Diffusion of organic solvents in thermoplastic elastomers: infinite dilution experiments

(Article begins on next page)

07 December 2025

Diffusion of organic solvents in thermoplastic elastomers: infinite dilution experiments

Ayşegül Aşkın [1]*, Sevilay Altınbaş [1], Marco Giacinti Baschetti [2]

[1] Department of Chemical Engineering, Faculty of Engineering and Architecture, Eskisehir Osmangazi University, Eskişehir, 26040, Turkiye

[2] Department of Civil, Chemical, Environmental and Material Engineering (DICAM), Alma Mater Studiorum, Università Di Bologna, via Terracini 28, I-40131 Bologna, Italy

*Corresponding Author's E-mail: aaskin@ogu.edu.tr

Abstract

Diffusion parameters, activity coefficients and Flory-Huggins interaction parameters of n-hexane, cyclohexane and benzene in several styrene-diene block copolymers (styrene-butadiene-styrene (SBS), styrene-ethylene/butylene-styrene (SEBS), and styrene-isoprene-styrene (SIS)) were obtained using the inverse gas chromatography (IGC) method with a packed column in the infinite dilution region and the range of 40-70 °C.

Diffusion coefficients based on the change in chromatographic peak width with carrier gas flow rate were calculated using the Van Deemter equation. The strong linear relationship indicated that using the Van Deemter equation was appropriate. The temperature increase caused the infinite dilution diffusion coefficient to increase, while the infinite dilution activity coefficient decreased; This proved the different behavior of the kinetics and thermodynamic parameters as a function of temperature. All solutes' infinite dilution diffusion coefficients decreased going from SBS to SEBS with the following order: SBS>SIS>SEBS. Activation energies were calculated from the Arrhenius equation, which provides the temperature dependence of diffusion coefficients.

Keywords: Activity Coefficient, Diffusion Coefficient, Inverse Gas Chromatography, Thermoplastic elastomers.

Introduction

Knowing the equilibrium and mass transfer properties is of great concern in various manufacturing operations, such as drying, devolatilization, polymerization, and vacuum/gas stripping involving polymers [1-4]. Understanding the solvents' activity and diffusion coefficients in melts of polymers helps analyze basic processing stages including plasticization, bulk polymerization, and devolatilization.

Furthermore, due to the tightening environmental and health regulations governing the volatile residuals in polymer products, there is now more interest in the activity and diffusion coefficients at infinite dilution for volatile solvents in polymer melts [5].

Most of the reported diffusion and activity coefficients have been measured by conventional methods. They are based on the bulk equilibration and gravimetric sorption/desorption experiments and allow the determination of the coefficients over a relatively extended range of solvent concentration. Applying these techniques to polymer-solvent systems presents challenges, such as longer experiment durations when the solvent is present in minimal amounts or near or below the glass transition temperature, particularly when the diffusion value is low [6].

Inverse gas chromatography is another standard method that proved very suitable for describing the sorption kinetics and the thermodynamic behavior of gas polymer mixtures in the limit of infinite dilution [7]. It avoids the time limitation imposed by other methods. It provides much valuable information regarding molecule-molecule interactions, which are visible only in the dilute regimes and can only be assessed by different methods through regression from data in the finite solvent concentration region [8]. However, data from the literature appears to support the similarities between thermodynamic data from IGC and other static techniques such as gravimetric sorption methods [9, 10].

Understanding polymer transition phenomena is crucial for choosing materials for different applications and comprehending polymer features. The crystalline melting point and the glass-rubber transition are the two main transitions. Therefore, in polymer chemistry, determining the glass transition temperature (T_g) and melting temperature (T_m) is crucial both theoretically and practically. Many researchers have utilized the IGC technique in the literature to find the T_g value of homopolymers, copolymers, and polymer blends [4, 11-13] since it was first suggested by Guillet et al. [14] in 1969 to assign phase transitions in polymers. Plotting the logarithm of the specific retention volume against the reciprocal of

temperature allows phase transition to be identified using IGC data [15, 16]. Studies have also been conducted using temperature-dependent change curves of the dispersive component of the surface energy of n-alkanes adsorbed on polymers to predict temperature transitions in polymers [17-19].

The stationary phase and mobile phase compositions in the IGC technique are known. Analysis is used to determine how the two phases interact with each other. Compared to the static method, this technique is simpler, cost-effective, and time-efficient, and it only needs a small quantity of solvent and polymer. Additionally, the IGC has been suggested as a tool for researching solute diffusion into polymers [6, 20-22]. The slow solute diffusion in the polymeric stationary phase causes the chromatographic peak distortion and broadening. Consequently, the elution curve can be associated with the solvent's diffusion coefficient at infinite dilution in the polymer, provided the proper testing conditions are met. Many of these investigations have used packed columns [6, 23-25].

Because of their mechanical qualities and processability, styrene-diene block copolymers are employed in various industrial applications. These materials also form phase-segregated structures that contain rubbery diene and glassy styrene domains [26-28]. Therefore, these thermoplastic polymers have mechanical properties similar to crosslinked polymers at low temperatures. Still, they show high flexibility and good processability at high temperatures, at which polystyrene domains behave like rubber. In the literature, there are many studies in which the interaction parameters of some solvents with styrene-based block copolymers are examined by the IGC method [29-32] and shown to be consistent with those obtained with other techniques such as those based on intrinsic viscosity [33].

Romdhane et al. [30], used the IGC method at infinite dilution to rank the solubility strengths of some solvents for two SBS triblock copolymers (with a styrene content of 31% and 17%), showing that aromatic hydrocarbons are potential solvents for both triblock copolymers. In contrast, hydrocarbons have a higher affinity for the material with higher diene content. Diez et al. [29], determined polymer-solvent interaction parameters of two SBS commercial rubbers with different structures (linear and radial), and similar styrene content by the IGC method, while Wu et al. [31], analyzed the compatibility of SEBS (styrene content of 30.3%) and SIS (styrene content of 15.6%) triblock copolymers with different organic solvents. Similar studies were also performed by Ovejero et al. [33] based on intrinsic viscosity measurements at 20 °C SEBS (styrene content of 32%).

Despite the number of works in the field, in the open literature, very little information about the diffusion coefficients in the infinite dilution region of organic solvent in these block copolymers can be found as most of the data refers to finite concentrations (through the gravimetric method) [27, 34-37].

In this concern, the present study focused on the mass transport properties of three common organic solvents, cyclohexane, n-hexane, and benzene, in three styrene-based block copolymers. The three polymers had similar styrene content, about 30%, and were linear (SIS and SEBS) or star-branched (SBS). The infinite dilution diffusion coefficients of the probes in styrene-diene block-copolymers were determined, at several different temperatures, by IGC based on the Van Deemter model of the chromatographic process [38].

Experimental

Materials and Methods

Three different monodisperse styrene-based block copolymers with the same glassy polymer content (SBS, SIS, and SEBS) were kindly supplied for testing by Versalis S.p.A. Their various properties are given in Table 1. The three penetrants, each representing a class of organics, were the reagent grade cyclohexane, purchased from Sigma-Aldrich, and n-hexane and benzene purchased from Merck.

