

tures of xenon and krypton, and the separation of pure xenon for the purpose of its purification. In the latter case, as membranes of PVMTS possess an "inverse" selectivity with respect to xenon and krypton ($\alpha_{Xe/Kr}$ of Silar = 1.7, and $\alpha_{Xe/Kr}$ of PVMTS = 0.45), they are placed advantageously in modules, including membranes of different types of selectivity, for example, in combination with Silar membranes. It is obvious that such modules will be characterized with significantly higher separation parameters than the normal membranes [11].

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MEMBRANE METHODS OF SEPARATION OF THE RADIOACTIVE NOBLE GASES.

II. INVESTIGATION OF DIFFUSION AND PERMEABILITY OF INERT GASES AND AIR COMPONENTS THROUGH FILMS BASED ON POLYDIMETHYLSILOXANE

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The transport characteristics of the inert gases, N_2 , O_2 , CH_4 , CO_2 , and H_2 as the main components of gaseous discharges have been measured by the differential permeability method at various temperatures, in homogeneous films of arylate-siloxane block copolymer (Silar) of various composition and also in its components viz. polydimethylsiloxane (PDMS) and polyarylate. The dependence of the diffusion and permeability coefficients on the inert gas atomic dimensions, and of the solubility coefficients on the force constants for the Lennard-Jones potential, were analyzed. It was shown that the selectivity of gas permeability of Silar was determined by the properties of the siloxane component and the sizes of the permeability coefficients were reduced with an increase in the proportion of polyarylate block due to the predominant reduction in diffusion coefficients in comparison with the solubility coefficients.

Preliminary investigations on the influence of irradiation on the permeability and selectivity of polymeric asymmetric membranes in relation to components of gaseous discharges [1] showed that membranes of Silar material superseded membranes of silicone rubber in their radiation stability. Silicone rubber membranes are acknowledged to be the best polymeric material for the purification of gaseous discharges of radioactive noble gases (RNG) [2]. It therefore seemed necessary to study in more detail the transport characteristics of this

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material and to determine the coefficients of diffusion, permeability, and solubility of the used gases, the temperature dependence of these coefficients, and to know their energies of activation. These data are necessary for selecting optimum conditions for the gas separation process and may serve as a basis for the modification of this polymer as applied to the problem set, viz. the isolation of RNG from gas-air discharges.

The aim of the present work was the measurement at various temperatures of the coefficients of permeability, diffusion, and indirectly of the solubility of the inert gases, oxygen, methane, carbon dioxide, and hydrogen as the main components of gaseous discharges, in the polymeric material Silar which is an arylate-dimethylsiloxane block copolymer [1]. Since it was evident that the indicated parameters of gas transfer must depend on the reciprocal content of the arylate and siloxane components it was expedient to use Silar of varied composition.

EXPERIMENTAL

The subjects of investigation were homogeneous films obtained by casting on cellophane from 3% solutions of Silar in methylene chloride, of thickness 956 and 1274 μm . Silar of two compositions was used in the work, 46/54 (weight ratio of polyarylate to polydimethylsiloxane) which corresponded to $N_{\text{Ar}}/N_{\text{Si}} = 10:70$ (N_{Ar} and N_{Si} respectively are the numbers of arylate and dimethylsiloxane units) and also 38/62 at $N_{\text{Ar}}:N_{\text{Si}} = 10:100$.

In order to characterize Silar as a gas-partitioning material more completely the transport characteristics of the components of this polymer, polydimethylsiloxane (PDMS) and polyarylate, were also studied. Films of PDMS manufactured by Rhone-Poulenc were used and had thickness 1010 μm . Films of polyarylate of thickness 77 μm were cast onto cellophane from a 5% solution of polyarylate in carbon tetrachloride.

Measurements of permeability and diffusion coefficients in the temperature range 20-120°C were carried out by the differential permeability method of [3] in which the dependence of time of gas flow rate through a membrane separating the reservoir and receiver was measured using detectors of the chromatographic type. The main characteristics of the equipment were given previously in [1].

