Article

Determining Hildebrand Solubility Parameter by Ultraviolet Spectroscopy and Microcalorimetry

Suzanny P. Carvalho,[a] Elizabete F. Lucas,[a] Gaspar González[b] and Luciana S. Spinelli*,[a]

[a]*Federal University of Rio de Janeiro, Institute of Macromolecules, Laboratory of Macromolecules and Colloids for Petroleum Industry – Av. Horácio Macedo, 2030, Cidade Universitária, 21941-598 Rio de Janeiro-RJ, Brazil*

[b]*PETROBRAS/CENPES, Av. Horácio Macedo, 950, Cidade Universitária, 21941-915 Rio de Janeiro-RJ, Brazil*

O parâmetro de solubilidade (δ) de uma molécula é extremamente importante, visto que novas moléculas são frequentemente desenvolvidas para serem aplicadas em sistemas líquidos. Neste trabalho, nós buscamos técnicas alternativas simples e confiáveis para determinar δ de moléculas de baixa e alta massa molar. Pireno, fenantreno e naftaleno tiveram seus δ determinados por microcalorimetria (μDSC), ultravioleta (UV) e calorimetria (DSC). Resultados de UV foram similares àqueles obtidos por DSC e àqueles citados na literatura. Amostras de poliestireno e poliestireno sulfonado tiveram seus δ determinados por UV, μDSC e viscosidade intrínseca ([η]). Os resultados de [η] foram similares àqueles obtidos por UV. Procedimento de UV foi relativamente simples, de fácil operação e confiável para determinação de δ de moléculas de ampla faixa de massa molar, podendo ser utilizado no desenvolvimento de novas moléculas. O procedimento utilizando μDSC ainda requer alguns ajustes a fim de torná-lo mais preciso do que [η].

The solubility parameter (δ) of a molecule is extremely important, since that new molecules are frequently developed to be applied in liquid systems. In this work, we looked for simple and reliable alternative techniques to determine δ of low and high molecular weight molecules. Pyrene, phenanthrene and naphthalene had their δ determined by microcalorimetry (μDSC), ultraviolet (UV) and calorimetry (DSC). UV results were similar to those obtained by DSC and to those cited in the literature. Polystyrene and sulfonated polystyrene samples had their δ determined by UV, μDSC and intrinsic viscosity ([η]). The [η] results were similar to those obtained by UV. UV procedure was relatively simple, easy operation and reliable for determining δ of molecules in a wide range of molar mass, can be used when developing new molecules. The μDSC procedure still requires some adjustments to become more accurate than [η] procedure.

Keywords: Hildebrand solubility parameter, differential scanning calorimetry, intrinsic viscosity, ultraviolet spectroscopy, microcalorimetry.

Introduction

The solubility parameter (δ) is related to a thermodynamic process that involves measures of intermolecular interactions derived from the cohesive energy density, which in turn are associated with the vaporization enthalpy of the substance.[1] This parameter is a very important physical-chemical criterion, although other parameters can also be used to assess the solubilization power of substances, such as the interaction parameter,

expansion factor and second virial coefficient, mainly to verify the interaction between polymer molecules and solvents.[2,3]

The Hildebrand solubility parameter provides a numerical estimate of the degree of interaction of materials. It is calculated by the square root of the cohesive energy density for non-polar substances, that is, in relation to the van der Waals interactions.[4-11]

In fact, all types of bonds holding the liquid together are broken by evaporation and the total energy of vaporization consists of several individual parts that come from dispersion forces (δ_D), permanent dipole – permanent

*e-mail: spinelli@ima.ufrj.br

Table 1. Characterization data of polymer samples[41,42]

Sample	Code	Sulfonic groups content / mol%	Number average molar mass / Mn	Weight average molar mass / Mw	Polydispersity
Polycardanol[41]	PC	–	8,350	17,600	2.10
Polystyrene[42]	PS	0.0	87,300	234,200	2.70
Sulfonated polystyrene[42]	PSS4a	5.0	90,580*	–	–
	PSS5a	7.0	98,070*	–	–
	PSS6a	10.0	102,680*	–	–

*calculated considering PS molar mass and sulfonic groups content

dipole forces (δ_P) and hydrogen bonding (δ_H), as proposed by Hansen.[4,7,8,11-14]

Solubility parameters can be calculated by different ways: using physical constants, such as heat of vaporization, thermal expansion coefficient, compressibility and critical pressure; estimated experimentally by direct measurements, such as solubility in solvents with known parameters and refraction index measurements.[15-17] Some techniques have been applied to determine solubility parameters indirectly, such as gas chromatography,[18-20] intrinsic viscosity,[15,21-24] molecular simulation,[25] molecular descriptors,[26,27] surface tension[17,28] and Small's technique, which is based on the contribution of the individual atoms and functional groups, to which empirical values are attributed.[29,30]

Specially for polymers, it must be applied indirect methods to estimate solubility parameter by experimentally rating the degree of physical interaction between polymer molecules and selected solvents with well-known solubility parameters. The solubility parameter attributed to the polymer is that in which it presents the greatest interaction.[13,15,21-24,31,32]

The solubility parameter concept is useful to the researchers that synthesize new molecules with specific properties that must be dissolved in an required moiety to be applied in several areas, such as pharmaceuticals,[12,33,34] polymers,[7,16,18,21,23,35,36] surfactants[17,19] and petroleum.[25,26,37-40] The aim of this study was to find simple and reliable methods to determine the solubility parameters of molecules with low and high molar mass, to contribute to studies of solubility, compatibility and synthesis of new molecules.

