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Evaluation of flotation reagents by normalization procedures

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Abstract: Froth flotation is a dynamic multiphase process in which particulate matter is separated with the help of chemical reagents by gas bubbles immersed in water. The original flotation results are usually presented in the form of kinetic curves relating recovered particulate matter mass (yield γ) or mass of a selected component (recovery ϵ), both shortly denoted as y , versus process time t at different concentrations c (g/dm³) of the applied reagents. The kinetic curves can be modified into three: incentive (maximum yield or recovery y_{\max} vs c), limits (y_{\max} vs kinetic constant k or specific rate) and half-life of flotation ($t_{1/2}$ vs c) curves. The original and modified curves can be normalized by taking into account either an external parameter such as molecular mass (MW), critical coalesce concentration (CCC), critical concentration at the minimum bubble velocity (CMV), dynamic foaming index (DFI), and many other parameters or an internal parameter such as time, concentration needed to achieve certain yield, recovery (y) or kinetic constant. Normalization leads to new flotation curves and provides additional useful information about flotation performance. Normalization can be fully effective, partial or ineffective. Normalization of the original flotation kinetic curves usually is ineffective. Also, normalization of the incentive curve with external parameters such as frother molecular mass, which changes reagent concentration from c (g/dm³) to C (mol/dm³), is also ineffective. Partially effective are normalizations with other external parameters such as CCC and CMV, usually within the same class of reagents, for instance alcohols. Only DFI seems to be a universal external normalization parameter for flotation results because it provides fully effective normalization and thus predicts the flotation results. Limited data on DFI restrict a full verification of this hypothesis. Normalization of the modified flotation curves with internal parameters such as k_{50} (value of 1st order kinetic constant when recovery or yield is 50% after a given flotation time), $C_{t1/2}$ (frother concentration in mol/dm³ at which the flotation half-life has an arbitrarily chosen value) and c_{y75} (frother concentration in g/dm³ at which recovery or yield is 75% after a given flotation time) is a good base for practical classification of flotation reagents.

Keywords: flotation, separation, foam, froth, frother, selectivity, efficiency, normalization, generic reagents, selective reagents, internal parameter, external parameter

1. Introduction

Flotation is one of many possible separation processes (Gaudin, 1957). It is a process in which particulate matter, due to collisions with gas bubbles, forms aggregates which travel up to the liquid/gas interface (Wills and Finch, 2016). The particulate matter must be either naturally hydrophobic or rendered hydrophobic by means of appropriate reagents called collectors (Fuerstenau et al., 2007). When the process involves formation of a layer of solid/water/gas mixture at the liquid/gas interface, it is called froth flotation, and requires an additional reagent which is referred to as frother (Laskowski, 1998). The frother should be able to produce a relatively stable froth helpful for evacuation it from the place of formation to the external concentrate compartment. Additional reagents, called modifiers, can also be used in flotation (Drzymala, 2007). The flotation reagents influence the results of flotation. Since the goal of flotation is to achieve the best separation of

hydrophobic particles from unwanted matter at projected economics, the choice of the reagents is very important.

Selection of flotation reagents depends on many factors including their type and dose, which influence the cost of flotation, as well as process selectivity determining the monetary value of the flotation products (Klimpel and Hansen, 1988; Wills and Finch, 2016). Also, kinetics of the process is important. One of the procedures, which can be adopted for evaluation and selection of flotation reagents is normalization. Normalization is a procedure making the observed property looking either more regular or identical, that is generic. Normalization is a very useful technique because it allows to find conditions under which different reagents behave identically. Sometimes it also allows to detect non-generic, that is specific, properties of the investigated reagents. Normalization can also be used for classification of reagents, especially frothers (Drzymala and Kowalczyk, 2017).

A normalization of frother concentration for evaluation of hydrophobic coal yield after a certain time of flotation with alcohols as frothers was proposed by the team of E. Malysa, K. Malysa and J. Czarnecki (1987). They applied a parameter originally called the dynamic frothability index, which is presently called the dynamic foamability index, or shortly DFI (Czarnecki et al., 1982; Malysa et al., 1978). It was demonstrated, that n-alcohols in the investigated system induce identical flotation. The applied alcohols were generic, provided that different concentrations of alcohols were applied which were next counterbalanced with DFI values.

The goal of this paper is to demonstrate that normalization is a useful tool for analysis, evaluation, comparison and classification of flotation results when yield or recovery are regulated with an incentive parameter, which usually is concentration of a reagent. The normalization can be also used for non-flotation separation systems. In this paper, a system of normalizations will be presented for the solid/liquid/gas/frother systems characterized by yield γ (for all solid), recovery ε (for a selected solid in the system), reagent (frother) concentration c (incentive parameter), process time t and names (types) of components in the system n .