On processing the kinetic curves obtained by this method to obtain reliable results it was important to consider such factors as the inertial of the apparatus and to observe conditions for the absence of dead zones. For this purpose the function of the apparatus response was determined at carrier gas flow rates in the receiver in the range from 0.1 to 1.4 cm^3/sec at a constant carrier gas flow rate in the reservoir of 0.6 cm^3/sec . For this air was introduced into the reservoir by the impulse method using a thin macroporous membrane in the cell. After recording the signal of the katharometer in the receiver with a recorder, the width δ of the obtained peak at half height was calculated. The smooth reduction of δ with increasing v showed that dead zones were absent from the cell and from the gas lines. In accordance with the obtained results the operating conditions were selected such that $\delta \ll \theta$ for a valid analysis of the kinetic curves (θ is the time lag [4]).

The permeability coefficients P of gases were calculated from the formula

$$P = \frac{C_i \cdot V \cdot H}{100 \cdot S \cdot \Delta p} \cdot \frac{\text{mole} \cdot \text{m}}{\text{m}^2 \cdot \text{sec} \cdot \text{Pa}}, \quad (1)$$

where C_i is the stationary concentration of the gas permeating the membrane (the penetrant) into the receiver, vol. %; V the carrier gas flow rate into the receiver, mole/sec; H the membrane thickness, m; S the membrane area, m^2 ; Δp the partial pressure of the penetrant in the reservoir, Pa.

From the ratio of the permeability coefficients a selectivity factor α_{ij} was calculated for the various pairs of gases.

$$\alpha_{ij} = \frac{P_i}{P_j}. \quad (2)$$

An analysis of the various means of calculating diffusion coefficients from a kinetic curve in a differential variant of the permeability method was given in [4]. Recently an original procedure for processing was proposed (the method of an infinite number of separate points or the linearization method) in [5] eliminating several of the inadequacies of the known methods. The method in question made it possible to use the whole shape of the dif-

TABLE 1. Parameters of Gas Permeability of PDMS at 25°C

Gas	$D \cdot 10^{11}$, m ² /sec	E_D , kJ/mole	$P \cdot 10^{14}$, mole · m/ m ² · sec · Pa	E_p , kJ/mole	$K_p \cdot 10^5$, mole/m ³ · Pa	ΔH_{K_p} , kJ/mole	$\alpha_{N_2} = \frac{P_i}{P_{N_2}}$
He	370	45	9.1	91	2.4	-45	1.2
Ar	108	69	15.8	38	14.4	-31	2.0
Kr	70	79	29.2	29	41.7	-50	3.8
Xe	45	88	50.4	24	111.9	-64	6.5
H ₂	330	57	16.8	79	5.0	+19	2.2
O ₂	115	64	16.1	55	14.1	-10	2.1
N ₂	94	59	7.7	67	8.4	+7	1.0
CO ₂	85	55	67.2	-19	79.0	-74	8.7
CH ₄	77	81	22.8	38	29.6	-43	3.0

TABLE 2. Parameters of Gas Permeability of Silar 38/62 at 25°C

Gas	$D \cdot 10^{11}$, m ² /sec	E_D , kJ/mole	$P \cdot 10^{14}$, mole · m/ m ² · sec · Pa	E_p , kJ/mole	$K_p \cdot 10^5$, mole/m ³ · Pa	ΔH_{K_p} , kJ/mole	$\alpha_{N_2} = \frac{P_i}{P_{N_2}}$
He	350	48	7.4	69	2.0	+22	1.3
Ar	83	69	12.8	29	15.4	-41	2.2
Kr	59	79	22.2	14	37.6	-65	3.9
Xe	33	93	36.3	-4.8	109.9	-98	6.4
H ₂	240	55	13.1	60	5.4	+7.2	2.3
O ₂	90	72	12.1	31	13.4	-41	2.1
N ₂	76	74	5.7	50	7.4	-24	1.0
CO ₂	48	67	60.5	-24	126.0	-91	10.6
CH ₄	58	79	16.5	29	28.6	-50	2.9

