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PREDICTING THE STABILITY OF ADVOCAAT TYPE EGG LIQUEURS ON A BASE OF SELECTED EVALUATION INDICATORS

Tomasz Tarko

Agricultural University of Cracow

Abstract. Attempts to work out a test for predicting the stability of Advocaat egg liqueurs revealed that centrifuging method appeared to be the most efficient in their quick destabilization. Measurements of conductivity, lipid droplet diameter as well as imbalance of emulsion with $MgSO_4$ addition may also be used as auxiliary indicators for evaluating the predicted stability of alcoholic egg emulsions. Making several tests at the same time is a condition for evaluation of credible liqueur stability time.

Key words: egg liqueurs stability, emulsion creams

INTRODUCTION

Despite of many-year tradition of egg liqueurs production in Poland, applied technologies do not ensure their full uniformity and stability during storage and distribution. Emulsion may break producing fat ring on a surface, alcoholic-water layer at the bottom or internal "cracks" [Dickinson 1992].

Emulsions are susceptible to destabilization due to various processes and physicochemical factors. Change of the size and shape of particles and their chemical structure is a result of instability [McClements 1999]. Creaming is an example of a physical instability of emulsion – fat droplets in O/W emulsion are of less density than surrounding solution, thus they tend to accumulate in upper liquid layer. Flocculation and coalescence as well as physical ripening (growth of droplets resulted from partial mixing of oil and water phases) are other instability reasons. Oxidation and hydrolysis processes that cause, among others, change of liqueur's colour, are recognized as chemical instability symptoms. In practice, almost all mentioned processes may occur at the same time leading to relatively fast and unfavourable visual changes [Gilewicz 1957, Dickinson and Stainsby 1982, Luyten et al. 1993].

Corresponding author – Adres do korespondencji: Dr inż. Tomasz Tarko, Department of Fermentation and Technical Microbiology of Agricultural University of Cracow, Balicka 122, 30-149 Cracow, Poland, e-mail: ttarko@ar.krakow.pl

Reduction of emulsion instability effects may be achieved by introduction of emulsifiers or other additives into the system, which elevates medium viscosity and makes particle migration slower and collisions frequency rarer. Also conditions, the final product is stored in – mainly temperature and light – play an important role.

Current stability monitoring, particularly its predicting on a base of simple indicators, would be helpful in protecting these valuable beverages against unfavourable quality changes. Up-to-date studies indicate that following measuring techniques should be considered as the storage stability tests: microscopy, nephelometry, conductometry and sedimentation [Dickinson 1992, Bury et al. 1995, McClements 1999, Chantrapornchai et al. 2001, Christov et al. 2002].

The microscopic observations serve to estimate the mean size of dispersed phase droplets, monitor aggregation progress and analyse the influence of different factors, e.g. temperature, pH, diluting, addition of other components or electric field on the emulsion [Gilewicz 1957, Kalab et al. 1995]. Traditional light microscopy is the most often applied for examining the emulsion uniformity. It is possible to monitor the coalescence process dynamics on a base of histograms presenting the dispersed phase droplet size recorded at different time after emulsion preparation [McClements 1999]. Confocal microscopy gives pictures of higher quality than common light microscopy and allows for generating 3D objects with no necessity of physical separation of sample parts [Vodovotz et al. 1996, McClements 1999]. Electron microscopes are also often applied for emulsion microstructure evaluation. Their relatively great depth of field is an advantage and pictures of even relatively large structures are very well exposed [Lee and Morr 1992, McClements 1999].

The measurement of light dispersion level (nephelometry) may supply information on droplets size and distribution, as well as their concentration in a system. Change of emulsion stability during its aging is characterized by a quick decrease of emulsion limiting surface and increase of droplets diameter. Droplets concentrate in larger conglomerates, they may have different shapes and changed refraction coefficient in emulsions that are flocculed [Hallet 1994, McClements 1999].

Conductometry is applied for studying the volumetric dispersion of fat phase in opaque emulsions with no necessity of earlier sample preparation. The electrolyte conductance mainly depends on its type, concentration and measurement temperature. This technique has its limitations when examining some products due to the necessity of diluting emulsion in the electrolyte. The electrolyte presence usually changes the nature of interactions between droplets with particular charge, which may influence on flocculation range as compared to original sample [Dickinson 1992].

Stability of multi-phase system at a long period may be also confirmed using the emulsion aging tests. Properly long centrifuging at various rotational speeds is a fastest way to destabilize emulsion naturally occurring as a result of gravity [Sherman 1995]. Comparison of time and force acting to sample during centrifuging allows for predicting the period, the gravity force would produce the same effect. Nevertheless, this accelerated creaming test must be thoroughly performed, because factors that determine the droplets movement in gravity field are often different than those in centrifugal field [McClements 1999].

