Physical Properties of Japanese Crude Oil Emulsions*

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(Received December 17, 1958)

Summary

All crude oil emulsions obtained from four districts were found to be of water-in-oil type, and their particle size distributions were determined by microscopic measurements.

Dielectric constants of these emulsions increased logarithmically as water contents increased, but high frequency losses measured by conductance changes in an L-C tank circuit (20 MC/sec) increased linearly.

Dielectric strengths at room temperature decreased at first as water contents increased, but they remained about 10–20 KV/cm in the range of 10–25 vol. % of water content.

Viscosities of these emulsions increased logarithmically as water contents increased, and non-Newtonian characters became predominant above 20 vol. % of water content. These critical concentrations were checked by Voet's theory.

Ultrasonic velocities and absorptions were measured at 1 MC/sec. The latter in high water content were two or three times larger than those calculated by Stokes' equation.

Interfacial tensions between crude oil and water were found to be influenced extremely by the hydrogen ion concentration of aqueous phase, and their interfacial tensions were about 10 dynes/cm smaller than those calculated by Antonoff's equation.

Introduction

To break, effectively and economically, the stable crude oil emulsions which are often produced in the oil wells in Japan is one of the most important matters for the Japanese petroleum industry to consider.

In solving this problem, however, adequate information concerning the nature of these emulsions is not available. For this reason, the authors have examined the physical properties of Japanese crude oil emulsions as they are affected, particularly, by the difference in the oil fields from where the

crude oils are produced and by the change in the water contents of the emulsions.

Nature of Dispersed Water

a) Type of emulsion:— Eleven samples obtained from four districts were examined by means of five methods (1,2). They all indicated to be of the water-in-oil type. The four districts and the samples prepared were as follows:

Akita district.....Hachimori (H), Toyokawa (T), Sunshirozawa (Su)

Niigata district.....Niitsu (N)

Yamagata district.....Kotaki (Ko), Shonai (Sh), Chokaisan (C), Yusa (Y), Kamihama (Ka), Innai (I)

Hokkaido district.....Kitatoyofu (Ki).

b) Particle size distribution:— Microscopic measurements were made. Some typical results

* Original papers published in J. Chem. Soc. Japan, Ind. Sec., **56**, 955, 958 (1953); **57** 328 (1954); **60** 410 (1957)

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Fig. 1 Particle size Distribution

obtained are summarized in Fig. 1. In these samples their statistic mean values and standard deviation in diameter are $1-3\mu$ and $0.8-1.9\mu$ respectively, and their skewnesses are all positive.

c) Salinity:—The following, i.e., (1) Specific resistance at room temperature by means of Kohlraush bridge (1000 cycle/sec), (2) salt content as NaCl by Mohr's method, and (3) pH were determined on the dispersed water separated from three samples. The results obtained are tabulated in Table 1.

Table 1

Name of Crude Oil	Spec. Resist. (Ω -cm)	NaCl (wt%)	pH
H	27.04	1.38	7.4
Ko	26.98	—	9.2
T	39.60	1.18	8.2

Electric Properties

a) *Dielectric Constant*:— One of the authors has already discussed about dielectric constant of dispersed systems in another paper (3). In this pa-

per only the results obtained in the measurements of five kinds of emulsions are reported. The measurements were made on the samples prepared by reducing the water contents of the emulsions by centrifuge at 950 kc/sec at room temperature by means of a series resonance circuit as shown in Fig. 2.

Fig. 2 Series Resonance Circuit for Dielectric Constant Measurement.

Dielectric constants are plotted against water contents (vol.%) in Fig. 3. In the same figure the calculated values from Wiener's (4) and Bruggeman's equations (5) are also plotted. The relation between dielectric constants and water contents can be represented by one curve for all of the five emulsions within the accuracy of this measurement, but the curve does not coincide with Wiener's equation, and it also deviates from Bruggeman's equation in the region of higher water content.

The values of $\log \epsilon$ increase almost linearly

Fig. 3 Relation between ϵ and Water Content.

against water content as shown in Fig. 4, agreeing with Lichtnecker's equation (6), but the inclination becomes larger at a certain water content. The authors suppose that any simple additive relationship could not be applied in the range of high water content of water-in-oil emulsions on account of a mutual interaction between dispersed particles.

Fig. 4 Relation between $\log \epsilon$ and Water Content.

b) **Dielectric Strength**:—Crude oil emulsions are often broken under high electric field, but only meager information about their dielectric strength has been reported. Three kinds of samples were investigated in this paper, and it was known that their dielectric strength became smaller than “dry” crude oils in accordance with their water content. However, it remained about 10–20 kV/cm at room temperature in the range of 10–25 vol. % of water content as shown in Fig. 5.

c) **High Frequency Loss**:—There is a relation between dielectric constant and water content

Fig. 5 Relation between Dielectric Strength and Water Content.

which is logarithmic as mentioned above, and this is not advantageous in the case of electric measurement of water content. The authors found that high frequency losses of crude oil emulsions measured by conductance changes in an L-C tank circuit (20 Mc/sec) as shown in Fig. 6, increased linearly when their water contents increased.

