

Correlation of Accessible Volume With Selectivity in Polyimides Having Voluminous Bridge in Diamine Component

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ABSTRACT

A number of 22 polyheteroarylenes including 18 polyimides, divided in five series, were studied with regard to the dependence of permeability, diffusion and solubility coefficients of gases on the reverse value of fractional accessible volume. It was shown that all these dependences are linear in semilogarithmic coordinates. Thus, the overall selectivity, which is determined by the slope of these dependences, is correlated with the free volume in each series of polymers. The introduction of volumetric bridging groups into the diamine component with the possibility of rotation around bonds with the polymer backbone near the bridge leads to an increase in the overall selectivity of permeability, diffusion and solubility of the polymer at sufficiently high values of the permeability, diffusion and solubility coefficients.

Keywords - Conformational parameters; polyimides; substituents; physical properties

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I. INTRODUCTION

The gas separation through membranes represents one of the most investigated domain inside membrane technology. Usually, the selective layers of gas separation membranes are prepared from glassy amorphous polymers. Thus, the correlation of the chemical structure of the repeating unit of polymers with their transport characteristics represents a traditional subject of study in the domain of membrane materials [1–3]. A very prospective class of polymers for gas separation membranes is represented by polyimides due to their high thermal and chemical stabilities together with high selectivity of gas separation [4–6]. At the same time, for a successful use of polymers for gas separation membranes, a high selectivity and a high permeability are required, which means that the diagram permeability-selectivity should be positioned above the Robeson „upper bound” [7–8]. For many gas pairs, such a permeability-selectivity diagram positioned above Robeson upper bound is exhibited by fluorine-containing polyimides. Thus, in recent years a series of fluorine-containing polyimides with voluminous substituents in the diamine fragment were synthesized and investigated [9–13], as well as other polycondensation polymers [13] which show high permeability and high selectivity for the pair of gases CO₂/CH₄ and O₂/N₂, and are situated above the Robeson line in the corresponding diagram. This characteristic is determined by the geometry of the polymeric chains

which influences their packing in polymer matrix. In our previous publications [14–17] we used certain calculation methods to explain the correlation between the geometry of the repeating unit of polymers and of that part of free volume which is accessible for gas molecules with permeability and diffusion coefficients of gases. The gas separation characteristics of polymers depend on the packing of polymeric chains into polymer matrix, that is on free volume (V_{fr}). Thus, it is considered that permeability (P) and diffusion (D) coefficients of polymers are linearly correlated with the free volume in semilogarithmic coordinates [1–3], which means that for a system one gas-different polymers at isothermic conditions we have the following equations, (1) and (2):

$$\ln P = a_p - b_p/V_{fr} \quad (1)$$

$$\ln D = a_D - b_D/V_{fr} \quad (2)$$

where a_p and b_p are inclination and slope for coefficient of permeability, and a_D and b_D are also for coefficient diffusion

The value of V_{fr} for polymers depends on the method of calculation.

In our previous works we have used analog dependences for the system one polymer-different gases, according to equations (3) and (4) and we calculated the volum of polymer which is accessible for molecules of gas of different dimensions and forms V_{acs} and the specific accessible volume FAV [17, 18]:

$$\ln P = A_p - B_p/FAV \quad (3)$$

$$\ln D = A_D - B_D/FAV \quad (4)$$

where A_P and B_P are inclination and slope for coefficient of permeability, and A_D and B_D are also for coefficient diffusion.

II. CALCULATION METHODS

To study the system one polymer – different gases, it is necessary to calculate the Van der Waals volume (V_w), free volume (V_{fr}) and the volume around the repeating unit which is not accessible to a certain gas due to its dimensions, the so-called „dead volume” (V_{dead}), and the volume which is accessible for a given gas (V_{acs}). Further, we construct the model of the repeating unit in which each atom is represented by a sphere having the corresponding radius of this type of atom. In this case, spheres with radii equal to the radii of the gas molecule are rolling up the monomer unit. By using the method described earlier [18], we calculate the Van der Waals and the dead volume. But, the gas molecules of CO_2 , N_2 and O_2 are represented by ellipsoids having two rotation axes, R_{min} and R_{max} . This is why for these molecules of gases we calculate two dead volumes: one for the maximum radius and the other for the minimum radius.

