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Controlled of colloidal parameters through gradual ternary association of new "homogeneous" nonionic structured lipids

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Abstract

In a previous work we have proposed a synergic optimization of synthetical colloidal basic parameters ("homogeneous" cumulated degree by oligomerisation) (n_{CB}) and cumulated hydrophile/hydrophobe values HLB_{CB}) of certain homogeneous conjugates PEG_n-L(2R'; R) (R'; 2R) (I) (structured by Williamson procedure) "colloidally disadvantage" (HLB = 2–7) through gradual binary association (1–70 % initially with "homogeneous" polyoxyethylene chains with (n = 3, 9, 18, 30, 40, 50) monoderivatized R(EH) and afterwards conjugates PEG_n-L(2R';R) (R';2R) "colloidally advantaged" (HLB = 9–13).

Encouraging results obtained suggested the idea of extending colloidal association systems from the binary to the ternary association, because operating range and degrees of liberty ensure the possibility of controlled modification a whole lot more extended.

To this purpose, there has by "homogeneous" conjugates PEG_n-L (2R'; R) (R'; 2R) $HLB_1/HLB_2/HLB_3$ = 2/6/13; 2/8/13; 2/10/13; 6/8/13; 6/10/13; 8/10/13 in gradual percentage ratios for each mentioned series by 10/34/56; 20/34/46; 33/34/33; 50/34/16; 60/34/6 for which it was assessed the evolution of the ternary cumulated "homogeneous" degree of oligomerisation (n_{CT}) and the ternary cumulated hydrophile/hydrophobe values (HLB_{CT}).

lt has been considered as a work premise, later on verified, the previous statement according to which hydrocarbonate chains R' and/or R only contributes insignificantly in the modification of the colloidal competences range.

Keywords: cumulated colloidal competences, ternary colloidal systems, polyoxyethylene conjugates, PEG-ylated lipids, structurated lipidic architectures

1. Introduction

Controlled administration, "additivation" of some structurated conjugate lipids (I) as biopolymers is appreciated in the formulation of some fungicides, germicides, growth regulators, herbicides, fertilizers, insecticides, minerals, oligoelement etc. [1]. To "adapt" a polymer to a specific biologic system, there must be considered simultaneously the following parameters: cost, environment conditions, eliberation kinetics imposed to the biologic system, length, accessibility of formulation and/or additivation. Other aspects include the nature of the polymer, thermostability and compatibility with bioactive agents, stability of the couple, processing conditions, shape and desired size of the final product [2].

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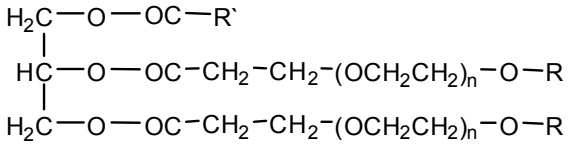
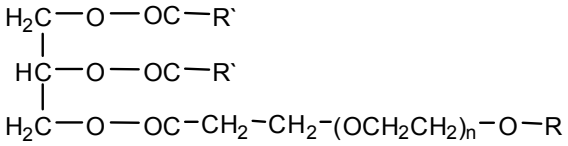


PEG_n-L (R`;2R)



PEG_n-L (2R`;R)

2. Materials and methods

We point out some of the most relevant application domains in horticultural and agroalimentary processing:

- soil conditioning or soil-seed-plant system [3-16];
- "covering" with edible pellicles (semipermeable barriers at gases and water vapours) as an optimum technological solution to extend preservation period post-harvesting. It is estimated that 25–80 % of horticultural products (fruits, freshly harvested vegetables) decay when stored and preserved [16] because they continue their metabolic activity after harvesting as "live cellular systems" [17], they rape climacterically and they age unclimacterically, if special procedures are not adopted to limit these biological processes. They can be simulated or they an substitute classical techniques used in fresh foods, controlled atmosphere (CA) or modified atmosphere (MA) [6,18,19], and they can be obstacles in the way of dehydration and gas transfer (carbon dyoxide and oxygen) [4]. The pellicles fortify simultaneously mechanical manipulation properties [20] and they ensure a structural integrity, the retention of volatile aromatized compounds [10] and they can serve as vehicle of technological additives in horticultural or agroalimentary processing, antioxidants E–300/E–324, antimicrobian agents (E–200/E–219) [17,21].

