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STRUCTURE CORRELATIONS – COLLOIDAL PROPERTIES AMONG SOME "HOMOGENOUS" POLYETHYLENE GLYCOLS (N = 3-18) DERIVATED WITH AROMA RADICALS AS POSSIBLE ADDITIVATION SYSTEMS

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Abstract

The "homogenous" polyoxyethylen chains ***(POE)*** *(*$\overline{n}$ *= 3-18) diversely split, as hydrophilic parts of a large series of additivation structures, cosmetics, pharmaceutics, agro-alimentary, represent „instruments" of controlled monitorization of* ***HLB value*** *because of the strictly quantified olygomerization degree, allowing fascinating colloidal performances (emulsifying, dispersion, micellar solubility, foaming / antifoaming, wetting / etallation, antistatic properties etc.). The knowing and the correlated interpretation of these in the ensemble structure – superficial active (colloidal) characteristics is a potential instrument of* ***GMP*** *controlled agro-alimentary processing. The limited (reduced) toxicity ("*n_0 *effective level") corroborated with the actual demanding regarding the alimentary security have encouraged the research of some characteristics in the "homogenous" polyoxyethylenic* ***(POE)*** *structures (*$\overline{n}$ *= 3-18) diversely split.*

Key words*: structure correlations–colloidal characteristics, "homogenous" polyethylene glycol, micellar critical concentration, superficial tension, alimentary additivation.*

Introduction

For over five decades the range of alimentary additives with heterogeneous polyoxiethylenic chains **(POE)** ($\overline{n}$ = **3-50**) as hydrophilic part with different oligomeriyation degrees ($\overline{n}$) is successfully accessed in the cosmetic, pharmaceutical, agro-alimentary etc. processing, because a controlled HLB balance may ensure the whole range of classical colloidal applications (the reduction of the

superficial tension at the separation interface of two phases, wetting / etallation, foaming / antifoaming, antistatic, dispersion, micellar solubility effect etc.).

After rediscovering the corronar polyethylene C_i (Pedersen, 1976) the attention has continuously been oriented towards the chains **(POE)**, towards the polyethyleneglycols **(PEG)** as acyclic structures ant towards their potential competences mainly due to their specific conformation but also to the oxygen coordination function. The "homogenous" (***n***) and / or heterogenic ($\bar{n}$) normal and derivated **POE** chains with different radicals have become accessible as hydrocolloids also for the alimentary additivation. In the previous researches there have also been obtained structures, which have been physical-chemically tested after purification and chemical (colloidal) characterization (Jianu, in press).

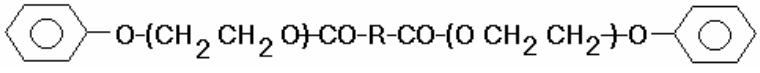
This works intends to propose by means of mathematics some colloidal structure-properties correlations in order to subsequently supervise the directions of their technological use.

Experimental

"Homogenous" polyethylenglycols ($\bar{n}$ = 3 - 18) (I) differently divided and purified anhydrous, was used. The stalagmometric method described in STAS 6118-5 with subsequently ISO modifications was used for measure superficial tension. To determine the equations of the regression curves with optimal correlation coefficients were computed (Cret, 2000).

Results and Discussions

For a determined number of given structures (I) there must be determined a connection relation between the number of drops and the concentration of the tested solution, in order to determine the micellar critical concentration (MCC).



From preliminary tries and by analyzing the values of the correlation coefficients for different types of regression curves, we have noticed that the biggest problem is at the form:

$$y = a \cdot x^{-b},\ a, b \succ 0$$

where the relations give the MCC coordinates:

$$x_0 = (ab)^{\frac{1}{b+1}},\ y_0 = a \cdot (ab)^{\frac{-b}{b+1}}$$

The experiments have been done successively for all the structures at the three temperatures: 20, 30 and 50°C. 11 values were retained**.** In tables 1-12 are presented the results of the measurements and then the expressions of the coefficients **a** and **b** of the mentioned regression function, the correlation coefficient, the MCC coordinates: A, B, C for 20, 30, respectively 50°C such as some graphic representations associated to the temperatures and to the MCC points.

