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## DEPENDENCE OF NATURAL RUBBER SWELLING INDEX UPON ORGANIC SOLVENTS PROPERTIES

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Received: October 30, 2009 / Revised: April 08, 2010 / Accepted: September 02, 2010

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**Abstract.** Mathematic analysis of the data on natural rubber swelling shows the degree of organic solvents penetrating dependence on their ability to nonspecific interaction and cohesion, which counteracts this process.

**Keywords:** linear multiparameter equation, swelling index, natural rubber, organic solvents.

### 1. Introduction

Polymer stability in different media including hydrocarbon ones is of a great practical importance [1, 2]. That is why it is no wonder that processes of swelling and dissolution of polymers, especially of rubber, are the subjects of intensive investigation over almost a hundred years. The review of earlier works on natural rubber swelling is presented in [3]. The quantitative data on adsorption of 135 organic solvents in crude and vulcanized rubber were presented for the first time here. Some conclusions on the effect of solvent nature on their penetrative ability were made as well. However, these conclusions are only qualitative. What is interesting, the authors based on the investigation of numerous solvents have disproved Ostwald's opinion about quantitative relation between swelling index of polymers and permittivity of adsorbed substance [4]. According to his opinion the amount of cc of liquid adsorbed by 1 cc of polymer  $Q$  is inversely proportional to its permittivity  $\epsilon$  in conformity with the equation:

$$\sqrt[n]{Q\epsilon} = \text{const} \quad (1)$$

where  $n$  changes within the limit from 2 to 3.

It can be noted as well that in homologous series with increasing of carbon chain length till 6–8 atoms the gradual (but not linear) increase of  $Q$  takes place. Thus, in

series of acids for  $C_1$   $Q = 0.12$ ;  $C_2 - 0.14$ ;  $C_4 - 1.57$ ;  $C_6 - 1.65$ ;  $C_7 - 1.94$ ; in series of alcohols for  $C_3$   $Q = 0.02$ ;  $C_3 - 0.06$ ;  $C_6 - 0.13$ ;  $C_7 - 0.60$ ;  $C_8 - 0.75$ ; however further increasing of the amount of carbon atoms stabilizes the value of  $Q$  or even diminishes it. The presence of branchings in the chain leads to decreasing of  $Q$  as compared to analogues with direct chains, probably, due to spatial difficulties. Even greater decreasing of  $Q$  is observed in the case when polar groups – carbonyl, carboxyl, nitrile, and especially hydroxyl ones – are incorporated into the structure [3].

The next attempts to establish the quantitative relation between physico-chemical characteristics of liquids and their ability to be adsorbed by polymers were based on the Flory-Huggins athermal solvents theory, according to which the swelling index  $Q$  depends on the molar volumes of polymer and solvent and their cohesion energy, that can be determined as the square of Hildebrand solubility parameter  $\delta^2$ . The maximal swelling index is observed when  $\delta$  for both components are equal. However, the relation between  $Q$  and  $\delta$  or  $\delta^2$  has the parabolic character with numerous deviations from the proposed curve [5] as a result of the deviation of the system from ideal, which is firstly due to the presence of specific interactions. The attempt to account the last ones incorporating correction factor  $\chi$ , which can be calculated from the viscosity measurements of polymer solutions [6], by establishing of the temperatures of complete dissolution of polymer in solvents (in cited articles these temperatures are designated incorrectly as “melting points”; probably, they may be more correctly designated as “temperatures of homogenization”) [7, 8] as well as by other methods does not essentially improve the calculation accuracy [9, 10].

The attempts to agree the values of  $Q$  with the solvent molar volume [11] or their Reichardt electro-

philicity parameters [12] failed as well. In the both cases the linear relations were obtained with some deviations only for the solvents of similar nature, mainly for their homologous series.

