



Fuel Processing Technology 86 (2005) 499–508

FUEL
PROCESSING
TECHNOLOGY

www.elsevier.com/locate/fuproc

An experimental study of stability of oil–water emulsion

Gonglun Chen, Daniel Tao*

Department of Mining Engineering, University of Kentucky, 234E MMRB, Lexington, KY 40506, USA

Received 31 August 2003; accepted 31 March 2004

Abstract

There has been much interest in alternative fuels made from coal which is much more abundant than oil. The coal–oil–water slurry is a new type of oil-based synfuel composed of finely pulverized coal, oil and water. It has lower viscosity, lower ignition point and higher heating value than coal–water slurry. The preparation of stable water-in-oil (W/O) emulsion is critical for the success of production of stable coal–oil–water slurry. The present study was undertaken to experimentally investigate the effects of different process variables on emulsion stability. The emulsion was prepared using 100 ml colloid mill with sorbitan monooleate (SM) as emulsifier. The variables studied include emulsifier dosage, ratio of oil to water, stirring intensity, emulsifying temperature and mixing time. The results showed that the optimum process conditions are: emulsifier dosage, 0.5%; oil to water ratio, 1:1; stirring intensity, 2500 rpm; and mixing temperature, 30 °C.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Emulsion; Emulsifiers; Coal–oil–water slurry; Stability; Surfactants

1. Introduction

An emulsion is defined as two immiscible liquids wherein droplets of one phase (the dispersed or internal phase) are encapsulated within sheets of another phase (the

* Corresponding author. Tel.: +1 859 257 2953; fax: +1 859 323 1962.

E-mail address: dtao@engr.uky.edu (D. Tao).



HERON_0021025

continuous or external phase) [1]. There are two basic forms of emulsion. The first is the oil-in-water (O/W) emulsion in which oil droplets are dispersed and encapsulated within the water column. The second is the water-in-oil (W/O) emulsion in which droplets of water are dispersed and encapsulated within the oil. For either type of stable emulsion to form, three basic conditions must be met:

- (1) the two liquids must be immiscible or mutually insoluble in each other;
- (2) sufficient agitation must be applied to disperse one liquid into the other; and
- (3) an emulsifying agent or a combination of emulsifiers must be present.

Emulsions have found numerous applications in foods, cosmetics, medicine, paints, hydraulic fluids, asphalt, polymerization, printing, fiber production, metal processing, wood processing, etc. [2–4].

Coal is the major energy source for the world. Fine coal slurry is a promising alternative fuel that may replace oil in some cases. However, the thermal energy per unit volume of coal slurry is low compared to oil. Moreover, burner nozzles and boilers have to be modified if oil is substituted with coal slurry, which has hindered commercialization of the technology. One of the most important tasks in developing coal slurry as the alternative fuel is to improve the combustion efficiency and reduce the environmental pollution. A new type of oil-based synfuel composed of finely pulverized coal, oil and water offers several advantages including lower viscosity, lower ignition point, higher heating value, higher combustion efficiency and lower particulate soot formation than coal–water slurry.

Coal–water slurries have been developed over the last 15 years as an alternative to fuel oil mainly in industry and power station boilers. Numerous processes are available for preparation of stable coal–water slurry. However, the technology for producing stable coal–oil–water slurry is much less sophisticated [5]. The effects of surfactants of different chain lengths have been investigated by Ghaicha et al. [6]. The consensus among most investigators is that prolonging the agitation beyond an optimum time does little to improve the quality of the emulsions, and the optimal time varies with different emulsion [7].

Given the ingredients of an emulsion and the emulsifying machine, the most significant parameter that can be varied to produce different emulsions is the stirring intensity. More efficient agitation gives better emulsion. Emulsion formation in simple mixers has been the subject of many detailed studies [8]. It has been found that the interfacial area increases with increasing rotational speed and diameter of the stirrer and with decreasing diameter of the container tank.

Temperature often has indirect effects on emulsification as a result of altering the interfacial tension, adsorption of emulsifier and viscosity. Because both viscosity and interfacial tension decrease with the increase in temperature, higher temperature is favorable for emulsification. There is also some evidence that a sharp increase or decrease of temperature tends to coagulate the particles, thereby causing the deterioration of emulsions. In recent years, considerable attention has been given by chemical engineers to the determination of the optimum emulsifying temperature for different emulsifiers.

