Chapter II

Some transparent immiscible liquid pairs

short running title: Transparent immiscible liquid pairs

(To appear in the Journal of Colloid and Interface Science)

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Abstract

This report identifies 121 transparent immiscible liquid pairs that have properties compatible with optical instrumentation based on laser-induced fluorescence. Physical data such as specific gravity, index of refraction, viscosity, flash point, and toxicity were found in the literature. Compatibility with plexiglas (PMMA), contact angles of the internal meniscus on glass and PMMA, meniscus formation times, and clearing times were measured. A useful non-invasive technique for determining interfacial tensions is explained and used. Some dependence of interfacial tension on molecular structure is found.

1 Introduction

The work reported here was undertaken as part of preparation for a proposed space experiment to study the relationship between container geometry and interface geometry for a free liquid surface at zero gravity. The research has involved a search for immiscible liquid pairs having properties compatible with optical instrumentation based on laser-induced fluorescence. The research was also guided by the peculiar requirements of space flight, including especially the prospect that any experiment will be highly automated and will be carried out only once.

In general, the capillary behavior of a liquid-vapor-solid system can be expected to be very sensitive to thermal effects. If the system is not closed or is not in thermodynamic equilibrium, evaporation and condensation at the liquid surface can change the temperature locally. Even in the absence of gravity, temperature inhomogeneities can affect the interfacial tension and thus lead to convective motions in both the liquid and the vapor. Condensation of vapor on the solid surface near a contact line can also produce an anomalous surface condition and thus affect the capillary behavior.

Although these difficulties are reduced in a closed system whose temperature is closely regulated, some means is still required to observe the shape of the capillary surface, including perhaps the static or dynamic contact angle. Either reflective or refractive properties of the interface are normally used for this purpose. However, total light reflection will occur at near-grazing angles of incidence if there is an appreciable discontinuity in index of refraction at the interface or at the container wall. One solution for this total-reflection problem is use of two immiscible liquids with closely matched indices of refraction. For detection of the interface, it is proposed to dissolve a fluorescent dye in one of the liquids and to use a laser light sheet to probe the meniscus by exciting the dye. Preliminary work suggests that this technique is feasible.

In section 2 of this paper, the methods used to select suitable liquids are outlined, and a table is provided of numerous transparent liquids with some of their physical properties. The main content of the paper is an associated table in section 2 of immiscible liquid pairs suitable

for research of the kind contemplated here, and perhaps for other purposes as well, such as experiments with stratified flow. Some approximate measurements of internal contact angle on glass and plexiglas are described in section 3. A non-intrusive technique, used to estimate Bond number and interfacial tension, is outlined in section 4. Some observed trends in the data are related to molecular structure in section 5, and a few comments are made about the reliability of the tables.

2 Liquid Properties

The primitive strategy of the initial search was first to generate lists of transparent liquids that can be classified either as strongly hydrophilic or as strongly hydrophobic, according to their solubility or lack of solubility in water. The hydrophilic group originally consisted of ten liquids, of which two (water and glycerol) were eliminated for reasons stated in the next paragraph. The hydrophobic group originally consisted of 130 liquids, of which 65 survived to be included in the final tables. A number of other hydrophobic liquids were considered but were disqualified on grounds of unsuitable freezing or boiling point, low flash point, lack of optical clarity, known toxicity, or other unattractive properties. It is possible that some of the accepted liquids, particularly formamide and several brominated hydrocarbons, have toxic properties that may eventually disqualify them when they are examined more carefully. In any event, the list of liquid pairs presented here is not claimed to be definitive.

Each liquid of one group was tested for miscibility with each liquid of the other group. The miscibility test consisted of placing approximately one milliliter of each liquid of a pair in a pyrex culture tube with a teflon-lined screw cap (VWR Scientific Catalog (1): Kimble: 45066A). The liquids remained in contact for a year or more, and were repeatedly mixed (emulsified) by vigorous shaking. There were several grounds for rejection of a liquid pair:

mutual solubility estimated as more than a few percent (some mutual solubility may be desirable);

chemical reaction, including discoloration (rare);

failure to de-emulsify or clear in a reasonable time (including especially persistence of a frost-like emulsion on the wall near the internal contact line);

permanent deposition of droplets of either liquid on the tube wall under the other liquid (water and glycerol were rejected on this ground).

Table I summarizes some physical properties of the 8 hydrophilic and 65 hydrophobic liquids, listed in each case in order of increasing specific gravity. In almost all cases the name assigned to a chemical is the popular name. An official identification number taken from the Chemical Abstracts Service register is also listed. The specific gravity (usually measured at 20°C) and the index of refraction (usually measured at 20°C for the sodium D line) are weighted in favor of values listed in the CRC Handbook of Chemistry and Physics (2). Default values are from the current Aldrich catalog (3) or from the Merck Index (4). The code for toxic hazard is from Sax (5). Values for flash point are taken from the Aldrich catalog (3) or from Sax (5). The property that is least certain in the table is the viscosity (measured or interpolated at 20°C except where noted). In some cases, no value for viscosity could be found in the literature even after a diligent computer search.

Of the 1300 pairs tested, 121 were found to be acceptable according to the criteria already mentioned. These pairs are listed in Table II in order of increasing nominal difference in index of refraction. Observations or estimates are provided for several other properties, including meniscus formation time and clearing time, and contact angle on glass and plexiglas. Estimates of interfacial tension, determined from measurements of meniscus height and contact angle, are also provided.

3 Measurements

In Table I, the entry for compatibility with plexiglas or poly(methylmethacrylate) or PMMA is the result of a test in which small strips of this material were partially immersed in each liquid for several months. This test was motivated by the fact that plexiglas is a popular material in some experimental work where these liquids may be used. The approximate meaning of the entries is:

good -- no readily apparent effect;

fair -- some swelling or softening and/or very slow crazing;

poor -- severe crazing; partial or complete solubility; occasional gel formation.

All of the hydrophilic liquids, and about half of the hydrophobic liquids, are judged to be compatible with PMMA. These combine to provide 66 compatible liquid pairs.

In Table II, the entries for meniscus formation time represent the time required for the two liquids to form a smooth, well-defined meniscus after vigorous shaking. The clearing time represents the additional time required for both liquids to become essentially clear. A clearing time of zero means that no emulsion was present after the meniscus was fully formed.

Direct measurements were made, using a cathetometer with a rotating angular eyepiece, of the height and the contact angle on borosilicate culture-tube glass of the internal meniscus for each liquid pair. These measurements are used in section 4 to estimate the interfacial tension. If the meniscus was concave upward, the contact angle refers to the lower liquid. If the meniscus was concave downward, the contact angle refers to the upper liquid and is enclosed in parentheses in Table II. It is worth noting that the hydrophilic liquid is always on the convex side of the interface in all the liquid pairs considered here. To remove distortion caused by refraction at the glass-air interface of the cylindrical culture tube, the tube was mounted in a square glass cell, and the intervening space was filled with a mixture of methanol and methyl benzoate whose composition was adjusted until the index of refraction closely matched that of the culture tube. Various modes of lighting were tried for observation of the meniscus, and diffuse polychromatic light was finally judged to be more effective than parallel and/or monochromatic light. Fig. 1 is a photograph of the culture-tube wall and a portion of the interface and contact region for 1-chlorohexane over formamide. The index of the matching solution has been deliberately detuned to show the location of the outer culture-tube wall.

There is a systematic distortion of the meniscus in Fig. 1. To analyze this distortion at a rudimentary level, assume that the culture tube is lighted from the rear by a diffuse light source and is viewed from a large distance using telescopic optics. The meniscus is convex to one of

the liquids, whose index of refraction n_i is assumed to be smaller than the index n_o of the culture tube and cell (this is the case for all of the liquid pairs in Table II). Fig. 2 shows a light ray that touches the interface and emerges from the cell along the line of sight. The geometry of the figure yields immediately the series of proportionalities

$$\frac{n_i}{n_o} = \frac{\sin\theta_o}{\sin\theta_i} = \frac{r'/L}{r/L} = \frac{r'}{r} \qquad [1]$$

of which the first is Snell's law of refraction. Thus the apparent radial position r' of the meniscus is related to the real position r by the affine transformation $r' = r\,\frac{n_i}{n_o} < r$, and the real contact angle γ is related to the apparent angle γ' by

$$\gamma = \tan^{-1}\left[\frac{n_o}{n_i}\tan\gamma'\right] \qquad [2]$$

This correction was applied to all of the measured contact angles. In most cases, the correction was less than 0.5 degrees, which is well within the estimated accuracy of ± 2 degrees for the measurement.