The occupied volume, V_{occ} , which is not accessible for gas molecules, is determined by the sum of Van der Waals volume and dead volume, according to equation (5):

$$V_{occ} = (V_w + V_{dead}) \quad (5)$$

The free volume is determined by the difference between the specific volume of polymer and the Van der Waals volume of the repeating unit, according to equation (6):

$$V_{fr} = \frac{1}{\rho} - \frac{N_A \cdot V_w}{M_o} \quad (6)$$

where ρ is the density of polymer, $N_A = 6.02 \cdot 10^{23}$ is the number of Avogadro, and M_o is the molecular weight of the repeating unit.

The volume which is accessible V_{acs} for gas molecules is determined by the difference between the specific volume of polymer and the occupied volume, according to equation (7):

$$V_{acs} = \frac{1}{\rho} - \frac{N_A \cdot V_{occ}}{M_o} \quad (7)$$

Usually, we used the specific accessible volume FAV , without any dimensions [17, 18], given by equation (8).

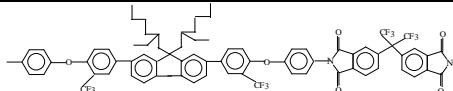
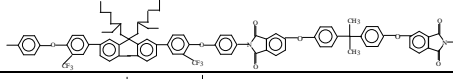
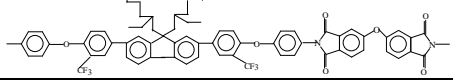
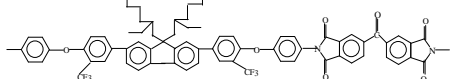
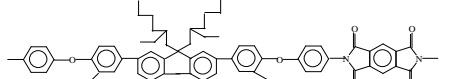
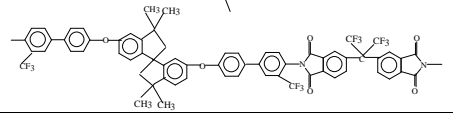
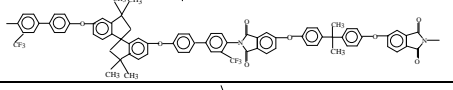
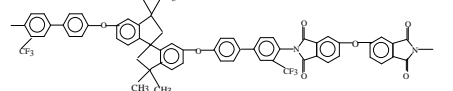
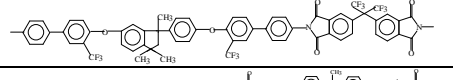
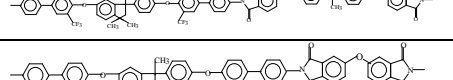
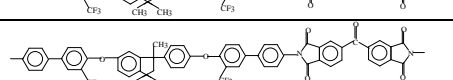
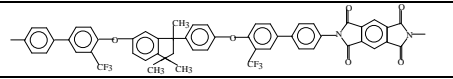
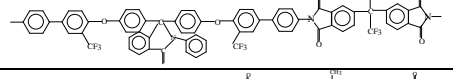
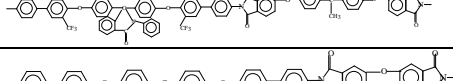
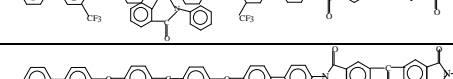
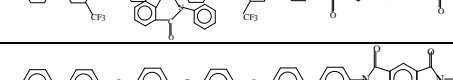
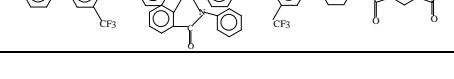

$$FAV = V_{acs} \cdot \rho \quad (8)$$

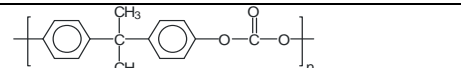

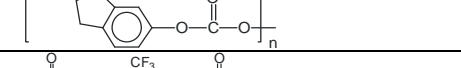
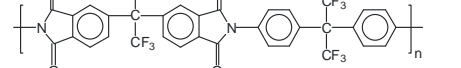
III. RESULTS AND DISCUSSION