## 2. Experimental

Since polymer swelling is the process the final effect of which is determined by the sum of different probable interactions we suggested the probability of describing it on the basis of the conception of free energies linearity by means of the linear multiparameter equations. This approach seems to be effective for generalization of the data on swelling of polyethylene [13], butyl rubber [14], some polyurethanes [15] and fluorocarbon polymers [16]. That is why it was expedient to examine its correctness in the case of natural rubber.

The data from [3] have been taken for calculations because of their great amount, however due to the fact that for the majority of investigated liquids the necessary characteristics are absent the data only for 30–35 solvents have been used. In [3] the values of  $Q$  were determined after 1, 2, 3, 7, 32, and 62 days of swelling. The fullest data on  $Q$  for 1 and 7 days of swelling in the case of vulcanized rubber and for 1 day of swelling for crude rubber were taken for the calculation. The investigation of the process of swelling was performed at 293 K using the samples of rubber vulcanized by 10 % of sulfur at 421 K during 75 min and crude rubber “smoked sheet” with the weight of ~ 0.1 g; the specific gravities of the samples were 0.9820 and 0.9146 g/ml.

The calculations were made using the formula from [13-16]

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

where  $n$  and  $\varepsilon$  are refractive index and permittivity of liquids, that characterize their polarizability and polarity, which determine nonspecific interactions in the system;  $B$  is Palm basicity and  $E_T$  is Reichardt electrophilicity, which determine specific interactions;  $\delta^2$  and the molar volume of solvent  $V_M$  characterize the structural factors.

The calculation methods are based on The IUPAC Group for Correlation Analysis in Chemistry recommendations [17] and were reported in details in the previous articles [13-16].

The data on rubber swelling  $Q$  are presented in [3] in ml of liquid, adsorbed by 1 ml of rubber. However, our previous investigations showed that the calculations with the use of the Eq. (2) usually can be performed rather in

moles of liquid, adsorbed by the unit of the polymer weight or volume, though the volume or the weight units may be used as well. That is why for comparison the data from [3]  $Q$  (ml/ml) have been expressed in ml and g of liquid, adsorbed by 1 g of rubber  $S_v$  and  $S_g$ , and also in the amount of moles of liquid, adsorbed by 1000 g of rubber  $S_M$  (for the convenience of calculations). The respective data on the amount of solvents, adsorbed during one day by the samples of vulcanized smoked-sheets rubber are presented in Table 1.

## 3. Results and Discussion

The calculation of  $S_v$  using the Eq. (2) for all 31 solvents from Table 1 leads to the expression with unacceptably low value of multiple correlation factor  $R = 0.911$ , however the exclusion from calculation (according to [17]) of the most deviating data for only two solvents – butyric acid and benzaldehyde – allows to obtain the adequate ( $R \geq 0.950$ ) Eq. (3). At plotting  $\lg S$  vs  $\lg \tau$  the satisfactory linear dependence in accordance with the known expression  $S_t/S_\infty = k \tau^n$  was found for the first seven days, however the data obtained for 31 days, deviate from it. Evidently, the mechanism of penetrating of solvents into polymer structure changes after seven days. Additionally, for some penetrants (nitromethane, nitriles, and higher alcohols) at the duration of experiments in 31 or 62 days one can observe constant values of  $S$ , *i.e.* complete saturation by solvent, or even the decrease of this value. Especially often such deviations take place for the samples of crude rubber. That is why for further quantitative analysis we use the data on  $S$  for one and for seven days, when the main part of the penetrant is absorbed. Additionally, most of results in [3] are presented for these time intervals.

$$\begin{aligned} \lg S_v = & -2.339 + (14.397 \pm 1.816)f(n^2) + \\ & + (3.009 \pm 1.155)f(e) - (2.230 \pm 1.255) \cdot 10^{-3} B - \\ & - (2.285 \pm 1.575) \cdot 10^{-3} E_T - (5.416 \pm 0.939) \cdot 10^{-3} d^2 - \\ & - (0.369 \pm 2.240) \cdot 10^{-3} V_M \end{aligned} \quad (3)$$

with  $R = 0.950$  and root-mean-square error  $s = \pm 0.217$ .