To obtain a rough estimate of the internal contact angle on PMMA, strips of this plastic were inserted into the culture tubes containing the 66 compatible pairs. The new contact region was viewed edge on, as in the photograph in Fig. 3, which shows diethyl diethylmalonate over formamide. The measured contact angles were in general larger and covered a wider range than those for glass. The inflection of the interface in the figure (the inversion of the contact angle) is typical for all but a few of the liquid pairs. Examination of the whole of the data suggests that the inversion is a result of stronger bonding of the hydrophilic liquid to glass compared with bonding of the hydrophobic liquid. In the few cases where inversion of the interface did not occur; the contact angle increased, but not past the 90 degrees required for inversion.

4 Non-intrusive Determination of Interfacial Tension

The dimensionless number that is characteristic of capillary phenomena is the Bond number, which is essentially the ratio of gravitational force to surface-tension force;

$$B = \frac{\Delta\rho\, g\, L^2}{\sigma} \qquad [3]$$

In this equation $\Delta\rho$ is the difference in density for two liquids separated by an interface, g is the acceleration of gravity, L is a characteristic length (here taken as the radius of the culture tube, 0.57 cm), and σ is the interfacial tension.

In the present context, all of the quantities in Eqn. [3] are known except B and σ. If the Bond number can be estimated, a value for the interfacial tension follows. The necessary estimate can be obtained from an analysis carried out by P. Concus (6) to determine the geometry of an equilibrium capillary surface inside a vertical cylinder of circular cross section. Along a diameter, the interface elevation $z(r)$ is determined by the capillary equation

$$\frac{1}{r}\frac{d}{dr}\left[\frac{r\, dz/dr}{[1+(dz/dr)^2]^{1/2}}\right] - Bz - \lambda = 0 \qquad [4]$$

where λ is a constant equal to twice the radius of curvature of the interface on the axis, where $r = z = 0$. All lengths are made dimensionless with L. The boundary conditions are

$$z = 0, \quad \frac{dz}{dr} = 0 \quad \text{at} \quad r = 0 \qquad [5]$$

$$z = h, \quad \frac{dz}{dr} = \cot\gamma \quad \text{at} \quad r = 1 \qquad [6]$$

where h is the meniscus height and γ is the contact angle. Concus used a shooting method to integrate Eqn. [4] and provided plots of h and λ as functions of B for fixed contact angles of 0 (10) 80 degrees. In the present work, the quantities h and γ are assumed to be known from the optical measurements. The same numerical methods used by Concus were applied to implement a two-parameter search for the quantities B and λ. Concus's plots

established a suitable starting point, given the measured contact angle and meniscus height. The values inferred for σ from Eqn. [3], using values of $\Delta\rho$ derived from Table I, are included in Table II.

5 Discussion and Conclusions

The properties listed in Tables I and II for the various liquids and liquid pairs should not be accepted uncritically. The culture tubes were not cleaned but were used as received, because the primary objective at the outset of the work was to identify acceptable liquid pairs. The manufacturer (Kimble; division of Owens, Illinois) states that the screw-top culture tubes were annealed at high temperature, hot enough to burn off organic deposits, before being packaged in sealed cardboard boxes. On arrival, the tubes were found to be clean, except for the occasional occurrence of fibers. The chemicals were purchased in small quantities, were not tested for purity, and in a few cases were labelled as "tech" or "pract" grade. Due to the large number of chemicals used and the small volume of each, custom purification of each liquid considered was simply out of the question. Handbook values for specific gravity or index of refraction were sometimes found to be inconsistent from one authority to another. For example, the four best visible matches in index of refraction, as judged by eye in terms of a weak color band as a vestigial indicator of interface position, are marked by asterisks in Table II. In one case, a pair having a difference in nominal index of 0.009 appeared to the eye to be much more closely matched than pairs having identical nominal indices. Nevertheless, the tables should be useful in making a preliminary choice of liquid pairs whose properties can then be established more rigorously for a particular application. The tables should also be useful in suggesting combinations (of pairs) that might be used to allow close control over either the difference in specific gravity or the difference in index of refraction or both.

Statements about compatibility of the various liquids with PMMA should also be treated as preliminary. Impurities in the various liquids may be a factor, and there are numerous formulations of PMMA. Considerable care may be required in fabrication of PMMA containers, including stress-relieving during and after machining to minimize crazing.

The measured contact angle itself may be in error by as much as two degrees in either direction. A more serious uncertainty in the measurement of contact angle arises from lack of control over the purity of the chemicals. One or two experiences with a second measurement of contact angle for a given liquid pair, but with one or both chemicals obtained from different vendors, showed discrepancies amounting to several degrees. More precise work aimed at a particular application therefore implies suitable care in specifying the purity of the liquids and the cleanliness of the container.

Errors in the measurements of contact angle γ and meniscus height h must be considered before determining the overall accuracy to which the Bond number is known. For an error of two degrees in contact angle, the error in Bond number varies from 28 percent to 5 percent as the Bond number varies from 1 to 60. It is important to note that the error in Bond number is also dependent upon the size of the angle being measured. A $\pm 2°$ error in a larger contact angle yields a larger error in the Bond number; this is demonstrated in Fig. 4 by the convergence of the Bond number curves as the contact angle approaches 90°. Therefore, the largest errors in Bond number occur for large contact angles and small Bond numbers. An error of 0.004 cm in the measurement of the meniscus height produces an error in Bond number of 10 percent to 7 percent over the same range. For Bond numbers greater than 10, the error due to contact angle measurement is less than 7 percent, while the error due to meniscus height measurement is also less than 7 percent. Note that these two errors are independent. The relative error in σ is the same as the error in B. For the test case, described in the following paragraphs, the Bond number was approximately 4. The estimated error in B computed for the average contact angle and meniscus height was approximately 22 percent, which is consistent with the observed spread in the data reported in Table III and displayed in Fig. 4.

A reviewer suggested that contact angles and therefore interfacial-tension measurements would be very sensitive to the cleanliness of the glass. The method described in this paper was therefore tested for a few liquid pairs for which interfacial tensions have been found in the literature. These liquid pairs were organic liquids; namely, heptanol, nonanol, decanol, benzene, ethyl ether, and carbon tetrachloride, all paired with water. The interfacial tensions quoted in the literature are for mutually saturated liquids, and the liquid pairs used in this test

were therefore emulsified several times to ensure mutual saturation. However, only carbon tetrachloride with water was found to be even marginally suitable for the technique used here. This liquid pair would have been rejected according to the specifications listed in section 2. The three alcohols were rejected because of the persistence of a frost-like emulsion on the wall near the contact line. Benzene and ethyl ether were rejected because their meniscus heights were of the order of the measurement resolution. The pair carbon tetrachloride and water tended to deposit droplets of either liquid on the tube wall under the other liquid. However, by rotating the inclined tube slowly, these droplets could be reduced in size and number, so that contact-angle and meniscus-height measurements could be performed with reasonable satisfaction. The method used was the same as for all the other measurements reported here.

This test also included a comparison of interfacial-tension values obtained from carefully cleaned tubes and tubes that were used as received. For this purpose, one tube was cleaned according to procedure 'C' as specified by Scientific Specialties Service (7). The tube was washed in biodegradable laboratory glassware cleaner, rinsed thoroughly with tap water, rinsed with 1:1 nitric acid, rinsed with triple distilled deionized water, air dried, and assembled in an organic-free environment. One milliliter of spectro-photometric grade carbon tetrachloride and one milliliter of triple-distilled deionized water were added to each tube. Measurements at ten circumferential locations were made of each interface after the liquids had been in contact for more than two weeks and had been shaken several times. The results of these measurements, given in Table III, indicate that cleaning of the tube reduces the dispersion in the data from 28 percent to 23 percent, and also yields an interfacial tension that is closer to the value interpolated from Harkins and Cheng (8). Nevertheless, the results obtained indicate that a reasonable estimate of the interfacial tension can be achieved by this method without first cleaning the tube.