Fig. 6 High Frequency Bridge Circuit for Loss Measurement.

Fig. 7 Relation between Unbalanced Current in Bridge Circuit and Water Content.

Fig. 8 Relation between Relative Viscosity and Water Content.

The values of unbalanced current of this bridge circuit at the time when the samples are put into the coil (L_p) are plotted against water contents in Fig. 7. Straight lines I and II were obtained at the plate voltages of 200 V and 90 V respectively. The values of water-in-spindle oil emulsions and butter fell on the same line. Other applications of this circuit for electric measurements of water content were discussed elsewhere. (7,8).

Flow Properties

Many reports have been published about viscosities of emulsions, but the effect of water content on water-in-oil emulsions and their non-Newtonian behaviors are not yet clear, especially in crude oil emulsions. It is necessary to know the flow properties of crude oil emulsions in connection with transportation or mixing problems.

Relative viscosities of four kinds of samples calculated from Saybolt seconds are plotted against water contents in Fig. 8, in which the calculated values from Einstein's (9), Taylor's (10), and Simha's (11) equations are also shown by E, T, and S, respectively. None of the equations represents satisfactorily the measured values;

Fig. 9 Relation between Logarithm of Relative Viscosity and Water Content.

rather a logarithmic relation agrees with them better as shown in Fig. 9.

Non-Newtonian behaviors of (K_0) and (T) were investigated by means of a modified Stormer viscometer (Fig. 10), expressing "fluidity" by reciprocal value of time (second) when the weight is moved down through the distance of 10 cm.

Fig. 10 Modified Stormer Viscometer.

Fluidities are plotted against shearing stress (gram of the weight) in Fig. 11, and Fig. 12. In the latter the sample containing 45 vol. % of water was prepared by mixing "dry" crude oil (T) with previously separated water.

In both (K_0) and (T) non-Newtonian character became predominant above approximately 20 vol. % of water content. This fact seems to correspond

Fig. 11 Flow Curves of (K_0).

Fig. 12 Flow Curves of (T).

to the changes of inclination shown in Figs. 4 and 9. The authors will discuss this point in the following section.

Relation Between Dielectric Constant and Fluidity

Voet (12, 13, 14) first found that a typical correspondence existed between dielectric constant and viscosity in some dispersed systems, and he insisted that an agglomeration factor (Av) was

Table 2 Values of Av Calculated from Voet's Equation

Name of Crude Oil	Water Content (vol. %)	Dielectric Constant	Av
(H)	trace	2.30	—
	6.4	2.69	1
	9.8	2.96	1
	11.0	3.19	1
	18.1	3.93	1
	19.2	4.24	1
	24.1	4.78	1
	24.4	5.00	2
	24.9	5.14	2
	25.0	5.07	2
(Ko)	trace	2.25	—
	6.5	2.86	1
	16.8	3.57	1
	29.3	5.90	1
	33.5	7.14	2
	36.5	8.00	2
	39.5	9.60	3
	42.0	11.1	3
	45.0	12.5	3
(T)	0.6	2.29	1
	11.4	3.22	1
	12.9	3.45	1
	15.8	3.82	1
	22.0	4.73	2
	23.0	4.78	2
(C)	0.4	2.29	1
	32.3	6.59	2
	37.1	8.07	2

equal to 1 in Newtonian flow and larger than 1 in non-Newtonian flow.

The calculated results of Av for four kinds of crude oil emulsions are tabulated in Table 2. In (C) and (T) 2.28 was chosen as the dielectric constant of "dry" crude oil, because measured values were not obtained.

It is supposed from the results of Table 2 that these crude oil emulsions exhibit non-Newtonian flow above 20–30 vol. % of water content. This assumption is justified by the observed results mentioned in the preceding section.

Any theoretical explanation for Voet's thought is not given, but the mutual interaction between dispersed particles in dispersed systems, if any, may be predominant at higher concentrations of dispersed phase. Eveson (15) and Myers (16) have also suggested such an interaction in suspensions. The authors believe further investigation on this subject is desirable.

Ultrasonic Propagation

On the propagation of ultrasonic vibration in dispersed systems only few reports have been published, among which Urlick's works (17, 18, 19) on the velocity and absorption of ultrasonics in some dispersed systems are most noteworthy. No data are found, at present, about crude oil emulsions, and it is necessary for considering the possible application of the ultrasonic method in breaking crude oil emulsions.

