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Removal of Emulsified Crude Oil From Produced Water by Electrophoresis

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ABSTRACT

Emulsified oil droplets in water are surrounded by negative zeta potential, and as a result, they move toward the positive electrode, when an electric potential is applied. This electrophoresis velocity of droplets was measured at various electric potentials, 1.569, 2.61 and 5.23 volts/cm, and various temperatures in the range from 71°F to 116°F. The measured electrophoresis velocity is in the range from 0.4 to 1.6 mm/min, depending upon the electric potential applied.

INTRODUCTION

Electrostatic force has been used for years in dehydration of crude oil, removing emulsified water droplets from crude oil to meet its market requirement [1-3]. The market requires the water content in crude oil to be 0.5 to 1.0% or less. However, to remove emulsified oil droplets in produced water is a new topic, mainly due to the recent environmental regulations.

After lengthy and vigorous mixing of crude oil and produced water in oil production tubings, valves and pumps, a small part of oil is emulsified and suspended in the produced water. Unlike free oil which can be separated from water by a water skimmer and flotation cells, as well as skim pile in some offshore oil wells, emulsified oil becomes small droplets of 1 µm or less in size, and can not be separated by these units. These small oil droplets later become an environmentally troublesome oil film floating on the surface of discharged water.

In the present practices, chemicals are used as coagulants and flocculants to remove emulsified oil droplets from water [4,5]. The process is very effective in most cases. However, there are circumstances where the use of chemicals is not preferred, such as the case when water must be discharged to an environmentally

sensitive wetland. Fired-tube heaters are known to be effective to some extent in breaking water-in-oil and oil-in-water emulsions in the oil field. However, the cost of fuels may be a concern. Therefore, in this work the application of electrophoresis is studied. It is the second physical method, after the conventional fired-tube heating.

ELECTROPHORESIS

Zeta Potential

The surface of oil droplets in oil-in-water emulsions has negative electric potential, though the bulk of emulsion is electrically neutral [4,6,7]. Figure 1 shows this uneven distribution of electric charge distribution. The potential diminishes in the diffuse layer where molecules of continuous phase move in and out freely. This potential at the surface of shear is referred to as zeta potential. The zeta potential of emulsified crude oil droplets is in the range of 10 to 200 mV, depending upon the pH value and temperature [8]. For most emulsions, it is in a narrow range, from 10 to 70 mV. Although this is a weak electric potential, it can cause emulsified oil droplets to respond to an electric field.

Electrophoresis Velocity

The electrophoretic motion of charged emulsified oil droplets or solid particles is presented in various physical or surface chemistry books. Two recent books are by Adamson [7] and Probstein [9]. The velocity of electrophoretic motion is referred to as electrophoresis velocity. When the Debye length of droplets is much smaller than the droplet diameter, the electrophoresis velocity is given by the Helmholtz-Smoluchowski equation [7,9]:

$$v_E = \frac{\epsilon_0 D_E \zeta E}{\mu_E} \quad (1)$$

References and illustrations at end of paper.

The electric potential is the applied electric voltage (V, volts) divided by the distance between electrodes (h, cm):

$$E = \frac{V}{h} \quad (2)$$

Dielectric constants, or relative permittivities, of various substances are given in standard chemistry and chemical engineering handbooks [10], and books by Smyth [11] and von Hippel [12]. Dielectric constant of water at room temperature is 78.5°F. Dielectric constant of water at 140 to 8,100 MHz frequency at temperature T (°C) other than room temperature is given by Wyman [11]:

$$D_o = 78.54[1 - 0.00460(T-25) + 0.0000088(T-25)^2] \quad (3)$$

Dielectric constant of crude oil is believed to be from 2 to 12, depending upon the composition of crude oil, according to the data provided by von Hippel [12].

Dielectric constant of emulsion, D_E , is given by Smyth [11] as follows:

$$D_E = D_o \left[1 + \frac{3\phi(D_1 - D_o)}{D_1 + 2D_o} \right] \quad (4)$$

For Equation (4) to be true, ϕ must be 0.3 or less.

The viscosity of emulsions can be calculated from the following equation [7]:

$$\mu_E = \mu_o \left[1 + 2.5\phi \left(\frac{f + 0.4}{f + 1} \right) \right] \quad (5)$$

In some literatures, permittivity is used in Equation (1), which is the product of ϵ_o and D_E , or $\epsilon_o D_E$. The ratio of electrophoresis velocity to electric potential, is referred to as electrophoresis mobility:

$$u_E = \frac{v_E}{E} = \frac{v_E h}{V} \quad (6)$$

where u_E is electrophoresis mobility in mm·cm/v·s after the units are properly converted.

