

A chromatographic and surface-activity analysis of the fractions of Rokopols, block Copolymers of propylene oxide and ethylene oxide separated from the technical product

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Summary

A method of refining technical Rokopols, products of copolymerization of ethylene oxide and propylene oxide of 30p160, 30p27 and 30p10 type was developed. The course of the relation between $R_f(R_m)$ and the number of oxyethylene segments n_{TE} in the molecule of the homological series of polyethyleneglycols (PEG) was used to examine the content of n_{TE} in the refined fractions of Rokopols. For the aqueous solutions of Rokopols weight-average molecular mass M_w was calculated and the surface tension coefficient γ^{25} was determined on the basis of the stalgmometric method. The value of the critical micellar concentration (cmc) and the thermodynamic potential for micelle formation (ΔG_m^0), which facilitates the assessment of the solubilizing abilities of the investigated class of copolymers, were estimated.

Key words: chromatographic analysis, surface activity, Rokopols

INTRODUCTION

Carbofluorines constitute a class of organic combinations which contain partly or completely replaced atoms of hydrogen or fluorine in their structure. This class of combinations is characterized by high solubility of oxygen, carbon dioxide, nitrogen and other gases [1,2].

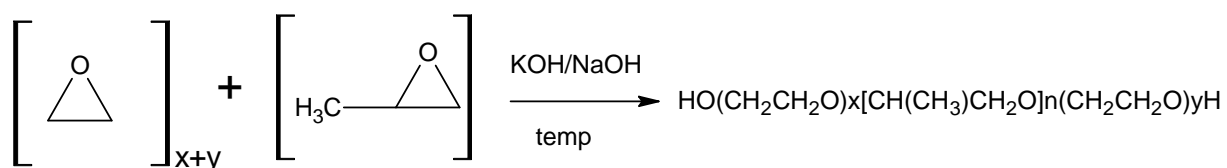
The basic difference between the operation of perfluoric carriers of oxygen and hemoglobin is that oxygen binds with hemoglobin in a coordinating fashion and the process is not subject to Henry's law. On the other hand, perfluorized organic compounds dissolve oxygen, carbon dioxide, nitrogen and other gases relatively well, but in a manner that accords with Henry's law.

Clinical research demonstrates that the most promising carriers of oxygen, i.e. those that are low-toxic, emulsify well and dissolve oxygen well, are the derivatives of perfluorodecalin[3-7].

As experiments prove, the safe use of carbofluoric substitutes of blood in the form of emulsion requires deep and durable disintegration of microdrops of the carrier of oxygen, because non-homogeneous emulsion may cause symptoms similar to those typical of poisoning. Most frequently, such durable emulsion is obtained from synthetic non-ionic emulsifiers, block copolymers of polypropylene oxide and polyethylene oxide known as Pluroniks.

Pluroniks are low-toxic, and thus can be used in relatively high concentration (2-3%). Another advantage of Pluronik F-68 with $M_n = 8350$ is that in the concentration 2.5% it is isooncotic with respect to blood serum.

Block copolymers of propylene oxide with ethylene oxide produced in Poland and labelled Rokopols are equivalents of Pluroniks. They are obtained through block condensation of propylene oxide (the hydrophobic element) and ethylene oxide (the hydrophilic element) with the use of the catalysts of concentrated aqueous solutions KOH and NaOH. The course of the reaction can be presented in the form of equation.



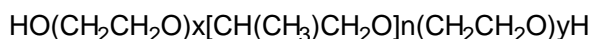
The product of the reaction retains all the properties of glycols and ethers, it contains both glycol and alcohol groups. The refining of the product is in fact elution of the excess of the catalyst (HCl), i.e. activation of the functional groups of glycols [12]. Those Rokopols whose lipophilic core contains at least 30 mols of isopropoxylo- segments are used as components in domestic detergents, ingredients of preparations that have emulsifying, washing, dispergating, moistening, and antistatic properties in different industries [8-11].

Current research has demonstrated that in equilibrium conditions Rokopols are good solubilizers for lipophilic therapeutic agents and can significantly complement the lithogenolitic index of bile A (duodenal content) [13-14].