The deviations of some regression coefficients which are close or even exceed their absolute values ( $V_M$ ) indicate probable insignificance of these terms of equation. In fact alternate exclusion of individual terms with determining for every case (according to [17]) of  $R$  values has indicated insignificance of the terms with  $E_T$  and  $V_M$ :

$$\begin{aligned} \lg S_v = & -2.457 + (14.391 \pm 1.452)f(n^2) + \\ & + (3.082 \pm 1.107)f(e) - (2.393 \pm 1.008) \cdot 10^{-3} B - \\ & - (5.458 \pm 0.591) \cdot 10^{-3} d^2 \end{aligned} \quad (4)$$

$R = 0.950; s = \pm 0.227.$

Table 1

The amounts of liquids adsorbed for 24 h by the samples of cured rubber in  $Q$  (ml/ml),  $S_V$  (ml/g),  $S_g$  (g/g) and  $S_M$  (mol/1000g), and experimental and calculated values of  $\lg S_g$  using the Eq. (6)

No.	Solvents	$Q$	$S_V$	$S_g$	$S_M$	$\lg S_g$ exp.	$\lg S_g$ calc.	$\Delta \lg S_g$
1	Pentane	1.16	1.181	1.887	26.199	0.2758	0.2709	-0.0049
2	Hexane	1.18	1.202	1.821	21.130	0.2603	0.3387	0.0784
3	Octane	2.36	2.403	3.418	29.930	0.5338	0.4074	-0.1263
4	Benzene	4.02	4.094	4.658	59.634	0.6682	0.5385	-0.1297
5	Toluene	4.17	4.246	4.897	53.147	0.6899	0.6391	-0.0509
6	<i>m</i> -Xylene	4.17	4.246	4.914	46.284	0.6914	0.6975	0.0060
7	Mesitylene	3.30	3.360	3.884	32.313	0.5893	0.6766	0.0873
8	Methylcyclohexane	2.60	2.648	3.443	35.065	0.5369	0.5134	-0.0235
9	Tetraline	4.87	4.959	5.112	38.666	0.7086	0.6853	-0.0233
10	Formic acid	0.12	0.122	0.100	2.172	-1.0000	-1.5614	-0.5614
11	Acetic acid	0.14	0.143	0.136	2.265	-0.8665	-0.5883	0.2782
12	Butyric acid*	1.57	1.599	1.667	18.922	0.2219	-0.5570	-0.7789
13	Benzaldehyde*	1.48	1.507	1.393	13.127	0.1440	0.9529	0.8090
14	Methylethylketone	0.72	0.733	0.911	12.632	-0.0405	-0.1248	-0.0843
15	Diethylketone	1.52	1.548	1.897	22.025	0.2781	0.0902	-0.1878
16	Ethylpropylketone	2.1	2.138	2.669	26.647	0.4263	0.2843	-0.1420
17	Methylisobutylketone	0.89	0.906	1.130	11.282	0.0531	0.2843	0.2312
18	Acetophenone	1.21	1.232	1.166	9.684	0.0667	0.3912	0.3245
19	Cyclohexanone	2.67	2.719	2.871	29.254	0.4580	0.0064	-0.4516
20	<i>n</i> -Propanol	0.02	0.020	0.025	0.416	-1.6021	-1.2874	0.3147
21	<i>tert</i> -Butanol	0.12	0.122	0.155	2.091	-0.8097	-0.6079	0.2017
22	<i>n</i> -Pentanol	0.06	0.061	0.075	0.851	-1.1249	-0.7535	0.3714
23	<i>n</i> -Hexanol	0.14	0.143	0.174	1.703	-0.7595	-0.5274	0.2320
24	<i>n</i> -Heptanol	0.60	0.611	0.742	6.386	-0.1296	-0.2138	-0.0842
25	<i>n</i> -Octanol	0.75	0.764	0.924	7.095	-0.0343	-0.2379	-0.2036
26	Benzyl alcohol	0.29	0.295	0.283	2.617	-0.5482	-0.3810	0.1672
27	Cyclohexanol	0.41	0.418	0.435	4.343	-0.3615	-0.3640	-0.0025
28	Acetonitrile	0.04	0.041	0.031	0.755	-1.5086	-1.5681	-0.0594
29	Propionitrile	0.06	0.061	0.078	1.416	-1.1079	-0.8407	0.2672
30	Benzonitrile	2.08	2.118	2.097	20.334	0.3216	0.0768	-0.2448
31	Nitromethane	0.03	0.031	0.027	0.0442	-1.5686	-1.7483	-0.1797