TABLE 3. Parameters of Gas Permeability of Silar 46/54 at 25°C

Gas	$D \cdot 10^{11}$, m ² /sec	E_D , kJ/mole	$P \cdot 10^{14}$, mole · m/ m ² · sec · Pa	E_p , kJ/mole	$K_p \cdot 10^5$, mole/m ³ · Pa	ΔH_{K_p} , kJ/mole	$\alpha_{N_2} = \frac{P_i}{P_{N_2}}$
He	240	48	4.7	74	2.0	+26	1.6
Ar	54	69	5.7	50	10.3	-19	1.9
Kr	36	91	10.1	36	27.9	-55	3.3
Xe	20	120	16.8	24	82.0	-96	5.7
H ₂	170	79	7.4	69	4.4	+14	2.4
O ₂	66	74	6.0	50	9.1	-24	2.0
N ₂	50	76	3.0	74	6.0	-2.4	1.0
CO ₂	44	57	29.6	-24	67.2	-81	9.8
CH ₄	39	86	7.7	38	19.8	-48	2.5

ferential curve to carry out analysis of it and to determine the extent of the deviation of the experimental curve from the theoretical model. This method was used previously using large computers, numerical tables, or special scale coordinate paper. In the present work a program has been developed and set down which effects this method on a minicomputer of type 15-VSM-5 and DZ-28. The program provides calculation of parameters D, their errors, and calculation of correlation coefficients, from which it is possible to form an opinion on the adequacy of the description of the diffusion process within the framework of the classical model and the determination of the confidence interval of the curve. An important special feature of the program is the possibility of carrying out an analysis of the kinetic curve from fragments of it which is particularly attractive for the diffusion of gases in complex media. All the experimental curves of permeability were processed with the aid of this program.

The solubility coefficient of a gas in a polymer K_p was calculated from the determined coefficients of permeability P and diffusion D.

$$K_p = \frac{P}{D}, \text{ mole/m}^3 \cdot \text{Pa}. \quad (3)$$

The values of P, D, and K_p obtained at various temperatures may be described by the Arrhenius equations for all the gases and investigated polymers.

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) = P_0 \exp\left[-\frac{(E_D + \Delta H_{K_p})}{RT}\right], \quad (4)$$

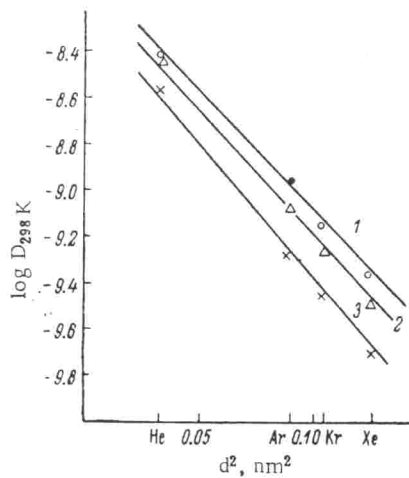


Fig. 1

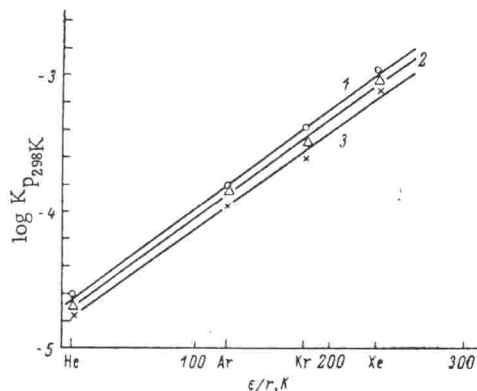


Fig. 2

Fig. 1. Relationship of diffusion constants of inert gases to their atomic sizes. 1) PDMS; 2) Silar 38/62; 3) Silar 46/54.

Fig. 2. Relationship of solubility constants of inert gases to the force constant for the Lennard-Jones potential. 1) PDMS; 2) Silar 38/62; 3) Silar 46/54.

