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LIGHT TRANSMITTANCE AS A MEASURE OF INTERFACIAL
AREA IN LIQUID-LIQUID DISPERSIONS

by

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ABSTRACT

Measurement of the interfacial area in liquid-liquid systems has been made photographically. The precision and accuracy of the method have been shown to be better than 10%. To avoid the tedium of counting drops, a simple light probe of an easily reproducible design has been developed to measure light transmission through the dispersions formed. Correlations of light transmission with interfacial area are presented and their usefulness and limitations discussed.

SUMMARY

A photographic technique was developed to measure the interfacial area of liquid-liquid dispersions. Data, based on a dispersion of glass beads in an organic liquid, demonstrated the accuracy and precision of the photographic method to be plus or minus 5%.

Equipment and techniques were developed to measure the light transmittance of liquid-liquid dispersions at optical path lengths of 1.0 to 2.0 centimeters. The reproducibility of transmittance measurements was found to be about 1% for consecutive measurements and about 3% for duplicate runs.

Generalized empirical correlations, based on theoretical considerations, were developed for light transmittance as a function of interfacial area, optical path length, and an optical parameter. The average per cent deviation in area as determined by transmittance readings was less than 6%. The optical parameter was found to be a function of the relative specific refraction of the drop phase.

The two correlations presented are based on light spectra in the yellow and near infrared regions, respectively. The application of these correlations is limited to disperse systems of nonabsorbing (water-white), immiscible liquid pairs in which the smallest particle size is greater than 50 microns and the volume fraction of the dispersed phase is 0.50. Experimental data are presented for several oil dispersed in water systems covering a range of relative refractive index from 1.005 to 1.165.

I. INTRODUCTION

Frequently investigators working with dispersions of immiscible liquids desire knowledge of the interfacial area of these systems. Such information would be particularly useful in the interpretation of liquid-liquid extraction data in terms of rate in addition to equilibrium concepts. Unfortunately, it is generally difficult or impossible to determine the interfacial area of liquid-liquid dispersions. In the few cases where interfacial areas have been determined, most investigators have relied on photographic techniques.

In recent years the phenomenon of light scattering by small particles has been the subject of a number of investigations.⁽¹⁴⁾ However, very little work has been reported in the literature concerning light scattering as a measure of particle size in liquid-liquid dispersions. Undoubtedly, a major deterrent to such investigations has been the problem of measuring the interfacial area of rapidly coalescing disperse systems by other than photographic methods.

In this report a photographic technique for measuring interfacial area is described. Also, empirical correlations based on theoretical considerations, which give the light transmittance of liquid-liquid dispersions as a function of interfacial area, are presented. Experimental data are presented for several nonabsorbing, (water-white) liquid pairs of differing relative refractive indices.

II. PREVIOUS WORK

Most of the interest in light scattering has been restricted to very dilute monodisperse* systems of small particles, generally less than one micron in diameter. Mathematical treatments of concentrated polydisperse** systems are not available. In addition, there are few quantitative data available relative to liquid-liquid or gas-liquid dispersions.

It is interesting to note that in 1925 Stamm and Svedberg⁽¹⁹⁾ were interested in the relationship between the right-angle scattering of light and the size distribution of soap-stabilized benzene-water emulsions. They suggested a linear relationship between light transmittance and concentration for a given particle size. Clark and Blackman⁽³⁾ investigated light transmittance as a measure of the interfacial area of foams. On the basis of admittedly qualitative data, a linear relationship between light transmittance and interfacial area was suggested.

* Monodisperse in the sense that all particles in the dispersion are the same size.

** Polydisperse in the sense that a distribution of particle sizes is present.

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Recently, Langlois and co-workers^(11, 12) published a correlation of light transmission with interfacial area for nonabsorbing liquid-liquid systems. Their results were correlated empirically by a linear equation in the following form:

$$\frac{I_0}{I} = 1 + \beta A \quad (1)$$

where

$$\frac{I_0}{I} = \text{the ratio of incident to emergent light intensity}$$

$$A = \text{interfacial area per unit volume of total mixed phases (volumetric area)}$$

$$\beta = \text{a constant characterizing a specific liquid pair.}$$

This relationship was considered to be independent of the volume fraction of the dispersed phase. The constant, β , was given as a function of the relative refractive index of the dispersed phase.

The papers by Langlois are of particular interest, because they represent the first successful attempt to establish a quantitative relationship between light transmission and volumetric area. However, the probe used was not designed to provide for variable optical path lengths, and, since the entire assemblage was mounted in the mixing vessel, it may have had an adverse effect on the mixing pattern. In addition, the reproducibility of results with different probes of the same design was poor and each probe required individual calibration.⁽¹⁰⁾ Duplication of this work would be difficult.

It is apparent from the literature that the quantitative equations relating particle size and concentration to light transmittance are limited and cannot be applied to concentrated polydisperse systems of large spherical particles. The available empirical relationships for polydisperse systems do not demonstrate satisfactory accuracy and precision. In addition, it is difficult to reproduce the equipment design and each detector unit requires individual calibration.

III. THEORY

A. Basic Theory

The light transmitted through a polydisperse system of non-absorbing isotropic spherical particles provides a measure of interfacial area if it can be demonstrated that light transmission is a function of the

total projected area. This means that it must be shown that the light transmission is a function of the mean surface-volume or sauter diameter, d_{sv} . Conversely, a correlation is not possible if the scattered light energy is sensitive to the particle size distribution. For a polydisperse system consisting of N_i particles of diameter d_i in a given size interval:

$$d_{sv} = \frac{\sum N_i d_i^3}{\sum N_i d_i^2} \quad (2)$$

For a volume fraction, ϕ , of the dispersed phase, the volumetric area is defined as follows:

$$A = \frac{6}{d_{sv}} \phi \quad (3)$$

The factors which control light transmittance are embodied in the familiar extinction or Beer-Lambert relationship:

$$SndL = \frac{dI}{I} \quad (4)$$

The scattering cross section, S , is the ratio of the light energy lost by scattering to the incident light energy per unit area, and n is the number of particles per unit volume. Integrating over the distance between light source and detector, L , as the incident light diminishes from I_0 to I , the conventional extinction equation is obtained:

$$\ln \frac{I_0}{I} = SnL = K_s \frac{d^2 \pi}{4} nL \quad (5)$$

where

$$K_s = \frac{4S}{d^2 \pi} = \text{the scattering area coefficient} ,$$

d = particle diameter .