Table 1. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

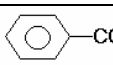
R =  —CO – (benzoic)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	41.28	43.56	49.18
0.5	41.99	44.19	49.98
0.25	42.78	45.51	51.68
0.125	43.52	46.91	51.68
0.0625	45.88	49.18	54.45
0.03125	46.48	50.82	55.44
0.01562	49.15	53.49	57.53
0.007812	54.33	59.78	60.98
0.003906	58.92	64.87	64.87
0.001953	64.14	70.91	67.76
0.000976	67.11	72.01	70.91
The equation of the function	$y = 38.6048 \cdot x^{-0.0734}$	$y = 40.8716 \cdot x^{-0.0792}$	$y = 47.4871 \cdot x^{-0.0540}$
CCM (mol/l · 10^{-2})	3.09	2.81	2.44
σ (dyne/cm)	40.25	47.02	49.83

Table 2. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  CH_2- (fenilacetil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.12	46.91	49.18
0.5	40.65	47.64	50.82
0.25	41.20	47.64	50.82
0.125	41.76	48.40	50.82
0.0625	43.56	50.82	53.49
0.03125	46.20	53.49	55.44
0.01562	50.82	56.46	58.63
0.007812	55.44	59.78	60.98
0.003906	62.22	63.52	64.87
0.001953	70.91	70.91	70.91
0.000976	74.71	74.27	74.08
The equation of the function	$y = 38128 \cdot x^{-0.0956}$	$y = 43.768x^{-0.0692}$	$y = 46.827x^{-0.0599}$
CCM (mol/l · 10^{-2})	3.09	2.81	2.64
σ (dyne/cm)	40.25	47.02	49.69

Table 3. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  CH_2- CH_2- (hidrocinalmoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.12	41.20	49.18
0.5	41.76	41.20	50.82
0.25	43.56	41.76	51.68
0.125	44.84	42.35	53.49
0.0625	46.20	43.56	56.46
0.03125	49.18	44.84	57.53
0.01562	52.57	49.18	58.63
0.007812	59.78	57.53	62.22
0.003906	64.87	63.52	64.87
0.001953	70.91	70.91	69.30
0.000976	70.14	74.61	74.22
The equation of the function	$y = 38.1670x^{-0.0893}$	$y = 36.5924x^{-0.0936}$	$y = 48.0463x^{-0.0567}$
CCM (mol/l · 10^{-2})	3.08	3.08	2.58
σ (dyne/cm)	42.20	40.65	50.70

Table 4. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  — CH = CH (cinamoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.37	41.58	48.90
0.5	40.92	41.64	49.88
0.25	42.98	41.90	51.47
0.125	44.54	42.48	53.52
0.0625	46.02	43.09	55.98
0.03125	48.87	44.11	57.34
0.01562	51.87	49.88	58.69
0.007812	59.18	57.48	61.80
0.003906	64.09	63.45	64.08
0.001953	69.88	69.94	70.87
0.000976	73.82	73.08	73.41
The equation of the function	$y = 37.6122x^{-0.0924}$	$y = 36.9208x^{-0.0904}$	$y = 47.6095x^{-0.0581}$
CCM (mol/l · 10^{-2})	3.05	3.02	2.61
σ (dyne/cm)	40.58	40.80	50.34

Table 5. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  —CO (α- naftoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	41.38	46.91	48.42
0.5	41.45	46.91	49.18
0.25	41.82	46.91	49.98
0.125	41.93	46.91	50.82
0.0625	43.05	48.40	52.57
0.03125	45.12	50.82	54.45
0.01562	49.43	54.45	56.46
0.007812	53.26	60.98	60.98
0.003906	57.18	64.87	67.76
0.001953	58.92	67.76	70.91
0.000976	60.31	70.91	71.94
The equation of the function	$y = 38.5214 \cdot x^{-0.0635}$	$y = 43.0363 \cdot x^{-0.0676}$	$y = 45.8368 \cdot x^{-0.0628}$
CCM (mol/l · 10^{-2})	2.31	2.72	2.70
σ (dyne/cm)	40.63	46.04	48.79

