

**DIFFUSION OF LOW MOLECULAR SUBSTANCES IN
COPOLYMER SYSTEMS USED FOR
ELECTRICAL INSULATION PURPOSES**

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Abstract: This research is connected with receiving information about diffusion processes in copolymer systems of statistical copolymers type: ethylene + styrene and ethylene - propylene in hexane diffuses molecules.

The chemical synthesis today allows the implementation of various co-polymer systems, used as polymer dielectrics. This refers, most of all, to the mass usage in the modern electronics and electrical engineering of polyene materials, such as polyethylene and polypropylene.

A research has been conducted of diffusion processes in co-polymer systems of the type ethylene + styrene and ethylene + propylene, which allows the obtaining of valuable information about changes in the physical characteristics depending on the mass per-cent content of one of the monomer components in the co-polymer systems, such as the micro-viscosity of the diffused molecules; the average square pin distance which the diffused molecules travel for a unit of time; the diffusion co-efficient; the activating energy of the diffusion processes.

Key Words: diffusion processes, copolymer systems, micro-viscosity of the diffused molecules, diffusion co-efficient, the activating energy of the diffusion processes

1. Introduction

Strict requirements for features and reliability in operation of modern electrical insulating materials need new polymer compositions. Modern chemical synthesis allows obtain different copolymer system used as polymer dielectrics with various and better electro-physical indicators. This primarity refers to, polyofelin materials, polyethylene and polypropylene, used in modern electronics and electrical engineer-

ing.

Examining diffusion of molecules of low molecular substances in the nano domain of the free volume of a copolymer systems allows to obtain valuable information about: micro viscosity (η) of the diffused molecules, average square distance ($\bar{\ell}$), which diffused molecules travelled per unit time ($t = 1s$), Van-der-Vaals interactions of the diffused molecules with its instantaneous neighboring groups at the formation of conformal conditions [1], activation energy (E_D) of diffusion processes and other physical characteristics [2-6].

This research is connected with receiving information about diffusion processes in copolymer systems of statistical copolymers type: styrene ethylene propylene and ethylene in hexane diffusing molecules.

Experimental results are used from [2], where the temperature dependence of the diffusion coefficient (D) in a limited temperature range $T \rightarrow (T_1 \div T_2)$ is given.

2. Theoretical and Experimental Part – Physical Interpretation of the Received Information

The processes of transmission of matter or energy from an area with a higher concentration to an area with a lower concentration occur at a molecular level and are determined by the random nature of molecules movement. According to the first law of Fick (*Adolf Fick*) the flow of the substance particles is proportional to the gradient of the potential

$$J = -D(dC/dx),$$

where $J [cm^{-2}s^{-1}]$ is the density of the substance flow, depending on coefficient of diffusion $D [(cm^2s^{-1})]$ and the gradient of the concentration. The diffusion coefficient D depends on temperature. In a study of $D = f(T)$ about diffusion processes in different substance system types (in particular, polymer, too) in limited temperature ranges (ΔT^*) is valid the dependence of Boltzmann - Arrhenius of the type (1)

$$D = D_0 \exp\left(-\frac{E}{k_B T}\right), \quad (1)$$

$$D_0 = D_C \exp\left(\frac{E}{k_B T_{\infty}}\right), \quad (2)$$

where: (D_0) is preexponential factor, (E) is the activation energy of diffusion processes (k_B) is the Boltzmann constant. Having experimental data for $D = f(T)$ we make the dependence $\ln D = f(1/T)$ and for obtained linear parts in the temperature range (ΔT^*), (1) is valid by (3) and (4) we define numerical values of (E) and (D_0).

$$E = (k_B T_1 T_2)(T_2 - T_1)^{-1} \ln(D_2/D_1), \quad (3)$$

$$\ln D_0 = \frac{1}{2} [\ln(D_1 D_2) + (T_1 + T_2)(T_2 - T_1)^{-1} \ln(D_2/D_1)]. \quad (4)$$

To determine micro-viscosity (η) in the movement of diffused molecules in copolymer systems we use equation (1) of the Stokes-Einstein [12] at $r = 2 \text{ \AA} = 2 \cdot 10^{-10} \text{ m}$ radius of the diffused molecules of hexane (C_6H_{14}).

$$\eta = k_B T (6\pi r D)^{-1}. \quad (5)$$

We present the dependence $\ln \eta = f(1/T)$ and define the relevant temperature range (ΔT^*) $\rightarrow (T_1 \div T_2)$ for which the dependence is linear. Then dependence (2) is valid where (η_0) is preexponential multiplier.

$$\eta = \eta_0 \exp\left(\frac{E^*}{k_B T}\right). \quad (6)$$

Determination of (E^*) and (η_0) we do respectively (3) and (4).

$$E^* = k_B T_1 T_2 (T_2 - T_1)^{-1} \cdot (\ln \eta_1 - \ln \eta_2), \quad (7)$$

$$\ln \eta_0 = \frac{1}{2} \left[\ln(\eta_1 - \eta_2) - (T_1 + T_2)(T_2 - T_1)^{-1} \cdot \ln\left(\frac{\eta_1}{\eta_2}\right) \right]. \quad (8)$$

The results obtained for: (η); (η_0) and (E^*) of the examined two types of copolymer systems are given in table 1 and table 2.