Scattering area coefficients may be calculated by means of complicated equations originally developed by Mie.⁽¹³⁾ With the aid of recently developed electronic computers, the Mie theory has been verified both by mathematical computation and by comparison of predicted and experimental data. Work by several investigators^(2, 5, 6, 7, 8, 9, 18) shows that K_s , the scattering area coefficient, is a function of the drop diameter, d , the incident light wavelength, λ , and the ratio m of the refractive index of the drop to that of the field phase:

$$K_s = f \left[\frac{\pi d}{\lambda} M \right] , \quad M = \left| \frac{m^2 - 1}{m^2 + 2} \right| \quad (6)$$

As shown in Fig. 1 the scattering area coefficient becomes increasingly more sensitive to values of the indicated function which are less than 2.0. As the particle diameter approaches the wavelength of the incident light and as the relative refractive index, m , approaches unity, a very rapid variation in K_s is apparent. However, for values greater than 10, K_s is relatively constant.

For practically all oil-water systems, M is greater than 0.01. By substituting this value of M in the function given in Eq. (6) and equating to 10, it may be shown that, at a wavelength of light of 0.5 micron, K_s is constant for all particle sizes above about 150 microns. Equating the function to 2.0 shows the absolute minimum particle size for the range of essentially constant K_s to be about 50 microns. Other investigators, Bailey⁽¹⁾ and Rose et al.,⁽¹⁶⁾ have verified certain of these observations by purely experimental means. They showed that for reflecting particles ($M=1.0$) K_s may be regarded as constant for particles greater than about 2.0 microns.

In this investigation the observed particle size distribution has generally been between 50 and 2000 microns and the scattering area coefficient may be considered as a constant with respect to particle diameter. Therefore, the drop diameter, d , may be defined as the sauter diameter, d_{sv} , and Eq. (5) may be written in terms of the interfacial area per unit volume of total mixed phases, A , and a scattering factor, α .

$$\ln \frac{I_0}{I} = \frac{K_s}{4} \pi d^2 n L = \frac{K_s}{4} \pi d^2 \left(\frac{6 N \phi}{N \pi d^3} \right) L = \frac{K_s}{4} \left(\frac{6 \phi}{d_{sv}} \right) L = \alpha A L \quad (7)$$

B. Applied Theory

The assumption was made in the basic relationship, Eq. (4), that light once scattered from the path of the primary beam was lost. This can be true only for very dilute dispersions. For the concentrated disperse systems studied, some of the light scattered from the primary beam is returned to the original path by secondary scattering. Hence, multiple scattering is a very important factor. Equation (7) shows α to be a function of K_s . The scattering area coefficient, K_s , is a constant which, within certain previously specified limitations, is independent of the oil-water system involved. If the phenomenon of multiple scattering did not exist, α would be identical for all systems. Therefore, α is in a sense a measure of the systems' ability or potential to cause multiple scattering, and the product αA is, to a limited extent, a measure of the total multiple scattering effected.

A number of other factors, such as the light source and detector geometry and the materials of construction, have a significant effect on the scattering factor, α . For example, consider the problem of measuring the emergent light intensity, I . The incident light, I_0 , is a collimated beam.

m = RELATIVE REFRACTIVE INDEX
 λ = INCIDENT LIGHT WAVELENGTH

d = PARTICLE DIAMETER
 K_s = SCATTERING AREA COEFFICIENT

Fig. 1

Comparison of Scattering Area Coefficients

Data Source: Boll, R. H , Gumprecht, R. O., Sliepcevich, C. M., J. Optical Society
44, 18, (1954)

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The emergent light, I , is defined as that portion of I_0 which passes unimpaird through L cm of dispersion. This means that the emergent light is that portion of the incident light scattered in the forward direction parallel to the path of the primary beam. Gumprecht and Sliepcevich⁽⁴⁾ point out that it is technically impossible to obtain an exact measure of the emergent light. Any detector design will measure, in addition to light scattered in the forward direction, some of the light scattered at small angles from the path of the primary beam.

The basic transmission relationship, Eq. (7) may be modified to conform with these practical considerations:

$$\ln \frac{I_0}{I} = f(\alpha, A, L) \quad . \quad (8)$$

Equation (8) shows that an exponential relationship exists between $\frac{I_0}{I}$ and some functions of α , A , and L . The exact nature of the function must be determined experimentally.

IV. EXPERIMENTAL

Experimental techniques and equipment were developed to measure the interfacial area per unit volume of total mixed phases (volumetric area) and the light transmittance of the dispersion at a specified optical path. The volumetric area was determined photographically and the light transmittance by photoelectric measurements.

A. Mixing Equipment

Dispersions were created in the 5.55-inch diameter Pyrex mixing vessel shown in Fig. 2. The vessel was equipped with four baffles, the width of each being $1/10$ of the diameter of the mixing vessel, and a 3-inch, six-blade, flat blade turbine. The baffles and agitator were constructed to conform with the design suggestions of Rushton.⁽¹⁷⁾ All metallic components were of 304 stainless steel; gaskets were of Teflon.