The emulsifying agent may be any surface-active substance which can form a thin interfacial film between the two liquids and maintain the emulsion by minimizing the

contact, coalescence and aggregation of the internal dispersed phase. The surfactant should surround the dispersed droplet as a nonadhering film. In water-in-oil emulsions, asphaltene, resins and paraffin waxes act as natural emulsifying agents stabilizing W/O mixture [9]. Presumably, these agents provide the required film around the water droplets which resists rupture, thus preventing water–water coalescence [10]. Jerzy and Bengt [11] pointed out that emulsion stability is dependent on the structure of the surfactant. An effective testing procedure of water-in-oil emulsion stability was investigated by Fingas et al. [12]. Their work shows that viscosity provides a more reliable measure of emulsion stability but that water content measurement is more convenient. Fingas et al. [12] also researched the effect of shaking time and water-to-oil ratio on emulsification. They concluded that shaking times longer than 2 h adversely affect the emulsion stability. Emulsifier loses effectiveness with the increased dilution of higher water-to-oil ratio values. Surfactant dosage and the ratio of oil-to-water are important factors influencing the stability of emulsions. However, the effects of these factors strongly depend on the ingredients of the specific emulsion.

The preparation of stable water-in-oil emulsion is essential for the production of stable coal–oil–water slurry. The effects of several process variables on the stability of oil-in-water emulsion were studied in the present work. The variables included emulsifier dosage, ratio of oil to water, stirring intensity, emulsifying temperature and mixing time, etc.

2. Experimental

The emulsifier used in the experiments was sorbitan monooleate (SM) acquired from Sigma-Aldrich, USA. The oil employed was a commercial diesel in China, which does not freeze at $-10\text{ }^{\circ}\text{C}$. Predetermined amounts of oil and emulsifier were introduced to a 100-ml colloid mill. All the measurements were made under the following conditions unless otherwise specified: the ratio of oil to water was 1:1 by volume; the stirring intensity, 2500 rpm; the mixing time, 15 min; the emulsifying temperature, $25\text{ }^{\circ}\text{C}$; pH value 6.0. The stability of the emulsion may be characterized by monitoring the droplet size distribution with the NMR self-diffusion method [13]. However, in the present study, the stability was characterized by the relative volume of emulsion defined as the ratio of emulsion volume to the total volume of water, oil and surfactant used to prepare the emulsion 24 h after preparation of the emulsion. The higher ratio indicates the greater stability [14].

3. Results and discussion

The most important task in preparation of emulsions is the selection of suitable surfactant which will satisfactorily emulsify the chosen ingredients at a given temperature. It has long been recognized that with a homologous series of surfactants, there is a range in which the polarity of the molecule, i.e., the relation between the contributions of the polar hydrophilic head and the nonpolar lipophilic tail, is optimal for a specific emulsion. Griffin [15] introduced a semiempirical procedure for selecting an appropriate emulsifier or blend

of emulsifiers to prepare an emulsion. The concept on which this procedure is based, the hydrophile–lipophile balance (HLB), is that the molecule of any emulsifier, or indeed of any surface-active material, contains both hydrophobic and hydrophilic groups, and the ratio of their respective weight percentages should influence emulsification behavior. A W/O emulsifier will have a low HLB, a solubilizing agent has a high HLB and an O/W emulsifier has an intermediate value [16]. It is well known that the emulsification is the best when the emulsifier and the emulsified material have the same HLB value [17]. Sorbitan monooleate was used as the emulsifier because its HLB is very close to the diesel's.

The stability of a W/O emulsion is defined as the resistance by the dispersed water droplets against coalescence. It is dependent on a variety of factors including the presence or absence of the emulsifying agent, viscosity (influenced greatly by temperature), specific gravity, water content and the age of the emulsion.

3.1. Effect of emulsifier dosage

Surfactant dosage is one of the most important factors influencing the stability of emulsions. Several investigations have demonstrated that emulsifier concentration can strongly influence emulsion stability [18]. It was observed that there existed a concentration window, out of which the stability quickly deteriorated. Fig. 1 shows that the relative volume of emulsion increased as surfactant concentration increased from 0.25% to 0.50%. As the concentration increased further, emulsion stability decreased. This is because at low surfactant concentrations, the emulsion is not stable due to agglomeration of the oil droplets; at high surfactant concentrations, the emulsion destabilization occurs as a result of rapid coalescence. The optimal sorbitan monooleate dosage for the emulsion system was 0.5%. The emulsifier dosage was thus determined to be 0.5% for the following experiments.