The calculation of FAV according to the equation (8) given above can be performed only in the case when we know the density of polymers; therefore to make the correlation with transport parameters we selected a series of polyimides

containing voluminous bridging groups reported in publications [9-12] (Table 1). These polyimides were divided into five series: the first series contains polymers **1**, **2**, **3**, **4** and **5**; the second series contains polymers **1a**, **2a** and **3a**; the third series contains polymers **1b**, **2b**, **3b**, **4b** and **5b**; the fourth series contains polymers **1c**, **2c**, **3c**, **4c** and **5c**; Besides, we examined the fifth series which contains four polymers of different structures **1d**, **2d**, **3d** and **4d** for comparison of their membrane characteristics with those of the selected polyimides. Thus, we have examined certain polyheteroarylenes such as polycarbonate **1d** [19], polycarbonate containing voluminous groups in the main chain **2d** [20], polyimide **3d** [21] and polybenzoxazol **4d** [22] having two hexafluoroisopropylidene bridges in the repeating unit of the main chain.

Table 1. Repeating unit, glass transition temperature, density, Van der Waals volume and free volume of selected polyheteroarylenes.

Poly-mer	Repeating unit	T _g (°C)	ρ (g/cm ³)	V _w (Å ³)	V _{fr} (cm ³ /g)	V _w (Å ³)	Reference
1		248	1.21	1140.416	0.2988	441.116	[9]
2		183	1.16	1276.936	0.3039		[9]
3		171	1.22	1068.286	0.2686		[9]
4		195	1.23	1078.188	0.2625		[9]
5		214	1.26	982.860	0.2432		[9]
1a		269	1.28	1006.468	0.2831	296.406	[10]
2a		232	1.34	1142.989	0.2015		[10]
3a		253	1.39	934.339	0.1852		[10]
1b		262	1.17	963.473	0.3489	255.588	[11]
2b		241	1.12	1099.993	0.3515		[11]
3b		249	1.14	891.343	0.3474		[11]
4b		252	1.15	901.240	0.3401		[11]
5b		265	1.27	805.917	0.2604		[11]
1c		292	1.25	1058.135	0.2991	362.773	[12]
2c		243	1.29	1194.655	0.2417		[12]
3c		276	1.319	986.005	0.2396		[12]
4c		280	1.332	995.907	0.2275		[12]
5c		327	1.323	900.579	0.2457		[12]

1d		150	1.2	246.356	0.2812	[19]
2d		227	1.395	229.838	0.2196	[20]
3d		305	1.48	553.663	0.2264	[21]
4d		290	1.461	522.791	0.2201	[22]

T_g = glass transition temperature; ρ = density; V_{fr} = free volume; V_w = Van der Waals volume

Such polymers were selected due to the reported data on permeability and diffusion coefficients for various gases and due to the similarity of the voluminous fragment in polycarbonate **2d** with the fragments of polymers in the first series, as well as due to the presence of four CF_3 - bridges in the repeating unit of polymers **3d** and **4d** analog to the polymers **1**, **1a**, **1b** and **1c**.

For each polymer we built the models of the repeating unit and we calculated the Van der Waals volume (V_w) and the free volume (V_f). All these data and the values of glass transition temperatures are shown in Table 1.

