УДК 630*.812.214

R. Makitra, **H. Midyana**, **L. Bazylyak**, **O. Palchykova**,
V. F. Shkodich, **A. M. Кochnev**, **G. E. Zaikov**

AN INFLUENCE OF THE SOLVENTS' PHYSICAL–CHEMICAL PROPERTIES ON THE PROCESS OF FUELS SWELLING

Ключевые слова: разбухание топлива, набухание угля, линейный принцип свободной энергии.

Подходы, применяемые до настоящего времени для оценки процесса набухания угля , которые основаны на теории регулярных растворов, не дают возможность количественно обобщить экспериментальные данные. Соотношение между физико-химическими свойствами растворителей и степенью разбухания угля в них может быть получено только с использованием линейных многопараметрических уравнений, учитывающих влияние всех процессов, протекающих в системе; при этом основной и молярный объем жидкостей являются определяющими. Такой подход эффективен при обобщении данных, относящихся к добыче угля.

Keywords: fuels swelling, coal swelling, linear free energies principle.

The approaches applying till the present time to the consideration of coal swelling process which are based on the theory of the regular solutions don't give the possibility quantitatively to generalize the experimental data. An adequate relationship between physical–chemical properties of the solvents and coal swelling degree in them can be obtained only with the use of the linear multiparametric equations which take into account the effects of the all processes proceeding into the system; at that, the basicity and the molar volume of the liquids are determining. This approach is effective under the generalization of data concerning to the coal extraction.

Introduction

An action of the organic solvents on solid fuels, *namely* black and brown coal or peat is under the active investigation for a long time. This is caused by two reasons; *specifically*, this is one among successful methods of the solid fuels structure study with the aim of their technological application for obtaining of the so–called montan–wax or it is used for obtaining of the low–molecular liquid extracts which can be next transformed into synthetic liquid fuel via the hydrogenation. It is necessary to add, that the interaction of coal with the solvents is taken as a principle of the coals liquefaction under their transformation into the liquid fuel.

The first stage of the interaction into the systems «coal–solvent» is their swelling and expansion as a result of the molecules of liquid invasion into the pores and into the structure of coal. Depending on the nature of solvent and also on coal itself its volume can be multiplied increase many times; correspondingly, the increment of weight for the investigated sample can achieve 100 and more percentage.

A review of the early works concerning to the coal swelling is presented in [1–2]. Let's note, that still in fifty years the coals swelling process was considered as the first stage of their extraction and it was connected with their physical–chemical interaction with the solvents [3]. The process itself was explained by two reasons: first is caused by the adsorption and absorption of liquid in pores, and accordingly to the second one the swelling process is connected with the change of the cohesion energy of the solid and liquid phases of a system. *Sanada* and coworkers [4–6] considered that the coal represents by itself the natural three–dimensional polymer, and in accordance with the *Flory–Huggin's* theory, the change of a free energy under the coal swelling represents by itself the conditional sum of the polymer and the solvent mixing energies; this free energy change is determined first of all by the difference in the *Hildebrand's* solubility parameters δ of both components:

$$\Delta G = [ln(1 - \O_2) + \chi\O^2 + \O_2], \qquad (1)$$

where $\O_2$ is a volumetrical part of the netting structure (of polymer) into the swollen system; and the parameter χ indicating the interaction of polymer and the solvent is equal to

$$\chi = \frac{\beta + (\delta_1 - \delta_2)^2 V_1}{RT}, \qquad (2)$$

where δ_1 and δ_2 are the *Hildebrand's* parameters of the solubility for the solvent and for the polymer and they are equal to $[(\Delta H_{vap} - RT) / V_{mol}]^{1/2}$ respectively; the empirical term β is the correction factor taking into account the number of the branching points into the structure of polymer.

After the insignificant transformations it can be obtained the *Flory–Renner's* equation. Such equation helps to calculate the sizes of the polymer link between the cross bonds M_c

$$M_c = \frac{\rho_2 V_1 \O_2^{1/3}}{[-ln(1-\O_2) - \chi\O_2^2 - \O_2]}, \qquad (3)$$

where ρ_2 is the density of a polymer into solution; V_1 is molar volume of the solvent.

Coefficient χ is determined empirically for each solvent and, of course, from the concentration dependence of the osmotic pressure taking into account a series of the assumptions.

In the work of *Sanada* [5] and subsequent works of other authors, the swelling degree in the volumetric parts Q is represented as a function on the δ of solvents. These data in the most cases form the parabolic, a so–called «bell–like» curve with a maximum for the solvent, δ_2 of which in accordance with the theory of the regular solutions is equal or is near to δ_1 of a polymer (coal). In reality, in the *ref.* [5] it was already maintained, that only the approximated dependencies are obtained for coal since a number of experimental data concerning to Q are visibly take one's leaved from the generalizing curve. Under the extraction of vitrain from the Yubary field (the content of carbon consists of 85,2 %) using the solvents into *Soxhlet's* apparatus it was determined in *ref.* [4], that the maximal yields of the extract are observed at their molar volume about 10 $cm^3/mole$ (ethylendiamine, dimethylformamide, cyclohexanone 24 – 26 %, acetophenone 35,6 %, pyridine 33,2 %); this fact authors explain by the influence of the value of cohesion energy. However, there are a plenty of exclusions, *for example*, for butanol V_{Mol} = 9,5, but the yield of an extract in this case is only 0,8 %. The explanation of this deviation as a result of the solvent association, which caused by the presence of the hydrogen bond, seems unconvincing, since under the experiments conditions (the extraction proceeds into *Soxhlet's* apparatus, and, so under the boiling temperature) such association will be insignificant. It was discovered in *ref.* [6], that the value M_c for Japanese coal with the carbon content less than 80 % is unreal low – only 10 *(!)*, next this value is sharply increased and achieves the maximum M_c = 175. Authors starting from the following positions at the explanation of this fact: *firstly*, experimental determinations were carried out in pyridine, in which the specific interactions can take place and, *secondly*, this deviation can be caused by the mistakes at the determination of χ coefficient. It is necessary to notify that although it is hardly to estimate the verisimilitude of determined in such a way molecular weights of structural links of a coal between the points of cross bonds, however, in a case of the synthetic polymers in a same way determined masses of links visible don't agree with the values obtained in accordance with others methods. The same approach was discussed especially in detail in the work of *Kirov* and co–authors [7] on example of swelling (and extraction) of three kinds of bituminous Australian coal. These authors confirmed the main observations of *Sanada, namely* the swelling degree Q increases from ~ 1,4 in hydrocarbons to ~ 2 in pyridine (δ – 11,0) and again is decreased to ~ 1,5 in alcohols. Calculated on this basis value δ of coal is increased steadily at the increase of the carbon content from 70 % till 87 % and in a case of more metamorphosed coal is sharply decreased again. Data concerning to the extraction of *Greta* coal are evidence of the maximal yield of extract (more than 20 %) under its treatment with ethylendiamine and dimethylformamide (δ – 11,5), however, authors admit a fact that this is a consequence of the specific interactions, since in alcohols from the δ by the same order the yield of the extract is only 1 – 2 %. But for all that, authors concluded, that although the swelling degree of coal is not directly connected with the molecular characteristics of the absorbed liquids, however the determining factor is their parameter of the solubility in spite of the fact that at the detailed consideration of the dependencies $Q = f(\delta)$ (or $f(\delta^2)$) there are a number of deviations (as same as in *ref.* [5]) from the ideal curve for many solvents are observed.

