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THE APPLICATION OF NOVEL ORGANIC DEEMULSIFIERS FOR THE SEPARATION OF OIL-IN-WATER EMULSIONS

ZASTOSOWANIE NOWYCH DEEMULGATORÓW ORGANICZNYCH DO ROZDZIAŁU EMULSJI OLEJ-WODA

Abstract

The paper summarizes the results of tests of separation of oil-in-water emulsions with the application of novel organic deemulsifiers. Fresh and used emulsions of different concentrations were tested. The manipulated variables were: the concentration of oil in the emulsion; the concentration and amount of deemulsifier solution; the temperature. The results of these tests are presented graphically.

Keywords: *separation of oil-in-water emulsions*, *organic deemulsifiers*

Streszczenie

W artykule przedstawiono wyniki przeprowadzonych badań rozdziału emulsji olej-woda z zastosowaniem nowych deemulgatorów organicznych. Badano rozdział emulsji świeżej i przepracowanej w zależności od stężenia emulsji, stężenia i ilości roztworu deemulgatora oraz temperatury. Wyniki badań zilustrowano na wykresach

Słowa kluczowe: *rozdział emulsji olej-woda*, *deemulgatory organiczne*

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Symbols

C_d – concentration of deemulsifier in mixture [dm^3/dm^3]
C_e – concentration of oil in emulsion sample [dm^3/dm^3]
C_m – concentration of oil in mixture [dm^3/dm^3]
m – slope of straight line
X_{vd} – volume of deemulsifier solution to volume of emulsion sample ratio [dm^3/dm^3]

1. Introduction

Various branches of industry generate oily waste water in the form of oil-in-water emulsions. Highly stable oil-in-water emulsions are often used in metal machining as emulsive cutting fluids. These emulsions are prepared from concentrates (soluble oil fluids) and are used in a diluted form (usual concentrations vary from 3 to 10% of oil). Soluble oil fluids consist mainly of a base mineral oil and emulsifiers to help produce stable emulsions. They also contain a variety of additives, e.g. rust inhibitors, bactericides.

The problem of utilizing used oil-in-water emulsions, particularly from machining processes, is of great importance because the quantity of these emulsions in Poland reaches 100.000 tons per year [1] and the 'producers' of these emulsions are spread all over Poland. In compliance with the Polish Act on Wastes [2], there is no option to dump these emulsions into the waste water treatment system. On the other hand, it is not profitable to transport the emulsions to a central point of processing because of the high water content in them. The emulsions have to be separated into their oil and water phases on the spot. The oil phase can be then transported to a recovery plant or can be burnt. The water phase can be recycled or diluted and discharged.

To separate oil-in-water emulsions into oil and water phases, various methods can be applied [3, 4] such as: thermal (vaporization); adsorptive methods; mechanical methods (micro and ultrafiltration); electrochemical methods (electrocoagulation and electrophoresis); chemical methods (with the use of salts, acids or deemulsifiers).

In this paper, investigations on the separation of some emulsive cutting fluids into their oil and water phases by means of various novel organic deemulsifiers have been described. The deemulsifiers are cation copolymers of polyamins with formula weights ranging from 75.000 to 200.000. Some types of this kind of organic deemulsifiers were tested by the authors in previous research [1, 5].

2. Range of investigations

Both fresh and used oil-in-water emulsions were used in the investigations. Fresh emulsions were prepared on a base of Emulgol ES-12 – a concentrate manufactured by Orlen Oil [6]. This concentrate is an amber-coloured transparent liquid. It consists mainly of lubricating oils, hydrocarbons $C_{20} - C_{50}$ and a neutral base oil. As a result of blending it with water in various proportions, very stable milky emulsions arise. The concentrations

of the tested fresh emulsions were 2, 5 and 8% by volume of oil. An unknown used emulsion was also tested.

For the separation of emulsions, the 1, 2 and 3% by volume aqueous solutions of the following organic deemulsifiers manufactured by SNF Floerger SA (France) were tested: FL 4340; FL 4820; FL 2565; FL 2949; EM 840TRM. The deemulsifiers were dense and viscous white liquids (except for yellow in the case of FL 4340) [7].

The investigations were carried out using 50 cm^3 volume samples of emulsions in 100 cm^3 capacity flasks at 20°C. Into each sample, small portions of solutions of deemulsifiers were added step by step. After each step, the flasks were shaken and the results of separation were observed. The tests were finished when a complete separation had taken place. In the investigations, two identical samples were used simultaneously. In the first sample the over-emulsification was reached in order to catch the sharpness of separation in the second. The final observations were made after 24 hours.

