Water Sorption Characteristics in Moderately Hydrophilic Polymers, Part 1: Effect of Polar Groups Concentration and Temperature in Water Sorption in Aromatic Polysulfones

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ABSTRACT: The water equilibrium concentration has been determined for three aromatic polysulfones differentiated essentially by the sulfone concentration, in the 0–0.9 activity range, at temperatures of 50, 60, and 70°C, using a dynamic vapor sorption apparatus. In all the cases, Henry's law was obeyed. The corresponding solubility S and heat of dissolution H_s were determined and their relationships with structure were investigated. The fact that S increases nonlinearly with the sulfone concentration and that H_s is also an increasing function of the latter leads one to abandon classical approaches to polymer–water interactions and propose a model in which water is doubly bonded. Then, S depends on the distribution of distances between polar groups, characterized by a function $P(r)$ and H_s depends on both $P(r)$ and the hydrogen bond potential $U(r)$. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 3279–3285, 2008

Key words: water solubility; heat of dissolution; structure-property relationships

INTRODUCTION

Water sorption in polymers has created an extensive literature owing to its practical applications in industrial domains such as membranes, textile, packaging, aerospace or naval composites, electrical insulation, etc. Early studies, as reviewed by Barrie[1] in 1968, revealed the diversity of sorption mechanisms. However, for a large family of amorphous glassy polymers of low to moderate hydrophilicity, sorption essentially results from the water dissolution in the polymer matrix and obeys Henry's law, at least, at low activities, typically when water activity $a \leq 0.5$. Our study focuses on structure–properties relationships in this domain characterized by the linearity of the sorption isotherms:

$$C = Sp \quad \text{or} \quad V = \alpha a \qquad (1)$$

where C is the water concentration in the polymer, V the water volume fraction, S the solubility coefficient of water in the polymer, p the water pressure, a the water activity, and α a dimensionless coefficient proportional to S.

Attempts were made to establish a link between C and the free volume fraction in the polymer, for instance in the case of epoxies.[2] But this theory fails to explain why free volume rich polymers such as hydrocarbons or polydimethylsiloxane elastomers have a very low hydrophilicity.

Better predictions can be made assuming water is hydrogen bonded to polar groups and its solubility is directly linked to the polar groups concentrations. The simplest theory[3] assumes a molar additive function H that can be defined as

$$H = MC = \sum_i H_i \quad \text{where } M = \sum_i M_i \qquad (2)$$

H is the number of water moles absorbed by a constitutive unit of molar mass M. This constitutive unit contains elementary groups of which the contribution to water absorption is H_i. For a given type of polar group, H_i would be independent of the surrounding structure. This concept was used with some success in the case of amine crosslinked epoxies,[4,5] but in wide structural series, H_i was found to increase with the group concentration.[6] With this theory, the main problem comes from the fact that H_i is not an integer meaning that all the polar groups are not equivalent. In the case of polyamides,[7,8] this observation led to the development of the concept of ''group accessibility.'' But how to demonstrate that the corresponding quantity is not an adjustable appropriate parameter?

In most of above cited studies, especially focused on polymers of low to medium hydrophilicity, C was found to be almost temperature independent, which encouraged authors to consider it as well representa-

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tive of the water–polymer interaction. In fact, C is not rigorously temperature independent: it tends to increase with temperature T for polymers of low polarity/low hydrophilicity such as polyethylene[9] for instance, and decrease with T for highly hydrophilic polymers such as certain epoxide-amine networks for instance.[6] These trends can be well explained by Henry's law.[10] Both the solubility S and the water pressure p obey Arrhenius law, at least, in a first approach:

$$S = S_0 \, \exp\left(-\frac{H_s}{RT}\right) \quad p_s = p_0 \, \exp\left(-\frac{H_w}{RT}\right) \quad (3)$$

where H_s is the heat of water solubility in the polymer and H_w is the heat of water vaporization ($H_w \approx 43$ kJ mol^{-1}). The water equilibrium concentration is thus expected to obey also Arrhenius law:

$$C = C_0 \, \exp\left(-\frac{H_c}{RT}\right) \quad \text{where } C_0 = S_0 p_0 \quad \text{and}$$

$$H_c = H_s + H_w \quad (4)$$

Since water establishes strong hydrogen bonds with polar groups, its dissolution in the polymer is exothermic: $H_s < 0$.