In spite of the indicated lacks, the described above approach is applied in later works concerning to the coal swelling for the results interpretation. It is necessary to indicate a plenty of investigations devoted to the swelling studies of coal № 6 from the Illinois State (standard in USA coal for the carbon–chemical investigations) [8 – 10]. General conclusions are in good agreement with the results of *ref.* [5, 7]. Comparison of the swelling degree for different coal in some solvents depending on the content of carbon has been done in *ref.* [11]. Similar investigation for Kansk–Achynsk Siberia coal was carried out in *ref.* [12, 13]. In both cases, as same as in *ref.* [**7**], it was proved the dependence of swelling degree of coal on the carbon content in it.

It's logically to assume the influence of the specific interactions during the swelling process, since the values of the parameters of coal solubility δ^2, which are determining accordingly to the *Flory–Renner's* equation, are differed. It depends on fact, if the data for all solvents are taking into account in calculations or such calculations are performed with the exclusion of results for the solvents which can be acceptors of the hydrogen bonds (amines, ketones). Different results have been obtained also at the application of other calculations methods, especially of the *Van–Krevelen's* method [14].

It is notified in *ref.* [15], that the swelling of some coal does not agree with the thesis of the regular solutions theory; that is why, to calculate the parameter χ for them is impossible. Authors explain this fact by the presence of oxygen atoms in the investigated coal. But also the molecular mass of separate sections (clusters) between the points of crossing for methylated or acetylated samples is equal only to 300 – 600 in accordance with the calculations (that is unreal).

It is necessary to notify, that the critical analysis of the *Flory* theory application for the determination of molecular mass and the crossing density of the coal structure has been done in the *Painter's* works [16]. Authors assert that the possible formation of the hydrogen bonds between the hydroxy groups of the low–metamorphized coal and the basic solvents plays an important role here; that is why, even a lot of the empirical amendments introduction into the calculations leads to the obtaining of the understated values of molecular masses of clusters.

Taking into account the above–mentioned lacks many authors concluded that the theory of regular solutions is insufficient for adequate description of the coals swelling process in different solvents (and also for their extraction) since such theory does not take into account the possible specific solvation of the active structures of coal and first of all its heteroatoms [17], especially by formation of the hydrogen bonds. In order to take into account the possible acid–base interactions it was proposed by *Marzec* and co–authors [18, 19] to determine the swelling degree as a function of donor number of *DN* solvents or as a function of their donor and acceptor numbers disparity accordingly to *Gutmann*. However, corresponding analysis of data concerning to the swelling of the silessian bituminous coal showed the following: although between the swelling degree Q and *DN* the visible symbasis exists and the deviations from the straight line are less than for the function $Q = f(\delta)$, *however*, it is complicated to confirm about the quantitative description of the process. The same conclusion about only qualitative character of such dependence has been done by authors in *ref.* [13] on example of swelling the brown *Kansk–Achynsk* coal and some kinds of the *Donbas* coal.

Above–mentioned facts and disagreements lead to the conclusions in *ref.* [20] that the sorption of solvents by coal is very complicated process covering also the changes under the action of a solvent into the coal structure and other possible nonequilibrium phenomena. That is why, an application for coal of the theories developed for the description of thermodynamically equilibrium process of the simple synthetic polymers swelling is unwarranted first of all due to neglect by existing chemical (specific) solvation interactions. As it was confirmed in many investigations, the swelling *Flory–Huggins's* model based on the theory of regular solutions is not sufficiently consistent with the real experimental data. It is caused by a range of simplifying assumptions putted into the base of this model and, first of all, by the presence of full isoentalpic mixing (solution) of two phases that is in disagreement with the reality – even in a case of the polymers which do not contain the donor–acceptor groups into the structure a swelling and solution processes are accompanied with a great enthalpy effect; it is known, that even non–specific solvation is often accompanied by the changes of free energy and enthalpy of the system. And isoentalpy will be not remained in a case of the possible donor–acceptor (acid–base) interaction, which is often observed in a case of the synthetic polymers with the content of heteroatoms (polyurethane, nitryle rubbers) and is observed in a case of coal as a result of the presence in it of such groups as *–OH*, *–COOH*, tertiary atom of nitrogen and *etc*.

The principle of the linearity of free energies *(LFE)* is applied in chemistry of solutions over 30 years for quantitative description of the solvents influence on the behavior of dissolved substances (spectral characteristics, constants of the reaction rate). In accordance with this principle general change of free energy of the system consists of the separate inter–independent terms and first of all consists of the non–specific and specific solvation effects and also needed energy for the formation of cavity in the structure of liquid phase with the aim of allocation the exterior molecule introducing there. And only full sum of these all possible energetic effects gives the final (equilibrium) energy of the system [21]:

$$\Delta G = \sum \Delta g_i \ , \tag{4}$$

With taken into account, that the constants of the reaction rates are determined via the equilibrium constants of the activated reactive complex formation, and the last in part depend on the solvation processes, it was proposed by *Koppel* and *Palm* [22] the following equation in order to determine the influence of medium properties on the reaction rates of the processes proceeding in it:

$$lg\,k = a_0 + \frac{a_1(n^2-1)}{(n^2+2)} + \frac{a_2(\varepsilon-1)}{(2\varepsilon+1)} + a_3B + a_4E_T \ , \tag{5}$$

This equation takes into account the influence of the polarization $f(n^2)$ and polarity $f(\varepsilon)$ of the solvents determining their ability to non–specific solvation and also their basicities B, and electrophilicity accordingly to *Reichardt* E_T characterizing their ability to introduce into acid–base interactions (specific solvation). Appropriateness of this equation for the generalization of experimental data of the dependencies of reactions rates (and also spectral characteristics of dissolved substances) on physical–chemical characteristics of the solvents has been proved by a number of hundred examples.

For the processes of the phase equilibria it was proposed by us to add to the *Koppel−Palm* equation the fifth term, which takes into account the density of the energy of solvents cohesion proportional to the squared *Hildebrand's* solubility parameter δ^2. Due to this fact necessary energy for the formation of cavity for the allocation of the molecule introducing into liquid phase is taking into account:

$$lg\,K = a_0 + a_1f(n^2) + a_2f(\varepsilon) + a_3B + a_4E_T + a_5\delta^2 \ , \tag{6}$$

Modified equation was turned out effective for the determination of the solvents influence on the equilibrium of such processes as solubility in different media of gases or solids, the distribution of substances between two phases, resembling equilibrium processes. So, it will be logically to try to use the equation (6) for the swelling processes. As a matter of fact, it was turned out, that with the use of this equation it is possible to determine the quantitative connection between the properties of the solvents and the equilibrium swelling degree for a number of polymers, and also for a coal [23 – 25].

