ELSEVIER

Chemical Engineering Journal 69 (1998) 63–67

Chemical Engineering Journal

Short communication

On the coalescence effects in a batch mixer–settler

G. Kyuchoukov *, R. Kounev [1]

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Blk. 103, Sofia 1113, Bulgaria

Received 10 January 1996; revised 3 October 1996; accepted 31 July 1997

Abstract

The effect of the agitation time on the behaviour of a dispersion during separation in a batch mixer–settler was studied. The studies were carried out on the four stages of copper transfer from hydrochloric acid to sulphuric acid medium using the bifunctional extractant Kelex 100®. The organic phase was a 20% (v/v) solution of Kelex 100®; the aqueous phase had different salt compositions and acidities in the different stages. The measurements were performed after completion of the mass transfer process. Four periods were distinguished in the behaviour of the dispersion. There were three cases of interfacial movement during the free motion of the droplets. © 1998 Elsevier Science S.A.

Keywords: Mass transfer process; Batch mixer-settler; Coalescence effects; Two-phase extraction system

1. Introduction

The processes of dispersion and coalescence in liquid–liquid extraction not only influence the mass transfer process, but are of significance for the design and dimensions of the corresponding equipment. In impeller-agitated apparatus, the dispersity of the two-phase system depends on the rpm number, type and geometric characteristics of the impeller, physicochemical properties of the system, availability of surface-active substances and performance of the mass transfer process.

The coalescence during dispersion separation is also affected by the factors mentioned above [1,2]. After a period of agitation, a steady state regime sets in which is characterized by a constant average droplet size. This results in a constant rate of sedimentation, provided that there is no coalescence or constant coalescence of the droplets. The separation of the dispersion is strongly dependent on the coalescence of the droplets with the surface [3]. When surface-active substances are present in the system, they accumulate at the interface. In the presence of electrolytes, a dielectric layer is formed [2] which also affects the coalescence. Provided that the agitation time is sufficient for the mass transfer process to be completed and a steady droplet size to be reached, but not sufficient for a constant rate of coalescence to set in, different times of separation will be registered depending on the duration of agitation. The steady state of the two-phase system (with respect to both sedimentation and coalescence) is reached in a finite time, whereas agitation is an infinite process. Therefore, the overall time of agitation and separation will have a minimum value with regard to agitation. It should be noted, however, that the system cannot reach steady state, but the completion of the mass transfer process should be achieved. In some cases, this minimum value coincides with the completion of the mass transfer process. Since several factors affect the processes of dispersion and coalescence, the behaviour of the system must be experimentally determined [4,5].

The purpose of this study was to follow the separation behaviour of a two-phase extraction system using various phase compositions and agitation times after completion of the mass transfer process.

2. Experimental details

As a model system, we used the four stages of the recently developed method for copper extraction from hydrochloric acid etching solutions and its subsequent transfer into chlorideless sulphuric acid medium by means of a bifunctional extractant [6]. The effects of the various phase compositions and acidities on the processes of dispersion and coalescence were studied. In all stages, the organic phase consisted of 20% (v/v) Kelex 100® (Kindly supplied by Schering), 15% (v/v) octanol and 65% (v/v) kerosene. The composition of

---

* Corresponding author. Tel.: +359-2-72-02-30; fax: +359-2-70-75-23.

[1] Tel. +359-2-72-02-30; fax: +359-2-70-75-23.

1385-8947/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved
PII S1385-8947(97)00103-4

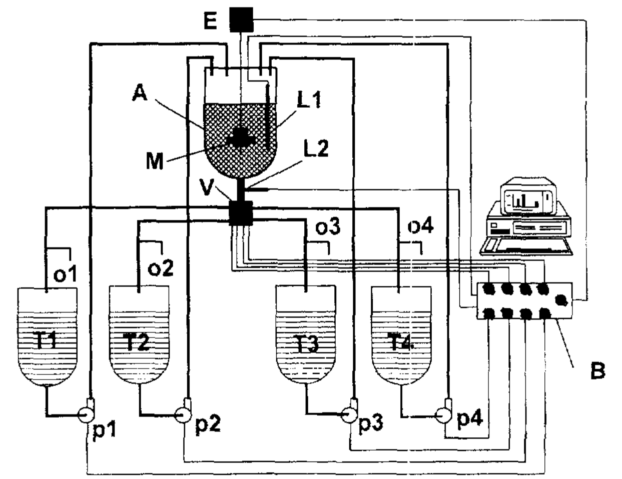

Fig. 1. Experimental equipment: A, mixer–settler; B, interface block; L1 and L2, level sensors; E, stirrer electromotor; M, turbine impeller; o1–o4, samplers; V, valve box; p1–p4, pumps; T1–T4, reservoirs.