The aim of the paper is to work out a test facilitating quick evaluation of storage stability of alcoholic egg emulsions.

MATERIAL AND METHODS

The egg liqueur of Advocaat-type industrially produced was material for study. Samples differing in storage stability were selected and necessary stability tests were performed. Additions of electrolytes accelerating the breaking of multi-phase systems and physical factors (centrifuging) were applied in study and then dynamics of changes in samples (fat droplets diameter and conductivity) was analysed.

Depending on experimental variant, emulsions were completed with various electrolytes (2% $MgCl_2$, 5% KJ, 1% $K_2Cr_2O_7$ and 30% $MgSO_4$) at the amount of 10% v/v. Applied amount (10%) was estimated on a base of preliminary tests consisting in introduction the electrolytes at the amounts from 1% to 20% in relation to initial sample volume.

Centrifuging

The aliquot of 10 cm^3 of tested emulsion was placed in a specially formed bottom-shaped vial, centrifuged (29 g, 3 min) in centrifuge MPW-340, and then thickness of fat ring produced on the emulsion surface was measured. Temporary centrifuging and measurement was made until complete sample breaking.

Microscopic observations

Aliquot of 1 cm^3 of tested emulsion was mixed with 3 droplets of dye (Sudan III), then using a glass baguette, one drop of solution was placed in Bürker's chamber with glass cover. Observations of fat droplets were carried out using light microscope equipped in a specialized ocular for diameter measurement. Size and number of fat droplets were evaluated in 5 different visual fields at 400x magnification. Measurements were performed just after electrolyte addition (control sample), after 3 hours and subsequent days of storage (1, 3, 5 and 7).

Conductance measurements

The emulsion conductance (expressed in μS/cm) was measured using MultiLab 540 conductometer at 20°C.

RESULTS AND DISCUSSION

Most of tested Advocaat-type egg liqueurs were characterized by similar stability. Four liqueurs differing in their storage stability were selected to tests. Table 1 presents the description of selected liqueurs in the aspect of visual changes occurring as a result of storage of the samples at room temperatures.

Table 1. Characterization of stability of selected Advocaat-type egg liqueurs
Tabela 1. Charakterystyka trwałości wybranych prób Advocaata

Symbol of liqueur Symbol kremu	Visual symptoms Ocena wizualna
I	Very high stability. First symptoms of destabilization – 10 months after production, first fat droplets on a surface in the 11th month. Bardzo duża trwałość. Pierwsze objawy destabilizacji po 10 miesiącach od daty zestawienia, a w jedenastym miesiącu pierwsze krople tłuszczu na powierzchni.
II	No breaking symptoms for 9 months after production. First fat droplets on a surface after 9 months, fat ring in the 10th month of storage. Brak objawów rozwarstwiania przez 9 miesięcy od daty zestawienia. Pierwsze krople tłuszczu na powierzchni kremu po 9 miesiącach, obrączka tłuszczowa w 10 miesiącu przechowywania.
III	No symptoms of characteristic emulsion breaking (fat ring on a surface) for 10 months after production. Gradual emulsion breaks observed in the 4th month after bottling. Brak objawów charakterystycznego rozwarstwiania kremu (obrączka tłuszczu na powierzchni płynu) przez 10 miesięcy od daty zestawienia. W czwartym miesiącu od rozlewu zaobserwowano postępujące „pęknięcia" emulsji.
IV	Very unstable, first fat droplets on a surface on the second day after bottling. Full fat ring after 1 week of storage. Bardzo niestabilny, pierwsze krople tłuszczu na powierzchni kremu w drugim dniu od daty rozlewu. Pełna obrączka po jednym tygodniu przechowywania.

Liqueurs I and II were characterized by a high stability during visual observation. First breaking symptoms were found just after 9-10 months of storage. Advocaat IV got broken very fast (second week of evaluation) producing fat ring on a liquid surface. Liqueur III was characterized by a typical destabilization – the emulsion breaks in all volume were observed in the 4th month of observation.

The rate of emulsion destabilization due to electrolyte addition was estimated on a base of microscopic evaluation and results are presented on Figures 1 and 2.