In order to achieve the satisfactorily high values of the coefficients of multiple correlations R, it is necessary to exclude from the calculations the data for some quantity (3 – 5) of the solvents. It is hard to explain this. Besides, it was not quite clear the model of the interactions into the system. In a case when the solvation processes are energetically advantageous (ΔG < 0) and that is why promote to the swelling process, that is to the solvent penetration into the structure of polymer, then the role of δ^2 factor is remained not clear. Such factor characterizes the energy needed for the cavity formation into the structure of the liquid; at the same time, unlike to the evaporation process, under the swelling of substances into liquid the following process takes place: liquid solvent penetrates into the structure of solid polymeric phase mostly as the whole.

At the beginning of the ninetieth the works of *Aminabhavi* are appeared [26]. These worked were concerned the polymeric membranes swelling into organic solvents and to the diffusion rate D of the liquids into their structure in which these values were considered as dependencies from the molar volume V_{Mol} of the liquids. Generalizations obtained in *ref.* [26] are rather unsatisfactory – approximately linear dependencies lgQ or lgD on V_{Mol} are observed only in the homologic ranges or in the case of similar solvents. But the approach itself must be considered as logical: it is clear, that the bigger sizes of the introducing molecule, the more difficult it will be penetrated into the structure of polymer including the adsorbent interstice. Low generalizing ability of the dependencies presented in the work [26] can be explained by fact that they do not take into account the solvation effects, which promote to liquids penetration. That is why the equation (6) has been expanded by us by the additional term taking into account the influence of the molar volume V_{Mol} of the solvents [27]:

$$lg\,Q = a_0 + a_1 f(n^2) + a_2 f(\varepsilon) + a_3 B + a_4 E_T + a_5 \delta^2 + a_6 V_M\,, \quad (7)$$

Such equation under the stipulation that *Q* is represented not in the volumetric parts accordingly to the *Flory–Huggins's* model but in accordance with the interpretation of equilibrium processes in the chemical thermodynamics as a moles of the solvent absorbed by one gram or by one cm^3 of polymer was turn out effective under the generalization of data for swelling degree of different synthetic polymers, *for example*, polyethylene, in different organic solvents depending on their physical–chemical parameters [28]. That's why, it was necessary to check the possibility of the equation (7) application for the generalization of data concerning to coal swelling since this equation takes into account *i)* the all most important possible energetic effects caused by possible donor–acceptor interaction of active groups of the coal with non–inert solvents including the formation of hydrogen bonds; *ii)* the effects of non–specific coal solvation with solvents which are caused by a presence in it the cyclic aromatic structures as a result of which the visible influence of the ability of some solvents for the polarization can be expected; *iii)* and also the endothermic effects as a result of steric complications of the solvents penetration *(V_M)* and *iv)* destruction of the liquid phase structure *(δ^2)*. The meaningfulness of the parameter V_M was confirmed in *ref.* [29−30], where it was shown that the quantity of the solvent's moles absorbed by the coal weight unit is decreased symbasis to the V_M of the solvent; at the same time, in *ref.* [31] it was shown, that under the coals swelling in homologous series of the solvents by the same basicity (amines, alcohols, *ect.*) the value *lgQ* is linearly decreased till the number of Carbon's atoms, that is, to their V_M. Also the values of the correction parameter χ from the equation (1) can be connected with the physical−chemical characteristics of the penetrants via the equation (7) [32].

Data concerning to a swelling of the most popular coal (namely, coal *Illinois № 6*) have been taken by us as a main object of our investigations. This coal is the standard object for the carbon–chemical investigations in USA. These data were already analyzed earlier in works [23 – 25] with the aim of their generalization accordingly to equation (6), but obtained results were unsatisfactory. Evidently this was caused by two factors: *i)* the influence of the molecules sizes of the solvents penetrating into the coal structure (their molar volume) was not taken into account in these works; *ii)* starting values of the swelling degree *Q* were given accordingly to original works [9 – 11] in *ml* (sometimes in *g*) of the solvent absorbed by 1 *ml* or 1 *g* of coal since the *Flory–Huggins's* model has been used by authors (this model uses the volumes of two liquids which are mutually mixed). If to consider the coal swelling process (and generally polymers swelling processes) as thermodynamically equilibrium process then the free energy change at the penetration and at the absorption of a solvent and, respectively, the equilibrium constant of this process, it is preferable to determine the quantity of connected solvent in molar units.

In the presented paper we have checked the efficiency of the above–mentioned factors considering studying the swelling process in organic solvents. Illinois coals are low–metamorphized, bituminous and contain 20 – 31 *%* of volatile substances, are characterized by ash content 8 – 12 *%* and sulphur content 4 – 7,8 *%*. Investigated in *ref.* [8−10] sample was characterized by following composition: *C* 79,8; *H* 5,11; *N* 1,8; $S_{org.}$ 2,0 and *O* 11,2 *%*. The samples were pulverized extracted from the soluble components with pyridine [8], were washed by water and after vacuum–drying they were saturated by solvent's steams till their full saturation at room temperatures in the closed vessels. Authors give the ratio of the weights for swelled samples respectively to the starting *W*; they were recalculated in the quantities of solvent moles absorbed by 1 *g* of coal S_M.

Table 1 - Experimental [8] and calculated in accordance with the two−parametric equation (8) values of the swelling degree S_M of the coal *Illinois №* 6

Solvent	Experiments			Calculations		
	W	$S_M 10^3$	lgS_M	lgS_M	ΔlgS_M	Δ %
Pyridine	1,87	11,00	–1,959	–1,958	–0,001	0,1
Dioxane	1,64	7,264	–2,139	–2,143	0,005	0,2
CH_2Cl_2	1,60	7,064	–2,151	–2,179	0,028	1,3
Clorobenzene	1,48	4,264	–2,370	–2,364	–0,006	0,3
Isopropanol	1,45	7,489	–2,126	–2,136	0,010	0,5
Toluene	1,41	4,450	–2,352	–2,364	0,012	0,5
Ethanol	1,40	8,682	–2,061	–2,069	–0,008	0,4
Benzene	1,38	4,864	–2,313	–2,283	0,030	1,3
Acetonitrile	1,34	8,283	–2,082	–2,056	0,026	1,2
Cyclohexene*	1,11	1,307	–2,884	–	–	–

Note: *data excluded from the final calculations

Generalization of studied data for 10 solvents in accordance with the fifth–parameter equation (6) leads to the expression with unsatisfactory low value of correlation coefficient *R* = 0,81 [23]. Exclusion from the consideration the most uncoordinated data for dioxane gives the possibility to obtain the fifth–parameter equation with low, but acceptable degree of connection *R* = 0,941. At the same time, consideration of the molar volume factor and the change of weight parts on the molar ones essentially improve the correlation – for all 10 studied solvents *R* = 0,940, and after the exclusion the data concerning to cyclohexene for the rest 9 solvents we obtain the equation with high connection degree *R* = 0,996 [33].

