One of us (G. B. Heisig) wishes to acknowledge a financial grant from the Fluid Research Funds of the Graduate College to aid in carrying out this work.

The authors wish to express their appreciation of the interest in and criticisms of the work by Dr. H. S. Taylor and Dr. H. Eyring.

Summary

The reaction between equivalent amounts of butadiene and bromine has been studied in small, medium and large spheres on "glass" and paraffined surfaces.

The rate of the reaction increases until the vapor pressure of the 1,4-dibromobutane formed is reached and the walls are covered by a unimolecular layer and then becomes constant.

The constancy of the product (*kd*) of the velocity constants (*k*) for a dimolecular reaction (calculated from the time that sufficient 1,4-dibromobutene is formed to saturate the gases and form a unimolecular layer on the surface, "glass" or paraffin) and the diameters of the spheres is evidence for a surface reaction.

The identity of the product (*kd*) of the velocity constants and the diameters of the "glass" and paraffined spheres indicates that the reaction must occur on a surface of reaction product rather than the wall itself and this is further proved by the small value of the velocity constant in the paraffined spheres in which an insufficient amount of reaction product is formed to coat the surface.

The large values of the velocity constants for the reaction in the packed spheres is further evidence for the reaction occurring at the surface.

The question is raised as to whether the reaction surface is actually glass in Norrish's studies of the reaction between ethylene and chlorine.

MINNEAPOLIS, MINN. RECEIVED MARCH 11, 1935

[CONTRIBUTION NO. 189, DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

Relation of Surface Tension to other Physical Properties of Liquid Mixtures

BY R. M. CONRAD AND J. L. HALL

Although attention has been called to the antibatic relation of surface tension to vapor pressure[1] and to compressibility[2] no attempt has been made to establish which of these two relations takes precedence in systems of completely miscible liquids where deviations from the ideal occur in surface tension, compressibility, or vapor pressure data. Obviously a serious difficulty arises in selecting systems which may demonstrate the unobscured relation of two properties to each other without any possible correlation with the third. Such investigations are made further difficult because of the scarcity of compressibility data. A simple apparatus has been designed for the purpose of measuring compressibility directly under pressures of two to three atmospheres. Compressibility measured under such low pressures was felt to be better suited for comparison with surface tension under atmospheric conditions than the high pressure data obtainable in some instances.

Fortunately a system was found which exhibited wide deviation from the normal in one of these properties but followed close to the ideal in the other two. Methanol–chloroform mixtures show wide deviation from the normal in respect to their vapor pressure data, as might be expected from the fact they form a minimum boiling mixture. Surface tension and compressibility data, however, were nearly ideal, indicating that this correlation has unquestionably greater significance in this system of liquids than the relation of vapor pressure to either compressibility or surface tension. This system was found to be strictly ideal with respect to density and index of refraction also, but it was radically abnormal with respect to fluidity.

Experimental Procedure

A technical grade of chloroform was extracted with concentrated sulfuric acid until the washings were no longer discolored. The chloroform was then refluxed for a short time over quicklime and distilled through an efficient fractionating column. The middle fraction, boiling within a 0.3° range covering the accepted boiling point given by the "International Critical Tables," was reserved and immediately made up into the mixtures with methanol.

A C. P. grade of methanol was taken through the standard procedure of preparing absolute alcohol and frac-

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[1] Worley, *J. Chem. Soc.*, **105**, 273 (1914).

[2] Freundlich, "Colloid and Capillary Chemistry," translated from third German edition, 1922, E. P. Dutton Co., New York, p. 78.

tionated to conform to the same standards set for the chloroform.