B. Light Source and Detector

The photoelectric equipment required for light transmittance measurements consisted of three major components: a light source to provide a uniform, collimated beam; a sensitive light detector unit; and an electronic circuit to measure the amplified output of the detector unit. In the design of the equipment, ruggedness and reproducibility were of prime importance. Of secondary concern was the desire to mount as much of the equipment as possible outside the mixing vessel to minimize contamination of the liquids and interference with the normal flow pattern.

Light Source (not shown) is located below the vessel

Fig 2 Experimental Mixing Vessel

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Both the light source and detector were externally located. The light source was located below and the detector above the mixing vessel. A light pipe or probe extended down from the detector into the dispersion. The distance from the bottom of the vessel to the end of the light pipe determined the optical path.

The light source was a Universal Microscope Illuminator, No. 353, made by the American Optical Company and fitted with a six-volt automobile bulb (GE 1493). Light from the microscope lamp converged at the focal point of a condensing lens. A series of preliminary tests (summarized in Fig. 3) showed that the percentage of the incident light which reached the detector varied directly with the diameter of the incident beam. Therefore a standard beam diameter was adopted and the collimated beam leaving the lens was restricted with a 18-mm aperture. The light leaving the aperture was filtered with either a Corning 3486 yellow filter or a 2404 red filter to obtain the desired light spectrum. The light source is shown schematically in Fig. 4.

The emergent light was transmitted to a photocell by a glass sensing probe extending into the dispersion. The probe was made adjustable to allow light paths of variable lengths through the dispersion. A 30-cm, 3/8-inch diameter Pyrex 7740 glass rod, polished on both ends, served as the probe. The detector unit is shown in Fig. 5. Very careful alignment of the light source and detector elements was necessary to obtain reproducible transmittance data. This was particularly true in the case of the 1P42 photocell because of its small diameter, which was less than the diameter of the light probe.

The microscope lamp did not provide a perfect point source of light. A more nearly perfect point source would be the filament of the auto lamp. However, the filament of the exposed bulb did not supply a sufficient amount of light energy to operate the phototube. Therefore, it was necessary to use the lens of the microscope lamp to concentrate the light produced by the auto lamp. Thus, the collimated beam leaving the system of lenses and aperture comprising the light source retained the image of the filament of the lamp. By looking directly down into the light beam, it was possible to see the image of the filament clearly outlined by its relatively higher light intensity. Therefore, in aligning the light source and detector it was the practice to center the end of the light probe carefully in the image of the lamp filament. This task was simplified by the fact that the greatest output of the phototube was obtained when the light source and detector were properly aligned. Substitution of lamps did not affect the reproducibility, even though for a given applied voltage some lamps were markedly brighter than others.

It was found that more reproducible readings were obtained if the sides of the probe were protected from stray light. Runs were made to compare the fraction of the incident light reaching the detector through

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Fig. 3

Effect of Incident Light Beam Diameter on Dispersion Light Transmittance

Fig. 4 Schematic Diagram of Light Source

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Fig 5
Light Detector Unit

uncoated and coated probes. The results of these comparisons are presented in Fig. 6. They showed that the uncoated probe permitted a larger percentage of the incident light to reach the detector because light reflected by the dispersed drops entered through the sides of the probe. The amount of stray light entering through the sides of the probe was found to increase with both the relative refractive index of the dispersed phase and the immersion depth of the probe. In order to eliminate this variable, the sides of the probe were coated with a platinum mirror finish. The mirror finish was obtained by painting the cleaned rod with a thin coat of "Liquid Bright Platinum No. 05," Hanovia Chemical and Manufacturing Company, then heating to dull cherry red to produce a bright finish. The several probes made in this manner gave reproducible results. Overheating resulted in a dull finish which caused inconsistent readings.

Light was transmitted from the probe to the photocell through a seal of Dow Corning No. 200 Silicon oil, which also lubricated the joint and prevented chipping. Black, 3/8-inch, rubber tubing covered the junction to prevent stray light from reaching the photocell.

End-type photocells, RCA 1P42 and RCA 1P41, were used rather than side entry types because they permitted a more compact detector design and also simplified the problem of obtaining an optical seal. A vacuum tube, such as the RCA 1P42, was preferable to the gas type RCA 1P41 because of the superior linearity of response. However, the gas tube (RCA 1P41) was larger and easier to fit to the end of the sensing probe. In addition, the gas tube had end fittings which matched conventional electrical connectors. In the case of the vacuum tube it was necessary to construct specially designed electrical connectors. Furthermore, the gas tube required a shorter warm-up period and was less sensitive to short circuits caused by moisture deposited on the electrical connectors during periods of high humidity.

The combination of the phototube and filter response characteristics determined the effective light spectrum. The 1P42 tube together with the yellow filter responded in the light band of 560 ± 50 millimicrons (Fig. 7). The 1P41 tube with the red filter responded in the light band from 600 to 1200 millimicrons (Fig. 8). It should be noted that the effective spectrum of the latter response curve is primarily in the near infrared region and for the most part is not visible to the human eye.

The output of the photocell was measured with the electronic circuit shown in Fig. 9. This circuit utilizes a high resistance in series with the photocell to produce a substantial voltage from the small currents produced by the photocell. The voltage produced was opposed by a variable voltage source and a constant net voltage was supplied through an amplifier circuit to an ammeter. The ammeter was maintained at a constant reading and therefore was in a sense a null indicator. The opposing variable voltage used to maintain the constant net voltage was controlled by a direct-reading, ten-turn, slidewire

Fig. 6

Effect of Platinum Coating on Light Detector Sensing Probe

Fig. 7

Wavelength Distribution of Filtered Light and Phototube Response for Yellow Light Spectrum

Fig. 8

Wavelength Distribution of Filtered Light and Phototube Response for Near Infrared Spectrum

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Fig. 9

Schematic Diagram of Light Detector Electronic Circuit

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helipot resistor. Since the photocell had a linear response, the helipot readings were a measure of the light reaching the photocell and were used in calculations without conversion since ratios of light energy were involved. A sample calculation showing the procedure used to calculate light ratios from the helipot readings is given in the Appendix.