In order to determine the effect of temperature on separation, some tests were also carried out for 2% oil emulsions at 50°C.

The purity of the water phase after separation was determined on the basis of its chemical oxygen demand (COD).

The number of tests was as follows:
- 45 tests of separation of fresh emulsions at 20°C,
- 10 tests of separation of fresh emulsions at 50°C,
- 10 tests of separation of used emulsion at 20°C,
- 1 test of water phase purity.

3. Results of investigations

3.1. Results of separation of emulsions at 20°C

The results of separation, showing the quantities of deemulsifiers needed for separation of 50 cm^3 emulsion samples, were collected in tables and depicted in graphs. In this paper, it is placed only one table for deemulsifier FL 4820 at 20°C (Table 1). The particular columns of this table contain:
- the concentration of oil in the tested emulsion sample,
- the concentration of the tested deemulsifier solution,
- the volume of deemulsifier needed for separation (both the volume of the added deemulsifier solution and the calculated volume of raw deemulsifier),
- descriptions of water and oil phases (colour, form).

The results of Table 1 show that separation usually occurs in a certain range of deemulsifier to emulsion ratio. The graphs showing the lower and the upper separation limits for ES-12 emulsion samples for each concentration of the tested deemulsifier solution are shown in Fig. 1. The *Y*-axis presents the ratio of definite deemulsifier solution volume to the emulsion sample volume. The area between the lower (minimum) and upper (maximum) separation limits represents the area of the two-phase mixture. Instead of three areas for each deemulsifier (one area for each applied concentration), it is possible to graphically show (Fig. 2) the separation range in the form of one area where the *X* and *Y*-axes describe

the concentration of oil and the concentration of pure deemulsifier respectively in the tested mixture (water from deemulsifier solution dilutes the oil in sample). The table in Fig. 2 gives the values of the slopes of the straight lines. The gentler the slope, the smaller the amount of deemulsifier needed for separation.

Table 1

Exemplary results of separation of fresh emulsion ES-12 (50 cm^3) with use of deemulsifier FL 4820 at 20°C after 24 h

Concentration of emulsion [% v/v]	Concentration of deemulsifier [% v/v]	Volume of deemulsifier [cm^3] (separation range)		Description of	
		solution	raw deemulsifier	water phase	oil phase
2	1	6.5–6.8	0.065–0.068	clear, colourless	white, thin
	3	2.0–2.8	0.060–0.840		
	5	1.1-1.6	0.055–0.080		
5	1	27.7	0.277		cream-coloured, thin
	3	7.3–10.0	0.219–0.300		white, thin
	5	4.3–5.8	0.215–0.290		
8	1	no separation			
	3	12.5–15.0	0.375–0.450	clear, colourless	cream-coloured, thin
	5	8.5	0.425		

3.2. The effect of temperature on separation

Some selected results of the effect of temperature on separation quality are given in Table 2.

Table 2

Exemplary comparison of selected results of separation of 2% fresh emulsion ES-12 (50 cm^3) with use of deemulsifier FL 4820 at 20°C and 50°C after 24 h

Deemulsifier		Required volume of deemulsifier solution		Description of	
kind	concentration [% v/v]	20°C	50°C	water phase	oil phase
FL 4820	1	6.5–6.8	3.1–4.2	clear, colourless	cream, thin
	5	1.1–1.6	0.8–0.9	clear, colourless	cream, thin