\* the data excluded from calculation

It is clear that the increasing of solvent cohesion diminishes their ability to penetrate into polymer structure (sign “minus” at the term with  $d^2$ ).

The basicity and polarity factors are also of relatively low significance – excluding the first of them we obtain the equation with  $R = 0.940$  and excluding the second one from the Eq. (4) leads to the three-parameter equation  $\lg Q_v = f(n^2, B, d^2)$  with  $R = 0.936$ .

At the same time the exclusion of the terms with  $f(n^2)$  or  $d^2$  destroys the correlation – the value of  $R$  for corresponding expressions becomes less than 0.8.

Non-coordination of the data for butyric acid and benzaldehyde with generalizing Eqs. (3) and (4) may cause the changing of the mechanism of their diffusion into polymer structure, which is confirmed by significant difference of the angles of the slopes of their dependences  $\lg S$  vs  $\lg \tau$  as compared with other liquids. But inaccuracies in defining of  $S$  due to the dispersion of the investigated samples of rubber in these solvents seem to be more probable cause, as it is noted in [3]. Non-coordination for some other solvents in following calculations may take place due to the similar reason.

Similar results have been obtained at generalization of  $S_g$  data for 31 solvents:  $R = 0.924$ , but after exclusion of the same solvents (butyric acid and benzaldehyde) the proper equation has been obtained:

$$\begin{aligned} \lg S_g = & -1.914 + (13.363 \pm 1.692)f(n^2) + \\ & + (2.684 \pm 1.076)f(e) - (1.846 \pm 0.117) \cdot 10^{-3} B - \\ & - (3.797 \pm 14.676) \cdot 10^{-3} E_T - (5.563 \pm 0.875) \cdot 10^{-3} d^2 - \\ & - (0.505 \pm 2.087) \cdot 10^{-3} V_M \end{aligned} \quad (5)$$

$R = 0.960; s = \pm 0.212$

and after excluding insignificant parameters  $V_M$ ,  $E_T$  and  $B$

$$\begin{aligned} \lg S_g = & -1.637 + (13.037 \pm 1.404)f(n^2) + \\ & + (0.922 \pm 0.608)f(e) - (5.313 \pm 0.533) \cdot 10^{-3} d^2 \end{aligned} \quad (6)$$

$R = 0.954; s = \pm 0.227$

In Table 1 the experimental and obtained with the use of the Eq. (6) values of  $\lg S_g$  and their divergences  $\Delta \lg S_g$  are compared. As one can see the values of  $\Delta \lg S_g$  (except those for benzaldehyde and butyric acid, which were not taken into account at calculation) are within the limits of the error corridor  $s \pm 0.227$  or only insignificantly overstep these limits (acetic acid, acetophenone, *n*-propanol).