C. Volumetric Area (Interfacial area per unit volume total mixed phases)

The volumetric area which exists in a liquid-liquid system during agitation was determined from photographs of the dispersion. Photographs were taken through the base of the mixing vessel with a 35-mm Leica camera fitted with an Ektar 5-cm lens, reflex prism, and close range bellows, using Kodak Plus-X film. Illumination was provided by a 0.0002-second Comet 100-watt-second strobe light mounted beside the vessel. Light from the droplets reached the camera by reflection. Pictures with good drop resolution were obtained by over-exposing the film by one stop and double-developing the negative. Resolution was improved by photographing through a G filter. A typical photograph is shown in Fig. 10.

Preliminary runs were made to establish techniques for area measurements in a mixing vessel of rectangular cross section specially designed to facilitate photographic study. An assortment of glass beads dispersed in a mixture of carbon tetrachloride and tetrabromoethane was photographed. These beads ranged in diameter from 210 to 710 microns. Several observers working independently determined the interfacial area from photographs by tracing the droplets in the plane of focus and by classifying the diameters. A sample calculation is given in the Appendix.

The precision of the technique is shown by the data of Table I. The accuracy of the technique is apparent from a size-frequency plot, Fig. 11, which compares the experimentally determined size distribution with the distribution determined by classification of the beads into sieve sizes. Both the accuracy and precision of the photographic method, based on measurements by several independent observers, is shown to be better than plus or minus 5%.

D. Procedure

Equal volume portions (1080 ml) of each phase were placed in the cylindrical mixing vessel shown in Fig. 2 and equilibrated from two to four hours to saturate the liquid pair mutually. Commercial or reagent grade organic liquids, pretreated by distillation, were used. The aqueous phase was distilled water or glycerin-water mixtures. Runs were made at $25 \pm 1^\circ\text{C}$ and refractive indices were determined at 25.0°C .

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System:	Cyclohexane in Water
Agitator Speed:	3.9 RPS
Turbine Diameter:	3 inches

Fig. 10

Typical Photograph of Dispersion

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Table 1

GLASS BEAD TEST FOR ACCURACY AND PRECISION OF
PHOTOGRAPHIC METHOD FOR MEASURING INTERFACIAL
AREA PER UNIT VOLUME DISPERSED PHASE

A. Photographically Determined Interfacial Area

<u>Observer</u>	<u>sq cm</u>
	<u>cu cm</u>
A	123
B	121
C	125
D	122
E	122

B. Interfacial Area Determined by Classification

	<u>sq cm</u>
	<u>cu cm</u>
Maximum Value	129
Minimum Value	107
Average Value	117
Average Value Determined Photographically	123

C. Size Distribution of Beads Used in Test

<u>Diameter (Micron)</u>	<u>Wt Per Cent</u>
210-297	4.1
420-500	35.1
500-590	29.6
590-710	31.2

Fig. 11

Comparison of Calculated Size Frequency of Dispersed Glass Beads with Measured Values

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For each system a series of transmittance measurements were obtained, and photographs of the dispersion were taken to provide a measure of the volumetric area at each of the impeller speeds employed. The specific volumetric area under a given set of conditions was found to be reproducible if surface active contamination were absent. To minimize contamination, the equipment was thoroughly cleaned with acetone, water, acid-dichromate cleaning solution, water, and distilled water in that order.

The incident light (I_0) was defined as the light energy per unit area measured through the clear field phase before emulsification, while the emergent light (I) was defined as that portion of the incident light which reached the detector probe after emulsification.

The reading of the incident light was arbitrarily controlled by the voltage applied to the light source. Mixing was begun and emergent light readings were taken when steady state conditions were reached (from 2 to 45 min) as indicated by a constant transmittance reading. Immediately after each emergent light reading, a measurement was taken to establish the reading for zero transmittance, as small changes in this quantity have considerable effect on the value obtained for the emergent light. Emergent light readings were taken at optical path lengths of 1.0, 1.5, and 2.0 cm.

The range of transmission readings that could be obtained was limited by the physical properties of the liquid pair. It was necessary to maintain sufficient agitation to insure complete emulsification but not enough to beat air into the system and change the optical properties.

V. CORRELATION OF TRANSMITTANCE DATA

The experimental data for the two light spectrums investigated were correlated empirically in the form of Eq. (8). For the yellow light spectrum:

$$\ln \frac{I_0}{I} = f(\alpha AL^{0.8}) \quad , \quad (9)$$

and for the near infrared light spectrum:

$$\ln \frac{I_0}{I} = f(\alpha AL^{0.65}) \quad . \quad (10)$$

The experimental data are tabulated in Tables 2 and 3. General correlations are presented in Figs. 12, 13, 14 and 15.

The scattering factor, α , is the optical parameter. It is primarily a measure of the effect of multiple scattering on the light transmittance as measured with the equipment employed in this investigation. For a

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Table 2

SUMMARY OF EXPERIMENTAL DATA

System	Symbol	Refractive Index*		Volumetric Area, sq cm/cu cm	In I_0/I at Specified Optical Path Length		
		Drop Phase	Field Phase		1.0 cm	1.5 cm	2.0 cm
Bromobenzene in Water	▷	1.5575	1.3335	33.2	4.17	5.03	-
Monochlorobenzene in Water	△	1.5221	1.3330	22.5	3.28	3.95	-
				27.7	3.62	4.34	-
Benzene in Water	○	1.4975	1.3332	22.2	2.73	3.33	3.82
				28.5	3.20	3.84	4.32
				35.6	3.56	4.20	4.65
Xylene in Water	◇	1.4877	1.3330	28.8	3.04	3.72	4.25
				34.0	3.57	4.21	4.72
				40.2	3.98	4.59	5.19
Kerosene in Water	○	1.4338	1.3330	49.6	3.49	4.17	4.82
				56.7	3.81	4.60	5.03
				71.5	4.33	5.01	5.62
Cyclohexane in Water	□	1.4181	1.3331	48.3	2.95	3.71	4.27
				52.6	3.28	3.93	4.53
				64.0	3.64	4.26	4.95
				73.3	3.88	4.52	5.35
Methyl Isobutyl Ketone in Water	○	1.3942	1.3349	39.1	2.19	2.66	3.04
				50.6	2.53	3.02	3.45
				62.1	2.87	3.40	3.83
Methyl Isobutyl Ketone in 60% Glycerin-Water	■	1.4118	1.3942	87.1	1.49	1.84	2.22
				91.2	1.68	2.03	2.43
Cyclohexane in 60% Glycerin-Water	▽	1.4182	1.4122	48.1	0.482	0.698	0.815

