Equilibrium constants of cellulose nitration by nitric acid under quasi-homogeneous conditions

V. A. Rafeev,* Yu. I. Rubtsov, T. V. Sorokina, and N. V. Chukanov

_Institute for Chemical Physics Research, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: rafeev@icp.ac.ru_

The equilibrium of nitration of cellulose was studied at 13.1 and 20 °C in aqueous solutions of HNO_3 (77.3—80.5 wt.%) forming quasi-homogeneous solutions with cellulose. At 20 °C under quasi-homogeneous conditions, the rates of cellulose nitration are comparable to those of homogeneous nitration of alcohols. The effective nitration constants differ substantially for heterogeneous and homogeneous reactions. Using IR spectra, the partial conversions in the nitration to the 2, 3 and 6 positions of the glucopyranose cycle and the effective equilibrium constants of formation of different isomeric nitrates were estimated.

Key words: cellulose, nitration, equilibrium, constants.

The equilibrium of the reaction of cellulose (1) nitration by aqueous solutions of HNO_3 has been studied in detail,[1—3] but the equilibrium constants of reactions of formation of different isomeric nitrates have been determined only in 1980—1990 [3,4] using ^{13}C NMR spectroscopy. At concentrations of HNO_3 below ~75 wt.% and above ~82 wt.%, the nitration of cellulose is heterogeneous,[1] which can be due to a specific influence of the solid phase. Therefore, it was of interest to study the regularities of nitration of cellulose by nitric acid under homogeneous or close to homogeneity (gel-like) conditions. The purpose of this work is to estimate the duration of nitration of a part of cellulose soluble in HNO_3, to analyze the effect of heterogeneity of the system on the equilibrium constants, and to study them in the region of formation of a quasi-homogeneous solution, using more accessible and widely abundant IR spectroscopy for the estimation of equilibrium constants of the cellulose nitration.

Experimental

Solutions of nitric acid with different concentrations were prepared by dilution of a stock 88.48% solution of HNO_3, and their concentrations were calculated from the weight of the stock solution and distilled water added. The stock solution was prepared by dilution of the concentrated acid distilled from fuming HNO_3 at a reduced pressure. Cotton cellulose with an ash content of 0.07% containing 98.4% α-cellulose was used.

To study the equilibrium of nitration at 13.1 °C, samples of nitrocellulose (2) were prepared in several stages: first, at room temperature cellulose was mixed with a solution of HNO_3 in a weight ratio of 1 : (40±0.01). The mixture was thoroughly homogenized and filtered through an acid-resisting filter. The

gel-like transparent mass obtained was placed in a vessel, which was thermostatted at 13.1 °C and had on the bottom several thick-walled capillaries with an inner diameter of ~1 mm closed with a ground plate. A vessel with a solution of nitrocellulose was hermetically mounted above another vessel thermostatted at the same temperature, provided with a magnetic stirrer, and containing a ~30-fold (relative to a solution of nitrocellulose) amount of 10% acetic acid. After thermostatting for 30 min, the vessel with aqueous acetic acid was evacuated, and a solution of nitrocellulose was added through capillaries with stirring to a vessel designed for washing nitrocellulose from HNO_3. Almost immediately after acetic acid was added to the aqueous solution of acetic acid, nitrocellulose precipitated, and several minutes after the precipitate was filtered off through a ceramic filter and washed with a large amount of water followed by keeping in water, which was changed from time to time, for several weeks. Washing out of HNO_3 was monitored by a litmus probe. As established previously[5] from the rate of thermal decomposition, this regime provides complete removal of HNO_3 from nitrocellulose. To stop the nitration reaction, diluted acetic acid was also used instead of water. Preliminary experiments showed that in this case, the content of nitrogen in the nitrocellulose obtained was higher by several tenths of a percent. Under these conditions, HNO_3 is faster displaced and, correspondingly, nitrocellulose is denitrated to a lower degree. A solution was admitted through capillaries, which provided a more reliable preparation of nitrocellulose corresponding to the equilibrium of nitration. According to the data on acid hydrolysis of trinitroglycerol by nitric acid,[6] it can be estimated that the degree of denitration of nitrocellulose at 13 °C during the time of isolation from the reaction mixture can be ~0.001% (calculated per starting nitrogen), and for washing from HNO_3 with water due to neutral hydrolysis, it is <0.05% (based on the starting nitrogen).