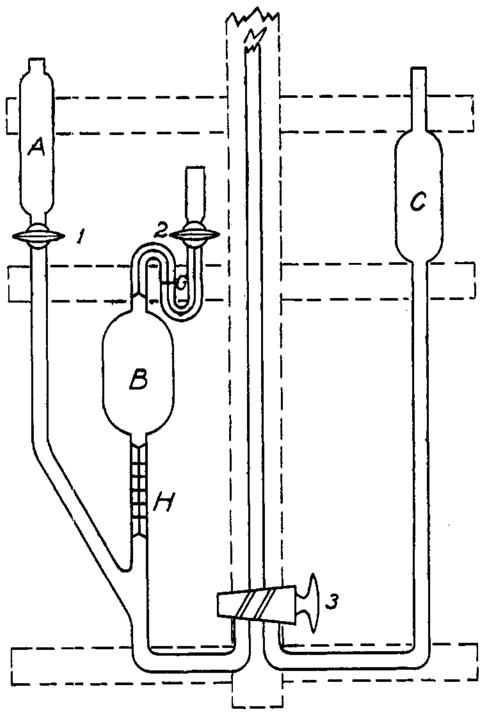

Fig. 1.—Design of apparatus for direct measurement of compressibility of liquids.

The mixtures were made up by weighing the portions directly in hooded glass-stoppered bottles. They were then stored in a dark cupboard until ready for use. All measurements were made at 25 ± 0.05°.

Density measurements were made with a vacuum walled pycnometer. The mixtures and the pycnometer were brought to temperature in the thermostat. Air buoyancy corrections were made to density *in vacuo*.

Surface tension was determined by measuring the capillary height with a traveling microscope and using the apparatus described by King, Hall and Ware.[3]

Fluidity was determined in an Ostwald viscosity pipet standardized with conductivity water.

Index of refraction was measured with a Bausch and Lomb Abbe refractometer using light from a mercury arc and referring readings to the D line by setting the instrument at 1.3325 for conductivity water. The instrument was also checked with a standard test plate. Temperature was controlled by siphoning water from the thermostat through the water jacket of the refractometer.

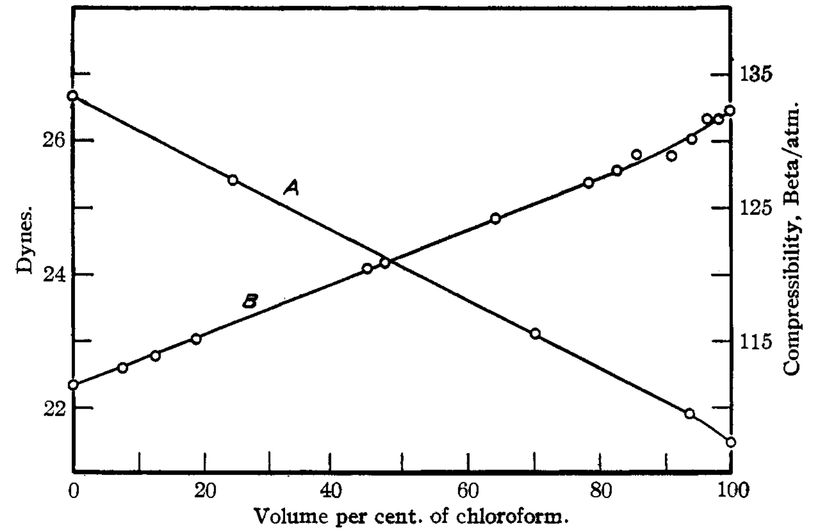

Fig. 2.—Chloroform–methanol mixtures: A, compressibility; B, surface tension.

Vapor pressures were determined on a Van Slyke blood gas analysis apparatus, by measuring directly the pressure of the vapor in contact with its liquid against a Torricellian vacuum. Water from the thermostat was circulated through the jacket surrounding the reaction pipet. Foreign gases were removed from the sample by alternately evacuating and returning to atmospheric pressure, forcing out any bubbles present with part of the sample, until the pressure reached a constant value. The pressures could be duplicated to 1 mm., which was accurate enough to show very clearly the character of the vapor pressure curve. The readings were corrected for the depth and pressure of the liquid sample, the final measurements always being made against a 0.5-cc. sample with the mercury brought to the 2-cc. mark in the pipet. The zero point on the manometer scale was found by opening both sides of the manometer to atmospheric pressure. But since the temperature correction for density of mercury in the manometer would amount to less than 1 mm. in every case, it was neglected.