In the same period it is also debated the effect of wax pellicles, oils and shellac on internal atmosphere, loss of weight and ethanol content from apples and citric fruits [10].

An oversight of these theoretical and practical considerations has suggested the idea to make the help of PEG-s new conjugates of the polyethylenglycols (PEG_n) with "homogeneous" degree of oligomerisation (n = 3 – 18) as new structurate lipids by diderivatisation (R) with nonylphenyl chains (NF) and/or 2-ethyl-hexyl (EH) respectively isolated high polyunsaturated fatty acids, purified and characterized as saponificable fractions from grapes seeds (*Vitis vinifera*) (R'_s), chestnut fruits (*Aesculus hippocastanum*) (R'_{ca}), wild rose (*Rosa canina*) (R'_m) coriander (*Coriandri fructus*) (R'_{co}).

2. Materials and methods

Materials

- conjugates PEGn-L (2R';R) (R';2R) (structured lipids) [22];
- "homogeneous" polyethylenglycols (n = 3 – 18) monoderivatised R (NF; EH) purified by water, polyethylenglycols (PEG_n), nonylphenol (NF) and/or 2-ethyl-hexyl alcohol;
- propionic acid (Merck) (CAS 79-09-4);
- ethanol 98 % (Merck) (CAS 64-17-5);
- phenol (Merck) (CAS 108-95-2);
- hydriodic acid (Merck) (CAS 10034-85-2).

Methods

Evaluation of water number (A) for polyoxyethylene chains (PEO) "homogeneous" (n = 3-18) per se and/or derivatized [22, 23]

Water number defined as the volume of aqueous phenol solution 2 % added until the appearance a 1 % solution of polyoxyethylene chains (PEO) "homogeneous" (n = 3–18) per se and/or derivatized chains [conjugates PEG_n-L (2R';R), (R';2R)] (ethyl alcohol solution 96 % at 25°C), opalescence determined by the clevage of "hydrogen linkages" of the of polyoxyethylene chains (PEO) with water molecules in a process of double exchange

(equilibrium) that exists in the solution. It is accepted where:

$$HLB = 0.89A + 1.11$$

A = water number (mL solutions 2 % phenol/ mL solution 10 % of polyoxyethylene chains PEO in ethyl alcohol 96 % at 25°C);

HLB = hydrophyle / hydrophobe value "homogeneous" (n = 3 – 18) polyoxyethylene chains (PEO) [conjugates PEG_n-L(2R'; R), (R'; 2R)] studied.

Weigh 0.5 g conjugates PEG_n-L (2R';R) (R';2R) to be studied in Jukov apparatus at 25 ± 0.5°C, dissolve in 5 mL ethyl alcohol 96 % and titrate it with aqueous phenol solutions 2 % from a biuret with double walls (thermostat as the Jukov apparatus).

Results are estimated with the relation:

$$A = \frac{\text{aqueous phenol solution 2 \%(mL)}}{\text{ethyl alcohol solution of } PEG_n - L\,(2R';R)(R';2R)\,(mL)}$$

Evaluation of HLB values after modified Karabinos [22, 23] method:

In 200–250 mL Erlenmeyer vessel weigh (analytical precision) 0.5 g conjugate PEG_n-L(2R';R) (R';2R), dissolve by stirring under controlled heating in 10–15 mL propionic acid (or 5–10 mL ethyl alcohol 98 % depending on the solubility of the studied product. Cooled by thermostatic bath at 25°C is titrated with aqueous phenol solution 2 % up to a permanent opalescence.