Ultrasonic velocities of three kinds of samples were measured by means of a ultrasonic interferometer of 1 Mc/sec, and the increase in the ultra-

Fig. 13 Relation between Ultrasonic Velocity and Water Content.

Fig. 14 Relation between Ultrasonic Velocity and Temperature.

Fig. 15 Block Diagram of Ultrasonic Absorption Measuring Device.

sonic velocity corresponded slightly to the increase in the water content as shown in Fig. 13. This resulted from the fact that the velocity (v) of dispersed water closely resembled that of "dry" crude oil: for instance, v of "dry" crude oil of Asahigawa emulsion was 1440 m/sec, and that of dispersed water was 1500 m/sec.

The influence of temperature upon ultrasonic velocities in (T, water content-trace) and (H, water content-27.5 vol. %) is shown in Fig. 14.

Ultrasonic absorptions at 1 Mc/sec were determined by the pulse method shown in Fig. 15, in the following two ways: Method (1)—The pulse heights on the cathod-ray oscilloscope were read by moving the receiving crystal. Method (2)—The attenuator was adjusted so as to keep the height of the received pulse on the oscilloscope constant during the alteration of the receiving crystal.

In Table 3 the values obtained by these two methods for medical linseed oil were compared with Hunter's published value (20), and the calculated value obtained from Stokes' equation (21).

In Fig. 16, the received pulse heights are plotted against the propagated distances in (T), and their absorption coefficients are tabulated in Table 4, in

Table 3 $\alpha/f \times 10^{17}$ in linseed oil (1 Mc/sec, @ 15°C)

Method (1)	Method (2)	Literature	Calculated
9,400	9,700	10,900	11,200

Fig. 16 Relation between Propagated Distance and Attenuation of Ultrasonic Pulse.

Table 4 Ultrasonic absorption of (T)
 $\alpha/f^2 \times 10^{17}$, 1 Mc/sec, @ 15°C

Sample	Water content (vol. %)	d(15/15)	Viscosity (poise)	Method (1)	Method (2)	Calculated
T-1	5.5	0.957	4.25	4,600	8,100	3,400
T-2	10.0	0.958	5.15	6,100	—	4,200
T-4	12.5	0.959	5.60	8,200	9,200	4,500
T-5	13.5	0.959	5.80	8,900	10,400	5,800
T-6	18.5	0.961	6.70	15,500	15,300	5,900

which the calculated values from Stokes' equation are also shown.

The ultrasonic absorption increased notably when the water content of emulsions increased be-

Fig. 17 Relation between Ultrasonic Absorption and Water Content.

yond approximately 20 vol. % as shown in Fig. 17. The authors believe that this is one of the proofs of our assertion that the mutual interaction between dispersed particles becomes predominant at higher concentrations of dispersed phase in these emulsions.

The observed absorption coefficients were two or three times larger than those calculated from Stokes' equation. The reason for this difference is not clear, and further investigation may be necessary.

Surface-chemical Properties

Surface-chemical properties of crude oil emulsions not only open a way for investigation as to its cause of emulsions, but also give important information for chemical methods of breaking them. However, the complex nature of the emulsions makes it difficult to discuss these properties in detail. In this paper the changes of interfacial tension between "dry" crude oils and water at various pH of the aqueous phase are chiefly discussed.

At first the interfacial tension between "dry" crude oils and distilled water was determined by means of Bartell's method (22) and A.S.T.M. (23). The results obtained are tabulated in Table 5.

The interfacial tension between "dry" crude oils and aqueous solutions of various pH adjusted by HCl or NaOH, was also determined by the two methods mentioned above. The results obtained are plotted against values of pH in Fig. 18 and Fig. 19. In the latter the dotted curves represent the interfacial tensions between "dry" crude oils and dispersed water separated from each crude oil emulsion by centrifuge and adjusted pH with HCl or NaOH.

It is known from these results that interfacial tension between crude oil and aqueous solution of HCl or NaOH decreases at the high acidic and also

Table 5 Interfacial Tensions between Crude Oils and Distilled Water (dynes/cm)

Name of Crude Oil	Temp. (°C)	Bartell's Method	A.S.T.M.
Ko	30	30.1	24.7
N	30	29.9	24.0
H	30	29.3	26.3
Sh	30	29.7	24.0
T	30	31.6	28.4

Fig. 18 Interfacial Tensions between Crude Oils and Aqueous Solution of Various pH by Bartell's Method.

Fig. 19 Interfacial Tensions between Crude Oils and Aqueous Solution or Dispersed Water of Various pH by ASTM.

high alkaline sides. Those between crude oil and dispersed water also decreases at the high acidic and high alkaline sides, but these changes occur in a much narrower pH range than in the aqueous solution of HCl or NaOH.

As tabulated in Table 6, Na_2SO_4 also gave nearly the same effect as NaOH.