Determination of the interfacial tension using the technique described here depends on measurement of both the contact angle γ and the meniscus height h. In calculations using the method of Concus (6), the Bond number is assumed fixed, although its value has to be determined. The Bond number is a dimensionless indicator of meniscus shape. Therefore, h and γ have a well-defined (nearly linear) relationship for fixed Bond number. This same

relationship turned out to be satisfied by the observed values of h and γ in the test just described. Fig. 4 shows the observed values of h and γ and the curves of constant Bond number for B = 5.06, 4.15, and 3.24 from bottom to top. These curves were calculated by fixing γ and B and shooting λ to find the meniscus height at the tube wall. The Bond number used to compute the solid curve, was found by a line fit to all the data. The dotted curves represent the estimated error in the Bond number caused by the uncertainty in the contact-angle and meniscus-height measurements. Note that the observed contact angle for the water/carbon tetrachloride pair in the cleaned culture tube varied from 19° to 48° at the ten points around the circumference, and from 26° to 63° for the tube used as received. However, in the main body of experiments reported in Table II, two contact-angle measurements were made 180° apart, and these contact angles rarely differed by more than the estimated accuracy of ±2° about the mean value. The eight cases where the contact angle difference was larger than ±2° but not more than ±4° are indicated by daggers † in Table II. Therefore the estimates of interfacial tension reported in Table II are dependable to the stated accuracy, unless indicated by daggers.

The interfacial tensions found for the 121 liquid pairs in Table II cover a broad range of values. The value of the interfacial tension for a particular liquid pair is a measure of the relative strength of intra-fluid attractions and inter-fluid attractions. A useful parameter is the hydrophilicity index (Table IV), which is the ratio of the number of OH groups to the number of carbon atoms in the molecule. A higher hydrophilicity index implies greater intra-fluid attraction and higher interfacial tension when paired with hydrophobic liquids. Indeed, this general trend was found, as recorded in Tables V and VI. Esters and ketones tended to have lower interfacial tensions than saturated hydrocarbons when paired with the same hydrophilic liquids. This observation indicates that inter-fluid forces are stronger between hydrophilic liquids paired with esters or ketones than they are for the same hydrophilic liquids paired with saturated hydrocarbons, probably because of oxygen-to-hydrogen attraction across the interface. The position of the OH groups on the hydrophilic molecules was also found to be important, as recorded in Table VII. When the OH groups are located on the first and second carbons, as for 1,2-propanediol, rather than the first and third, as for 1,3-propanediol, the interfacial tension is decreased dramatically. Note that dipropylene glycol was omitted from these tables, since it formed only one acceptable immiscible pair. Formamide was also omitted, because although it

formed many successful liquid pairs, its structure is very different from the other hydrophilic liquids and therefore does not lend itself well to comparison. A final note is that the three alcohols, octanol, nonanol, and decanol, formed acceptable immiscible pairs only with formamide. Alcohols have non-zero hydrophilicity indexes and stronger inter-fluid attraction when paired with hydrophilic liquids; hence greater solubility.

In summary, 121 suitable liquid pairs have been found. They exhibit a wide range of contact angles, interfacial tensions, and viscosities. In addition, 66 of these pairs are compatible with plexiglas. Suggested relationships between molecular structure and interfacial tension may aid in the extension of Table II and in the choice of a liquid pair best suited to a specific application. The method described here for determination of the interfacial tension may be adequate if other more intrusive techniques are not feasible.

This material is based upon work supported by the U.S. National Aeronautics and Space Administration and the University of California. The opinions, findings, conclusions and recommendations are those of the authors and not necessarily of the U.S. National Aeronautics and Space Administration or the University of California.

References

1. VWR Scientific Catalog 84/85, p 1551.

2. Weast, R.C. (ed.), "CRC Handbook of Chemistry and Physics (59th edition)". CRC Press, West Palm Beach, Florida, 1978.

3. "Aldrich Catalog Handbook of Fine Chemicals (1984-1985)". Aldrich Chemical Co., Milwaukee, Wisconsin, 1984.

4. Windholz, M. (ed.), "The Merck Index (9th edition)". Merck and Co., Rahway, New Jersey, 1976.

5. Sax, N., "Dangerous Properties of Industrial Chemicals (6th edition)". Van Nostrand Reinhold, New York, 1984.

6. Concus, P., *J. Fluid Mech.* **34**, 481-495 (1968).

7. Scientific Specialties Service Inc. Randallstown, MD 21133. Pre-Cleaned Bottle Book 1988, p 16.

8. Harkins, W.D. and Cheng, Y.C., *J. Amer. Chem. Soc.* **43**, 35-53 (1923).

Figure Captions

Figure 1 Internal meniscus against borosilicate glass culture tube (1-chlorohexane over formamide).

Figure 2 Ray trace diagram of affine contraction.

Figure 3 Internal meniscus inversion from borosilicate glass culture-tube wall to PMMA blade (diethyl diethylmalonate over formamide).

Figure 4 Meniscus height versus contact angle for water/carbon tetrachloride. (Contact angle measured in upper liquid) Bond number = 5.06, 4.15, and 3.24 from bottom to top.

Table I
Collected physical properties of some transparent liquids

[ ]	=	Chemical Abstracts Service identification number.
SG	=	specific gravity, usually measured at 20 °C and referred to water at 4 °C.
IR	=	index of refraction, usually measured at 20 °C for the yellow D line of sodium.
ν	=	kinematic viscosity, usually at 20 °C, in stokes (cm^2/sec). (ν^*, computed from formulas, usually with reference to experimental data; ν^{25}, viscosity at different temperature, usually 25 °C; ν^+, extrapolated or interpolated from experimental data.)
Toxic hazard	=	symbol from Sax (4). Usually refers to 50-percent lethal dose in laboratory animals ("3" means 0.04-0.4 g/kg: "2" means 0.4-4 g/kg: "1" means 4-40 g/kg). More than one code means that the chemical is more toxic to some species of laboratory animals than to others.
Flash point	=	usually closed cup in °F, from Aldrich catalog (2) where possible.
Compat PMMA	=	compatibility with unstressed plexiglas = poly(methylmethacrylate). ("good", no easily visible effect; i.e., the chemical can be stored in a PMMA container; "fair", noticeable crazing, swelling, or softening; "poor", severe interaction, often in a period of minutes.)

Name [CAS number]	SG	IR	ν cm^2/sec	Toxic hazard	Flash point °F	Compat PMMA
			HYDROPHILIC LIQUIDS			
1,5-pentanediol [111-29-5]	0.992	1.449	1.290	1	265	good
dipropylene glycol [106-62-7]	1.021	1.440	0.746^{25}	1	280	good
1,2-propanediol [57-55-6]	1.036	1.432	0.541	3-2-1	225	good
1,3-propanediol [504-63-2]	1.060	1.440	0.440	1	175	good
ethylene glycol [107-21-1]	1.109	1.432	0.179	2-1	230	good
diethylene glycol [111-46-6]	1.116	1.447	0.320	3	290	good
triethylene glycol [112-27-6]	1.124	1.453	0.436	3-1	330	good
formamide [75-12-7]	1.133	1.447	0.034	3	310	good
			HYDROPHOBIC LIQUIDS			
octane [111-65-9]	0.703	1.397	0.008	1	60	good
nonane [111-84-2]	0.718	1.405	0.010	3	88	good
decane [124-18-5]	0.730	1.410	0.012	3	115	good
1-decene [872-05-9]	0.741	1.422	0.011	--	118	good