Experimental

Materials

Toluene (99.5%), *n*-hexane (99.5%), 1,4-dioxane (99.5%), tetrahydrofuran (99.5%), ethyl alcohol (99.8%) and isopropyl alcohol (99.0%) were supplied by Vetec Química Fina, Rio de Janeiro, Brazil, while naphthalene (98.5%), phenanthrene (97.0%) and pyrene (96.0%) were supplied by Merck, São Paulo, Brazil. All compounds were used as received. Samples of polystyrene, sulfonated polystyrene and polycardanol were obtained from the Laboratory of Macromolecules and Colloids in the Petroleum Industry of Federal University of Rio de Janeiro (LMCP/UFRJ). Polycardanol was obtained by addition polymerization[41] and its molar mass was determined by size exclusion chromatography on a Waters, model 510, equipped with refractive index detectors (Waters 410) and data acquisition software Millenium 2.10, using styragel columns and tetrahydrofuran as solvent. The characterization data are presented in Table 1.[42]

Methods

Determination of the solubility parameter by differential scanning calorimetry (DSC)

The solubility parameters of samples of naphthalene, phenanthrene and pyrene were determined by applying equation 1,[43] which relates the solubility parameter (δ) with the vaporization enthalpy (ΔH_v), gas constant (R), temperature (T) and molar volume of the sample (V). Therefore, obtaining the material's solubility parameter requires determining the variation of the vaporization enthalpy, which can be measured by differential scanning calorimetry. The analyses were carried out in pans with laser-perforated lids containing a mass of 5 to 10 mg of the sample, under 30 psi nitrogen, at a heating rate of 10 ºC min^{-1} and in the temperature range from 20 ºC to about 10 ºC above the boiling point of each sample. A TA Instruments DSC Q200 calorimeter was used and the analyses were performed in duplicate. Table 2 presents the data on molar volume and boiling temperature obtained from the literature[44] and used in this experiment. The values of vaporization enthalpy used in equation 1 were those at respective vaporization temperatures of the compounds.

$$\delta =\left(\frac{\Delta H_v - RT}{V}\right)^{1/2} = \left(\frac{\Delta E}{V}\right)^{1/2} \tag{1}$$

Table 2. Molar volume and boiling point of naphthalene, phenanthrene and pyrene[44]

Sample	Molar volume / ($cm^3\,mol^{-1}$)	Boiling Temperature / °C
Naphthalene	110.51	218
Phenanthrene	151.10	336
Pyrene	159.13	393

Determination of the solubility parameter by intrinsic viscosity measurement ([η])

Determination of the solubility parameter using equation 1 is restricted to samples that can be vaporized before degradation of their molecular structure occurs. Hence, this method cannot be used to determine solubility parameters of polymers. For this purpose, the method generally used is based on determining the intrinsic viscosity of polymer solution in solvent systems with different solubility parameters. Since for a particular polymer-solvent pair and constant temperature, the intrinsic viscosity increases with stronger polymer-solvent interaction, the polymer's solubility parameter will be equal to the parameter of the solvent in which its intrinsic viscosity is highest.[13]

Only the polystyrene and sulfonated polystyrene samples (PSS4a and PSS6a) were analyzed with this procedure.

For this purpose, toluene and isopropanol were used (δ of 18.2 and 23.5 $MPa^{1/2}$, respectively),[13] along with their mixtures in varied proportions. The solubility parameters of the mixtures were calculated through the weighted average in function of the volume ratio of each component (ϕ) and the solubility parameters of the pure solvents (δ), using equation 2.[45] This same calculation has been used by authors in previous articles.[41,42]

$$\delta_m = \delta_1\,\phi_1 + \delta_2\,\phi_2 \qquad (2)$$

Stock solutions were prepared of each polymer in each of the solvent systems chosen, at a concentration of 1 wt/v%. These solutions were passed through a 0.45 μm mesh filter. Then 2 mL aliquots of each were transferred to previously weighed aluminum capsules and placed in a heated chamber at 50 °C until they reached constant weight. The concentration of each solution was calculated based on the average of the masses contained in each of the two capsules.

A 10 mL aliquot of the filtered polymer solution was placed in a Ubbelohde (0B) capillary viscometer coupled to a Haake C25P thermostatically controlled bath operated at 25 °C. The flow time was timed to obtain at least five reproducible readings. Then, 2 mL of the solvent used to prepare the solution, after passage through a 0.22 μm filter, was added to the viscometer to dilute the sample. The system was homogenized and reproducible readings were again taken. This procedure was repeated with three further additions of 2 mL of solvent, as well as for the pure solvent. The flow times attributed to each dilution were the average of all reproducible readings. From the flow time of the pure solvent, flow times of the solutions at varied concentrations and the real concentrations of these solutions, the intrinsic viscosity of each polymer-solvent pair was calculated by extrapolation of the inherent viscosity (η_{inh}) (Schulz-Blaschke equation) and reduced viscosity (η_{red}) (Huggins equation) to the concentration equal to zero, following equations 3 to 7, in which the variables are: t = flow time of the solution; t_0 = flow time of the solvent; and c = concentration of the solution.[46] All the analyses were performed in duplicate.

The solubility parameter attributed to the sample was that of the solvent system at which the highest intrinsic viscosity was observed.

$$\text{Relative viscosity } \eta_r = \frac{t}{t_0} \qquad (3)$$

$$\text{Specific viscosity } \eta_{sp} = \eta_r - 1 = \frac{t - t_0}{t_0} \qquad (4)$$

$$\text{Reduced viscosity } \eta_{red} = \frac{\eta_{sp}}{c} \qquad (5)$$

$$\text{Inherent viscosity } \eta_{inh} = \frac{\ln \eta_r}{c} \qquad (6)$$

$$\text{Intrinsic viscosity } [\eta] = \lim_{c \to 0}\left(\frac{\eta_{sp}}{c}\right) = \lim_{c \to 0}\left(\frac{\ln \eta_r}{c}\right) \qquad (7)$$

Determination of the solubility parameter by ultraviolet-visible spectroscopy (UV-Vis)

The solubility parameters of all the samples listed in Table 3 were measured by this technique. The methodology applied is not based on thermodynamic, as DSC, but uses the same principle of intrinsic viscosities, that is, the solubility parameter of the compound would be the same as that of the solvent system in which the compound exhibit the highest interaction. In this case, the absorbance of each system was measured, with attribution to the solute of the solubility parameter of the solvent system in which the absorbance was greatest.