Two cases can be thus distinguished:

– Low water–polymer interactions: $|H_s| < H_w$ so that $H_c > 0$; C is an increasing function of T,
– High water–polymer interactions: $|H_s| > H_w$ so that $H_c < 0$; C is a decreasing function of T.

It appears thus that the polymer–water interaction cannot be represented by a single quantity (the water equilibrium concentration); at least two quantities S_0 and H_s are necessary, which imposes us to study experimentally the water sorption at several temperatures.

For such investigations on structure-water solubility relationships, where polar groups concentration is probably a key parameter, it appears interesting to work on sample families containing only one type of polar groups of which the concentration can significantly vary from one member to another. Aliphatic polyamides, for instance, have been widely studied, but they display several drawbacks, especially their morphological heterogeneity and the fact that in wet state their amorphous phase can be glassy to rubbery dependant on the temperature and water concentration in the usual investigation domain.

Aromatic polysulfones don't display these drawbacks: they are fully amorphous and they remain in the glassy state even when saturated by water. They can be considered as an aromatic polyether matrix of low polarity/hydrophilicity containing highly polar sulfone groups which are strong hydrogen acceptors in hydrogen bonds. The sulfone concentration can be significantly varied, for instance from 2.3 mol kg^{-1} in bisphenol A polysulfone to 4.3 mol kg^{-1} in polyethersulfone. Furthermore, their practical applications in membrane technology lead to extensive research work on their water transport properties.

From the point of view of structure-water solubility relationships, the data reported by Schult and Paul[11] well illustrate the above reported trends: the solubility coefficient (at low activity) displays no correlation with the free volume fraction as defined by Van Krevelen[3] but tends to increase with the sulfone concentration although other factors are obviously involved.

Unfortunately, Arrhenius parameters of S were not reported. The aim of our work is to determine them, on three distinct commercial polysulfones: Bisphenol A polysulfone (PSU), biphenolpolysulfone (PPSU) and polyethersulfone (PES) and to compare various models of polymer–water interaction on the basis of experimental results.

EXPERIMENTAL

Samples

The investigated polysulfones are polymers free of additives, processed into thin films. Their density, trade name, and thickness are given in Table I. The three polymers are totally amorphous.

Equipment

A dynamic vapor sorption (DVS) apparatus supplied by Surface Measurements Systems was used to record sorption isotherms. Its principle is shown in Figure 1.

The DVS system is based on an ultrasensitive recording microbalance capable of measuring changes in sample mass of about 0.1 µg. This instrument is installed in a constant controlled temperature chamber which permits measurements at temperatures from 10 to 70°C. The required humidities are generated by mixing dry and saturated vapor gas flows in the right proportion using mass flow controllers. The maxi-

TABLE I
Characteristics of the Polysulfone Under Study

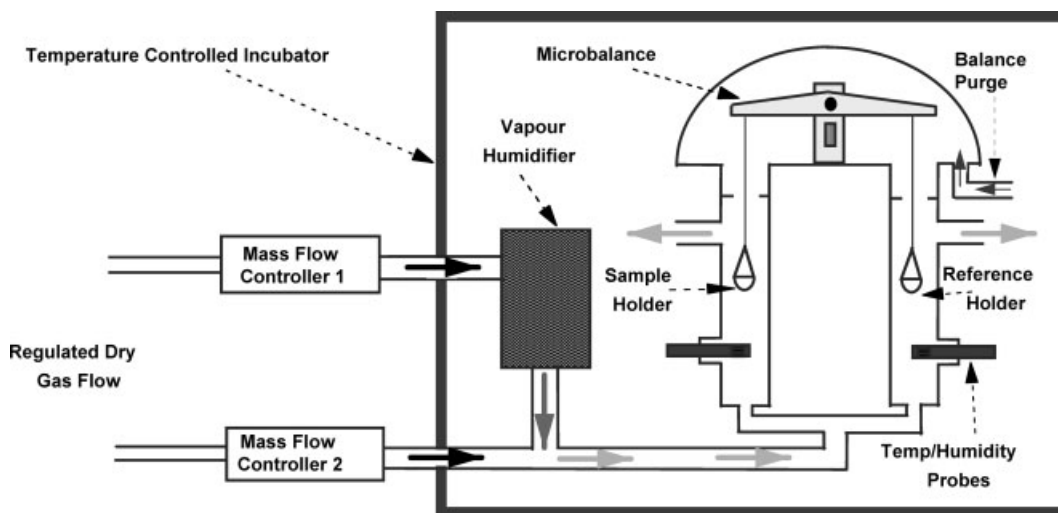| Polymer	ρ (kg m^{-3})	T_g (K)	[sulf] (mol kg^{-1})	Trade name	Film thickness (µm)
PSU	1240	463	2.3	Udel	90
PPSU	1290	493	2.5	Radel R	70
PES	1370	488	4.3	Ultrason	75