EXPERIMENTAL MEASUREMENTS

Apparatus

A Particle Electrophoresis Apparatus Mark II, made by Rank Brothers (Cambridge, England) was used to measure the electrophoresis velocity of emulsified oil droplets, at various electric potentials and temperatures. The apparatus consists of (1) microscope with binocular head and gratings for measuring distance; (2) electrophoresis cell; (3) quartz-iodine illuminator; (4) constant temperature bath with a water circulation pump and a heating element; (5) electrodes which can be placed at the ends of the electrophoresis cell; (6) control instrument; (7) DC power supply. Figure 2 shows the schematic diagram of the apparatus.

The electrodes inserted into the electrophoresis cell provide 12, 20 and 40 volts of DC power. The distance between electrodes is 7.65 cm ($h = 7.65$ cm). Therefore, when the power is applied, the electric potentials applying to the cell are 1.569, 2.61 and 5.23 volts/cm, depending upon the voltage of the DC power.

The inside diameter and stationary level (distance from the inner tube-wall surface) of the cell are, respectively, 2.1 and 0.307 mm.

Sample Preparation

A mixture of 50 ml crude oil and 200 ml deionized water were mixed with a Sunbeam kitchen mixer at its maximum speed (1060 rpm) for 5 minutes. It simulated the rapid mixing of oil and water in oil production tubings and transmission pipelines. The resulting mixture was set on the bench for one hour to allow free oil to separate from water by gravity. The bottom layer (water layer) was used as samples. The layer was clear, but contained emulsified oil droplets as shown in Figure 3. The size of droplets varied from 30 μ m to about 1 μ m. Most of them are about 4.0 μ m in diameter.

Experimental Procedures

In each run the electrophoresis cell was filled with sample, and placed in the constant temperature bath, which was maintained at a constant temperature. If the measurement was to be made at the temperature above the room temperature, the sample and the cell were heated either by hot water in the bath or by microwave heating in a domestic microwave oven. After the illuminator was turned on and the focus of microscope was adjusted to observe oil droplets inside the cell at its stationary level, a constant electric voltage (12, 20 or 40 volts) was applied to the sample through electrodes at the ends of the cell.

Oil droplets were found to move. The velocity was measured by reading the distance which an oil droplet traveled in a given length of time. The voltage was reversed in each run to measure the electrophoresis velocity in both directions. In each run, 15 to 20 readings of velocities were taken.

EXPERIMENTAL RESULTS

The experimental results, electrophoresis velocities, electrophoresis mobilities and zeta potentials at various electric potentials and temperatures, are summarized in Tables 1 through 6. In these tables "C" indicates the experimental run with conventional heating (using hot water), while "M" indicates the run with microwave heating.

Table 1 shows electrophoresis velocities of emulsified oil droplets at 12 volts of DC voltage. The velocity varies from 0.4 to 0.545 mm/min. It appears that the effects of temperature and heating method are not significant. The same observation can be made in Tables 2 and 3, which show electrophoresis velocities at 20 and 40 volts, respectively.

Electrophoresis velocity increases, as electric potential increases. From Figure 4, where measured electrophoresis velocities are plotted versus electric potentials, the following empirical equation is obtained:

$$v_E = 0.280 E \quad (7)$$

If the effects of temperature and heating method are neglected, the average values of electrophoresis velocities at 1.569, 2.61 and 5.23 volts/cm of electric potentials are respectively, 0.439, 0.713 and

1.40 mm/min. These velocities are moderate, but enough to provide separation of oil droplets from water.

Based on the experimental data shown in Tables 1, 2, and 3, electrophoresis mobilities and zeta potentials were calculated. The results are shown in Tables 4, 5, and 6, for 12, 20, and 40 volts respectively.

APPLICATIONS

Separation of Emulsified Oil

As demonstrated by the measured data of electrophoresis velocity, emulsified oil droplets have negative zeta potentials, and move toward the anode when electric potential is applied on them. The velocity is not fast, but it is enough to provide the separation of emulsified oil from water. Equations for sizing the separator are shown as follows.