1-octyne [629-05-0]	0.746	1.416	0.008^{25}	--	64	fair
4-octyne [1942-45-6]	0.751	1.425	--	--	68	good
dihexyl ether [112-58-3]	0.794	1.420	0.016*	1	170	good
2,6-dimethyl-4-heptanone [108-83-8]	0.805	1.413	0.012	2-1	120	good
squalane [111-01-3]	0.808	1.453	0.467	--	424	good
2-heptanone [110-43-0]	0.811	1.409	0.010	2-1	117	poor
4-heptanone [123-19-3]	0.817	1.407	0.009	2	120	poor
3-heptanone [106-35-4]	0.818	1.406	--	2	106	poor
2-octanol [123-96-6]	0.819	1.420	0.098	3	160	good
2-octanone [111-13-7]	0.820	1.415	0.013+	2	145	poor
5-nonanone [502-56-7]	0.822	1.420	0.016	2	141	good
3-octanone [106-68-3]	0.822	1.415	--	3	115	fair
4-decanone [624-16-8]	0.824	1.424	--	--	160	good
1-nonanol [143-08-8]	0.827	1.433	0.135	2-1	168	good
1-decanol [112-30-1]	0.830	1.437	0.172	3	180	good
isopropyl myristate [110-27-0]	0.853	1.435	0.066	3	--	good
isobutyl isobutyrate [97-85-8]	0.854	1.400	0.010^{25}	2-1	111	good

ethyl laurate [106-33-2]	0.862	1.431	0.039	--	234	good
isopropylbenzene [98-82-8]	0.862	1.492	0.009	2	115	poor
ethyl caprate [110-38-3]	0.865	1.426	0.027[+]	1	216	good
ethyl isovalerate [108-64-5]	0.866	1.396	--	2-1	80	poor
ethyl caprylate [106-32-1]	0.869	1.418	0.018	1	167	good
methyl laurate [111-82-0]	0.870	1.432	0.036	--	235	good
butyl butyrate [109-21-7]	0.871	1.408	0.012	2-1	128	good
2-ethylhexyl acetate [103-09-3]	0.872	1.420	0.017	2	187	good
methyl caprylate [111-11-5]	0.878	1.417	0.026	1	163	good
1-chlorohexane [544-10-5]	0.879	1.420	0.008	--	80	good
ethyl butyrate [105-54-4]	0.879	1.400	0.008	1	67	poor
methyl caproate [106-70-7]	0.885	1.405	0.010	--	113	poor
butyl acrylate [141-32-2]	0.890	1.419	0.010[*]	2	103	poor
bis(2-ethylhexyl) adipate [103-23-1]	0.922[25]	1.447	0.140[+]	--	380	good
dibutyl carbonate [542-52-9]	0.925	1.412	0.019[25]	--	--	fair
dibutyl sebacate [109-43-3]	0.937	1.442	0.096	1	353	good
dibutyl adipate [105-99-7]	0.962	1.437	0.037[38]	1	--	good

dipropyl adipate [106-19-4]	0.979	1.431	--	--	--	poor
diethyl diethylmalonate [77-25-8]	0.988	1.424	0.038	--	202	good
diethyl pimelate [2050-20-6]	0.994	1.431	0.040	--	235	poor
dipropyl succinate [925-15-5]	1.002	1.425	--	3-1	--	poor
diethyl adipate [141-28-6]	1.008	1.427	0.035	2	235	poor
dimethyl azelate [1732-10-1]	1.008	1.437	0.050	--	--	poor
butyl benzoate [136-60-7]	1.010	1.496	0.021^{38}	2-1	225	fair
dipentyl phthalate [131-18-0]	1.024	1.489	0.321^{+}	--	245	good
glycerol tributanoate [60-01-5]	1.035	1.436	0.112	3	345	good
ethyl benzoate [93-89-0]	1.047	1.501	0.021	2-1	184	poor
dimethyl adipate [627-93-0]	1.060	1.428	0.031	--	225	poor
diethyl maleate [141-05-9]	1.066	1.442	0.033	2	200	poor
1-bromodecane [112-29-8]	1.070	1.456	0.024^{+}	--	202	good
2-phenylethyl acetate [103-45-7]	1.088	1.517	0.022^{25}	3	230	poor
methyl benzoate [93-58-3]	1.089	1.516	0.019	2-1	181	poor
glycerol tripropanoate [139-45-7]	1.098	1.432^{19}	0.130	2	--	poor
1,5-dichloropentane [628-76-2]	1.101	1.456	0.016	3	80	poor

1-bromooctane [111-83-1]	1.112	1.452	0.015	1	173	good
1-bromohexane [111-25-1]	1.174	1.448	0.009	--	135	good
1-bromo-3-methylbutane [107-82-4]	1.207	1.442	0.006^{+}	--	90	fair
2-bromopentane [107-81-3]	1.208	1.441	--	3	69	fair
1-bromopentane [110-53-2]	1.218	1.445	0.007	3	88	poor
2-bromobutane [78-76-2]	1.259	1.437	0.005^{+}	3	70	poor
1-bromobutane [109-65-9]	1.276	1.440	0.005	1	75	poor
bromocyclohexane [108-85-0]	1.336	1.496	0.017	--	145	good
1-bromopropane [106-94-5]	1.354	1.434	0.004	1	78	poor
1,1,2-trichlorotrifluoro-ethane [76-13-1]	1.575	1.358	0.005	2	high	good

Table II
Capillary properties of some immiscible liquid pairs

CA	=	internal contact angle on borosilicate glass or on poly(methylmethacrylate), degrees.
Men. form	=	time required for formation of internal meniscus, minutes.
$\sigma_{int.}$	=	interfacial tension of internal meniscus, dynes/cm (see section 4).
Clear	=	time required for liquid pair to become clear after meniscus is formed, minutes.
SG	=	specific gravity, upper liquid/lower liquid (usually measured at 20°C and referred to water at 4°C).
IR	=	index of refraction, upper liquid/lower liquid (usually measured at 20°C for the yellow D line of sodium).

LIQUID PAIRS

NAMES	CA glass (deg)	CA PMMA (deg)	Men. form. (min)	$\sigma_{int.}$ dyne/cm	Clear (min)	SG	IR
glycerol tripropanoate / ethylene glycol	15	-	2.3	0.9	0	1.098 / 1.109	1.432 / 1.432
bis (2–ethylhexyl) adipate / formamide	13	(70)	3.0	14.4	80	0.922 / 1.133	1.447 / 1.447 *
1,3–propanediol / 1–bromobutane	(13)	-	4.8	9.7	60	1.060 / 1.276	1.440 / 1.440
methyl laurate / ethylene glycol	10	(37)	1.2	10.8	60	0.870 / 1.109	1.432 / 1.432
methyl laurate / 1,2–propanediol	11	(24)	3.0	4.1	0	0.870 / 1.036	1.432 / 1.432
1,3–propanediol / 2–bromopentane	9	-	4.0	9.7	120	1.060 / 1.208	1.440 / 1.441
ethyl laurate / ethylene glycol	15	(44)	1.0	10.1	0	0.862 / 1.109	1.431 / 1.432
dipropyl adipate / ethylene glycol	16	-	1.4	7.0	0	0.979 / 1.109	1.431 / 1.432
1,5–pentanediol / 1–bromohexane	(8)	28	5.3	3.7	240	0.992 / 1.174	1.449 / 1.448
ethyl laurate / 1,2–propanediol	13	(59)	6.7	3.9	0	0.862 / 1.036	1.431 / 1.432
dipropyl adipate / 1,2–propanediol	29	-	4.4	0.3	18	0.979 / 1.036	1.431 / 1.432
diethylene glycol / 1–bromohexane	(7)	44	6.0	5.5	120	1.116 / 1.174	1.447 / 1.448
diethyl pimelate / ethylene glycol	27	-	1.9	1.7†	0	0.994 / 1.109	1.431 / 1.432
1,3–propanediol / 1–bromo –3–methylbutane	(10)	-	5.0	9.6†	60	1.060 / 1.207	1.440 / 1.442
1,3–propanediol / diethyl maleate	(15)	-	6.9	2.1	0	1.060 / 1.066	1.440 / 1.442

