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Influence of Electrolytes and High Viscosity on Liquid-Liquid Separation

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***Abstract*—**Liquid-liquid extraction is a process using two immiscible liquids to extract compounds from one phase without high temperature requirement. Mostly, the technical implementation of this process is carried out in mixer-settlers or extraction columns. In real chemical processes, chemicals may have high viscosity and contain impurities. These impurities may change the settling behavior of the process without measurably changing the physical properties of the phases. In the current study, the settling behavior and the affected parameters in a high-viscosity system were observed. Batch-settling experiments were performed to experimentally quantify the settling behavior and the mixer-settler model of Henschke [1] was used to evaluate the behavior of the toluene + water system. The viscosity of the system was increased by adding polyethylene glycol 4000 to the aqueous phase. NaCl and Na_2SO_4 were used to study the influence of electrolytes. The results from this study show that increasing the viscosity of water has a higher influence on the settling behavior in comparison to the effects of the electrolytes. It can be seen from the experiments that at high salt concentrations, there was no effect on the settling behavior.

***Keywords*—**Coalescence; electrolytes; liquid-liquid separation; high viscosity; mixer- settler.

I. Introduction

LIQUID-liquid extraction is one important separation process in chemical industries besides distillation. The principle of the separation has been studied by many researchers such as Jeelani and Hartland [2], Henschke et al. [3].

The main step of liquid-liquid extraction is to contact both phases for mass transfer to occur. To enhance the mass transfer, the interfacial surface area is increased by creating dispersion. The direction of the dispersion depends on the system itself, as well as the phase ratio of the two liquids. For further treatment the separation of the phases is necessary. To understand better and to investigate the settling behavior of the dispersion, batch settling experiments can be used. The processes during the batch settling according to Henschke [1] are shown in Fig. 1 schematically for the lighter phase being dispersed.

When the mixing is stopped, the droplets start sedimenting to the top. At the boundary of the continuous phase the droplets coalesce to the bulk of the dispersed phase. Plotting the boundary between dispersed bulk and continuous phase over time, the coalescence curve can be constructed. Accordingly, the sedimentation curve is derived from the height parting the droplet free continuous phase from the sedimentation zone, where droplets still sediment towards their bulk. If the sedimentation is faster than the coalescence of the droplets a dense packed zone forms. In this zone drop-drop coalescence occurs, causing the drop diameter to increase.

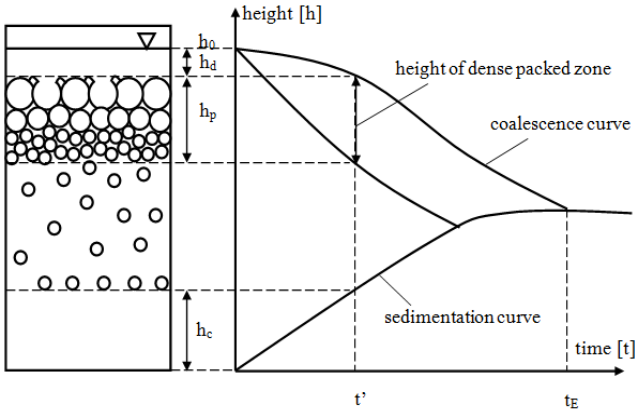


Fig. 1 Schematic representing the curves during a batch settling-experiment according to Henschke [1]

Henschke [1] and Henschke et al. [3] gave a complete overview of the description of drop sedimentation during the settling experiment. Since the sedimentation curve almost represents a linear curve, the swarm sedimentation velocity of the drops v_S can be determined. Henschke [1] applied the model of sedimentation for drop swarms which was developed by Pilhofer and Mewes [4]. This model is valid for Archimedes numbers

$$\mathrm{Ar} = \frac{\rho_c \Delta\rho g d_{32,0}^3}{\eta_c^2} \quad (1)$$

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Open Science Index, Chemical and Molecular Engineering Vol:6, No:12, 2012 publications.waset.org/12029/pdf

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larger than 1 and volume fractions of the dispersed phase (ε_0) between 0.06 and 0.55.