Sizing Separator

When an oil-in-water emulsion is fed to an electric field provided by two parallel plates as shown in Figure 5, oil droplets have horizontal velocity component u due to the flow of emulsion, and vertical velocity component v_E which is electrophoresis velocity. If the distance between two electrodes is h , the retention time of emulsion required for all oil droplets to be separated is given by:

$$t = \frac{h}{v_E} \quad (8)$$

With this length of time, emulsion will travel the distance L . That is:

$$u t = L \quad (9)$$

where u is equal to the volumetric flow rate of emulsion (Q) divided by the flow area (hW).

Combining Equations (8) and (9), the surface area of electrodes (A or LW) is related to the flow rate and electrophoresis velocity by:

$$A_s = \frac{Q}{v_E} \quad (10)$$

Since h is small, a practical design of separator will be a combination of many compartments, as shown in Figure 6. The total flow rate to the separator is nQ , if it has n identical compartments.

Example

Find the size and operating conditions of a separator to remove emulsified crude oil from a stream of 100 gal/min of crude oil-in-water emulsion.

Solution - This separator can be sized as follows:

Operating conditions are:

$$u = 2 \text{ ft/min}$$

$$t = 20 \text{ min}$$

$$E = 2.61 \text{ volts/cm}$$

$$\text{Number of compartments} = 20$$

Dimensions of separator are:

$$h = (0.0713 \text{ cm/min}) (20 \text{ min.}) \quad \text{Eq. (8)}$$

$$= 0.0468 \text{ ft}$$

$$L = (2 \text{ ft/min.}) (20 \text{ min.}) \quad \text{Eq. (9)}$$

$$= 40 \text{ ft}$$

$$\text{Since } u(hW) = \frac{100}{(20)(7.481)}$$

$$W = 7.14 \text{ ft}$$

Voltage required for each compartment is:

$$V = (2.61 \text{ volt/cm}) (1.426 \text{ cm})$$

$$= 3.72 \text{ volts}$$

Total height of separator is:

$$H = (20)(0.0468 \text{ ft}) = 0.936 \text{ ft}$$

Surface area of separator is:

$$A_s = \frac{\left(\frac{100}{7.481}\right)\left(\frac{1}{20}\right)}{(0.0713)(1/100)(3.281)} \quad \text{Eq. (10)}$$

$$= 285.7 \text{ ft}^2$$

Reynolds number of flow is:

$$R_e = \frac{(2 \text{ ft/min})(62.4 \text{ lbm/ft}^3)(0.0935 \text{ ft})}{(60 \text{ sec/min})(1 \text{ cp})(6.72 \times 10^{-4} \text{ lbm/ft} \cdot \text{sec} \cdot \text{cp})}$$

$$= 289 \text{ (Laminar flow)}$$

where 0.0935 ft is the equivalent diameter of each compartment.

CONCLUSIONS

Emulsified crude oil in water can be separated by electrophoresis process. The electrophoresis velocity of emulsified crude oil droplets at various electric potentials and temperatures were measured. The velocity is moderate, but enough to provide the separation of oil, which cannot be separated by the conventional oil separators.

An important variable, diameter of oil droplets, needs a further study. This work prepared its samples at the condition similar to that in the oil production operation. Therefore, the diameter of droplets in these samples used in measurements is believed to be in the range of interest in the oilfield.

NOMENCLATURE

A_s = surface area of separator

f = viscosity of continuous phase divided by that of dispersed phase

E = electric potential, volts/cm

D_E	= dielectric constant
D_O	= dielectric constant of continuous phase (water)
D_1	= dielectric constant of dispersed phase (oil)
h	= distance between electrodes, cm
L	= length of separator
Q	= volumetric flow rate of emulsion to a compartment of separator
T	= temperature, °C
t	= retention time, min
u	= horizontal velocity of oil droplets
u_E	= electrophoresis mobility
V	= electric voltage, volts
\vec{V}	= velocity of oil droplets in separator
v_E	= electrophoresis velocity, mm/min
W	= width of separator
ϵ	= permittivity
ϵ_r	= relative permittivity, or dielectric constant
ϵ_O	= permittivity constant
ζ	= zeta potential, mv
μ_E	= viscosity of emulsion, cp
μ_O	= viscosity of continuous phase (water), cp
ϕ	= volume fraction of dispersed phase (oil)

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Table 1 Electrophoresis Velocity at 12 Volts