diethylene glycol / 1–bromopentane	(7)	-	2.0	4.9	180	1.116 / 1.218	1.447 / 1.445
bis (2–ethylhexyl) adipate / 1,5–pentanediol	9	(43)	8.5	5.3	180	0.922 / 0.992	1.447 / 1.449
dibutyl sebacate / 1,3–propanediol	30	(33)	6.0	14.1	0	0.937 / 1.060	1.442 / 1.440
ethylene glycol / 1–bromopropane	(18)	-	4.8	10.1	0	1.109 / 1.354	1.432 / 1.434
1–bromodecane / triethylene glycol	11	86	8.2	6.1	60	1.070 / 1.124	1.456 / 1.453
1,5–pentanediol / 1–bromooctane	(12)	54	5.0	7.0	0	0.992 / 1.112	1.449 / 1.452 *
dimethyl azelate / 1,3–propanediol	13	-	2.7	5.0	120	1.008 / 1.060	1.437 / 1.440
dimethyl adipate / ethylene glycol	11	-	2.1	2.1	12	1.060 / 1.109	1.428 / 1.432
glycerol tributanoate / ethylene glycol	13	(18)	1.6	8.4	12	1.035 / 1.109	1.436 / 1.432
1,5–pentanediol / 1–bromopentane	(8)	-	1.6	5.8	180	0.992 / 1.218	1.449 / 1.445
glycerol tributanoate / 1,2–propanediol	8	(8)	11.5	0.3	1680	1.035 / 1.036	1.436 / 1.432
1,3–propanediol / 1–bromopentane	(12)	-	4.6	8.9	60	1.060 / 1.218	1.440 / 1.445
diethyl adipate / ethylene glycol	16	-	2.0	3.6	0	1.008 / 1.109	1.427 / 1.432
1,2–propanediol / 2–bromobutane	(49)	-	1.1	2.9†	60	1.036 / 1.259	1.432 / 1.437
diethylene glycol / 1–bromo –3–methylbutane	(5)	-	3.2	5.8	240	1.116 / 1.207	1.447 / 1.442
dimethyl azelate / ethylene glycol	9	-	1.5	5.2	120	1.008 / 1.109	1.437 / 1.432
isopropyl myristate / dipropylene glycol	23	13	3.5	1.7	60	0.853 / 1.021	1.435 / 1.440
1–bromooctane / formamide	9	(59)	5.8	13.6	180	1.112 / 1.133	1.452 / 1.447 *

squalane / formamide	16	(35)	60.0	14.1	120	0.808 / 1.133	1.453 / 1.447
1,3–propanediol / 1–bromopropane	(17)	-	0.8	7.9	120	1.060 / 1.354	1.440 / 1.434
ethyl caprate / 1,2–propanediol	18	(57)	3.1	4.2	60	0.865 / 1.036	1.426 / 1.432
bis (2–ethylhexyl) adipate / triethylene glycol	12	(89)	1.8	6.4	80	0.922 / 1.124	1.447 / 1.453
dipropyl succinate / ethylene glycol	26	-	2.2	0.1†	60	1.002 / 1.109	1.425 / 1.432
4–octyne / ethylene glycol	18	(27)	3.1	6.7	16	0.751 / 1.109	1.425 / 1.432
diethylene glycol / 1–bromobutane	(19)	-	2.5	3.5	120	1.116 / 1.276	1.447 / 1.440
1,5–pentanediol / 1,5–dichloropentane	(5)	-	4.4	5.7	120	0.992 / 1.101	1.449 / 1.456
1,5–pentanediol / 1–bromo –3–methylbutane	(9)	-	2.2	8.7	240	0.992 / 1.207	1.449 / 1.442
formamide / 1–bromobutane	(6)	-	5.8	41.4	120	1.133 / 1.276	1.447 / 1.440
bis (2–ethylhexyl) adipate / 1,3 propanediol	10	(50)	9.1	10.5	180	0.922 / 1.060	1.447 / 1.440
1,5–pentanediol / 1–bromodecane	(8)	63	8.0	8.3	120	0.992 / 1.070	1.449 / 1.456
1,2–propanediol / 1–bromobutane	(15)	-	2.1	5.4	18	1.036 / 1.276	1.432 / 1.440
4–decanone / ethylene glycol	11	(38)	0.8	9.3	0	0.824 / 1.109	1.424 / 1.432
1,3–propanediol / 1–bromohexane	(10)	31	5.0	10.8	120	1.060 / 1.174	1.440 / 1.448
ethylene glycol / 1–bromobutane	(9)	-	4.1	14.9	18	1.109 / 1.276	1.432 / 1.440
4–decanone / 1,2–propanediol	20	(42)	2.3	2.7	0	0.824 / 1.036	1.424 / 1.432
diethyl diethylmalonate / ethylene glycol	10	(16)	1.0	7.8	180	0.988 / 1.109	1.424 / 1.432

1,5–dichloropentane / formamide	11	-	4.6	large	120	1.101 / 1.133	1.456 / 1.447
1,2–propanediol / 2–bromopentane	49	-	1.3	4.6	60	1.036 / 1.208	1.432 / 1.441 *
ethylene glycol / 2–bromopentane	(6)	-	3.8	19.8	20	1.109 / 1.208	1.432 / 1.441
ethyl laurate / 1,3–propanediol	13	(37)	2.3	7.2	180	0.862 / 1.060	1.431 / 1.440
1,5–pentanediol / 1–bromobutane	(8)	-	2.3	5.6	180	0.992 / 1.276	1.449 / 1.440
diethyl maleate / ethylene glycol	14	-	1.9	3.8	12	1.066 / 1.109	1.442 / 1.432
1,2–propanediol / 1–bromo –3–methylbutane	24	-	3.4	4.8	120	1.036 / 1.207	1.432 / 1.442
ethylene glycol / 1–bromo –3–methylbutane	(8)	-	3.7	16.6	60	1.109 / 1.207	1.432 / 1.442
1–decanol / formamide	12	(54)	1.7	5.5	20	0.830 / 1.133	1.437 / 1.447
dibutyl sebacate / 1,2–propanediol	14	(42)	3.0	3.9	180	0.937 / 1.036	1.442 / 1.432
dibutyl adipate / formamide	15	(28)	1.7	6.7	80	0.962 / 1.133	1.437 / 1.447
dimethyl azelate / formamide	14	-	1.0	3.2	0	1.008 / 1.133	1.437 / 1.447
glycerol tributanoate / diethylene glycol	14	(25)	3.9	2.4	120	1.035 / 1.116	1.436 / 1.447
glycerol tributanoate / formamide	12	(15)	4.8	7.2	12	1.035 / 1.133	1.436 / 1.447
1–chlorohexane / ethylene glycol	15	(24)	1.5	5.7	60	0.879 / 1.109	1.420 / 1.432
5–nonanone / ethylene glycol	18	(28)	1.2	9.8	13	0.822 / 1.109	1.420 / 1.432
2–ethylhexyl acetate / ethylene glycol	10	(25)	1.2	7.1	120	0.872 / 1.109	1.420 / 1.432
1,3–propanediol / dimethyl adipate	(8)	-	8.7	0.1	1680	1.060 / 1.060	1.440 / 1.428