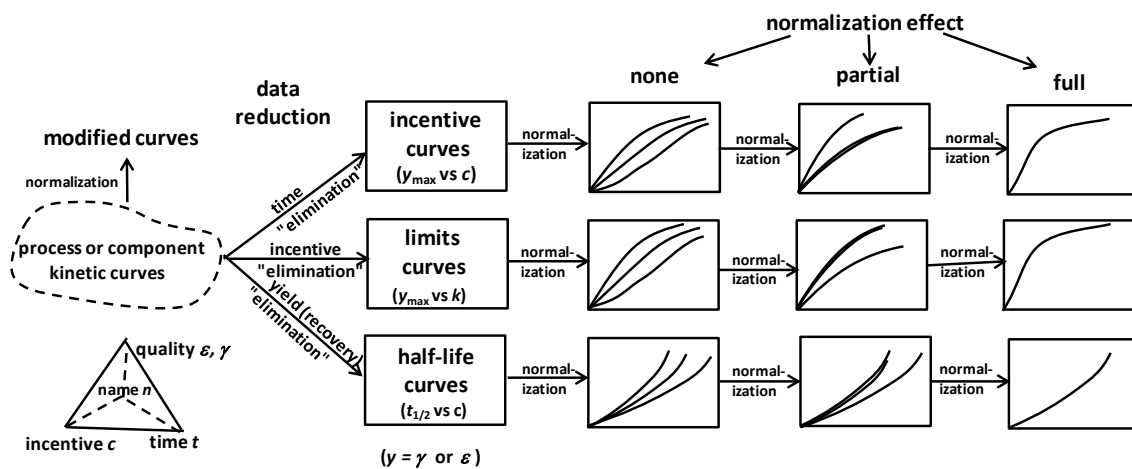


Fig. 1. Application of normalizations in the solids/liquid/gas system in which γ (or ε), t , c , n variables are considered. Normalization can be performed for original kinetic curves as well as for their modifications.

Normalization leads to either full, partial or none superposition of separation curves.

Symbols are explained in the text

The system of normalizations for y (γ or ε), t , c , n variables is graphically presented in Fig. 1. As can be seen from Fig.1. the normalization procedure can be applied directly to the original separation data, that is kinetic curves, as well as to their modifications such as incentive (maximum yield or recovery y_{max} vs c), limits (y_{max} vs kinetic constant k or specific rate) and half-life of flotation ($t_{1/2}$ vs c) curves. The outcomes of normalizations can be full (generic property), partial (generic and specific) and none when the curve does not overlap. It provides useful information for analysis, evaluation, comparison and classification of reagents used for regulation of the process selectivity. The details of the normalization procedure involving frothers will be discussed in the following sections of the paper.

2. Original kinetic curves and their normalization

Flotation experiments performed in the solid(s)/water/gas system provide important parameters such as yield of the floating fraction γ , recovery of a considered component ε at a given concentrations of a reagent c , time of the process t and types (names) of system components n . These parameters can be related by means of process kinetic curves (γ vs. t) or component kinetic curves (ε vs. t) (Drzymala et al., 2017) with concentration and names indicated in the legend, as shown in Fig. 2a.

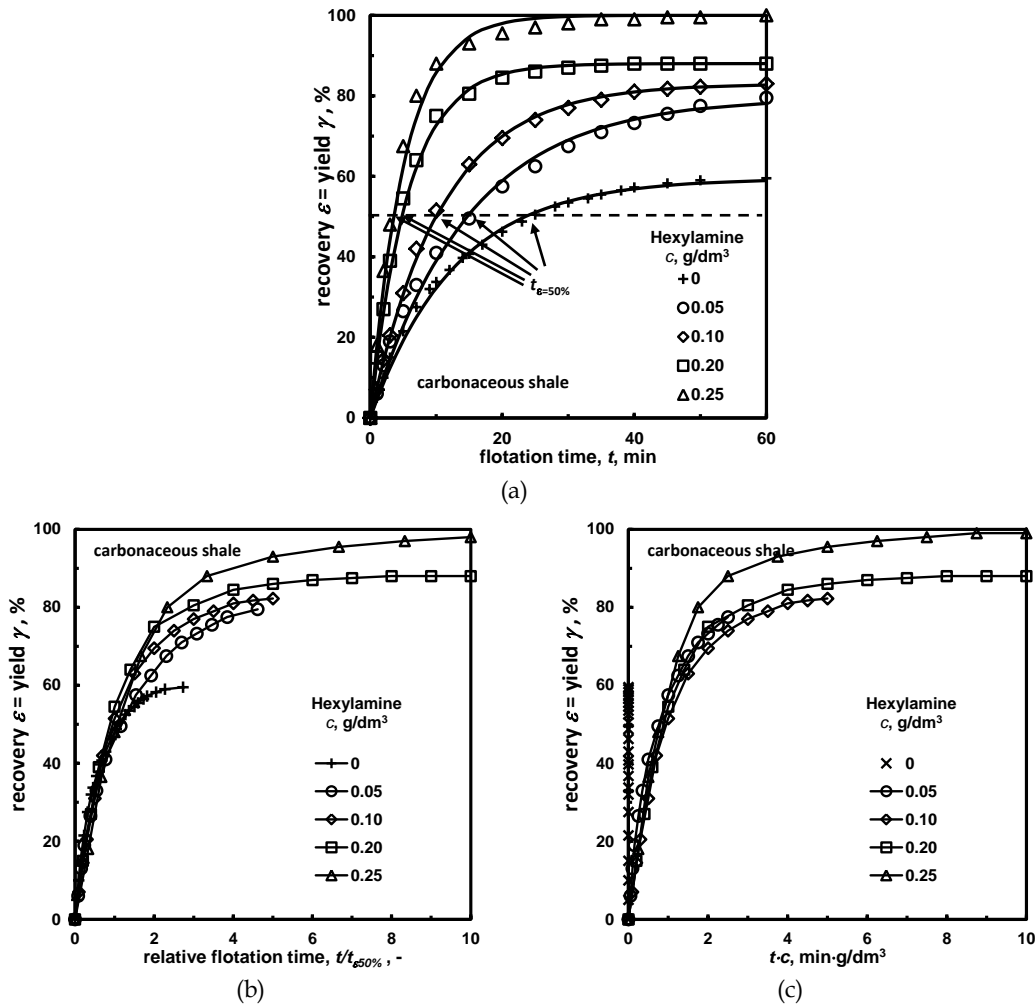


Fig. 2. Influence of varying concentrations of a reagent (here hexylamine) on flotation results of a solid (here carbonaceous shale) as a function of time (data of Kudlaty, 2016, Drzymala et al., 2017).