For these analyses, a Varian Cary 50 UV-Vis spectrophotometer was used. First, scans were performed (200-800 nm) of solutions of the materials in good solvents, to determine the specific wavelength for each material and the best concentration for each analysis. This choice was

based on the device's sensitivity and satisfaction of the Lambert-Beer law.[47]

Sample and solvent were placed in a glass tube and agitated at 150 cycles *per* minute for a period of 300 s at room temperature. Then the absorbance of each solution was read. All these analyses were performed in triplicate and the results were expressed in graphs of absorbance as a function of the solvent system's solubility parameter.

The solvent systems used in these analyses and the concentrations and wavelengths are reported in Table 3.

Determination of the solubility parameter by microcalorimetry (µDSC)

This method was applied to the samples of naphthalene and sulfonated polystyrenes (PSS4a, PSS5a and PSS6a). The principle of the methodology was the same as that used for intrinsic viscosities and ultraviolet spectroscopy, that is, the solubility parameter of the compound would be the same as that of the solvent system in which the compound exhibit the highest interaction. In this case the solubilization heat of each system was measured, attributing to the solute the solubility parameter of the solvent system at which the solubilization heat was highest.

The assays were carried out using a Setaram µDSC III containing two mixture cells, one for the reference and the other for the sample. These cells have two compartments. In the upper compartment we placed 1 µL of the solvent system and in the lower compartment 1 mg of the sample. The apparatus was programmed to operate isothermally at 25 ºC, under N_2 flow. After stabilization of the baseline, the solvent was added to the solid material manually by downward movement of the piston located in the cell's upper compartment, resulting in a first peak. Then after the baseline stabilized, the piston was moved again, producing a second peak. The solubilization enthalpy was calculated from the difference between the heats detected in the first and second peaks. This procedure was performed because the movement of the piston itself during addition results in

detection of the heat, due to the device's sensitivity.

These analyses were performed in triplicate and the solubilization enthalpy values were calculated as the mean of the three readings.

Results and Discussion

Selection of the molecules

For this study we selected molecules with low and high molar mass. Naphthalene, phenanthrene and pyrene were chosen for having low molar mass and solubility parameters (δ) already reported in the literature: 20.2 MPa$^{1/2}$ [13,48] and 20.3 MPa$^{1/2}$;[49] 20.0 MPa$^{1/2}$ [48] and 20.1 MPa$^{1/2}$;[49] 24.5 MPa$^{1/2}$ [50] and 25.2 MPa$^{1/2}$;[48] respectively. The reason for the slight differences in the parameter values for the same substance is the different sources consulted.[13,48-50] Phenanthrene (three condensed rings) and naphthalene (two condensed rings) have very similar solubility parameters, although differing by one aromatic ring, allowing assessment of the sensitivity of the methods used. In turn, pyrene, containing four condensed rings, has a higher solubility parameter. For purposes of illustration, we can mention the solubility parameter of benzene of 18.5 MPa$^{1/2}$.[49] It contains only one aromatic ring, evidencing the tendency for the solubility parameter to increase with a greater number of condensed rings for the molar mass range analyzed. Polystyrene was selected for its high molar mass and δ values cited in the literature (17.0-20.8 MPa$^{1/2}$).[51] The range of solubility parameter values is attributed to the fact that polymers have chains with different molar masses. Polycardanol, obtained by addition polymerization,[41,52] was chosen for having a chemical structure similar to that of polystyrene, but with a significantly different ratio of aromatic groups/aliphatic segments. The three sulfonated polystyrene samples were chosen for presenting slightly different polarities than the polystyrene but mutually very close among the three, also allowing assessment of the sensitivity of the procedures applied to determine δ.

Table 3. Solvent system, concentration of the solution and wavelengths used in the UV-Vis analyses

Sample	Concentration / %, wt/v	Solvent system	Wavelength / nm	Optical path / mm
Naphthalene	0.5	hexane-dioxane	310	1
Phenanthrene		dioxane-ethanol	347	1
Pyrene	0.05	dioxane-ethanol	345	2
Polystyrene				1
PSS4a	0.5	toluene-isopropanol	335	1
PSS5a				1
PSS6a				1
Polycardanol	0.2	toluene-tetrahydrofuran	344	5

Determination of the solubility parameter by differential scanning calorimetry

Figure 1 presents the heat flow curve in function of temperature for naphthalene. Two endothermic events can be observed: one relative to the melting of the material, at lower temperatures, and the other related to vaporization. The curves for phenanthrene and pyrene were similar. The melting and vaporization enthalpy values obtained for each sample (Table 4) are in good agreement with literature evidencing the accuracy of the data.[53] Table 4 also shows the solubility parameters calculated from equation 1, using vaporization enthalpy. The solubility parameters are expressed according to the International System of Units ($MPa^{1/2}$).

