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REGULARITIES OF ORGANIC SOLVENTS DIFFUSION INTO FLUOROPOLYMER STRUCTURE

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Abstract. Diffusion coefficients of organic solvents into tetrafluoroethylene-propylene copolymer structure may be generalized by multiparameter equations. Molar volume and cohesion energy of penetrating liquids are suggested to be determining their values and retarding the process.

Keywords: multiparameter equation, diffusion coefficient, swelling.

1. Introduction

Process of diffusion of organic solvents into polymer structure is of both theoretical and practical interest, especially in view of membrane technologies development. That is why a great number of investigations are devoted to it [1]. However, unlike diffusion in homogeneous medium which complies with Fick, Einstein-Stocks and other equations, the problem of relation between diffusion rate of a penetrant into polymer structure and its properties has not been solved till now [2]. For instance, in case of diffusion into polymer membranes numerous deviations from the known expression $Q_\tau / Q_\infty = k\tau^{n\,a}$ are noted (where Q_τ is the amount of solvent absorbed during the time τ; Q_∞ is the same value at saturation, k and n are constants.) At $n = 0.5$ the process complies with Fick law, however, as a rule, $n > 0.5$, which implies that the process occurs in the field of so called anomalous transport. When considering this problem from the position of the theory of regular solvents, the suggested relation between the characteristics of swelling and diffusion processes and the Hildebrand solubility parameter δ has only semiquantitative character since it does not take into account the effect of possible specific interactions. The attempts to describe the diffusion via molar volume of liquid $V_м$ failed too. Although according to the Einstein-Stocks formula $D = kT/6\pi\eta r$ diffusion coefficient D must be inversely proportional to the radius of diffusing molecule r, in real cases linear relation between these values is observed only within homologous or structurally close solvents and even here with numerous exceptions [3].

We have made an assumption that in the diffusion processes both molecules' sizes and their solvation interactions ability are significant. Simultaneous consideration of all these factors is possible by employing the free energies linearity concept by means of linear multiparameter equations. The authors [4, 5] show that in case of low-polarity polymers (*cis*-isoprene, butadiene-styrene *etc.*) relation between diffusion coefficient and penetrants' properties is satisfactorily described by equation (1):

$$\lg D = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{\varepsilon - 1}{2\varepsilon + 1} + \\ + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M \qquad (1)$$

In this equation D is diffusion coefficient; n is refractive index and ε is permittivity of liquids, that characterize their polarizability and polarity, which define their ability to nonspecific solvation; B is Koppel-Palm basicity, and E_T is Reichardt electrophilicity, that characterize possible specific (acid-base) interactions; the square of solubility parameter δ^2 is proportional to the cohesion energy of liquids and reflects inputs of energy for destruction of their structure; $V_м$ is molar volume of liquids; a_i is regression coefficient.

2. Results and Discussion

Correlation analysis of the obtained equations has shown that in all cases the molar volume of liquid is determinative and counteractive as to diffusion; however acceptable values of multiple correlation coefficient R may be obtained only by taking into account some other factors. It is worth noting that in case of aliphatic polymers nonspecific solvation ability, which is connected with polarizability $f(n^2)$ of liquids, increases the value of D, while specific solvation ability, which is determined by their basicity B, decreases it. Similarly as in *cis*-isoprene polymer, dependence of diffusion on solvent properties is also observed for chloroisoprene polymer. In case of butadiene-

styrene polymer the influence of medium basicity is reverse. Therefore it was of interest to examine the influence of electronegative but smaller in size fluorine atoms on the values of diffusion coefficients. In [6-9] the investigation results of diffusion of a series of solvents into copolymer tetrafluoroethylene-propylene (Aflas FA 100S, 3M Industrial Chemical Products Division) are presented. The investigations were carried out at 303, 318 and 333 K using membranes (14.7×0.225cm), filled by 30 % carbon black. Diffusion coefficients were defined based on Fick equation:

$$\frac{\partial c}{\partial \tau} = D(\frac{\partial^2 c}{\partial x^2}),$$

where c is liquid concentration at x distance during τ period of time. The numerical values D were determined from the slope of relations $lg\ (1 - S_\tau / S_\infty)$ *vs* time τ, where S is the quantity of solvent, adsorbed during time τ. Corresponding values of D for the investigated liquids are presented in Table.