a) Original experimental data curves (kinetic curves) approximated with the 1st order kinetics, b) ineffective normalization with time needed to achieve 50% yield (or recovery), c) ineffective normalization of time with concentration

The process and component kinetic curves can be normalized with various parameters. Figure 2b shows normalization of the flotation time with the time needed to achieve 50% of the yield, while Fig. 2c shows example of normalization by multiplication of the time by the reagent concentration. Both normalizations do not change the character of the curves, and therefore, do not provide any new information about the system. Other normalizations of the kinetic curves are possible but no improvement is expected. Therefore, another approach is needed. The most useful seems to be the apparent elimination of one of three system parameters that either γ (ε), t or c . The apparent elimination relies on approximation of the kinetic curve data points with a kinetic equation, preferably of the 1st order, either in the differential:

$$dy/dt = (y_{\max} - y) \cdot v \quad (1a)$$

or integral

$$y = y_{\max}[1 - \exp(-kt)] \quad (1b)$$

form, where y stands for either yield γ or recovery ε , while k is the 1st order kinetic constant and v is the 1st order kinetics specific process rate. It should be noticed that v and k are numerically identical (shortly $\text{num } k = \text{num } v$), though their units are different (Drzymala et al., 2017). The unit of k is 1/min or 1/s, while the unit of v is percent of mass recovered in the concentrate per percent of mass present as the tailing per unit time (%/(%·s)).

Due to the modification of the process data with the 1st order kinetics, the whole individual kinetic curve is transformed into two new parameters, that is y_{\max} (γ_{\max} or ε_{\max}) and process rate (v or k). This approach opens new possibilities for normalization. It also reduces the number of curves delineating the results of the separation process. In some cases, instead of γ_{\max} or ε_{\max} , which are calculated by approximation of the separation data with kinetics equations, the yield, or recovery, after an arbitrarily chosen separation time is used for the plotting of the separation curves.

The modification of the kinetic plot leads to three new separation curves that is incentive, limits, and half-life curves, which are presented in the following sections of the paper.

3. Normalization of the incentive curves

The apparent elimination of time from the original kinetics curves can be accomplished by approximation of each kinetic curve with the 1st order kinetic equation (Eq. 1) to obtain the limit of y (γ or ε), that is maximum y or y after a certain time of the process, and next plotting the relation between limit of y as a function of the value of the incentive parameter, which usually is concentration. Typical incentive curves are shown in Fig. 3a. The incentive curves can be normalized. There are two types of normalization: with internal or external parameter. The first one takes into account a characteristic parameter already measured and utilized as it was demonstrated in Fig. 2, where the relations were normalized with internal parameter $c_{\gamma 75}$, that is frother concentration in g/dm³ at which yield is 75% after a given flotation time. The performed internal normalization with $c_{\gamma 75}$ (Fig. 3b) is effective, and the $c_{\gamma 75}$ values can be used for classification of the used frothers. However, it is an internal (already used) parameters, meaning that the prediction of flotation results is not possible without actual running the experiment.

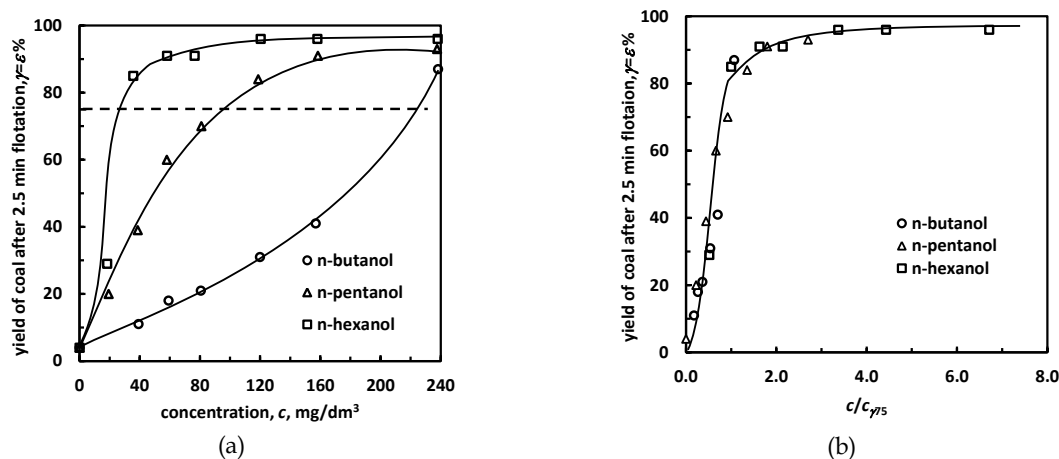


Fig. 3. a) Original incentive curve of Malysa et al. (1987) of coal flotation, b) internal normalization of flotation data with characteristic frother concentration needed to achieve coal yield equal to 75% ($c_{\gamma 75}$)