Voltage Applied = 12.0 volts (Electric Potential, $E = 1.569$ volts/cm)
 pH = 5.90

Runs	Temp. °F	No. of Data Points	Ave. Electrophoresis Velocity, v_E , mm/min	Range of v_E , mm/min
1C	116.8	15	0.442	0.227-0.604
1M	"	"	0.398	0.222-0.511
7bC	116.0	"	0.402	0.257-0.586
7bM	"	"	0.401	0.301-0.566
3C	103.8	"	0.545	0.320-0.739
3M	"	"	0.518	0.403-0.643
7C	"	"	0.532	0.461-0.635
7M	"	"	0.495	0.352-0.682
15bC	103.5	20	0.391	0.297-0.487
15bM	"	"	0.513	0.348-0.650
9C	97.0	15	0.473	0.355-0.603
9M	"	"	0.502	0.386-0.612
5C	96.0	"	0.385	0.245-0.573
5M	"	"	0.351	0.188-0.452
16bC	"	17	0.388	0.294-0.480
16bM	"	"	0.428	0.313-0.626
11C	71.4	15	0.374	0.348-0.445
11M	"	"	0.370	0.319-0.411

(ave. = 0.439)

Table 2 Electrophoresis Velocity at 20 volts

Voltage Applied = 20 volts (Electric Potential, $E = 2.61$ volts/cm)
 pH = 5.90

Runs	Temp. °F	No. of Data Points	Ave. Electrophoresis Velocity, v_E , mm/min	Range of v_E , mm/min.
2M	117.5	15	0.768	0.616-0.986
2C	116.8	"	0.938	0.608-1.18
8bC	116	20	0.701	0.453-0.942
8bM	"	"	0.630	0.457-0.768
4C	103.8	15	0.866	0.562-1.19
4M	"	"	0.709	0.480-0.968
8C	"	15	0.881	0.741-1.08
8M	"	"	0.727	0.513-0.984
10bC	103.5	20	0.698	0.388-0.912
10bM	"	"	0.629	0.518-0.756
10C	97.0	15	0.770	0.618-0.917
10M	"	"	0.798	0.667-0.980
6C	96.0	15	0.546	0.350-0.774
6M	"	"	0.497	0.264-0.716
12bC	"	15	0.661	0.486-0.779
12bM	"	"	0.793	0.681-0.914
12C	71.4	15	0.639	0.503-0.779
12M	"	"	0.584	0.501-0.753

(ave. = 0.713)

Table 3 Electrophoresis Velocity at 40 Volts

Voltage Applied = 40 volts (Electric Potential, $E = 5.23$ volts/cm)
 pH = 5.90

Runs	Temp. °F	No. of Data Points	Ave. Electrophoresis Velocity, v_E , mm/min	Range of v_E , mm/min.
13C	117.2	14	1.64	1.29-1.89
13M	"	16	1.04	0.812-1.73
17C	116.0	20	1.06	0.645-1.74
17M	"	"	1.91	1.18-2.38
14C	103.9	15	1.30	1.03-1.59
14M	"	"	0.990	0.773-1.24
18C	103.5	20	1.52	1.29-1.76
18M	"	"	1.79	1.25-2.77
19C	96.0	15	1.38	1.20-1.51
19M	"	"	1.36	1.18-1.65

(ave. = 1.40)

Table 4 Electrophoresis Mobilities and Zeta Potentials at 12 Volts

Voltage Applied = 12.0 volts (Electric Potential, $E = 1.569$ volts/cm)
pH = 5.90

Runs	Temp. °F	Electrophoresis Mobility u_E mm·cm/v·s x 1000	Zeta Potential ζ , mv
1C	116.8	4.70	43.3
1M	"	4.23	39.0
7bC	116.0	4.46	41.1
7bM	"	4.26	39.2
3C	103.8	5.79	58.5
3M	"	5.50	55.6
7C	"	5.65	57.2
7M	"	5.26	53.2
15bC	103.5	4.15	41.9
15bM	"	5.45	55.1
9C	97.0	5.03	54.9
9M	"	5.33	58.1
5C	96.0	4.09	44.6
5M	"	3.73	40.7
16bC	"	4.12	44.6
16bM	"	4.55	49.2
11C	71.4	3.97	53.8
11M	"	3.93	53.4