A is estimated with the relation:

$$A = \frac{\text{aqueous phenol solution 2 \% (mL)}}{\text{ethyl alcohol solution of } PEG_n - L\,(2R';R)\,(R';2R)\,(mL)}$$

$$B = \frac{\text{aqueous phenol solution 2 \% (mL)}}{\text{propionic acid solution of } PEG_n - L\,(2R';R)\,(R';2R)\,(mL)}$$

$$HLB = 0.89\,(A)B + 1.11$$

Assessing ethyleneoxide content in "homogeneous" (n = 3–18) polyethyleneoxy (PEO) chains [22] partially or full derivatised

The polyethyleneoxy (PEO) chain "homogeneous" (n = 3–18) partially or full derivatised are (divide) quantitative with hydriodic acid (d = 1,7–1,9), and with the resulted iode are titrate it with sodium thiosulphate solution. One mol (structural unit) of ethyleneoxyde (EO) (form) one mole of iode (I_2). It is weigh with (analytical precision) 0.1-0.5 g "homogeneous" polyethyleneoxy (PEO) chain (n = 3-18) per se and/or derivatised (without water or polyethyleneglycols PEG_n) in a 100 mL vessel (NS 29/32), 5 mL hydriodic acid (d = 1.7–1.9) is exactly added and warmed up 90 minutes at reflux (110-115°C), on the glycerol bath in parallel with a mirror sample.

After full breaking it is introduce in the open upper part of the refrigerant 50 mL aqueous solution KI 20 % for washing and solvating the formed iodine (sublimated), and it is titrate the $Na_2S_2O_3$ solution 0.1 n in presence of starch aqueous solution 1 % fresh prepared.

If it is proceeding with hydriodic acid of low density (d < 1.7) the determinations is effectuated at 130–135°C, 3 hours.

$$\text{etyleneoxyde (EO)} = \frac{(V_2 - V_1)\cdot F \cdot 2{,}2}{a \cdot 1000}\ (\%)$$

where:
V_1 = volume of $Na_2S_2O_3$ solution 0.1 n used in mirror sample (mL);
V_2 = volume of $Na_2S_2O_3$ solution 0.1 n used in the analyzed sample (mL);
f = factor of $Na_2S_2O_3$ solution 0.1 n;
a = weight of sample analyzed (g).

3. Results and Discussions

In the series of the preoccupations to diversify the range of optimized structurated lipids (OSL) by gradual monitorised associations, after encouraging results have been obtained in binary systems with "homogeneous" polyoxyetylene chains with degrees of oligomerisation (n = 3, 9, 18, 30, 40, 50) monoderivatized with R(EH;2-ethyl-hexyl) chains respectively conjugates PEG_n-L(2R'; R) (R'; 2R) with HLB ≥ 9, has been considered as synthetic and the access to ternary systems of gradual conjugates association PEG_n-L (2R'; R) (R';2R) "coloidally disadvantaged" [24,27-29].

As an operation premise it has been "accepted" the previous observation according to which hydrocarbonate chains R' saponifiable lipidic

fractions from grapes seeds (*Vitis vinifera*) (R'_s), wild chestnut (*Aesculus hippocastanum*) (R'_{ca}) wild rose (*Rosa canina*) (R'_m) and coriander (*Coriandri fructus*) (R'_{co}) and R[(EH)-2-ethyl-hexyl and (NF) nonylphenyl] do not influence negatively the range of colloidal competences, their major role being insured by an advanced degree of polyunsaturation (fatty acids with 1Δ, 2Δ 3Δ) allocated according to gas chromatographic evaluations thus R's [C_{16} (0Δ) 10,10 %; C_{18}(1Δ) 24,80 %; C_{18}(2Δ) 64,90 %; R'_{ca} [C_{16}(0Δ) 10,90 %; C_{18} (1Δ) 57,00 %; C_{18}(2Δ) 28,80 %; C_{18}(3Δ) 3,72 %], R'_m [C_{16}(0Δ) 3,19 %; C_{18} (1Δ) 15,92 %; C_{18}(2Δ) 67,50 %; C_{18}(3Δ) 13,30 %], R'_{co}[C_{16}(0Δ) 2,7 %; C_{18} (1Δ) 83,00 %; C_{18}(2Δ) 13,40 %].