The second type of normalization relies on incorporation into consideration an additional external parameter such as molecular mass (weight) (MW), critical coalescence concentration (CCC), critical concentration at the minimum bubble velocity (CMV), dynamic foamability index (DFI) etc. The normalization of flotation data of Malysa et al. (1987) (Fig. 4a) with external parameters such as

molecular mass as $1/MW$ (Fig. 4b) is ineffective since none of the curves overlap. However, it was demonstrated by Malysa et al. (1987) that normalization of the incentive curve with DFI leads to a full normalization (Fig. 4d).

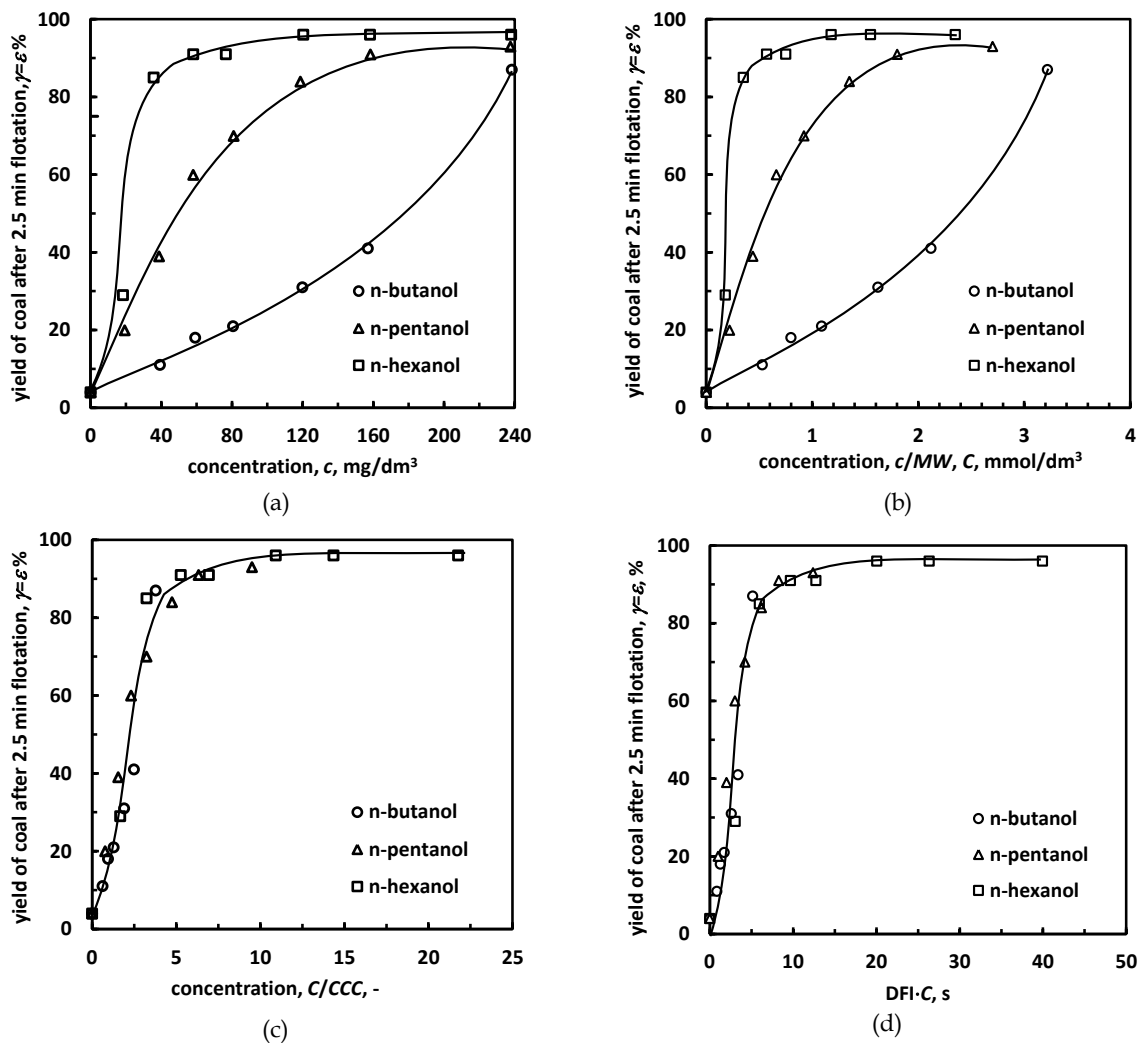


Fig. 4. (a) Incentive (yield of coal vs. frother concentration) curve with alcohol as frother and its normalizations: (b) ineffective with molecular mass MW, (c) fully effective with CCC and (d) fully effective with DFI (based on Malysa et al., 1987)

In the case of the flotation data considered by Malysa (1987) (Fig. 4a), normalization of the frother concentration with the inverse value of the critical coalescence concentration CCC (Laskowski, 2004) is also successful (Fig. 4c) and similar to that of DFI (Fig. 4d). The similar effect of normalization is a result of observed $1/x$ type dependence of DFI on CCC for certain groups of reagents.

