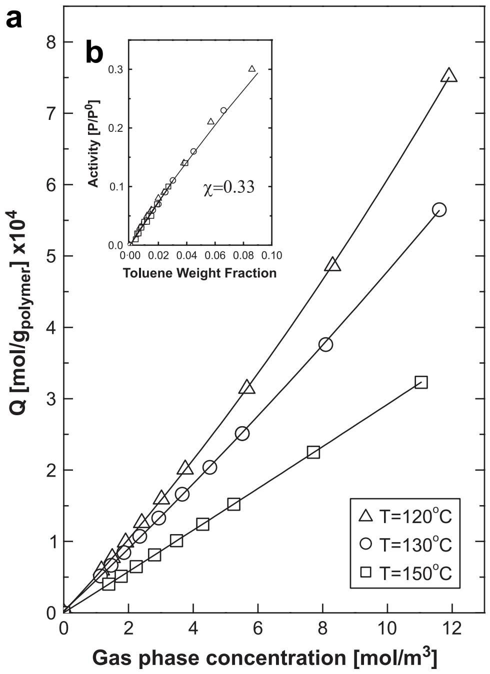

Fig. 7. Absorption isotherms (a) and activities (b) of toluene at equilibrium with a polystyrene-*co*-acrylonitrile copolymer at several temperatures.

The mutual diffusion coefficients of the toluene–poly(styrene-*co*-acrylonitrile) system are illustrated in Fig. 8. They show a strong dependence on the concentration of toluene in the polymeric phase, especially at the lowest temperature studied. Unfortunately, a free-volume correlation could not be made for this system

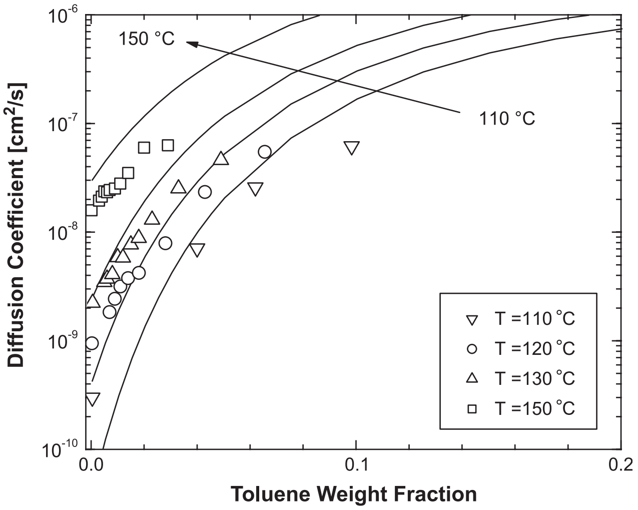

Fig. 8. Experimental diffusion coefficients for toluene in poly(styrene-*co*-acrylonitrile) at several temperatures. Lines are free volume predictions using PS free-volume parameters for comparison.

because of the lack of a set of free-volume parameters for the copolymer. The curves shown in Fig. 8 are, instead, the free-volume prediction for toluene in pure polystyrene using the parameters reported by Duda et al. [22]. Because of the low acrylonitrile content in the copolymer small differences were expected between the diffusion coefficients for neat PS and this poly(styrene-*co*-acrylonitrile). This plot also shows the same trend, a decrease of diffusivity with acrylonitrile content, found in previous experiments with gases and at infinite dilution.

In this work we are extending the use of IGC to multicomponent systems since most of the diffusion processes encountered in industry involve more than one component. These processes are often treated as pseudo-binary systems because the lack of reliable diffusivity data. Unfortunately, the number of techniques capable of measuring diffusion and thermodynamic properties in multicomponent systems is very limited. The technique presented in this work can be readily applied to the study of the effect of one solute on the diffusivity and thermodynamic of a second solute present in trace amounts, and with the necessary equipment modifications it can also be used to the study of true multicomponent systems [5].