2–ethylhexyl acetate / 1,2–propanediol	14	(19)	2.2	1.4	360	0.872 / 1.036	1.420 / 1.432
1,5 pentanediol / 2–bromobutane	(67)	-	0.7	5.2†	180	0.992 / 1.259	1.449 / 1.437
1,2–propanediol / 1–bromopentane	(11)	-	1.8	4.2†	120	1.036 / 1.218	1.432 / 1.445
ethylene glycol / 1–bromopentane	(4)	-	3.8	11.7	120	1.109 / 1.218	1.432 / 1.445
isopropyl myristate / diethylene glycol	12	(49)	2.9	9.7	60	0.853 / 1.116	1.433 / 1.447
ethyl caprylate / 1,2–propanediol	14	(45)	1.8	2.9	270	0.869 / 1.036	1.418 / 1.432
1–nonanol / formamide	9	(58)	1.0	4.9	60	0.827 / 1.133	1.433 / 1.447
bis (2–ethylhexyl) adipate / 1,2–propanediol	8	(69)	2.5	4.9	120	0.922 / 1.036	1.447 / 1.432
1–octyne / ethylene glycol	17	-	0.9	7.1	15	0.746 / 1.109	1.416 / 1.432
ethyl laurate / diethylene glycol	10	(73)	5.2	5.0	60	0.862 / 1.116	1.431 / 1.447
2–octanone / ethylene glycol	9	-	0.6	7.3†	120	0.820 / 1.109	1.415 / 1.432
dihexyl ether / dipropylene glycol	13	14	2.5	1.5†	120	0.794 / 1.021	1.420 / 1.440
dibutyl carbonate / 1,2–propanediol	19	-	1.3	3.3	1440	0.925 / 1.036	1.412 / 1.432
2–heptanone / ethylene glycol	12	-	0.7	7.1	60	0.811 / 1.109	1.409 / 1.432
4–decanone / diethylene glycol	19	(50)	1.1	4.2	60	0.824 / 1.116	1.424 / 1.447
diethyl diethylmalonate / diethylene glycol	12	(15)	4.6	2.5	120	0.988 / 1.116	1.424 / 1.447
4–decanone / formamide	9	(61)	0.3	3.8	0	0.824 / 1.133	1.424 / 1.447
diethyl diethylmalonate / formamide	9	(29)	0.3	7.1	20	0.988 / 1.133	1.424 / 1.447

1–decene / formamide	10	(50)	3.5	8.3	60	0.741 / 1.133	1.422 / 1.447
3–heptanone / ethylene glycol	10	-	0.9	8.0	12	0.818 / 1.109	1.406 / 1.432
2–octanol / formamide	13	(47)	1.5	4.2	120	0.819 / 1.133	1.420 / 1.447
dihexyl ether / formamide	8	90	0.3	19.4	60	0.794 / 1.133	1.420 / 1.447
1–chlorohexane / formamide	8	(68)	1.6	20.9	60	0.879 / 1.133	1.420 / 1.447
2–ethylhexyl acetate / formamide	12	(27)	0.4	7.9	20	0.872 / 1.133	1.420 / 1.447
butyl acrylate / formamide	13	-	0.2	10.0	12	0.890 / 1.133	1.419 / 1.447
ethyl caprylate / formamide	9	(54)	0.4	12.8	240	0.869 / 1.133	1.418 / 1.447
4–decanone / triethylene glycol	13	(52)	1.4	3.8	18	0.824 / 1.124	1.424 / 1.453
methyl caprylate / formamide	12	(39)	0.7	10.6	240	0.878 / 1.133	1.417 / 1.447
2–octanone / formamide	11	-	0.3	5.8	12	0.820 / 1.133	1.415 / 1.447
3–octanone / formamide	18	-	0.3	9.7	13	0.822 / 1.133	1.415 / 1.447
2–ethylhexyl acetate / triethylene glycol	12	(49)	1.3	2.6	120	0.872 / 1.124	1.420 / 1.453
2,6–dimethyl–4–heptanone / formamide	12	(54)	0.7	10.8	12	0.805 / 1.133	1.413 / 1.447
decane / diethylene glycol	11	72	5.5	12.8	1440	0.730 / 1.116	1.410 / 1.447
butyl butyrate / formamide	12	(44)	0.8	10.9	1440	0.871 / 1.133	1.408 / 1.447
4–heptanone / formamide	17	-	0.2	7.2	18	0.817 / 1.133	1.407 / 1.447
2,6–dimethyl–4–heptanone / triethylene glycol	13	(49)	2.0	3.5	270	0.805 / 1.124	1.413 / 1.453

dipentyl phthalate / diethylene glycol	10	(26)	5.5	2.9	240	1.024 / 1.116	1.487 / 1.447
methyl caproate / formamide	9	-	0.5	6.2	12	0.885 / 1.133	1.405 / 1.447
nonane / formamide	8	(89)	2.2	28.3	120	0.718 / 1.133	1.405 / 1.447
dipentyl phthalate / formamide	14	(41)	8.2	12.9	180	1.024 / 1.133	1.489 / 1.447
octane / 1,3–propanediol	10	(88)	2.7	13.2	60	0.703 / 1.060	1.397 / 1.440
decane / triethylene glycol	12	61	4.0	13.1	180	0.730 / 1.124	1.410 / 1.453
isopropylbenzene / formamide	12	-	2.6	19.3	120	0.862 / 1.133	1.492 / 1.447
ethyl butyrate / formamide	12	-	0.5	5.5	0	0.879 / 1.133	1.400 / 1.447
formamide / bromocyclohexane	(13)	34	0.6	21.6	12	1.133 / 1.336	1.447 / 1.496
butyl benzoate / formamide	10	-	15.0	13.8	180	1.010 / 1.133	1.496 / 1.447
ethyl isovalerate / formamide	12	-	0.2	9.5	12	0.866 / 1.133	1.396 / 1.447
isobutyl isobutyrate / triethylene glycol	20	(58)	2.2	3.1	80	0.854 / 1.124	1.400 / 1.453
ethyl benzoate / formamide	14	-	0.9	7.9	120	1.047 / 1.133	1.501 / 1.447
methyl benzoate / formamide	13	-	2.1	9.5	0	1.089 / 1.133	1.516 / 1.447
2–phenylethyl acetate / formamide	10	-	2.0	3.4	20	1.088 / 1.133	1.517 / 1.447
triethylene glycol / Freon 113	(15)	(74)	1.9	4.5	60	1.124 / 1.575	1.453 / 1.358

* Freon 113 = 1,2,2-trifloro-1,1,2-trichloroethane

Culture tube	σ estimated (28^{o}C) (dynes/cm)	Error from published* value: 44.2 dynes/cm
as received	49.7 ± 14.0	12%
cleaned	46.0 ± 10.7	4%

*(interpolated from Harkins and Cheng (8))

Table III

Interfacial tension measurements for water/CCl_4

	Hydrophilicity Index $\left(\frac{\#\ OH}{\#Carbon}\right)$
ethylene glycol	1.00
1,3 propanediol	0.67
1,2 propanediol	0.67
diethylene glycol	0.50
1,5 pentanediol	0.40
dipropylene glycol	0.33
triethylene glycol	0.33
formamide	0.00

Table IV

Hydrophilicity index of hydrophilic compounds

	Hydrophilicity Index (# OH / # Carbon)	Esters				Ketone	Saturated Hydrocarbons			
		2-ethylhexyl acetate	glycerol tributanoate	ethyl laurate	diethyl diethyl malonate	4-decanone	1-bromobutane	1-bromo-3-methyl butane	1-bromopentane	decane
ethylene glycol	1.00	7.1	8.4	10.1	7.8	9.3	14.9	16.6	11.7	---
diethylene glycol	0.50	---	2.4	5.0	2.5	4.2	3.5	5.8	4.9	12.8
triethylene glycol	0.33	2.6	---	---	---	3.8	---	---	---	13.1

Table V

Decrease of interfacial tension (dyne/cm) with decreasing hydrophilicity

	Hydrophilicity Index (# OH / # Carbon)	Esters					Saturated Hydrocarbons					
		dimethyl adipate	diethyl maleate	dimethyl azelate	ethyl laurate	bis (2-ethylhexyl) adipate	1-bromopropane	1-bromobutane	1-bromo-3-methyl butane	1-bromopentane	2-bromopentane	1-bromohexane
ethylene glycol	1.00	2.1	3.8	5.2	10.1	---	10.1	14.9	16.6	11.7	19.8	---
1,3-propanediol	0.67	0.1	2.1	5.0	7.2	10.5	7.9	9.7	9.6	8.9	9.7	10.8
1,5-pentanediol	0.40	---	---	---	---	5.3	---	5.6	8.7	5.8	---	3.7

Table VI

Decrease of interfacial tension (dyne/cm) with decreasing hydrophilicity

	Hydrophilicity Index (# OH/ # Carbon)	Esters			Sat. Hydrocarbons			
		ethyl laurate	dibutyl sebacate	bis (2-ethylhexyl) adipate	1-bromobutane	1-bromo-3-methyl butane	1-bromopentane	2-bromopentane
1,3-propanediol	0.67	7.2	14.1	10.5	9.7	9.6	8.9	9.7
1,2-propanediol	0.67	3.9	3.9	4.9	5.4	4.8	4.2	4.6