Table 5 Electrophoresis Mobilities and Zeta Potentials at 20 Volts

Voltage Applied = 20 volts (Electric Potential, $E = 2.61$ volts/cm)
pH = 5.90

Runs	Temp. °F	Electrophoresis Mobility u_E mm·cm/v·s x 1000	Zeta Potential ζ , mv
2M	117.5	4.90	45.1
2C	116.8	5.99	55.2
8bC	116	4.47	41.2
8bM	"	4.02	37.0
4C	103.8	5.53	55.9
4M	"	4.53	45.8
8C	"	5.63	56.9
8M	"	4.64	46.9
10bC	103.5	4.45	45.0
10bM	"	4.01	40.6
10C	97.0	4.92	53.7
10M	"	5.09	55.6
6C	96.0	3.48	38.0
6M	"	3.18	34.7
12bC	"	4.22	46.1
12bM	"	5.08	55.5
12C	71.4	4.08	55.4
12M	"	3.73	50.6

Table 6 Electrophoresis Mobilities and Zeta Potentials at 40 Volts

Voltage Applied = 40 volts (Electric Potential, $E = 5.23$ volts/cm)
pH = 5.90

Runs	Temp. °F	Electrophoresis Mobility u_E mm·cm/v·s x 1000	Zeta Potential ζ , mv
13C	117.2	5.22	48.1
13M	"	3.31	30.5
17C	116.0	3.39	31.2
17M	"	6.09	56.1
14C	103.9	4.15	41.9
14M	"	3.16	31.9
18C	103.5	4.83	48.9
18M	"	5.69	57.5
19C	96.0	4.40	47.6
19M	"	4.33	46.9

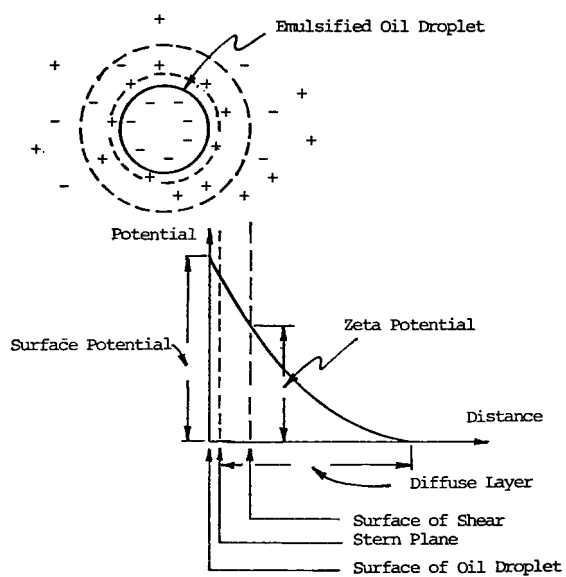


Figure 1 Zeta Potential of Emulsified Oil Droplets

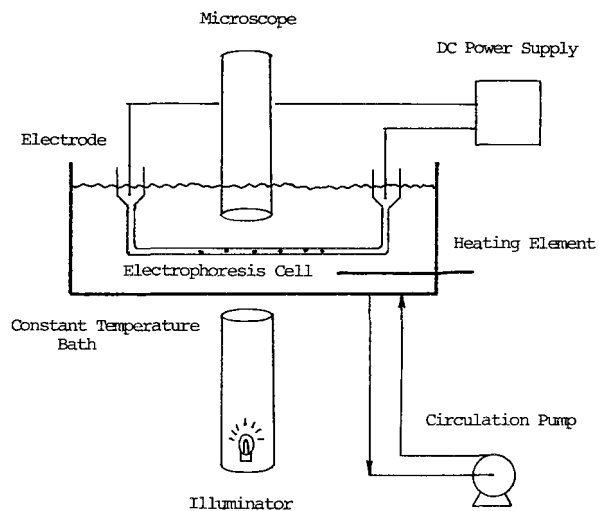


Figure 2 Experimental Apparatus

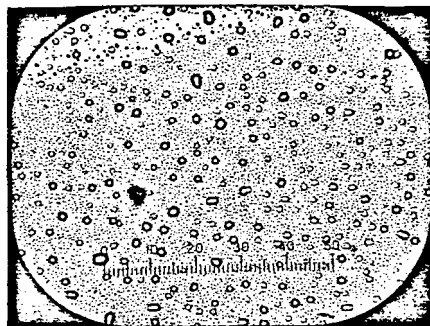


Figure 3 Droplets of Emulsified Crude Oil in Water Used in Zeta Potential Measurements (250X)

