1. Introduction An adsorption of the polymeric molecules at an interface layer of liquid and solid phases essentially changes energy and the entropy of the interfacial interaction. That is why it widely used in many practical applications, in particular, for the improvement of the properties of composite materials by functionalization of the filler’s surface, for the stabilization of nanoparticles in solutions [1–3] and for the giving of property of the biological compatibility to the (bio)artificial organs in medicine [4]. The scientific interest to the problem of the polymers adsorption is determined also by the variety of factors having an influence on its equilibrium value and dynamics, namely: an availability, number and nature of the functional groups in molecule of polymer, its length N and conformation, thermodynamical quality of the solvent and nature of the adsorptive (active) centers of the surface of solid. In accordance with the earlier model [5–9] of the separate molecule of polymer ad-sorption, on the surface of the adsorbent the polymeric chains having the conformation of balls in solution are straighten up and form the plate although «diffusive», that is with loops and tails layer by h thickness, which is considerably less than the conformational radius Rf of the Flory ball in solution: h Rf. An essential argument for benefit of this model is fact, that it supposes a considerable energy of the Langmuir interaction of active centers of the adsorbent with more number of polymer’s links. It seems, that the investigations [10–11] with the use of the IR–spectroscopy confirm of this fact indicating on the great part (from 0.2 till ∼ 1) connected with the active centers of monomeric links of a chain. However, the modern experimental methods, in particular, an ellipsometry and the neutron reflection [12], give the values of the adsorption layer thickness h neared to the sizes of the Flory ball in solution, h ≈ Rf, that points on the volumetric character of the polymer adsorption but not on the plate one. These and others experimental facts have been theoretically analyzed with the use of the methods of the self–consistent field and scaling [13–17]. The results of an analysis can be lined in the following simplified model: in the flocculent adsorption layer (a distance between the centers of the adsorptive molecules l ≥ 2Rf, the polymeric chain is in practically the same conformational state as in the solution; in dripless adsorptive layer (l 2Rf) an interaction between the adsorbed chains compresses the polymeric balls in the adsorption plate and stretches them in a form of the chain by blobs [16], cylinders [13] or rotation ellipsoids [18] along the normal to the surface. Presented model doesn’t not take into account that the interaction of polymeric chains in the dripless adsorptive layer can leads to the overlapping of their conformational volumes with the formation of physical network of the intertwined between themselves polymeric chains. A model of flocculent and dripless adsorptive layers also is good agreed with the experimental ellipsometric data on kinetics of adsorption of different upon nature and length polymeric chains and also on number and distribution in them of the functional groups [19–23]. It is follows from these references that the kinetic curves of adsorption of the polymeric chains from the diluted solutions consist of two sections: the first is starting – quick and short with the characteristic time by 102 s order and the second one (final)

– slow and long with the characteristic time ~ 103 s. It was notified in ref. [19–23], that the kinetic constant of quick and slow process, the capacity of flocculent and dripless adsorptive layers, practically (that is via the measurements error limits), do not depend on the nature, number and type of the functional groups location in polymeric chain, but depend considerably on its length and consequently, on its conformational state. Thereby, a question about the conformational state of the polymeric chain in the adsorptive layer consists in the following: what is the more advantageous from the point of view of the free energy (Helmholtz): the plate (h Rf) form of an adsorption (to which a high energy of the Langmuir interaction «adsorbate – adsorbent» and low entropy of the conformation of the adsorbed polymeric chain correspond), or the volumetric (h ≈ Rf) form of an adsorption (at which a loss of the part of energy of Langmuir interaction can be compensated by a high entropy of the conformational state of the polymeric chain in the adsorption layer). In the presented paper we will be started from the imagination about the volumetric form of the polymeric chains adsorption assuming that the «anchor» fit of the polymeric chain on the surface of adsorbent is realized via little number of z (z N, where N is a general number of links of the polymeric chain) of the end links forming the Langmuir connection with the active centers of adsorbent. In spite of fact, that the presented model, as it was mentioned earlier, in detail was analyzed with the use of the methods of self–consistent field and scaling, but it was not obtained its thermodynamical evolution. Here the thermodynamical analysis of the polymeric chains adsorption will be based on the full taking into account of free energy of conformation of polymeric chains in solution and adsorptive layer. The notions «flocculent and dripless adsorptive layers» will be substituted on thermodynamically more determined notions of diluted and concentrated adsorption layers. 