the aqueous phase depended on the process taking place and is given in the corresponding stage. The experiments were performed in the batch pilot installation presented schematically in Fig. 1. The mixer–settler A was filled with the organic phase. The aqueous solutions used in the different stages were fed from the reservoirs T1–T4 into the mixer–settler by means of the pumps p1–p4. The liquid flows in the various directions were regulated by the electromagnetic valves operated by means of the interface block B. The mixer–settler was of 20 l capacity and 25 cm in diameter. It had a vertical graduation for volume determination. The turbine-type impeller M of 13.5 cm in diameter was set in motion by means of the stirrer electromotor E. The impeller was situated at the interface. The phase ratio was 1:1 and the total working volume was 10 l. After feeding the two phases into vessel A, agitation was started. The movement of the two fronts (of sedimentation and coalescence) was clearly visible, permitting their location to be followed along the height of the apparatus and the process taking place to be observed. The precondition for a completed mass transfer process was obeyed in all experiments. The high impeller velocity (400 rpm) maintained in all stages provided relatively short agitation times to validate the abovementioned precondition. The observed phenomena and the results obtained are discussed below.

3. Results and discussion

The dispersion separation was followed by studying the movement of the two demarcation lines between the separated aqueous or organic phase and the non-separated dispersion with time. Fig. 2 shows a typical pattern of the movement of these two fronts. Because in all experiments, the aqueous (heavy) phase was the dispersed phase, curve c represents the movement of the surface on which the droplets coalesce. Curve s depicts the movement of the surface between the dispersion and the separated organic (light) phase. For each τ_S value from the start of dispersion separation, the intercept below curve c corresponds to the volume of separated aqueous phase as a result of coalescence, that between both curves to the volume of non-separated dispersion and that above curve s to the volume of separated organic phase. Line I corresponds to the location of the interface prior to agitation and after complete separation of the dispersion.

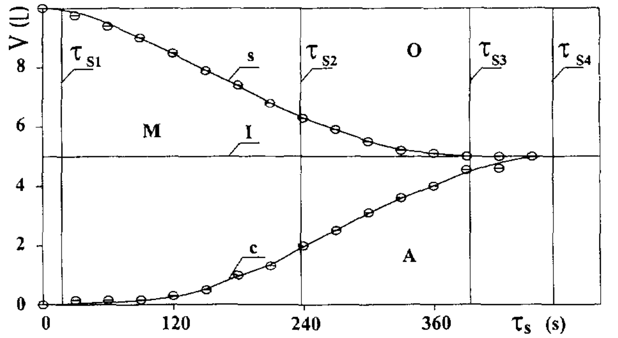

Fig. 2. Separation profiles of the dispersion obtained in the extraction stage (agitation time, 30 s).

Four periods were distinguished during the process of separation of the dispersion. The first period (from 0 to τ_{S1}) was the shortest (10–15 s). It was characterized by a very low rate of sedimentation due to the residual agitation of the dispersion by internal forces. The second period (from τ_{S1} to τ_{S2}) was a period of free sedimentation of the droplets with a constant rate. As a result, the organic phase brightened. The droplets formed a packed zone directly above the coalescing front c. At point τ_{S2}, the surface of the packed zone overlapped with s.

During this period, the ratio between the volumes of the continuous and dispersed phases in the dispersions continuously changed as a result of the difference between the rates of sedimentation and coalescence. The coalescence of the droplets pressed together in the packed bed began to play a decisive role. This was most clearly manifested in the third period (τ_{S2} to τ_{S3}), when the rate of the volume change of the aqueous phase as a result of coalescence with the aqueous surface exceeded the rate of the volume change of the liberated organic phase. In contrast with the former periods, in the third period, the liberation of the organic phase from the dispersion was due to restructuring of the packed bed caused by interdroplet coalescence. The larger droplets thus obtained needed a longer time to achieve coalescence with the aqueous surface [1,2]. In the examined case, a larger droplet size led to a higher rate of liberation of the aqueous phase, since the volume liberated by coalescence exceeded that liberated by the small droplets during the same time interval. In the fourth period (τ_{S3}–τ_{S4}), the rate of coalescence changed again. This was a specific period which was strongly dependent on the phase composition and had a considerable effect on the separation time. In some cases, only mechanical destruction of the dispersion was possible. In this period, the dispersion was characterized by the small volume of the continuous phase, thin films of which enveloped irregularly shaped volumes of coalesced droplets pressed together. The initial thickness of the packed bed in the fourth period was approximately 10–15 mm.