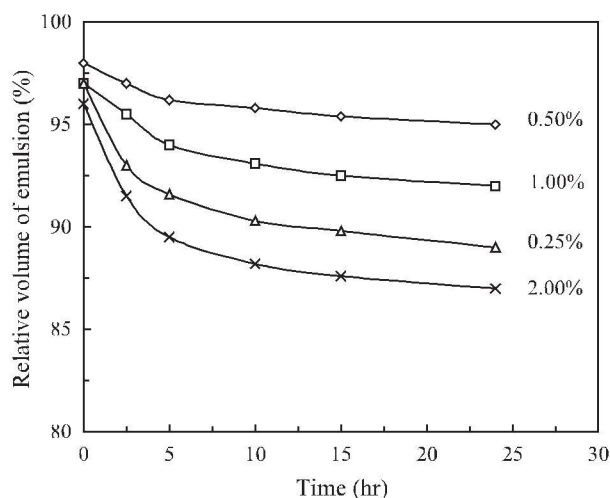


Fig. 1. Effect of sorbitan monooleate dosage on emulsification.

3.2. Effect of oil/water ratio

It has been reported that emulsion type is dependent on the relative phase volume. Ostwald [19] concluded that at a phase volume $\phi > 0.74$, the emulsion would be packed more densely than was possible. This means that any attempt to exceed a phase volume of 0.74 for the internal phase must result in either inversion or breaking.

Fig. 2 shows the effect of volume ratio of oil to water on emulsion stability at the sorbitan monooleate dosage of 0.5%. When the ratio of oil to water was reduced progressively from 9:1 to 5:5, the relative volume of emulsion was increased consistently. After 24 h, the relative volume of emulsion was 19.6% at the ratio of 9:1. The relative volume of emulsion was 29%, 60% and 84%, respectively, as the ratio of oil to water was reduced to 8:2, 7:3 and 6:4, respectively. When the ratio was 5:5, the relative volume was 97%. At this ratio, the relative volume was essentially constant over a period of 24 h, indicating that the emulsion was very stable.

3.3. Effect of stirring intensity

There are many different ways of preparing emulsions of two liquids that are insoluble or possess only slight mutual solubility. Emulsification is usually achieved by the application of mechanical energy. Initially, the interface between the two phases is deformed to such an extent that large droplets are formed, and these large droplets are subsequently broken up into smaller ones.

During emulsification, the interfacial area between two liquids increases. Liquids tend to minimize this surface area; therefore, mechanical energy is required for emulsification to proceed. It was reported that increasing local dissipation of energy in breaking zone due to the rise of circulation consumption through mixer zone is found to be the most effective

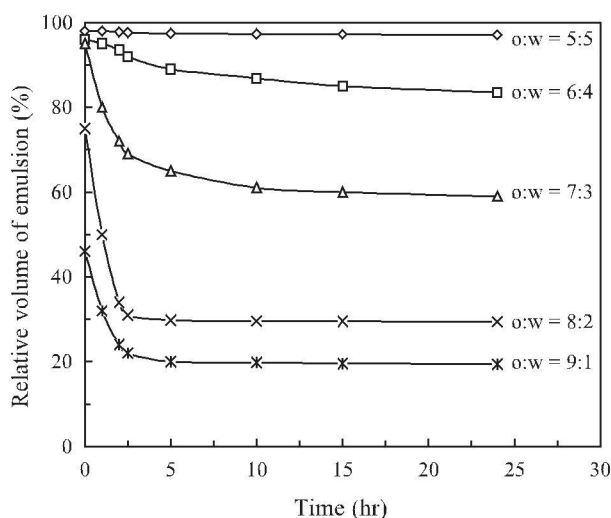


Fig. 2. Effect of oil/water ratio on emulsification.