Table

Logarithms of diffusion coefficients of the solvents into polymer FA-100S at 303, 318 and 333 K according to [6-8] and calculated using equations (4-6)

No	Solvent	$lg(D\times10^7)$								
		303 K			318 K			333 K		
		Exp.	Calc.	$\Delta lg(D\times10^7)$	Exp.	Calc.	$\Delta lg(D\times10^7)$	Exp.	Calc.	$\Delta lg(D\times10^7)$
1	Hexane	0.2014	0.3503	0.1489	0.4082	0.5144	0.1061	0.6375	0.6463	0.0088
2	Heptane	-0.0757	-0.0746	0.0011	0.1173	0.2338	0.1166	0.4216	0.4208	-0.0008
3	Octane	-0.4559	-0.5030	-0.0471	0.0414	-0.0618	-0.1032	0.2504	0.1789	-0.0715
4	Isooctane	-0.3872	-0.3059	0.0814	0.1173	0.1401	0.0228	0.2601	0.3403	0.0802
5	Nonane	-1.0000	-0.8952	0.1048	-0.2441	-0.3227	-0.0786	0.0086	-0.0345	-0.0431
6	Dichloro-methane	0.9886	0.8029	-0.1856	-	-	-	-	-	-
7	1,2-dichlo-roethane	0.3692	0.5085	0.1393	0.6590	0.6548	-0.0042	0.0651	0.8937	0.0286
8	Chloroform	0.7482	0.7524	0.0042	0.8235	0.8084	-0.0151	0.9680	0.9972	0.0292
9	Trichloro-ethylene	0.7917	0.5310	-0.2607	0.8432*	0.3283	-0.5149	0.9090*	0.4680	-0.4410
10	Tetrachloro-methane	0.3655	0.6237	0.2582	0.3962	0.3093	-0.0869	0.4900	0.3876	-0.1024
11	1,1,1-trichloro-ethane	0.3838	0.5583	0.1745	0.4166	0.3944	-0.0222	0.6304	0.4440	-0.1864
12	Tetrachloro-ethylene	0.4065	0.1963	-0.2102	0.4502*	-0.2860	-0.7363	0.4914*	-0.1885	-0.6798
13	Tetrachoro-ethane	-0.1487	-0.1100	0.0387	-0.0223	-0,1798	-0.1575	0.0086	0.0542	0.0456
14	Methylacetate	0.7825	0.6502	-0.1323	-	-	-	-	--	-
15	Ethyl-acetate	0.6263	0.4120	-0.2143	-	-	-	-	-	-
16	Methyl-benzoate	-0.6021	-0.6139	-0.0119	-	-	-	-	-	-
17	Ethyl-benzoate	-0.7212	-0.9280	-0.2068	-	-	-	-	-	-
18	Acetone	0.7243	0.6578	-0.0665	0.7825	0.6688	-0.1136	0.7931	0.7453	-0.0478
19	Methyl-ethylketone	0.4814	0.4923	0.0108	0.5587	0.6242	0.0655	0.5866	0.6848	0.0982
20	Acetonitrile	-0.2924	0.0255	0.3179	-0.1308	-0.1452	-0.0144	0.1206	0.0937	-0.026
21	Tetrahydro-furan	0.7356	0.6753	-0.0603	0.8195*	0.2623	-0.5572	0.8802*	0.0959	-0.7843
22	1,4-dioxane	0.1173	0.3231	0.2059	0.1732	0.2293	0.0561	0.1875	0.2052	0.0177
23	Dimethyl-acetamide	-0.1675	-0.2574	-0.0899	-0.0969	-0.0588	0.0381	0.0492	-0.0060	-0.0552
24	Butyl-acetate	0.3181*	-0.1470	-0.4651	-	-	-	-	-	-
25	Cyclo-hexanone	-1.2218*	-0.2435	0.9783	-0.5686	-0.3780	0.1906	-0.4202	-0.3272	0.0931
26	Cyclohexane	-0.7959*	0.5260	1.3219	-0.1079*	0.2399	0.3478	0.1790	0.3118	0.1328

* These data are excluded from the calculations

Generalization of these data by equation (1) was made using solvents characteristics from reviews [10, 11]. The calculations were performed in compliance with recommendations of the IUPAC Group for Correlation Analysis in Chemistry [12].

