O-A8

The comparison of stability among three types of emulsions in the emulsion liquid membrane separation processes

Hongjing Liu [a], Gaohong He* [a] and Guohua Chen [b]

[a] R&D Center of Membrane Sci. & Tech., Dalian University of Technology, Dalian 116012, China

[b] Dept. of Chem. Eng., The Hong Kong University of Sci. and Tech., Clear Water Bay, Kowloon, Hong Kong

1 Introduction

Since emulsion liquid membrane (ELM) was found by Li in the late 1960s[1], a great amount of work has been conducted on the research and application of ELM[2~8].

Generally, during a process of ELM separation, three types of emulsions will be shown in turn. They are primary emulsion, multiple emulsion, namely ELM, and recovered emulsion respectively. Those three types of emulsions inevitably share some common properties, and at the same time, because those three types of emulsions emerge in different stages of ELM separation, some differences will be observed. Hitherto, no paper reporting the differences and commons in the stability of those three types of emulsions in the process of ELM separation was found.

In this paper, attention has been focused on the stability of those three types of emulsions respectively in the W/O/W ELM system, and some commons and differences among them were studied. Four kinds of solvents were used to produce every emulsion respectively where different oil phases have different impacts on the stability of primary emulsion.

2 Materials and methods

2.1 Material

n-heptane, hexahydrobenzene, methylbenzene, o-xylene(Shenyang Reagent Factory), were chosen as oil solvent of the W/O/W multiple emulsion. The surfactant, Span-80(Dalian University of Technology Chemical Factory), was used to stabilize the W/O/W globule. $Ni(NO_3)_2$ (Tianjin Reagent Factory) was used as a tracer to detect the breakage of emulsion.

2.2 Method

The stability of primary emulsion was evaluated by its viscosity. Measurements were carried out at 25°C with a capillary viscosimeter. Breakage of multiple emulsion and recovered emulsion was measured as a function of time by using a tracer. $Ni(NO_3)_2$ was a tracer existed in the internal phase. Spectrophotometer 721(Shanghai China Analytical Instrusment Deneral Factory) was used to analyze the concentration of Ni^{2+} in the external phase according to GB-11910-89. The state of natural demulsification was observed by a Olympus BX50 microscope (Olympus Corporation) equipped with camera.

3 Results and discussion

3.1 Effect of water volume on viscosity of emulsion

The resistance to flow is one of importance property of emulsion. Emulsion with required viscosity will keep it stability, which had been explained by the rheological study. So the change in emulsion viscosity will reveal the extension of stability of primary emulsion. It is necessary to define the relative viscosity, that is to say, relative viscosity is the ratio between emulsion viscosity and membrane solvent viscosity.

Figure1 shows the change of viscosity emulsion with time. The samples of Figure1 was gotten from the upside emulsion of gauging-tank.Figure1 shows that viscosit y was incline to decrease with time. What cause these trends? Figure2 gives reasons for it. Figure2 shows the change in density of upside emulsion with time, becoming low with time, and at the same time, the concentration of oil was increasing. Since primary emulsion was put staticly in the gauging-tank, it was inevitable that creaming would happen, that is to say, disperse phase upside of gauging-tank was less than that of the downside emulsion of gauging-tank, which indicates that the decrease of water volume faction is the result of the decrease of emulsion density. Therefore, the decrease of water-volume faction brings about the decrease of viscosity. So the change of viscosity embodies that the stability become bad. It should be pointed out that the change of viscosity in Figure3 is interesting, who comes from the downside of gauging-tank. In Figure3, the viscosity increases first with time due to the increase of water volume faction.

---

* Corresponding author. Tel (086)-411-84016845, Email: hgaohong@dlut.edu.cn

However, after it attained some higher value, the viscosity began to decrease rapidly. Ostwald had proposed that the volume of disperse phase is not more than 0.74, otherwise inversion will happen. He thought that viscosity of emulsion will increase with the increase of volume faction and there is a dramatic reduction in viscosity of W/O emulsion when volume faction is beyond 74%. In this paper, the reason for decrease of viscosity after attained the highest viscosity value is not because of inversion, but demulification, which can be observed by visualization. Figure 4 (a~d) displays the demulsificating state of n-heptane emulsion. Figure 4 (a~b) shows a network structure, where continuous phase forms a net path and some big water bodies form net caves. There are a lot of water globules in net path, furthermore, more and more water droplets will gather together, which cause flocculation and coalescence with time. According to c and d, much bigger body has formed and less water globules has existed in the net path, which note that the demulsification process is near to finish, and during this period, the viscosity of primary emulsion has been decreasing all the time.