Compressibility was determined in a specially constructed apparatus shown in Fig. 1, by measuring with a traveling microscope the linear expansion of the sample through a capillary when the pressure was reduced from two or three atmospheres to barometric pressure.

Referring to the drawing, the operation was as follows. The sample is placed in reservoir A, the mercury forced below the junction of the tubes from A and B, and the sample run into B by opening stopcocks 1 and 2. When the compression limb had been filled above stopcock 2, mercury was forced through stopcock 3 from the manometer until it stood near the middle of capillary H, and well past the junction into the tube to A. Stopcock 3 was closed, and by applying pressure at A, the mercury was forced high enough in H so that when a drop of mercury was introduced at 2 and drawn down to the mark in the center vertical section of capillary G, the manometer mercury stood near the lower end of capillary H. The drop of mercury was then drawn back and forth through

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(3) King, Hall and Ware, THIS JOURNAL, 52, 5128 (1930).

the stopcock 2 several times to sweep all the sample out of the region of the stopcock. The two limbs of the compression member were then brought to pressure equilibrium by opening stopcocks 1 and 2 simultaneously. Mercury equivalent to 1, 2 or 3 atmospheres was then forced into the manometer by turning 3 so as to connect the manometer with C, and applying air pressure to C. With stopcocks 1 and 2 closed, pressure was next applied to the sample by connecting the manometer to B through stopcock 3. The mercury level in H was measured by a traveling microscope, and when this level became constant, stopcock 3 was closed and 1 was opened, releasing the pressure in the pipet; the level in H was again immediately measured. The difference in levels corresponds to the expansion of the sample in B. The capillary cross section at every half centimeter had been determined previously, by measuring the length of a weighed pellet of mercury in it. The volume of the compression pipet had been previously determined by the weight of water it contained at 25° corrected for air buoyancy. The bulb B was constructed from heavy-walled Pyrex tubing 35 mm. in diameter. The pressure change was simply the difference in height of the mercury in the manometer and in the side arm leading to A, corrected for the pressure of the overlying excess sample; for pressure equilibrium had previously been allowed in the two limbs of the compression member, A and B. Since the manometer and side arm were substantially the same size, capillary effects were equalized. Compressibility was calculated by the following expression

$$\beta = \frac{-10^6}{V}\left(\frac{\Delta V}{\Delta P}\right)$$

The apparatus was a one-piece Pyrex glass construction, mounted on a structural iron support. The manometer was supported on a 3.2 cm. channel iron 2.7 meters long.