I_0/I = ratio of incident to emergent light intensities

Experimental data were obtained at 25°C

*Refractive indices of mutually saturated liquids measured at sodium D line

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Table 3

SUMMARY OF EXPERIMENTAL DATA FOR NEAR INFRARED LIGHT SPECTRUM

System	Symbol	Refractive Index*		Volumetric Area, sq cm/cu cm	In I_0/I at Specified Optical Path Length		
		Drop Phase	Field Phase		1.0 cm	1.5 cm	2.0 cm
Monochlorobenzene in Water		1.5221	1.3330	22.5	2.53	3.06	3.51
				27.7	2.84	3.41	4.06
Benzene in Water		1.4975	1.3332	23.8	2.68	3.33	3.94
				27.7	3.10	3.80	4.26
Xylene in Water		1.4877	1.3330	31.4	3.25	3.78	4.39
				42.4	3.73	4.14	4.89
				48.7	4.15	4.44	5.32
Kerosene in Water		1.4338	1.3330	49.6	3.09	3.53	4.20
				56.7	3.36	3.89	4.60
				71.5	3.96	4.48	5.35
Kerosene in Methyl Alcohol		1.4311	1.3427	27.3	-	2.39	-
				36.8	-	2.92	-
				50.3	-	3.34	-
				57.3	-	3.78	-
Cyclohexane in Water		1.4181	1.3331	48.3	2.61	3.09	3.53
				52.6	2.84	3.38	3.77
				64.0	3.24	3.77	4.27
				73.3	3.52	4.06	4.57
Methyl Isobutyl Ketone in Water		1.3942	1.3349	39.1	1.69	2.25	2.59
				50.6	2.01	2.67	3.01
				62.1	2.31	2.89	3.30
Isobutanol in Water		1.3890	1.3416	79.2	2.52	2.99	3.43
				82.0	2.71	3.17	3.69
60% Glycerin-Water in Hexone		1.4118	1.3941	87.1	1.16	1.54	1.84
				92.0	1.37	1.74	2.08
Cyclohexane in Glycerin-Water		1.4182	1.4122	48.1	0.252	0.347	-

I_0/I = ratio of incident to emergent light intensities

Experimental data were obtained at 25°C

*Refractive indices of mutually saturated liquids measured at sodium D line

Fig. 12

General Correlation of Light Transmittance with Volumetric Area for Yellow Light Spectrum

Fig. 13

Scattering Factor, α , as a Function of the Relative Specific Refraction, M , for Yellow Light Spectrum

Fig. 14

General Correlation of Light Transmittance with Volumetric Area for Near Infrared Light Spectrum

Fig. 15

Scattering Factor, α , as a Function of the Relative Specific Refraction, M , for Near Infrared Light Spectrum

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specified light source and detector geometry, the scattering factor was found to be a complex function of the relative refractive index.

Bailey⁽¹⁾ and Rose et al.,⁽¹⁶⁾ working with small (less than 10 microns) solid particles, obtained a satisfactory correlation by presenting their optical parameter as a function of the relative specific refraction, M . The relative specific refraction or Lorenz-Lorentz coefficient is a simple function of the relative refractive index:

$$M = \left| \frac{m^2 - 1}{m^2 + 2} \right| \quad (11)$$

$$m = \frac{\text{refractive index of drop}}{\text{refractive index of field phase}}$$

For the experimental data obtained in this investigation, the Lorenz-Lorentz coefficient proved to be a satisfactory correlating tool for the poly-disperse systems of large spherical particles ranging from 50 to 2000 microns in diameter, as is evident from Figs. 13 and 15. Note that individual correlations were required for the light spectra investigated and that experimental data were obtained only for systems where the relative refractive index was greater than unity.

The area-transmittance data of Rea and Vermeulen⁽¹⁵⁾ for 40 and 20% dispersions were correlated for comparison purposes by means of the exponential relationship (Eq. 8) employed in this investigation. It was found that, by considering each volume fraction individually, their data were correlatable in an exponential form which showed marked improvement over their linear correlation in the case of the data for 40% dispersions. The relative specific refraction (M) was found to be a satisfactory correlating tool for the scattering factors determined for their data, which included oil in water ($m > 1.0$) and water in oil ($m < 1.0$) systems.

The present investigation employed 50% dispersions and the relative refractive index was always greater than unity. It was found that satisfactory correlations of the scattering factor could be obtained with the relative refractive index or the refractive index difference. The Lorenz coefficient was employed because a unique curve was obtained which should hold for values of the relative refractive index greater than or less than one.

The relative refractive index should be evaluated at the wavelength of the incident light. However, a satisfactory correlation was obtained with the refractive index measured at the more convenient sodium D line.