2. Conformation and free energy of conformation of the linear polymeric chains in adsorptive layer 2.1. Diluted adsorptive layer Equilibrium conformational state and its free energy for linear polymeric chains in adsorptive layer let’s determine starting from the following characteristics of the diluted solution in which r ≤ r*, where r and r* are density and critic density of the solution upon polymer, corresponding to the beginning of the polymeric chins conformational volumes overlapping. Self–avoiding random walks statistics (SARWS) [24] for diluted solution determines the distribution density w (x, N) of the end of a chain from its beginning in d–measured space via expression: , i = 1, d (1) Here: a is a linear size of the link of a chain, xi is the displacement of the end of a chain from its beginning along the i direction, si is the mean square deviations of the Gaussian part of the distribution (1), connected via the ratio: , i = 1, d (2) Among the all possible states of the polymeric chain let’s choice the most probable or thermodynamically equilibrium in accordance with the condition: at (3) This leads to the determination of the equilibrium semi–axes of the conformational ellipsoid of the polymeric chain in the real solution: (4) In the ideal solution the all directions of the chain’s end walk are equiprobable, that leads to the condition resulting from the (2): (5) By combining the (4) and (5) we find the conformational radius of the polymeric chain in the ideal solution or the radius of the un–deformed Flory ball: (6) In the real solution the Flory ball is deformed into the rotation ellipsoid, compressed or elongated along the axe connecting the beginning and the end of a chain. The semi–axes Xi of the conformational ellipsoid can be expressed via the Rf and vie the multiplicities li of the linear deformation: (7) The volumetric deformation we determine via the ratio: (8) in which is the multiplicity of the volumetric deformation. The multiplicities of the linear and volumetric deformation are not undefined and are connected via the ratio [24]: (9) As the analysis in ref. [24] shows, at any deformations of the Flory ball the conformational volume is decreased , that is why . Thereby, in general case , and the sign «=» corresponds to the ideal solution, and the sign «» corresponds to the real solution. An entropy S and free energy F of the equilibrium conformational state of polymeric chain let’s determine via the expressions: , at (10) It is follows from the determination of (10) and from the expressions of (1) and (7) for the real solution: (11) for the ideal one (12) Here (13) Accordingly to the formulated above starting positions the distribution density ws (x, N) of the end of a linear polymeric chain from its beginning in the adsorbed layer can be written in the same form (1), but with the correction that due to the presence of reflecting surface a half of the d–measured volume becomes inaccessible for the displacements xi of the end of a chain. That is why an expression for ws (x, N) we will obtained from the (1) by the substitution instead of . So, we will obtain: (14) Using the conditions (5) we find the equilibrium values Xsi of the semi–axes of conformational ellipsoid of polymeric chain in the real adsorption layer: (15) For the ideal adsorptive layer accordingly to the (5) we have: (16) So, in adsorption layer the conformational radius of the polymeric chain is even more, than in the solution: . This is connected with fact that the demand of the absence of the self–avoiding walks trajectories at the inaccessibility of the volume under the reflecting surface leads to the capture of more volume above the reflecting surface. We will obtain the expressions for the free energy Fs equilibrium to the conformation of polymeric chain in the real adsorption layer from the determination of (10) with taking into account of (7), (8), (15) and (16): (17) and in the ideal one (18) Here is the multiplicity of the volumetric deformation of conformational volume in real adsorbed layer connected with the multiplicities of the linear deformations λsi via the ratio similar to (9). It is follows from the ratios (6) and (9): (19) That is why it can be written instead of the (18) with taking into account of (12): (20) So, at the transition of a polymeric chain from the ideal diluted solution into the ideal one adsorption layer the change of the free energy of conformation will be positive and will be as follow: (21) 2.2. Concentrated adsorption layer As same as earlier, the discussion let’s start from the concentrated solution, in which accordingly to condition the conformational volumes of the polymeric chains are overlapped. That is why, an object of the SARW statistics in this case is some volume of the d–measured space, in which there are m intertwined between themselves polymeric chains. It is follows from the analysis [25] that the distribution density of the end relatively the beginning for any undefined chosen from the m–ball of polymeric chain will be determined by the expression: (22) We find from this accordingly to the same condition (3) the equilibrium semi–axes of the conformational ellipsoid in the real concentrated solution: (23) and in accordance with the condition (5) the conformational radius of any undefined chain and m–ball in wholly in the ideal concentrated solution will be equal: (24) At this, it can be again written (25) (26) where is the multiplicity of the