Table 1. Series of hydrophile/hydrophobe values for conjugates PEG_n-L(2R'; R) (R'; 2R) selected for the structuring and evaluation cumulated colloidal parameters (HLB_{CT}) in ternary associated

No	Partially hydrophile/hydrophobe values of conjugates PEG_n-L (2R'; R) (R'; 2R)		
	First series (HLB_1)	**Second series (HLB_2)**	**Third series (HLB_3)**
1	2,00 ± 0,5	6,00 ± 0,5	13,00 ± 0,5
2	2,00 ± 0,5	8,00 ± 0,5	13,00 ± 0,5
3	2,00 ± 0,5	10,00 ± 0,5	13,00 ± 0,5
4	6,00 ± 0,5	8,00 ± 0,5	13,00 ± 0,5
5	6,00 ± 0,5	10,00 ± 0,5	13,00 ± 0,5
6	8,00 ± 0,5	10,00 ± 0,5	13,00 ± 0,5

In Table 1 it is presented the series of hydrophile/hydrophobe values for conjugates PEG_n-L (2R'';R) (R';2R) selected for the structuring and evaluation of ternary associated systems:

It has also been selected the series of gradual ternary association ratios (10/34/56; 20/34/46; 33/34/33; 50/34/16; 60/34/6). Experimental values (Table 2,3) offer an overview of the chances to ameliorate HLB_{CT}. One can formulate some preliminary observations:

- in the first series, at reduced values of HLB_1/HLB_2 = 2/6 the most favorable results are obtained for ratio of ternary gradual association 10/34/56 when HLB_{CT} = 9,52 ± 0,5 (9 associated conjugates). As gradual ternary association reports is shifting in the disadvantage of HLB_3 = 13,00 ± 0,5 resulted ternary systems have HLB_{CT} < 8,00;
- in the second series, at reduced but modified values HLB_1/HLB_2 = 2/8 and the same HLB_3 the best values HLB_{CT} = 10,20 ± 0,5 (16 associated conjugates) one can encounter the series of association reports (10/34/56; 20/34/46). Shifting the report of gradual association towards adverse values HLB_3 = 13,00 ± 0,5 is negatively affecting HLB_{CT} < 8;
- in the third series, the modification of the participation percentage HLB_2 = 10,00 ± 0,5 in association report HLB_2/HLB_2 = 2/8 with constant maintaining of the HLB_3 = 13,00 ± 0,5 has lead to a total of 15 optimized associated conjugates. It is remarked the same adverse tendency with the displacement of the association report of ternary association, towards the extreme values of the series;
- in the four series the modification of the participation percentage of HLB_1 = 6,00 ± 0,5 and HLB_2 = 8,00 ± 0,5 with constant maintaining of the HLB_3 = 13,00 ± 0,5 determines as a whole a full formulation of a 23 optimized associated conjugates;
- in the five series the modification of the participation percentage of HLB_2 = 10,00 ± 0,5 in ternary association system with constant maintaining of the HLB_3 = 13,00 ± 0,5

determines a new displacement HLB_{CT} with the formulation of 18 colloidal ameliorated associated conjugates for ternary association ratios 20/34/46; 33/34/33;

- in the six series the displacement of participation percentage of $HLB_1 = 8,00 \pm 0,5$ with constant maintaining of the $HLB_2 = 10,00 \pm 0,5$ respectively $HLB_3 = 13,00 \pm 0,5$ ensures colloidal amelioration of 28 associated conjugates especially with the 33/34/33; 50/34/16; 60/34/6 ternary ratios association.

Experimental values obtained in ternary association have allowed extending the efforts of correlation of "homogeneous" cumulated degrees of oligomerisation (n_{CT}) and HLB_{CT} with the percentage of the participation in the system. In the paper, in order to verify the statements, there were selected from the mentioned series $HLB_1/HLB_2/HLB_3$ (Table 1) a representative of the PEG_n-L(2R'; R) (R'; 2R). Simultaneous evaluation confirmed a very good similarity of the values [25,26].

4.Conclusions

The idea of gradual ternary association of some conjugates PEG_n-L(2R'; R)(R'; 2R) "colloidally disadvantaged" from different mixed systems proved to be benefic especially because of optimization possibility Supplementary, the range covered by ternary systems resulted is a lot more uniformly marked, fact that enlarges the area of technological application.