Figure 1 Schematics of the dynamic vapor sorption.

mum capacity of the balance is 1.5 g. It is calibrated with certified loads of 100 mg supplied by Troemner. Relative humidity measurements are calibrated using saturated salt solutions.[12] The relative humidities at 50°C of the three salt solutions used in this study are given in Table II. The calibration method, based on the determination of the deliquescent point, is shown by Figure 2. At a given temperature, relative humidity RH varies and mass m of a saturated solution is recorded. The equilibrium RH for the solution under study corresponds to the RH value at which $dm/d\underline{RH} = 0$. This calibration is repeated at each temperature for each solution.

Sorption tests

The sorption isotherms are recorded between 0 and 90% RH, measurements being made in 10 steps, each one of 10% RH. It is the minimum step to have a good signal/noise ratio. Measurements are done at three temperatures: 50, 60, and 70°C. The procedure used is the following: insert sample in the quartz pan, do a cycle 0-90-0% RH during 30 min for each step, leave the sample till the achieving of a stabilized mass that will be considered as the initial mass of the sample. The stabilization time depends on temperature: 2 h at 50°C, 1 h at 60°C, and 30 min at 70°C. A longer waiting time will bring static into the balance due to the fact that the instrument is made of glass.

TABLE II
Salt Solutions Used for Calibration and Their Corresponding Relative Humidity at 323 K

Salt solution	Relative humidity at 50°C (%)
LiCl	11.10
$MgCl_2$	30.54
NaCl	74.43

Expression of results

If m_0 was the initial sample mass (in dry state) and Δm the mass uptake, the relative mass uptake is $w = \Delta m/m_0$ and the corresponding mass fraction is $\mu = w/(1 + w)$. The water volume fraction is $v = \mu \rho_p / [\mu \rho_p + (1-\mu)\rho_w]$, where ρ_p and ρ_w are the respective densities of the polymer and water. The water concentration is: $C = v/V_w$, where V_w is the molar volume of the water molecule.

RESULTS

Examples of sorption isotherms of PSU, PPSU, and PES are shown in Figure 3. They are linear in the whole activity ($0 \leq a \leq 0.9$) and temperature ranges ($323 \text{ K} \leq T \leq 343 \text{ K}$) under investigation. The slopes $\alpha = (\partial v/\partial a)_T$ obtained at 50, 60, and 70°C are listed in Table III. From water concentration C values, the solubility coefficient S was calculated and its (apparent) Arrhenius parameters S_0 and H_s were determined and reported in Table III.
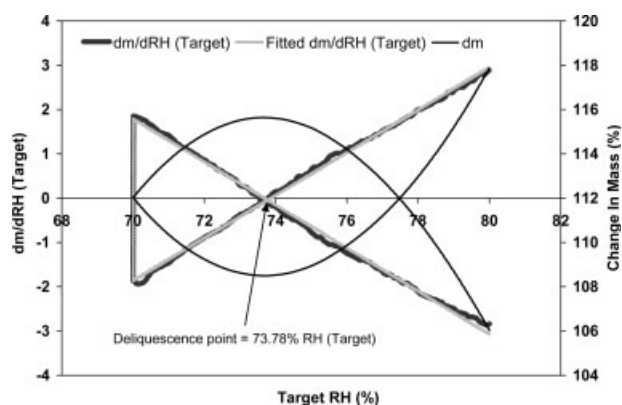

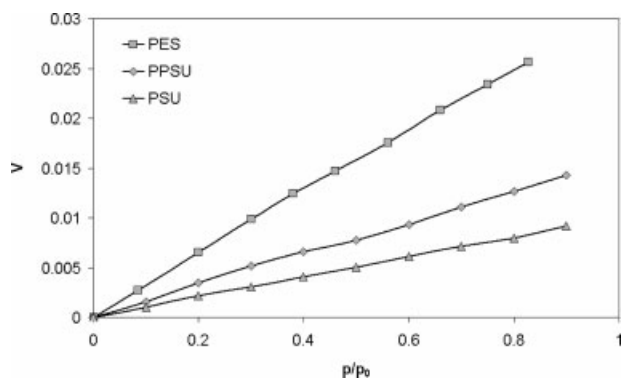**Figure 2** Salt validation calibration with NaCl at 50°C.