Then the sedimentation velocity of swarm drops v_s can be determined from:

$$v_s = \frac{\mathrm{Re}_s \eta_c (1 - \varepsilon_0)}{\rho_c d_{32,0}} \tag{2}$$

Pilhofer and Mewes used the equation:

$$\mathrm{Re}_s = \frac{3q\varepsilon_0}{c_w \xi (1-\varepsilon_0)} \left[\left(1 + \mathrm{Ar} \frac{c_w \xi (1-\varepsilon_0)}{54 q^2 \varepsilon_0^2} \right)^{0.5} - 1 \right] \tag{3}$$

to calculate the Reynolds number for sedimentation, with the parameter:

$$\xi = 5 K_{HR}^{-3/2} \left(\frac{\varepsilon_0}{1-\varepsilon_0} \right)^{0.45} \tag{4}$$

which is derived from the Hadamard–Rybczynski factor:

$$K_{HR} = \frac{3(\eta_c + \eta_d)}{2\eta_c + 3\eta_d} . \tag{5}$$

The parameter q used in (3) depends on the volume fraction of the dispersed phase (ε_0):

$$q = \frac{1-\varepsilon_0}{2\varepsilon_0 K_{HR}} \exp\left(\frac{2.5\varepsilon_0}{1 - 0.61\varepsilon_0} \right), \quad \text{if } \varepsilon_0 < 0.55 \tag{6}$$

$$q = \frac{2.2(1-\varepsilon_0)}{\varepsilon_0 K_{HR}} \exp\left(\frac{0.4\varepsilon_0}{1 - 0.61\varepsilon_0} \right), \quad \text{if } \varepsilon_0 \geq 0.55 \tag{7}$$

The friction coefficient

$$c_w = \frac{\mathrm{Ar}}{6\mathrm{Re}_\infty^2} - \frac{3}{K_{HR}\mathrm{Re}_\infty} \tag{8}$$

can be calculated with the help of the Reynolds number in an infinitely extended fluid. A model was developed by Ishii and Zuber [5] which is given as follows:

$$\mathrm{Re}_\infty = 9.72 \left[(1 + 0.01\mathrm{Ar})^{4/7} - 1 \right] \tag{9}$$

Henschke [1] developed an approach for the Reynolds number for sedimentation which is valid for Archimedes number between 1 and 2:

$$\mathrm{Re}_s = \frac{\mathrm{Ar}(1-\varepsilon_0)^2}{36\varepsilon_0 q} \tag{10}$$

Moreover, Hartland et al. [2] developed the equation for predicting sedimentation and coalescence profiles in terms of the slope of the coalescence curve and the height of the dense packed zone. When the sedimentation is complete, sedimentation and height of dense packed zone can be described as in (11) to (13) respectively.

$$\frac{dh_d}{dt} = \frac{2\varepsilon_i d_{32,i}}{3\tau_i} \tag{11}$$

The height of dense packed zone between $0 < t < t'$ can be described as:

$$h_p = \frac{(h_0 - v_s t)\varepsilon_0 - (1-\varepsilon_0)h_d}{\varepsilon_{p,0} - \varepsilon_0} \tag{12}$$

For $t \geq t'$, the height of the dense packed zone is:

$$h_p = \frac{h_0 \varepsilon_0 - h_d}{\varepsilon_p} \tag{13}$$

The model of Hartland et al. [2] does not describe the coalescence times τ_i which depends on the drop deformation. However, Henschke et al. [3] gave a complete description of drop deformation and the coalescence parameter. The successful model from Henschke [1] and Henschke et al. [3] has been used in the Settler program developed by AVT-TVT, RWTH Aachen University, Germany and CEET, Graz University of Technology, Austria. This program allows users to design horizontal and vertical settlers for clear systems based on a simple settling experiment on laboratory scale.

In an industrial scale, impurities such as electrolytes even in trace amounts may have a significant impact on process operation and process efficiency. These impurities may change the settling behaviour although their effect on the phase properties cannot be detected. Until now, the design method has mostly been validated for simple systems. For technically more relevant systems e.g. with high viscosity which is often encountered in the industries or impurities, systematic validation is still required. Thus in this work, the influence of impurities such as electrolytes and high viscosity has been investigated.

II. Materials and Methods

A. Materials

Polyethylene glycol with a specified mean molecular weight of 4000 g/mol was obtained from Sasol Germany GmbH. The toluene used for the experiments was a toluene distillation from TVT-AVT, RWTH Aachen University, Germany. NaCl (analytical grade) and Na_2SO_4 (analytical grade) were obtained from Merck GmbH Germany and Sigma-Aldrich, respectively.

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B. Methods

The mixer-settler cell of Henschke [1] as shown in Fig. 2 was used for mixing toluene and water (with PEG 4000 and salt) at 800 rpm for 30 seconds. The settling experiment is recorded on video and evaluated by the Settler program.