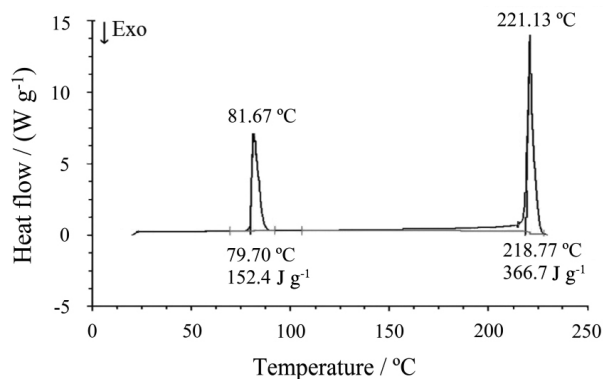**Figure 1.** Curves of heat flow in function of temperature for naphthalene

The δ values obtained for naphthalene, phenanthrene and pyrene, respectively, 19.7, 19.3 and 25.2 $MPa^{1/2}$, are very near those reported in the literature (20.2, 20.0 and 25.2 $MPa^{1/2}$) and mutually coherent, that is, naphthalene has a slightly higher solubility parameter than phenanthrene, with pyrene being well above both. This method was only applied to the samples with low molar mass since molecules with high molar mass undergo thermal degradation before reaching their vaporization energy.[15]

Determination of the solubility parameter by intrinsic viscosity [η]

Macromolecules do not volatilize, so it is not possible to determine their solubility parameters using equation 1.

Instead, the measurement is done by preparing various solutions using solvents with different solubility parameters and determining the respective intrinsic viscosities. The macromolecule's solubility parameter will be the same as that of the solvent in which it presented the greatest interaction, that is, the system with the highest [η]. The intrinsic viscosity permits making inferences about the polymer-solvent interaction, because it refers to an infinitely diluted solution, in the limit of vanishing concentration. At this point, only one macromolecule is considered to be present in the solution, which does not undergo the influence of other macromolecules, so that its behavior depends only on its interaction with the solvent molecules:[15] the stronger the molecule-solvent interaction, the greater the expansion of the molecular coil in the solvent and the higher the intrinsic viscosity. Since this method is very arduous and time-consuming, we only performed these tests with samples PS, PSS4a and PSS6a. The principle of observation of the phenomenon limits the application of this method to molecules with high molar mass.

Figure 2 shows the extrapolations of the reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) to concentration zero for the solution of PSS6a in the toluene:isopropanol solvent mixture at 82:18. The curves presented acceptable correlation coefficients and the extrapolations of the reduced and inherent viscosities, as expected, were practically equal: 0.5521 and 0.5512 dL g^{-1}, respectively. The curves for all the other systems evaluated behaved similarly, but not all the extrapolations of η_{red} and η_{inh} converged to the exactly same value. The intrinsic viscosity results for all the systems, obtained from these extrapolations at concentration zero, are presented in Table 5.

For the polystyrene sample, although the extrapolations of η_{red} and η_{inh} did not converge to the same value, it was
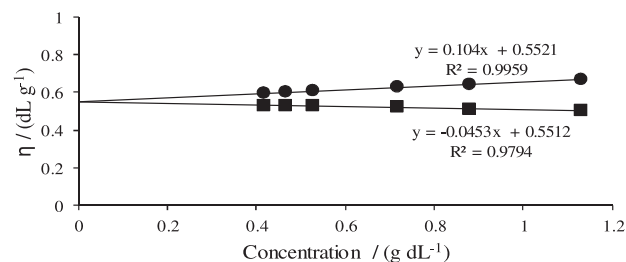

Figure 2. Viscosity as a function of concentration for the solution of PSS6a in the toluene:isopropanol solvent mixture at 82:18.

Table 4. Experimentally determined melting enthalpy, vaporization enthalpy and calculated solubility parameter using equation 1

Samples	ΔH_m Experimental / (J g^{-1})	ΔH_v Experimental / (J g^{-1})	ΔE_v / (J mol^{-1})	δ Calculated / $MPa^{1/2}$
Naphthalene	152.4	366.7	42,917.7	19.7
Phenanthrene	97.8	344.5	56,336.8	19.3
Pyrene	91.5	528.1	101,396.0	25.2

Table 5. Solvent systems, respective solubility parameters and intrinsic viscosities determined by extrapolation of reduced viscosity to concentration zero ($\eta_{red\ c\to0}$) and inherent viscosity to concentration zero ($\eta_{inh\ c\to0}$)

Polymer sample	Solvent system toluene:isopropanol / (v:v)	δ of solvent system / MPa$^{1/2}$	[η] ($\eta_{red\ c\to0}$) / (dL g^{-1})	[η] ($\eta_{inh\ c\to0}$) / (dL g^{-1})
	95:5	18.44	0.8204	0.7834
PS	90:10	18.73	0.9327	0.8633
	85:15	18.99	0.7944	0.7713
	82:18	19.15	0.7254	0.7090
	85:15	18.99	0.5281	0.5217
PSS4a	82:18	19.15	0.5237	0.5272
	80:20	19.26	0.4804	0.4779
	82:18	19.15	0.5521	0.5512
PSS6a	80:20	19.26	0.5613	0.5695
	78:22	19.37	0.4400	0.4344

possible to identify the highest value of [η] for a single solvent system whose solubility parameter was equal to 18.73 MPa$^{1/2}$. We therefore attributed this value to the polymer, which is within the solubility range described in the literature (17 to 20.8 MPa$^{1/2}$).[51] For sample PSS4a, the extrapolation differences hampered identification of the system with the highest [η] value. In any event, the values of [η] for the systems prepared with solvents having solubility parameters of 18.99 and 19.15 MPa$^{1/2}$ were very similar. We consider the δ of PSS4a to be within this range. These values of δ were higher than that found for pure polystyrene, which was expected since the sulfonation increases the polarity. For sample PSS6a, the value of δ was 19.26 MPa$^{1/2}$. This is higher than the value for PSS4a, which is also coherent with the fact that sample PSS6a has a sulfonation degree of 10 mol% while for sample PSS4a this is only 5 mol%.