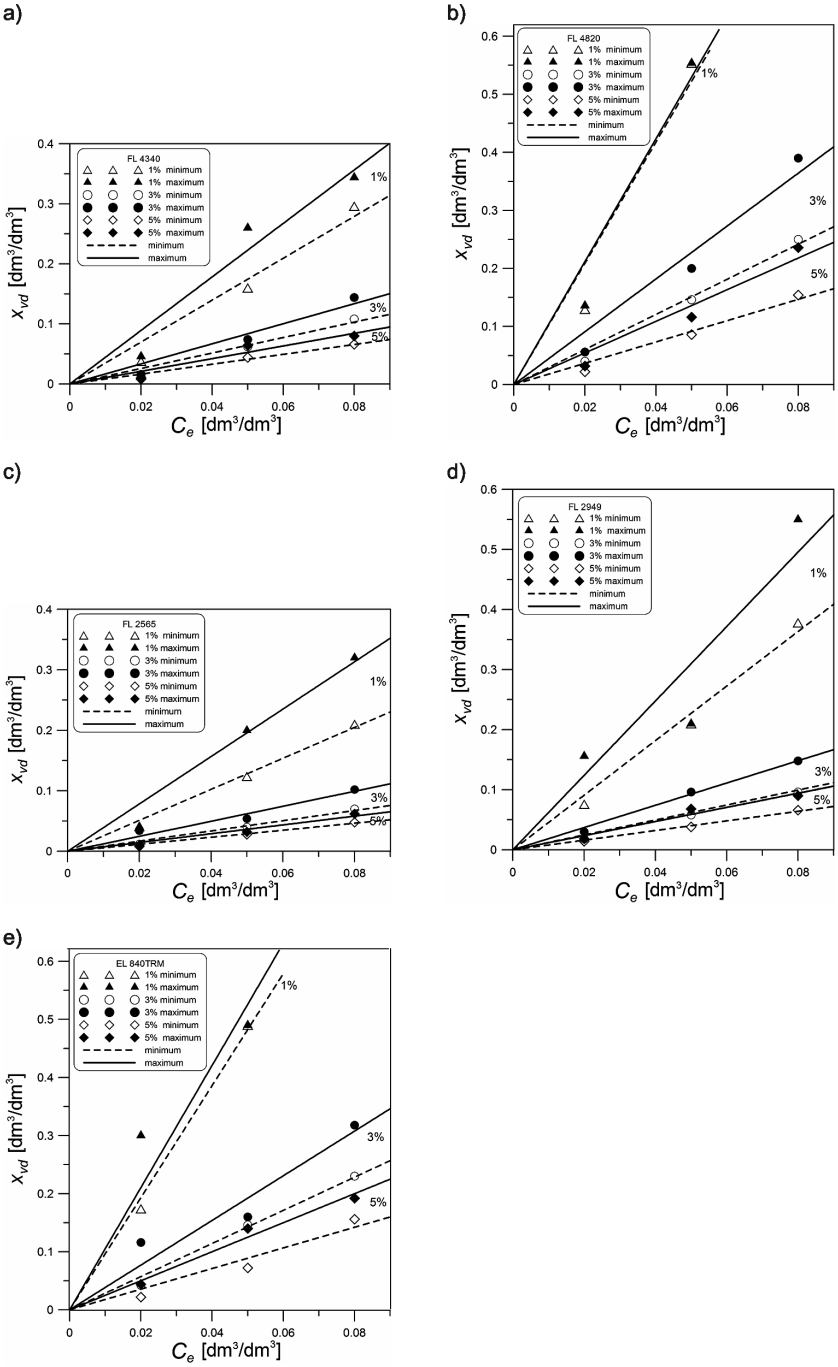
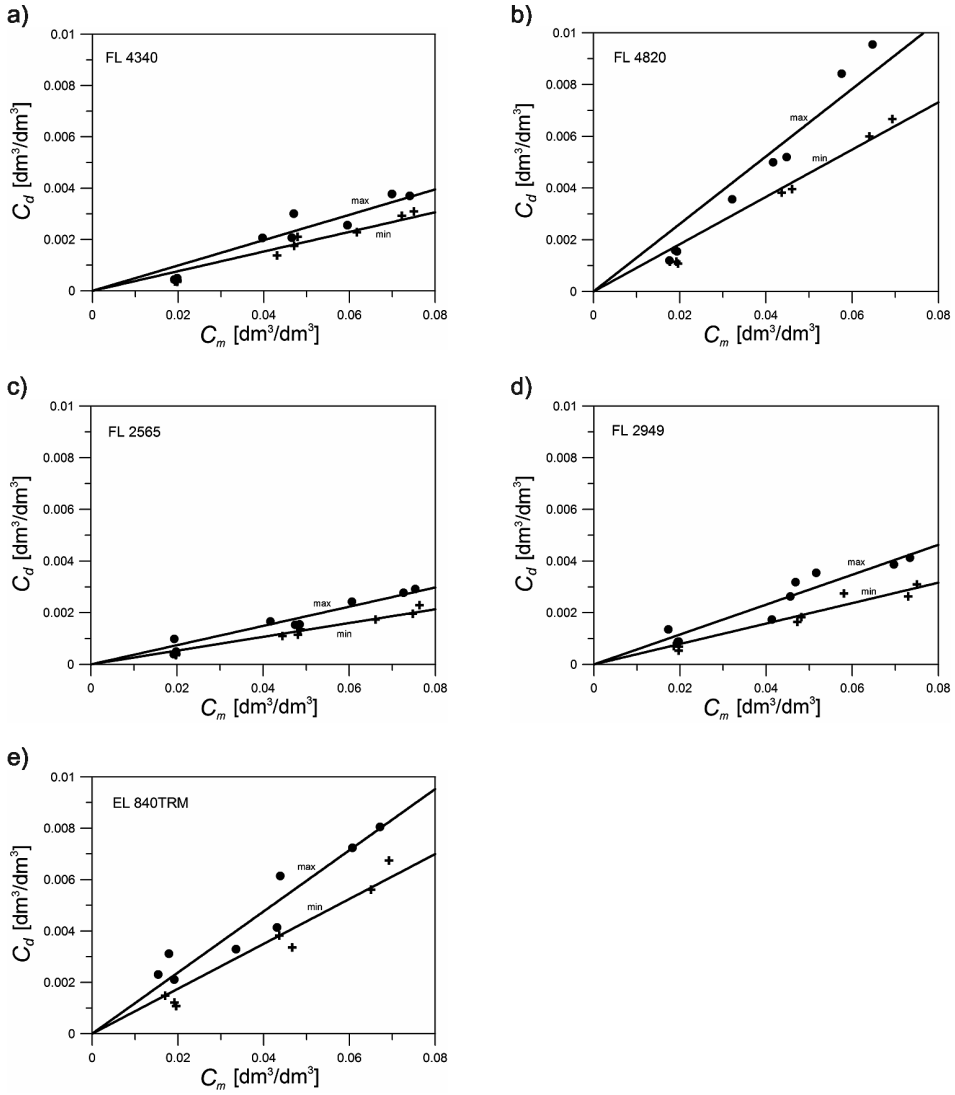