Figure 3 Sorption isotherms for PES, PPSU, and PSU at 50°C.

It is clear that the pre-exponential factor of water solubility and its apparent activation energy are decreasing functions of the sulfone content. It is also interesting to remark for PSU: $|H_s| < H_w$, so the solubility tends to be a slowly increasing function of temperature, whereas the reverse is observed for PPSU and PES.

In a first attempt, we tried to correlate the water sorption characteristics to the polymer cohesive properties and polymer–water interaction parameter χ. The molar cohesive energy E_{coh} was first calculated using the molar increments reported by Van Krevelen[3] except for the sulfone group for which Porter's data[13] ($E_{sulfone} = 45{,}000$ J mol^{-1}) was used. Then, the cohesive energy density $d_{coh} = \rho E_{coh}/M$, where ρ is the specific mass of the polymer and M the molar mass of the monomer unit used for the calculation of E_{coh}, the solubility parameter $\delta = d_{coh}^{1/2}$, and the water–polymer interaction parameter:

$$\chi = \frac{V_w}{RT}(\delta_{coh} - \delta_w)^2 \tag{5}$$

where V_w and δ_w are respectively, the molar volume and water solubility parameter, were calculated and listed in Table IV.

There is another possible method for determining the polymer–water interaction, based on the Flory-Huggins sorption isotherms equation:

$$\ln(a) = \ln(v) + (1 - v) + \chi(1 - v)^2 \tag{6}$$

of which the initial slope is α such as:

$$\alpha = \exp\left[-(1 + \chi)\right] \tag{7}$$

The values of χ calculated from eq. (7) are also listed in Table III. They are significantly higher than those calculated from eq. (5). In fact, simulations of Flory-Huggins isotherms using eq. (8) lead to curves displaying a positive concavity in the high activities, the deviation from linearity being as marked as the sulfone concentration is high. It can be concluded that the Flory-Huggins theory is not pertinent to describe the sorption behavior of the systems under study. More generally, there is no linear correlation between the slope of sorption isotherms and the sulfone concentration [Fig. 4(a)], or the cohesive energy [Fig. 4(b)].

On the contrary, these figures indicate a strong nonlinearity and, eventually, the existence of critical conditions (for instance a critical sulfone concentration $[sulf]_c$ below 1 mol kg^{-1} or a critical cohesive energy density $d_{coh\,c} \sim 300$ MPa) above which the influence of sulfone concentration (or cohesive energy density) on water solubility increases suddenly. For instance, for $d_{coh} > d_{coh\,c}$, the dependence of hydrophilicity to cohesive energy density could be approximated by

$$\alpha \approx k(d_{coh} - d_{coh\,c})^3 \tag{8}$$

where k is a characteristic parameter of the polysulfone family.

DISCUSSION

It appears thus that classical approaches to the structure-water solubility relationships cannot explain the strong nonlinearity of the solubility variation with polar group concentration, cohesivity, solubility parameter or any other cohesive parameter. Furthermore, Arrhenius parameters S_0 and H_s display surprising trends: S_0 and H_s are decreasing functions of the sulfone concentration whereas, in the simplest case, H_s would be expected to be constant (only depending on the nature of polar groups) whereas S_0 would be an increasing function of the polar group concentration.