Applied salts contributed to faster emulsion destabilization and increase of dispersed phase grains size. Less fat droplets below 20 μm diameter were found in emulsions directly after electrolyte introduction, as compared to the control (Fig. 1). High-stability liqueur (sample I) was characterized by a much higher dispersion as compared to quickly breaking emulsions (III and IV). Significant growth of lipid fraction grains was recorded during short-term storage in all tested liqueurs. In Advocaat I, droplets of 70 μm diameter were found after 5 days of observation. In unstable liqueur IV, such particles were visible just at the beginning of the observation. Initially, emulsions with magnesium chloride addition showed great increase of fat particles (droplets of 70-80 μm diameter were present after 3 hrs in unstable samples), but longer action of the electrolyte caused the dispersed phase particles became more uniform in all samples. Probably, emulsion stability imbalance occurred directly after electrolyte ($MgCl_2$) introduction into the solution, which resulted in the increase of fat droplets diameter. Further storage of the liqueur with Mg^{2+} ions probably caused the solution cross-linking making a specific balance that reduced coalescence [McClements 1999]. A similar tendency of changes was found after addition of potassium iodide as a destabilizing agent. In unstable

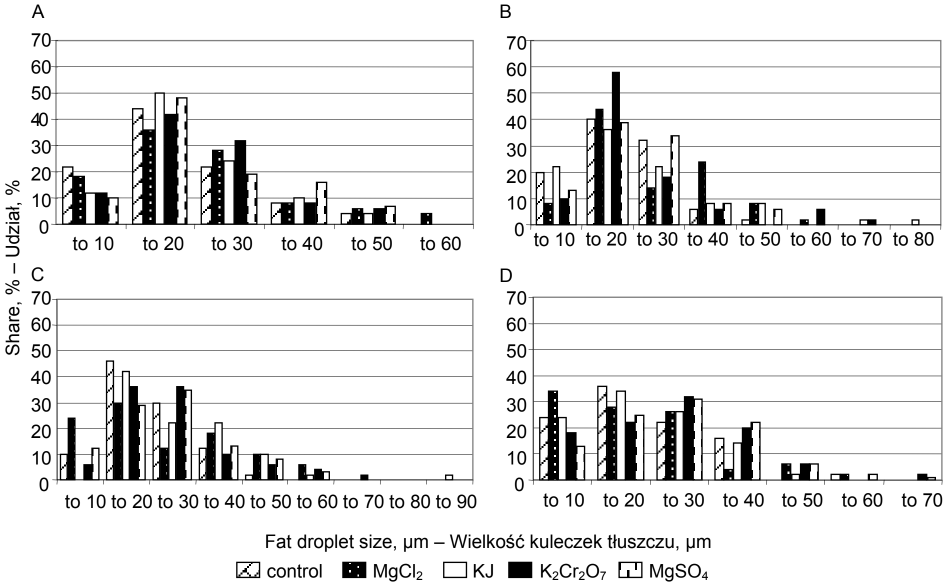

Fig. 1. Fat droplet characteristic in cream samples with various destabilization additives, after preparing: A – sample I, B – sample II, C – sample III, D – sample IV
Rys. 1. Charakterystyka kuleczek tłuszczu w próbach kremów z różnymi dodatkami destabilizującymi, bezpośrednio po zestawieniu: A – próba I, B – próba II, C – próba III, D – próba IV