Table VII

Dependence of interfacial tension (dyne/cm) on OH placement

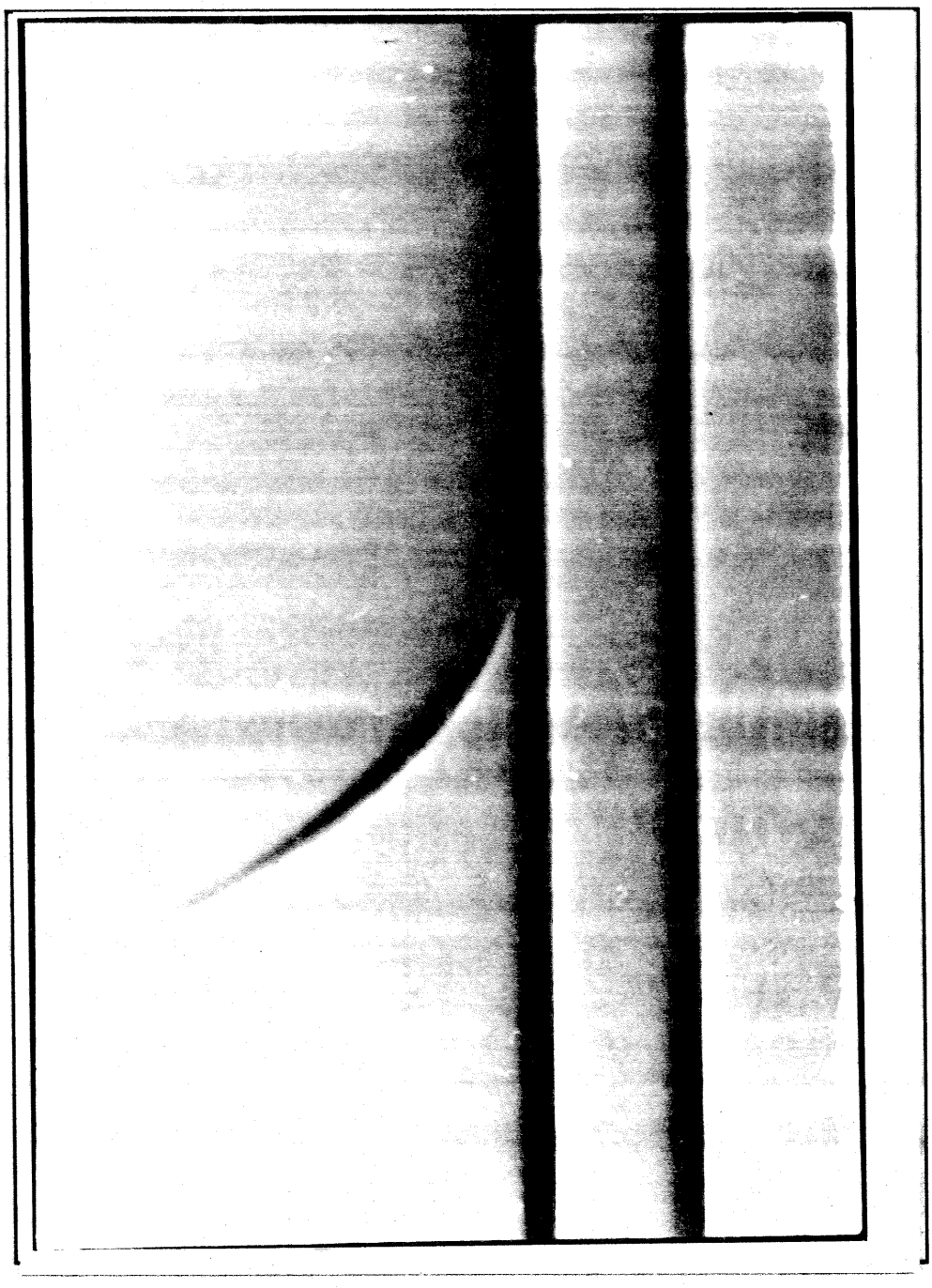

Figure 1

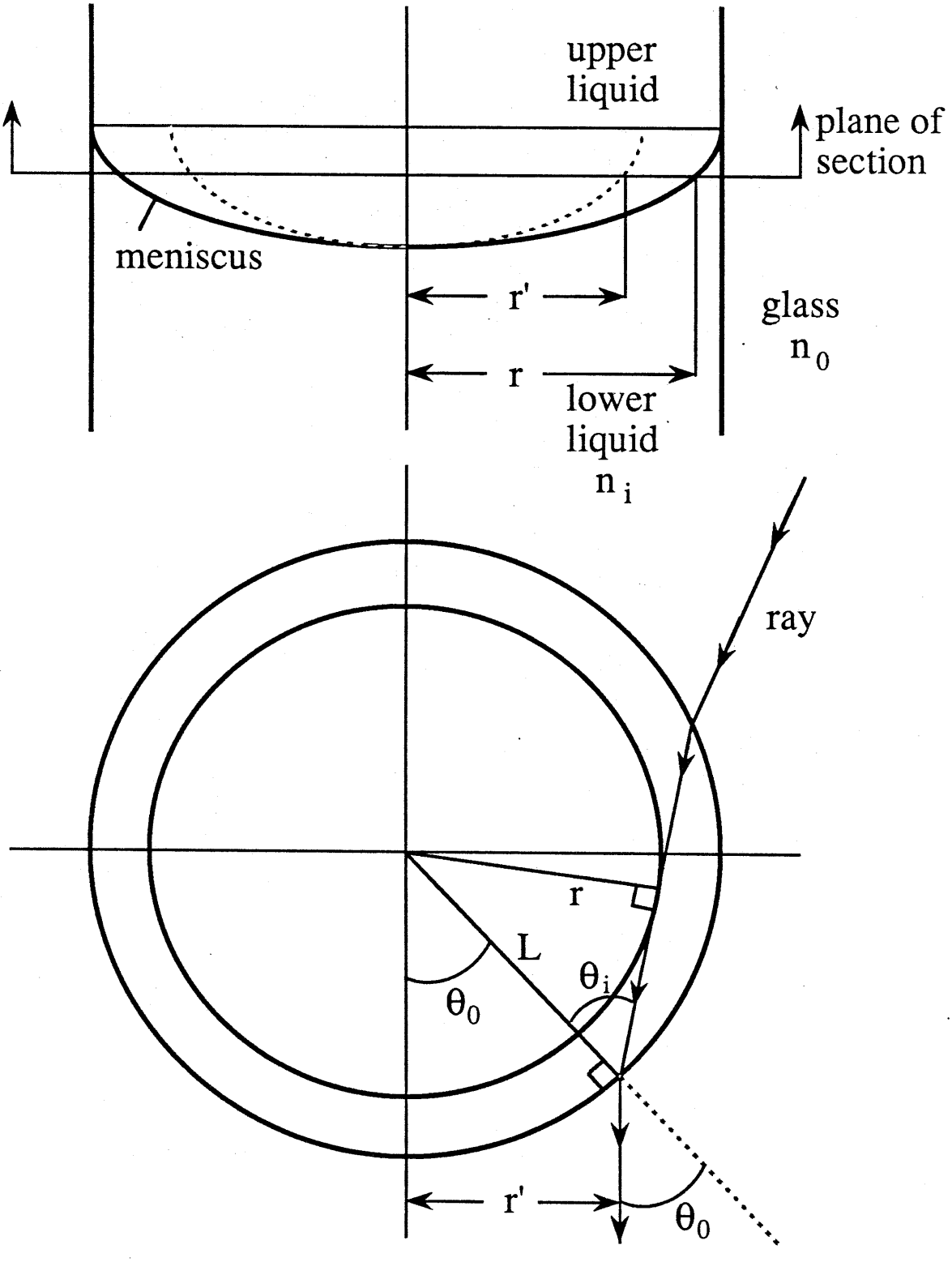

Figure 2 Ray-trace diagram of affine contraction