VI. DISCUSSION

A. General Observations

Several observations were made during the course of this investigation. The most interesting of these was in connection with the geometric pattern formed by the light beam as it passed through the emulsion. In passing through the dense dispersions, such as benzene in water, the beam formed a wide angle cone. In systems where the relative refractive index approached unity, such as cyclohexane in glycerin-water, little deformation of the incident collimated beam could be noticed. This cone-shaped pattern of the light beam lends credence to the assumption that the optical parameter, α , is to some extent a measure of the effect of multiple light scattering and should be a function of the relative refractive index. The angle between the cone of light passing through the emulsion and the bottom of the mixing vessel could probably be used to correlate interfacial area data. A simple trigonometric derivation is sufficient to show that a mathematical relationship may exist between the angle of the cone with the base of the vessel and the percentage of light transmitted through the emulsion.

For the conditions of this investigation, the average value of the scattering area coefficient was about 2.1 (see Fig. 1). For a value of K_s of 2.1, the scattering laws predict the essentially complete dispersal, by the concentrated dispersions, of the incident light in less than one centimeter. However, substantial light intensities were measured at one centimeter. The experimentally determined values of the scattering factor (α) were found to be less than the theoretical value of $0.53 (K_s/4)$ by as much as a factor of 50. This shows that multiple scattering and the equipment geometry have an important effect on the observed light transmittance.

The combined effects of geometry and multiple scattering may be assumed to account for the fact that different correlations were necessary for the two light spectra considered. The differences cannot be attributed to a change in the value of the scattering area coefficient. Consideration of Fig. 1 is sufficient to show that the minor difference in the light spectra would have little effect on the scattering area coefficient.

The assumption of a constant scattering area coefficient (K_s) becomes suspect for values of the relative specific refraction (M) less than 0.01. Both correlations include data for systems where M is as low as 0.003. It may be significant that the scattering factor plots deviate from relatively straight lines at the lower values. However, the fact that the curvature is more pronounced in the case of the plot based on the yellow light spectrum is not readily reconciled. Actually, the shorter wavelength of the yellow light spectrum should produce more reliable data for low

values of M than the near infrared spectrum. At low values of M , the ratio of diameter to wavelength becomes increasingly important because, as shown in Fig. 1, the validity of the assumption of a constant K_s increases directly with this ratio.

Perhaps most surprising was the limited range of particle sizes present in any given dispersion. It was evident from the photographs that the particle sizes usually varied by not more than a factor of five. In rare cases, the particle size was found to vary by as much as a factor of fifteen. Generally, the drops appeared to be perfect spheres except in cases where they were relatively large. It was interesting to note that systems characterized by large drops, of the order of 1.5 mm, do not correlate quite as well as others, possibly because of deformation of the large drops.

Investigators have occasionally reported difficulty in deciding which phase is dispersed and which is continuous. It should be borne in mind that a phase present in a volume fraction greater than 0.50 may still be the dispersed phase. The dispersed phase may be detected by simply observing the settling pattern of the dispersion to determine the direction of travel of the droplets towards the interface.

The continuous phase is usually that phase which best wets the mixing vessel. This may explain why the dispersions obtained in this work were oil-in-water with the exception of the MIBK-glycerin-water system, where MIBK (methyl isobutyl ketone) was the continuous phase. In the case of the one run involving two organic liquids, kerosene dispersed in methyl alcohol, the more polar compound, the alcohol, was the continuous phase.

Experimental data for values of the relative refractive index less than unity were not obtained because attempts to develop the required water in oil dispersions at a volume fraction dispersed phase of 0.50 were unsuccessful. Of the systems investigated, the more polar component always exhibited a definite propensity for the role of the continuous phase. In some cases, it was possible to invert the phases by increasing the impeller speed, thereby putting more energy into the system. However, the water in oil dispersions produced by this procedure were unstable. Photographs showed that these dispersions consisted of drops of water in an oil continuum with very small drops of oil suspended in the larger water drops. A typical photograph of a water in oil dispersion is presented in Fig. 16.

Two correlations are presented which were prepared from data obtained with differing effective light spectra. It is difficult to assign a preference to either correlation, there being advantages and disadvantages to both.

It was easier to obtain reproducible results from the 1P41 phototube because it was larger than the sensing probe. Therefore, all light leaving the probe was picked up by the phototube. This was not the case

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Fig. 16

Photograph of Water in Oil Dispersion

Photograph shows a dispersion of water in carbon tetrachloride. Note the presence of small drops of carbon tetrachloride in the larger water drops.

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with the 1P42 phototube, because its diameter was less than that of the sensing probe. The effect of the size of the phototube was most apparent when there was some slight movement of the phototube relative to the sensing probe, caused by the vibration or accidental jarring of the equipment. Any angle between the ends of the 1P42 phototube and the sensing probe would reduce the effective light sensitive area. This effect was much less apparent with the 1P41 phototube simply because of its larger size.

B. Reproducibility of Data

A number of preliminary runs were made which proved that, for any given supply of a liquid pair, a reproducible relationship existed between impeller speed and interfacial area. The small differences in the photographically determined areas for a specified impeller speed were usually less than 5% and well within the limits of the precision of the photographic technique. The existence of the speed-area relationship made it possible to reduce the number of area measurements necessary. At a given impeller speed, transmittance measurements were obtained for several optical path lengths and related to a single area measurement.

Consecutive transmittance readings were reproducible to within 3% and in most cases to within 1%. In the case of duplicate runs, with the same supply of the liquid pair, the introduction of additional variables, such as substitution of probes and readjustment of the optical path length, caused some loss in reproducibility. However, transmittance measurements for these duplicate runs were usually within 3% and rarely varied by as much as 5%.

The reproducibility of duplicate runs with an apparently identical but fresh supply of both liquid phases was subject to the presence of minute quantities of surface active contamination. Unfortunately, the role of surface active agents is not fully understood, but it is known that trace quantities of certain contaminants cause considerable change in settling and mixing characteristics of liquid-liquid systems. In cases where there was contamination, the precision of the usual physical property measurements, including interfacial tension, was not adequate to provide a satisfactory measure of the effect of surface activity. However, the presence of surface activity was qualitatively indicated by the formation of surface films, a marked increase in the dispersion settling time, and a change in the impeller speed-volumetric area relationship.