TABLE III
Sulfone Concentration, Slope of Sorption Isotherms and Arrhenius Parameters of the Water Solubility in the Three Polymers Under Investigation

Polymer	[sulf] (mol kg^{-1})	α ($\times 10^{-4}$) (50°C)	α ($\times 10^{-4}$) (60°C)	α ($\times 10^{-4}$) (70°C)	S_0 ($\times 10^{-9}$) (mol m^{-3} Pa^{-1})	H_s (kJ mol^{-1})
PSU	2.3	102	119	128	12	−40.6
PPSU	2.5	158	175	183	3.6	−45.1
PES	4.3	307	335	336	2.1	−48.4

TABLE IV
Cohesive Parameters and Slope of the Sorption Isotherm for the Three
Polysulfones Under Consideration

Polymer	[sulf] (mol kg^{-1})	E_{coh} (kJ mol^{-1})	d_{coh} (MPa)	δ_p (MPa)$^{1/2}$	χ [eq. (5)]	χ [eq. (7)]	α ($\times 10^{-4}$) (50°C)
PSU	2.3	215	604	24.6	3.0	3.6	102
PPSU	2.5	204	659	25.7	2.7	3.1	158
PES	4.3	137	810	28.5	2.0	2.5	307

From a careful investigation on water sorption by polyethylene samples differing by the content of oxygen containing polar groups, McCall et al.[9] showed that S doesn't obey Henry's law but it is rather the sum of two "Arrhenian" terms: one (index m) relative to the low polarity matrix, the other (index p) relative to the polar groups of which concentration is s:

$$S = S_{m0} \exp\left(-\frac{H_m}{RT}\right) + sS_{p0} \exp\left(-\frac{H_p}{RT}\right) \quad (9)$$

where H_m and H_p (sorption heat of respectively, matrix and polar groups) are negative and $|H_m| < |H_p|$. S_{m0} and S_{p0} are parameters related respectively, to the nature of matrix and the nature of polar groups.

This model is obviously unsuitable for the polysulfone series under study since, extrapolating at zero the sulfone concentration, we would obtain a negative solubility value for the matrix, which would be lacking physical sense.

It seems interesting to explore a new way for modeling polymer–water interactions (in the Henry's regime, e.g., at low activities), starting from the hypothesis that water is always doubly bonded to polar groups by hydrogen bonds. This hypothesis is supported by IR and NMR observation[14] and also by the fact that the heat of dissolution H_s values are generally too high to correspond to single hydrogen bonds.[15]

Then, a hydrophilic site would be composed of two polar groups, that imposes constraints on the distance r between polar groups. Let us consider three possible configurations of polymer–water complex in Figure 5. The hydrogen bond distance x is linked to the distance r between polar groups by

$$x = \frac{r}{2\sin\left(\frac{\theta}{2}\right)} - 1 \quad (10)$$

where l is the length of the OH bond in water (0.96 Å) and θ is the HOH valence angle in water (104°).

The potential $U(x)$ of the hydrogen bond is defined, whatever its mathematical form, by two extreme bond distances: x_v corresponding to a Van der Waals contact, and x_g, the distance above which the bond dissociation energy becomes negligible. The equilibrium bond distance x_0 ($x_v < x_0 < x_g$) corresponds to the maximum bond strength. The values of x_v, x_g, and x_0 can be found in literature.[16] Typically, for an O—H bond, $x_v \sim 1.4$–1.5 Å and $x_g \sim (2.3 \pm 0.1)$ Å. This determines the limit values of the distance between polar groups:

$$r_v = 2(x_v + 1) \sin\left(\frac{\theta}{2}\right) \quad \text{and} \quad r_g = 2(x_g + 1) \sin\left(\frac{\theta}{2}\right) \quad (11)$$

It is possible to define an hydrophilic site as a pair of polar groups such as

$$r_v \leq r \leq r_g \quad (12)$$

where typically $r_v \sim 3.8$ Å and $r_g \sim 5.1$ Å.