There are only two decisive parameters here – *the basicity* which assists to the swelling process and *the molar volume*, which opposites to this process; taking into account the needed energy and the negotiation of the cohesion forces have only insignificant influence and the exclusion of this parameter from the calculations practically does not worsen the equation

$$lg\,S_M = -1{,}96 + (0{,}665 \pm 0{,}074)10^{-3} B - (4{,}12 \pm 0{,}58)10^{-3} V_M\,;$$

$$R = 0{,}984 \;\; and \;\; S = 0{,}030\,, \quad (8)$$

Obtained equations have greater predicted ability comparatively to the fifth–parameter equation obtained in the *ref.* [23], which does not take into account the factor of the molar volume.

The influence of the factor of molar volume is confirmed by fact that between lgS_M and V_M the neatly marked symbasis is observed, *namely*: with increasing of

V_M the value lgS_M is decreased. The action of other decisive factor – solvents basicity – is opposite, in other words, with the basicity increasing the symbate increasing of lgS_M is observed. Evidently, this is caused by the specific solvation of acid centers, which are in the macromolecule of coal and, first of all, of hydroxy groups. Their presence can be assumed taking into account a great number of the oxygen in the Illinois coal. Comparison of these two oppositely directed dependencies leads to the conclusion, that they are mutually compensated. Although these dependencies are only symbate, but the algebraic sum of the influence of these two factors is practically linearly connected with the respective values lgS_M [34]. The third factor is the density of the cohesion energy, which is proportional to needed energy for separation of absorbed molecules from the structure of liquid phase; this factor respectively also decreases the swelling value. However, the influence of this value is insignificant; this fact is confirmed by negligible decreasing of the R value at its exclusion only from 0.991 to 0,984. The possible processes of non–specific and electrophilic solvation practically do not impact on the value S_M.

In *ref.* [10] authors also have been studied the swelling process of the coal *Illinois № 6* in the liquid phase. Swelling degree S_V has been studied volumetrically as the ratio of volumes of swelling sample to the starting one. Unlike to [9], it was investigated the process in a range of amines including the primary ones, able to the formation of hydrogen bonds and also alcohols. At the generalization of these data in accordance with the fifth–parameter equation without taking into account of V_M for the all 17 solvents it was obtained the equation with the low value R = 0,861; in order to obtain the satisfactory correlation it is necessary to exclude from the consideration the data for the methyl– and dimethylanilines [25].

Table 2 - Experimental [10] and calculated in accordance with the equation (10) values of swelling degree for the coal *llinois №* 6

Solvent	*Experiments*			*Calculations*	
	S_V	S_M10^3	lgS_M	lgS_M	ΔlgS_M
2–Picoline	2,76	17,84	–1,749	–1,794	0,045
Pyridine	2,75	21,72	–1,663	–1,808	0,145
Butylamine	2,64	16,57	–1,781	–1,941	0,160
Propylamine	2,45	17,62	–1,754	–1,655	–0,099
Aniline	1,99	10,86	–1,964	–2,205	0,241
2–Hexanon	1,98	8,120	–2,090	–2,312	0,221
Methylaniline	1,44	4,052	–2,392	–2,037	–0,355
Propanol	1,36	4,820	–2,317	–2,240	–0,077
Ethanol	1,34	5,824	–2,235	–2,194	–0,041
Butanol	1,34	3,715	–2,430	–2,242	–0,188
Methanol	1,23	5,690	–2,245	–2,204	–0,041
Dimethylaniline*	1,10	0,789	–3,103	—	—
Isopropanole*	1,06	0,784	–3,106	—	—
Toluene	1,06	0,562	–3,250	–3,311	0,061
p–Xylene	1,06	0,487	–3,312	–3,326	0,013
m–Xylene	1,05	0,407	–3,390	–3,293	–0,097
Benzene	1,04	0,447	–3,350	–3,362	0,012

Note: *data excluded from the calculations

In Table 2 presented the starting values of S_V from *ref.* [10] and calculated on their basis quantities of solvent's moles absorbed by 1 *g* of coal – S_M and lgS_M. In this case for 17 solvents it was obtained by means of the six–parametric equation (7) a relatively low value of R (only 0,884) too, but after the exclusion of data for isopropanol and dimethylaniline we will obtain the equation (9) with a high correlation degree:

$$lgS_M = -2{,}91 + (0{,}454 \pm 1{,}40)f(n^2) + (5{,}73 \pm 1{,}22)f(\varepsilon f + (1{,}43 \pm 0{,}37)10^{-3}B - (2{,}99 \pm 2{,}20)10^{-3}E_T - $$
$$-(0{,}722 \pm 0{,}947)\delta^2 - (6{,}52 \pm 4{,}54)10^{-3}V_M$$

$$N = 15\,,\ R = 0{,}981,\ S = 0{,}160\,, \qquad (9)$$

and after the exclusion of insignificant factors

$$lg\,S_M = -4{,}34 + (3{,}42 \pm 0{,}69)f(\varepsilon) + (2{,}02 \pm 0{,}27)10^{-3}B - (0{,}86 \pm 2{,}55)10^{-3}V_{Mol}$$

$$R = 0{,}968 \text{ and } S = 0{,}172\,, \qquad (10)$$

In this case *the basicity* and *the molar volume* of the solvents are decisive factors too, the influence of which is oppositely directed. An appearance of the polarity as significant factor is connected with the specific selection of high polar solvents (alcohols, amines).

Accordingly to [9] the swelling process of the Illinois coal № 6 has been carried out principally under other conditions, *namely*: the samples were previously extracted with pyridine, dried coal was standed till the full saturation with vapors at 100 ^0C in closed metallic ampoules (with the exception of phenol, investigating temperature of which is 182 ^0C). Authors presented the results of investigations as the ratio of swelling W (in percentages) that is the ratio of weights of swelling sample after 1 hour to the dried sample. These data have been previously generalized in the work [24]. Low value R for the all 12 solvents equal to 0,876 after the exclusion from the consideration data concerning to the phenol and tetrahydrophurane is increased till 0,972. Essentially better results were obtained with taken into account the molar volume factor and after recalculation of W in S_M.