Finite concentration experiments, in addition to the finite binary experiments (where the same solute used to saturate the polymer is injected), were conducted in which the column was saturated with toluene and a trace amount of hexane was injected. The concentration of toluene in the polymer was determined from the gas phase concentration as per Fig. 7. The small amount of hexane injected does not affect the equilibrium. The influence of toluene on the diffusion coefficient of a third species (hexane) was studied using the IGC-MSD. Fig. 9 shows the diffusion coefficient of hexane in toluene–poly(styrene-*co*-acrylonitrile) mixtures. The diffusion coefficients for hexane increase with the concentration of toluene. The same behavior was reported by Galdámez et al. [5] for mixtures of THF and cyclohexane in PVAc. The increase of the diffusivity is more significant at the lower temperatures where an increase of several orders of magnitude for the diffusion coefficient is observed by increasing the solvent concentration up to 10%. Unfortunately, at 110 °C, the low value of the diffusion coefficient at infinite dilution and the low partition coefficient of hexane make difficult the accurate measurement of the diffusion coefficient and therefore it is not shown in Fig. 9. At these conditions a poor fitting between the theoretical and elution profile was found and the diffusion coefficient could only be estimated to be of the order of 10^{-12} $\mathrm{cm^2/s}$. In this region of low solute concentrations, the diffusion coefficient is limited by the lack of free volume in the polymer, and the additional free volume introduced by toluene dissolved in the copolymer has a great influence on the diffusion coefficient of hexane.

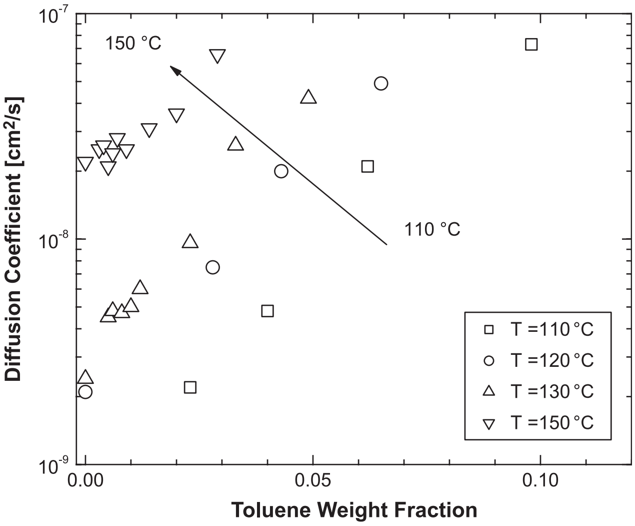

Fig. 9. Experimental diffusion coefficients for hexane at finite concentration as a function of the toluene weight fraction in poly(styrene-*co*-acrylonitrile).

5. Conclusions

Polymer–solvent interactions, partition, and diffusion coefficients at infinite dilution of solute were obtained for various solutes in poly(styrene-*co*-acrylonitrile) by IGC. Since the IGC technique is rapid, simple, and reliable; this technique is ideal for industrial purposes. In this study, both thermodynamic and diffusion measurements were performed at infinite and finite concentrations using an IGC-mass spectrometer technique.

The thermodynamic results at infinite dilution are useful to determine the degree of compatibility between poly(styrene-*co*-acrylonitrile) and the various solutes used. Aromatics were shown to be the most suitable solvents for the copolymer as they have more affinity than other paraffins or saturated rings. Also this study shows that the acrylonitrile groups, at the composition studied, have little effect on the partition coefficient of the solutes but they systematically decrease the diffusion coefficients of the migrating species compared to pure PS.

Finally, with minimal modifications the IGC technique was used to determine the thermodynamic and transport properties of toluene and hexane in the poly(styrene-*co*-acrylonitrile)–toluene mixture at concentrations of up to 10 wt.% toluene. One advantage of this technique is that multiple data points can be obtained much more expediently than with standard sorption techniques without compromising accuracy. Also it can be readily used to study the effect of a solvent in the thermodynamic and transport behavior of a second solvent, expanding the applicability of the technique to regions where the conventional sorption studies cannot be applied.

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