Indeed, the concentration C_H of hydrophilic sites will depend on the distribution $P(r)$ of the distances
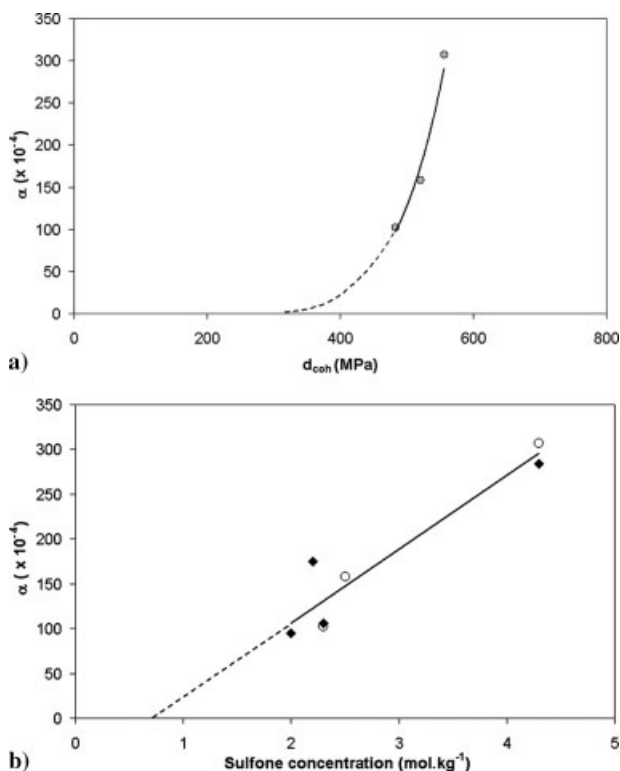
Figure 4 (a) Plot of α as a function of d_{coh} (b) Plot of α as a function of the sulfone concentration. ○: this work; ◆: Data from Schult and Paul.[11]
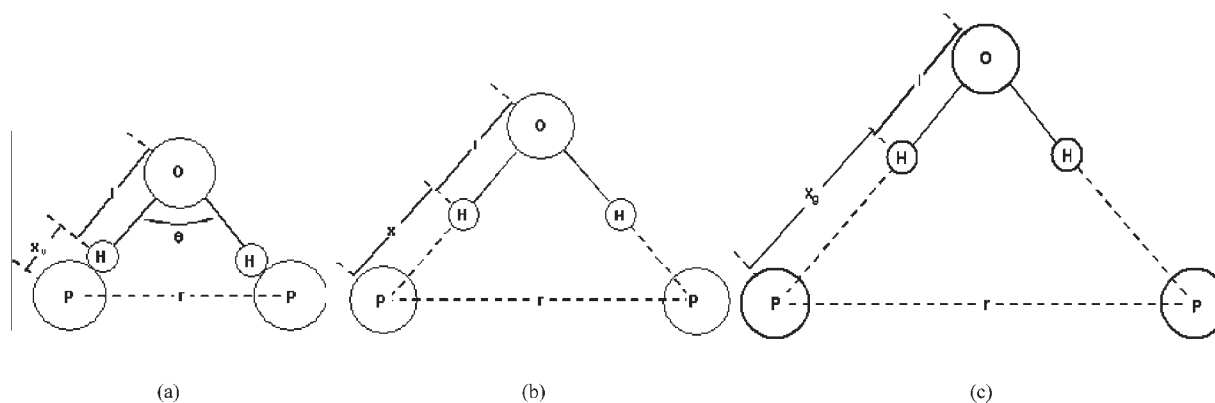
Figure 5 Three possible configurations of the system composed of one water molecule and two polymer polar sites (P) separated by a distance r.

between neighboring pairs of polar groups. It is given by

$$C_H = \int_{r_v}^{r_g} P(r)dr$$

(provided that C_H is expressed in adequate units)

(13)

The boundaries r_v and r_g have to be compared with the average distance r_0 between polar groups determined assuming a cubic array:

$$r_0 = \left(\frac{M}{\rho N_a}\right)^{1/3}$$

(14)

where M is the molar mass of the monomer unit, ρ is the specific weight and N_a the Avogadro's number. r_0 ranges from 8.4 Å (PSU) to 6.5 Å (PES). In other words, only the pairs of polar groups belonging to the lowest tail of the distribution $P(r)$ can act as hydrophilic sites. In the case under study, the "intramolecular component" of the distribution, e.g., the distance between two sulfones belonging to adjacent monomer units in the same chain, corresponds to distances of the order of 10 Å or higher so that this component is not expected to play a significant role in water absorption. It can be reasonably supposed that

each water–polymer complex contributes to the heat of solubility H_s proportionally to its bonding energy. Then, we would have:

$$H_s = K \int_{-\infty}^{+\infty} U(r)P(r)dr$$

(15)

where the constant K depends only on the chosen system of units.

Making the reasonable assumption that the curves $P(r)$ are almost parallel or at least not secant at $r < r_0$, we can schematize the situation, for the polysulfones under study, by Figure 6.