Examples showing the effect of surface active contamination are given in Table 4. In the first example, MIBK in water, for a given agitator speed the dispersion settling time was increased 500% and the volumetric area 35% because of the presence of contamination. In the second example the light ratios, which are a measure of the volumetric area, showed a marked change. In general, it appears that the settling time was the most sensitive test for contamination.

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Table 4

EXAMPLES SHOWING EFFECT OF SURFACE ACTIVE CONTAMINATION

Example 1: Comparison of runs made on 9-7-54* (contamination present) and 11-19-54 (purified liquids)

System: Methyl isobutyl ketone in water; equal volumes of each phase

Agitator Speed (RPS)	Settling Time (min)		Volumetric Area $\left(\frac{\text{sq cm}}{\text{cu cm}}\right)$	
	Contaminated	Purified	Contaminated	Purified
3.66	0.59	0.11	59.8	-
4.24	0.59	0.12	63.0	46.9
5.45	0.60	0.12	72.8	54.2
7.0	0.60	0.125	-	65.3
8.0	-	0.11	-	80.4

Example 2: Comparison of runs made on 4-24-55** (contamination present) and 4-25-55 (purified)

System: Cyclohexane in water, equal volumes of each phase

Agitator Speed (RPS)	Transmittance Ratio, I_0/I	
	Contaminated	Purified
7.27	34.4	6.33
9.04	56.3	19.9
13.75	126.0	35.0

*Contamination indicated by film on interface and drops clinging to wall of mixing vessel; liquids used in repeat run were purified by distillation.

**Contamination indicated by heavy interfacial film; source of contamination was grease from an impeller shaft bearing, liquids used in both runs originally pretreated by distillation.

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Although surface activity has no effect on the validity of the light transmittance - volumetric area correlation, which depends only on the optical properties of the liquid pair, it was desirable to eliminate or at least minimize contamination. This was especially true in cases where it was desired to check the reproducibility of a system by means of duplicate runs with fresh liquids. For that reason, the previously mentioned rigorous cleansing methods were employed.

In cases where the cleansing procedures were followed and no residual interfacial film or foam could be detected, it was possible to obtain satisfactory reproducibility with a different supply of the liquid pair. Substantiating data are presented in Table 5. These examples are for duplicate runs made after time intervals of several months where there was no indication of surface active contamination in the form of interfacial films or foams. In most cases the photographically determined areas agree within 10%. However, it should be noted that in two cases the areas for a pair of runs appear to differ by a small, fairly constant percentage. This indicated the possibility of minute contamination even after stringent precautions and emphasized the desirability of correlating transmittance data only with area data for that particular run.

Both area and transmittance data used in the correlation were obtained from measurements at the bottom of the mixing vessel. For that reason, there can be little doubt that the photographically determined areas represented the area at the point where the transmittance measurements were obtained. However, even considering the extreme degree of turbulence in these agitated systems, there might be some question concerning the homogeneity of the bulk of the dispersion, particularly near the agitator. To resolve this question a simple test was devised which showed the dispersions to be essentially homogeneous. A portable, one-piece detector-source unit, consisting of phototube and a flash light bulb, was placed in several different locations in the settling cell. Within the limits of experimental precision, no variation in light transmittance was observed, indicating essentially complete homogeneity of the dispersion.

C. Conclusions

Previous investigators working with liquid-liquid or gas-liquid dispersions have suggested empirical linear correlations for transmittance-area data. However, their suggestions were based on limited data. The present work was designed to cover a useful range of relative specific refraction, M , and to provide a sufficient quantity of experimental data to test adequately various methods of interpreting these data. Although attempts to develop linear correlations were unsuccessful, it was established that these data may be correlated by a modified form of the theoretical light extinction exponential equation.

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Table 5

EXAMPLES SHOWING REPRODUCIBILITY OF DATA*

Example 1

System: Methyl Isobutyl Ketone in Water

Volume Fraction: 0.50

<u>3" Agitator Speed, RPS</u>	Volumetric Area $\left(\frac{\text{sq cm}}{\text{cu cm}}\right)$	
	<u>11-19-54</u>	<u>2-16-55</u>
3.66	-	38.3
4.24	46.9	44.1
5.45	54.2	49.9
7.0	65.3	58.3

Example 2

System: Kerosene in Water

Volume Fraction: 0.50

<u>3" Agitator Speed, RPS</u>	Volumetric Area $\left(\frac{\text{sq cm}}{\text{cu cm}}\right)$	
	<u>11-28-54</u>	<u>3-1-55</u>
3.89	51.8	49.6
4.38	61.5	56.7
5.66	83.5	71.5

Example 3

System: Kerosene in Water

Volume Fraction: 0.25

<u>3" Agitator Speed, RPS</u>	Volumetric Area $\left(\frac{\text{sq cm}}{\text{cu cm}}\right)$	
	<u>12-28-54</u>	<u>3-2-55</u>
3.89	-	35.7
4.38	38.4	38.6
5.66	45.1	44.1
7.27	51.7	-

Example 4

System: Cyclohexane in Water

Volume Fraction: 0.50

<u>3" Agitator Speed, RPS</u>	Volumetric Area $\left(\frac{\text{sq cm}}{\text{cu cm}}\right)$	
	<u>12-3-54</u>	<u>3-4-55</u>
3.89	47.0	46.3
4.38	58.0	58.4
5.66	77.5	66.9
7.27	-	74.0

*These data are from runs made with a fresh supply of the liquid pair. The liquids were pretreated by atmospheric or steam distillation in each case.

The generalized correlations (Figs. 12 and 14), which show light transmittance as a function of interfacial area, optical path, and an optical parameter, are valid only for the conditions of this investigation. The physical conditions are: the light source and detector design as shown in Figs. 4 and 5, and the appropriate incident light spectra as shown in Figs. 7 and 8.