Association in ternary systems is a major staging the extension and/or completion of structural and colloidal map of the conjugates PEG_n-L(2R'; R)(R'; 2R) propose for the study and which allow integral access to the conjugates PEG_n-L(2R'; R)(R'; 2R).

Table 2. Series of hydrophile/hydrophobe values and structures for conjugates (PEG_n-L (2R';R) (R';2R) selected for evaluation cumulated colloidal parameters (HLB_{CT}) in ternary associated

No	Hydrophile/hydrophobe values for selected conjugates PEG_n-L (2R'; R) (R'; 2R)		
	First series (HLB_1)	**Second series (HLB_2)**	**Third series (HLB_3)**
1	2,00 ± 0,5	6,00 ± 0,5	13,00 ± 0,5
			PEG_{18}-L(R'$_{ca}$; 2NF)
		PEG_9-L(2R'$_{ca}$; 1NF)	PEG_{18}-L(R'$_S$; 2NF)
	PEG_3-L(2R'$_{ca}$; 1NF)	PEG_9-L(2R'$_S$; 1NF)	PEG_{18}-L(R'$_m$; 2NF)
	PEG_3-L(2R'$_{co}$; 1NF)	PEG_9-L(2R'$_{co}$; 1NF)	PEG_{18}-L(R'$_{co}$; 2NF)
		PEG_9-L(2R'$_{co}$; 1EH)	PEG_{18}-L(R'$_{ca}$; 2EH)
			PEG_{18}-L(R'$_S$; 2EH)
			PEG_{18}-L(R'$_{co}$; 2EH)
2	2,00 ± 0,5	8,00 ± 0,5	13,00 ± 0,5
			PEG_{18}-L(R'$_{ca}$; 2NF)
			PEG_{18}-L(R'$_S$; 2NF)
	PEG_3-L(2R'$_{ca}$; 1NF)		PEG_{18}-L(R'$_m$; 2NF)
	PEG_3-L(2R'$_{co}$; 1NF)	PEG_9-L(2R'$_m$; 1EH)	PEG_{18}-L(R'$_{co}$; 2NF)
			PEG_{18}-L(R'$_{ca}$; 2EH)
			PEG_{18}-L(R'$_S$; 2EH)
			PEG_{18}-L(R'$_{co}$; 2EH)