The exceptionally low toxicity of these block copolymers inspired research into the possibility of separating from the technical product the fraction with relatively slight dispersion of molar masses with simultaneous use of thin-layer chromatography to define their homogeneity and estimate the number of oxyethylene segments.[15,16]

MATERIALS

1. Block copolymers of propylene oxide and ethylene oxide of a generalized formula



Types Rokopol 30p10 ($x+y \approx 10$ $n \approx 30$) Rokopol 30p27 ($y+x \approx 27$ $n \approx 30$) and Rokopol 30p160 ($x+y \approx 160$ $n \approx 30$), were produced in Zakłady Chemiczne Rokita S.A. in Brzeg Dolny n/Odra (Chemical Plant Rokita S.A. in Brzeg Dolny n/Odra).

2. Alcohols: metanol, propanol, isopropanol, all analytically pure, POCH Gliwice.
3. Methyl ethyl ketone, analytically pure, Loba-Chemie.
4. Ammonia, 25% solution, POCH Gliwice.
5. Bases for thin-layer chromatography
 - a.) DC-Kieselgel 60 F₂₅₄ Merck (put on a gel plate 0.25 mm thick)
 - b.) 4N Kieselgel HF₂₅₄₊₃₆₆ (put on a gel plate 0.25 mm thick).
6. Iodine, analytically pure, POCH Gliwice.
7. Thin-layer chromatography chambers.
8. Stalagmometers with $v = 28.20 \text{ cm}^3$ and 45 cm^3 , Medingen.
9. Active carbon, following FP.
10. Standard polyethylene glycols PEG with $M_n = 200-6000$, Merck and POCH Gliwice.

METHODS

Selection of conditions for the examination of separated fractions of Rokopols by means of thin-layer chromatography

The solutions of standard polyethylene glycols PEG and technical and refined Rokopols were prepared on the basis of the analytical sample of 0.05–0.1g of polymer in the

volume of 50cm³ of adequate developing system (the mobile phase). About 0.05–0.1 cm³ of thus prepared solution was put on the chromatoplate by means of a micropipette. The plates were developed in the temperature of 25⁰C ±0.1, and after drying they were detected in a chamber with J₂ (sublimating iodine).

The retention factor R_f (R_F=b/a) served as a basis for calculating R_M (its logarithmic function) based on the following equation:

$$R_M = \log \frac{1 - R_F}{R_F} = \log \left[\frac{1}{R_F} - 1 \right]$$

The most important R_F coefficients that were reproducible with close accuracy on HF₂₅₄₊₃₆₆ base for appropriate developing systems are provided in Tables 1 and 2.

Surface activity of aqueous solutions of Rokopols

The measurement of surface tension of aqueous solutions of Rokopols (separated fractions) was conducted in accordance with the Polish Standard PN-90CO4809 (equivalent to ISO 304 and 6889) “Środki powierzchniowo czynne oznaczenie napięcia powierzchniowego(γ_s)i napięcia międzyfazowego(γ_i)” [“Surface-active agents. Determining surface tension (γ_s) and interfacial tension (γ_i)]. The values of cmc are presented in Table 3.

Refining of technical Rokopols

The high solubility of Rokopols in polar solvents, alcohols and ketones, combined with their non-reactivity with respect to the structure was the reason why they were used in the process of fractionation of the technical product.

Fractionation of technical Rokopol 30p160

A. 88.0g of technical Rokopol 30p160 was weighed, disintegrated and inserted into 200.0cm³ of mixture of isopropanol and n-butanol (1:1 parts by volume). It was heated slowly up to 70-85⁰C and mixed until the product dissolved entirely. The orange and brown solution was quickly cooled down to 0±0.2⁰C. The sediment obtained, which had a distinct crystalline structure, was filtered out (very fast), drained, and washed

with the aforementioned system of solvents, and dried. 75.5g of white product with a characteristic odour was obtained. The fraction was labelled 30p160 A-1.