Other conditions, as defined by the range of the experimental data and the restrictions imposed by the underlying theoretical and practical considerations, are:

1. Liquids which are transparent in the incident light spectrum.
2. Dispersions consisting of 50% by volume dispersed phase.
3. Systems in which the relative specific refraction (M) is between 0.01 and 0.116.
4. Dispersions in which the smallest particle size present is greater than 50 microns.
5. Dispersions through which the percentage light transmittance ($\frac{I}{I_0} \times 100$) is greater than 0.65%.

The results of this investigation deviated widely from those that may be predicted from theoretical light extinction theory which ignores the effect of multiple light scattering. First, considerably more light reached the detector than would be predicted theoretically. Secondly, the attenuation of the incident light passing through these dispersions was less than would be predicted, as evidenced by the fact that optical path length entered both correlations as reduced power functions. These wide deviations may be attributed to the combined effects of multiple scattering of light, caused by the high concentration of drops, and the equipment geometry.

The correlations with average deviations of less than 6% in area based on transmittance show that the ability of a nonabsorbing liquid-liquid dispersion to transmit light may be of value as a method of estimating the amount of interfacial area present. However, considerable additional work is necessary before this technique can be regarded as a standard service tool. Some criterion of absorbancy, other than simply nonabsorbing liquid, must be established. This is especially important in the case of the near infrared spectrum which extends into the region where water begins to exhibit absorbancy peaks. Also the work should be extended to volume fractions other than 0.50. Work in progress with 25 and 10% dispersions indicates that similar correlations may be developed for these systems.

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NOTATION

- A - interfacial area per unit volume total mixed phases
(volumetric area), sq cm/cu cm
 d - drop diameter, cm
 d_i - drop diameter in interval "i," cm
 d_{sv} - mean surface-volume or sauter drop diameter, cm
 I_0 - incident light intensity
 I - emergent light intensity
 K_s - scattering area coefficient
 L - optical path length, cm
 M - relative specific refraction of drop
(Lorenz-Lorentz coefficient)
 m - relative refractive index of drop
 N_i - number of drops in interval "i"
 n - number of drops per unit volume total mixed phases,
(cu cm)⁻¹
 S - scattering cross section, sq cm
 α - scattering factor (optical parameter)
 β - optical parameter
 ϕ - volume fraction dispersed phase

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APPENDIX

A. Sample Calculations1. Volumetric Area (Interfacial area per unit volume total mixed phases), A

The diameters of between 150 and 300 drops were measured for each determination. These measurements were obtained from photographs of the dispersions and the total number of measurements were normalized to 100 to facilitate comparison of drop size distributions. The magnification factor of the photograph was determined from the image of a metal strip of known dimension which was included in each photograph.

Equations used to calculate volumetric area (A) were:

$$d_{sv} = \frac{\sum N_i d_i^3}{\sum N_i d_i^2} \quad (1)$$

and

$$A = \frac{6\phi}{d_{sv}} \quad (2)$$

The following sample calculation is based on the data of Table 6.

$$d_{sv}(\text{cm}) = \left(\frac{6526}{328.8} \right) \left(\frac{1}{32.8} \right) \left(\frac{1 \text{ cm}}{10 \text{ mm}} \right)$$

$$A = (6) (0.50) \left(\frac{328.8}{6526} \right) \left(\frac{32.8}{1} \right) \left(\frac{10}{1} \right) = 49.6 \frac{\text{sq cm}}{\text{cu cm}}$$

2. Emergent to Incident Light Ratio, I_0/I

The emergent to incident light ratio was calculated directly from readings of a turn counter attached to the helipot resistor shown as item C in Fig. 9. The following example shows the procedure used to obtain incident to emergent light ratios from turn counter readings.

If A = turns required to balance 100 per cent transmittance
(no emulsion present)

B = turns required to balance X per cent transmittance
(emulsion present)

C = turns required to balance zero per cent transmission or
"dark current" (shield over light source, no light reaching photocell)

then

$$\frac{I_0}{I} = \frac{C - A}{C - B}$$

Let

$$A = 0.0155, \quad B = 8.537, \quad C = 8.801$$

Then

$$\frac{I_0}{I} = \frac{8.801 - 0.0155}{8.801 - 8.537} = 32.8$$

Table 6

DETAILED DATA FOR VOLUMETRIC AREA SAMPLE CALCULATION

System: kerosene dispersed in water
Volume Fraction Dispersed Phase = 0.50
Magnification Factor = 32.8

Drop Diameter (mm)	N_i	$N_i(\%)$	$d^2/100$	$d^3/100$	$(N_i \%)d^2/100$	$(N_i \%)d^3/100$
6 - 8	2	0.8	0.49	3.43	0.4	3
8 - 10	8	3.2	0.81	7.29	2.6	23
10 - 12	14	5.6	1.21	13.31	6.8	74
12 - 14	24	9.5	1.69	21.97	16.1	209
14 - 16	46	18.3	2.25	33.75	41.2	618
16 - 18	56	22.2	2.89	49.13	64.2	1091
18 - 20	36	14.3	3.61	68.59	51.6	981
20 - 22	31	12.3	4.41	92.61	54.2	1139
22 - 24	15	6.0	5.29	121.67	31.7	730
24 - 26	6	2.4	6.25	156.25	15.0	375
26 - 28	8	3.2	7.29	196.83	23.3	630
28 - 30	4	1.6	8.41	243.89	13.5	390
30 - 32	1	0.4	9.61	297.91	3.8	119
32 - 34	1	0.4	10.89	359.37	4.4	144
	252	100.2			328.8 sq mm	6526 cu mm

NOTE: Table lists drop diameters as obtained from photographs. The actual drop diameter is the diameter given in the table divided by the magnification factor of the photograph.