volumetric deformation of the m–ball. The values li and lv are connected as before by the ratio (9). From the determination of (10) after the substitution in (22) of the equilibrium values accordingly to (23) with taking into account of (25) and (26) we will obtain the expression for free energy of conformation Fm for any undefined chain in m–ball in concentrated solution: real (27) and ideal (28) Here accordingly to (24) (29) Let's transfer the obtained ratios into concentrated adsorptive layer. From the considerations above presented a distribution density in concentrated adsorption layer takes a form: (30) Therefore, we have for the real concentrated adsorptive layer: (31) for ideal (32) Here ms is a number of the chains in ms–ball of the adsorption layer. Free energy of conformation for any undefined chain in the ms–ball in concentrated adsorbed layer is determined by the expressions: for real (33) for ideal (34) where again is the multiplicity of the volumetric deformation of ms–ball in real concentrated adsorbed layer. From the comparison of (32) and (6) follows (35) That is why it can be also written: (36) So, at the transfer of polymeric chain from the ideal concentrated solution into the ideal concentrated adsorption layer a free energy of conformation increases on the value: (37) The values m and ms depend on the concentration of polymer in solution and in the adsorption layer correspondingly. Let's determine of their dependence on a density upon polymer of the solution r and adsorption layer rs. In concentrated solution and in adsorption layer the density upon polymer in the conformation volumes m– and ms–ball is the same as in the whole volume of the solution and in the whole volume of the adsorption layer. That is why: (38) (39) Here M0 is a molar mass of the link of a chain. In the last expression (39) the number 2 was appeared in order to take into account, that at presence of the reflecting surface, the conformational volume of the polymeric chain in the adsorption layer is equal to . At the value m = 1 we have , and is the critic concentration of the polymeric chains in the solution corresponding to the beginning of their conformational volumes overlapping: (40) Similarly, at ms = 1 we have , and , where (41) From the comparison of (38) and (40), (39) and (41) with taking into account of the expressions for Rf, Rm, Rs and Rsm accordingly to (6), (24), (16) and (32) we find (42) (43) Critical concentrations of the beginning of the polymeric chains conformational volumes overlapping in solution r* and in adsorption layer rs* can be expressed in the form of clear dependence on the length of a chain: (44) (45) Where (46) is per sense the density in the volume of the monomeric link. 3. Adsorption isotherm of the polymeric chains 3.1. Overall view of the adsorption isotherm At the adsorption of polymeric chains from the solution the dislodgment of the molecules of a solvent from the active centers of adsorbent takes place; that is why the adsorption process can be considered as quasi–chemical reaction by the following view [3] (47) Here: P and B, Ps and Bs is a polymer and a molecule of the solvent into solution and into adsorption layer correspondingly. A condition of the adsorbed equilibrium (47) has the following standard view (48) where mi and ui are the chemical potential and the stoichiometric coefficient of the i participant in (47). Chemical potentials of the polymeric chains in the solution mp and in the adsorbed layer mps we will determin with taking into account of their free energy of conformation via the following expressions: (49) (50) As it can be seen, the values mp0 and mps0 were determined by the choice of the standard states of the solution at r = r* and of the adsorption layer at rs = rs*. Next we will be suppose that even in concentrated solution and in adsorption layer accordingly to conditions r > r* and rs > rs* the molar part of the solvent considerably more than the molar part of the polymeric chains. That is why taking into account also the position z N, it can be assumed, that at the adsorption of polymer the change of the molar part of the molecules of the solvent in solution and in adsorption layer will be little and it can be neglected. That is why, chemical potentials of the solvent in the solution and in the adsorption layer we will determine by the expressions (51) (52) in which mв0 and mвs0 are standard chemical potentials of the solvent in solution and in adsorption layer. Let’s rewrite the condition of chemical potential of the equilibrium (47) as follows: (53) Let’s note (54) (55) where Kp and KB are equilibrium constants of the Langmuir interaction of polymeric chain and molecule of the solvent with one active center of the adsorbent correspondingly. It is follows from this that the equilibrium constant K of the displacing adsorption of polymer accordingly to (47) will be equal to (56) Using the determinations (54) - (56) and the expressions (49) and (52) in (53) we will obtain the overall view of the adsorption isotherm of polymeric chains: (57) where is a change of a free energy of conformation of polymeric chain at its transfer from the solution into the adsorption layer. Since the value DF can depends on the ratio of the concentrations of polymer in solution and in adsorption layer at r ³ r* and rs ³ rs*, the overall expression (57) can be filled by the essentially different content. An analysis of the partial forms of the adsorption isotherms let’s carry out under the approximation of the idealness of the solution and of the adsorption layer. Peculiarities of the adsorption polymer from the real solution let’s discuss on the qualitative level. 