The flotation data of Malysa et al. (1987) for selected alcohols after normalization can be approximated with the following equation:

$$\gamma_{max} = 96\% \cdot \exp[-0.2(DFI \cdot c)^2]^{-1}. \quad (2)$$

Since Malysa et al. (1987) considered only a homologous series of alcohols as frothers, it became necessary to check the usefulness of normalization of separation results with DFI, CCC and CMV for other frothers. It was done with the data of Kowalczyk et al. (2014) and Melo (2005). Figure 5a is the incentive curve for all investigated by Kowalczyk et al. (2014) frothers, that is alcohols (Cn), propylene glycols (Pn) and ethylene (CE) and propylene (CP) glycol ethers. Figures 5b-f present normalization of the carbonaceous shale flotation data with MW, CMV, CCC and DFI, respectively, for selected frothers, because only limited data on DFI are available.

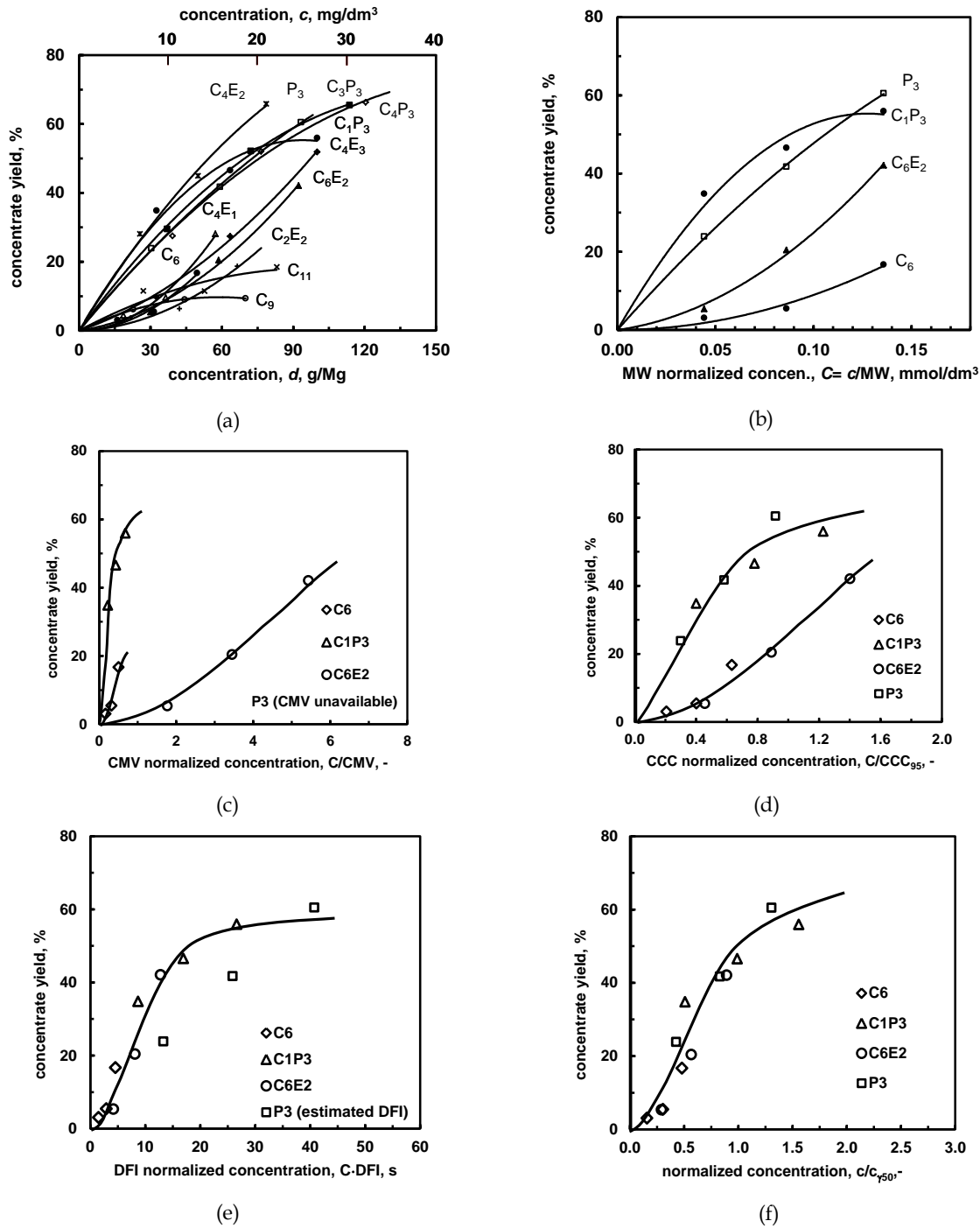


Fig. 5. (a) Incentive (carbonaceous shale yield vs. concentration of different frothers after 7 minutes of flotation) curves and their normalizations, (b) as figure 5a but for selected frothers as representatives of different frothers families - ineffective normalization with molecular mass MW, (c) ineffective normalization with CMV, (d) partially effective normalization with CCC, (e) nearly fully effective normalization with DFI, (f) nearly fully effective normalization with characteristic concentration needed for $\gamma=50\%$ (based on data of Kowalczyk et al., 2014)

It appears that only DFI provides full normalization of the incentive curves (Fig. 5e) of the considered flotation data. The normalization with CCC is partially effective, while with CMV and MW normalization is ineffective. Internal type of normalization with c_{50} (concentration expressed in g/dm³ needed to obtain yield or recovery equal to 50% after a given time of flotation) is also effective (Fig. 5f). It allows to classify the frothers as to the dose of frother needed for a certain yield or

recovery. However, c_{50} is not able to predict the separation results because it must be obtained from the flotation experiments.