Determination of the solubility parameter by ultraviolet-visible spectroscopy (UV-Vis)

Since this technique has no limitations regarding molar mass of the material, all the samples were assessed by it. Figures 3 and 4 present the graphs of absorbance in function of the solubility parameter of the solvent systems for the naphthalene and polystyrene, respectively. As expected, the absorbance increases up to a maximum value and then decreases. The solubility parameter of the solvent system at this maximum absorbance was attributed to the solute being studied. At this solubility parameter there is a strong intermolecular interaction between the product and solvent, which provides greater solvatation, meaning more molecules in solution are able to absorb light. This behavior was observed for all the

samples analyzed and the solubility parameter values attributed to the samples were: naphthalene (19.94 MPa$^{1/2}$); phenanthrene (20.5 MPa$^{1/2}$); pyrene (25.3 MPa$^{1/2}$); PS (18.99 MPa$^{1/2}$); PSS4a (19.15 MPa$^{1/2}$); PSS5a (19.15 MPa$^{1/2}$); PSS6a (19.26 MPa$^{1/2}$) and polycardanol (18.53 MPa$^{1/2}$). The values found for the samples with low molar mass were in agreement with those obtained by DSC and those mentioned in the literature. For the samples with high molar mass, the values for PS, PSS4a and PSS6a were equal to or very near those determined by [η]. The values found for PSS4a (5 mol% of sulfonation) and PSS5a (7 mol% of sulfonation) were equal, demonstrating that it was not possible to perceive the polarity differences that comes from the difference of 2 mol% in the degrees of sulfonation. However, it was possible to observe solubility differences between polystyrene (18.99 MPa$^{1/2}$) and polycardanol (18.53 MPa$^{1/2}$). Polycardanol is an oily soluble polymer, obtained from the addition polymerization of cardanol, which structure is constituted of a phenol meta substitute with a C_{15} unsaturated hydrocarbon chain containing one to three double bonds. In hydrocarbon compounds, the aromatic ring is responsible for a more polar character. Since the aromatic/aliphatic ratio is lower for polycardanol than for polystyrene, we expected the solubility parameter of polycardanol also to be lower.

Determination of the solubility parameter by microcalorimetry (µDSC)

The solubilization enthalpy values were obtained from the curves of heat flow in function of time. Figure 5 shows the curve obtained for naphthalene dissolved in hexane:dioxane (5:95). The first peak (endothermic) refers to the heat involved in the processes of sample
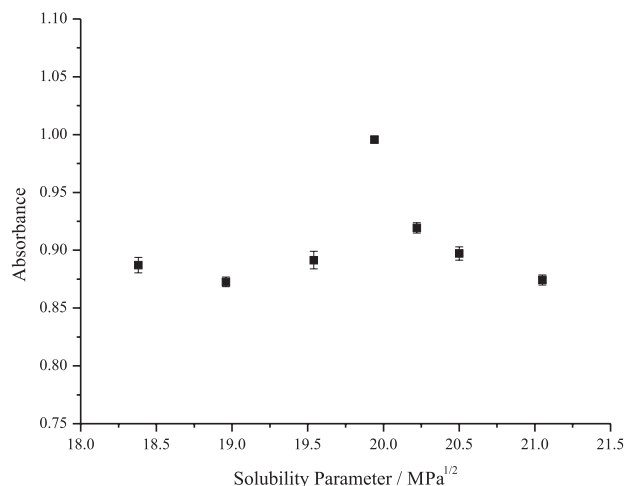
Figure 3. Absorbance as a function of solubility parameter of the solvent system for naphthalene, at 310 nm.
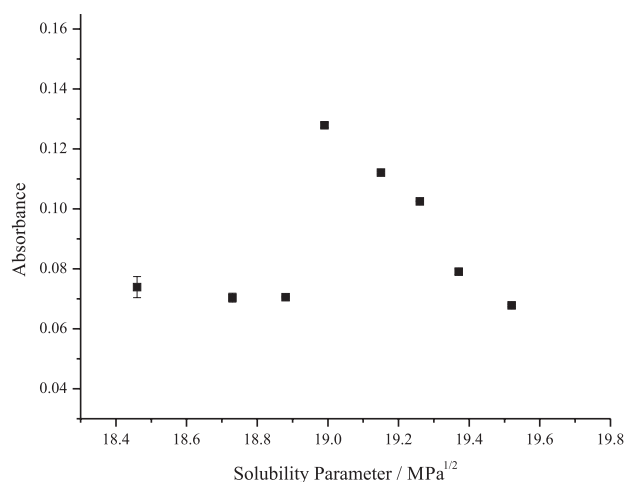

Figure 4. Absorbance as a function of solubility parameter of the solvent system for polystyrene, at 335 nm.

solubilization and movement of the piston for addition of the solvent. The second peak (exothermic) refers only to the heat involved in the piston movement. The solubilization enthalpy was calculated from the difference between the enthalpy values associated with the first and second peaks. Figure 6 shows the heat flow curve in function of time for PSS5a solubilized in the toluene:isopropanol (82:18). All the polymer samples presented similar curves. In these cases, unlike for the samples with low molar mass, two exothermic peaks can be observed, the first with less area than the second. This happens because the heat involved in the endothermic process of solubilization of the sample is lower than the heat involved in the exothermic process of the piston movement. The calculation of the difference between the peaks ($\Delta H_{solub} = \Delta H_{1st\,peak} - \Delta H_{2nd\,peak}$) evidences the endothermic character of the process of dissolving the polymers in the chosen solvents. This behavior is associated

with the fact that solute molecules need to absorb energy to overcome their attractive interactions and separate.[54]
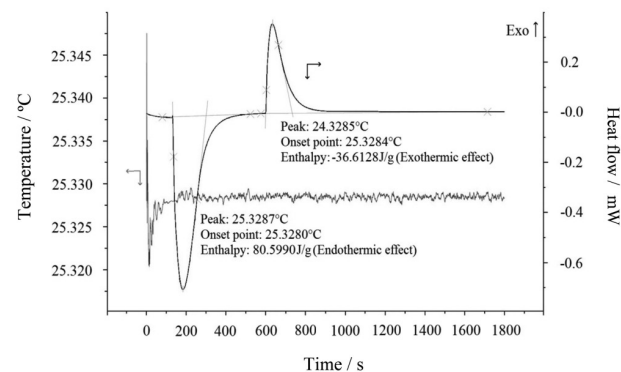