- B. 88.0g of technical Rokopol 30p160 was weighed, disintegrated and inserted into 600.0cm³ of methanol. It was stirred and heated under a reflux condenser until it dissolved completely, i.e. up to 60-70⁰C. A real solution with strong orange and brown colouring was obtained. Then, 150.0g of active carbon was added and the solution was heated under a reflux condenser for 15 minutes up to the boiling point. The hot solution was infiltrated and the adsorbent was separated. The colourless methanol solution was thickened up to the volume of ~230,0 cm³ and then quickly cooled down to the temperature of 5.0±0.2⁰C. Strong white sediment was obtained and then quickly filtered out, drained and washed with methanol. As a result, 27.5g of white fine crystalline product with a characteristic odour was obtained. The fraction was labelled 30p160 A-2.
- C. After the separation of the fraction 30p160 A-2, the methanol solution was vaporized to dryness. The residue was dissolved in 300.0cm³ of isopropanol, then 50g of active carbon was added and the whole was heated under a reflux condenser up to the temperature of 76-82⁰C. The hot solution was infiltrated and the adsorbent was separated. The colourless solution was cooled down to the temperature of 14±0.2⁰C very quickly. The white sediment that was obtained was filtered out, drained and washed with the aforementioned alcohol. 41.5g of the product was obtained after drying. The fraction was labelled 30p160 A-3.

Fractionation of technical Rokopol 30p27

- A. 40.5g of technical Rokopol 30p27 was weighed and dissolved in 250cm³ of isopropanol. 15.0g of active carbon was added to the dark brown and orange solution and it was heated under a reflux condenser for 15 minutes. The hot solution was infiltrated and the adsorbent was separated. A solvent was distilled off the solution in the temperature of 85-87⁰C with 26-32mmHg. After cooling down, 35.5g of white product of the consistency of wax was obtained. The fraction was labelled 30p27 B-1.
- B. As in A, the process of technical fractionation of technical Rokopol 30p27 was conducted with the use of the solvent system isopropanol : methanol (1:1 parts by volume). Out of 40.5g of technical Rokopol 30p27, 22.85g of the product was obtained. The fraction was labelled 30p27 B-2.

C. As in A, the process of fractionation of technical Rokopol 30p27 with the use of methanol as the solvent. The process of refining with active carbon was carried out under a reflux condenser at the temperature of 50-55°C. Methanol was separated on the vacuum evaporator at the temperature of 50°C with 26-28mmHg. Out of 55.65g of technical Rokopol 30p27, 38.5g of the white product of the consistency of paste and with no visible indicators of crystallinity was obtained. The fraction was labelled 30p27 B-3.

Fractionation of technical Rokopol 30p10

A. 75.65g of technical Rokopol 30p10 was weighed and dissolved cold in methanol. 22.0g of active carbon was added to the light-yellow solution and the solution was heated under a reflux condenser up to the boiling point. After cooling down the adsorbent was separated and the colourless methanol solution was vaporized on the vacuum evaporator at the temperature of 50°C with 26-28mmHg. 70.8g of the product, liquid of the consistency of paraffin, was obtained. The fraction was labelled 30p10 C-1.

RESULTS

Through the modification of the developing system (the mobile phase) of type A (Table I), significant variation of R_f coefficient was obtained for standard PEG with M_n within the range of 200-1500 on both Silicagel HF₂₅₄₊₃₆₆ and Silicagel 60F₂₅₄ bases. M_n of PEG declared by the manufacturer enabled calculation of the number of oxyethylene segments $-n_{TE}$ ($-OCH_2CH_2-$)_n in their structure.

At the same time the chromatographic homogeneity of the technical product was estimated. The results obtained in the course of research demonstrate that the process of adsorption on active carbon (Freundlich adsorption isotherm) makes it possible to separate fractions with relatively little variation in M_w . The results are presented in Tables I, II, and III.

The calculated values of R_f ($\bar{x} \pm t_s$ dla $n=10$) and R_M served as a basis for examining the course of the relation between R_f and R_M , and the estimated structural number of n_{TE} , $R_f, R_M = f(n_{TE})$.