The duration of nitration in the region of dissolution of nitrocellulose was studied on the same installation, but at first a solution of HNO_3 was thermostatted at 20 °C, then cellulose was added, and the mixture was manually stirred thoroughly to homogeneity. Duration of nitration was characterized by the

nitrogen content in nitrocellulose achieved for different times of nitration. In these experiments, the solution was not filtered, and distilled water was used to stop the nitration reaction.

The content of nitrogen in nitrocellulose 2 was determined from the heat of combustion in an oxygen atmosphere[7,8] and calculated based on the weight of a fully dried sample.

The degree of substitution of OH groups at $C(2)$, $C(3)$, and $C(6)$ atoms of the glucopyranose cycle by NO_3 groups was determined from the total conversion and the ratio of absorption intensities at 1298, 1267, and 1282 cm^{-1} characterizing the corresponding positions of NO_3 groups in model compounds.[9] IR spectra were recorded on a Specord-75 IR spectrophotometer.

Results and Discussion

Preliminary experiments showed that at 20 °C the cellulose used passes into a gel-like state (with the visually observed disappearance of the cellulose phase) in the range of HNO_3 concentrations from 78 to 83%. Therefore, all further experiments were carried out with solutions of HNO_3, whose concentration was in the range indicated.

The data in Table 1 show that for quasi-homogeneous nitration the equilibrium of nitration is achieved already within several minutes, perhaps during the time of mixing of cellulose with a solution of HNO_3, which is indicated by the unchanged (within the measurement accuracy equal to ±0.07%) nitrogen content in nitrocel-
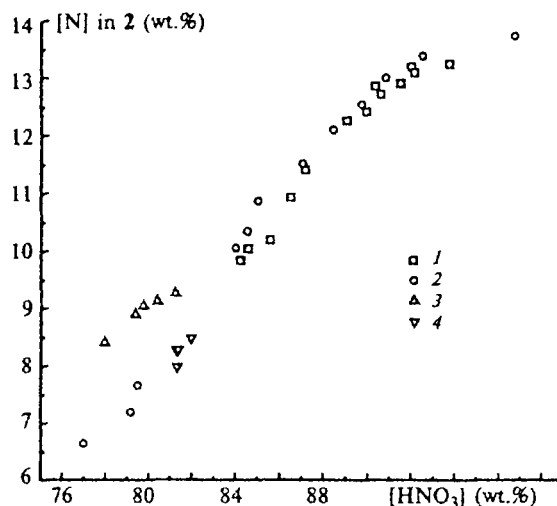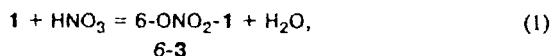

Fig. 1. Dependences of the nitrogen content in nitrocellulose on the concentration of HNO_3 used for nitration: *1*, data in Ref. 1, 20 °C; *2*, data in Ref. 4, 20 °C; *3*, this work, 13.1 °C; and *4*, this work, 20 °C.

lulose in time. (In Table 1 and hereinafter, the concentration of HNO_3 is presented taking into account its consumption in nitration and dilution with water contained in the starting cellulose.) The rate constant of nitration of secondary hydroxyl groups is most likely not more than 10 times[10] lower than that of primary groups (the maximum estimation). Using the value of the rate constant of nitration of MeOH in 82% HNO_3 at 20 °C $(0.15\ s^{-1})[10]$ and assuming that the nitration of cellulose obeys the first-order kinetic law, we can estimate that under homogeneous conditions, the nitration of cellulose occurs by 99% during less than 5 min, which was observed in our experiments.
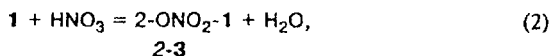
The data on the nitrogen content in nitrocellulose samples obtained by the nitration of cellulose at 13.1 °C by solutions of HNO_3 with different concentrations, the total depth of nitration (η), and the depths of nitration at positions 2, 3, and 6 of the glucopyranose cycle (η_2, η_3, and η_6, respectively) are presented in Table 2. The average values of three or four measurements of the nitrogen content are presented. The ratios of partial pressures of HNO_3 and H_2O above solutions of the acid (p_{HNO_3}/p_{H_2O}) were calculated from the nomograms.[11]