Table 6 Interfacial Tensions between (T) crude oils and aqueous solutions of Na_2SO_4 at 30°C.

pH	7.2	7.9	9.2	10.4	ca. 12	ca. 13
Bartell's method	30.4	29.8	28.6	23.0	ca. 6	ca. 5.5
A.S.T.M.	29.0	27.9	28.1	7.1	unmeasured	

The interfacial tensions between four kinds of crude oils and distilled water or separated water are calculated by Antonoff's equation from the measured values in Table 7. The observed values in all systems of crude oils against the separated water were about 10 dynes smaller than those calculated.

Surface-chemical properties known in these measurements indicate that these crude oils contain ampholytic surfactants, and adequate care

Table 7 Calculated and Observed Interfacial Tension (dynes/cm).

Sample	Calculated	Observed @ 30°C	
		Bartell's method	A.S.T.M.
(Sh)-distilled water	37.9	29.7	24.0
(Sh)-separates water	33.6	22.1	—
(T)-distilled water	38.4	31.6	28.4
(T)-separated water	25.0	11.5	13.1
(H)-distilled water	36.9	29.3	26.3
(H)-separated water	15.4	—	11.3
(Ko)-distilled water	39.9	30.1	24.3
(Ko)-separated water	31.4	18.5	—

has to be taken in the case when acid, alkali or surfactants are used for breaking these emulsions.

Conclusion

Many unknown properties of Japanese crude oil emulsions have been made clear, and the authors believe that the information obtained is not only helpful in the treatment of these emulsions, but also for future researches on the properties of other dispersed systems; for example, desalting of crude oils with water, soda washing of distillates, treating emulsified lubricating oils, and improving the properties of soluble cutting oils.

Acknowledgment

The authors wish to express their appreciation to Dr. Ken-ichi Yamamoto and Dr. Tadatsugu Ito of Waseda University, to Dr. Rempei Goto of Kyoto University, and to Dr. Toshizo Isemura of Osaka University. They are also grateful to the

members of Teikoku Sekiyu Co. for offering the samples, and to the management of the Nippon Oil Co. for permission to publish this article.

References

- 1) T. Fukushima & T. Ichimura : *Waseda Applied Chemical Society Bulletin*, **20**, No. 2,9 (1952), Waseda Univ., Tokyo, Japan.
- 2) T. Ito & T. Fukushima : *Kagaku (Science)* **23**, 628 (1953), Japan P. 218, 962 (20, Jan. 1956)
- 3) T. Fukushima : *Waseda Applied Chemical Society Bulletin*, **21**, No. 58, 20, (1952), Waseda Univ., Tokyo, Japan.
- 4) O. Wiener : *Physik. Zeit.*, **5**, 322 (1940)
- 5) D.A. Bruggeman : *Ann. Physik.* **24**, 636 (1935)
- 6) K. Lichtnecker : *Physik. Zeit.*, **27**, 115 (1926)
- 7) T. Fukushima & T. Ito : *OHM* **40**, 1274 (1953) : Japan P. 216, 622 (5, Oct. 1955)
- 8) T. Fukushima & K. Imazu : *J. Japan Oil Chemists's Soc.*, **4**, 188 (1955)
- 9) A. Einstein : *Ann. Physik*, **4**, 289 (1906) : **34**, 591 (1911)
- 10) R. Taylor : *Proc. Roy. Soc., London*, **A138**, 41 (1932)
- 11) R. Simha : *Kolloid-Zeit.*, **74**, 266 (1936)
- 12) A. Voet : *J. Phy. & Colloid Chem.*, **51**, 1037 (1947)
- 13) " : *Proc. Intern. Rheol. Congr.*, **2**, 15 (1948)
- 14) A. Voet & L.R. Suriani : *J. Colloid Sci.*, **7**, 1 (1952)
- 15) G.F. Eveson, S.G. Ward & R.L. Whitmore : *Discuss. Faraday Soc.*, No. 11, 11 (1951)
- 16) R.R. Myers, J.C. Miller & A.C. Zettlemoyer : *J. Applied Phys.*, **27**, 468 (1956)
- 17) R.J. Urlick : *J. Applied Phys.*, **18**, 983 (1947)
- 18) " : *J. Acoust. Soc. Am.*, **20**, 283 (1948)
- 19) " : *J. Acoust. Soc. Am.*, **21**, 115 (1948)
- 20) J.L. Hunter : *J. Acoust. Soc. Am.*, **13**, 36 (1941)
- 21) G.G. Stokes : *Cambr. Trans. Phil. Soc.*, **8**, 287 (1845)
- 22) F.E. Bartell & F.L. Miller : *J. Am. Chem. Soc.*, **50**, 1961 (1928)
- 23) A.S.T.M. D 971-50 (1950)