The course of regression equations at the probability level $p=0.05$ with high numerical values of the correlation coefficient $r \geq 0.955$ (Table 4) indicates that they can be used to

calculate the number of oxyethylene segments n_{TE} in the fractions of block copolymers of 30p160, 30p27 and 30p10 type separated from the technical product.

The above shows that on Silicagel HF₂₅₄₊₃₆₆ base, irrespective of the polarity of the developing system (the mobile phase), the highest values of the correlation coefficient are found for regression equations of $R_f=a+b \cdot n_{TE}$ and $1/R_f=a+b \cdot n_{TE}$ types.

What is interesting from the perspective of analytic application is that on Silicagel 60 F₂₅₄ base the highest value of the correlation coefficient was found for the logarithmic form of exponential equation of $y=a \cdot x^b$ ($R_f=a \cdot n_{TE}^b$, $\log R_f=a'+b \cdot \log n_{TE}$) type.

The mathematical analysis of the results obtained was complemented with the investigation of the relation between the numerical value of R_M coefficient and the calculated structural number of oxyethylene segments n_{TE} in the molecule of PEG, $R_M = f(n_{TE})$. Regression equations at $p=0.05$ and the numerical values of the correlation coefficient are provided in Table IV.

The separated fractions of Rokopols 30p160 (A-1, A-2, A-3), 30p27 (B-1, B-2, B-3) and 30p10 (C-1) were tested on Silicagel HF₂₅₄₊₃₆₆ and Silicagel 60F₂₅₄ bases with the use of developing systems in which R_f PEG were characterized by significant regressive variation (systems C, D and E).

The numerical values of R_f presented in Table V demonstrate that the separated fractions of Rokopols are characterized by small dispersion of M_w and retain significant homogeneity. R_f was given as $\bar{x} \pm t_s$ for $n=10$.

Regression equations from Table IV were used to estimate the number of oxyethylene segments n_{TE} in the structure of copolymer for the examined systems and bases. The results are presented in Table V.

The averaging values of n_{TE} provided in Table 6 were used to calculate the weight-average molecular weight (M_w) of the separated copolymer (M_w of the lipophilic core of copolymer composed of 30 mols of propylene oxide $30p = 1742.4\text{g/mol}$) based on the equation $M_w=1742,4+44,053 \cdot n_{TE}$.

The stalagmometric method was used to estimate surface-tension coefficients of aqueous solutions of copolymers and the equation $\gamma^{25}=f(c, g \cdot 100\text{cm}^3)$ served to calculate the numerical value of critical micellar concentration, which was used to determine the thermodynamic potential of micelle formation (ΔG_m^0) on the basis of the equation $\Delta G_m^0 = 2,303RT \log cmc$.

It should be observed that the numerical value of decrease in surface tension in the critical region γ_{cmc}^{25} (mJ/m²) does not exceed its physiological value in human body fluids (52-48 mJ/m² serum, tear) in a significant way.

This state of affairs makes it possible to use Rokopols as solubilizers for lipophilic therapeutic agents administered parenterally.

The results obtained were used to observe the relation between ΔG_m^0 and the estimated number of oxyethylene segments n_{TE} (Table 6) in the molecule of the copolymer, $\Delta G_m^0 = f(n_{TE})$ (Fig.).

The course of the relation above (Fig. 1) shows that the thermodynamic stability of micelle increases along with an increase in the number of oxyethylene segments in the molecule of the copolymer, which ensures that the process of equilibrium solubilization gives a time-stable adduct with a lipophilic therapeutic agent.

The relation $\Delta G_m^0 = f(n_{TE})$ (Fig.) is described at the probability level $p=0.05$ and $r=0.9313$ in terms of the following regression equation:

$$\frac{1}{\Delta G_m^0} = -5,1806 \cdot 10^{-2} + 3,4494 \cdot 10^{-5} \cdot n_{TE}$$

The equation given above may be useful in determining the influence of the number of oxyethylene segments on the thermodynamic stability of micellarly solubilized therapeutic agent during the process of mass exchange at the phase boundary.