The four periods described above were observed in all stages of the model reaction examined.

3.1. Extraction

In this stage, the aqueous phase was an industrial hydrochloric acid etching solution of copper with the following concentration: hydrochloric acid, approximately 2.9 M; copper, approximately 120 g l^{-1}; chlorides, approximately 4.0 M. The mass transfer process taking place was the extraction of the copper chloride complex by a preconditioned bifunctional extractant:

$$2OHRNHCl + CuCl_4^{2-} \leftrightarrow (OHRNH)_2CuCl_4 + 2Cl^- \qquad (1)$$

In this stage (as in the others), the aqueous (heavy) phase was the dispersed phase. Fig. 3 presents the location of the two fronts. The analysis of the curves obtained showed that, in the period of free droplet sedimentation, the rate of movement of the sedimenting front exceeded that of droplet coalescence with the aqueous surface c, i.e., the process of coalescence limited the separation. The strongest effect was observed with an agitation time of 60 s (highest curve asymmetry) and the weakest effect with an agitation time of 15 s. There was a continuous increase in the content of the dispersed phase (aqueous droplets) in the non-separated dispersion with time. For example, with an agitation time of 30 s, 1.2 l of aqueous phase and 3.33 l of organic phase separated at the end of the period of free droplet sedimentation ($\tau_{S2} = 240$ s), i.e., the content of the dispersed phase in the packed bed formed increased from 50 to 69%. During the third period, the condensation of the layer continued and, at 360 s, the content of the dispersed phase reached 80%. This value, which exceeds the theoretical value for the most dense spherical packing (74%), can be attributed to droplet polydispersity. The droplets were pressed together by their weight, and the film around them became thinner, broke down and pulled out, leading to droplet coalescence and deformation. The slower the coalescence with the aqueous surface, the denser the packed bed. The droplets were replaced by volumes of aqueous phase of irregular form, enveloped by thin films of organic phase. As a result of thinning, breaking down and pulling out of the films, there were no distinguishable volumes of the organic phase in the fourth period. As shown in Fig. 3, there is no significant difference in the movement of the upper front s as a function of the agitation time (the difference between the curves is within 20%), whereas, for the movement of the lower front, these differences exceed 50%. For instance, with an agitation time of 15 s, the two-phase system was fully separated after 390 s, whereas, with an agitation time of 60 s, less than 50% of the aqueous phase separated within this time. The dependence of the separation time on the agitation time (see Fig. 4) in the transition period, when steady state of the system has not been achieved, shows a maximum. Hence, the minimum agitation time should be applied in this stage, but sufficient for the completion of the mass transfer process (15 s).

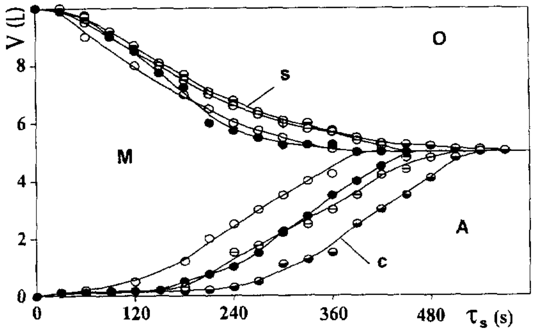

Fig. 3. Separation data in the extraction stage for various agitation times: ○, 15 s; ⊖, 30 s; ◒, 60 s; ●, 120 s.

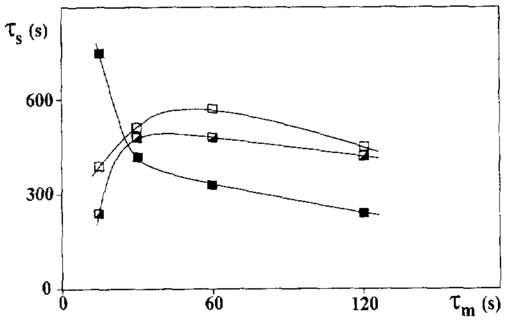

Fig. 4. Effects of the agitation time (τ_m) on the separation time (τ_S): □, extraction; ■, stripping; ◪, conditioning.