3.2. Particular forms of the adsorption isotherm 3.2.1. High affinity of polymer to the active centers of adsorbent K >> 1. a) Solution and adsorption layer are diluted accordingly to condition , . In this variant the change of a free energy of conformation at the transfer of the polymeric chain from the solution in the adsorption layer is determined by the expression (21), which let’s rewrite taking into account of (13) for real d = 3 space: (58) Therefore, the adsorption isotherm takes a following view: (59) This expression describes the initial linear section of the dependence rs / rs* on r / r*, as it was shown on the Fig. 1 a and b at three values of K and two values of N. As we can see, at K >> 1 the ratio rs / rs* achieves the value, equal to 1, earlier than the ratio r / r*. That is why the next section of the adsorption isotherm is characterized by the condition: b) Solution is diluted , adsorption layer is concentrated In the presented variant free energy of conformation of polymeric chain in solution is determined by the expression (12), in the adsorption layer by the expression (34) or (36) with taking into account of (42). Combining them we will obtain: (60) An adsorption isotherm takes a view: (61) As we can see from the (60) and (61), at the transfer of polymeric chain from the diluted solution into the concentrated adsorption layer at rs / rs* increasing the value ΔF is sharply increased that gives a strong counteracting to the following adsorption effect. That is why the second section of the adsorption isotherm is characterized by a great deceleration of the adsorption value with the growing of polymer concentration in solution and gives the visibility of the going out on plateau (see Fig. 1). Determined on the basis of this quasi–plateau value of adsorption rs is insignificantly more than rs* and weakly depends on the equilibrium constant K of the displacing adsorption: thus, at the transition from the curve 2 to the curve 4 on Fig. 1 the constant K is increased on two orders, whereas the value of adsorption on ~ 20 %. At the growth of the length of chain N the value of adsorption on the quasi–plateau is decreased. Presented section of the adsorption isotherm is continued till the value . Thus, the next third section of the adsorption isotherm is characterized by the transition of polymeric chains from the concentrated solution in the concentrated adsorption layer. c) Concentrated solution and adsorption layer: , . In accordance with the previous analysis in the presented variant ΔF is determined by the expression (37), which with taking into account of (42) and (43) can be written as (62) Fig. 1 - Calculated adsorption isotherms of linear polymeric chains at different values of K and N in coordinates rs / rs* – r / r* Using the (62) and taking into account of (13) in general expression (57), at d = 3 we will obtain (63) Therefore, at transition in a field of the concentrated solution, as it was illustrated by numerous calculations on Fig. 1, the adsorption of polymer is sharply increased forming the third practically linear section of the adsorption isotherm. Comparing of these sections at different equilibrium constants K of the displacement adsorption (curves 2, 3 and 4) it can be note again that the main factor determining the rate of the adsorption change on this section is not the constant K, but the change of a free energy of conformation. Calculated adsorption isotherms (curves 2 – 4 on Fig. 1) are typical at the considerable affinity of a polymer to the adsorbate. Let’s consider however the view of the adsorption isotherm with relatively weak affinity of a polymer to the adsorbate. 3.2.2. Weak affinity of a polymer to adsorbate accordingly to condition K ≤ 1 In this case some previous variants are also possible but in other sequence and in a new quality. a) Diluted solution and adsorption layer: , . In presented concentration interval a change of a free energy of conformation ΔF is described by the expression (58), and the adsorption isotherm by the expression (59). Therefore, presented section of the adsorption isotherm is linear, but with very little angle of inclination (see Fig. 1, curve 1 at K = 1), that cannot permit experimentally find it. As we can see, at low values of K the critical concentration of polymer is achieved earlier than in the adsorbed layer. That is why the second section of the adsorption isotherm is characterized by the condition: b) Concentrated solution and diluted adsorption layer: , . In this variant an expression for ΔF of the polymer adsorption we will obtain by the combination of the expressions (20), (28), (29) with taking into account of (42): (64) It’s follows from this (65) Accordingly to (64) and (65) in presented concentration interval and up to the value with growth of the concentration of polymer in solution ΔF is decreased, that sharply, practically exponentially increases of the polymer adsorption (see Fig. 1, curve 1). At the achievement of critical concentration of polymer in the adsorption layer the third section of the adsorption isotherm is started corresponding to the condition , . It is wholly identical to the considered above and is described by the same expression (63), but at little values of K. At this, comparing the presented on Fig. 1 adsorption isotherms (curves 1 – 4), it can be again noted that on the third section of the isotherm the rate of the adsorption growth, that is , is practically the same in spite of the difference between the constants K on four orders. 