Table 1. Nitrogen content in nitrocellulose 2 at different times and moduli ($\beta = m_{HNO_3}/m_1$) of nitration of cellulose by aqueous solutions of HNO_3 (20 °C)

t/min	[N] in 2 (wt.%)	
	$[HNO_3] = 81.31\%$, $\beta = 50$	$[HNO_3] = 81.96\%$, $\beta = 150$
5	8.36	8.51
15	8.22	—
45	8.26	—
60	—	8.41
90	8.32	—
120	8.40	8.53
180	8.25	—

Table 2. Parameters of nitrocellulose 2 obtained under conditions of quasi-homogeneous nitration of cellulose at 13.1 °C

$[HNO_3]$ (wt.%)	[N] in 2 (wt.%)	η	η_2	η_3	η_6	p_{HNO_3}/p_{H_2O} [11]
77.32	8.40	0.4442	0.3465	0.2865	0.6996	2.346
78.67	8.90	0.4808	0.3750	0.3043	0.7630	2.97
79.05	9.06	0.4928	0.3711	0.3238	0.7836	3.175
79.68	9.13	0.4988	0.3771	0.3472	0.7722	3.55
80.50	9.27	0.5094	0.3836	0.3622	0.7824	4.12

The dependences of the nitrogen content in the nitrocellulose samples nitrated under equilibrium on the concentration of HNO_3 at 20 °C (Fig. 1), which were obtained by different authors,[1,4] agree satisfactorily with the results of this work. However, for the nitration at 13.1 °C, the nitrogen content in the nitrocellulose samples is higher by 1.2—1.5% (see Fig. 1). This can be related not only to the close approach to equilibrium of nitration in the nitrocellulose samples obtained by the method described above but also to the substantial temperature dependence of the position of equilibrium of cellulose nitration under quasi-homogeneous conditions.
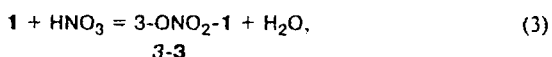
The formation of all possible nitrates for the elementary unit of cellulose **1** (2-, 3-, and 6-mononitrates (*2-3*, *3-3*, and *6-3*, respectively); 2,3-, 2,6-, and 3,6-dinitrates (*2,3-4*, *2,6-4*, and *3,6-4*, respectively), and cellulose trinitrate (**5**)) can be represented by seven independent equations:
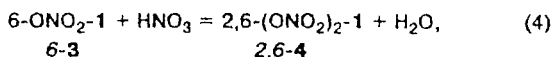
$$1 + HNO_3 = 6\text{-}ONO_2\text{-}1 + H_2O, \qquad (1)$$
$$6\text{-}3$$
$$K_1 = (\alpha_{6\text{-}3}/\alpha_1)(a_{H_2O}/a_{HNO_3});$$

$$1 + HNO_3 = 2\text{-}ONO_2\text{-}1 + H_2O, \qquad (2)$$
$$2\text{-}3$$
$$K_2 = (\alpha_{2\text{-}3}/\alpha_1)(a_{H_2O}/a_{HNO_3});$$

$$1 + HNO_3 = 3\text{-}ONO_2\text{-}1 + H_2O, \qquad (3)$$
$$3\text{-}3$$
$$K_3 = (\alpha_{3\text{-}3}/\alpha_1)(a_{H_2O}/a_{HNO_3});$$

$$6\text{-}ONO_2\text{-}1 + HNO_3 = 2,6\text{-}(ONO_2)_2\text{-}1 + H_2O, \qquad (4)$$
$$6\text{-}3 \qquad\qquad 2,6\text{-}4$$
$$K_4 = (\alpha_{2,6\text{-}4}/\alpha_{6\text{-}3})(a_{H_2O}/a_{HNO_3});$$