3.2 The stability of different primary emulsions

From Figure3, we also know that primary emulsions with the different oil solvents had different lifetime. The time lasted before most emulsion was demulsificated was shown at Table1. Hexahyddrobenzene emulsion kept stability longer, then n-heptane, methylbenzene, and o-xylene.

Volume faction of the highest viscosity was calculated through Hatschek equation amended (equation 1) , and the result is shown at Table1.

$$\eta_r = \eta_0 \left[\frac{1}{(1 - (h\phi)^{1/3})} \right] \qquad (1)$$

where η is viscosity of emulsion, η_0 is viscosity of continuous phase, Φ is volume faction of internal phase, and h is volume factor. h is near 1.3. η_r is called relative viscosity, whose value is η/η_0. The values of volume faction were all near 0.75, shown in the Table1, which seemed the water volume factions of four primary emulsions were similar when attained the highest viscosity value.

3.3 Breakage of W/O/W emulsion and recovered emulsion

Breakage of ELM is one of calibrations to describe the degree of stability of ELM. The breakage of emulsion was defined as follows:

$$\varepsilon = \frac{CeVe}{C_0V_0} \times 100\% \qquad (2)$$

where Ce is concentration of Ni^{2+} in external phase, Ve is volume of external phase, C_0 is original concentration of Ni^{2+} in internal phase, V_0 is original volume of Ni^{2+} in internal phase.

The breakage ratios of four different oil phase ELM under the stirring are shown in Figure5. The degree of rupturing from good to bad is hexahydrobenzene, n-heptane, o-xylene, and methylbenzene. The breakage trend of hexahydrobenzene was unstable, and the possible reason is that hexahydrobenzene is more sensitive to the behavior of stirring. The result of experiment tells us that the trend of stability of primary emulsion does not always agree with that of multiple emulsion compared with table1. Although the primary of hexahydrobenzene and n-heptane can last more time without demulsification, they can not keep their stability very well under the action of shearing. On the contrary, o-xylene and methylbenzene have more stability under the action of shearing. So from the viewpoint of breakage, o-xylene and methylbenzene are better oil solvent than hexahydrobenzene and n-heptane in ELM separation.

After 5 minutes' stirring, no other components permeated into the internal phase except water. Putting the recovered emulsion as well as external phase into the gauging-tank, every one hour the concentration of Ni^{2+} in external water phase was analyzed. The result is shown at Figure6. The sequence of breakage from good to bad is n-heptane, methylbenzene, o-xylene and hexahydrobenzene. This result does not keep accordance with the breakage of ELM. Among different ELM systems o-xylene has the smallest value of breakage. But it seems that the stability of hexahydrobenzene recovering emulsion resumes its best stability without the action of stirring, that is to say, hexahydrobenzene emulsion is more sensitive to the behavior of stirring than other emulsion membrane systems which will limit the application of hexahydrobenzene.

3.4 Swelling of emulsion

After 30ml primary emulsion was stirred for 10 minutes in the external phase, the volume of emulsion was changed. As shown in Table1, the phenomenon of the increase in the volume of emulsion is called swelling. The swelling ratio is defined by the recovered emulsion volume to primary emulsion volume. The swelling ratio calculated is shown in the Table1. It should be noted that two main kinds of cases cause the swelling of emulsion. One is osmotic swelling behavior due to the transfer of water from the external aqueous phase to the internal water droplet. Besides osmotic swelling, there is another swelling process-entrainment swelling because of the entrainment and emulsification of external aqueous phase in the emulsion globules. There is no doubt that the volume increase of multiple emulsion will affect the property of recovered emulsion, and make it difficult reuse. The higher swelling ratio is, the more unstable the emulsion liquid membrane is. So the value of stability of emulsion liquid membrane according to the swelling ratio from high to low is methylbenzene, o-xylene, n-heptane and hexahydrobenzene.