3	2,00 ± 0,5 PEG_3-L(2R'$_{ca}$; 1NF) PEG_3-L(2R'$_{co}$; 1NF)	10,00 ± 0,5 PEG_9-L(R'$_{ca}$; 2EH) PEG_9-L(R'$_{co}$; 2EH) PEG_9-L(2R'$_{s}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1EH) PEG_{18}-L(2R'$_{co}$; 1EH)	13,00 ± 0,5 PEG_{18}-L(R'$_{ca}$; 2NF) PEG_{18}-L(R'$_{s}$; 2NF) PEG_{18}-L(R'$_{m}$; 2NF) PEG_{18}-L(R'$_{co}$; 2NF) PEG_{18}-L(R'$_{ca}$; 2EH) PEG_{18}-L(R'$_{s}$; 2EH) PEG_{18}-L(R'$_{co}$; 2EH)
4	6,00 ± 0,5 PEG_9-L(2R'$_{ca}$; 1NF) PEG_9-L(2R'$_{S}$; 1NF) PEG_9-L(2R'$_{co}$; 1NF) PEG_9-L(2R'$_{co}$; 1EH)	8,00 ± 0,5 PEG_9-L(2R$_{m}$; 1EH)	13,00 ± 0,5 PEG_{18}-L(R'$_{ca}$; 2NF) PEG_{18}-L(R'$_{c}$; 2NF) PEG_{18}-L(R'$_{m}$; 2NF) PEG_{18}-L(R'$_{co}$; 2NF) PEG_{18}-L(R'$_{ca}$; 2EH) PEG_{18}-L(R'$_{s}$; 2EH) PEG_{18}-L(R'$_{co}$; 2EH)
5	6,00 ± 0,5 PEG_9-L(2R'$_{ca}$; 1NF) PEG_9-L(2R'$_{S}$; 1NF) PEG_9-L(2R'$_{co}$; 1NF) PEG_9-L(2R'$_{co}$; 1EH)	10,00 ± 0,5 PEG_9-L(R'$_{ca}$; 2EH) PEG_9-L(R'$_{co}$; 2EH) PEG_9-L(2R'$_{s}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1EH) PEG_{18}-L(2R'$_{co}$; 1EH)	13,00 ± 0,5 PEG_{18}-L(R'$_{ca}$; 2NF) PEG_{18}-L(R'$_{s}$; 2NF) PEG_{18}-L(R'$_{m}$; 2NF) PEG_{18}-L(R'$_{co}$; 2NF) PEG_{18}-L(R'$_{ca}$; 2EH) PEG_{18}-L(R'$_{s}$; 2EH) PEG_{18}-L(R'$_{co}$; 2EH)
6	8,00 ± 0,5 PEG_9-L(2R'$_{m}$; 1EH)	10,00 ± 0,5 PEG_9-L(R'$_{ca}$; 2EH) PEG_9-L(R'$_{co}$; 2EH) PEG_9-L(2R'$_{s}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1NF) PEG_{18}-L(2R'$_{m}$; 1EH) PEG_{18}-L(2R'$_{co}$; 1EH)	13,00 ± 0,5 PEG_{18}-L(R'$_{ca}$; 2NF) PEG_{18}-L(R'$_{s}$; 2NF) PEG_{18}-L(R'$_{m}$; 2NF) PEG_{18}-L(R'$_{co}$; 2NF) PEG_{18}-L(R'$_{ca}$; 2EH) PEG_{18}-L(R'$_{s}$; 2EH) PEG_{18}-L(R'$_{co}$; 2EH)

Table 3. Correlation of the HLB_{CT} values with conjugates PEG_n-L (2R': R); (R': 2R) in various gradual ternary association systems

