

EFFECT OF PRESSURE AND TEMPERATURE ON OIL-WATER INTERFACIAL TENSIONS FOR A SERIES OF HYDROCARBONS

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ABSTRACT

An apparatus was constructed for the measurement of interfacial tensions over a range of temperatures and pressures. This apparatus utilized the pendent drop method, and resembles in construction similar apparatus recently described in the literature and in use in some petroleum research laboratories. The interfacial tensions of benzene, propane, n-pentane, n-hexane, n-octane, and iso-octane against water were measured at temperatures ranging from 26° to 82° C and at pressures ranging from 1 to 204 atm. Values of interfacial tensions for the benzene-water system and their variations with temperature and pressure are generally in good agreement with values of previous investigations.

The data in all cases showed a slight decrease of interfacial tension with pressure at constant temperature in the range studied. The effect of pressure became less as the pressure was increased, with an indication of a reversal of the effect at higher pressures. There was a decrease of interfacial tension with temperature at constant pressure in all cases, as would normally be expected. This rate of decrease became greater the higher the temperature.

A general equation is presented for the interfacial tensions as a function of pressure and temperature over the range

studied, and the constants calculated for each system. A definite trend was found in the effect of molecular weight on the interfacial tension at a given temperature and pressure, for the homologous series from propane to n-octane. Data for n-decane from the literature fitted well into this trend.

INTRODUCTION

It has been recognized for many years that surface forces play an active part in the production history of an oil reservoir as well as in determining the amount of unrecoverable oil. The magnitudes of these forces are governed by the values of the interfacial tensions. These vary greatly with composition, pressure, and temperature. The effect of composition is greater than that of pressure and temperature over the ranges normally encountered. In fact, because of the variety of compounds present in a crude, no attempt has yet been made to correlate crude composition with its surface tension or with its interfacial tension against water. The amount of dissolved methane greatly affects the surface properties of an oil, and there are "surface-active" compounds in crudes which have a much greater effect on boundary tensions than do equal amounts of hydrocarbons.

The purpose of the present work was partly to contribute data that would eventually be used in correlations applicable

¹References given at end of paper.

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APPARATUS

The High Pressure Cell

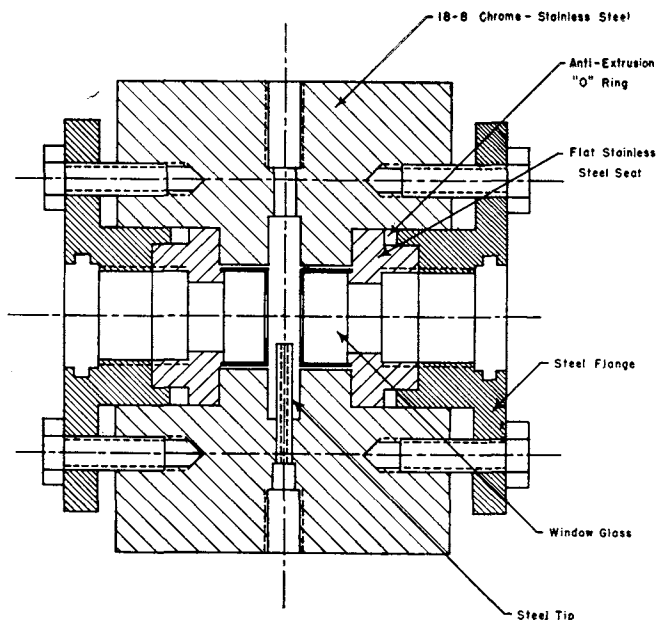


FIG. 1 — INTERFACIAL TENSION CELL.

The basic design of the cell used in this study follows that of other investigators. However, a two-windowed cell was preferred for the reason that direct illumination of the drop, rather than illumination from behind, might produce reflections that would change the appearance of the drop profile. The cell body (Fig. 1) is a hollow cylinder 5½ in. in diameter and 4 in. long, machined from a rod of 18-8 chrome stainless steel Type 303. Stainless steel was used so that the cell would possess adequate structural strength and resist corrosion. This is of importance since these factors can seriously affect the values of the interfacial tensions of the systems being studied. The windows are standard optical flats 0.5 in. thick, 30 mm in diameter, of the type usually used as gauge blocks and secondary micrometer testing standards. They are attached to stainless steel seats by means of stainless steel retainers that screw into the seats. The sides of the seats that are in contact with the glass are highly polished to the degree of almost optical flatness, since the glass is in direct contact with the metal seat. No gasket has been used for fear of unequal strains in the windows that might cause them to break. This feature of the design is similar to that suggested by Poulter⁵ and Bridgman,⁶ and has been used successfully at high pressures without any reported leak or failures except at pressures below 500 psi.⁶

to petroleum, and partly to construct precise and adequate equipment for future measurements. It was decided to limit the investigation to pure liquid hydrocarbons.