The data concerning to W taken from [**9**] and calculated on their basis swelling values in moles S_M and lgS_M are presented in *Table* 3; the generalization of these data in accordance with the sixth parameter equation (7) leads to higher degree of relationship R = 0,909, and the exclusion from the consideration of one solvent (butylamine) gives the possibility to obtain the equation with satisfactory degree of relationship R = 0,974; an additional exclusion of the dimethylformamide gives the equation (11) with R = 0,991:

$$lg\,Q = -2{,}61 + (3{,}50 \pm 0{,}82)f(n^2) + (2{,}30 \pm 0{,}46)f(\varepsilon f - (0{,}33 \pm 0{,}14)10^{-3}B - (2{,}37 \pm 6{,}8)10^{-3}E_T +$$
$$+ (0{,}70 \pm 0{,}24)10^{-3}\delta^2 - (1{,}5 \pm 2{,}1)10^{-3}V_M$$

$$N = 10,\ \ R = 0{,}991 \text{ and } S = 0{,}055\,, \qquad (11)$$

and after the exclusion of insignificant factors

$$lg\,Q = -2{,}51 + (2{,}66 \pm 1{,}20)f(n^2) + (1{,}80 \pm 0{,}60)f(\varepsilon) - (7{,}4 \pm 5{,}0)10^{-3}E_T - (2{,}8 \pm 2{,}9)10^{-3}V_M$$

$$R = 0{,}964 \text{ and } S = 0{,}086\,, \qquad (12)$$

With the molar volume of the solvents increasing the coal swelling degree is decreased; the same is an effect of the ability to electrophilic solvation. Unlike to both previous cases, the positive influence of the solvents basicity (*namely* their ability to form the donor–acceptor bonds with acid groups of the coal) here is insignificant evidently as a consequence of especial influence of the conditions of experiment carrying out. Under higher temperatures the hydrogen bonds are easy decomposed. At the same time, the possible positive influence of the factors of non–specific solvation $f(n^2)$ and $f(\varepsilon)$ is observed. Calculated values lgS_M and their discrepancy with the experiment ΔlgS_M are presented for the comparison in *Table* 3.

Table 3 - Experimental [9] and calculated in accordance with the equation (12) values of «swelling ratio» of soluble part of coal for the coal *Illinois* № 6

Solvent	*Experiments*			*Calculations*	
	W	$S_M 10^3$	lgS_M	lgS_M	ΔlgS_M
Dimethylformamide	6,2	60,54	–1,218	—	—
N–Methylpyrrolidone	5,7	37,17	–1,430	–1,503	0,073
Dimethylsulphoxide	5,5	49,19	–1,308	–1,407	0,099
Ethylendiamine	4,6	33,24	–1,478	–1,466	–0,012
Aniline	4,6	34,13	–1,467	–1,513	0,047
Butylamine*	3,8	29,82	–1,525	—	—
Pyridine	3,7	28,67	–1,543	–1,475	–0,068
Phenol	3,4	22,49	–1,648	–1,512	–0,136
Pipyridine	3,0	19,26	–1,543	–1,475	–0,068
Tetrahydrofuran	2,8	22,97	–1,639	–1,615	–0,024
Toluene	2,6	16,65	–1,779	–1,874	0,095
Hexane	1,6	6,902	–2,161	–2,134	–0,027

Note: *data excluded from the calculations

Both the equilibrium swelling degree and the kinetics of this process depend on the character of the solvent. In the work [10] it has been studied the swelling rate of the coal Illinois № 6 volumetrically in different solvents; on the starting stages it is ordered to the pseudo–first order reactions kinetics as is observed in the case of polymers swelling too. It helped to determine the respective constants rate of the process *k*, which are presented in *Table* 4. In *ref.* [25] we have generalized these data for 24 solvents with the use of the fifth–parameter equation (6). For the all maximal sequence of the data the value of correlation multiple coefficient *R* was very low and equal to 0,694 and only after the exclusion from the calculation the data for five solvents (that is practically 20 %) it could obtain the satisfactory value of *R* = 0,957. Additional taking into account the influence of molar volume, that is transition to sixth parameter equation, gives the possibility to obtain the expression with *R* = 0,883. And in order to obtain the satisfactory correlation it was enough to exclude from the calculations data for only two solvents, *namely* 2–hexanone (methylbutyl ketone) and triethylamine:

$$lg\,k = 2{,}20 - (2{,}55 \pm 3{,}84)f(n^2) + (1{,}08 \pm 4{,}26)f(\varepsilon) + (4{,}17 \pm 1{,}12)10^{-3}B - (71{,}7 \pm 62{,}5)10^{-3}E_T - $$
$$- (0{,}92 \pm 2{,}45)\delta^2 - (42{,}8 \pm 9{,}1)10^{-3}V_M$$

$$N = 22,\ \ R = 0{,}959 \text{ and } S = 0{,}448, \qquad (13)$$

The equation terms characterizing the influence of non–specific solvation and also cohesion energy that have a great standard deviations which are more than the absolute values of the coefficients and is why are evidently insignificant. Checking the value *R* decreasing at the exclusion of these terms confirmed this assumption and helped to obtain the equation with lesser quantity of significant terms. This equation also adequately characterizes the influence of the solvents properties on the rate of their penetration into the coal structure; besides, the decisive factor in this case as same as in a case of swelling value is the influence of molar volume of the solvents, increasing of which leads to the process rate decreasing.

$$lg\,k = 1{,}12 + (4{,}85 \pm 0{,}52)10^{-3}B - (66{,}0 \pm 19{,}5)10^{-3}E_T - (42{,}1 \pm 6{,}2)10^{-3}V_M$$

$$R = 0{,}957 \text{ and } S = 0{,}418, \qquad (14)$$

Significant factor as same as in a case of the swelling degree is the solvents basicity. With the solvents basicity increasing, the process rate is also increased. The less essential is a role the solvents ability to electrophilic solvation; although this factor increases the process rate but it exclusion from the consideration decreases *R* till 0,928. The values *lgk* calculated in accordance with the equation (14) are represented in *Table* 4.

Decisive role of the V_M factor during the adsorption process of the solvents by coal is in agreement with the determined in the work [25] proportionality for the alcohols between *lgk* and steric factor E_s of the *Hammet–Taft's* equation.

So, the swelling characteristics of the Illinois coal are determined by total influence of molar volume of liquids and their ability to specific solvation. The same conclusion has been done by authors of the works [35–36] explaining the adsorption growing by increasing the donor number of the solvents via the formation of hydrogen bond by *OH*–groups of coal. But these authors have not done respective quantitative generalization giving the possibility on the basis of the linearity of free energies principle adequately to connect the properties of the liquids with their ability to interact with a coal; it was confirmed that the approaches based on the theory of regular solutions equitable only at the consideration of the swelling process in the «inert» (so–called low–basic) solvents, mainly of low–polar.