Series	HLB₁	HLB₂	HLB₃	HLB'$_{CT}$ Association ratio 1	Association ratio 2	Association ratio 3	Association ratio 4	Association ratio 5
1	2	6	13	9.52 (±0.5) PEG_9-L(R'_{cc}; 2NF) 9.17 PEG_9-L(R'_{ccc}; 2NF) 9.19 PEG_9-L($2R'_{ccc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 — PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 PEG_{12}-L($2R'_{cc}$; 1EH) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.44 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.82 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39	8.42 (±0.5) (7.92 – 8.92)	Ternary systems		
2	2	8	13	10.20 (±0.5) PEG_9-L(R'_{cc}; 2EH) 10.54 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_9-L(R'_{ccc}; 2EH)10.88 PEG_9-L($2R'_{ccc}$;2EH) 10.1 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 — PEG_{12}-L($2R'_{cc}$; 1EH) 9.95 PEG_{12}-L($2R'_{ccc}$; 1EH) 10.30 PEG_{12}-L($2R'_{ccc}$; 1NF) 10.22 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.82	9.10 (±0.5) PEG_9-L(R'_{cc}; 2NF) 9.17 PEG_9-L(R'_{ccc}; 2NF) 9.19 PEG_9-L($2R'_{ccc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 — PEG_{12}-L($2R'_{cc}$; 1EH) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.44 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39	Ternary systems		
3	2	10	13	10.88 (±0.5) PEG_9-L(R'_{cc}; 2EH) 10.54 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_9-L(R_{cc}'; 2EH)10.88 PEG_{12}-L($2R'_{ccc}$;1EH) 10.3 PEG_{12}-L($2R'_{ccc}$;1NF) 10.2	9.78 (±0.5) PEG_9-L($2R'_{ccc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 PEG_{12}-L($2R'_{cc}$; 1NF) 9.58 — PEG_{12}-L($2R'_{cc}$;1EH) 9.95 PEG_{12}-L($2R'_{ccc}$;1EH) 10.30 PEG_{12}-L($2R'_{ccc}$;1NF) 10.22 PEG_{12}-L($2R'_{ccc}$;1EH) 9.82 PEG_{12}-L($2R'_{ccc}$;1NF) 9.39	8.35 (±0.5) (7.85 – 8.85)	Ternary systems	
4	6	8	13	10.60 (±0.5) PEG_9-L(R_c'; 2EH) 10.54 PEG_9-L(R_{cc}'; 2EH) 10.44 PEG_9-L(R_{cc}'; 2EH)10.88 PEG_{12}-L($2R_{cc}'$;1EH) 10.3 PEG_{12}-L($2R'_{ccc}$;1NF) 10.2	9.90 (±0.5) PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_9-L($2R'_{ccc}$; 2EH) 10.11 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 PEG_{12}-L($2R'_{cc}$; 1NF) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.95 — PEG_9-L(R'_{ccc};2EH) 10.44 PEG_{12}-L($2R'_{ccc}$;1EH) 10.30 PEG_{12}-L($2R'_{ccc}$;1NF) 10.22 PEG_{12}-L($2R'_{ccc}$;1NF) 10.22 PEG_{12}-L($2R'_{ccc}$;1EH) 9.82 PEG_{12}-L($2R'_{ccc}$;1NF) 9.39	9.99 (±0.5) PEG_9-L(R'_{cc}; 2NF) 9.17 PEG_9-L(R'_{ccc}; 2NF) 9.19 PEG_9-L($2R'_{ccc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.44 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39	Ternary systems	
5	6	10	13	11.28 (±0.5) PEG_9-L(R'_{ccc}; 2EH)10.88	10.58 (±0.5) PEG_9-L(R'_{cc}; 2EH) 10.54 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_9-L(R'_{ccc}; 2EH)10.88 PEG_{12}-L($2R'_{ccc}$; 1EH) 10.30 PEG_{12}-L($2R'_{ccc}$; 1NF) 10.22 — PEG_9-L(R'_{cc}; 2NF) 9.17 PEG_9-L(R'_{ccc}; 2NF) 9.19 PEG_9-L($2R'_{cc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88	9.67 (±0.5) PEG_{12}-L($2R'_{cc}$; 1EH) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.95 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.82 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39	8.48 (±0.5)) Ternary systems	
6	8	10	13	11.48 (±0.5)	10.98 (±0.5) PEG_9-L(R'_{cc}; 2EH) 10.54 PEG_9-L(R'_{ccc}; 2EH)10.88	10.33 (±0.5) PEG_9-L(R'_{cc};2EH) 10.54 PEG_9-L(R'_{ccc};2EH) 10.44 PEG_9-L(R'_{ccc};2EH)10.88 PEG_{12}-L($2R'_{ccc}$;1EH) 10.30 PEG_{12}-L($2R'_{ccc}$;1NF) 10.22 — PEG_{12}-L($2R'_{cc}$;1EH) 9.88 PEG_{12}-L($2R'_{ccc}$;1EH) 10.30 PEG_{12}-L($2R'_{ccc}$;1NF) 10.22 PEG_{12}-L($2R'_{ccc}$;1EH) 9.82	9.48 (±0.5) PEG_9-L(R'_{cc}; 2NF) 9.17 PEG_9-L(R'_{ccc}; 2NF) 9.19 PEG_9-L($2R'_{ccc}$; 2NF) 9.34 PEG_9-L($2R'_{ccc}$; 2NF) 9.37 PEG_{12}-L($2R'_{cc}$; 1EH) 9.88 — PEG_{12}-L($2R'_{cc}$; 1EH) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.95 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.82 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39	8.98 (±0.5) (PEG_{12}-L($2R'_{cc}$; 1EH) 9.58 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.95 PEG_9-L(R'_{ccc}; 2EH) 10.44 PEG_{12}-L($2R'_{ccc}$; 1EH) 9.82 PEG_{12}-L($2R'_{ccc}$; 1NF) 9.39

Notice: association ratio 1 – 10/34/56; association ratio 2 – 20/34/46; association ratio 3 – 33/34/33; association ratio 4 – 50/34/16; association ratio 5 – 60/34/6

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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