It is known that with the increase of free volume, the glass transition temperature decreases

because the probability of conformational transitions is higher [23]. The dependence of glass transition temperature on free volume is represented in Figure 1. In all three dependences the point corresponding to the first polymer in that series goes out of the overall dependence. This is due to the presence of those 12 fluorine atoms in the repeating unit; the repulsion between these fluorine atoms leads to the increase of free volume. The points corresponding to the polymer **2** from the first series and to the polymer **5** from the fourth series do not fall on the overall dependence, probably due to incomplete removal of the solvent [24].

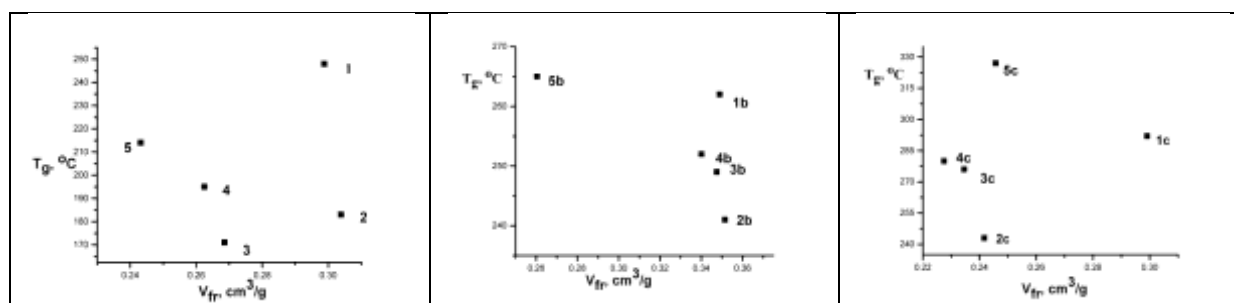


Figure 1. The dependence of glass transition temperature (T_g) on the free volume (V_f) for polymers of the series 1, 3 and 4.

For four gases, CO_2 , O_2 , N_2 and CH_4 , we calculated the values of the occupied volume (V_{occ}), the accessible volume (V_{acs}) and the specific accessible volume **FAV**. Then we built the dependence of permeability and diffusion coefficients on the reverse value of **FAV** according to the equations 3 and 4. The results of these calculations are shown in Table 2. In Figures 2a and 2b we built these dependences for the first polymer of the first group.

Now we examine the correlation $P(1/FAV)$ according to the equation 3. As it was shown in our previous publications [14–17], for all gases except

Table 2. The parameters of equation $y=A+Bx$ for the permeability and diffusion solubility coefficients.

Polymer	P			D			S		
	A	-B	R%	A	-B	R%	-A	B	R%
1	44.13	12.71	95.38	26.61	7.48	99.98	24.97	7.06	97.37
2	44.73	12.59	96.14	24.76	6.82	89.78	25.40	7.00	97.42
3	36.59	9.24	96.92	19.89	4.89	93.22	21.14	5.19	97.24
4	36.60	9.09	96.30	18.54	4.48	95.08	20.89	5.03	93.76
5	26.72	6.21	88.50	19.31	4.36	96.88	17.21	3.84	95.45
1a	26.71	7.45	95.39	17.93	4.87	87.02	27.14	9.02	92.90
2a	22.76	4.36	93.53	12.67	2.34	86.10	14.88	2.74	99.89
3a	16.64	2.89	88.18	10.83	1.79	86.31	12.58	2.08	95.24
1b	57.84	20.05	98.48	42.63	14.43	95.57	29.15	10.04	90.65
2b	55.69	18.56	98.54	38.10	12.55	93.29	26.52	8.77	88.78
3b	55.95	18.92	98.84	38.41	12.77	97.01	27.14	9.02	92.97
4b	56.92	18.91	98.56	37.14	12.22	97.14	27.00	8.88	96.16
5b	36.45	9.66	99.63	27.45	7.17	94.01	19.08	5.02	90.11
1c	74.26	23.64	99.99	70.22	22.38	99.97	21.71	6.04	94.81
2c	45.20	11.44	99.89	53.97	13.65	98.32	14.39	3.62	97.02
3c	42.28	10.67	99.57	47.03	11.84	99.99	17.76	4.41	72.86
4c	45.95	11.32	99.67	42.93	10.53	99.80	24.18	5.83	82.36
5c	59.22	16.08	99.88	49.49	13.40	99.52	33.64	9.01	80.40
1d	29.81	8.64	83.20	37.38	10.68	98.48	16.38	4.88	92.49
2d	18.35	4.39	93.92	25.38	6.15	96.20	10.34	2.80	96.70
3d	34.65	9.36	92.90	35.61	9.66	97.20	10.19	3.13	90.13
4d	26.10	6.62	91.98	36.74	9.44	98.30	13.96	3.94	94.14