Generalization of the data obtained for 26 solvents at 303 K leads to an equation with unsatisfactorily low value of multiple correlation coefficient R 0.848; however, exclusion (according to the recommendations [12]) of the most deviating data for only three solvents, namely cyclohexane, cyclohexanone and butylacetate allows obtaining an adequate equation with $R > 0.95$:

$$lg(D\times10^7) = 4.853 - (1.485\pm1.500)f(n^2) + (1.380\pm1.224)f(\varepsilon) + \\ +(0.140\pm0.406)\times10^{-3}B + (2.312\pm3.813)\times10^{-2}E_T - \\ -(6.269\pm1.012)\times10^{-3}\delta^2 - (23.441\pm1.494)\times10^{-3}V_M \qquad (2)$$

$N = 23$, $R = 0.965$, root-mean-square error $s = \pm\ 0.146$.

Maximum value of pair correlation coefficient r was observed between lgD and $V_м$ – 0.598 for 26 initial solvents and 0.729 for 23 solvents used in calculations. Correlation was not observed with other terms of equation: the calculated coefficients r are smaller than 0.3, which does not allow to ascertain their direct influence on lgD.

Significant root-mean-square deviations of regression coefficient at a number of equation terms, which often exceed their absolute value, are indicative of their probable insignificance. That is why, with the goal to establish a probable effect of individual factors on the value of D, the successive exclusion of separate terms of equation each time followed by determining R values for equations containing smaller number of terms was carried out. In case when this value decreases insignificantly, the corresponding excluding term is considered to be insignificant. Thereby real insignificance of solvation terms $f(n^2)$ and B as well as low significance of E_T were established. Based on the above stated we can conclude that dependence of D on liquid properties may be described adequately by three-parameter equation (3):

$$lg(D\times10^7) = 4.570 + (0.695\pm0.514)f(\varepsilon) - \\ -(6.324\pm0.671)\times10^{-3}\delta^2 - (2.278\pm0.151)\times10^{-3}V_M \qquad (3)$$

$R = 0.961$, $\quad s = \pm\ 0.155$

and to some extend less adequately by two-parameter equation (4), which takes into account only the cohesion energy and the molar volume of the penetrants, whose penetration into polymer structure gets hindered as it increases:

$$\lg(D\times10^7) = 4.682 - (5.817\pm0.579)\times10^{-3}\delta^2 - \\ -(2.330\pm0.152)\times10^{-3}V_M \qquad (4)$$

$R = 0.957$, $s = \pm\ 0.161$.

In Table the values of lgD, calculated using equation (4), as well as their deviations from experimental values $\Delta\, lgD$ are given. The relation between $lgD_{cal.}$ and $lgD_{exp.}$ is shown on Fig. 1. As one can see, deviations values, are normally within the range of mean-root-square error $s = \pm\ 0.160$ or exceed it insignificantly (chloroethylene, tetrachloromethane, ethylacetate, and acetonitrile), but not more than by $\pm\ 2s$. More significant deviations are observed for the three solvents that have been excluded from the calculations.

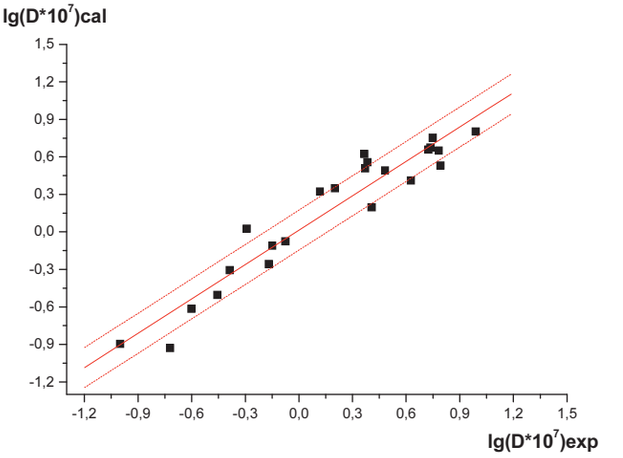

Fig. 1. Relation between experimental values of $lg\ (D\cdot10^7)$ at 303 K calculated using equation (4)