Table 1. Characteristics of the block-copolymers

Block-copolymers	Styrene content (wt%)	M g/mol	Polydispersity	Diene (1,2)
SBS (radial)	34	234000	1.2	9%
SIS (linear)	26	131000	1.14	3%
SEBS (linear)	34	54000	1.02	25%

IGC Measurements

Utilizing an autosampler and a thermal conductivity detector, the Agilent 6890 gas chromatograph was used to perform the chromatographic measurements. The carrier gas was high-purity helium. Air was employed as an unretained compound to calculate the dead volume. A stainless steel column, 2 m long and 5.35 mm i.d. was cleaned with methanol and acetone before packing. Block-copolymers were soaked using Al-Saigh and Munk's method [39] to coat Chromosorb W-AW-DMCS from Alltech (60-80 mesh) at an amount of about 12% (w/w). Using typical ashing processes [38], the total loadings of SBS, SIS, and SEBS on the support were 11.73 %, 11.77 %, and 11.73 % (w/w), respectively.

The column was packed and conditioned in an 80 °C helium stream for an entire night. Tests were then performed by injecting a known amount of the solvent to be tested in the column and by observing the elution peak. Symmetric peaks were measured for each solvent probe, and the peak maximum was determined by taking the retention duration. Elution times were independent of the amount of solvent injected, confirming that tests were carried out in the Henry's Law region. Three determinations were used to average the net retention volume required for computations.

Theory

Infinite Dilute Diffusion Coefficient

The following equation gives an infinite dilute diffusion coefficient following van Deemter's model [38].

$$D_{12}^{\infty} = \frac{8d_2^2}{\pi^2 C} \frac{k}{(1+k)^2} \tag{1}$$

where C is a parameter associated with column properties, d_2 is the average thickness of the polymer on the support particles, and k is the so-called partition ratio. By using the following equations, d_2 and k values can be determined;

$$d_2 = \frac{w_2 \rho_s d_s}{6 \rho_2 w_s} \qquad (2)$$

$$k = \frac{t - t_o}{t} \qquad (3)$$

where d_s is the average support particle diameter, t and t_o are the solvent and unadsorbed material retention times (methane, air, etc.), w_2 is the weight of the polymer coating on the support material, w_s is the weight of the support material, ρ_2 is the density of the polymer, and ρ_s is the density of the support material.

According to Plate Theory, C in Eq 1 is derived from the following equation:

$$H = A + \frac{B}{u} + Cu \qquad (4)$$

where A is an eddy diffusion-related constant, and B is related to axial diffusion in the gas *phase* based on the structural elements or tortuosity of the column. At sufficiently high flow rates, the B/u term is small relative to $A + Cu$ and can be neglected. C is related to the other parameters of the probe diffusion in the liquid phase, H is the plate height equivalent to a theoretical plate (HEPT), and u is the carrier gas's linear velocity.
From the experimentally eluted peak, H is computed as follows [38, 40].

$$H = \left(\frac{l}{5.54} \right) \left(\frac{t_{1/2}}{t} \right)^2 \qquad (5)$$

where t is the solvent retention time determined at the peak's maximum, l is the column length, and $t_{1/2}$ is the complete peak broadness at half maximum. The carrier gas's linear velocity (u) can be computed using the following expression:

$$u = \frac{jF_o}{\overline{a}} \frac{T_c}{T_o} \qquad (6)$$

where T_c and T_o are respectively the temperatures of the column and room temperature; F_o is the carrier gas flow rate, $\overline{a}$ is the gas phase volume per unit length, which is the ratio of the

retention volume of unadsorbed material to the column length, and j is the compressibility factor obtained from the following relationship:

$$j = \frac{3}{2}\left[\frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1}\right] \tag{7}$$

Where P_i and P_0 are the inlet and outlet pressures of the column, respectively, thus, the compressibility factor can be obtained immediately from the measured values of P_i and P_0 at any temperature and carrier gas velocity.

Activation Energy

The Arrhenius equation typically provides the diffusion coefficient's temperature dependency [25, 41, 42]:

$$D^\infty = D_0 e^{-\Delta E_D / RT} \tag{8}$$

where D_0 is the preexponential factor of the diffusion process independent of temperature, T is the absolute temperature, R is the gas constant, and ΔE_D is the activation energy required for a diffusing molecule in a particular polymer matrix to diffuse into a neighboring environment that is distinct from its current surroundings. The diffusion rate is constrained in diluted solutions because it takes energy for the diffusing species to leave its current surroundings and migrate into a nearby environment when it does not frequently come into contact with a polymer molecule.

Infinite Dilute Activity Coefficient and Flory–Huggins Interaction Parameter

The generalized equations that relate the measured data to the solvent activity coefficients in the polymer can be found below [6, 41, 42]:

$$\Omega_1^\infty = \gamma_1^\infty \frac{M_2}{M_1} = \frac{273.15R}{v_g^0 M_1} \frac{1}{\varphi_1^s P_1^s} \tag{9}$$

where M_2 is the molar mass of the polymer on the support solid, M_1 is the solvent's molar mass, P_1^s is the pure solvent's saturated vapor pressure, is the solvents' saturated fugacity coefficients, R is the gas constant, Ω_1^∞ and γ_1^∞ are the solvents' activity coefficients in mass fraction and mole fraction scale, respectively. The Antoine constants were used to determine the solvents' saturation vapor pressures (P_1^s), and the Soave equation of state was used to determine the solvents' saturated fugacity coefficients (φ_1^s) [43]. The following equation can be used to determine the retention volume per gram of polymer phase ($v_g{}^0$) in Eq. 9 based on the retention time at temperature. $v_g{}^0$ is calculated at 273.15K at infinite dilution of the solute.

$$v_g{}^0 = \frac{jF}{w_2}\frac{273.15}{T_o}(t - t_o)\tag{10}$$

where F is the carrier gas flow rate, t is the solvent retention time, t_o is the hold-up time required for inert gas to pass through the column, and w_2 is the polymer mass on the column-packed support material.

According to the Flory-Huggins approach, the interaction parameter for a specific solute-polymer pair is defined as [44-46]

$$\chi_{12}^\infty = \ln\frac{273.2Rv_2}{V_g^0 V_1 p_1^o} - \frac{p_1^o}{RT}(B_{11} - V_1) - 1\tag{11}$$

where v_2, V_1, B_{11}, and p_1^o are the specific volume of the polymer, the sorbate's molar volume, the sorbate's second virial coefficient, and saturated vapor pressure, respectively. V_1 and B_{11} values are calculated at column temperature as described by Voelkel and Fail [46].

Results and Discussion

Diffusion coefficient

The infinite dilution diffusion coefficients of cyclohexane, n-hexane, and benzene in styrene block copolymers at various temperatures were measured using inverse gas chromatography. Every solvent-polymer pair was measured at multiple carrier flow rates.