Figure 5. Heat flow (right axis) and temperature (left axis) in function of time for naphthalene solubilized in hexane:dioxane (5:95).
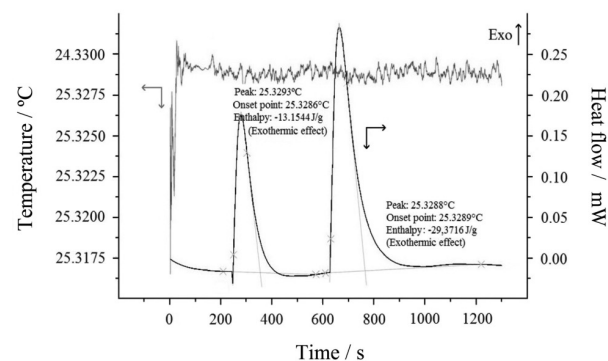

Figure 6. Heat flow (right axis) and temperature (left axis) in function of time for 7 mol% sulfonated polystyrene (PSS5a) solubilized in toluene:isopropanol (82:18).

Table 6 presents the average solubilization enthalpy values as well as the standard deviations for all the solute-solvent systems evaluated. The standard deviations were relatively high, mainly for the analyses of naphthalene, but it was possible to observe differences between the solubilization enthalpies in the different solvent mixtures. As was observed in the UV-Vis tests, the solubilization enthalpy increases with rising solubility parameter, reaches a peak and then decreases. The δ value of the solvent system, at the maximum solubilization heat, was attributed to the solute. For naphthalene, the maximum solubilization enthalpy value was observed in the hexane:dioxane 10:90 solvent mixture, which presented a solubility parameter of 19.94 MPa$^{1/2}$, thus being the solubility parameter attributed to naphthalene by this experimental procedure. This result is in accordance with that obtained by UV-Vis spectroscopy (19.94 MPa$^{1/2}$) and calorimetry (19.7 MPa$^{1/2}$), which in turn are very near the values found in the literature (20.2 and 20.3 MPa$^{1/2}$).[13,48,49]

It should be highlighted that to obtain a more exact measurement of the solubility parameter of naphthalene

Table 6. Average solubilization enthalpies obtained for the selected samples and correlation with solubility parameters of the solvent systems

Samples	Solvent mixtures	Solvent content	δ of solvent mixtures / $MPa^{1/2}$	Average solubilization enthalpy / $(J\ g^{-1})$	Standard deviation / $(J\ g^{-1})$
Naphthalene	hexane:dioxane	30:70	18.96	102.8982	7.1011
		20:80	19.54	121.7297	3.0006
		10:90	19.94	143.9015	3.3948
		5:95	20.22	117.9409	2.7941
		0:100	20.50	115.7718	4.8068
PSS4a	toluene:isopropanol	90:10	18.73	12.0016	0.9308
		85:15	18.99	18.3009	1.9491
		82:18	19.15	21.9868	1.0622
		80:20	19.26	12.5671	1.6879
		78:22	19.37	11.7037	1.2781
PSS5a	toluene:isopropanol	85:15	18.99	14.7719	1.1576
		82:18	19.15	16.9905	0.4626
		80:20	19.26	12.5252	1.2957
		78:22	19.37	12.1729	0.0774
PSS6a	toluene:isopropanol	85:15	18.99	15.5075	0.6876
		82:18	19.15	17.0002	0.8384
		80:20	19.26	12.6917	0.9594
		78:22	19.37	12.1472	0.6779
		75:25	19.52	12.9986	1.0127

using techniques based on evaluation of solutions in solvents with distinct solubility parameters, it would be necessary to evaluate other solvent systems with solubility parameters between 19.54 and 19.94 $MPa^{1/2}$ and between 19.94 and 20.22 $MPa^{1/2}$. However, such an exacting procedure would not have led to a δ value equal to that cited in the literature, since in the mixture of solvents with δ equal to 20.2 $MPa^{1/2}$, both the values, of absorbance obtained by the UV-Vis and those of solubilization enthalpy obtained by the μDSC, were lower than those found for the solvent mixtures with δ of 19.94 $MPa^{1/2}$.

The three types of sulfonated polystyrene presented maximum solubilization enthalpy values in the toluene:isopropanol 82:18 solvent mixture, which has a solubility parameter of 19.15 $MPa^{1/2}$. These results are in agreement with those obtained by UV-Vis for samples PSS4a and PSS5a, but differ from the result found for PSS6a (19.26 $MPa^{1/2}$). The result obtained using UV-Vis is more coherent with the fact that the samples had distinct sulfonation degrees; since the sulfonic groups make the molecules more hydrophilic, the solubility parameter is higher.

The experimental procedure using the μDSC technique was not able to identify small variations in the solubility parameter of the molecules with high molar mass. However,

since the results were very near those expected, just as for molecules with low molar mass, we believe a more detailed investigation is necessary for adjustment, mainly of movement of the piston and the preparation and storage of the solvent mixtures.