3.2. Scrubbing

In this stage, the aqueous phase was ammonia and ammonium chloride solution of pH 8. This stage aimed to liberate the organic phase from the chloride ions by destroying the organic copper chloride complex and binding the copper ion in a chelate complex by a cation exchange reaction as follows:

$$(OHRNH)_2CuCl_4 + 4NH_3 \leftrightarrow (NRO)_2Cu + 4NH_4Cl \qquad (2)$$

i.e., copper was transferred from the organic to the aqueous phase and back to the organic phase. This was the slowest stage. The process required a minimum of 120 s to reach completion even at the high rpm number used (400 rpm). In this stage, phase inversion took place immediately after completion of the mass transfer process: at the start of the process, the organic phase was the dispersed phase, whereas, at the end, the aqueous phase was the dispersed phase. The inversion was also observed in experiments with separatory funnels. After phase inversion at the end of separation (fourth period), classical evidence of 'film dispersion' was observed. The whole volume of the organic phase was separated (approximately 5 l), the volume of the thin film enveloping the volume of the aqueous phase being within error limits. The film dispersion took about one-third of the whole volume of the system, only two-thirds of the aqueous phase being separated by coalescence with the surface. Irrespective of the duration of agitation after completion of the mass transfer process, the same result was observed. The film dispersion was extremely stable and no change in its volume, except for thinning of the film, was registered after several days. Due to the dark-blue colour of the copper-loaded organic phase, the dispersion initially had a blue colour, which gradually faded as a result of the thinning of the organic film. The dispersion could only be mechanically destroyed by agitation with a velocity of several rpm which caused film breakage and accelerated the coalescence.

After several days, mechanical treatment of the dispersion led to instantaneous coalescence due to the thinned organic layer.

3.3. *Stripping*

In this stage, the aqueous solution was sulphuric acid with an initial concentration of 3.0 M. As a result of both stripping of copper and coupling of sulphuric acid to the tertiary nitrogen of the extractant according to:

$$(NRO)_2Cu + 2H_2SO_4 \leftrightarrow 2OHRNH\cdot HSO_4 + Cu^{2+} + SO_4^{2-} \quad (3)$$

the final concentration of sulphuric acid dropped to 2.6 M. In this stage, the agitation time (after completion of the mass transfer process) strongly affected both the behaviour of the dispersion and the separation time. Three different types of separation profile were observed (see Fig. 5). The first type, registered with agitation times of 15 and 30 s, was that discussed in the extraction stage. It was characterized by a prevalent separation of the continuous phase during the free sedimentation of the droplets, i.e., the rate of sedimentation exceeded that of coalescence. Here, a detailed study of the other two types of separation profile is presented. With an agitation time of 60 s, the two curves in Fig. 5 are symmetrical to the interface location (I) after dispersion destruction and, correspondingly, prior to the start of agitation and during most of the period of free droplet sedimentation. This signifies that the separated volume of the organic phase, obtained as a result of the sedimentation of aqueous droplets per unit time, equals that obtained by their coalescence with the aqueous surface. Thus, the initial (1:1) ratio of the phase volumes was also preserved in the non-separated dispersion. The third and fourth periods during which the type of dispersion changed strongly were short. The third type of separation profile was observed with an agitation time of 120 s. The phase ratio in the bulk of the dispersion (M) was in favour of the continuous (organic) phase. During most of the second period, the rate of coalescence with the aqueous surface exceeded that of the free sedimentation of the droplets. For instance, with a separation time of 150 s, the droplets represented 40% of the non-separated volume (50% at the start). This may be related to interdroplet coalescence during the process of sedimentation, as a result of which they move faster to the surface where they coalesce. On the other hand, the sedimentation of smaller droplets defined a lower rate of movement of the upper front s. Here also, large droplets up to 10–15 mm were observed after packed bed formation (in the third and fourth periods). They existed for a much shorter time than in the first type of separation.

Fig. 5 illustrates the favourable effect of the agitation time on the separation of the dispersion obtained. In this stage of the mass transfer process, agitation creates a dispersion with different separation profiles as discussed above. The ratio between the duration of the third and fourth periods and that of the first and second periods, calculated for the different sedimentation types, is at a maximum for the first type, where coalescence of the droplets with the aqueous surface during the period of free sedimentation (second period) limits the separation, and is at a minimum for the third type, where sedimentation limits the separation. In contrast with the extraction stage, in the stripping stage, longer agitation times lead to shorter separation times of the dispersion (Fig. 4).