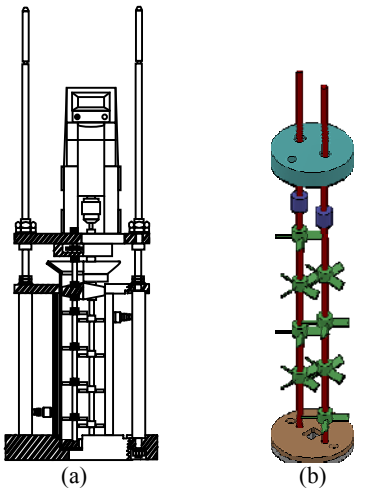


Fig. 2 (a) Settling apparatus according to Henschke, 1994
(b) Stirrer

The experiments were split into two parts in this study. The influence of electrolytes was investigated in the first part and the influence of viscosity on the settling behavior in the second.

In both parts the experiments were performed for two volumetric phase ratios between the organic and aqueous phase, namely 1/2 and 2/1.

Sodium chloride and sodium sulfate were separately used as salts in these experiments. The concentration of each salt was varied from 50 to 500 mmol/L_{aq}. The viscosity of the aqueous phase in the second part was increased by adding polyethylene glycol 4000 with variation of 5%wt. to 50%wt.

III. Results and Discussion

Sedimentation and coalescence behavior of the system toluene + water was studied by evaluating the influence of volume phase ratios, salt concentration and viscosity. The information from the settling experiments (coalescence and sedimentation data) and the physical properties (density, viscosity and interfacial tension) of the system were used to evaluate the mean drop diameter d_{32} and the coalescence parameter r_s^* by the Settler program.

A. Settling Behavior of Pure System

The experimental results without PEG and electrolytes for the phase ratios (o/a) of 1/2 and 2/1 are shown in Fig 3. In the case of the phase ratio (o/a) of 1/2, toluene droplets are dispersed in the water phase while for the phase ratio (o/a) of 2/1, water was the dispersed phase. This phenomenon is called phase inversion where the dispersed phase changes to become the continuous and vice versa. It can be seen from the result that for the phase ratio (o/a) 1/2, the settling time is much lower than for the phase ratio (o/a) 2/1. This is due to the different dispersed phase and the smaller size of Sauter mean diameter (d_{32}), the effect of which is described in (2).

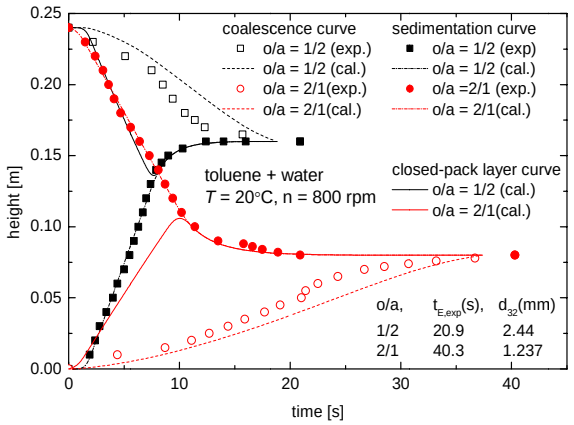


Fig. 3 Coalescence and sedimentation curve of toluene + water system o/a =1/2 and 2/1

Similar results were obtained for the system MIBK and water by Effertz [6] as well as Manodumrongthum [7]. Phase inversion takes place between the volume phase ratios of 1/2 and 2/1. Also the settling time increases for MIBK + water system. But MIBK system has settling time slower than toluene system as shown in Fig. 3 (toluene + water system) and Fig. 4 (MIBK + water system). It can be concluded that as expected the settling time depends on the investigated systems.

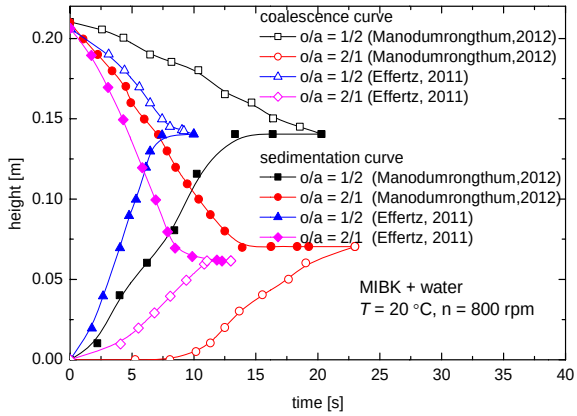


Fig. 4 Coalescence and sedimentation curve of MIBK-water system o/a =1/2 and 2/1 [6]-[7]