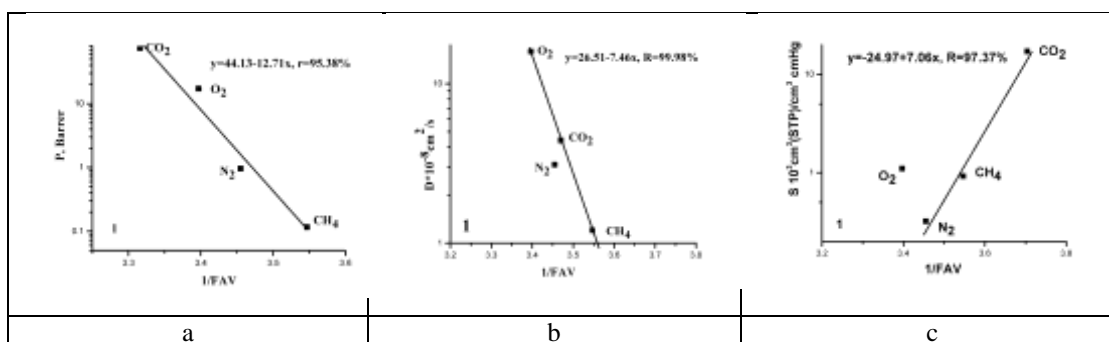


Figure 2. The dependence of permeability (a), diffusion (b) and solubility (c) coefficients on the specific accessible volume (FAV) for the polymer 1 of the series 1

for CO₂, the accessible volume for the permeability coefficient is calculated by taking into consideration the dead volume for the maximum axis. On the dependence $P(1/FAV)$ the point corresponding to CO₂ is situated on the overall line when the accessible volume is calculated by taking into consideration the dead volume with the minimum radius of gas molecule. As seen in Table 2, all the dependences $P(1/FAV)$ calculated according to equation 3 have high correlation coefficients.

The B_p value represents the overall selectivity of gas separation of polymer. The increase of the slope of $P(1/FAV)$ dependence and of the B_p value indicate the increase of the selectivity of this polymer.

As seen in Table 2, the highest overall selectivity in each series of polymers corresponds to

the first polymer – which contains a hexafluoroisopropylidene bridge in the dianhydride fragment. The free volume (Table 1) corresponding to the first polymer in each series is maximum, in the limits of the accuracy of density measurement. This is explained by the presence of those 12 fluorine atoms in the repeating unit of these polymers that leads to the increase of free volume due to the repulsion between these negative atoms of different chains and as a consequence to the loosening of the packing in glassy state [25]. The polymer 5 from the first and the third series, containing the pyromellitimide fragment, being the most rigid of all these polymers, shows the lowest overall selectivity. An exception is made by polymer 5 in the fourth series. The overall selectivity of polymers 3 and 4 in all series is practically identical.

The selectivity of polymers **3d** and **4d** having 6 fluorine atoms in the repeating unit is also high, although substantially lower than that of analog polymers reported in publications [9-12].