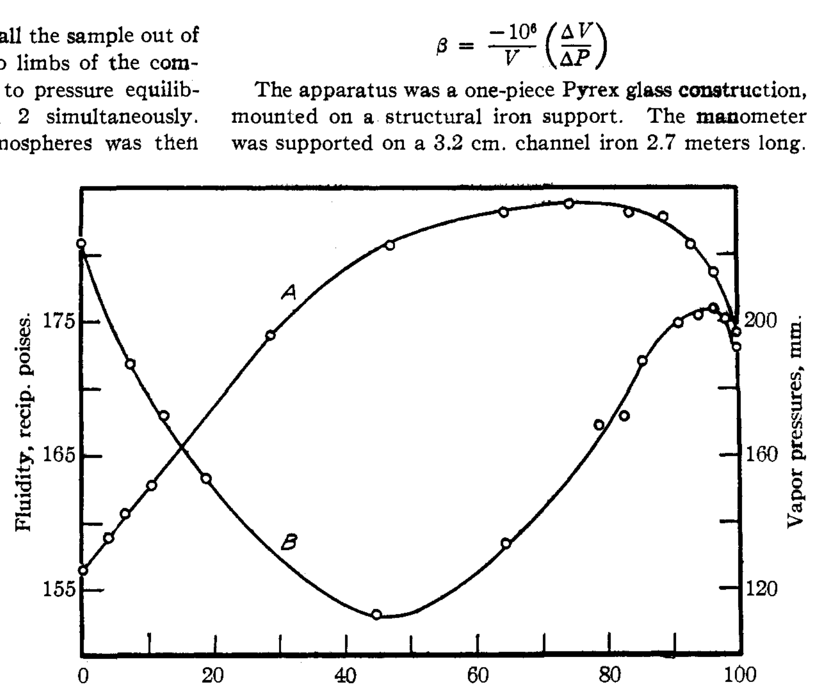

Fig. 3.—Chloroform–methanol mixtures: A, vapor pressure–mole percentage diagram; B, fluidity–volume percentage diagram.

The apparatus was firmly mounted on supports bolted to the top of the thermostat.

The principal difficulty encountered was in maintaining a sufficiently constant temperature, as a change of 0.1° introduces an error of approximately 100% at the pressure used. In using a Freas thermostat at 25° and with the room temperature at 23–25°, the bath cooled from 25.03 to 24.97° in ten or fifteen minutes, which was a much too rapid temperature change to permit accurate determinations. However, when the room temperature was held at 28° and a loose cover was laid over the thermostat, it took two to three hours for the water-bath to cool through the same range. Under these conditions, the mercury in the capillary was observed with the sample under pressure until it came to a constant level for several minutes. The pressure was then released, and the height in H read again as soon as possible—in less than a minute from the time of the previous reading. These readings gave values for volume change very slightly affected by temperature changes.

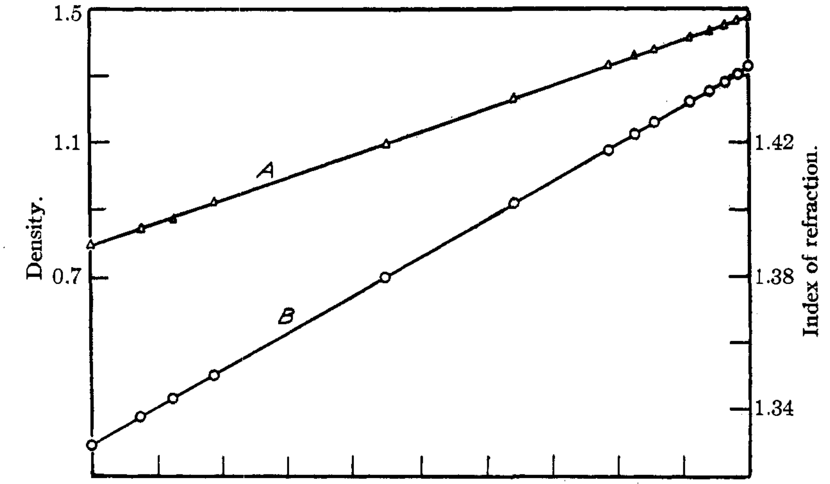

Fig. 4.—Chloroform–methanol mixtures: A, density: B, index of refraction.

Comparison of the experimentally determined constants for chloroform and methanol with values found in the "International Critical Tables" is shown in Table I.

TABLE I

EXPERIMENTALLY DETERMINED CONSTANTS FOR CHLOROFORM AND METHANOL USED IN MIXTURES COMPARED WITH CONSTANTS IN "INTERNATIONAL CRITICAL TABLES"

Temperature 25°

Constant	Chloroform Exptl.	Chloroform "I. C. T."	Methanol Exptl.	Methanol "I. C. T."
Density, g./ml.	1.4793	1.4795	0.7909	0.7866
Surf. tens., dynes	26.48	26.46	22.33	22.18
Fluidity, rec. poises	173	173.6	181	181
Refr. index, n_D	1.4424	1.4426	1.3290	1.3289
Vap. pressure, mm.	196	199	126	123
Compress., beta/atm.	107.1	106.4	133.3	[a]

[a] No low pressure compressibility data are given. The chloroform value is for a range of 1 to 6 megabaryes.