$$6\text{-}ONO_2\text{-}1 + HNO_3 = 3,6\text{-}(ONO_2)_2\text{-}1 + H_2O, \qquad (5)$$
$$6\text{-}3 \qquad\qquad 3,6\text{-}4$$
$$K_5 = (\alpha_{3,6\text{-}4}/\alpha_{6\text{-}3})(a_{H_2O}/a_{HNO_3});$$

$$2\text{-}ONO_2\text{-}1 + HNO_3 = 2,3\text{-}(ONO_2)_2\text{-}1 + H_2O, \qquad (6)$$
$$2\text{-}3 \qquad\qquad 2,3\text{-}4$$
$$K_6 = (\alpha_{2,3\text{-}4}/\alpha_{2\text{-}3})(a_{H_2O}/a_{HNO_3});$$
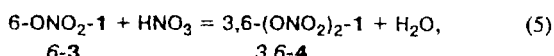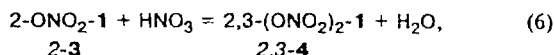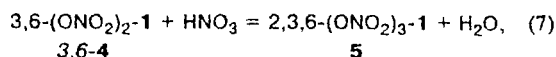
$$3,6\text{-}(ONO_2)_2\text{-}1 + HNO_3 = 2,3,6\text{-}(ONO_2)_3\text{-}1 + H_2O, \qquad (7)$$
$$3,6\text{-}4 \qquad\qquad\qquad 5$$
$$K_7 = (\alpha_5/\alpha_{3,6\text{-}4})(a_{H_2O}/a_{HNO_3}).$$

Here *a* is the activity, and α is the fraction of the total number of units of equilibrium isomeric nitrates. Equations (1)—(7) assume that the ratios of activity coefficients of equilibrium isomeric nitrates are independent of the acidity of the medium, which evidently can be performed in a narrow range of HNO_3 concentrations. Based on the equations of material balance for partial depths of substitutions η_2, η_3, and η_6

$$\eta_2 = \alpha_{2\text{-}3} + \alpha_{2,6\text{-}4} + \alpha_{2,3\text{-}4} + \alpha_5, \qquad (8)$$

$$\eta_3 = \alpha_{3\text{-}3} + \alpha_{3,6\text{-}4} + \alpha_{2,3\text{-}4} + \alpha_5, \qquad (9)$$

$$\eta_6 = \alpha_{6\text{-}3} + \alpha_{2,6\text{-}4} + \alpha_{3,6\text{-}4} + \alpha_5, \qquad (10)$$

the expressions for the fraction of nonprotonated units of cellulose

$$\alpha_1 = 1 - \alpha_{2\text{-}3} - \alpha_{3\text{-}3} - \alpha_{6\text{-}3} -$$
$$- \alpha_{2,3\text{-}4} - \alpha_{2,6\text{-}4} - \alpha_{3,6\text{-}4} - \alpha_5, \qquad (11)$$

using Eqs. (1)—(7) and taking into account that

$$3\eta = \eta_2 + \eta_3 + \eta_6, \qquad (12)$$

we can obtain the following expressions:

$$\eta = a(K_8 + 2aK_9 + 3a^2K_{10})/[3(1 + aK_8 + a^2K_9 + a^3K_{10})], \qquad (13)$$

$$\eta_2 = a\alpha_1[K_2 + a(K_1K_4 + K_2K_6) + a^2K_{10}], \qquad (14)$$

$$\eta_3 = a\alpha_1[K_3 + a(K_1K_5 + K_2K_6) + a^2K_{10}], \qquad (15)$$

$$\eta_6 = a\alpha_1[K_1 + a(K_1K_4 + K_1K_5) + a^2K_{10}], \qquad (16)$$

where $a = a_{HNO_3}/a_{H_2O}$; $K_8 = K_1 + K_2 + K_3$; $K_9 = K_1K_4 + K_1K_5 + K_2K_6$; $K_{10} = K_1K_5K_7$; $\alpha_1 = 1 + aK_8 + a^2K_9 + a^3K_{10}$.