A review of the methods used for interfacial tension measurements at high pressure and a range of temperatures indicated that the pendent drop method was the most satisfactory. This method has been used, for instance, by Hough, Rzasa, and Wood¹ in the Stanolind Research Laboratories.

The pendent drop method is based on the shape and size of the profile of a hanging drop, coupled with a knowledge of the densities of the two fluids at the experimental conditions. The basic equations of this method were derived by Bashforth and Adams.² The method was further developed by Andreas, Hauser and Tucker.³ The latter authors prepared accurate tables, based on experiment, from which the interfacial tension may be calculated from certain measurements on the drop. They define a "shape factor" *S* as *d*/*D*, where *D* is the maximum diameter, and *d* is the diameter at a vertical distance from the apex equal to the maximum diameter. Their tables contain values of the reciprocal of a function *H*, defined by:

$$H = \frac{\Delta\rho g d^3}{\gamma} \dots \dots \dots (1)$$

where $\Delta\rho$ is the density difference for the fluids, *g* is the acceleration of gravity, and γ the interfacial tension, all in c.g.s. units. Values of 1/*H* are given as a function of *S*, the shape factor. Niederhauser and Bartell later calculated more accurate tables than those of Andreas, Hauser, and Tucker.

To obtain accurate interfacial tension values *D*, *d*, and $\Delta\rho$ must be measured accurately. The diameters are usually determined by forming an enlarged and undistorted picture of the drop profile on a photographic plate or film. The magnification can be determined by including the tip in the photograph, the size of the tip being known from micrometer measurements. Densities must be known from accurate PVT measurements on the substances used.

To provide a tight seal and prevent leaks through the annular space between the seats and the cell body, anti-extrusion "o" rings were used. These rings are especially designed for use in high pressure cells. They consist of ordinary "o" rings with leather gaskets on both sides. The assembled seats with the "o" rings are followed by steel flanges to hold them in place. These flanges are provided with "o" rings to prevent water leakage from the bath to the cell.

The tip (Fig. 1) from which the drop is suspended is made of stainless steel. It has a capillary hole 0.047 in. in diameter. It is designed so that it can be dropped into the proper position and then followed by high pressure fittings, permitting ready interchange of tips without disturbing the cell windows. The tip is also provided with an "o" ring to prevent leakage past the space between it and the body of the cell.

Since the liquids whose interfacial tensions were studied are of lower density than the surrounding fluid (water), the cell was inverted. However, it can be rotated 180° in its

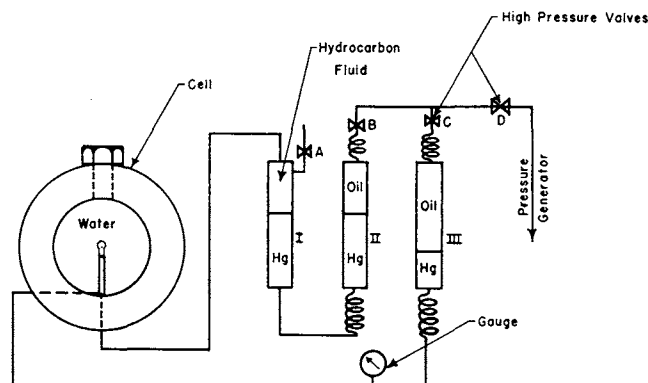


FIG. 2 — GENERAL PLAN OF APPARATUS FOR CONTROL OF PRESSURE AND RATE OF DROP FORMATION.

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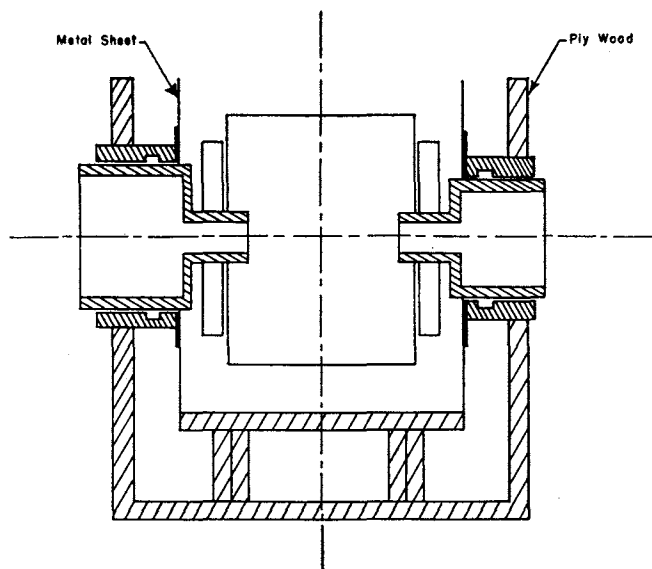


FIG. 3 — WATER BATH WITH CELL IN PLACE.

mounting to study drops of a fluid of higher density than that of the fluid surrounding the tip. A tap of fairly large diameter, with a straight thread and seat to fit a plug, facilitates filling and emptying the cell. The cell has been designed for ease of assembly and cleaning.