Plots of plate height (H) vs linear velocity (u) were generated for each solvent in several styrene block copolymers at various temperatures to demonstrate the applicability of the Van Deemter equation. As an example, graphs of plate height (H) versus linear velocity (u) for SIS-Cyclohexane are given in Figure 1. For all solvents in all block copolymers, the slope of the linear relationships between H and u was used to calculate the values of A and C at each temperature (40–70 ºC). From the latter parameter in particular the calculation of values was possible using Equation 1-7. The results are given in Table 2 and Figure 2 as a function of the different solvents' kinetic diameter (σ). From the plot, it is possible to notice that the diffusion kinetics of the various solvents are reduced in the following order n-hexane> benzene>cyclohexane which is the same as the kinetic diameter of the different penetrants, thus highlighting the direct relationship between these two parameters. The existence of a correlation between diffusivity and penetrant size is often used to describe the transport behavior of different penetrants in polymers qualitatively. Among the others, Teplyakov and Meares [47] also tried to build a more quantitative relationship and from an empirical approach they noticed that a straight line with a slope of k_1 and an intercept of k_2 is frequently produced by fitting the logarithm of the diffusion coefficients as a function of the square of the kinetic diameter as follows:

$$\ln D^{\infty} = -k_1 \sigma^2 + k_2 \tag{12}$$

A greater k_1 value generally denotes stronger diffusivity selectivity of the polymer films. In Figure 2. the diffusivity data measured in the present work for the three-block copolymers, were plotted against the solvent's kinetic diameters according to Eq.(12). The linearity was very good in the case of SIS with an R^2=0.998. At the same time, SEBS and SBS showed lower correlation coefficient values that always remained above 0.85, confirming the good correlation between the two quantities. The k_1 values increased in the SBS <SIS <SEBS sequence, suggesting that the latter polymer shows a stronger dependence of diffusivity from the kinetic diameter.
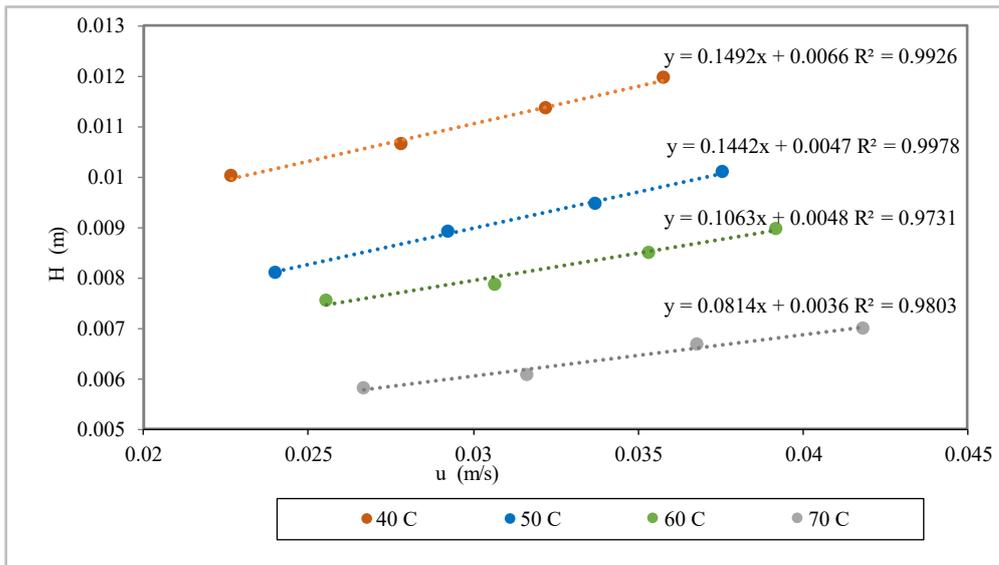
Figure 1. The plots of plate height (H) against linear velocity (u) for SIS-Cyclohexane
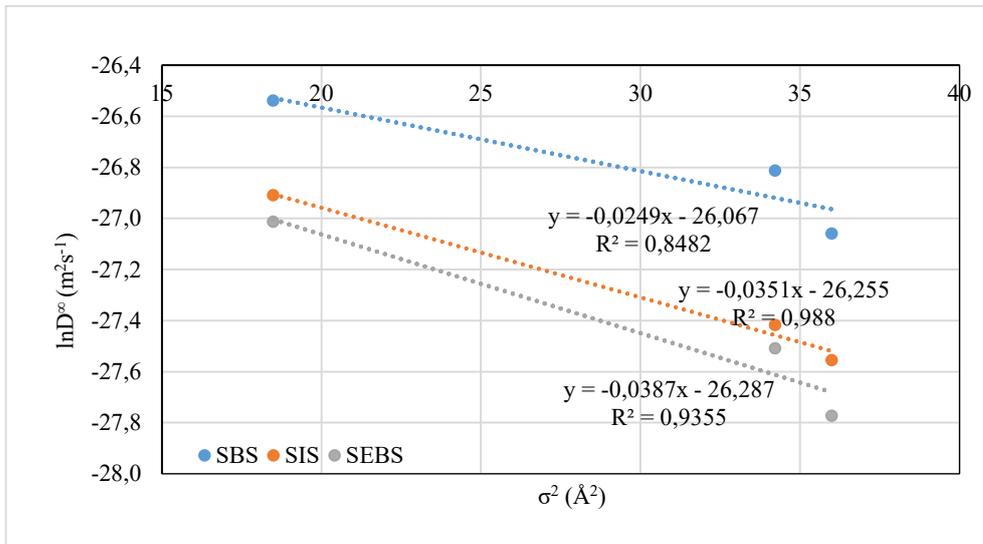

Figure 2. The logarithm of Infinite dilute diffusion coefficients (D^{∞}) at 40°C as a function of the kinetic diameter of the solvents squared (σ)*. Kinetic diameters are taken from www.mdpi.com/2073-4344/5/4/2147/s1 [48]. ($\sigma_{benzene}$=5.85Å; $\sigma_{n\text{-}hexane}$ =4.3; Å; $\sigma_{cyclohexane}$ =6.0 Å)

Table 2. Infinite dilute diffusion coefficients (D^∞), diffusion constants (D_0), and activation energies for diffusion (ΔE_D) of the solvents

SOLVENT	T (°C)	$D^\infty.10^{12}$ (m^{2}s^{-1})			$D_0.10^8$ (m^{2}s^{-1})			$-\Delta E_D$ (kJ.mole^{-1})		
		SBS	SIS	SEBS	SBS	SIS	SEBS	SBS	SIS	SEBS
Cyclohexane	40	1.77±0.01	1.08±0.00	0.87±0.01	14.01±0.7	39.5±1.1	77.70±2.2	29.17±1.9	33.5±2.9	35.94±3.9
	50	2.67±0.02	1.39±0.00	1.01±0.01						
	60	3.71±0.02	2.24±0.03	1.92±0.02						
	70	4.70±0.01	3.22±0.09	2.69±0.02						
n-Hexane	40	2.98±0.02	2.06±0.02	1.85±0.02	2.70±1.0	3.84±1.3	7.20±0.8	23.61±2.6	25.71±3.5	27.63±2.2
	50	4.36±0.01	2.44±0.05	2.33±0.02						
	60	5.62±0.00	3.82±0.07	3.31±0.02						
	70	6.58±0.00	4.63±0.05	4.62±0.01						
Benzene	40	2.26±0.02	1.24±0.02	1.13±0.04	7.90±0.9	6.72±0.8	16.80±1.3	27.22±2.3	28.40±0.5	30.98±3.7
	50	3.15±0.09	1.71±0.02	1.60±0.03						
	60	4.61±0.01	2.39±0.05	2.62±0.08						
	70	5.49±0.01	3.19±0.10	3.04±0.06						