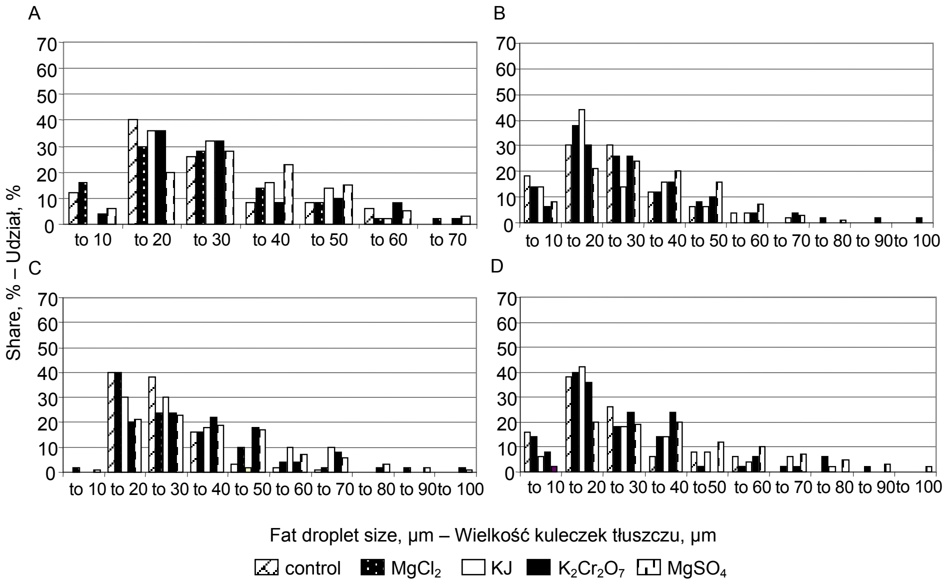

Fig. 2. Fat droplet characteristic in cream samples with various destabilization additives, after seven days storage: A – sample I, B – sample II, C – sample III, D – sample IV
Rys. 2. Charakterystyka kuleczek tłuszczu w próbach kremów z różnymi dodatkami destabilizującymi, po siedmiu dniach przechowywania: A – próba I, B – próba II, C – próba III, D – próba IV

liqueurs, particles of 90-100 μm diameter were observed just after 5 days; in the stable sample (I), the largest droplets did not have diameter larger than 60 μm at the 7th day of storage (Fig. 1). Addition of potassium dichromate initially (3 hrs) caused the fat droplets coalescence, but after 5 days, destabilizing interaction of the electrolyte was delayed. Relatively fast growth of dispersed phase particles was found in samples with magnesium sulfate. Size of fat droplets in stable liqueurs did not exceed 70 μm after 7-day storage. Less stable emulsion (IV) contained droplets of more than 90 μm diameter (Fig. 1 and 2). Influence of $MgSO_4$ confirmed the usefulness of bivalent ions application, particularly Mg^{2+}, in tests associated with destabilization of multi-phase systems [Dickinson 1992, Agboola and Dalgleish 1996].

Conductance changes in industrially produced liqueurs tested after storage are presented on Figure 3.

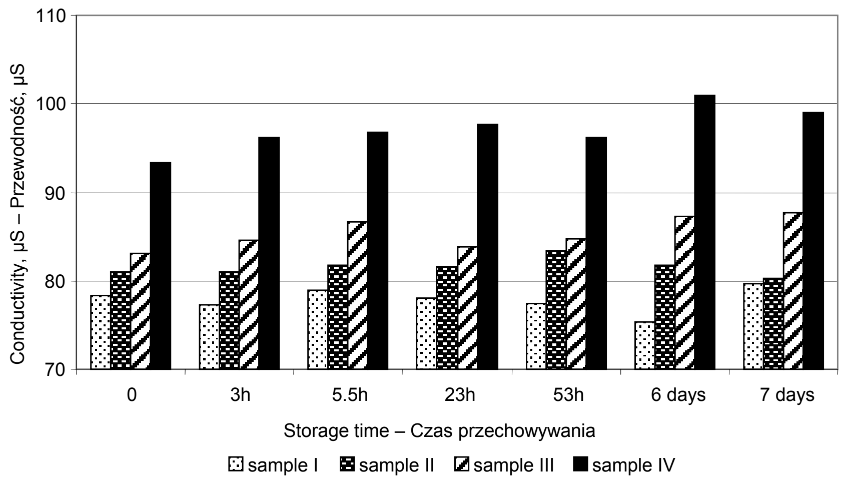

Fig. 3. The influence of storage time on conductivity changes in creams
Rys. 3. Wpływ czasu przechowywania na zmiany przewodności alkoholowych kremów emulsyjnych

Conductometric measurements revealed that the conductance during storage changed very slightly in tested Advocaat-type liqueurs. However, significant changes of particular liqueurs conductance, depending on their stability, were recorded. Conductance of sample IV (Fig. 3) that was characterized by the lowest stability, ranged from 93 μS to 100 μS; the value for more stable Advocaat (sample I) was much lower (78-80 μS). Conductance values of other samples were within 80-85 μS range. The increase of conductivity along with the fat globules size may be accounted for by the presence of the so-called double electric layer within the emulsion. Every droplet suspended in the solution is surrounded by a layer of anions causing their repulsion [McClements 1999]. Larger conglomerates are formed during dispersed phase particles agglomeration and their total surface area is lower than that of particular globule. Therefore, part of ions transfers into the solution making conductivity higher [Latreilla and Paquin 1990]. It is supposed that aging of the liqueur with initial conductance from 70 μS to 80 μS is much slower than that of similar solutions with conductance of about 90-110 μS.

The centrifuging tests are another group of methods simulating the destabilization during the storage. The method is one of the best indicators of emulsion stability, because comparison of the force acting towards a sample during centrifuging allows for predicting the time, the gravity force would produce similar destabilization effects [Aken 2003]. Results of such experiments are presented on Figure 4.