TABLE 4. Parameters of Gas Permeability of Polyarylate at 25°C

Parameter	$D \cdot 10^{11}$, m^2/sec	$P \cdot 10^{14}$, mole· $m/m^2 \cdot sec \cdot Pa$
He	29.0	0.6
Ar	0.23	0.02
Xe	0.11	—

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right), \quad (5)$$

$$K_p = K_{p_0} \exp\left(-\frac{\Delta H_{K_p}}{RT}\right), \quad (6)$$

where E_p is the permeability energy of activation, kJ/mole; E_D the diffusion energy of activation, kJ/mole; ΔH_{K_p} the heat of solubility, kJ/mole. This made it possible to determine the energy parameters of the process of gas transfer through the polymeric films.

RESULTS AND DISCUSSION

Characteristics of the gas permeability of Silar and PDMS for each investigated gas are given in Tables 1-3. In addition, values are shown in Table 4 for the coefficients of permeability and diffusion for certain inert gases in polyarylate. Values of selectivity factors are also given in Tables 1-3 in relation to nitrogen (α_{N_2}) as the main component of air.

As is seen from Tables 1-3 the permeability of Silar for each gas was reduced with the increase in content of polyarylate block in relation to pure PDMS. The sizes of P and D of gases for polyarylate were appreciably less than those for PDMS (Table 4) so that this component may be considered as a filler of the polymeric system. It is evident from Tables 1-3 that the solubility coefficient of gases K_p in the investigated systems was practically the same as for pure PDMS but the diffusion coefficient of gases D was reduced with an increase in the fraction of polyarylate.

The observed effects are conveniently illustrated by the example of the inert gases. Thus in Fig. 1 the relationship of $\log D$ for gases in PDMS and Silar to the square of their atomic diameters is represented [6]. It is evident that the reduction in the size of D for

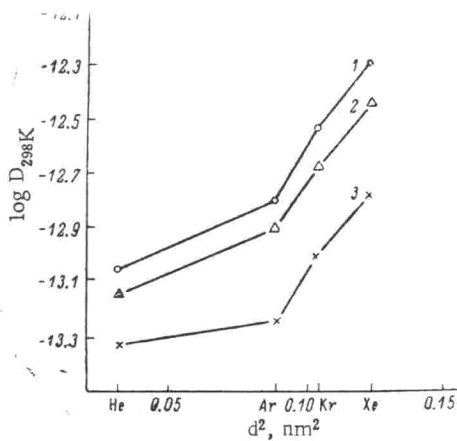


Fig. 3. Relationship of permeability coefficients of the inert gases to their atomic dimensions. 1) PDMS; 2) Silar 38/62; 3) Silar 46/54.

the gases in Silar is not accompanied by a significant change in the selectivity of diffusion, i.e., the slope of the relationship in coordinates $\log D$ vs. d^2 was practically unchanged. On the other hand, the solubility of the inert gases in the investigated polymers increased with atomic size since the boiling points of the gases and the size of the force constant for the Lennard-Jones potential [7], which determine the inclination of the gas molecules towards condensation, increased in the same order. The relationship of the logarithm of solubility coefficient on the force constant for the Lennard-Jones potential ϵ/R , K for PDMS and Silar of both compositions are shown in Fig. 2. As is evident the solubility of the gases is reduced insignificantly with the increase in polyarylate fraction but the selectivity of the solubility [slope of the $\log K_p \sim f(\epsilon/R, K)$] was practically constant.

Superposition of the relationships of Figs. 1 and 2, allowing for $P = K_p \cdot D$, also leads to the unusual, at first sight, growth in the permeability of the inert gases with the increase in their atomic dimensions in polymers based on polydimethylsiloxane (Fig. 3).

Thus the selectivity of gas permeability for Silar of different compositions is determined by the properties of the siloxane component (Tables 1-3), but the sizes of the gas permeability coefficients in comparison with pure PDMS was reduced 2-3 fold with an increase in the fraction of polyarylate block to 46 portions by weight. On the other hand the film-forming properties of Silar make it possible to obtain asymmetric membranes with an effective operating layer of submicron dimensions in comparison with the homogeneous films of PDMS of several tens of microns thickness which bridge over the loss of gas permeability properties of the polymeric material of the membrane. In view of the radiation stability of Silar with retention of selectivity it is suggested that membranes of this polymer may find use for solving problems of purifying gaseous discharges of RNG.

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