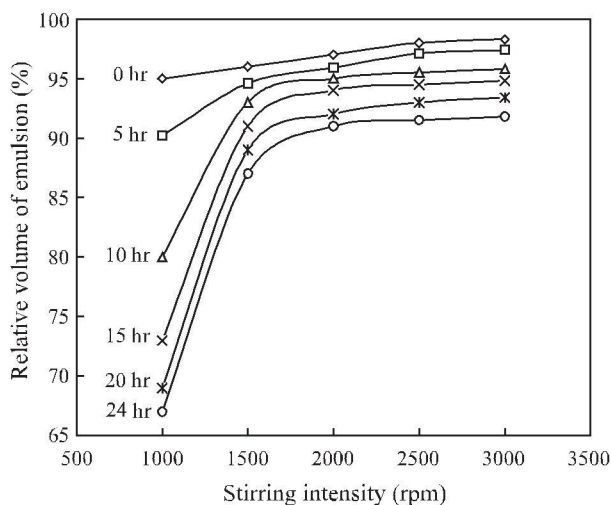


Fig. 3. Effect of stirring intensity on emulsification.

method of drops diameter decrease [20]. The purpose of stirring is to form a stable and homogeneous emulsion by breaking large liquid drops into smaller drops. Fig. 3 shows the relative volume of emulsion as a function of stirring intensity after stirring the mixture for 15 min. The relative volume of emulsion prepared using 1000 rpm stirring speed decreased sharply with time, indicating that a 1000 rpm was not sufficient for this emulsion system. To better show the dependence of emulsion stability on stirring speed, the relative emulsion volume after 15-min stirring followed by 24-h resting is plotted against time in Fig. 4, which clearly indicates that a more stable emulsion was achieved with higher stirring speed. A stirring speed higher than 2500 rpm was, however, not

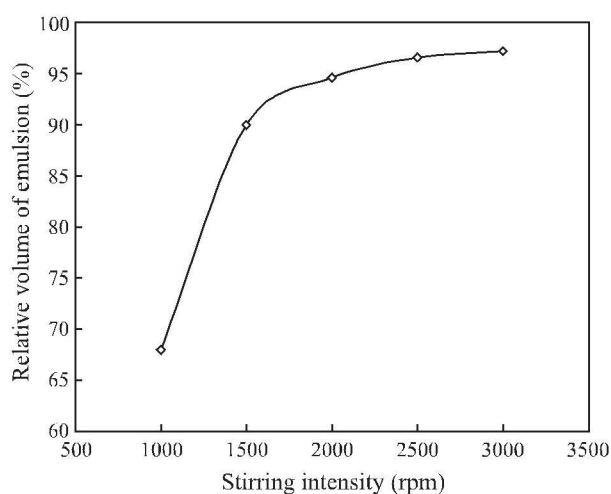


Fig. 4. The relationship between stirring intensity and relative emulsion volume after 24 h.

required because higher stirring speed will lead the emulsifier to break away from the oil–water interface.

3.4. Effect of mixing temperature

To investigate the effect of temperature on the emulsion stability, the relative emulsion volume was determined at temperatures ranging from 30 to 70 °C. The mixture was stirred for 15 min at different temperatures, with increments of 10 °C. The results of relative emulsion volume vs. time are shown in Fig. 5. Fig. 6 shows the emulsion stability of emulsions prepared at different mixing temperatures after 24-h resting. Obviously, the emulsion was more stable at lower temperature, and the most stable emulsion was generated at 30 °C. It is well known that the surface tension of most liquids decreases with increasing temperature. The increased kinetic energy imparted to the surface molecules at higher temperature will tend to overcome the net attractive force of the bulk liquid. Furthermore, as the temperature of the liquid approaches the critical value, the cohesive force between the molecules approaches zero. It is expected, therefore, that the surface tension will vanish at the critical temperature. This is well shown in Eotvos's equation [21]:

$$\gamma(Mv)^{\frac{2}{3}} = \kappa(T_c - T) \quad (1)$$

where γ is the surface free energy, M the molecular weight, v the specific volume, T_c the critical temperature of the liquid, T the temperature, and κ is a universal constant, which is approximately 2.2 for a large number of liquids. Usually, both viscosity and interfacial tension decrease with increasing temperature; any increase in temperature usually makes emulsification easier. However, an abnormal increase of temperature is to be avoided because it tends to coagulate the particles, thereby causing a deterioration of the emulsions. The interfacial adsorption of the emulsifier is adversely affected to some extent by increasing temperature. The surfactant which is loosely adsorbed on the oil–

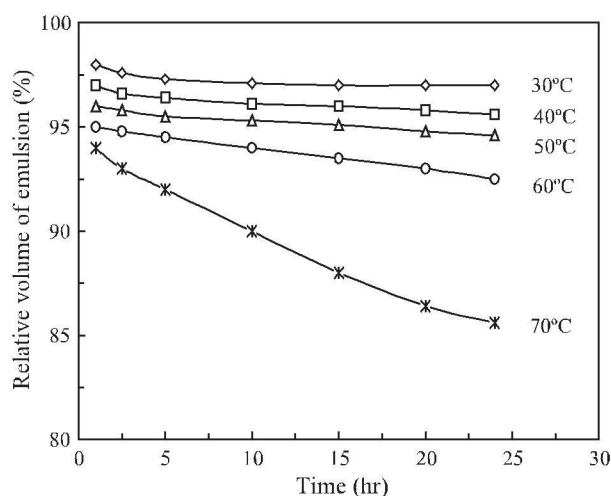


Fig. 5. Effect of mixing temperature on emulsification.