Comparison of the solubility parameter values obtained by the methods using DSC, [η], UV-Vis and μDSC

Table 7 summarizes the solubility parameters found by the various techniques employed. From a practical standpoint, all the techniques supplied information, at least approximate, regarding the solubility of the samples. However, consideration should go to the advantages and disadvantages of each method. DSC applying equation 1 is a simple, fast and reliable technique to determine δ, but it is limited to analysis of molecules with relatively low molar mass, that is, molecules that vaporize at temperatures below their thermal degradation. The technique involving determination of [η] in solvents with different solubility parameters is very laborious and susceptible to procedural mistakes. Besides this, it was not able to perceive small differences of polarity between samples of the same family. UV-Vis spectroscopy can be applied to measure the solubility parameter of molecules without limitation

Table 7. Solubility parameters obtained by DSC, [η], UV-Vis and μDSC

Sample	δ / MPa$^{1/2}$				
	Literature	DSC	UV	μDSC	[η]
Naphthalene	20.2/ 20.3	19.7 ± 0.05	19.94 ± 0.2	19.94 ± 0.2	[b]
Phenanthrene	20.0/ 20.1	19.3 ± 0.05	20.50 ± 0.2	[c]	[b]
Pyrene	24.5/ 25.2	25.2 ± 0.05	25.30 ± 0.4	[c]	[b]
Polystyrene	17.0-20.8	[b]	18.99 ± 0.1	[c]	18.73
PSS4a (5 mol%)	[a]	[b]	19.15 ± 0.04	19.15 ± 0.1	18.99 – 19.15
PSS5a (7 mol%)	[a]	[b]	19.15 ± 0.1	19.15 ± 0.1	[c]
PSS6a (10 mol%)	[a]	[b]	19.26 ± 0.05	19.15 ± 0.1	19.26
Polycardanol	[a]	[b]	18.53 ± 0.05	[c]	[c]

[a]Not found; [b]Not possible to determine; [c]Not analyzed.

as to molar mass, since the solubility parameter values found experimentally were very close to those reported in the literature, and for unknown samples the values were highly coherent with the structures presented. μDSC is also adequate for a wide molar mass range and has the main advantage over the other techniques of requiring a smaller quantity of material, even though it has only provided approximate solubility parameter values when applying the procedure used in this work.

Conclusions

Among the methods assessed to measure the solubility parameter, the one based on the maximum absorbance, of the sample dispersed in solvents with different solubility parameters, determined by ultraviolet-visible (UV-Vis) spectroscopy was the most suitable for a wide molar mass range. It is a relatively simple and fast method not prone to operational errors. Besides this, it is easily repeatable and highly sensitive to small solubility differences of the samples. Specifically for molecules with low molar mass, the technique of determining the vaporization enthalpy by differential scanning calorimetry is better than the UV-Vis technique because it requires a smaller sample quantity. However, for new molecules, it is necessary to determine the density of the sample, which requires more material. Therefore, it can be said that the two techniques are comparable in terms of advantages. On the other hand, for molecules with relatively high molar mass, it is not possible to determine the vaporization enthalpy, and so the procedure using UV-Vis is more suitable. The procedure involving determination of the intrinsic viscosity [η], adequate only for molecules with high molar mass, is very laborious, susceptible to operational errors and has low sensitivity. Finally, the procedure involving microcalorimetry (μDSC)

is suitable for a broad molar mass range and needs only small sample quantities, but it only supplies approximate information on solubility, so it needs adjustments to obtain more exact solubility parameter values.

References

1. Mark, J. E.; *Physical Properties of Polymers Handbook*, 2nd ed.; Springer: New York, EUA, 2007.
2. Mark, H. F.; Bikales, N.; Overberger, C. G.; Menges, G.; *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley e Sons: New York, EUA, 1989.
3. Holmberg, K.; Jönsson, B.; Kronberg, B.; Lindman, B.; *Surfactants and Polymers in Aqueous Solution*, 2nd ed.; Wiley: England, 2002.
4. Redelius, P. G.; *Fuel* **2000**, *79*, 27.
5. Goodarzi, M.; Duchowicz, P. R.; Freitas, M. P.; Fernandéz, F. M.; *Fluid Phase Equilib.* **2010**, *293*, 130.
6. Matelet, F.; Ekulu, G.; Solimando, R.; Rogalski, M.; *Energy Fuels* **2004**, *18*, 667.
7. Hansen, C. M.; *Prog. Org. Coat.* **2004**, *51*, 77.
8. Martina, L.; Redelius, P.; *Energy Fuels* **2008**, *22*, 3395.
9. Ya, L.; Jia-Jia, S.; Lei, S.; *J. Fuel Chem. Technol.* **2008**, *36*, 297.
10. Eslamimanesh, A.; Esmaeilzadeh, F.; *Fluid Phase Equilib.* **2010**, *291*, 141.
11. Machui, F.; Langner, S.; Zhu, X.; Abbott, S.; Bradec, C.; *Sol. Energy Mater. Sol. Cells* **2012**, *100*, 138.
12. Adamska, K.; Voelkel, A.; *Int. J. Pharm.* **2005**, *304*, 11.
13. Hansen, C. M.; *Hansen Solubility Parameters: A User's Handbook*, 2nd ed.; CRC Press: New York, EUA, 2007.

14. Levin, M.; Redelius, P.; *Energy Fuels* **2008**, *22*, 3395.

15. Lucas, E. F.; Soares, B. G.; Monteiro, E. E. C.; *Caracterização de polímeros: determinação de peso molecular e análise térmica*, 3a. ed.; E-papers: Rio de Janeiro, Brasil, 2001.