The compressibility–volume per cent. composition diagram and the corresponding surface tension diagram (Fig. 2) were nearly ideal, though their slight deviations were in strict antibatic relation to each other. The maximum compressibility deviation from the ideal is plus 2% and that of the surface tension is minus 4%.

Fluidity and vapor pressure (Fig. 3) showed wide deviations from the normal, and with no apparent correlation with any other property investigated. Vapor pressure is shown in its relation to mole per cent. composition, in accordance with Raoult's law. All other properties are shown in relation to volume per cent. composition as simple additive properties.

Index of refraction (Fig. 4) follows strictly a straight line function of volume per cent. composition, so that it is an accurate means of determining the composition of mixtures of chloroform and methanol from the indices of the pure components.

Density also follows a straight line function very closely (Fig. 4). The maximum deviation from the ideal was found to be 0.0009.

Summary

1. In the system, chloroform–methanol, close correlation was found between surface tension and compressibility, both being nearly ideal functions of composition.

2. Vapor pressure data deviated widely from the ideal. The system does not conform to Worley's rule of the antibatic relation between surface tension and vapor pressure.

MANHATTAN, KANSAS RECEIVED MARCH 11, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Solubility. XIV. Experimental Tests of a General Equation for Solubility

BY JOEL H. HILDEBRAND

The writer, with the collaboration of Mr. S. E. Wood,[1] derived the equation

$$\mathrm{E}' = \frac{2\pi N^2}{\mathrm{v}} \int^{\infty} \varphi W r^2 dr \qquad (1)$$

for the potential energy of an assemblage of molecules of the same species and the equation

$$E' = \frac{2\pi N_2}{V} \left[n_1^2 \int \varphi_{11} W_{11} r^2 dr + n_2^2 \int \varphi_{22} W_{22} r^2 \mathrm{d}r + 2n_1 n_2 \int \varphi_{12} W_{12} r^2 \mathrm{d}r \right] \qquad (2)$$

for the potential energy of a mixture of n_1 moles of one species with n_2 moles of another. In these equations, N is the Avogadro number; v, the molal volume; V, the volume of the mixture; the φ's are the potential functions between pairs of molecules whose species are denoted by the subscripts; the W's are the "probability functions" expressing the structure of the assemblage, as used by Prins,[2] and by Debye and Menke.[3]

These equations are perfectly general, regardless of the type of molecule or molecular field; indeed, Equation 1 reduces to familiar forms, both in the case of a gas, when W becomes unity immediately above the collision diameter, and in the case of the solid, where W is discontinuous. For the liquid state, in the absence of more exact knowledge concerning the probability functions and the repulsive potentials, we are forced at present to make certain approximations, as set forth in the original publication. These include non-polar character and spherical symmetry for the molecular species considered, the identity of the probability functions when expressed in terms of molecular diameters, the neglect of the repul-

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(1) J. H. Hildebrand and S. E. Wood, *J. Chem. Physics*, **1**, 817 (1933); *cf.* also, G. Scatchard, *Chem. Rev.*, **8**, 321 (1931); THIS JOURNAL, **56**, 995 (1934); J. H. Hildebrand, *ibid.*, **56**, 996 (1934).

(2) J. A. Prins, *Physica*, **6**, 315 (1926); *Z. Physik*, **56**, 617 (1929); *Physik. Z.*, **30**, 525 (1929); F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).

(3) P. Debye and H. Menke, "Fortschritte der Röntgen-forschung," Akademische Verlagsges., Leipzig, 1931, Chap. I; H. Menke, *Physik. Z.*, **33**, 593 (1932); *cf.* also O. Kratky, *ibid.*, **34**, 482 (1933).