In general, the infinite dilution diffusion coefficients of the solvents are reduced with the order of SBS> SIS> SEBS, with SBS showing higher diffusivity for the other materials which are instead rather close to each other. The results may suggest that the presence of pendant groups in the rubbery domains reduces the ability of the penetrant molecules to travel within the polymeric matrix, however, it is likely that the structure of the block copolymers, that is the distribution of the rubbery and glassy domains, plays a more important role in determining the effective diffusivity of the materials. It is well known that at the temperature inspected the styrene domains are well below Tg thus behaving as a glassy impermeable phase. Consequently, the transport mainly happens in the dienic phase, where the molecules are free to move. However, they are still strongly affected by the glassy phase, forcing them to follow a tortuous path to diffuse into the polymers. For example, data obtained here are at least 1 order of magnitude lower than those obtained in pure polybutadiene ($5.7 \cdot 10^{-7}$ and $1.1 \cdot 10^{-6}$ cm^2/s at 25°C for n-hexane and cyclohexane respectively) [49] showing the non-negligible effect of the glassy phase on the overall properties of the materials.
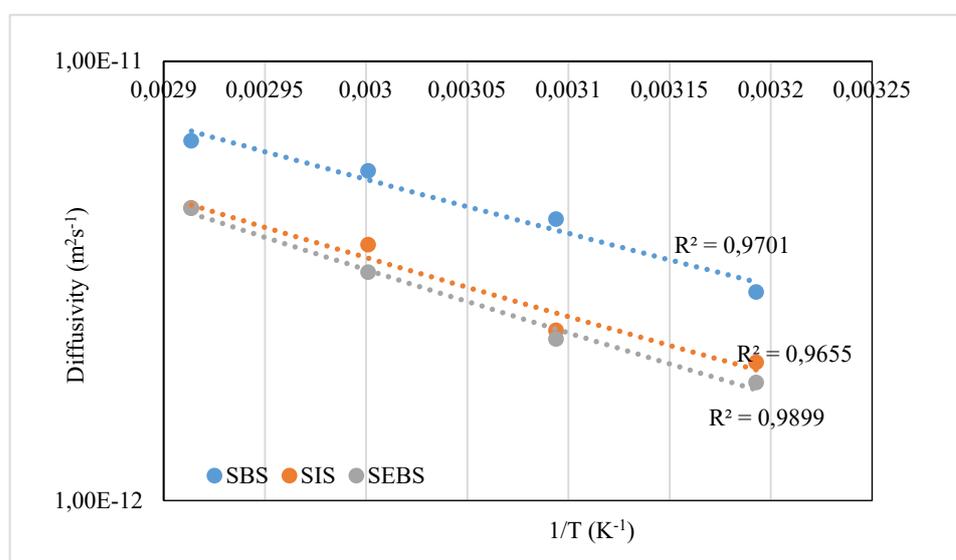
Romdhane and Danner [3] demonstrated the validity of the IGC method by measuring the diffusivity and solubility of toluene and benzene in polystyrene above the polymer's glass transition temperature. The diffusion coefficient of benzene in polystyrene varies between $12.6.10^{-9}$- 117.10^{-9} $cm^2.s^{-1}$ in the range of 130 and 160 ^0C operating temperatures.

There is no study in the literature where the diffusion parameters for concerned copolymers are determined by the IGC method. However, gravimetric studies (at finite concentration regions) have been conducted to examine the mass transport properties of cyclohexane, toluene, chloroform, n-nonan [27, 34, 36, 37, 50].
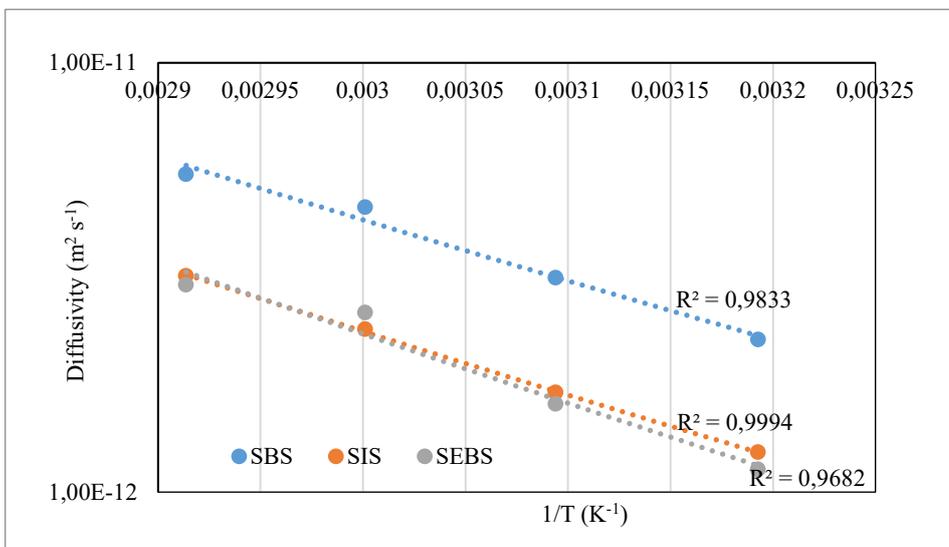
In an experimental study by Chiang et al. based on measuring the weight change over time for the adsorption of cyclohexane by SBS (styrene content 27.7% by weight), the approximate value of the equilibrium diffusion coefficient was found to be $3.2.10^{-7}$ cm^2/s [27] According to Bacchelli et al.'s study [50], diffusion increased with penetrant (cyclohexane) concentration for all copolymers, but it increased more for SBS than for SIS and SEBS. In their experiments with the pressure decay technique at 60°C up to 0.8 activity (0.015-0.2 g/g_{pol} penetrant concentration range), the diffusion coefficient of cyclohexane in copolymers decreased in the order SBS>SEBS>SIS at high penetrant values. Diffusion coefficients in SIS and SEBS approached each other at low penetrant concentrations.