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Tabela I. Rezultaty analizy chromatograficznej PEG i Rokopoli na podłożu Silicagel HF₂₅₄₊₃₆₆₄ Przy użyciu układów rozwijających „A” i „B”

Table I. The results of PEG and Rokopols chromatographic analysis on Silicagel HF₂₅₄₊₃₆₆₄ base with the use of developing system „A” i „B”

PEG Mn	n _{TE} wyliczone calculated	Układ rozwijający „A” Developing system „A”		Układ rozwijający „B” Developing system „B”	
		R _f ±t _s *	R _M	R _f ±t _s	R _M
PEG-200	4,14	0,679±0,018	-1,6745	0,524±0,019	-1,9582
PEG-300	6,14	0,592±0,011	-1,8383	0,487±0,017	0,0224
PEG-400	8,68	0,670±0,018	-1,6924	0,392±0,014	0,1906
PEG-600	13,22	0,681±0,014	-1,6706	0,144±0,019	0,7741
PEG-1000	24,32	0,696±0,017	-1,6401	0,132±0,024	0,8179
PEG-1500	33,68	0,692±0,014	-1,6484	0,152±0,028	0,7464
PEG-2000	45,04	0,688±0,090	-1,6564	0,068±0,012	1,1367
PEG-6000	135,95	0,632±0,012	-1,7656	0,009±0,002	2,0417
Rokoppol tech.	n _{TE} oznaczone determine	R _f □(\bar{x})	R _M	R _f □(\bar{x})	R _M
30p160	95,6	0,596	-1,8311	0,074	1,0972
		0,640	-1,7501		
		0,692	-1,6484		
30p27	25,7	0,680	-1,6725	0,082	1,0488
		0,823	-1,3326	0,411	0,1562
30p10	4,2	0,895	-1,0693	0,745	-1,5342

* R_f (\bar{x} ±t_s) dla n=10; * R_f (\bar{x} ±t_s)for n=10

Układ rozwijający A: izopropanol 4 cz obj., izobutanol -2cz obj., MEK -2 cz obj. NH₃H₂O 25% 3 cz obj. Układ Rozwijający B: izopropanol 4 cz obj., izobutanol -2cz obj., MEK -2 cz obj. NH₃H₂O 25% 1 cz obj.

Developing system A : izopropanol 4 parts by volume., izobutanol -2 parts by volume, MEK -2 parts by volume NH₃H₂O 25% 3 parts by volume. Developing system B : izopropanol 4 parts by volume, izobutanol -2parts by volume, MEK -2 parts by volume NH₃H₂O 25% 1 parts by volume.

Tabela II. Rezultaty analizy chromatograficznej PEG i Rokopoli na podłożu Silicagel HF₂₅₄₊₃₆₆₄ Przy użyciu układów rozwijających „C” i „D”
 Table II The results of PEG and Rokopols chromatographic analysis on Silicagel HF₂₅₄₊₃₆₆₄ base with the use of developing system „C” and „D”

PEG Mn	n _{TE} wyliczone calculated	Układ rozwijający „C” Developing system „C”		Układ rozwijający „D” Developing system „D”	
		R _f ±t _s *	R _M	R _f ±t _s	R _M
PEG-200	4,14	0,679±0,028	-1,6745	0,543±0,023	-1,9251
PEG-300	6,14	0,662±0,032	-1,7080	0,512±0,022	-1,9792
PEG-400	8,68	0,631±0,018	-1,7595	0,463±0,024	0,0641
PEG-600	13,22	0,590±0,026	-1,8598	0,262±0,034	0,4495
PEG-1000	24,32	0,535±0,017	-1,9390	0,251±0,027	0,4748
PEG-1500	33,68	0,557±0,022	-1,9005	0,245±0,028	0,4868
PEG-2000	45,04	0,498±0,032	0,0034	0,144±0,017	0,7741
PEG-6000	135,95	0,286±0,027	0,3972	0,058±0,012	1,2106
PEG-9000	204,14	0,132±0,028	0,8179	0,044±0,018	1,3368
PEG-12000	272,32	0,095±0,018	0,9789	0,035±0,012	1,4404
PEG-15000	340,50	0,083±0,017	1,0429	0,011±0,009	1,9538
Rokoppol tech.	n _{TE} oznaczone	R _f (\bar{x})	R _M	R _f (\bar{x})	R _M
30p160	160	0,225	0,5371		
	68,8	0,425	0,1313		
30p27	61,6	0,440	0,1062		
	21,5	0,575	-1,8687		
30p10	12,4	0,611	-1,3673		

* R_f($\bar{x} \pm t_s$) dla n=10; * R_f($\bar{x} \pm t_s$)for n=10.