Thus, under the assumptions presented above, the dependence of η on the ratio of activities of molecular forms of HNO_3 and H_2O (p_{HNO_3}/p_{H_2O}) is described by the three-parameter expression (13), from which K_8, K_9, and K_{10} values can be estimated by the known optimization methods. Based on these values and experimental data for η_2 and η_3, using Eqs. (17) and (18) obtained from Eqs. (14) and (15):

$$\eta_2/(a \cdot \alpha_1) - a^2K_{10} = K_2 + a(K_1K_4 + K_2K_6), \qquad (17)$$

$$\eta_3/(a \cdot \alpha_1) - a^2K_{10} = K_3 + a(K_1K_5 + K_2K_6), \qquad (18)$$

we can calculate the K_2, K_3 ($K_1K_4 + K_2K_6$), and ($K_1K_5 + K_2K_6$) values by the least-squares method and then, using K_8, K_9, and K_{10}, the K_1, $K_4—K_7$ values can be calculated.

Another variant of calculation of the $K_1—K_7$ parameters is related to the optimization of dependences (19) and (20) relative to eight parameters:

$$\frac{\eta_2}{\eta} = \frac{3(1 + aK_{11} + a^2K_{12})}{1 + K_{13} + 2aK_{11} + 2aK_{14} + 3a^2K_{12}}, \qquad (19)$$

$$\frac{\eta_3}{\eta} = \frac{3(1 + aK_{15} + a^2K_{16})}{1 + K_{17} + 2aK_{15} + 2aK_{18} + 3a^2K_{16}}, \qquad (20)$$

where $K_{11} = (K_1 K_4 + K_2 K_6)/K_2$; $K_{15} = (K_1 K_5 + K_2 K_6)/K_3$; $K_{12} = K_{10}/K_2$; $K_{16} = K_{10}/K_3$; $K_{13} = (K_1 + K_3)/K_2$; $K_{17} = (K_1 + K_2)/K_3$; $K_{14} = K_1 K_5/K_2$; $K_{18} = K_1 K_4/K_3$.

Based on the K_{11}—K_{18} values used, the K_2/K_1, K_3/K_1, K_{10}/K_1, $K_1 K_4/(K_2 K_6)$, and $K_1 K_5/(K_2 K_6)$ ratios can be calculated. Then using the equation

$$3\eta/[a(1 - 3\eta)K_{19} + 3a^3(1 - \eta)K_{10}/K_1] =$$
$$= K_1 + a(2 - 3\eta)K_{20}/[a(1 - 3\eta)K_{19} + 3a^3(1 - \eta)K_{10}/K_1], \quad (21)$$

where $K_{19} = 1 + K_2/K_1 + K_3/K_1$ and $K_{20} = K_2 K_6[1 + K_1 K_4/(K_2 K_6) + K_1 K_5/(K_2 K_6)]$, the K_1 and K_{20} values and then K_2—K_7 can be calculated by the least-squares method. Expression (21) was obtained by the transformation of Eq. (13).

The search for only positive values of K_8, K_9, and K_{10} of Eq. (13) by the first variant and K_{11}—K_{18} by the second variant of the calculation was performed in the region of positive values by the Nelder—Mid[12] simplex method with explicit restrictions. In the first case, the mean-average relative deviation of experimental η values from calculated values was the minimized function, and in the second case, the function was minimized as the sum of mean-average relative deviations of experimental η, η_2, and η_3 values from those calculated from Eqs. (13), (19), and (20). In both variants of optimization, the stability of the position of the found minimum of the function was checked by changing the increment from 0.2 to 2.5 and variation of the initial values of parameters. In the calculations, the a_{HNO_3}/a_{H_2O} values were taken as equal to the ratio of partial pressures of HNO_3 and H_2O above the neat aqueous solutions of the acid (see Table 2). The values of equilibrium constants of nitration estimated by both methods are presented below.