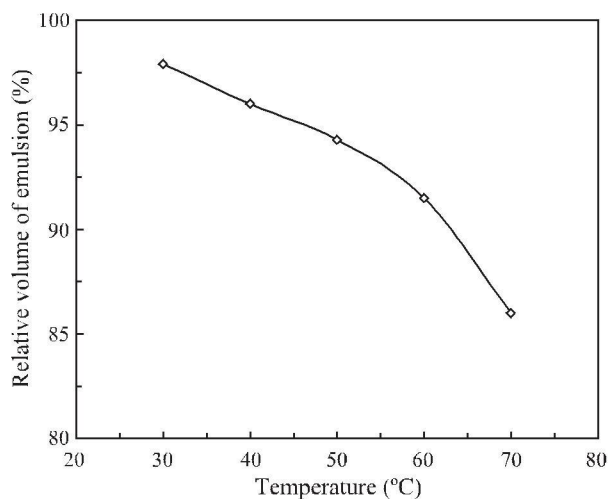


Fig. 6. The relationship between mixing temperature and emulsification after 24 h.

water interface will separate out from the emulsion. This will increase the probability of collision and coalescence, thus destabilizing water-in-oil emulsions [22]. It can be seen that the optimum emulsifying temperature is 30 °C when sorbitan monooleate is used as the emulsifier.

3.5. Effect of mixing time

The mixing time is another important factor for emulsification. Verbich et al. [23] reported that the radii of the droplets in the emulsion decreased with increasing stirring

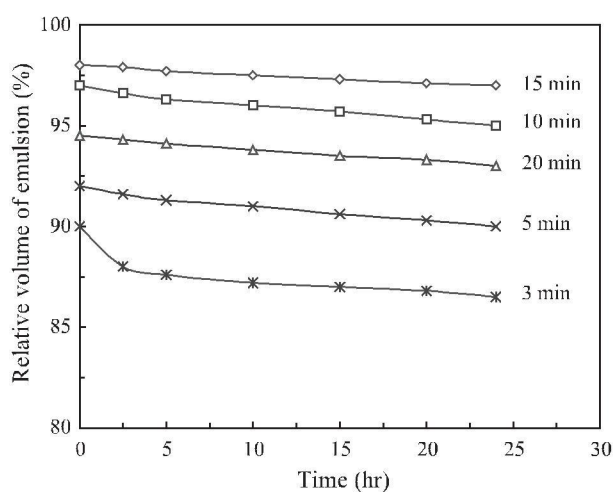


Fig. 7. Effect of mixing time on emulsification.

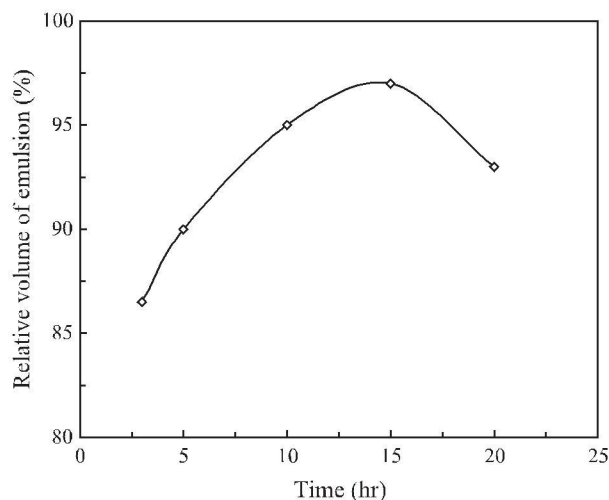


Fig. 8. The relationship between mixing time and relative volume of emulsion after 24 h.

speed and emulsifying time. The emulsifier becomes more effective with increased mixing time. However, if the mixing time is too long, the effectiveness of emulsifier will be decreased because the intense stirring will cause the emulsifier to drop out from the oil–water interface. Fig. 7 shows the relative volume of emulsion increased as mixing time increased from 3 to 15 min. As the mixing time increased further, emulsion stability decreased. This experiment also shows that the mean size of the particles decreased very rapidly in the first few seconds and then gradually attained the limiting value after 15 min. To better show the dependence of emulsion stability on mixing time, the relative emulsion volume after 24 h is plotted against mixing time in Fig. 8, which clearly indicates that the optimum mixing time is 15 min.