In all three copolymers, the diffusion coefficients of all solvents increased with temperature. The graphs plotted according to the results of $\ln D^{\infty}$ versus are presented in Figure 2. a, b, c for the three-block copolymers in n-hexane, benzene and cyclohexane respectively and results are consistent with the Arrhenius equation (Eq. 8). From the fitted straight lines, the activation energies of the three solvents are determined (in all lines, R^2 values greater than 0.95 were obtained) and shown in Table 2.
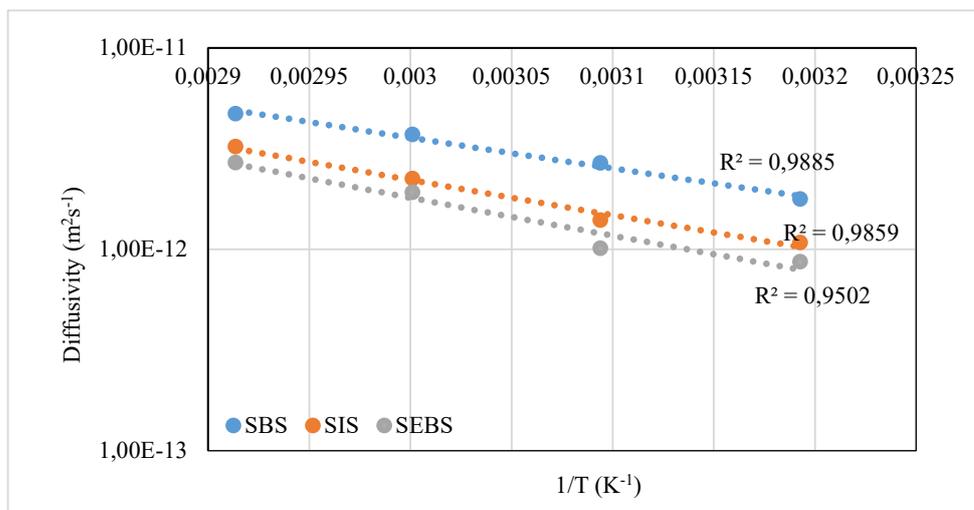
It can be seen from Table 2 that the diffusion activation energy is positive, as expected for such type of thermally activated process, with values ranging from 23 to 35 kJ/mol in line with the values found for the same solvent in other polymeric materials [25, 51, 52]. The activation energies increase in the SBS <SIS <SEBS order for all solvents. n-Hexane, then, shows lower activation energy than Benzene and Cyclohexane showing once again a clear effect of the kinetic diameter in determining the diffusion behavior of the different molecules. In infinite dilution conditions indeed, the effect related to swelling of the polymer phase or penetrant-penetrant interaction can be neglected and the activation energy is strictly related to the required energy for the penetrant molecules to jump from one polymer cavity to the next one. This latter energy is of course higher when bigger molecules are involved.

(a)

(b)

(c)

Figure 3. $\ln D^{\infty}$ versus $1/T$ (a) n- hexane; (b) benzene and (c) cyclohexane

Activity coefficient

The activity coefficients (Ω_1^∞) in the polymer phase were estimated using Equations 9 and 10 and presented in Table 3. At constant temperature, the Ω_1^∞ values of solvents increase in the following order: benzene<cyclohexane<n-hexane for SBS and SIS, and cyclohexane<benzene<n-hexane for SEBS.

Benguergoura et al. [53] used capillary column inverse gas chromatography to determine the thermodynamic properties of poly(styrene-co-butadiene) rubber-various solvent systems. They compared their results with those of packed column studies in the literature. They determined that polar solvents had higher Ω_1^∞ values than nonpolar solvents. Furthermore, they noted that the parameter is largely temperature-dependent in non-polar and weakly polar solvents. When the Ω_1^∞ values of the solvent-SBS rubber pairs used in this study are compared with the values found in their study, it is seen that the coefficients are in a similar order (benzene<cyclohexane<n-hexane).

Table 4 gives infinite dilute Flory-Huggins interaction parameters obtained using Equation 11. The uncertainty of the data in Tables 3 and 4 is between ±%1 and ±%5. Uncertainties were estimated as stated by Wang et al [42].

In the three copolymers, the Flory-Huggins parameters of n-hexane increased with temperature, while cyclohexane and benzene decreased with temperature. This parameter measures the free energy of the interaction between the components and the tested polymers. The dependence of the calculated parameters on the technologically specific temperature can be used to predict how the interactions between the compounds in the polymer-solvent systems will change with temperature. The decrease in the Flory-Huggins parameter with increasing temperature indicates that the interaction between the investigated polymers and compounds is increased when temperature is raised.

Table 3. Infinite Dilute Activity Coefficients of Solvents in Block-copolymers at Different Temperatures.

	Ω_1^{∞}								
	Cyclohexane			n-Hexane			Benzene		
T (°C)	SBS	SIS	SEBS	SBS	SIS	SEBS	SBS	SIS	SEBS
40	6.114	6.285	5.666	8.730	8.546	7.581	4.850	5.666	6.028
50	6.059	6.221	5.594	9.094	8.856	7.724	4.789	5.423	5.827
60	6.018	6.169	5.458	9.285	9.140	7.865	4.748	5.154	5.666
70	5.961	6.131	5.335	9.569	9.319	8.036	4.684	4.944	5.513

Table 4. Infinite dilute Flory-Huggins Interaction Parameters

	χ_{12}^{∞}								
	Cyclohexane			n-Hexane			Benzene		
T (°C)	SBS	SIS	SEBS	SBS	SIS	SEBS	SBS	SIS	SEBS
40	0.625	0.661	0.545	0.792	0.782	0.649	0.494	0.661	0.710
50	0.601	0.639	0.519	0.818	0.803	0.653	0.470	0.606	0.665
60	0.581	0.617	0.482	0.825	0.820	0.657	0.451	0.544	0.625
70	0.567	0.597	0.448	0.840	0.825	0.663	0.433	0.491	0.587

According to data in the literature, the temperature dependence of the Flory-Huggins parameter may vary depending on the type of solvent. For example, Romdhane et al. [30] in their study where they determined the Flory-Huggins parameters of SBS triblock copolymers using various solvents, the Flory-Huggins parameter of cyclohexane decreased with temperature, while that of chloroform increased.

Diez et al. [29] evaluated the effect of carbon number on Flory Huggins interaction parameters for two commercial SBS rubbers and different solvent pairs using the IGC method. They found that aromatic compounds had the lowest value and paraffinic compounds had the highest value. They attributed this result to the olefinic and aromatic character of SBS. They also stated that n-alkanes were the worst solvents for both rubbers due to the high values of the Flory-Huggins parameter and that the effect of temperature on the parameter was negligible in most of the polymer-solvent pairs examined. Similarly, it is observed that n-hexane has the highest value for SBS and benzene has the lowest value in this study conducted at identical temperatures.

The compatibility between polymers and solvents is examined using the polymer-solvent interaction parameter. The more compatible the polymer and solvent are, the lower its value. Benguergoura et al. [53] examined the Flory Huggins interaction parameter change depending on the molecule's molar mass and carbon number for poly(styrene-co-butadiene) rubber-various polymer solvent systems. They concluded that the parameter increases as the molar mass of the molecule increases and that aromatic and cyclic solvents containing the same number of carbons are more compatible with polymers. Similarly, in Table 4, it can be seen from the parameters of SBS that cyclohexane and benzene are more compatible with polymer than hexane.

The Flory-Huggins theory criterion of $\chi_{12}^{\infty} < 0.5$ states that a polymer and solvent must be perfectly miscible throughout the composition range. In addition, for Ω_1^{∞}, the following rule has been built for the polymer–solvent systems [54]: $\Omega_1^{\infty} < 5$: good solvents; $\Omega_1^{\infty} > 5$: moderate solvents or poor solvents. The solubility of each probe for a given polymer was consistent based on the two theories mentioned above and comparisons with the values of Ω_1^{∞} and χ_{12}^{∞}.

Evaluating the values of and Ω_1^{∞} together, it was found that the solving capacity of the solvents increased in the sequence: n-hexane <cyclohexane< benzene for SBS and SIS; n-hexane ≈ benzene < cyclohexane for SEBS.