Układ rozwijający C: izopropanol 4 cz obj., izobutanol -2cz obj., MEK -2 cz obj. NH₃H₂O 25% 2 cz obj. Układ Rozwijający B rozwijający D: n-butanol -5 cz obj. izopropanol 3,5 cz obj., NH₃H₂O 25% 1,5 cz obj.

Developing system C: izopropanol 4 parts by volume, izobutanol -2parts by volume, MEK -2 parts by volume NH₃H₂O 25% 2 parts by volume. Developing system B and D: n-butanol -5 parts by volume izopropanol 3,5 parts by volume, NH₃H₂O 25% 1,5 parts by volume.

Tabela III. Rezultaty analizy chromatograficznej PEG i Rokopoli na podłożu Silicagel HF₂₅₄₊₃₆₆ i 60E₂₅₄ Przy użyciu układu rozwijającego „E”

Table III.. The results of PEG and Rokopols chromatographic analysis on Silicagel HF₂₅₄₊₃₆₆ base with the use of developing system „E”

PEG Mn	n _{TE} wyliczone calculated	Układ rozwijający „E” Developing system “E”		Układ rozwijający „E” Developing system “E”	
		R _f ±t _s	R _M	R _f ±t _s	R _M
PEG-200	4,14	0,533±0,033	-1,8843	0,582±0,018	-1,8562
PEG-300	6,14	0,501±0,028	-1,9982	0,525±0,024	-1,9565
PEG-400	8,68	0,480±0,023	0,0346	0,445±0,024	0,0958
PEG-600	13,22	0,402±0,026	0,1723	0,323±0,011	0,3211
PEG-1000	24,32	0,411±0,022	0,1562	0,231±0,028	0,5223
PEG-1500	33,68	0,358±0,024	0,2535	0,250±0,032	0,4771
PEG-2000	45,04	0,302±0,024	0,3638	0,205±0,025	0,5881
PEG-6000	135,95	0,209±0,017	0,5886	0,132±0,012	0,8179
Rokoppol tech.	n _{TE} oznaczone	R _f (\bar{x})	R _M	R _f (\bar{x})	R _M
30p160	210,6	0,176	0,6703	0,196	0,6130
	13,7	0,428	0,1242	0,369	0,2330
30p27	37,5	0,335	0,2977	0,233	0,5173
	6,5	0,496	0,0068	0,433	0,1169
30p10	2,2	0,596	-1,8311	0,494	0,0103
		0,632	-1,7650	0,745	-1,5342
Podłoże Silicagel 60 F ₂₅₄ Układ rozwijający “E”: n-butanol- 5cz obj, n-propanol – 1cz. obj. NH ₃ H ₂ O 25% 4 cz. obj. Silicagel 60 F ₂₅₄ base Developing system “E”: n-butanol- 5cz obj, n-propanol – 1parts by volume NH ₃ H ₂ O 25% 4 parts by volume					

Tabela IV. Równania regresji opisujące przebieg zależności między R_f i R_M a wyliczoną zawartością segmentów oksyetylenowych n_{TE} w strukturze PEG

Table IV The Regression equations descriptions the course of the relation between R_f i R_M and the number of oxyethylene segments n_{TE} in the molecule of PEG