Generalization of the data on the amount of adsorbed moles of liquid  $S_m$  (for obtaining the adequate expression) requires excluding from calculations of three solvents – butyric acid, formic acid, and benzaldehyde:

$$\begin{aligned} \lg S_m = & 0.670 + (10.891 \pm 1.435)f(n^2) + (1.854 \pm 0.918)f(e) - \\ & - (0.381 \pm 1.047) \cdot 10^{-3} B - (25.153 \pm 13.373) \cdot 10^{-3} E_T - \\ & - (4.809 \pm 0.753) \cdot 10^{-3} d^2 - (1.792 \pm 1.789) \cdot 10^{-3} V_M \end{aligned} \quad (7)$$

$R = 0.964; s = \pm 0.179$

and after excluding of insignificant parameters  $B$  and  $V_M$ :

$$\begin{aligned} \lg S_m = & 0.786 + (0.941 \pm 1.215)f(n^2) + (1.603 \pm 0.573)f(e) - \\ & - (3.148 \pm 1.099) \cdot 10^{-2} E_T - (4.241 \pm 0.553) \cdot 10^{-3} d^2 \end{aligned} \quad (8)$$

$R = 0.962; s = \pm 0.183$

Thus, calculations indicate only insignificant differences at the use of three dimensions of adsorbed liquid – ml/g, g/g and mol/g, although in the case of  $V_M$  it is desirable to use a four-parameter equation, since excluding the term  $f(e)$  decreases  $R$  till 0.951 and  $E_T$  till 0.950. In all three cases factors that determine the swelling index are nonspecific solvation of structural parts of rubber chains by solvents, caused firstly by their polarizability and solvents cohesion, which counteracts their penetration into polymer (sign “minus” at the corresponding term). Surprisingly, possible specific interaction of solvents and polymers is insignificant, as well as the molar volume of solvent  $V_M$ , that is size of its molecules.

At longer contact of polymer with organic solvents its swelling factor usually increases, evidently, due to gradual destroying of its structure (Table 2, column I). For alkanes this increasing is insignificant (in [3] the authors observed in some cases even its insignificant decreasing), while in the case of aromatic hydrocarbons it reaches 15–20 %. For other solvents, especially for acids, one can observe the increasing of  $Q$  even till 100 %. Therefore to examine the approach for generalization of the experimental data proposed in this article as well as to determine factors that govern the swelling chemism we have generalized the data on swelling index after rubber was in contact with solvents during seven days. In Table 2 the respective data from [3] on  $Q$  (ml/ml) for 7 days of rubber swelling and calculated on their basis values of  $S_v$  (ml/g),  $S_g$  (g/g) and  $S_m$  (mol/1000g) are presented. They also may be generalized by the Eq. (2), however, the obtained results are worse since for obtaining of the adequate expressions exclusion of the data for 4–6 solvents (*i.e.* till 20 % of their total amount) from the calculations is necessary.

In the case of generalization of the data on  $S_v$  for 35 solvents the initial value of  $R$  is equal to 0.880 and for obtaining of the acceptable correlation score the values of  $S_v$  not only for formic and butyric acids, but also for cyclohexanone, acetone, and benzaldehyde must be excluded from consideration for obtaining of the acceptable correlation score. The multiparameter equation with  $R = 0.952$  has been obtained. The terms that reflect the influence of the molar volume  $V_M$  ( $R$  decreases till 0.951), polarity  $f(e)$  ( $R = 0.950$ ) and  $E_T$  ( $R = 0.949$ ) were found to be insignificant:

$$\begin{aligned} \lg S_v = & -1.864 + (13.645 \pm 1.255)f(n^2) + \\ & + (0.7 \pm 0.6) \cdot 10^{-3} B - (4.6 \pm 0.4) \cdot 10^{-3} d^2 \end{aligned} \quad (9)$$

$R = 0.949; s = \pm 0.226$ .

The value of the term with  $B$  is insignificant as well – after excluding it  $R$  decreases till 0.946. The same factors as those in the previous case –  $f(n^2)$  and  $d^2$  – are determinative.