It should be mentioned that the window system used in the design of this cell disqualifies the use of the equipment for the study of liquid drops formed in a surrounding gas phase because the windows are not gas tight except at extremely high pressures. However, to study boundary tension at liquid-vapor interfaces the liquid phase can be placed in the cell, and the "drops" of vapor or gas can be formed.

Drop Forming System

The system that has been used to form the drops is essentially that of Hauser and Michaels⁷ and is shown in Fig. 2. It consists of three thick-walled stainless steel (Type 304) cylinders, $1\frac{1}{4}$ in. OD and $\frac{1}{4}$ in. thick. Stainless steel end plugs machined to fit American Instrument Co. super-

pressure fittings were screwed and soldered to both ends of the cylinders. The upper plug of the cylinder containing the hydrocarbon was made to receive two fittings in order to facilitate filling and emptying of the cylinder. Two cylinders are threaded the whole length on the outside and each is provided with two nuts so that they can be raised or lowered. Capillary stainless steel tubing $1/16$ in. OD is used to connect the various cylinders and the cell together. Cylinder 3 is connected to a pressure generator at one end and to the cell at the other. Cylinder 2 is connected to the same pressure generator at the top, while its lower end is connected to the lower end of Cylinder 1. One of the fittings in the upper plug of Cylinder 1 is connected to the filling plug and the other to the cell. Cylinders 1 and 2 form a differential pressure to form the required drop. Mercury is used to transfer the pressure to the cell and the hydrocarbon reservoir.

The hydrocarbon liquid is placed above the mercury in Cylinder 1, and is led through the stainless steel capillary tubing to the drop forming tip in the cell. In order to produce a differential pressure necessary to form the drop, either Cylinder 2 is raised or Cylinder 1 is lowered.

Thermostat Bath

The system used for temperature maintenance is shown in Fig. 3. It consists of a water bath made of sheet metal, surrounded by a plywood box, the intervening space being filled with granulated cork as an insulator. The brass tubes which form part of the optical system (see below) are fitted with "o" rings, which in turn fit into the larger brass tubes soldered to the walls of the bath. To minimize corrosion, the bath liquid consisted of a 0.1 per cent solution of sodium chromate with a *pH* of 7. A heater, relay, and thermostat maintain the bath at the desired temperature within $\pm 0.0^{\circ}\text{C}$.

The Optical Systems

One of the major difficulties in the pendent drop method is the design of the optical system. Two alternatives appear for obtaining results with high precision. The first is to produce large photographs and make measurements by simple means. This necessitates the use of cumbersome apparatus. The sec-

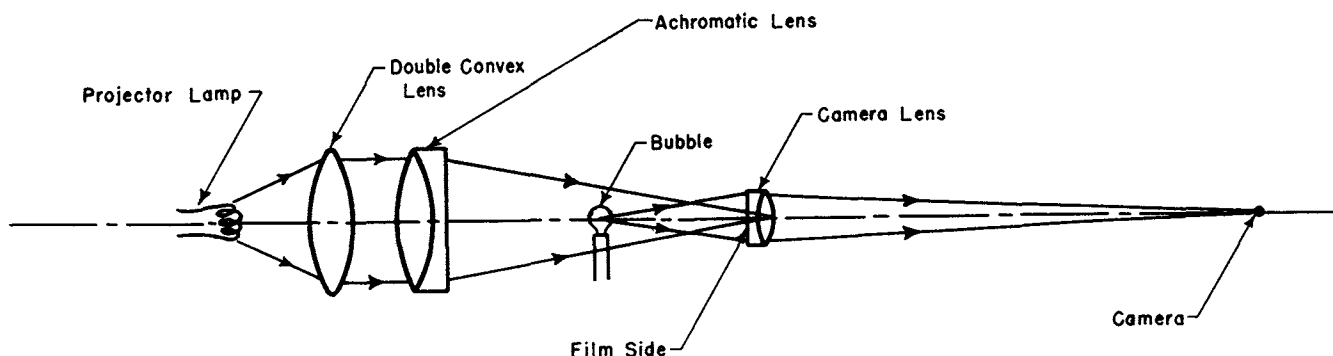


FIG. 4 — OPTICAL SYSTEM.