Table 6. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

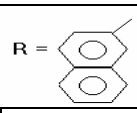
R =  (β- naftoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	41.42	46.34	48.02
0.5	41.02	46.33	49.34
0.25	41.34	46.52	49.41
0.125	41.22	47.03	50.18
0.0625	43.21	48.92	53.02
0.03125	45.29	50.24	54.03
0.01562	49.11	55.02	56.92
0.007812	53.34	61.14	60.25
0.003906	57.38	64.55	67.83
0.001953	58.28	66.92	70.35
0.000976	60.41	70.42	70.91
The equation of the function	$y = 38.2487x^{-0.0645}$	$y = 42.7992x^{-0.0680}$	$y = 45.6905x^{-0.0624}$
CCM (mol/l · 10^{-2})	2.33	2.71	2.68
σ (dyne/cm)	40.39	45.81	48.59

Table 7. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R = O_2N  CO — (p-nitrobenzoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.33	43.42	49.24
0.5	41.03	44.32	49.37
0.25	42.75	45.63	51.03
0.125	43.42	46.92	51.98
0.0625	45.75	49.32	54.92
0.03125	46.42	50.74	55.67
0.01562	43.25	53.92	57.88
0.007812	54.02	59.34	60.43
0.003906	58.74	64.50	64.53
0.001953	64.19	70.48	67.53
0.000976	67.26	72.11	70.82
The equation of the function	$y = 37.8084x^{-0.0745}$	$y = 40.9380x^{-0.0785}$	$y = 47.3808x^{-0.0541}$
CCM (mol/l · 10^{-2})	2.62	2.95	2.44
σ (dyne/cm)	40.62	44.56	49.72

Table 8. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) $\overline{n} = 8$

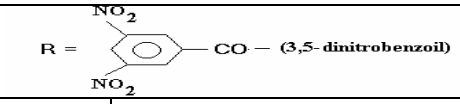
			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	43.56	46.91	49.98
0.5	43.56	47.64	50.82
0.25	43.56	49.18	51.68
0.125	46.20	49.18	55.44
0.0625	46.20	49.98	57.53
0.03125	46.91	51.68	60.98
0.01562	52.57	57.53	62.22
0.007812	58.63	63.52	64.87
0.003906	64.87	67.76	67.76
0.001953	67.76	70.91	70.91
0.000976	69.14	71.14	71.91
The equation of the function	$y = 39.9201x^{-0.0771}$	$y = 44.1433x^{-0.00693}$	$y = 49.1369x^{-0.0571}$
CCM (mol/l · 10^{-2})	2.83	2.84	2.65
σ (dyne/cm)	43.26	47.46	51.59

Table 9. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

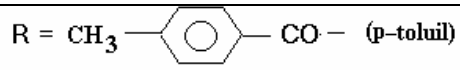
			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	41.32	43.62	49.25
0.5	42.03	44.45	50.14
0.25	42.48	45.63	51.79
0.125	43.67	46.75	52.24
0.0625	45.74	49.28	54.42
0.03125	46.54	50.92	55.54
0.01562	49.28	53.54	56.38
0.007812	54.58	58.34	59.22
0.003906	58.32	63.47	63.84
0.001953	63.92	70.02	66.74
0.000976	66.80	71.60	69.90
The equation of the function	$y = 38.6366x^{-0.0728}$	$y = 41.0942x^{-0.0762}$	$y = 47.8206x^{-0.0499}$
CCM (mol/l · 10^{-2})	2.62	2.88	2.28
σ (dyne/cm)	41.44	44.55	49.83

Table 10. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R = CH_3 — O —  — CO — (p-anisoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	41.48	43.56	50.82
0.5	42.37	46.91	52.57
0.25	42.88	47.64	52.57
0.125	43.77	48.40	54.45
0.0625	45.68	48.40	54.45
0.03125	46.38	49.98	56.46
0.01562	49.95	56.46	60.98
0.007812	55.03	60.98	64.87
0.003906	58.88	64.87	70.91
0.001953	63.44	70.91	70.47
0.000976	66.88	78.90	71.70
The equation of the function	$y = 38.8762x^{-0.0722}$	$y = 41.6419x^{-0.0809}$	$y = 49.0691x^{-0.0558}$
CCM (mol/l · 10^{-2})	2.61	3.07	2.59
σ (dyne/cm)	41.67	45.60	51.75