K_i	Variant		K_i	Variant	
	first	second		first	second
K_1	1.470	1.040	K_5	0.3450	0.383
K_2	0.824	0.583	K_6	0.0164	0.041
K_3	0.186	0.031	K_7	0.0021	0.0002
K_4	0.265	0.275			

Dependences (17) and (18) obtained with the values of K_8, K_9, and K_{10} parameters found by the optimization using the first variant are presented in the corresponding coordinates in Fig. 2. As can be seen from the results obtained, both variants of optimization give close values of equilibrium constants K_1 and K_2, K_4 and K_5, but the reliability of estimations of K_3, K_6, and K_7 is much worse, which is related to a considerably lower content of the corresponding nitrates in the equilibrium mixture.

The η, η_2, η_3, and η_6 values calculated from Eqs. (13)—(16) using the values of equilibrium constants of nitration K_1—K_7 obtained by both optimization variants agree within 3% with the experimental data.

The K_8, K_9, and K_{10} values estimated from dependence (13) by the Origin Microsoft Word standard optimization methods using our experimental results and the
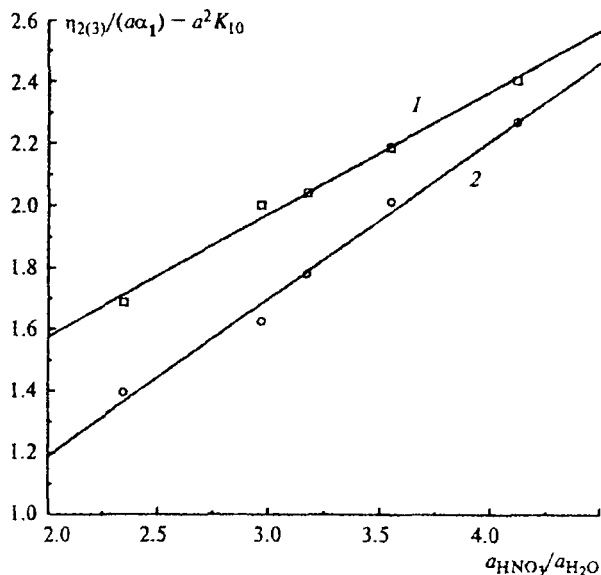

Fig. 2. Dependences using K_8, K_9, and K_{10} for determination of values of equilibrium constants of nitration in coordinates of Eqs. (17) and (18) ($\alpha_1 = 1 + aK_8 + a^2 K_9 + a^3 K_{10}$): *1*, η_2; *2*, η_3.

published data of other authors[4] at 20 °C were 8.87, 2.58, and 0.205 in the heterogeneous region and 5.06, 0.65, and 0.095 in the region of quasi-homogeneous nitration of cellulose. The equilibrium constants K_8, K_9, and K_{10} calculated from the literature data[4] and estimated by the optimization methods in the region of heterogeneous nitration agree with each other, but describe unsatisfactorily the experimental data in the region of homogeneous nitration. The substantial differences between the values of equilibrium constants of cellulose nitration observed under heterogeneous and homogeneous conditions can be due to different reasons, for example, the influence of the solid phase on the effective rate constant. It can be estimated from the data obtained that in a solution at 13.1 °C the equilibrium constant of formation of cellulose 6-mononitrate is higher than those of 2- and 3-mononitrates by 1.8 and 8—30 times, respectively, and the equilibrium constant of formation of cellulose 6,3-dinitrates is higher than the corresponding constants for 6,2- and 2,3-dinitrates by 1.3 and 9—20 times, respectively (see above). No 2- and 3-mononitrates and 2,3-dinitrate were observed by the high-resolution ^{13}C NMR spectroscopic study of the equilibrium of cellulose nitration[3,4] performed mainly under heterogeneous conditions. The specificity of the steric structure of the glucopyranose cycle of cellulose most likely hinders substantially the formation of these isomers. At the same time, the increase in the equilibrium constants K_8, K_9, and K_{10} observed in the solid phase indicates facilitation of the formation of other nitrate isomers.