B. Influence of Electrolytes

The influence of the investigated salt concentrations is shown in Fig. 5 for both phase ratios. The experimental results indicate that for the phase ratio (o/a) 1/2 NaCl has a higher effect on the settling time of the toluene + water system than Na_2SO_4. In the case of the volume phase ratio (o/a) of 1/2 the results from both salts show that the settling time increases with increasing salt concentration. The effect is that at small salt concentrations an increase of the concentration leads to a

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further increase in the settling time. For salt concentrations above a certain limit of 200 mmol/L Na_2SO_4 and 100 mmol/L NaCl a further increase of the salt concentration does not affect the settling time any further.

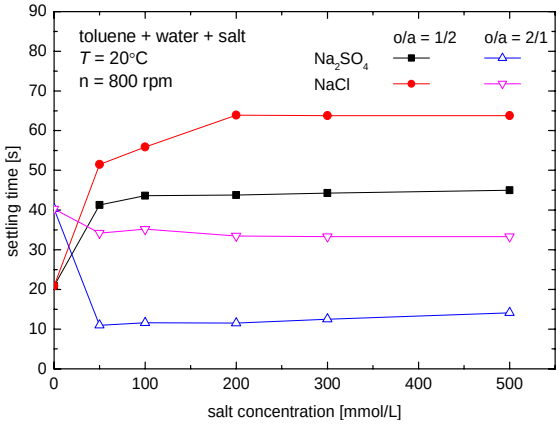


Fig. 5 Influence of salt on the settling time

In the case of the volume phase ratio (o/a) of 2/1, it was observed that sodium sulfate has a higher effect than sodium chloride. The settling time decreases with increasing concentration of sodium chloride and it becomes nearly constant for salt concentration above 200 mmol/L. For sodium sulfate, the settling time is rapidly declining when 50 mmol/L of the salt were added. For the Na_2SO_4 concentrations above 100 mmol/L only a slight effect on the settling time could be observed.

These results agree with the investigated behavior for the MIBK + water system, investigated by Effertz [6]. Additionally, the result of the settling time as a function of salt concentration for the system 1-butanol + water at the volume phase ratio (o/a) of 5/2 varied NaBr and NaCl concentrations from 10^{-3} to 10^{3} mol/m^3 showed that a little amount of salt has a strong influence on settling behavior. Increasing salt concentration from 10^{-3} to 1 mol/m^3 increases settling time by several decades and subsequently further increasing salt concentration from 10 to 100 mol/m^3 results to reduce settling time down to that of salt-free systems [8].

Furthermore, Soika and Pfennig [9] also studied the volume phase ratio (o/a) of 2/5, their results showed that the settling time of this system was different when different salts were added and by increasing salt concentration, settling time decreased.

C. Influence of Viscosity

In the experiments on varying viscosity, the concentration of NaCl and Na_2SO_4 were fixed at 100 mmol/L of water. Both volume phase ratios (o/a) of 1/2 and 2/1 were studied. The viscosity of the aqueous phase for each system is shown in Table I.

TABLE I
THE VISCOSITY OF AQUEOUS PHASE FOR EACH SYSTEM

c_{NaCl}[a]	c_{Na2SO4}[a]	$c_{PEG4000}$[b]	Viscosity[c]
-	100	5	1.99
-	100	20	9.16
-	100	35	36.84
-	100	50	120.03
100	-	5	1.63
100	-	20	7.76
100	-	35	27.21
100	-	50	106.13

[a]Concentration is in unit mmol/L of aqueous phase, [b]concentration is in unit %wt. of aqueous phase, [c]viscosity is in unit mPa·s

The coalescence and sedimentation curve for the volume phase ratio (o/a) of 1/2 are shown in Fig. 6. The results from both salts show the same behavior where the organic phase (toluene) is dispersed in the aqueous phase (water + PEG4000 + salt) and an increase of the viscosity leads to higher settling times. This behavior can be explained by previous equations. Especially the Archimedes number (1) depends on the physical properties of the system, therefore by increasing the concentration of PEG4000 the physical properties and consequently the settling time of the system change.