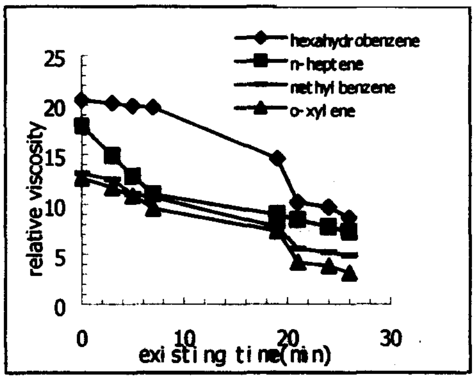


Figure1 Relative viscosity of upside emulsion vs existing time

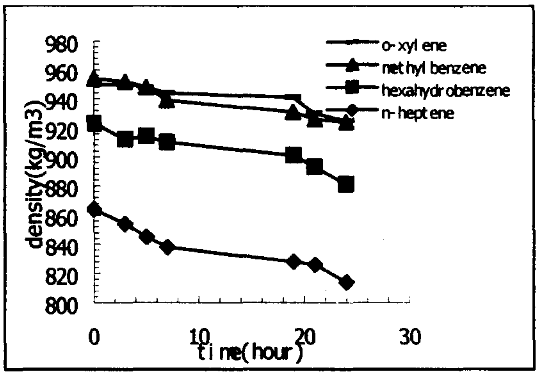


Figure2 The density change of upside emulsion vs time

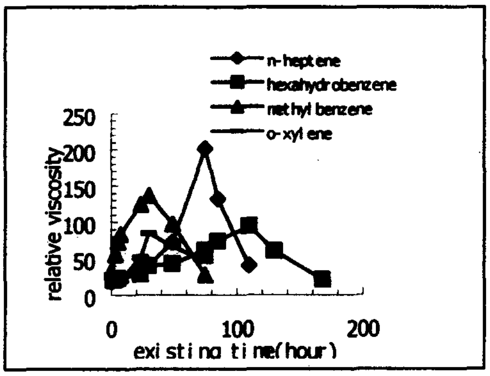
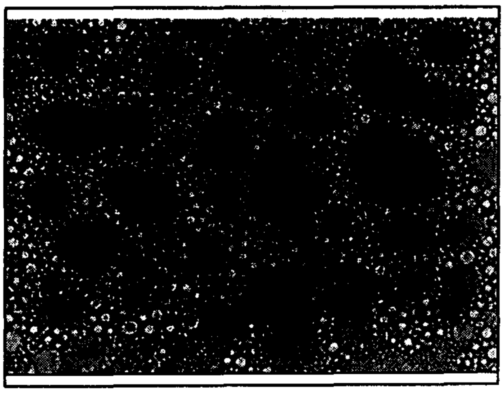


Figure3 Relative viscosity of downside emulsion vs existing time

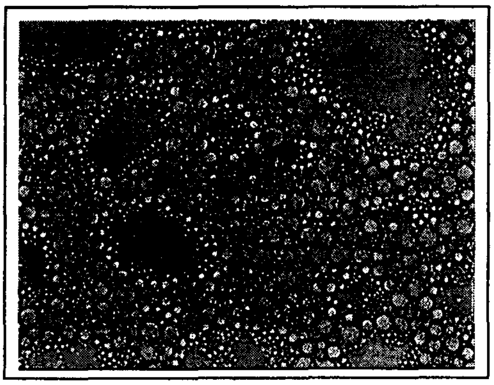
emulsion	hexahydrobenzene	n-heptane	methylbenzene	o-xylene
time(day)	4	3	1	1
volume faction	0.754	0.757	0.752	0.742
Volume (ml)	37	39	45	43
swelling ratio	1.23	1.3	1.5	1.43