Table 4 - Experimental [10] and calculated accordingly to equation (14) values of the logarithms of the constants rate of the coals *Illinois* № 6 swelling

№	*Solvent*	*Experiments*		*Calculations*	
		$k10^5$, s^{-1}	*lgk*	*lgk*	*Δlgk*
1	Propylamine	1167,0	–1,933	–1,679	–0,254
2	Butylamine	614,0	–2,212	–2,974	0,763
3	Pyridine	316,7	–2,499	–2,655	0,155
4	2–Picoline	126,7	–2,897	–3,124	0,226
5	2–Hexanone*	125,0	–2,903	—	—
6	Methanol	53,30	–3,273	–3,183	–0,091
7	Ethanol	21,30	–3,672	–3,624	–0,048
8	Aniline	20,0	–3,699	–3,962	0,263
9	Propanol	10,90	–3,963	–4,290	0,328
10	Butanol	3,84	–4,416	–4,926	0,511
11	Isopropanol	2,54	–4,595	–4,152	–0,443
12	Methylaniline	2,47	–4,607	–4,063	–0,545
13	Butanole–2	1,32	–4,879	–4,694	–0,185
14	Toluene	0,90	–5,046	–5,334	0,288
15	Isobutanol	0,833	–5,079	–4,859	–0,220
16	Dimethylaniline	0,59	–5,229	–4,578	–0,651
17	Benzene	0,45	–5,347	–4,675	–0,671
18	Pentanol	0,376	–5,425	–5,510	0,085
19	*p*–Xylene	0,375	–5,426	–5,924	0,498
20	*m*– Xylene	0,225	–5,648	–5,919	0,271
21	*o*– Xylene	0,118	–5,928	–5,891	–0,037
22	Ethyl benzene	0,113	–5,947	–6,032	0,086
23	Cumene	0,009	–7,046	–6,716	–0,330
24	Triethylamine*	0,00038	–8,420	—	—

Note: *data excluded from the calculations

Correctness of the sixth parameter equation (7) and its simplified forms for the generalization of the swelling data was proved for other coals including the Donbas coal [37] at the parameters B and V_M, for lignites from the *Rawhile* and *Big Brown* mines (USA) and also for the *Silesian* coal (Poland).

In *ref.* [18] presented data concerning to the bituminous *Silesian* coal swelling in 21 solvents. It can be assumed, that such coal is situated between the cannel coals and gas coal (such assumption has been done on the basis of the *Silesian* coal characteristics, *namely*: *(% per daf)*: C = 80,7; H = 5,6; N = 1,9 and S = 0,9; a content of the volatile substances consists of 39,5 *%*). The swelling degree Q has been determined volumetrically at 25 ^0C starting from the increase of the volume of coal under the solvent excess till the equilibrium achievement (2−7 weeks). Appropriating values of Q are represented in Table 5.

Table 5 - Experimental [8] and calculated values of the bituminous *Silesian* coal swelling degree

Solvent	*Experiments*			*Calculations*		
	Q	S_M10^3	lgS_M	lgS_M	ΔlgS_M	*Δ %*
Benzene*	1,00	0,00	–	–	–	–
Nitrobenzene	1,10	0,98	–3,009	–3,003	0,006	0,2
Diethyl ether*	1,15	1,44	–2,842	–	–	–
Isopropanol*	1,14	1,83	–2,738	–	–	–
1,4–Dioxane	1,16	1,88	–2,726	–2,704	–0,022	0,8
Ethyl acetate	1,26	2,66	–2,575	–2,481	–0,094	3,6
Acetonitrile	1,15	2,86	–2,544	–2,499	–0,045	1,8
n–Propanol	1,23	3,08	–2,511	–2,316	–0,196	7,8
Nitromethane*	1,18	3,36	–2,474	–	–	–
Methyl acetate	1,32	3,99	–2,399	–2,528	0,128	5,4
Acetone	1,30	4,08	–2,389	–2,366	–0,023	1,0
Ethanol	1,25	4,28	–2,369	–2,316	–0,052	2,2
Methanol	1,19	4,70	–2,328	–2,402	0,075	3,2
Methyl ethyl ketone	1,49	5,47	–2,262	–2,256	–0,006	0,2
Dimethoxyethane	1,60	5,75	–2,240	–2,327	0,087	3,9
Tetrahydrofuran	1,59	7,28	–2,138	–2,138	0,000	0,0
Dimethyl formamide	1,69	8,92	–2,050	–2,118	0,069	3,3
Pyridine	2,08	13,40	–1,873	–1,711	–0,162	8,6
N–Methylpirrolidone	2,38	14,28	–1,845	–1,912	0,067	3,6
Dimethyl sulfoxide	2,04	14,66	–1,834	–2,014	0,180	9,8
Ethylenediamine*	2,08	16,17	–1,791	–	–	–

Note: *data excluded from the final calculations

Authors in *ref.* [8] consider, that inherently of the presented coal swelling process is the donor−acceptor interaction of the coals' acidic groups with the basic ones of the solvents. However, really they determined only the symbasis between the swelling degree Q and donor number of the solvent DN; at that, incomprehensible sharp bend is observed at DN = 12−13 on this dependence. In a case of hydrocarbons, ethers, alcohols it is observed only the slow increasing of Q at the DN increase, while for the carbonyl compounds of amines and dimethyl sulfide *(DMSO)* the inclination of line is essentially steeper [8]. The same peculiarity is observed also for the S_M. At the same time, the dependence between Q and δ was not determined.

In *ref.* [24] we had a go to generalize the results presented in *ref.* [8] via the fifth−parametric equation (6) without taking into account a factor of the molar volume. The obtained value R for 21 solvents was unsatisfactory (0,887) and in order to achieve the acceptable value of R = 0,958 it was necessary to exclude from the consideration the data for three solvents.

In accordance with the approach developed in *ref.* [29] we had a go to generalize the data from the *ref.* [8] by means of the equation (1), *i. e.* with taking into account of influence of the molar volume of the solvents V_M; the logarithm of the moles of solvent absorbed by 1 sm^3 of coal lgS_M determined based on the W *(see Table 5)* was used as the correlated value. However, in a case for 20 solvents (data for benzene are excluded from the consideration since for this solvent W and respectively S_M are equal to zero) the correlation is also unsatisfactory: R = 0,818; sequential exclusion of data for diethyl ether (*№* 3), isopropanol (*№* 4), nitromethane (*№* 9) and ethylenediamine (*№* 21) increases the value R till 0,877; 0,911; 0,934 and 0,969. Thus, for the 16 solvents it was obtained the sixth−parametric equation (15) which with the acceptable accuracy connects the swelling degree with the physical−chemical characteristics of the solvents:

$$lg\,S_M = -2{,}72 - (6{,}07 \pm 1{,}45)f(n) + (2{,}26 \pm 0{,}55)f(\varepsilon) + (3{,}53 \pm 0{,}33)10^{-3}B - (0{,}130 \pm 0{,}063)E_T +$$
$$+ (1{,}17 \pm 0{,}55)10^{-3}\delta^2 - 9{,}92 \pm 3{,}36)10^{-3}V_M$$

$$N = 16,\ R = 0{,}969 \text{ and } S = 0{,}104, \qquad (15)$$

By−turn exclusion of the separate terms of an equation denotes on the lesser significance of the terms with E_T (the R of the corresponding fifth−parametric equation is equal to 0,954) and with the δ^2 (R is equal to 0,951). Thereby, the swelling process of the presented coal can be adequately described with the use of the fourth−parametric equation:

$$lg\,S_M = -3{,}47 - (4{,}11 \pm 1{,}27)f(n) + (1{,}82 \pm 0{,}51)f(\varepsilon) + (3{,}50 \pm 0{,}36)10^{-3}B - (6{,}66 \pm 2{,}45)10^{-3}V_M \qquad (16)$$

$$N = 16,\ R = 0{,}951 \text{ and } S = 0{,}117$$

At the same time, the equations which do not take into account the factors of the non−specific solvation give the essentially poor results:

$$lg\,S_M = \ 3{,}02 + 3{,}0 \cdot 10^{-3}B - 3{,}85 \cdot 10^{-3}V_M;$$

R = 0,872; S = 0,171. And the three−parametric equations with taken into account of *f(n)* or *f(ε)* give the value or R ~ 0,9.