For sake of clarity, the difference between the three polymers has been exaggerated, but the figure allows to understand why $|H_s|$ increases with the sulfone concentration. This figure explains why there is a critical sulfone concentration close to 1 mol kg^{-1} [Fig. 4(b)], corresponding (in Figure 6) to the virtual PSUC (critical polysulfone), below which water absorption is practically negligible. Tetramethylhexafluoro-bisphenol polysulfone studied by Schult and Paul[11] of which the solubility is 1.8 times lower than PSU is probably close to this limit.

CONCLUSIONS

The water sorption characteristics (S and H_s) of three aromatic polysulfones differentiated by the sulfone concentration have been experimentally determined in the range 50–70°C and 0–90% RH. It appears the dependence of solubility S on the sulfone concentration or any cohesive parameter is strongly nonlinear, and the heat of water dissolution in the polymer increases with the sulfone concentration. These characteristics are not compatible with the classical idea that each polymer–water complex is formed from one water molecule linked to a single polar group. We tried to build a model in which water is doubly bonded e.g., an hydrophilic site is composed of two
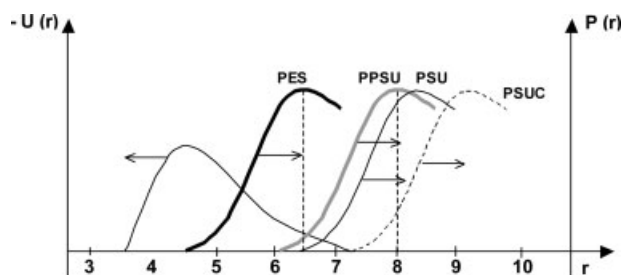

Figure 6 Presumed shape of the potential $U(r)$ and $P(r)$.

polar groups (sulfone groups in the case under study). Two elements must be taken into account: the hydrogen bond potential $U(r)$, which imposes a restricted range for the distance r between polar groups of which the distribution $P(r)$ is characterized by an average value r_0. Then the concentration of hydrophilic sites would be given by the integral $\int_{r_v}^{r_g} P(r)dr$ where r_v and r_g are respectively, the minimum and the maximum O—H distance for the hydrogen bond. The heat of dissolution of water in the polymer H_s would be given by the integral $\int_{-\infty}^{+\infty} U(r)P(r)dr$. Assuming that $P(r)$ curves are not secant in the polysulfone family under consideration, this model predicts well the trends of variation of the solubility and its activation energy H_s with the sulfone concentration.

NOMENCLATURE

S	solubility coefficient
H_s	water heat of dissolution
$P(r)$	distribution of the distances between polar groups
$U(r)$	potential of the hydrogen bond
C	water concentration in the polymer
p	water pressure
p_s	water vapour pressure at saturation
C_s	water concentration in the polymer at saturation
H_i	molar contribution of the ith group to hydrophilicity
M	molar mass
H	molar additive function to hydrophilicity
p_0	pre-exponential coefficient of p
H_w	water heat of vaporization
R	gas constant
T	temperature
S_0	pre-exponential coefficient of S
s	polar group concentration
S_{m0}	pre-exponential coefficient referred to low polarity matrix
S_{p0}	pre-exponential coefficient referred to polar groups
H_m	water heat of dissolution in the matrix
H_p	water heat of sorption on polar groups
RH	Relative humidity
α	initial slope of the water sorption isotherm
d_{coh}	cohesive energy density
ρ	density
E_{coh}	molar cohesive energy
M	molar mass
δ	solubility parameter
χ	water-polymer interaction parameter
V_w	water molar volume
δ_{coh}	molar solubility parameter of studied polymer
δ_w	molar solubility parameter of water

a	water activity
v	water volume fraction in the polymer
$[sulf]_c$	critical sulfone concentration
$d_{coh\ c}$	critical cohesive energy density
k	constant
s	polar group concentration
S_{m0}	pre-exponential coefficient refered to low polarity matrix
S_{p0}	pre-exponential coefficient refered to polar groups
H_m	water heat of dissolution in the matrix
H_p	water heat of sorption on polar groupsθ: valence angle of HOH
x	hydrogen bond length
r	distance between two polar groups
l	length of the O—H bond in water
x_v	minimum bond distance
x_0	equilibrium bond distance
x_g	maximum bond distance
r_v	distance between polar groups when x = x_v
r_g	distance between polar groups when x = x_g
r_0	average distance between sulfone groups
r_c	minimum distance between sulfone groups
M	Molar mass of the monomer unit
N_a	Avogadro's number
K	constant

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