Układ rozwijający Developing system	Równanie regresji – typ Regression equation - typ	„r”	Współczynniki kierunkowe równań Regression factors	
			a±da	b±db
„B”	$1/R_f = a + b \cdot n_{TE}$	0,9721	$9,0751 \pm 10,6551$	$0,8321 \pm 0,2007$
	$\log R_f = a + b \cdot n_{TE}$	0,9527	$-0,4156 \pm 0,2135$	$-0,0126 \pm 0,0041$
	$R_M = a + b \cdot 1/n_{TE}$	0,9467	$1,6404 \pm 0,5289$	$-13,6071 \pm 4,6217$
„C”	$1/R_f = a + b \cdot n_{TE}$	0,9847	$0,9526 \pm 0,6532$	$0,0322 \pm 0,0043$
	$\log R_f = a + b \cdot n_{TE}$	0,9901	$-0,1779 \pm 0,0471$	$-0,0029 \pm 0,0003$
	$R_M = a + b \cdot n_{TE}$	0,8961	$-1,6332 \pm 0,5521$	$0,0097 \pm 0,0036$
„D”	$\log R_f = a + b \cdot n_{TE}$	0,9649	$-0,4259 \pm 0,1387$	$-0,0044 \pm 0,0009$
	$R_f = a + b \cdot \log n_{TE}$	0,9627	$0,6774 \pm 0,1015$	$-0,2793 \pm 0,0592$
	$R_M = a + b \cdot 1/n_{TE}$	0,9332	$1,3652 \pm 0,4356$	$-15,3771 \pm 4,4620$
„E”	$R_f = a + b \cdot \log n_{TE}$	0,9830	$0,6693 \pm 0,0535$	$-0,2123 \pm 0,0395$
	$1/R_f = a + b \cdot n_{TE}$	0,9790	$1,9942 \pm 0,2361$	$0,0214 \pm 0,0044$
	$R_M = a + b \cdot 1/n_{TE}$	0,8992	$0,7030 \pm 0,6410$	$-11,5245 \pm 5,6008$
„E”* 60F ₂₅₄	$\log R_f = a + b \cdot n_{TE}$	0,9871	$0,0307 \pm 0,0949$	$-0,4328 \pm 0,0700$
	$R_f = a + b \cdot \log n_{TE}$	0,9545	$0,7291 \pm 0,1304$	$-0,3085 \pm 0,0962$
	$R_M = a + b \cdot 1/n_{TE}$	0,9150	$0,9705 \pm 0,6405$	$-12,7104 \pm 5,5968$

Tabela V. Oznaczona na podłożu silicagel HF₃₅₄₊₃₆₆ i silicagel 60F₂₅₄ przy użyciu odpowiedniego układu rozwijającego (C,D,E) zawartości segmentów oksyetylenowych w oczyszczonych frakcjach Rokopoli

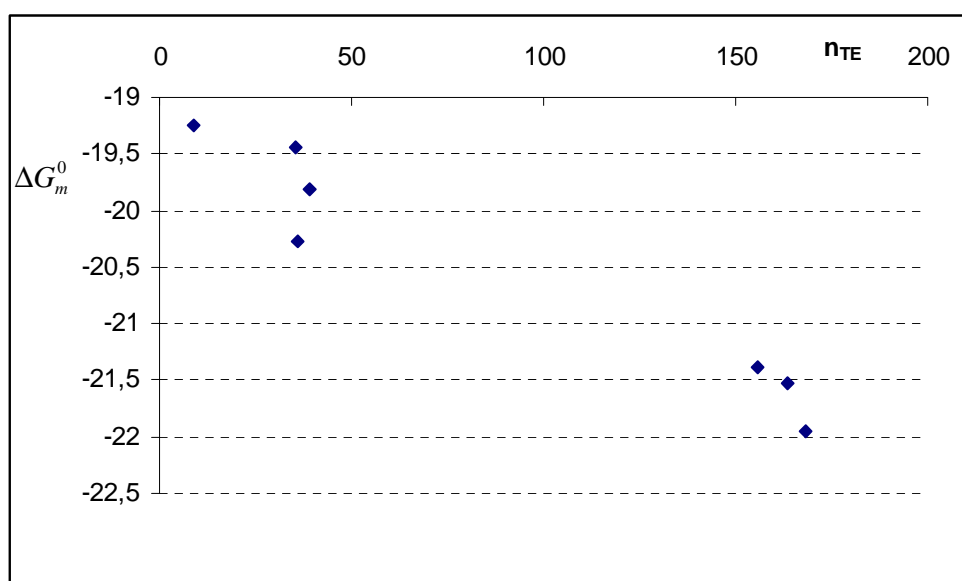
Table V. Determine on silicagel HF₃₅₄₊₃₆₆ i silicagel 60F₂₅₄ basis with the use of developing system (C,D,E) content of oxyethylene segments in the refined fractions of Rokopols