In Table 5 presented the values of lgS_M which were determined in accordance with the above presented equation. As we can see, the deviations more than ± 0,117 are observed only for the propanol, pyridine and *DMSO*. Essentially more deviations were observed also for the excluded from the calculations solvents. In a case of the isopropanol such disagreement of the calculations and experiment was caused probably by the steric difficulties, and in a case of the ethylene diamine – by the extreme high basicity. It's interesting, that in a case of the benzene, in which the swelling practically does not proceed (S_M is equal to zero), the calculation accordingly to the equation (16) gives the values $lgS_M = -3{,}49$, *i. e.* it is differed only insignificantly from zero by the value S_M.

It is necessary to stop on a role of the separate terms into equation (16). Between lgS_M and V_M the symbate decrease of the swelling degree with the liquid molar volume increasing is observed (as same as in the previous cases). In accordance with the earlier developed principles it very important is also the contribution of the acid−base interaction – the swelling degree is distinctly increased at the value of B of solvents (*see Fig.* 1), though the correlation between these values is only medium (R = 0,752 for the all points).

After the exclusion of the most deviating solvents, the value R becomes equal to 0,870. Significantly is also the influence of the non−specific solvation. After the exclusion of one among terms *f(n)* or *f(ε)* the R is decreased till 0,9, and in a case of the exclusion of both together terms this value is decreased till 0,872.

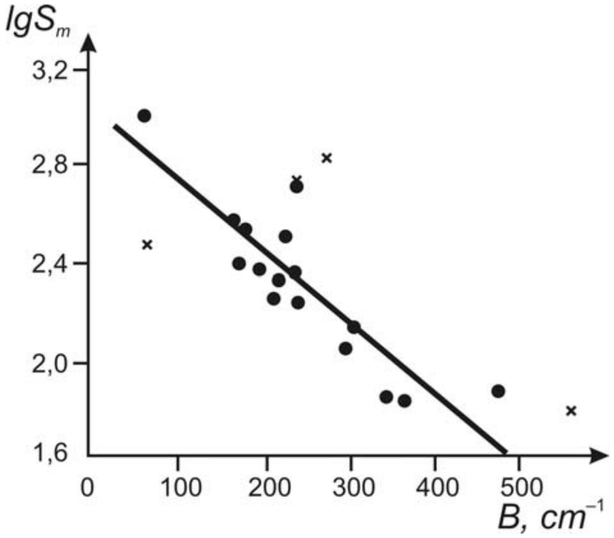

Fig. 1 - The correlation between the quantity of the absorbed solvent lgS_M by the bituminous silesian coal and the basicity B; × − data excluded from the calculation

But if to apply the equation (7) to the coal extraction data, then the factor of molar volume V_M is insignificant, and the connection between quantities of extracted substance (in *g/mole* of the solvent) and physical–chemical characteristics can be satisfactorily described by fifth parameter equation (6) or by its simplified forms; in this case possible acid–base interaction is the decisive factor, that is factor B [38 – 40]. 38This confirmation is in good agreement with the above–said: bigger molecules harder introduce into the coal structure and after equilibrium state their size does not play the role. Let us notify, that the same approach has the positive results at the data generalization concerning to the solubility of the synthetic low–molecular coal analogous – diphenylolpropane – in 20 solvents [41].

This approach is also applicable for the generalization of data concerning to the coal extraction under sub–critical conditions, but the role of the specific solvation is also insignificant, evidently as a result of its suppression at high temperatures.

So, it was discovered the lack of fit the description of the coal swelling process with the use of one–parametric dependencies including those dependencies based on the theory of regular solutions on the solubility parameter of liquids. It was shown, that the quantitative connection between the swelling degree of coal and physical–mechanical properties of the solvents is achieved only on the basis of principle of the linearity of free energy under condition of taking into account the all solvation process. *The basicity of the solvents and their molar volume are the factors determining the swelling degree for low–metamorphized coal.*

References

1. *Kibler M. V.* The Solvents Action on Coals // In Book «*Chemistry of Solid Fuels*», 1, (1951), p. p. 145−267 *(in Russian)*.
2. *Keller D. V., Smith C. D.* Spontaneous Fracture of Coal // «*Fuel*», 55 (4), (1976), p. p. 272 – 280.
3. *Kröger K.* Die Steinnohleextraction // «*Erdöl und Kohle*», 9 (7), (1956), s. s. 441−446.
4. *Sanada Y., Honda H.* Solvent Extraction of Coal // Bull. «*Chem. Soc. Japan*», 35 (8), (1962), p. p. 1358−1360.
5. *Sanada Y., Honda H.* Equilibrium Swelling of Coals in Various Solvents // «*Fuel*», 45 (4), (1966), p. p. 451−456.
6. *.Sanada Y., Honda H.* Swelling Equilibrium of Coals by Pyridine // «*Fuel*», 45 (4), (1966), p. p. 295−300.
7. *Kirov N. Y., O'Shea J. N., Sergeant G. D.* The Determination of Solubility Parameters of Coal // «*Fuel*», 47, (1967), p. p. 415−424.
8. *Green T. K., Kovac J., Larsen J. W.* A Rapid and Convenient Method for Measuring the Swelling of Coals // «*Fuel*», 63 (7), (1984), p. p. 935−938.
9. *Mayo F. R., Zevely J. S., Pavelka L. A.* Extractions and Reactions of Coals Below 100 ^oC // «*Fuel*», 67 (5), (1988), p. p. 595−599.
10. *Aida T., Fuku K., Fujii M. et al.* Steric Requirements for the Solvent Swelling of Illinois № 6 *Coal* // «*Energy and Fuels*», 5 (6), (1991), p. p. 74−83.
11. *Nelson J. F., Mahajant O. T., Walker P. L.* Measurement of Swelling of Coals in Organic Liquids // «*Fuel*», 59 (12), (1980), p. p. 831−837.
12. *Skrypchenko G. B., Khrennikova O. V., Rybakov S. I. // «Khimiya Tviordogo Topliva»*, 5, (1987), p. 23−28 *(in Russian)*.
13. *Osipov A. M., Bojko Z. V. // «Khimiya Tviordogo Topliva»*, 3, (1987), p. p. 15−18 *(in Russian)*.
14. *Van Krevelen W.* Chemical Structure and Properties of Coal // «*Fuel*», 44 (4), (1965), p. p. 229−242
15. *Larsen J. W., Shawyer S.* Solvent Swelling Studies // «*Energy and Fuels*», 4 (1), (1990), p. p. 72−74.
16. *Painter P. C., Graf J., Coleman M. H.* Coal Solubility and Swelling / *Parts* 1−3 // «*Energy and Fuels*», 4 (4), (1990), p. p. 379−397.
17. *Weyrich O. R., Larsen J. W.* Thermodynamics of Hydrogen Bonding in Coal–Derived Liquids // «*Fuel*», 62 (8), (1983), p. p. 976−977.
18. *Marzec A., Kisielow W.* Mechanism of Swelling and Extraction and Coal Structur*e* // «*Fuel*», 62 (8), (1983), p. p. 977−979.
19. *Szeliga J., Marzec A.* Swelling of Coal in Relations to Solvent Electron–Donor Numbers // «*Fuel*», 63 (10), (1983), p. p. 1229−1231.