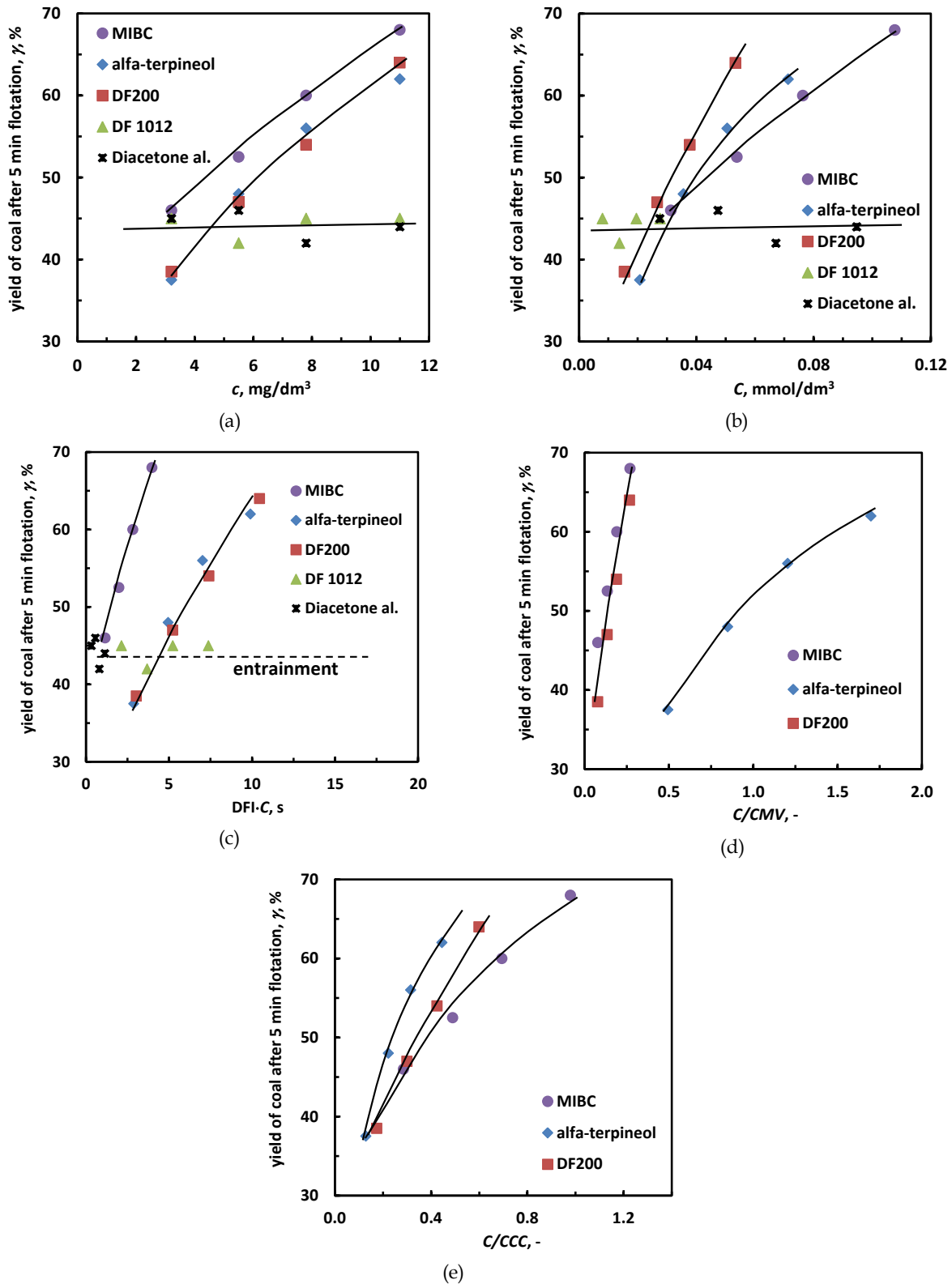


Fig. 6. (a) Incentive flotation curves and their normalizations, (b) ineffective normalization with molecular mass MW, (c) partially effective normalization with DFI, (d) partially effective normalization with CMV, (e) ineffective normalization with CCC (based on data of Melo (2005) for coal-quartz mixture, 5 min flotation in Leeds cell in the presence of only frother)

In the case of data of Melo (2005) (Fig. 6a), DFI also seems to be the best normalization parameter (Fig. 6c) disclosing generic properties of the applied frothers. Among the investigated by Melo (2005) frothers only MIBC seems to behave specifically. Partially effective normalization is observed with CMV (Fig. 6d) while normalizations with MW (Fig. 6b) and CCC (Fig. 6e) are ineffective. Very effective normalization of flotation results with DFI, if confirmed with data of other authors, provides an opportunity to predict the concentration of frother needed for achieving certain yield or recovery of separation without performing experiments.