The overall selectivity B_p depends on the free volume inside of each series of polymers. The dependence of overall selectivity on the free volume for all four series of polymers is shown in Figure 3. Each of them is well described by the line $B_p = E + F/V_{fr}$. As seen in Figure 3, the most visible dependence on free volume is shown by polymers belonging to the fourth series. In this series the value of the slope of the line to the axis of abscissa, F , is maximal. The bridging groups in the diamine component of all four series of polymers can be described in the following way: in the first and the second series the bridges are totally rigid, in the third series the bridge is semirigid (the rotation is possible around one bond phenyl – carbon), and finally in the

fourth series the rotation is possible around both bonds phenyl – carbon.

Table 3 presents the fragments of diamine component, rotation conditions around the bridge in these fragments, the value of slope F and the Van der Waals volume of fragments of diamine components of all four series. On one hand, the rotation conditions around the bridge in the main chain of polymer show the possibility of conformational transitions in polymer matrix during passing of gas molecules through membrane. On another hand, the increase of the volume of bridging group leads to the increase of the free volume of polymer matrix. This can be seen in the case of the first polymer in the first series: the value of F is high enough and the coefficient of permeability for CO_2 is 73.91 Barrer [12]. The polymers of the fourth series have the highest value of F , the Van der Waals volume of the bridge is the second regarding the