During generalization of the data expressed in the units of weight  $S_g$   $R$  of the initially obtained equation is equal to 0.895; excluding from consideration of the data for

Table 2

The amounts of liquids adsorbed by vulcanized rubber in 7 days (I) and by crude rubber in 24 h (II)

No.	Solvents	I				II			
		$Q$	$S_v$	$S_g$	$S_M$	$Q$	$S_v$	$S_g$	$S_M$
1	Pentane	1.10	1.120	1.789	24.838	6.67	6.792	10.850	150.640
2	Hexane	1.15	1.171	1.774	20.590	-	-	-	-
3	Octane	2.43	2.475	3.521	30.832	-	-	-	-
4	Benzene	4.50	4.582	5.213	66.739	26.08	26.558	30.214	386.813
5	Toluene	4.62	4.705	5.427	58.900	28.25	28.768	33.181	360.115
6	<i>m</i> -Xylene	4.29	4.369	5.057	47.631	-	-	-	-
7	Mesitylene	3.67	3.737	4.320	35.940	20.47	20.845	24.098	200.483
8	Methylcyclohexane	2.56	2.607	3.390	34.525	28.70	29.226	38.005	387.056
9	Tetraline	6.31	6.426	6.625	50.110	16.65	16.955	17.479	132.206
10	Formic acid	0.21	0.214	0.175	3.802	0.33	0.336	0.275	5.974
11	Acetic acid	0.18	0.183	0.174	2.898	0.22	0.224	0.214	3.564
12	Butyric acid	1.70	1.183	1.234	14.007	3.31	3.371	3.515	39.898
13	Acetic anhydride	0.07	0.071	0.066	0.646	0.03	0.031	0.029	0.284
14	Benzaldehyde	1.73	1.762	1.692	15.944	1.23	1.253	1.203	11.336
15	Acetone	0.03	0.031	0.039	0.671	-	-	-	-
16	Methylethylketone	0.87	0.886	1.101	15.266	0.70	0.713	0.886	12.285
17	Diethylketone	1.83	1.864	2.284	26.518	7.35	7.485	9.173	106.502
18	Ethylpropylketone	2.45	2.495	3.112	31.101	8.10	8.248	10.288	102.716
19	Methylbutylketone	1.02	1.039	1.296	12.952	-	-	-	-
20	Acetophenone	1.40	1.426	1.387	11.520	0.63	0.642	0.624	5.183
21	Cyclohexanone	4.80	4.888	5.162	52.598	6.55	6.670	7.043	71.765
22	<i>n</i> -Propanol	0.02	0.0204	0.025	0.416	0.01	0.0102	0.013	0.216
23	<i>tert</i> -Butanol	0.19	0.193	0.245	3.305	0.13	0.132	0.167	2.253
24	<i>n</i> -Pentanol	0.09	0.092	0.113	1.282	0.11	0.112	0.138	1.566
25	<i>n</i> -Hexanol	0.21	0.214	0.261	2.555	0.22	0.224	0.273	2.672
26	<i>n</i> -Heptanol	0.76	0.774	0.939	8.081	0.94	0.957	1.161	9.991
27	<i>n</i> -Octanol	0.98	0.998	1.207	9.268	0.72	0.733	0.886	6.803
28	Amyl alcohol	-	-	-	-	0.04	0.0407	0.048	0.826
29	Benzyl alcohol	0.37	0.377	0.362	3.347	0.09	0.092	0.088	0.814
30	Cyclohexanol	1.27	1.293	1.344	13.419	0.60	0.611	0.635	6.340
31	Acetonitrile	0.04	0.041	0.031	0.755	0.02	0.0204	0.015	0.365
32	Propionitrile	0.05	0.051	0.065	1.180	0.08	0.081	0.104	1.888
33	Benzonitrile	2.36	2.403	2.379	23.068	3.00	3.055	3.025	29.332
34	Nitromethane	0.04	0.041	0.036	0.590	0.06	0.061	0.054	0.885
35	Nitrobenzene	1.13	1.151	0.937	7.612	1.01	1.029	0.837	6.799
36	<i>o</i> -Nitrotoluene	1.94	1.976	1.699	12.390	1.06	1.079	0.928	6.767