For normalizations of the flotation results the values of DFI were taken from Khoshdast et al. (2015) and Melo (2005), CCC from Zang et al. (2012), Kowalczyk (2013) and Melo (2005), while CMV from Kowalczyk et al. (2017).

4. Normalization of the limits curves

The original flotation data based on y (ε or γ), t , c , and n can also be reorganized and reduced by apparent elimination of the incentive parameter, which in our case is the concentration. As it was discussed earlier, approximation of the data with the 1st order kinetics provides two new flotation limits parameters, that is y_{max} and k ($=v$). The new parameters can be used for a separation plot called the limits (Drzymala et al., 2017) or R-K (Bhattacharya and Dey, 2008) curve. The limits curves for flotation of carbonaceous shale with different flotation reagents taken from the paper of Nowak and Drzymala (2017) are presented in Fig. 7a. The limits curves can be used directly for characterization of flotation systems as presented in Fig. 7b.

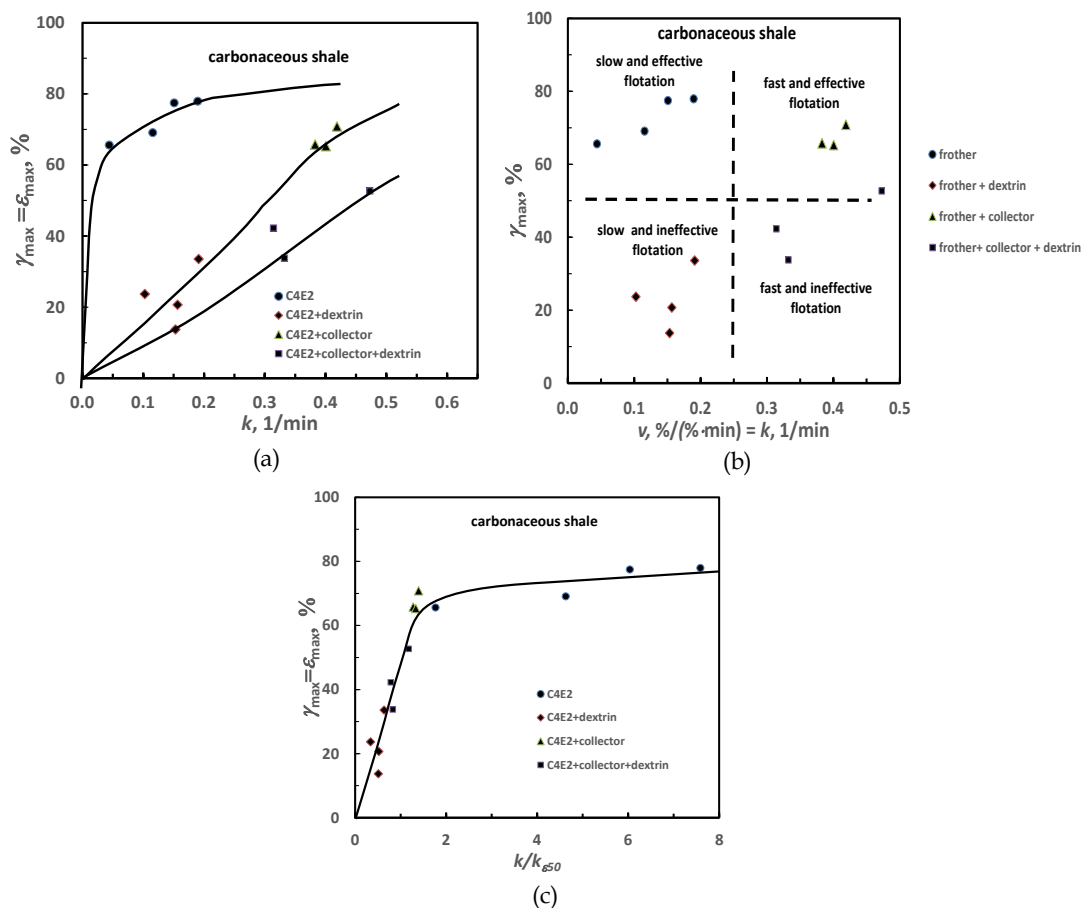


Fig. 7. Limits kinetic curves (a) and resulting classification of flotation systems (b) as well as total normalization using $k_{y50\%}$ (c)

The limits curve can also be normalized. Figure 7c presents normalization of the kinetic constant (specific rate) with the internal parameter such as the constant needed to obtain 50% maximum y (yield or recovery). In such a case normalization is totally effective and the k_{50} values can be used for

classification of frothers. Such a classification was offered in the paper of Drzymala and Kowalczyk (2017).

5. Normalization of the half-life curves

The considered here flotation curves are based on y (ε or γ), t , c and n . It has been already presented that either c or t can be eliminated leading to limits or incentive curves, respectively. The third option of modification of the kinetic curves is the apparent elimination of the yield or recovery. This can be accomplished by reducing the original flotation curves to specific plot of time versus concentration. Such approach was presented by Kowalczyk et al. (2016) in the form of $1/k$ versus c , as shown in Fig. 8a. The $1/k$ parameter is in fact a specific time, that is time of the half-life of flotation $t_{1/2}$, when the flotation follows the 1st order kinetics because $1/k = t_{1/2}/\ln 2 = t_{1/2}/0.693$. The parameter $t_{1/2}$ is related to y_{\max} via the 1st order kinetic equation (Eq. 1). The advantage of this type of curve over other modifications of the kinetic curves has to be established. The $t_{1/2}$ versus concentration plots will be called the half-life curves.