Table1 The relative properties of four series primary emulsion

a



b



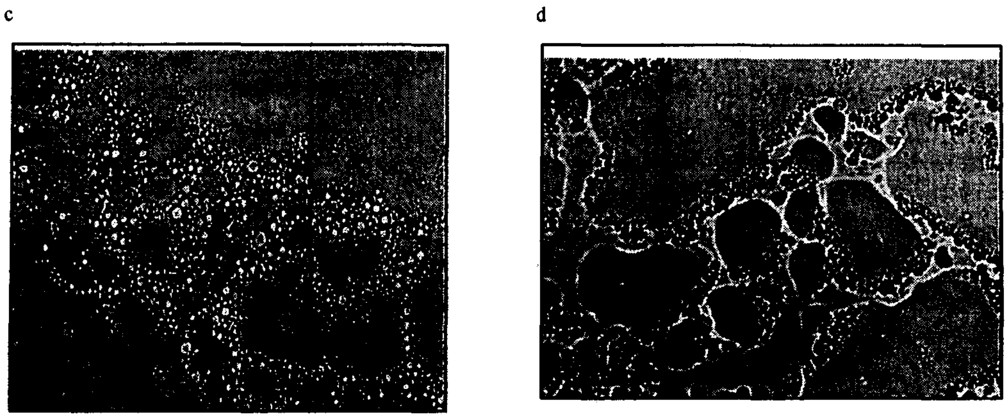
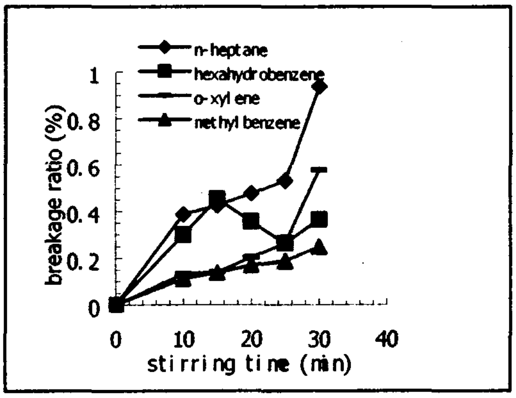


Figure4 (a~d) The process of demulsification of primary emulsion with n-heptane oil solvent



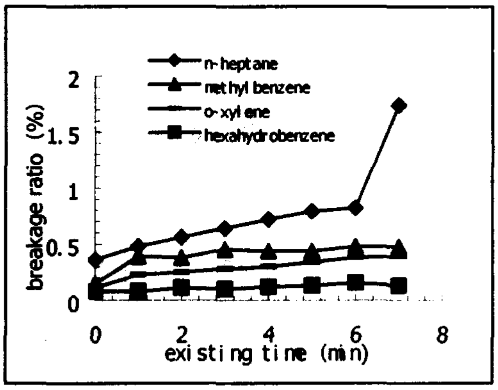


Figure5 The breakage ratio of four different oil phase emulsions vs the stirring time

Figure6 The breakage ratio of recovered emulsion vs existing time

Conclusions

Primary emulsions, multiple emulsions and recovered emulsions prepared by n-heptane, hexahydrobenzene, methylbenzene and o-xylene respectively, have different stability sequence. The results above reveal some facts as follows: On the one hand, water volume faction will induce the change of viscosity of emulsion. On the other hand high stability of primary emulsion can not surely promise high stability of multiple emulsion, namely, the stable trend of primary, multiple emulsion and recovered emulsion can not always keep consistent.

ACKNOWLEDGMENT

The financial support from the National Natural Science Foundation of China, grant #20006001, is greatly appreciated.

Reference

1. N.N.Li, US Patent 3,410,794 (1968).
2. A.K.Chakravarti, S.B. Chowdhury, D.C. Mukherjee. "Liquid membrane multiple emulsion process of separation of copper(II) from waste water." Colloid and Surfaces 166 (2000) 7-25.
3. Prashant S. Kulkarni, Krishnakant K Tiwori and Vijaykumar V mahajan. "Membrane stability and enrichment of nickel in the liquid emulsion membrane process." J Chem Technol Biotechnol 75 (2000) 553-560.
4. T. M. S. Chang, "Liguid-Membrane-Encapsulated Enzymes," Biomedical Applictions of Immobilized Enzymes and Proteins, 1 (1977) 171.
5. F. Bonina, S. Bader, L. Montenegro, C. Scrofani, M. Visca, Three phase emulsions for controlled delivery in the cosmetic field, Int. J. Cosmet. Sci. 14 (1992) 65-74.
6. N.S. Tokgoz, A. Fructus, P. Prognon, M. Seiller, J.L. Grossiord, Incorporation of the L-ascorbic acid and the N-acetyl L-cysteine in the inner aqueous phase of a W/O/W multiple emulsion: stability, characterization and aging studies, in: Proceedings of the !st Word Meeting APGI/APV, Budapest, (1995),. 666-667.
7. S. Matsumoto, W/O/W multiple emulsion with a view to possible food applications, J.Text. Stud. 17(1986) 141-159.
8. B. De Cindio, G. Grasso, D. Cacace, Water-in-oil-in-water double emulsions for food applications: yield analysis and rheological properties, Food Hydrocolloids 4(1991) 339-352.