3.4. *Conditioning*

The organic phase was conditioned with a NaCl solution of approximately 5.0 M according to the reaction:

$$OHRNH\cdot HSO_4 + Cl^- \leftrightarrow OHRNH\cdot Cl + HSO_4^- \quad (4)$$

the conditioned extractant being fed for reusage in the extraction stage.

The behaviour of the dispersion in this stage is shown in Fig. 6. It was similar to that in the extraction stage, but the separation of the two phases was more rapid. This mainly

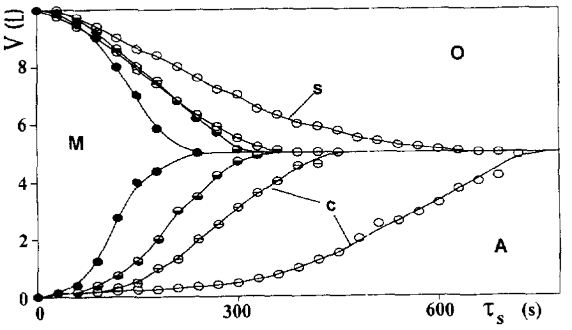

Fig. 5. Profiles of phase separation in the stripping stage for different agitation times: ○, 15 s; ⊖, 30 s; ◒, 60 s; ●, 120 s.

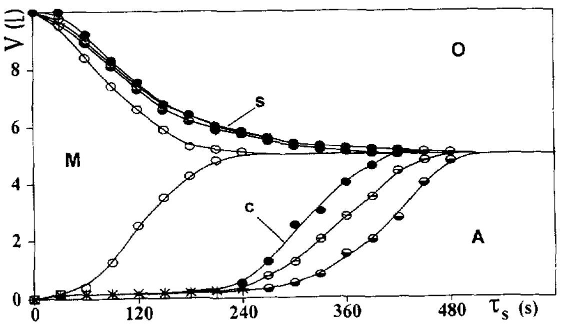

Fig. 6. Separation data during conditioning for various agitation times (400 rpm): ○, 15 s; ⊖, 30 s; ◒, 60 s; ●, 120 s.

applied to the dispersion obtained with an agitation of 15 s. With the other agitation times, the effect of interdroplet coalescence in the packed bed formed (third and fourth periods) on the time required for complete dispersion separation was clearly observed. The volume increase of the organic (continuous) phase had practically the same course for all three agitation times used (30, 60 and 120 s). This was probably due to the same dispersity of the system resulting in equal rates of sedimentation. The first two periods were characterized by equal rates of droplet coalescence with the aqueous surface. The picture totally changed after free sedimentation was complete and interdroplet coalescence in the packed bed started to play a dominant role. It also affected the coalescence with the aqueous surface, which, in this system, was strongly dependent on the agitation time.

It follows from the results presented in Fig. 4 that, similar to the extraction stage, there is no proportionality in this stage between the agitation time and the separation time of the dispersion; 15 s was the optimum agitation time, which led to a separation time of 255 s. The behaviour of the dispersion and its structure during separation varied considerably with other agitation times with respect to both the rate of droplet sedimentation and coalescence with the aqueous surface.

4. Conclusions

The results obtained indicate that the behaviour of a two-phase system during separation depends not only on the phase composition, intensity of agitation and performance of the mass transfer process, but also on the duration of agitation. During the period of free sedimentation of the droplets (after completion of the mass transfer process), three sedimentation types were observed as a function of the time of agitation:

1. the rate of settling is higher than the rate of coalescence;
2. the rate of settling is equal to the rate of coalescence;
3. the rate of settling is lower than the rate of coalescence.

References

[1] G.V. Jeffreys, G.A. Davies, Recent Advances in Liquid–Liquid Extraction, C. Hanson (Ed.), Pergamon, 1971, pp. 495–584.
[2] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction, Part I, Elsevier, 1984, pp. 207–228.
[3] M.J. Kourio, C. Gourdon, G. Casamatta, Conference Papers, ISEC'88, Vol. 2, 1988, pp. 179–182.
[4] J.C. Gogfrey, D.K. Chang-Kakoti, M.J. Slater, S. Tharmalingam, CIM 21 (Special Volume) (1979) 406–412.
[5] A. Assenov, M.J. Slater, Hydrometallurgy 2 (1976) 157–170.
[6] G. Kyuchoukov, R. Kounev, Hydrometallurgy 35 (1994) 321–342.