Compared to these limit values, benzene is a good solvent for SBS at all operating temperatures and for SIS at 70°C. For SEBS on the other hand, cyclohexane can be defined as a good solvent at 60 and 70°C. In all other conditions tested these materials can be considered poor solvents for the considered copolymer, similar to n-hexane which showed limited affinity with all the materials investigated.

The same results were estimated for these solvents in the study by Jeong and Lee [55] in which a solubility test investigated the dissolution behavior of SBS, intrinsic viscosity measurements, and group additive test.

The comparison of the values found and the selected values presented in the literature by different authors are given in Table 5 for the three-block copolymers. It can be said that the small differences between the values and the ones in the literature are due to the molecular weight and styrene ratios of rubbers. The polymer's molecular weight and polydispersity can affect polymer dissolution in solvents. Polydisperse samples dissolved approximately twice as quickly as monodisperse samples with the same molecular weight [56]. On the other hand, Ovejeva et al. [57] demonstrated that polymer-solvent interaction parameters are not affected by rubber linear and radial structures for SBS.

The SIS data in the table shows how the styrene content affects the parameter values. The values of copolymers with similar styrene content appear to be closer. The effect of molecular weight is less apparent. The SEBS data in the table shows this situation. In Table 5 it can be said that the small difference between the IGC and intrinsic viscosity measurement results of the parameters for SBS and SEBS is related to the polymer concentration rather than temperature. While viscosity measurements are performed at low polymer concentrations, IGC measurements are performed in the high range of polymer levels [32].

Table 5. Comparison of the present and the literature data

	χ_{12}^{∞}			Ω_1^{∞}			**Reference**
	Cyclohexane	n-Hexane	Benzene	Cyclohexane	n-Hexane	Benzene	
SBS	0.60	0.82	0.47	6.06	9.09	4.79	In this study
By IGC with a styrene (radial) content of 34% by weight M_w: 234,000 g.mol^{-1}, T=50 $^{\circ}$C							
	0.56	0.79	0.40	5.88	8.79	4.46	[30]
By IGC with a styrene (linear) content of 31% by weight M_w:110,800 g.mol^{-1}, T=55 $^{\circ}$C							
	0.43	___	0.39	___	___	___	[57]
By intrinsic viscosity, with a styrene (radial) content of 30% by weight M_w=237,000 g.mol$^{-1,}$ T=30 $^{\circ}$C							
	0.33	0.69	0.34	4.40	7.43	3.93	[29]
By IGC, with a styrene (radial), content of 30% by weight M_w=237,000 g.mol^{-1}, T=50 $^{\circ}$C							
	0.71	0.94	0.53	6.94	10.32	5.10	[29]
By IGC, with a styrene (linear) content of 31% by weight M_w=113,000 g.mol^{-1}, T=50 $^{\circ}$C							
SIS	0.64	0.80	0.61	6.22	8.86	5.42	In this study
By IGC with a styrene (linear) content of 26% by weight M_w: 131,000 g.mol^{-1}, T=50 $^{\circ}$C							
	0.48	0.46	___	5.52	6.57	___	[31]
By IGC, with a styrene (linear) content of 15.6 % by weight M_w=130,960 g.mol^{-1}, T=50 $^{\circ}$C							
SEBS	0.52	0.65	0.63	5.59	7.72	5.83	In this study
By IGC with a styrene (linear) content of 34% by weight M_w: 54,000 g.mol-1, T=50 $^{\circ}$C							
	0.47	0.63	0.58	5.57	7.76	5.47	[32]
By IGC, with a styrene content of 32% by weight M_w: 90,000 g.mol^{-1}, T=50 $^{\circ}$C							
	___	___	___	4.54	7.09	5.98	[32]
By UNIFAC-FV group contribution method [58]							
	0.45	0.61	0.52	___	___	___	[32]
By intrinsic viscosity, with a styrene content of 32% by weight, M_w=86,238 g.mol^{-1}, T=20 $^{\circ}$C							
	0.44	0.38	___	5.25	5.99	___	[31]
By IGC with a styrene (linear) content of 30.3 % by weight, M_w=71,880 g.mol^{-1}, T=50 $^{\circ}$C							

Therefore, the general affinity for the three-block copolymer seems to decrease in the following order benzene > cyclohexane > n-hexane, in line with previous studies on the subject as visible in Table 2. This behavior can be related to the different interactions with the styrenic and dienic domains in the materials. For example, studying the solubility of various solvents in SBS triblock copolymers with different styrene content; showed that Flory-Huggins parameters of some aromatic (such as benzene, toluene ethyl-benzene, p-xylene) and aliphatic (such as n-hexane, n-heptane) solvents decreases increasing the butadiene content of the materials suggesting higher affinity with this domain inside the system.

Considering the segregated structure of the considered block copolymer it can be interesting to analyze the results concerning the behavior in the corresponding homopolymers: polystyrene and polybutadiene. In this concern, the literature has reported that aliphatic hydrocarbons have higher solubility against polybutadiene than polystyrene [59, 60]. The affinity for polystyrene instead, decreased in the aromatic > alicyclic > aliphatic order, as reported by Tümsek et al. [61], which also observed that benzene was the best dissolving agent among the solvents studied. The affinity of the different solvents for the various materials therefore seems to be somewhat dominated by their affinity for the styrenic phase despite this having a lower concentration than the dienic one in the considered block copolymers.

Conclusions

In the present study, mass transport properties of n-hexane, cyclohexane, and benzene in three block copolymers based on styrene (SIS and SEBS SBS) were examined at column temperatures between 40 and 70 °C by infinite dilution IGC experiments.
The diffusion coefficient was calculated using the data from the chromatography peak and the retention period using the Van Deemter model of the chromatographic process. The infinite dilution diffusion coefficients of the solvents are reduced with the order of SBS> SIS> SEBS. In all three copolymers, the diffusion coefficients of all solvents increase with temperature. The logarithm of the diffusion coefficient is linearly related to the square of the kinetic diameter. Diffusion activation energies are positive and increase in the SBS <SIS <SEBS order for all solvents.

Additionally, χ_{12}^{∞} and interaction parameters are used to analyze polymer-solvent compatibility. Assessing the values of these parameters together, it was found that the solving

capacity of solvents increased in the following order: n-hexane <cyclohexane< benzene for SBS and SIS; n-hexane ≈ benzene < cyclohexane for SEBS. The interaction parameters obtained were compared with the literature.