4. Conclusions

- 1) A stable O/W emulsion was produced using the diesel as the oil and sorbitan monooleate as the emulsifier. The optimal emulsifier dosage was 0.5% by volume. At lower emulsifier dosages, the emulsion was unstable; the instability at higher emulsifier dosages was a result of rapid coalescence and concentration.
- 2) The emulsion stability increased with decreasing oil-to-water ratio. The optimum ratio was 1:1 by volume.
- 3) Higher stirring intensity resulted in more stable emulsion. The optimum stirring intensity was 2500 rpm for the emulsion system investigated.
- 4) High temperature reduced emulsion stability, and the optimum emulsifying temperature was 30 °C.
- 5) Emulsion stability increased with stirring time up to 15 min, beyond which the stability decreased with further increase in stirring time due to the drop-out of emulsifier from oil–water interface.

References

- [1] R.P. James, R.P. Charles, *Petroleum Spills* (1985) 3.
- [2] U. Stiegler, *Nuclear Instruments and Methods in Physics Research. Section A, Accelerators, Spectrometers, Detectors and Associated Equipment* 454 (1) (2000) 197–200.
- [3] H.G. Saunders, F.A. Kamake, *Forest Products Journal* 46 (3) (1996) 56–62.
- [4] T. Nakashima, M. Shimizu, M. Kukizaki, *Advanced Drug Delivery Reviews* 45 (1) (2000) 47–56.
- [5] P.D. Bergman, *Coal Mining and Processing* 19 (10) (1982) 34–41.
- [6] L. Ghaicha, R.M. Leblanc, F. Villamagna, A.K. Chattopadhyay, *Langmuir* 11 (2) (1995) 585–590.
- [7] J.R. Campanelli, D.G. Cooper, *Canadian Journal of Chemical Engineering* 67 (5) (1989) 851–855.
- [8] C. Washington, *Advanced Drug Delivery Reviews* 20 (2-3) (1996) 131–145.
- [9] N. Zaki, P.C. Schorling, I. Rahimian, *Petroleum Science and Technology* 18 (7) (2000) 945–963.
- [10] G.P. Canvari, *Marine Pollution Bulletin* 13 (1982) 49–54.
- [11] K. Jerzy, K. Bengt, *Colloids and Surfaces* 50 (1990) 131–140.
- [12] M.F. Fingas, B. Fieldhouse, L. Bier, D. Conrod, E. Tennyson, *Author Affiliation: Environmental Technology Cent Source: ASTM Special Technical Publication, 1252, ASTM, Philadelphia, PA, USA, 1994 (Oct 10–11), pp. 41–54.*
- [13] R. Ivanova, B. Balinov, R. Sedev, D. Exerowa, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects* 149 (1) (1999) 23–28.
- [14] X. Li, Z. Chen, H. Li, S. Han, *Chinese Journal of Chemical Engineering* 9 (2) (2001) 200–203.
- [15] W.C. Griffin, *Journal of the Society of Cosmetic Chemists* 1 (1985) 311.
- [16] P. Sherman, *Emulsion Science* (1968) 18–23.
- [17] G. Li, R. Guo, *China Petroleum Industry Press* (1995) 54.
- [18] G. Ostberg, B. Bergenstahl, M. Hulten, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects* 94 (2-3) (1995) 161–171.
- [19] W. Ostwald, *Kolloid-Zeitschrift* 6 (103) (1910) 7.
- [20] C. Graillat, M. Lepais-Masmejean, C. Pichot, *Journal of Dispersion Science and Technology* 11 (5) (1990) 455–477.
- [21] R. Eotvos, *Annalen der Physik* 27 (1886) 448.
- [22] R.P. James, R.P. Charles, *Petroleum Spills* (1985) 3.
- [23] S.V. Verbich, S.S. Dukhin, A. Tarovski, O. Holt, O. Saether, J. Sjoblom, *Colloids and Surfaces. A, Physicochemical and Engineering Aspects* 123–124 (1997) 209–223.