16. Bozdogan, A. E.; *Polymer* **2003**, *44*, 6427.

17. Somasundaran, P.; Krishnakumar, S.; Mehta, S. C.; *J. Colloid. Interf. Sci.* **2005**, *292*, 373.

18. Karim, K. A.; Bonner, D. C.; *Polym. Eng. Sci.* **1979**, *19*, 1174.

19. Proverbio, Z. E.; Bardavid, S. M.; Arancibia, E. L.; Shulz, P. C.; *Colloids Surf., A* **2003**, *214*, 167.

20. Voelkel, A.; Strzemiecka, B.; Adamska, K.; Milczewaska, K.; *J. Chomatogr. A* **2009**, *1219*, 1551.

21. Elias, H. G.; *Macromolecules: Structure and Properties*, 2nd ed.; Plenum Press: New York, EUA, 1984.

22. Bozdogan, A. E.; *Polymer* **2004**, *45*, 6415.

23. Bustamante, P.; Navarro-Lupión, J.; Escalera, B.; *Eur. J. Pharm. Sci.* **2005**, *24*, 229.

24. Johansson, B.; Friman, R.; Laitinen, H. H.; Rosenholm, J. B.; *Adv. Colloid Interface Sci.* **2009**, *147–148*, 132.

25. Rogel, E.; *Colloids Surf., A* **1995**, *104*, 85.

26. Jouyban, A.; Khoubnasabjafari, M.; Soltani, S.; Soltanpour, S.; Tamizie, E.; Acree Jr., W. E.; *J. Braz. Chem. Soc.* **2008**, *19*, 604.

27. Jouyban, A.; Fakhree, M. A. A.; Shayanfar, A.; Ghafourian, T.; *J. Braz. Chem. Soc.* **2011**, *22*, 684.

28. Yanke, L.; Shufen, Z.; Jinzong, Y.; Qinghui, W.; *Colloids Surf., A* **2004**, *248*, 127.

29. Fedors, R. F.; *Polym. Eng. Sci.* **1974**, *14*, 147.

30. Roberts, G. A. F.; Thomas, I. M.; *Polymer* **1978**, *19*, 459.

31. Launay, H.; Hansen, C. M.; Almdal, K.; *Carbon* **2007**, *45*, 2859.

32. Kusano, Y.; Teodoru, S.; Hansen, C. M.; *Surf. Coat. Technol.* **2011**, *205*, 2793.

33. Gröning, R.; Braun, F. J.; *Pharmazie* **1996**, *51*, 337.

34. Minguetti, P.; Cilurzo, F.; Casiraghi, A.; Montarani, L.; *Int. J. Pharm.* **1999**, *190*, 91.

35. Evans, K. M.; Hardy, J. K.; *J. Appl. Polym. Sci.* **2004**, *93*, 2688.

36. Çavuş, S.; Çakal, E.; Sevgili, L. M.; *Swelling behavior and solubility parameters of poly(Nvinylcaprolactam-co-itaconic acid) gels*, "Annals of 20th Polychar POLYCHAR World Forum on Advanced Materials", P1.23, Croatia, 2012.

37. Garreto, M. S. E.; González, G.; Ramos, A. C.; Lucas, E. F.; *Chem. Chem. Technol.* **2010**, *4*, 317.

38. Ramos, A. C. S.; Rolemberg, M. P.; Moura, L. G. M.; Zilio, E. L.; Santos, M. F. P.; González, G.; *J. Pet. Sci. Eng.* **2013**, *102*, 36.

39. Garreto, M. S. E.; Mansur, C. R. E.; Lucas, E. F.; *Fuel* **2013**, *113*, 318.

40. Honse, S. O.; Mansur, C. R. E.; Lucas, E. F.; *J. Braz. Chem. Soc.* **2012**, *23*, 2204.

41. Moreira, L. F. B.; González, G.; Lucas, E. F.; *J. Appl. Polym. Sci.*, **1999**, *73*, 29.

42. Lima, A. F.; Mansur, C. R. E.; Lucas, E. F.; González, G.; *Energy Fuels* **2010**, *24*, 2369.

43. Huggins, M. L.; *J. Phys. Chem.* **1942**, *46*, 151; Huggins, M. L.; *Ann. N. Y. Acad. Sci.* **1942**, *43*, 1.

44. Lide, D. R.; *Handbook of Chemistry and Physics*, 81st ed., CRC Press: Boca Raton, Florida, USA, 2001.

45. Prausnitz, J. M.; Lichtenthaler, R. N.; Gomes, A. E.; *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: New Jersey, USA, 1999.

46. Flory, P. J.; *Principles of Polymer Chemistry*, 6th ed.; Cornell University Press: New York, USA, 1995.

47. Svanderg, S.; *Atomic and Molecular Spectroscopy: Basic Aspects and Practical Applications*, 4th ed.; Springer: New York, USA, 2004.

48. Weast, R. C.; *Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Raton, Florida, USA, 1985.

49. Barton, A. F. M.; *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed.; CRC Press: Boca Raton, Florida, USA, 1983.

50. Fornari, T.; Ebãnez, E.; Reglero, G.; Stateva, R.; *Open Thermodyn. J.* **2011**, *5*, 40.

51. Barton, A. F. M.; *Handbook of Polymer-Liquid Interaction Parameters and solubility parameter*, CRC Press: Boca Raton, Florida, USA, 1990.

52. Moreira, L. F. B.; González, G.; Lucas, E. F.; *Polímeros* **1998**, *3*, 46.

53. Acree Jr., W.; Chickos, J. S.; *J. Phys. Chem. Ref. Data*, **2010**, *39*, 043101.

54. Brown, T. L.; LeMay, H. E.; Bursten, B. E.; Burdge, J. R.; *Química: A ciência central*, 9a. ed.; Pearson Education do Brasil Ltda.: São Paulo, Brasil, 2005.