Fig. 1. Lower and upper separation limits for selected concentrations of deemulsifiers



Slope of the straight lines (above)

m	FL 4340	FL 4820	FL 2565	FL 2949	EL 840TRM
minimum value	0.0383	0.0914	0.0267	0.0395	0.0874
maximum value	0.0494	0.1305	0.0372	0.0578	0.1191

Fig. 2. General lower and upper separation limits for each deemulsifier

Graphs showing the effect of temperature on quantity of deemulsifier needed for separation of 2% oil emulsion are presented in Fig. 3.

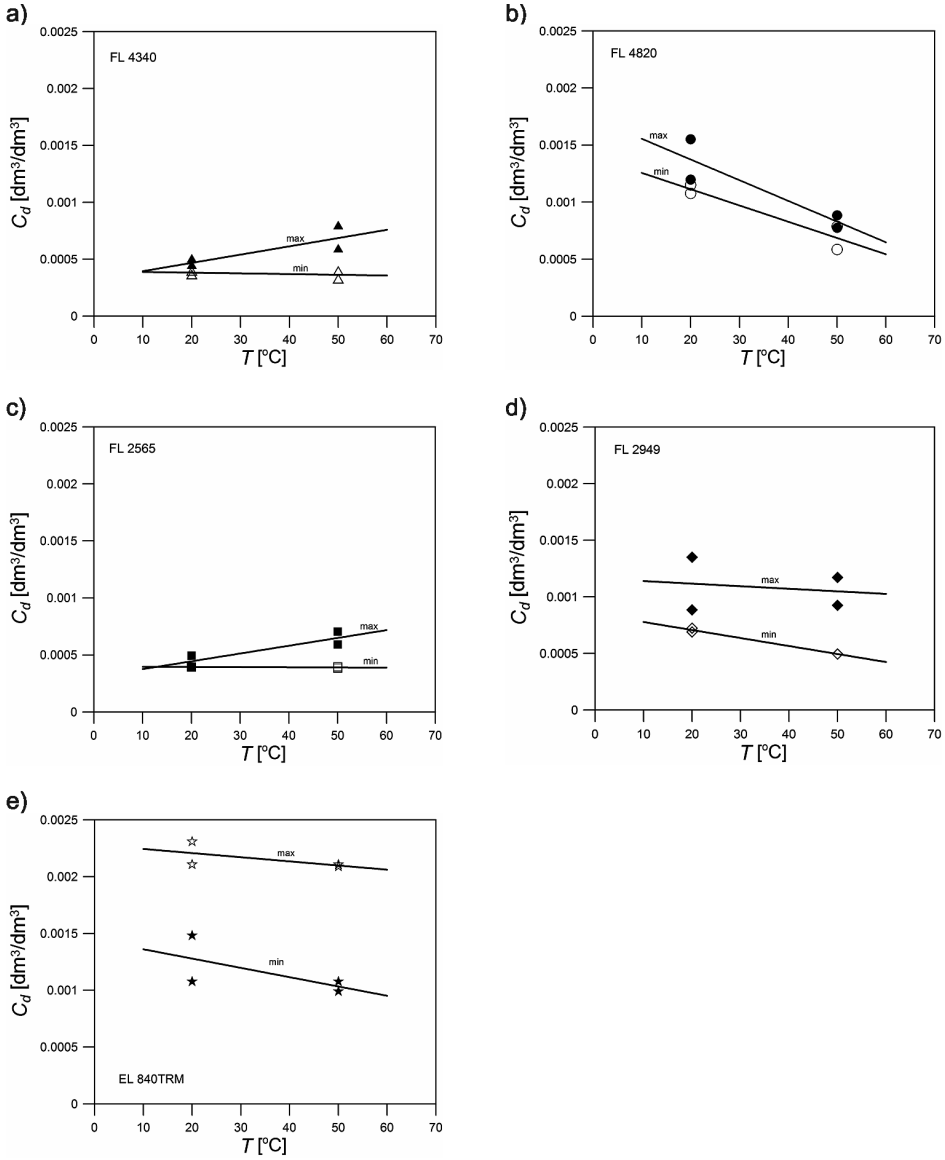


Fig. 3. Effect of temperature on quantity of deemulsifier (lower and upper limits) needed for the separation of 2% emulsion

3.3. Purity of water phase

For the testing of water phase purity, a sample of water phase obtained as a result of separation of the used emulsion with the aid of a 5% solution of deemulsifier FL 4820 was chosen. The water phase was light-yellow and turbid. Its value of COD (Chemical Oxygen Demand) was equal to 11.950 mgO_2/dm^3.

4. Conclusions

On the basis of the obtained results of these investigations, the following conclusions have been formulated below.

- From among the five tested organic deemulsifiers, the best results of separation, taking into account both the amount and the separation quality, were obtained for FL 4340 and FL 2565. Compared to other deemulsifiers, the quantity of them needed for separation was the smallest. When FL 4340 was used, the fresh emulsion separated into a clear, colourless water phase and a thin oil phase. In the case of FL 2565, the quality of separation was worse. The worst results were obtained for EM 840TRM – the separation of both fresh and used emulsions required large volumes. Additionally, the water phase was always turbid.
- The graphs depicting the quantities of the deemulsifier solutions needed for the separation of emulsions show the following relationships:
  - the higher the concentration of the deemulsifier solution, the smaller the volume needed for the separation of the emulsion of the definite oil concentration,
  - the higher the concentration of oil in the emulsion, the larger the volume of deemulsifier of a definite concentration needed for emulsion separation.