20. *Hsieh S. T., Duda J. L.* Probing Coal Structure with Organic Vapor Sorption // *«Fuel»*, 66 (2), (1987), p. p. 170−178.
21. *Mayer U.* Eine Semiempirische Gleichung zur Beschreibung des Lösungs–Mitteleinflusses auf Statik und Kinetik Chemischer Reaktionen. *Th.* 1, 2. // «*Monutsh. Chemie*», 109 (H. 2), (1978), s. s. 421−433, s. s. 775−790.
22. *Koppel I. A., Palm V. A.* The Influence of the Solvent on Organic Reactivity // In: *«Advances in Linear Free Energy Relationships»* / Ed. N. B. Chapman & J. Shorter. London, New York: Plenum Press (1972), p. p. 203−281.
23. *Makitra R. G., Pyrig Ya. M.* // *«Khimiya Tviordogo Topliva»*, 6, (1988), p. p. 41−45 *(in Russian).*
24. *Makitra R. G., Pyrig Ya. M.* // *«Khimiya Tviordogo Topliva»*, 6, (1992), p. p. 11−20 *(in Russian).*
25. *Makitra R. G., Pyrig Ya. M., Vasiutyn Ya. M.* // *«Khimiya Tviordogo Topliva»*, **3**, (1995), p. p. 3−13 *(in Russian).*
26. *Aminabhavi T. M.*, *Harogopadd S. B., Khinnavar R. S. et al.* // Rubber Solvent Interactions // «*Rev. Macromol. Chem. Phys.*», C 31 (4), (1991), p. p. 433−497.
27. *Makitra R. G.*, *Turovsky A. A.*, *Zaikov G. E.* Correlation Analysis in Chemistry of Solutions // Eds. *VSP, Utrecht−Boston* (2004), 324 p.
28. *Makitra R. G.*, *Pyrig Ya. M.*, *Zaglad'ko E. A.* // *«Plastics»*, **3**, (2001), p. p. 23−27 *(in Russian).*
29. *Makitra R. G.*, *Midyana G. G.*, *Palchykova E. Ya.*, *Bryk D. V.* // *«Solid Fuel Chemistry»*, 44 (**6**), (2010), p. 407.
30. *Makitra R. G.*, *Prystansky R. Ye.* // *«Khimiya Tviordogo Topliva»*, 4, (2003), p. 24 *(in Russian).*
31. *Makitra R. G.*, *Bryk D. V.* // *«Solid Fuel Chemistry»*, 44 (3), (2010), p. 164.
32. *Makitra R. G.*, *Midyana G. G.*, *Palchykova E. Ya.* // *«Solid Fuel Chemistry»* 45 (6), (2011), p. 430.
33. *Makitra R.*, *Polyuzhyn I.*, *Prystansky R.*, *Smyrnova O.*, *Rogovyk V.*, *Zaglad'ko O.* Application of Free Energies Linearity Principles For Sorption and Penetration of the Organic Substances // *«Works of the Scientific Society named after Shevchenko»*, 10, (2003), p. p. 152−163 *(in Ukrainian).*
34. *Makitra R. G.*, *Prystansky R.* Ye. // *«Khimiya Tviordogo Topliva»*, 5, (2001), p. 316 *(in Russian).*
35. *Larsen J. W.*, *Green T. K.*, *Kovac J.* // «*J. Org. Chem.*», 50 (10), (1985), p. p. 4729−4735.
36. *Hall P. G.*, *Marsh H.*, *Thomas K. M.* Solvent Induced Swelling of Coals to Study Macromolecular Structure // «*Fuel*», 67 (6), (1988), p. p. 863−866.
37. *Makitra R. G.*, *Prystansky R.* Ye. // *«Khimiya Tviordogo Topliva»*, 4, (2003), p. p. 24−36 *(in Russian).*
38. *Vasiutyn Ya. M.*, *Makitra R. G.*, *Pyrig Ya. M.*, *Turovsky A. A.* // *«Khimiya Tviordogo Topliva»*, 4, (1994), p. p. 66−73 *(in Russian).*
39. *Makitra R. G.*, *Pyrig Ya. M.* // *«Khimiya Tviordogo Topliva»*, 1, (1991), p. p. 67−70 *(in Russian).*
40. *Makitra R. G.*, *Pyrig Ya. M.* // *«Khimiya Tviordogo Topliva»*, 3, (1993), p. p. 14−18 *(in Russian).*
41. *Makitra R. G.*, *Bryk S. D.*, *Palchykova O. Ya.* An Investigation of Interaction of Low−Metamorphized Coal with Organic Solvents (on Example of Diphenilolpropane) // «*Geology and Geochemistry of Combustible Minerals*», № 3–4, (2003), p. p. 126−130 *(in Ukrainian).*

© **R. Makitra** - Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–Organic Chemistry & Coal Chemistry named after L.M. Lytvynenko;National Academy of Science of Ukraine, bazyljak.L.I@nas.gov.ua; **H. Midyana -** Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–Organic Chemistry & Coal Chemistry named after L.M. Lytvynenko;National Academy of Science of Ukraine, bazyljak.L.I@nas.gov.ua; **L. Bazylyak -** Chemistry of Oxidizing Processes Division; Physical Chemistry of Combustible Minerals Department; Institute of Physical–Organic Chemistry & Coal Chemistry named after L.M. Lytvynenko;National Academy of Science of Ukraine; **O. Palchykova -** Institute of Geology and Geochemistry of Combustible Minerals; National Academy of Science of Ukraine; **V. F. Shkodich** – Ph.D, Assoc. Professor Department of technology of synthetic rubber, shkodich@mail.ru; **A. M. Kochnev -** Professor Department of technology of synthetic rubber, kochnev55@bk.ru; **G. E. Zaikov -** Professor Department of plastics technology, ov_stoyanov@mail.ru.