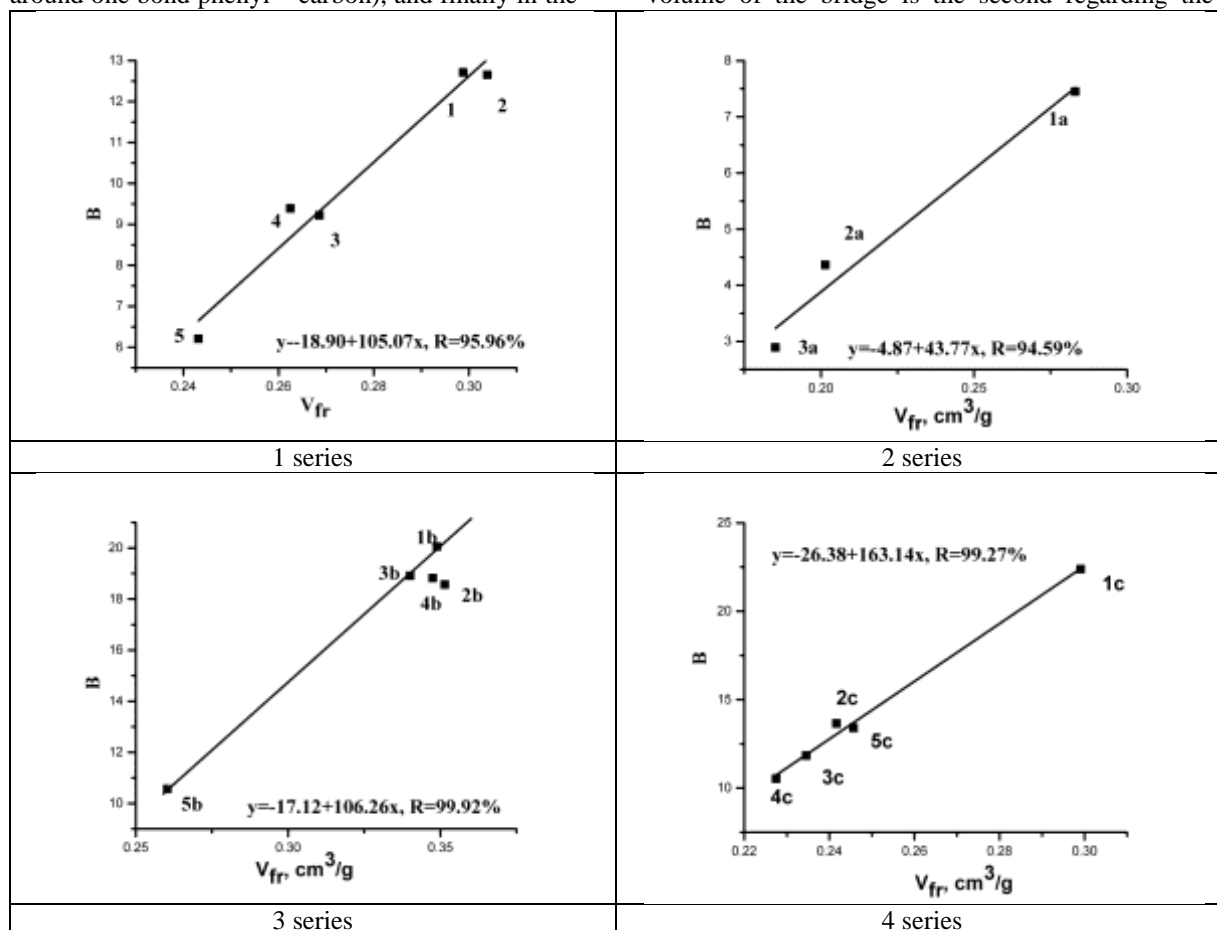

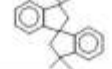




Figure 3. The dependence of overall selectivity of permeability B on the free volume.

Table 3. The characteristics of voluminous bridges.

Series	Voluminous bridge	Rotation conditions	F	V _v (Å ³)
1		Hindered	105.07	441.116
2		Hindered	43.77	296.406
3		Possible around one bond	106.21	255.588
4		Possible around both bonds	163.14	362.773

value, and the highest overall selectivity is shown by the first polymer in this series. But the coefficient of permeability for CO₂ is not too high, being only 17.04 Barrer [12].

Thus, the introduction of bridging groups in the diamine component having the possibility of rotation around the bonds of the main chain which are close to these bridges leads to the increase of the overall selectivity of permeability of the polymer at a high enough permeability.

Now we examine the correlation D(1/FAV) according to equation 4.

As we have shown in previous publications [14–17] for all gases, except CO₂, the accessible volume for diffusion coefficient is calculated taking into account the dead volume for the maximum radius. The accessible volume for CO₂ is calculated with formula 0.4 R_{max} + 0.6 R_{min}. Only in this case the point of CO₂ is on the overall direct line. This can also be seen for other polymers [25, 26]. As can be seen in Table 2, the dependences D(1/FAV) calculated with equation 4 have a high correlation coefficient.

The coefficient B_D in this case represents also the overall selectivity of diffusion. In all four series, the first polymers having 12 fluorine atoms in the main chain show the highest overall selectivity. But the highest selectivity of diffusion, as in the case of permeability coefficients, is shown by the first polymer of the fourth series.

The overall selectivity of permeability coefficients in most cases is higher than the overall selectivity of

diffusion coefficients (Table 2). This can be easily seen when we compare the selectivity of the first polymers in all four series. A similar behavior was observed for other polymers, as well [27].

At low pressure of gases the permeability and diffusion coefficients are correlated by equation 9:

$$P = D \cdot S \quad (9)$$

where S is the solubility coefficient.

All these polymers show linear correlations, with high accuracy, in equations 3 and 4. Therefore, according to equations 3, 4 and 9, it can be concluded that solubility coefficients should linearly depend on the specific accessible volume, as shown in equation 10:

$$\ln S = A_S + B_S/FAV \quad (10)$$

where A_S and B_S are the inclination and overall selectivity of solubility.

Figure 2c presents the dependence of solubility coefficients on the specific accessible volume according to equation 10. Here we can see the increase of solubility with the increase of 1/FAV, which means that the solubility increases with the decrease of specific accessible volume. In all these diagrams showing the dependence S(1/FAV), the points corresponding to oxygen go out of the overall dependence. Here, the behavior of CO₂ is unusual: the point corresponding to the solubility coefficient of this gas is situated on the overall dependence if the calculation of accessible volume takes into consideration the dead volume calculated for the maximum radius of the gas molecule.