References

1. Caruthers JM (1998) Handbook of diffusion and thermal properties of polymers and Polymer Solutions. American Institute of Chemical Engineers, New York
2. Vrentas JS, Duda JL (1979) Molecular diffusion in Polymer Solutions. AIChE Journal 25:1–24. https://doi.org/10.1002/aic.690250102
3. Romdhane IH, Danner RP (1993) Polymer-solvent diffusion and equilibrium parameters by inverse gas-liquid chromatography. AIChE Journal 39:625–635. https://doi.org/10.1002/aic.690390411
4. Davis PK, Danner RP, Duda JL, Hadj Romdhane I (2004) Use of inverse gas chromatography to study binary polymer−solvent systems near the glass transition temperature. Macromolecules 37:9201–9210. https://doi.org/10.1021/ma0347767
5. Tihminlioglu F, Surana RK, Danner RP, Duda JL (1997) Finite concentration inverse gas chromatography: Diffusion and partition measurements. Journal of Polymer Science Part B: Polymer Physics 35:1279–1290. https://doi.org/10.1002/(sici)1099-0488(199706)35:8<1279::aid-polb14>3.3.co;2-c
6. Zhang S., Tsuboi A., Nakata H., Ishikawa T., 2002, Activity Coefficients and Diffusivities of Solvents in Polymers, Fluid Phase Equilib. 194–197,1179-1189. https://doi.org/10.1016/S0378-3812(01)00772-5
7. Xia Y, Chen J, Wu Z, et al (2015) Measurement of solubility thermodynamic and diffusion kinetic characteristic of solvents in PDMS by inverse gas chromatography. European Polymer Journal 73:259–267. https:// doi.org/10.1016/j.eurpolymj.2015.10.019
8. Voelkel A, Strzemiecka B, Adamska K, Milczewska K (2009) Inverse gas chromatography as a source of physiochemical data. Journal of Chromatography A 1216:1551–1566. https://doi.org/10.1016/j.chroma.2008.10.096
9. Surana RK, Danner RP, Tihminlioglu F, Duda JL (1997) Evaluation of inverse gas chromatography for prediction and measurement of diffusion coefficients. Journal of Polymer Science Part B: Polymer Physics 35:1233–1240. https://doi.org/10.1002/(SICI)1099-0488(199706)35:8<1233::AID-POLB9>3.0.CO;2-U
10. Etxabarren C, Iriarte M, Etxeberria A, et al (2003) Determination of the diffusion coefficients of organic solvents in polyepichlorohydrin: A comparative study of inverse gas chromatography and sorption methods. Journal of Applied Polymer Science 89:2216–2223. https://doi.org/10.1002/app.12423
11. Etxeberría A, Alfageme J, Uriarte C, & Iruin JJ (1992) Inverse gas chromatography in the characterization of polymeric materials. Journal of Chromatography A 607:2:227-237. https://doi.org/10.1016/0021-9673(92)87080-R
12. Benabdelghani Z, Etxeberria A, Djadoun S, Iruin J, & Uriarte C (2006) The phase behavior of poly(styrene-co-methacrylic acid)/poly(2,6-dimethyl-1,4-phenylene oxide) by inverse gas chromatography. Journal of Chromatography A 1127:1-2:237-245. https://doi.org/10.1016/j.chroma.2006.05.093
13. Nastasović AB, & Onjia AE (2008) Determination of glass temperature of polymers by inverse gas chromatography. Journal of Chromatography A 1195:1-2:1-15. https://doi.org/10.1016/j.chroma.2008.05.009
14. Lavoie A, Guillet JE (1969) Estimation of Glass Transition on Temperatures from Gas Chromatographic Studies on Polymers. Macromolecules 2:4:443–446.

https://doi.org/10.1021/ma60010a027

15. Guillet J, Al-Saigh ZY (2016) Inverse Gas Chromatography in Analysis of Polymers:Polymers and Rubbers. Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation https://doi.org/10.1002/9780470027318.a2016

16. Voelkel A (2020). Physicochemical measurements (inverse gas chromatography). Gas Chromatography (Second Edition), 561-579. https://doi.org/10.1016/B978-0-12-820675-1.00013-7

17. Hamieh T, Rezzaki M, Schultz J (2001) Study of the second order transitions and acid–base properties of polymers adsorbed on oxides by using inverse gas chromatography at infinite dilution. I Theory and Methods. Journal of Colloid and Interface Science 233:343–347. https://doi.org/10.1006/jcis.2000.7271

18. Hamieh T, Rezzaki M, Schultz J (2001) Study of the second order transitions and acid–base properties of polymers adsorbed on oxides by using inverse gas chromatography at infinite dilution. II Experimental Results. Journal of Colloid and Interface Science 233:343–347. https://doi.org/10.1006/jcis.2000.7271

19. Hamieh T, Schultz J (2002) New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite dilution. II. Study of the transition temperatures of poly(methyl methacrylate) at various tacticities and of poly(methyl methacrylate) adsorbed on alumina and silica. Journal of Chromatography A 96:1-2:27-36. https://doi.org/10.1016/s0021-9673(02)00358-8

20. Gray DG, Guillet JE (1973) Studies of diffusion in polymers by Gas Chromatography. Macromolecules 6:223–227. https://doi.org/10.1021/ma60032a014

21. Braun J -M., Poos S, Guillet JE (1976) Determination of diffusion coefficients of antioxidants in polyethylene by Gas Chromatography. Journal of Polymer Science: Polymer Letters Edition 14:257–261. https://doi.org/10.1002/pol.1976.130140502

22. Öner M, Dinçer S (1987) Thermophysical properties of polymer-probe pairs by Gas Chromatography. Polymer 28:279–282. https://doi.org/10.1016/0032-3861(87)90417-4

23. Munk P (1991) In: Barth HG, Mays JW (eds) Modern Methods of Polymer Characterization. Wiley and Sons. Ch 5.

24. Zhao C, Li J, Zeng C (2006) Determination of the infinite dilution diffusion and activity coefficients of alkanes in polypropylene by inverse gas chromatography. Journal of Applied Polymer Science 101:1925–1930. https://doi.org/10.1002/app.23658

25. Zhao C, Li J, Jiang Z, Chen C (2006) Measurement of the infinite dilution diffusion coefficients of small molecule solvents in silicone rubber by inverse gas chromatography. European Polymer Journal 42:615–624. https://doi.org/10.1016/j.eurpolymj.2005.08.019

26. Aggarwal SL, Livigni RA (1977) Structure and properties of micro composites and macrocomposites from block polymers. Polymer Engineering & Science 17:498–505. https://doi.org/10.1002/pen.760170803

27. Chiang KT, Sefton MV (1977) Structure of styrene–butadiene–styrene block copolymers by diffusion analysis. Journal of Polymer Science: Polymer Physics Edition 15:1927–1935. https://doi.org/10.1002/pol.1977.180151105

28. Adams JL, Graessley WW, Register RA (1994) Rheology and the microphase separation transition in styrene-isoprene block copolymers. Macromolecules 27:6026–6032. https://doi.org/10.1021/ma00099a014

29. Díez E, Ovejero G, Romero MD, Díaz I (2011) Polymer–solvent interaction parameters of SBS rubbers by inverse gas chromatography measurements. Fluid Phase Equilibria 308:107–113. https://doi.org/10.1016/j.fluid.2011.06.018

30. Romdhane IH, Plana A, Hwang S, Danner RP (1992) Thermodynamic interactions of solvents with styrene–butadiene–styrene triblock copolymers. Journal of Applied Polymer Science 45:2049–2056. https://doi.org/10.1002/app.1992.070451120

31. Wu P, Qi S, Liu N, Deng K, Nie H (2011) Investigation of thermodynamic properties of SIS, SEBS, and naphthenic oil by inverse gas chromatography. Journal of Elastomers & Plastics 43:369–386. https://doi.org/10.1177/0095244311405000