- Temperature considerably affects the separation efficiency, but the effect of temperature on separation is irregular. Usually, at higher temperatures the area of separation (the range of deemulsifier concentrations in the separated mixture) is larger.
- Generally, separation efficiency is time dependent. The longer the separation time, the sharper the separation and the clearer the water phase.
- The measure of the purity of the water phase is the index of Chemical Oxygen Demand (COD). If this exceeds the maximum permissible value of 125 mg O_2/dm^3 [8], the water phase has to be treated before being drained off. Usually, this treatment is necessary.

The method of the separation of oil-in-water emulsions with the use of organic deemulsifiers is possible for practical realization and can find widespread industrial application. The advantages of this method are low capital and power costs. Equipment necessary for the method's realization in industrial processes consists mainly of a storage tank for used emulsion, a mixer, a deemulsifier feeder and storage tanks for the oil and water phases. The total operating costs depend on the price of the deemulsifier. One inconvenience of this method is the necessity to select the kind and quantity of deemulsifier for each batch of used emulsion.

References

[1] Komorowicz T., Magiera J., Pacholarz M., Papka L., *Badania rozdziału emulsji olej-woda z zastosowaniem deemulgatorów*, Czasopismo Techniczne, 1-Ch/2007.

[2] Ustawa o odpadach z dn.14 grudnia 2012 roku, Dz. U. Nr 21 z 2013 r.

[3] Kąkol M., *Utylizacja przepracowanych cieczy chłodząco-smarujących*, Paliwa, Oleje i Smary w Eksploatacji, Nr 70, 2000.

[4] Komorowicz T., Magiera J., *Zatężanie zużytych emulsji olejowych w procesie ultrafiltracji okresowej*, Czasopismo Techniczne, 5-M/2003.

[5] Komorowicz T., *Deemulgatory organiczne w ochronie środowiska*, Inżynieria i Ochrona Środowiska, T. 10, Nr 10, 2007.

[6] Orlen Oil, *Katalog produktów*, 2011 (http://www.orlenoil.pl).

[7] NF Floerger S.A. (France), Catalogue of products, 2011.

[8] Rozporządzenie Ministra Środowiska z dn. 28 stycznia 2009 r., Dz. U. Nr 27, poz. 169 z 2009 r.