formic and butyric acids, acetone and benzaldehyde leads to the Eq. (10) with  $R = 0.952$ :

$$\lg S_g = -0.646 + (12.499 \pm 1.343) f(n^2) + (2.238 \pm 0.753) \cdot 10^{-3} B - (0.029 \pm 0.016) E_T - (4.273 \pm 0.669) \cdot 10^{-3} \delta \quad (10)$$

$$R = 0.951, s = \pm 0.229$$

In this case the terms with  $f(\varepsilon)$  and  $V_M$  were found to be insignificant as well; more evidently the effect of  $E_T$  can be observed – its exclusion decreases the value of  $R$  of the obtained three-parameter equation till 0.945.

Although the expression obtained for all solvents that generalize their swelling amounts in moles  $S_M$  may be characterized by  $R$  of the same order – 0.879, for obtaining of the equation with the acceptable value of  $R = 0.956$  it is necessary to exclude from consideration the data for already 6 solvents, *i. e.* ~ 20 % of the total amount – formic

and butyric acids, acetone, benzaldehyde, acetophenone, and nitrobenzene. In this case the factors  $f(\varepsilon)$  and  $E_T$  are found to be insignificant again:

$$\lg S_M = 0.889 + (10.793 \pm 1.354) f(n^2) + (2.293 \pm 0.738) \cdot 10^{-3} B - (0.037 \pm 0.015) E_T - (3.553 \pm 0.624) \cdot 10^{-3} \delta^2 \quad (11)$$

$$R = 0.951, s = \pm 0.212$$

Further excluding of the term with  $E_T$  leads to decreasing of  $R$  till 0.941 and of the term with  $B$  – till  $R = 0.934$ .

Hence, at the large contact time between rubber and organic solvents the swelling index is determined by the same factors – the solvents' ability to nonspecific solvation, which depends on their polarizability and their cohesion that counteracts swelling. However, some influence (although insignificant) of the factor of specific solvation is observed.

The same regularities were noted at generalization of the data on crude rubber swelling (Table 2, column II). First it must be noted here that almost all solvents (except lower alcohols) are adsorbed several times better than in the case of cured rubber probably due to both its less dense structure and the presence of double bonds. In the limit this rubber dissolves in a number of solvents.

The generalization of the respective data on  $S_v$  for 31 solvents after swelling during one day leads to the expression with  $R = 0.890$ , however the excluding from calculation of the data on rubber swelling in formic and butyric acids, benzaldehyde, and nitromethane allows to get the adequate Eq. (12):

$$\begin{aligned} \lg S_v = & 1.065 + (13.695 \pm 2.476) f(n^2) - \\ & - (1.040 \pm 1.147) f(\varepsilon) + (2.439 \pm 1.360) \cdot 10^{-3} B - \\ & - (0.032 \pm 0.022) E_T - (7.182 \pm 1.284) \cdot 10^{-3} \delta^2 - \\ & - (1.497 \pm 3.302) \cdot 10^{-3} V_M \end{aligned} \quad (12)$$

$$R = 0.951, \quad s = \pm 0.306$$

After exclusion of insignificant parameters the acceptable correlation score can be achieved taking into account only two parameters, namely  $f(n^2)$  and  $\delta^2$ :

$$\begin{aligned} \lg S_v = & 0.046 + (13.485 \pm 1.860) f(n^2) - \\ & - (8.3 \pm 0.6) \cdot 10^{-3} \delta^2 \end{aligned} \quad (13)$$

$$R = 0.950, \quad s = \pm 0.328$$

At generalization of the data on  $S_g$  for the increase of the initial value of  $R = 0.902$  the exclusion of the data for the same four solvents is necessary, thus the equation with  $R = 0.960$  has been obtained:

$$\begin{aligned} \lg S_g = & 0.826 + (15.558 \pm 2.253) f(n^2) - \\ & - (2.487 \pm 1.057) f(\varepsilon) + (3.609 \pm 1.382) \cdot 10^{-3} B - \\ & - (0.014 \pm 0.020) E_T - (7.925 \pm 1.230) \cdot 10^{-3} \delta^2 - \\ & - (2.838 \pm 3.254) \cdot 10^{-3} V_M \end{aligned} \quad (14)$$

$$R = 0.960, \quad s = \pm 0.302$$

and after excluding insignificant parameters

$$\begin{aligned} \lg S_g = & 0.024 + (14.533 \pm 2.181) f(n^2) + \\ & + (1.30 \pm 1.00) \cdot 10^{-3} B - (9.00 \pm 0.70) \cdot 10^{-3} \delta^2 \end{aligned} \quad (15)$$

$$R = 0.950, \quad s = \pm 0.336$$

The influence of the factor of basicity is also relatively insignificant. A two-parameter equation obtained after the exclusion of this factor is characterized by the value of  $R = 0.940$ .

The results obtained in the case of the generalization of the data expressed in moles ( $S_m$ ) are rather worse. The initial value  $R = 0.889$  may be increased till the acceptable level by exclusion of the data for formic acid, benzaldehyde, nitromethane, and acetophenone:

$$\begin{aligned} \lg S_m = & 2.945 + (13.788 \pm 2.494) f(n^2) - (2.862 \pm 1.041) f(\varepsilon) + \\ & + (4.001 \pm 1.361) \cdot 10^{-3} B - (0.020 \pm 0.019) E_T - (7.689 \pm \\ & \pm 1.231) \cdot 10^{-3} \delta^2 - (6.554 \pm 3.205) \cdot 10^{-3} V_M \end{aligned} \quad (16)$$

$$R = 0.956, \quad s = \pm 0.297$$

However, only one parameter was found to be insignificant here –  $E_T$ ; its exclusion decreases  $R$  insignificantly – till 0.955. The exclusion of any other parameter leads to obtaining of a four-parameter equation with  $R$  lower than the acceptable limit of 0.95. The parameter of the molar volume is also relatively insignificant:  $\lg S_m = 2.035 + (11.466 \pm 2.131) f(n^2) - (2.458 \pm 1.122) f(\varepsilon) +$

$$+ (2.30 \pm 1.20) \cdot 10^{-3} B - (7.50 \pm 0.80) \cdot 10^{-3} \delta^2 \quad (17)$$

$$R = 0.947, \quad s = \pm 0.327$$

Further exclusion of the terms  $f(\varepsilon)$  or  $B$  leads to the equations with  $R \approx 0.940$ .

## 4. Conclusions

The performed mathematical analysis of the data from [3] on swelling of both vulcanized and crude rubber in solvents of different nature makes it possible to conclude that the swelling index is determined mainly by nonspecific solvation, defined by solvent polarizability, and by their cohesion, that counteracts this process. Contrary to the common opinion that the swelling index for rubber depends on penetrants' polarity, the above mentioned factor, as well as their molar volume, is insignificant. The influence of possible specific solvation is insignificant as well.

In contrast to the data of [14-16] on some other polymers swelling, according to which the data may be generalized rather in moles of liquid adsorbed by rubber, in the case of crude rubber statistically better results may be obtained at generalization of the data expressed in volume parts.

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## ЗАЛЕЖНІСТЬ СТУПЕНЯ НАБРЯКАННЯ ПРИРОДНОГО КАУЧУКУ ВІД ВЛАСТИВОСТЕЙ ОРГАНІЧНИХ РОЗЧИННИКІВ

**Анотація.** Математичний аналіз даних з набрякання природного каучуку показує, що ступінь поглинання розчинників каучуком залежить, в основному, від їхньої здатності до неспецифічної взаємодії і когезії, що протидіє цьому процесу.

**Ключові слова:** лінійні багатопараметрові рівняння, ступінь набрякання, органічні розчинники.