32. Ovejero G, Pérez P, Romero MD, et al (2009) SEBS triblock copolymer–solvent interaction parameters from inverse gas chromatography measurements. European Polymer Journal 45:590–594. https://doi.org/10.1016/j.eurpolymj.2008.11.022

33. Ovejero G, Pérez P, Romero MD, et al (2007) Solubility and Flory Huggins parameters of SBES, poly(styrene-B-butene/ethylene-B-styrene) triblock copolymer, determined by intrinsic viscosity. European Polymer Journal 43:1444–1449. https://doi.org/10.1016/j.eurpolymj.2007.01.007

34. Mateo JL, Bosch P, Serrano J, Calvo M (2000) Sorption and diffusion of organic solvents through photo-crosslinked SBS block copolymers. European Polymer Journal 36:1903–1910. https://doi.org/10.1016/s0014-3057(99)00260-8

35. Xia Y, Chen J, Wu Z, et al (2015) Measurement of solubility thermodynamic and diffusion kinetic characteristic of solvents in PDMS by inverse gas chromatography. European Polymer Journal 73:259–267. https://doi.org/10.1016/j.eurpolymj.2015.10.019

36. Iwai Y, Miyamoto S, Ikeda H, et al (1993) Measurement and correlation of mutual diffusion coefficients for styrene-butadiene rubber(SBR)-n-nonane systems. Polymer Engineering & Science 33:322–327. https://doi.org/10.1002/pen.760330603

37. Caneba GT, Soong DS, Prausnitz JM (1983) Diffusion and sorption of cyclohexane vapor in SBS and SBR Copolymers. Journal of Macromolecular Science, Part B 22:693–711. https://doi.org/10.1080/00222348308245750

38. van Deemter JJ, Zuiderweg FJ, Klinkenberg A (1995) Longitudinal diffusion and resistance to mass transfer as causes of nonideality in chromatography. Chemical Engineering Science 50:3869–3882. https://doi.org/10.1016/0009-2509(96)81813-6

39. Al-Saigh ZY, Munk P (1984) Study of polymer-polymer interaction coefficients in polymer blends using inverse gas chromatography. Macromolecules 17:803–809. https://doi.org/10.1021/ma00134a047

40. Conder JR, Young CL (1979) Physicochemical Applications of Gas Chromatography. Wiley, NewYork.

41. Zeng C, Li J, Wang D, et al (2006) Infinite dilute activity and diffusion coefficients in polymers by inverse gas chromatography. Journal of Chemical Engineering Data 51:93–98. https://doi.org/10.1021/je050241s

42. Wang D, Li J, Zeng C, et al (2007) Measurement of the infinite dilute activity coefficients and diffusion coefficients of water and straight chain alcohols in cross-linked polyvinyl alcohol by Inverse Gas Chromatography. Journal of Chemical Engineering Data 52:368–372. https://doi.org/10.1021/je0602871

43. Soave G (1972) Equilibrium constants from a modified Redlich-Kwong equation of State. Chemical Engineering Science 27:1197–1203. https://doi.org/10.1016/0009-2509(72)80096-4

44. Yampolskii Y, Belov N (2015) Investigation of polymers by inverse gas chromatography. Macromolecules 48:6751–6767. https://doi.org/10.1021/acs.macromol.5b0089

45. DiPaola-Baranyi G (1982) Estimation of polymer solubility parameters by inverse gas chromatography. Macromolecules 15:622–624. https://doi.org/10.1021/ma00230a080

46. Voelkel A, Fall J (1996) Influence of prediction method of the second virial coefficient on inverse gas chromatographic parameters. Journal of Chromatography A 721:139–145. https://doi.org/10.1016/0021-9673(95)00763-6

47. Teplyakov V, Meares P (1990) Correlation aspects of the selective gas permeabilities of polymeric materials and membranes. Gas Separation & Purification 4:66–74. https://doi.org/10.1016/0950-4214(90)80030-o

48. www.mdpi.com/2073-4344/5/4/2147/s1. Accessed 2 March 2024.

49. Uyeda T, Odani H (1991) Solution and diffusion of vapor mixtures in polybutadiene, Bulletin of the Institute for Chemical Research, Kyoto University, 69(4):412-420. http://hdl.handle.net/2433/77401

50. Bacchelli F, Coppola S, Baschetti MG, De Angelis MG, Doghieri F (2007) Diffusion of cyclohexane in styrene block copolymers, relationship between mass transport and viscoelastic properties, AIChE Annual Meeting Conference Proceedings ISBN 978-081691022-9

51. Zeng C, Huang M, Zhao H, et al (2011) Solution and diffusion properties of cyclohexane, cyclohexanol, and cyclohexanone in poly(ethylene glycol) by inverse gas chromatography. Journal of Applied Polymer Science 123:124–134. https://doi.org/10.1002/app.34447

52. Randová A, Bartovská L, Hovorka Š, et al (2010) Diffusion coefficients in systems LDPE+cyclohexane and LDPE+benzene. e-Polymers. 68: 1-6. https://doi.org/10.1515/epoly.2010.10.1.742

53. Benguergoura H, Allel A, Sharaf Saeed W, & Aouak T (2021). Capillary column inverse gas chromatography to determine the thermodynamic parameters of binary solvent poly (styrene-block-butadiene) rubber systems. Arabian Journal of Chemistry 14:4:103040. https://doi.org/10.1016/j.arabjc.2021.103040

54. Hansen CM (2000) Hansen Solubility Parameters A User's Handbook, 2nd. Edn., CRC Press, https://doi.org/10.1201/9781420006834

55. Jeong JK, & Lee DC (1996). Solubility parameter of a SBS triblock copolymer. Korea Polymer Journal, 4:1:9-15.

56. Miller-Chou BA, Koenig JL (2003) A review of polymer dissolution. Progress in Polymer Science 28:1223–1270. https://doi.org/10.1016/s0079-6700(03)00045-5

57. Ovejero G, Romero MD, Díez E, Díaz I (2010) Thermodynamic interactions of three SBS (styrene–butadiene–styrene) triblock copolymers with different solvents, by means of intrinsic viscosity measurements. European Polymer Journal 46:2261–2268. https://doi.org/10.1016/j.eurpolymj.2010.10.016

58. Oishi T, & Prausnitz JM (1978) Estimation of solvent activities in polymer solutions using a group-contribution method. Industrial & Engineering Chemistry Process Design and Development 17:3:333-339. https://doi.org/10.1021/i260067a021

59. Romdhane IH, Danner RP (1991) Solvent volatilities from polymer solutions by gas-liquid chromatography. Journal of Chemical Engineering Data 36:15–20. https://doi.org/10.1021/je00001a005

60. Newman RD, Prausnitz JM (1972) Polymer-solvent interactions from gas-liquid partition chromatography. The Journal of Physical Chemistry 76:1492–1496. https://doi.org/10.1021/j100654a022

61. Tümsek F, Börekçi M, Topaloğlu Yazıcı D, Aşkın A (2011) Examination of polystyrene by inverse GC: Part 2. above glass transition temperature. Chromatographia 73:117–122. https://doi.org/10.1007/s10337-010-1830-4

.