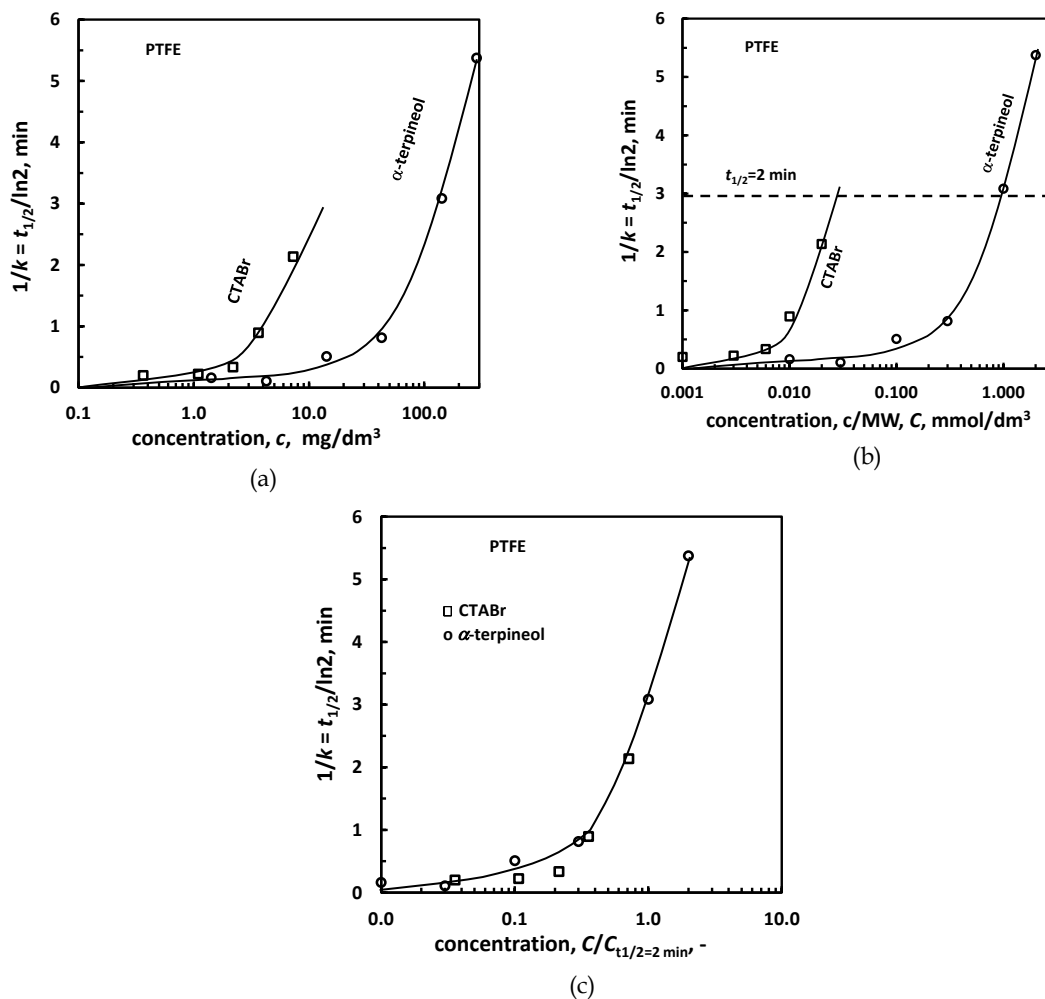


Fig. 8. Half-life curves for flotation of PTFE in the presence of two surfactants. (a) Original curve (Kowalczyk et al., 2016), (b) after ineffective normalization with MW providing concentration in mol/dm^3 , (c) after fully effective normalization with $C_{t_{1/2}=2 \text{ min}}$

The normalization of the half-life curves is possible and Fig. 8b shows ineffective normalization of it with the external parameter MW, while Fig. 8c presents a totally effective normalization with internal parameter $C_{t_{1/2}=2 \text{ min}}$, that is frother concentration in mol/dm^3 at which the flotation half-life is two minutes (Fig. 8c).

6. Conclusions

The original flotation kinetic process curves relating either yield or recovery with the time of flotation for a given concentration of a reagent can be transformed into three, that is incentive (y_{\max} vs c), limits (y_{\max} vs k) and half-life ($t_{1/2}$ vs c) curves. The original and modified curves can be normalized leading to either full, partial or lack of normalization. Normalization can be performed with either internal, that is already obtained from the same experiment, or external, parameters. Normalization of the original flotation kinetic curves usually is ineffective. The normalization of the modified curves with an internal parameter is very useful because all of them can be efficiently and fully normalized providing parameters, which can be used for classification of the flotation reagents.

The normalization of the modified curves with an external parameter depends on the used parameter. For instance the normalization of the incentive curve with molecule mass leading to changing the reagent concentration units from g/dm^3 to mol/dm^3 is totally ineffective. The most effective and universal normalization is obtained for the incentive curves with DFI. This parameter is able to predict the results of flotation having only DFI and the generic form of the incentive curve.

All of the discussed curves and their normalizations are very useful because they are able to provide additional information about considered reagents.

Acknowledgments

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