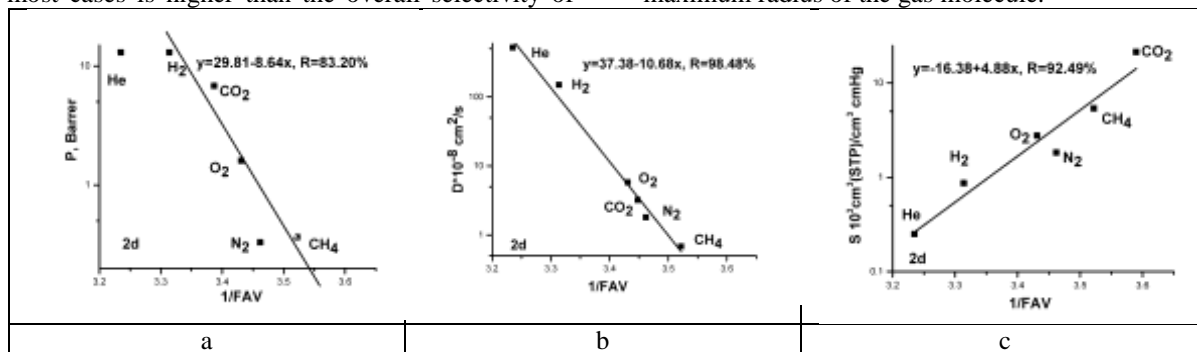


Figure 4. The dependence of permeability (a), diffusion (b) and solubility (c) coefficients on the specific accessible volume (FAV) for the polymer 2d. from the fifth series d.

In order to prove this effect for other polymers, we examined four polymers of different structures which make the fifth series (d) (Tables 1 and 2). For these polymers, are published not only the permeability and diffusion coefficients, and therefore the solubility coefficients for CO₂, O₂, N₂, CH₄, but also for helium and hydrogen. Figure 4 presents these dependences according to equations 3, 4 and 10 for the polymer **2d**. As seen in Figure 4 and Table 2, all these dependences have a high accuracy.

There are articles which report the dependence of solubility coefficients of gases on the accessible contact surface of gas molecule and on the surface of the repeating unit of the polymer [28, 29], based on the Van der Waals interactions. Here it is considered that higher the surface of the gas molecule, higher the solubility and therefore the solubility coefficient. Indeed, the surface of CO₂ molecule is substantially higher than that of methane, for example, and as a consequence the solubility coefficient is higher [28, 29]. This is why the use of the maximum radius of CO₂ for the calculation of FAV in correlation with the solubility coefficient is totally logic.

The correlations according to equations 1 – 4 have been intensively discussed [1–3, 14–17, 24–27], but the linear aspect of the dependence of solubility coefficients on the specific accessible volume has not been investigated. However, the increase of solubility coefficients with the increase of free volume, or the dimensions of elements of free volume have been studied in the literature [1–3, 28, 30–33]. Usually, the dimensions of the elements of free volume were studied in correlation with the value of Langmuir sorption capacity according to the double-sorption model [1–3, 30–33], and then the correlations one gas – different polymers were discussed. For the case one polymer – different gases, a linear dependence of the dependence of solubility coefficients on the accessible volume was found.

IV. Conclusions

It was shown that the study of the system one – polymer different gases allows to differentiate the polymers in function of the overall selectivity of permeability, diffusion and solubility. The overall selectivity depends on the free volume of the polymer. Detailed analysis of the overall selectivity of the polymers showed that the van der Waals volume of the bridge in the diamine component of the polyimide monomer unit along with the conditions of the rotation around the bridge bonds with the main chain, has a great influence on the characteristics of the transport polymer. The bridging group in the dianhydride component is also of great importance.

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