Oczyszczone frakcje	Układ Rozwijający „C” Developing system „C”		Układ Rozwijający „D” Developing system „D”		Układ Rozwijający „E” Developing system „E”		Układ Rozwijający „E*” Developing system „E*”	
Rokopoli/ Refined fractions of Rokopols	R _f ±t _s	Oznaczone Determine n _{TE}	R _f ±t _s	Oznaczone Determine n _{TE}	R _f ±t _s	Oznaczone Determine n _{TE}	R _f ±t _s	Oznaczone Determine n _{TE}
30p160 A-1	0,330±0,031	104,7	0,057±0,004	186,9	0,176±0,012	210,6	0,122±0,012	152,0
30p160 A-2	0,437±0,022	97,2	0,059±0,007	182,5	0,182±0,014	197,4	0,124±0,011	146,4
30p160 A-3	0,312±0,023	174,4	0,068±0,011	168,5	0,184±0,009	193,1	0,126±0,017	141,1
30p27 B-1	0,536±0,032	32,1	0,259±0,011	36,5	0,331±0,017	39,2	0,233±0,011	34,1
30p27 B-2	0,489±0,018	45,8	0,251±0,016	39,6	0,335±0,008	37,5	0,238±0,013	32,5
30p27 B-3	0,529±0,024	34,1	0,253±0,012	38,8	0,342±0,015	34,8	0,228±0,012	35,8
30p10 C-1	0,625±0,018	9,1	0,428±0,014	13,1	0,486±0,011	7,3	0,494±0,011	6,0
* podłoże (faza stała) silicagel 60F ₂₅₄ ; * silicagel 60F ₂₅₄ basis								

Tabela VI. Parametry fizykochemiczne określające aktywność powierzchniową wydzielonych frakcji Rokopoli

Table VI. The parameters defined surface activity of aqueous solutions refined fraction of Rokopols

Oczyszczone frakcje Rokopoli refined fraction of Rokopols	Oznaczona ilość segmentów Determined content of segments $-n_{TE}(\bar{x})$	M_W^*	cmc g/100cm ³	cmc mol/l	ΔG_m^0 kJ/mol	γ_{cmc}^{25} mJ/m ²
30p160 A-1	163,55	9035,4	0,1524	$1,6867 \cdot 10^{-4}$	-21,5290	57,1
30p160 A-2	155,87	8680,9	0,1538	$1,7864 \cdot 10^{-4}$	-21,3868	56,2
30p160 A-3	168,02	9144,2	0,1298	$1,4195 \cdot 10^{-4}$	-21,9565	52,5
30p27 B-1	35,47	3305,2	0,1298	$3,9272 \cdot 10^{-4}$	-19,4337	45,8
30p27 B-2	38,85	3453,8	0,1164	$3,3701 \cdot 10^{-4}$	-19,8138	47,1
30p27 B-3	35,87	3322,8	0,0928	$2,7982 \cdot 10^{-4}$	-20,2747	46,2
30p10 C-1	8,87	2133,3	0,0912	$4,2750 \cdot 10^{-4}$	-19,2389	45,1
M_W (CH ₂ CH ₂ O) _{n=1} =44,053; M_W [CH(CH ₃)CH ₂ O] _{n=1} =58,080; M_W [CH(CH ₃)CH ₂ O] _{n=30} =1742,4						



Ryc. Przebieg zależności między termodynamicznym potencjałem tworzenia miceli - ΔG_m^0 a oznaczoną zawartością segmentów oksyetylenowych n_{TE} w strukturze wydzielonych frakcji kopolimerów

Fig. The course of relationship between - ΔG_m^0 and n_{TE} in the structure of refined fractions of polymers