The comparison of the results of NaCl and Na_2SO_4 at 35% and 50% PEG4000 by weight, the settling behavior of both salts is the same and the settling times were similar. Therefore, it can be concluded that NaCl and Na_2SO_4 have a small effect on the settling time for systems of higher viscosity.

Fig. 7 shows the influence of viscosity on the settling curve of the toluene-water system for both investigated salts for the volume phase ratio (o/a) of 2/1. The results from both cases show a similar effect, that the settling time increases when 5%wt. and 20%wt. PEG4000 are added to system. The velocity of the droplets decreases as the viscosity increases (see Eq. 2), therefore a longer settling time is required. In the case of 35%wt. and 50%wt. PEG4000, the organic phase changed to be the continuous phase whereas the aqueous phase became the disperse phase. Moreover, the addition of 35%wt. and 50%wt. PEG4000 in aqueous phase caused a decrease in the settling time.

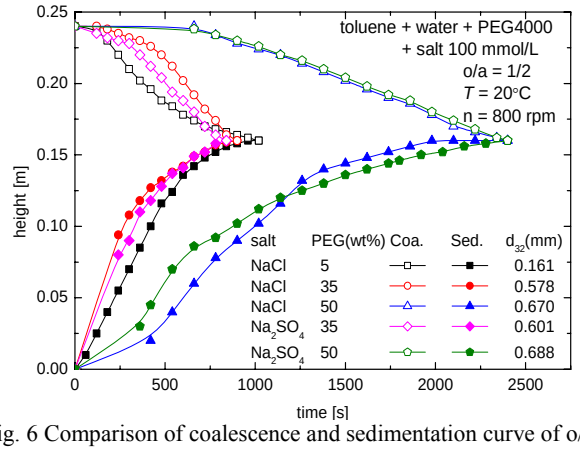


Fig. 6 Comparison of coalescence and sedimentation curve of o/a = 1/2 at different concentrations of PEG4000 and 100 mmol/L NaCl and Na_2SO_4

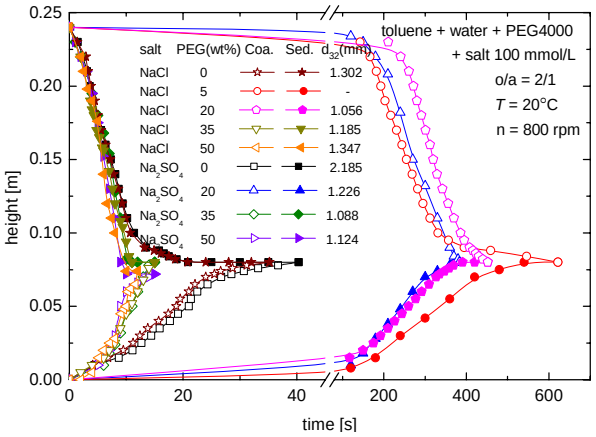


Fig. 7 Comparison coalescence and sedimentation curve of o/a = 2/1 at different concentrations of PEG4000 and 100 mmol/L NaCl and Na_2SO_4

In addition, it can be concluded from the results that the electrolytes had essentially no effect on the settling time in viscous systems.

IV. Conclusion

The results show that the volume phase ratio (between organic and aqueous phase) and the system's viscosity affect the settling behavior and the settling time of the system toluene + water. The settling time depends on the investigated system. Moreover, the influence of electrolytes on settling behavior was only little depended on the type of salt since both salts showed similar behavior in the toluene + water system. However, a major criterion is the investigated system. Lastly, the investigation of the influence of viscosity on the settling time showed that increasing the viscosity results in the increase of the settling time. In addition, 100 mmol/L of both salts had no influence on settling time and settling behavior in the viscous system.

Greek letters

ε	volume fraction of dispersed phase
η	viscosity, Pa·s
ξ	defined by (2)
ρ	density, kg/m^3
σ	interfacial tension, N/m
τ	coalescence time, s
Δ	difference

Nomenclature

Ar	Archimedes number
c_w	friction coefficient
d_{32}	Sauter diameter, m
h	height, m
H	Hamaker coefficient, N·m
K_{HR}	Hadamard–Rybczynski factor
q	defined by (4) and (5)
r	radius, m
Re	Reynolds number
t	time, s
v	velocity, m/s

Subscripts

0	initial value (after mixing is stopped)
∞	in infinite extended fluid
aq	aqueous phase
c	continuous phase
d	dispersed phase
E	end
i	at the interface
p	dense-packed zone
s	sedimentation
vdW	van der Waals

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