4. Conclusions Usually the experimental values of the adsorption of polymer are described not in the coordinates rs / rs* – r / r*, but in coordinates As – ρ, where As is a mass of the adsorbed polymer, referred to the unit of the surface of adsorbent. Let’s determine the relationship between As and rs. Since As = mass / s, rs = mass / sRs, where s is the value of the surface of adsorbent, for diluted adsorption layer we have at (66) In concentrated adsorption layer at (67) Critical value of the adsorption As*, corresponding to the beginning of the polymeric chains conformational volumes overlapping in the adsorption layer will be equal: (68) Using the ratios (45), (46) and (16) we will obtain the clear form of the dependence of As* on the properties of polymeric chain: (69) A view of the calculated adsorption isotherms in coordinates As – ρ is shown on Fig. 2. They keep the same peculiarities as the presented on Fig. 1. Fig. 2 - Calculated adsorption isotherms for linear polymeric chains at different values of K and N in coordinates As – ρ Comparing of these calculated adsorption isotherms and experimental ones, additionally let’s note. 1. At the growth of the length of a chain N, the work, that is the value ΔF of the polymeric chain transfer from the solution into the adsorption layer is increased and the value of adsorption is decreased that is in good agreement with the experimental data, obtained with the use of the ellipsometric methods on the ideally smooth surfaces of the adsorbent. However, the experiments concerning to the adsorption of polymers on the porous adsorbents indicates sometimes on the increasing of the values of adsorption on the quasi–plateau of the isotherm at the growth of the molecular mass of the polymer. From our point of view, this is not the contradiction with the theoretical analysis of the presented work. Evidently that the adsorption of polymeric chains in the pores of adsorbent can characterized by the peculiarities depending on ratio of the sizes of pores and on the conformational volume of polymeric chains. It is not excluded that in this case the equilibrium constant K of the displacing adsorption of polymer can depend on the molar mass of the polymer at the expense of the additional Langmuir interaction of monomeric links with the active centers of adsorbent on the walls of the pores, that is at the expense of the z increasing. The behavior of polymeric chains in the pores of adsorbent having the size of the pores commensurable with the conformational volume of the chains needs more detailed analysis. However, let us note that the growth of the K on some orders weakly increases the value of the adsorption of polymer on quasi–plateau; that is why the influence of the molar mass of the polymer on values z and correspondingly K, will be also small visualized on the value of the adsorption on quasi–plateau, that is observed in the experiments. An absence of the visible influence of nature of the ω–functional groups of polymer on the value of adsorption on quasi–plateau is also explained by these reasons. 2. The numerous experimental data indicates that at the growth of the polymeric chains hardness and at the impairment of the thermodynamic quality of the solvent the adsorption of polymer is increased. We combine of these variants comparing the adsorption of polymer from the ideal and from the real solutions limiting concretely by the field of the quasi–plateau, in which at K >> 1 the solution is dilute, and the adsorption layer is concentrated. In this variant for the estimation of ΔF it is needed to use the expression (33) for Fsm in a case of the real concentrated adsorption layer and to use the expression (11) for F in a case of the real diluted solution. By combining of them we will obtain: (70) where λsv and λv are multiplicity of the volumetric deformation and conformational volume of polymeric chain in the real adsorption layer and in the solution correspondingly. In accordance with general expression (57), we find (71) At the transfer of the polymeric chain from the ideal into the real solution its conformational volume is deformed with the transformation of the spherical Flory ball into the conformational ellipsoid elongated or flattened along the axis connecting the begin and the end of a chain [26], that leads to decrease of the conformational volume and accordingly to the expression (8) to decrease of λv: at any deformations of the Flory ball λv became less than the one. That this why the effects related with the notions «hardness of the polymeric chain» and «the thermodynamic quality of the solvent» can be quantitatively estimated via the multiplicity of the volumetric deformation λv ≤ 1. The indicated effects are visualized in the adsorption layer weaker than in the solution: firstly, because the conformational volume in the adsorption layer equal to Rsd/2, is less, than in solution. This increases the elastic properties of the conformational volume of polymeric chain and thereafter increases the deformation work. Moreover, the concentrated adsorption layer corresponding to the quasi–plateau on the adsorption isotherm is more near to the ideal than the diluted real solution. That is why under other equal conditions λsv > λv. This means, that the adsorption of polymer from the real solution is more than from the ideal one.