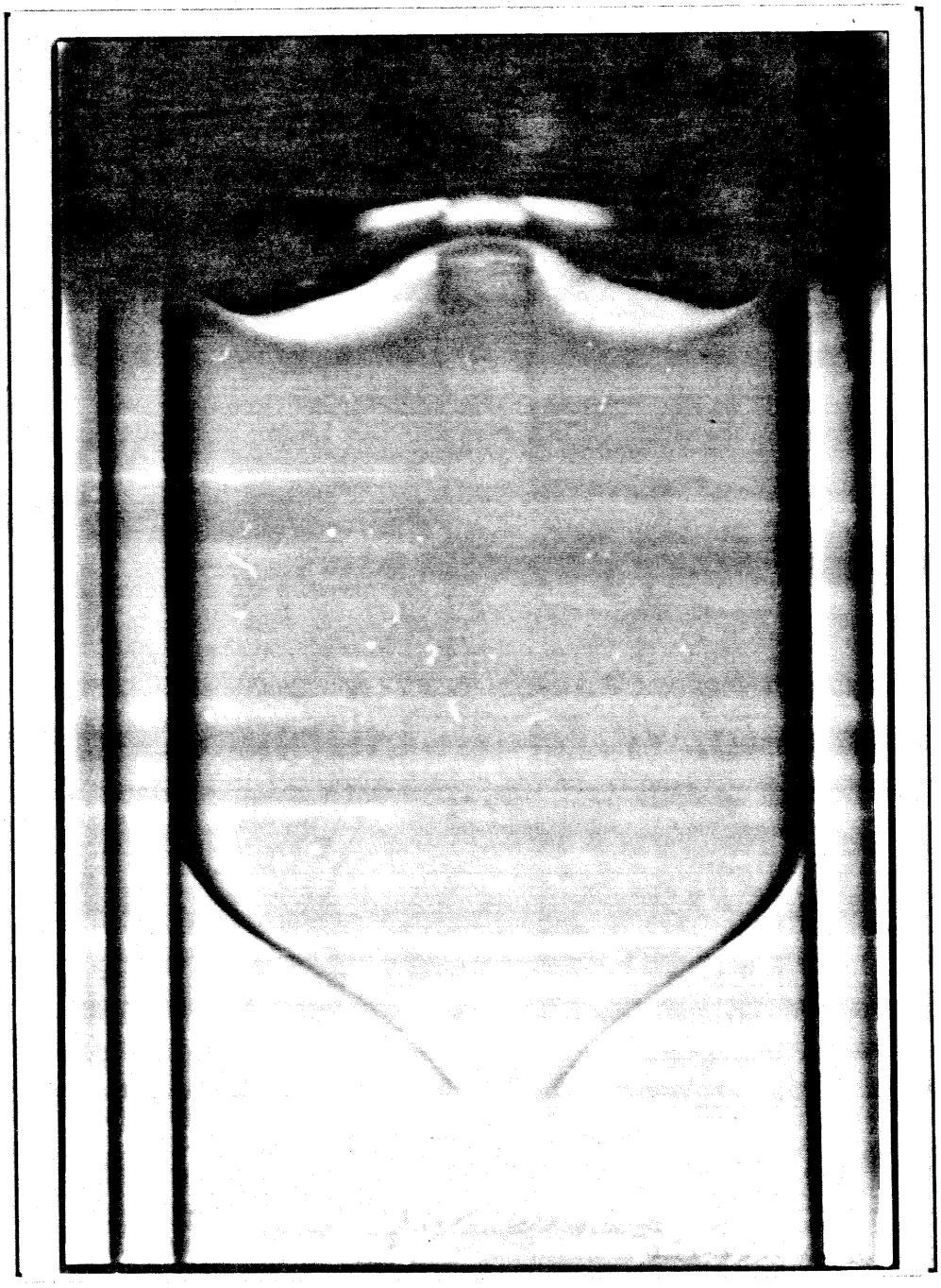

Figure 3

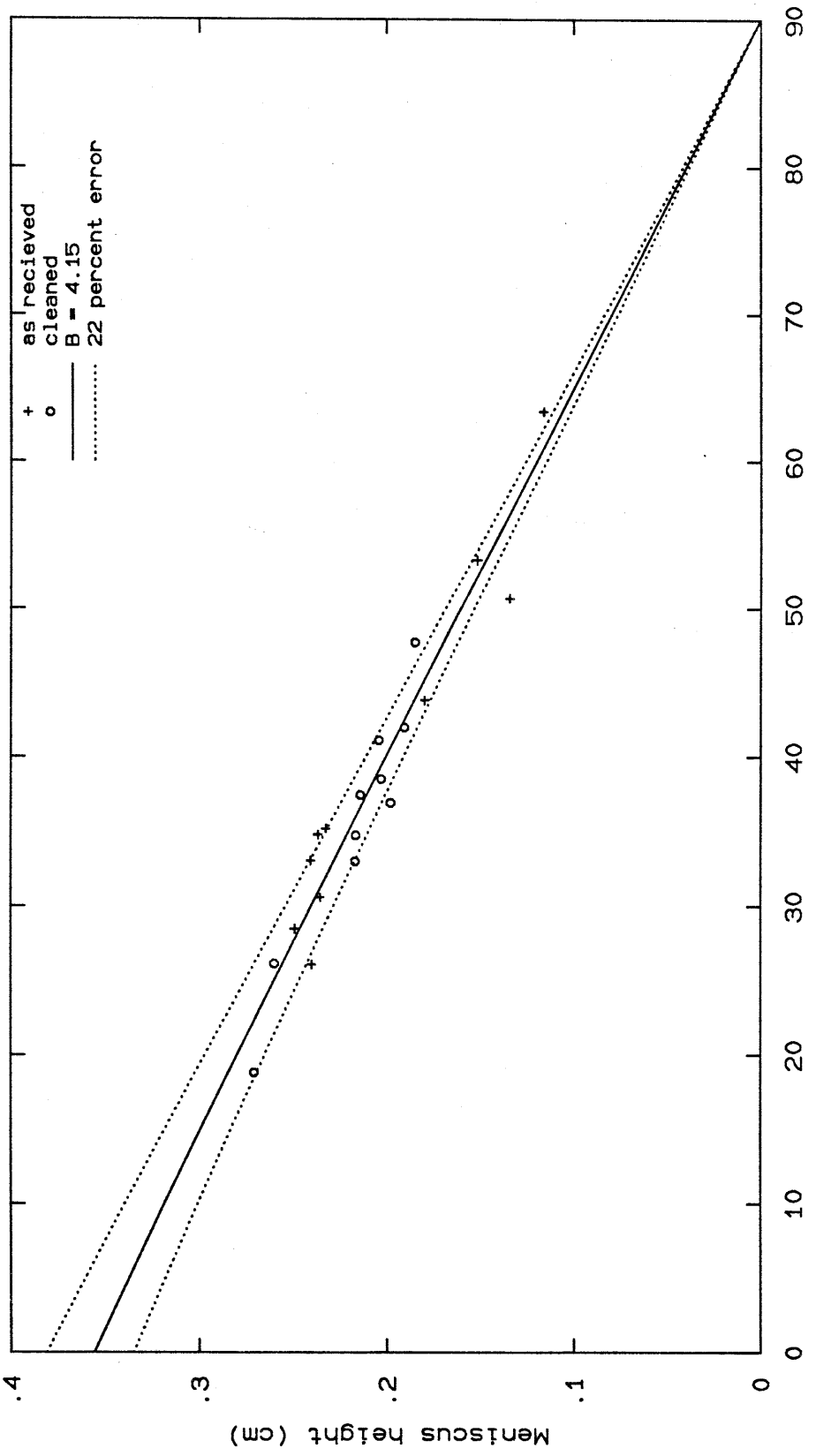

Figure 4 Meniscus height vs. contact angle for water/carbon tetrachloride
Bond number = 5.06, 4.15, and 3.24 from bottom to top