Table 11. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  — (2- furoil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.55	46.91	48.48
0.5	41.76	46.91	49.18
0.25	42.35	47.64	50.82
0.125	42.35	48.40	51.68
0.0625	43.56	49.18	51.68
0.03125	49.18	51.68	56.46
0.01562	54.45	54.45	60.98
0.007812	57.53	58.63	62.22
0.003906	66.28	63.52	66.28
0.001953	70.91	67.76	67.76
0.000976	69.50	70.91	70.91
The equation of the function	$y = 37.4280x^{-0.0917}$	$y = 43.6368x^{-0.0641}$	$y = 46.7067x^{-0.0592}$
CCM (mol/l · 10^{-2})	3.09	2.62	2.61
σ (dyne/cm)	41.51	46.42	49.43

Table 12. The dependency on temperature of the main colloidal characteristics (σ, CCM) of (I) for $\overline{n} = 8$

R =  — CO – (2-tiofuroil)			
Concentration, mol/l · 10^{-2}	Number of solution drops		
	20°C	30°C	50°C
1	40.78	47.12	49.32
0.5	41.84	47.22	49.99
0.25	42.38	48.18	50.98
0.125	42.48	48.98	51.24
0.0625	43.78	49.38	51.48
0.03125	48.88	51.58	55.74
0.01562	53.28	54.29	59.74
0.007812	57.42	58.49	62.08
0.003906	65.32	63.12	65.35
0.001953	69.32	67.02	67.14
0.000976	70.03	69.50	69.40
The equation of the function	$y = 37.5732x^{-0.0894}$	$y = 44.1730x^{-0.0604}$	$y = 47.2170x^{-0.0546}$
CCM (mol/l · 10^{-2})	1.80	2.52	2.45
σ (dyne/cm)	38.68	46.71	49.58

Conclusions

Could be notice that for the studied series, the correlation coefficients have values close to the unit, which justifies the selection of the power function as mathematic model for the observed phenomena.

To notice is also the linear dependence of the MCC coordinated on the temperature to which the experiments are done. Table 13 presents the equations of the regression lines and the correlation coefficients corresponding to the points experimentally obtained for all the structures selected and analyzed.

References

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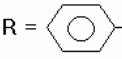
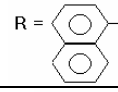
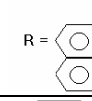
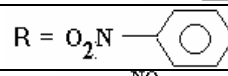
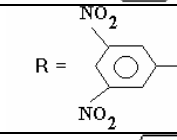
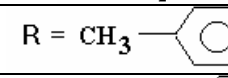
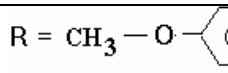
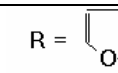
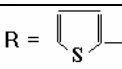
Pedersen, C.J. (1967). *J. Amer. Chem. Soc*., 89(9), 7017, 1967

Table 13. The equations of the regression lines of MCC on temperature

R Structure	The equations of the lines, the correlation coefficient
	y = 5,65 – 0,06x; r = –0,95
	***y = 4,96 – 0,04 x; r = –0,99***
	***y = 5,26 – 0,05 x; r = –0,98***
	***y = 4,82 – 0,04 x; r = –0,99***
	***y = 0,24 + 0,05 x; r = 0,90***
	***y = 0,48 + 0,04 x; r = 0,91***
	***y = 3,73 – 0,02 x; r = –0,41***
	***y = 3,79 – 0,02 x; r = –0,68***
	***y = 4,77 – 0,04 x; r = –0,68***
	***y = 3,15 – 0,008 x; r = –0,16***
	***y = 5,70 – 0,06 x; r = –0.93***
	***y = –0,71 + 0,06 x; r = 0,94***