The average square distance ($\bar{\ell}$), which the diffused molecules travel per unit time ($t = 1 \text{ s}$) for one dimensional diffusion can be determined [6] by dependence (5), at transition from one state to a neighbouring conformal state. In this case the diffused molecules + neighbouring atom groups from macromolecular chains of copolymer systems [7], Table 2

$$\bar{\ell} = (4Dt)^{1/2} = 2(Dt)^{1/2} \quad (9)$$

In [8] it is written that $D = f(A^*, B^*, T, T_g)$ and according to [9] can be represented in the form (10). We compare (10) with (1)

$$\ln D = A^* - B^* T_g (T)^{-1}, \quad (10)$$

and we obtain the dependences (11) and (12):

$$A^* = \ln D_0, \quad (11)$$

$$B^* = E^* (k_B T_g)^{-1}. \quad (12)$$

The glass transition temperature (T_g) of copolymer system is determined by (13), as we know temperatures (${}_1T_g$) and (${}_2T_g$) of homopolymers, obtained by the relevant polymerization of the given monomer

$$T_g(\text{copolymer system}) = X_1({}_1T_g) + X_2({}_2T_g), \quad (13)$$

<i>copolymer system – (ethylene + styrene) + hexane</i>										
<i>mas. % styrene</i>	$T_1 - T_2$	$\ln \eta$ [η] = <i>la.S</i>	$\ln \eta_o$ [η_o] = <i>Pa.S</i>	E^* <i>eV</i>	ℓ μm	B^*	T_g <i>K</i>	X <i>m%</i>		
8	296	÷	1.97	-26.54	0.73	0.78	÷	15.69	243	4.69
	329		÷	-13.12	0.26	3.25		6.02		÷
	372	÷	0.79			30.5	÷			20.71
	411		-5.14			46.7				
			÷							
			-5.89							
22	297	÷	1.57	-28.99	0.78	0.99	÷	15.34	259	7.76
	329		÷	-14.62	0.32	4.39		6.86		÷
	357	÷	-1.39			18.8	÷			36.63
	411		-4.21			39.9				
			-							
			-5.58							
35	297	÷	0.56	-27.12	0.71	1.57	÷	13.47	275	9.53
	329		÷	-13.57	0.30	6.32		6.00		÷
	340	÷	-2.12			12.92	÷			45.79
	411		-3.51			33.73				
			÷							
			-5.24							

Table 1

as (X_1) and (X_2) are the mass percentage of each monomer components in the copolymer systems.

The resulting numerical values (C^*) and (T_g) of the examined two types of copolymers systems are given in table 1 and table 2.

It is evident from (12) that (*) is a number, which shows how many times (*) is bigger than the elementary quantum heat (kT_g) temperature (T_g) of a copolymer systems.

In [10] problems related to the permeability, diffusion processes of gases, vapours and liquids in them are thoroughly discussed. A summary [11] of experimental results on diffusion of gases in different polymers is made. By the obtained linearity [11] of the dependence $lgD_0 = f(E_0)$ for elastomers and glassy polymers (plastics) the validity of the compensation law for diffusion processes is shown. The obtained summarized dependencies of $D_0 = f(E_D)$ are represented by dependencies (14) and (15), respectively for elastomers and plastomers, at room temperature of $25^0C =$

<i>copolymer system – (ethylene + styrene) + hexane</i>								
<i>mas. % stirol</i>	$T_1 - T_2$	$\ln \eta$ $[\eta] = P d^{[13]} = Pa.s$	$\ln \eta_0$	E^* <i>eV</i>	ℓ μm	B^*	T_g <i>K</i>	X <i>m%</i>
5	297-352 390-413	0.67 ÷ - 2.40	-19.12	0.51	1.49 ÷ 7.53	11.48	235	1.91 ÷ 6.36
10	297-392 390-413	- 0.38 ÷ - 3.32	-19.38	0.49	2.52 ÷ 11.92	10.91	238	1.89 ÷ 6.31
15	297-352 390-413	- 0.66 ÷ - 5.39	-31.24	0.79	2.90 ÷ 10.63	9.05	240	1.88 ÷ 6.27
25	297-352 390-413	- 2.95 ÷ - 3.96	-18.31	0.41	7.09 ÷ 15.86	8.93	245	1.85 ÷ 6.18

Table 2

298⁰K.

$$\lg D_0 = 0,5[E_D \cdot (1000)^{-1} - 8, 0], \quad (14)$$

$$\lg D_0 = 0,4[E_D \cdot (1000)^{-1} - 10]. \quad (15)$$

In (14, 15) activation energy (E_D) of the diffusion processes is in the measuring unit $[E_D] = cal/mol$.

We can use (14) and substitute $E_D = 0,76V = 17518 cal/mol$ for the sample with 8 weight % styrene - Table 1 [12]. Then for (D_0) we obtain a result $\ln D_0 = 10,96$, which we compare with $\ln D_0 = 9,25$ from table 1 [12]. A relative deviation of 15.6% is obtained.

If we consider the generalized dependence $(E_D/d^2) = f(T_g)$ [10] and assume $T_g = 243^0 K$ and $d = 2r = 4 \text{ \AA} = 4 \cdot 10^{-10} m$ (for hexane) the result is $E_D = 0,79 eV$ at experimentally obtained $E = 0.76 eV$ from table 1 [12]. The relative deviation obtained is 3.8%.

3. Conclusions

A study of diffusion processes type in copolymers system of the type ethylene + styrene and ethylene + propylene:

a) with increasing (T) we observe: decreasing (η) and ($*$) and increasing (η_0) and ($\bar{\ell}$) - as expected.

b) there are no substantive changes of the physical characteristics in dependence of mass percentage of one of the monomer components in copolymer systems.

c) an unilateral decreasing ($*$) is received with increasing mass percentage of propylene in the second type of copolymer systems – table 2.

d) a comparison is made between the obtained rates of ($\ln D_0$) and ($E = E_D$) with those of generalized dependences in [10] obtained by the method of additive atomic group contributions, and the relative deviations are respectively 15.6% and 3.8%.

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