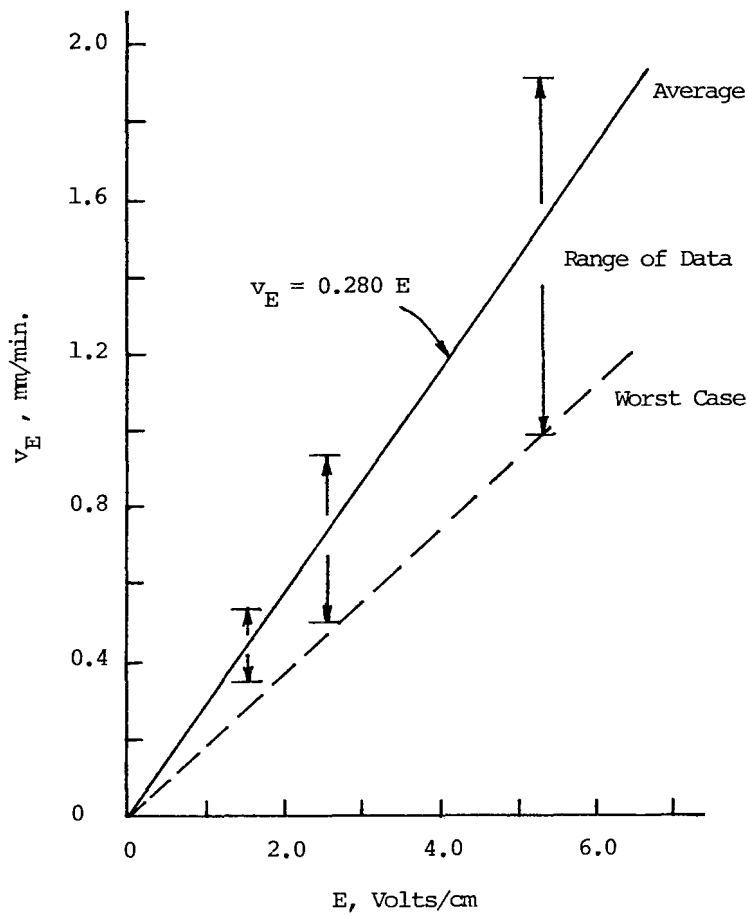


Figure 4 Electrophoresis Velocity

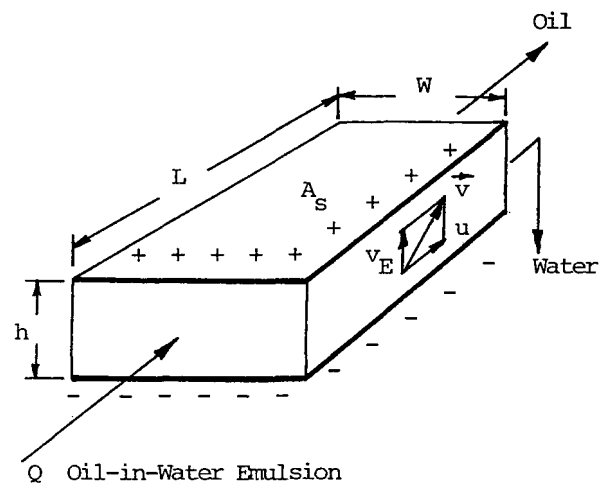


Figure 5 Compartment of Separator for Separating Emulsified Oil from Water

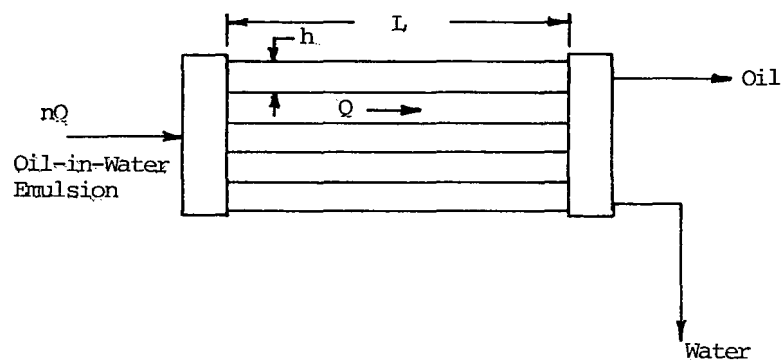


Figure 6 Schematic Diagram of Separator