The specific behavior of cellulose in the nitration reaction follows from the comparison: for the homogeneous nitration of glycerol by aqueous solutions of HNO_3 (17 °C) studied[13] by the ^1H NMR spectra, the ratio of equilibrium constants of nitration of the primary to secondary OH groups is 2.5. The very low rates of attainment of thermodynamically equilibrium concentrations of H_2O and HNO_3 between the solution and solid phase during heterogeneous nitration can be another reason for the differences between the values of equilibrium constants. Because of the difference between the rates of diffusion of water and HNO_3 to cellulose[14] due to the lower chemical affinity of water to nitrocellulose, a relative increase in the concentration of HNO_3 appears in the solid phase and, as a consequence, higher values of effective equilibrium constants are observed. Exposure of cellulose to the nitrating mixture for a long time, necessary for establishment of thermodynamic equilibrium between the solution and solid phase, is combined with the competing oxidation reaction, resulting in a decrease in the degree of esterification of cellulose. Thus, the equilibrium constants of nitration by aqueous solutions of HNO_3 are sensitive to the phase state of cellulose. When equilibria of nitration of cellulose are studied in other nitrating systems, for example, in sulfuric-nitric mixtures, this effect of the phase state can also appear and should be taken into account.

References

1. F. D. Miles, *Cellulose Nitrate*, London, 1955.
2. J. Chedin, A. Tribot, and S. Feneant, *Compt. Rend.*, 1948, **226**, 2068.
3. T. K. Wu, *Macromolecules*, 1980, **13**, 74.

4. A. A. Chicherov, A. V. Kuznetsov, Yu. M. Kargin, V. V. Klochkov, G. N. Marchenko, and G. G. Garifzyanov, *Vysokomol. Soedin., A*, 1990, **32**, 502 [*Polym. Sci. USSR, Ser. A*, 1990, **32** (Engl. Transl.)].
5. E. A. Panina, V. A. Rafeev, Yu. I. Rubtsov, and N. V. Chukanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1273 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1143 (Engl. Transl.)].
6. B. S. Svetlov and V. P. Shelaputina, *Zh. Fiz. Khim.*, 1966, **40**, 2889 [*J. Phys. Chem. (USSR)*, 1966, **40** (Engl. Transl.)].
7. R. S. Jessup and E. J. Prosen, *J. Research of the National Bureau of Standards (U.S.)*, 1950, **44**, 387.
8. V. A. Rafeev, Yu. I. Rubtsov, V. V. Avdonin, T. V. Sorokina, and A. M. Korolev, *Zav. labor. [Plant Laboratory]*, 1993, No. 3, 39 (in Russian).
9. N. V. Chukanov, L. N. Leksina, Yu. N. Rogov, S. I. Firgang, and A. I. Usov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1763 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1631 (Engl. Transl.)].
10. A. I. Kazakov, Yu. I. Rubtsov, L. V. Zabelin, Yu. M. Kargin, G. B. Manelis, and G. N. Marchenko, *Dokl. Akad. Nauk SSSR*, 1984, **277**, 618 [*Dokl. Chem.*, 1984 (Engl. Transl.)].
11. B. D. Mel'nikov and E. B. Mel'nikov, in *Kratkii inzhenernyi spravochnik po tekhnologii neorganicheskikh veshchestv. Grafiki i nomogrammy* [*Brief Engineering Reference Book on Technology of Inorganic Substances. Plots and Nomograms*], Khimiya, Moscow, 1968, 105 (in Russian).
12. B. D. Bunday, *Basic Optimisation Methods*, Edward Arnold Publishers, London, 1984.
13. A. I. Kazakov, G. V. Lagodzinskaya, L. P. Andrienko, N. G. Yunda, A. M. Korolev, Yu. I. Rubtsov, G. B. Manelis, and L. T. Eremenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1723 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1560 (Engl. Transl.)].
14. V. A. Rafeev, Yu. I. Rubtsov, and T. V. Sorokina, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1981 [*Russ. Chem. Bull.*, 1996, **45**, 1879 (Engl. Transl.)].