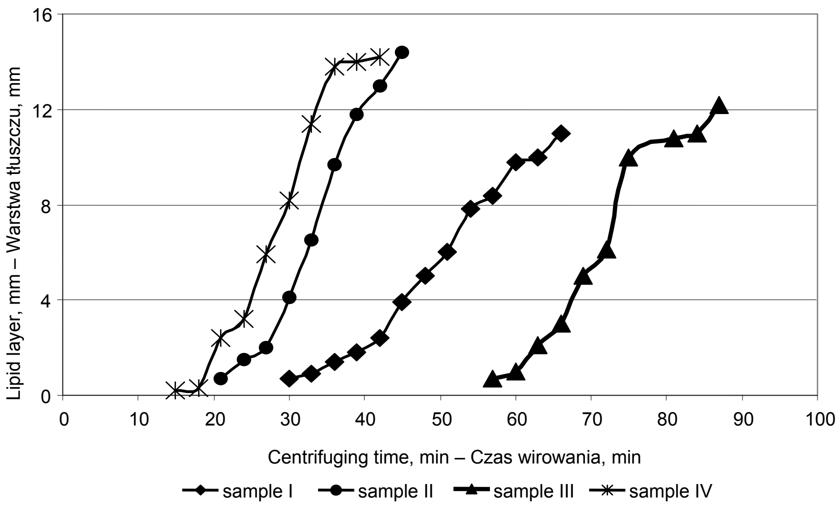

Fig. 4. Velocity delamination characteristic in centrifuging test (29.09 g)
Rys. 4. Charakterystyka szybkości rozwarstwiania badanych kremów podczas testu wirowania (29.09 g)

Tests were carried out using liqueurs characterized by a different storage stability (Table 1). The thickness of lipid layer on the emulsion surface after a given time of centrifugal force action (29.09 g) was measured. The first breaking symptoms were observed in liqueurs with low stability (IV) after 15 minutes. In Advocaat-type liqueurs characterized by high stability (sample I), separation of fat layer occurred after 30 minutes of centrifuging (Fig. 4). First destabilization symptoms under the influence of centrifugal force occurred after 57 minutes of centrifuging in egg liqueur with "cracks" formed during storage. Centrifuging tests may be considered as a relatively simple and quick method for achieving relatively credible information on predicted stability of tested emulsion. However, all experimental parameters (rotational speed and centrifuging time) as well as shape of a vessel that should facilitate credible reading of fat layer thickness, should be on mind [Britten and Giroux 1991, McClements 1999].

Measurements of conductivity, diameter of lipid droplets and time of liqueur breaking during centrifuging may be used as indicators of predicted stability of alcoholic emulsion liqueurs. The centrifuging method was characterized by the highest efficiency at evaluating the predicted stability of Advocaat-type liqueurs. Microscopic observations may be accepted as useful for evaluation of liqueur structure changes during the storage, and conductance changes reflect the level of system emulsification. Application of water solutions of electrolytes, namely $MgSO_4$, as a compound that accelerates the emulsion breaking, is also a clue in predicting the stability of tested liqueurs. Several methods applied at the same time are the conditions of evaluating a credible time of predicted emulsion stability. This condition for multi-phase systems was earlier underlined by other authors [Bury et al. 1995, O'Brien et al. 1995, McClements 1999].

CONCLUSIONS

1. The centrifuging tests are characterized by a relatively high efficiency at evaluating the predicted stability of Advocate-type liqueurs.
2. Measurements of conductance and destabilization using $MgSO_4$ may be the auxiliary indicators at predicting the stability of alcoholic egg emulsions.
3. Application of several tests at the same time is a condition for proper and credible evaluation of emulsion stability time.

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PROGNOZOWANIE STABILNOŚCI KREMÓW EMULSYJNYCH TYPU ADVOCAAT NA PODSTAWIE WYBRANYCH WSKAŹNIKÓW OCENY

Streszczenie. Próby opracowania testu prognozowanej trwałości kremów typu Advocaat wykazały, że bardziej skuteczna w przeprowadzaniu szybkiej destabilizacji była metoda wirówkowa. Pomiary przewodności, średnicy kuleczek lipidowych oraz naruszenie równowagi emulsji z udziałem $MgSO_4$ mogą być również wykorzystane jako pomocnicze wskaźniki oceny prognozowanej trwałości alkoholowych emulsji jajowych. Warunkiem określenia wiarygodnego czasu stabilności kremów jest równoczesne wykonanie kilku testów.

Słowa kluczowe: stabilność likierów jajowych, kremy emulsyjne

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