Similarly, the data obtained at higher temperatures 318 and 333 K were generalized (Table). However in this case the factor of the electrophilic solvation has to be additionally considered. This factor increases the value of D, which is probably due to the fact that values of r between lgD and $V_м$ are considerably smaller here. Having generalized 20 available data obtained at 318 K we have got an expression with $R = 0.835$; to obtain an acceptable value of R data for cyclohexane, tetrahydrofuran, tetrachloroethylene and trichloroethylene need to be excluded from consideration. Thus, for 16 solvents a six-parameter equation with $R = 0.978$ has been obtained, in which polarizability and basicity terms are insignificant.

$$lg(D\times10^7) = -0.397 - (3.496\pm0.762)f(\varepsilon) + \\ +(16.405\pm2.692)\times10^{-2}E_T - \\ -(8.247\pm0.134)\times10^{-3}\delta^2 - (1.297\pm0.134)\times10^{-2}V_M \qquad (5)$$

$N = 16$, $\quad R = 0.978$, $\quad s = \pm\ 0.094$.

Further excluding of a relatively insignificant term with $f(\varepsilon)$ decreases R more significantly – up to 0.926.

A similar effect is observed for the data obtained at 333 K. The value of $R = 0.852$ for all 20 solvents after excluding from consideration the data for tetrahydrofuran, trichloroethylene, and tetrachloroethylene increases to 0.975. Factor $f(n^2)$ in this case is insignificant; the effect of basicity is of low significance as well.

$$lg(D\times10^7) = -1.352 - (4.210\pm0.867)f(\varepsilon) + \\ +(19.372\pm2.879)\times10^{-2}E_T - \\ -(8.355\pm0.724)\times10^{-3}\delta^2 - (1.042\pm0.144)\times10^{-2}V_M \quad (6)$$

$N = 17$, $R = 0.953$, $s = \pm 0.111$.

In this case further excluding of any term of the equation from consideration decreases R to undesirably low values (< 0.95).

Thus, the obtained generalizing equations denote a common for other polymers mechanism of liquids diffusion – diffusion decreases with increase of cohesion and molecules sizes. At the same time insignificance of solvents basicity factor B allows speculating about the absence of the assumed donor-acceptor interaction between fluorine atoms of polymer and electron-donor carboxylic groups of the solvent, such as carboxylic groups in esters. The effect of solvents polarity is not quite clear either. It must be noted that predominantly polyhalogenderivatives, which have enhanced polarizability, deviate from general regularities.

In [6-9] the diffusion process activation energies values E_D (кJ/mol) are given. Although the exactness of their determination by values of D for only three temperatures seems to be moderate, these values may still be generalized using the equation of type (1). After excluding data for cyclohexane, dichloroethane and chloroform the following equation has been obtained:

$$E_D = 108.87 - (424.91\pm71.88)f(n^2) + \\ +(104.13\pm44.96)f(\varepsilon) - \\ (31.95\pm15.33)\times10^{-3}B - (4.28\pm1.67)E_T + \\ +(0.22\pm0.04)\delta^2 + (0.62\pm0.06)V_M \quad (7)$$

N=17, $R = 0.962$ $s = \pm 4.78$.

Molar volume $V_м$ has maximum influence on E_D value – r between these values equals 0.776. Large standard deviations at the majority of regression terms indicate their relative insignificance. Excluding the basicity parameter decreases R to 0.950, while further exclusion of the terms with $f(n^2)$ and E_T makes the correlation invalid.

3. Conclusions

Thus, obtained generalizing equations are evidences of common with other polymers mechanism of liquids diffusion, that is decrease of diffusion with increasing their cohesion and molecules sizes. At the same time insignificance of the solvents basicity B allows to express the opinion about the absence of the assumed donor-acceptor interaction between fluorine atoms of polymer and electron-donor carboxylic groups of the solvent, such as carboxylic groups in esters. It should be noted that predominantly polyhalogenderivatives, which have enhanced polarizability, deviate from general regularities.

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ЗАКОНОМІРНОСТІ ДИФУЗІЇ ОРГАНІЧНИХ РОЗЧИННИКІВ У ФТОРВМІСНИХ ПОЛІМЕРАХ

Анотація. *Коефіцієнти дифузії органічних розчинників у структуру тетрафторетилен-пропіленового кополімера узагальнені багатопараметровими рівняннями. Визначаючими їх значення і сповільнюючими процес є мольний об'єм і енергія активації проникаючих рідин.*

Ключові слова: *багатопараметрове рівняння, коефіцієнт дифузії, набрякання.*