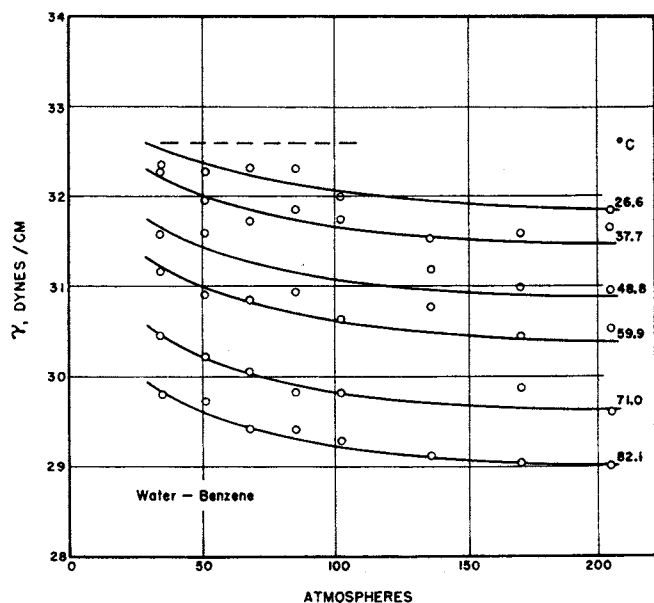


FIG. 5—INTERFACIAL TENSIONS FOR THE WATER-BENZENE SYSTEM. DOTTED LINE SHOWS DATA OF MICHAELS AND HAUSER AT 23.25°C.

ond is to take small pictures and make measurements with highly specialized equipment. Between these two limits there must lie a region wherein drop images can be produced so that neither large-scale photographic equipment nor sensitive measuring devices need be employed. In designing the optical system used in this study, such a compromise was sought. This might have been at the expense of the degree of accuracy, but it is believed that this is overbalanced by the ease of measurement and speed of operation.

The system used consists of an ordinary photographic camera equipped with a Wirgin lens, 75 mm. This lens is intended for use in cases where increased depth of field and wider coverage are considered more important than good definition at the corners of the film. It works equally well at all distance-settings from infinity to about four focal lengths.

As shown in Fig. 4, the lens is used in a reverse manner, *i.e.*, the side that ordinarily faces the film is facing the object. It is attached to the camera by means of an aluminum tube about 5½ in. long.

An achromatic lens of focal length 7-3/32 in. and diameter 2-1/64 in. is used to focus the parallel incident rays into the center of the camera lens. This produces an image of the source of light in the middle of the camera lens which is placed at a short distance from the objective. An ordinary projector lamp of 500 watts is used as a source of light. It is connected to a variable-voltage transformer to change the intensity. The lamp is placed in the focus of a double convex lens, 82 mm in diameter; this lens and the achromatic lens are mounted in a brass tube. The use of photographic films for recording drop profiles is desirable, since errors due to distortion and shrinkage during the process of making positive prints is eliminated. Kodak Safety Film Super Panchro-Press, Type B, was used. The magnification obtained by this method is of the order of eight to nine diameters. Photographs are made with full opened diaphragm and with 1/25 of a second exposure.

The entire camera assembly is mounted by means of two strap clamps on a movable bed. It can be moved back and

forth for focussing by means of a rack and pinion. The rear strap clamp on the movable bed also serves to lock the sliding tube carrying the plate holder. A thumb screw at the front of the camera platform locks the bed after focussing is complete.

MATERIAL USED AND PROCEDURE

One of the serious limitations imposed on this study is the lack of reliable data about the compressibility coefficients and thermal expansion coefficients of the hydrocarbons. These coefficients are necessary to determine the densities of the phases at the elevated temperatures and pressures. This study has been confined to the following hydrocarbons: benzene, iso-octane, propane, n-butane, n-pentane, n-hexane, and n-octane. Benzene of the highest purity, free from thiophenes purchased from Fisher Scientific Co. was used. "Extra pure" n-butane, 99.9 per cent, and "extra pure" propane, 99.9 per cent were purchased from Matheson Co., Inc. Iso-octane of high purity was purchased from Phillips Petroleum Co. This grade is used as reference fuel in knock test engines. N-hexane, 99 per cent and n-octane, 98± per cent were obtained through the courtesy of M. R. Fenske, Director of the Petroleum Refining Laboratory, The Pennsylvania State College.

The reservoirs and the cell were first cleaned with concentrated sulfuric acid containing potassium dichromate. This cleaning was followed by rinses with distilled water and ethyl alcohol. Ninety cc of clean mercury were put in both Reservoirs 1 and 2. Reservoir 3 contained 20 cc of clean mercury. Reservoirs 2 and 3 and the connecting tubing were filled with Nourse White Cream Separator Oil. Tubings connecting these

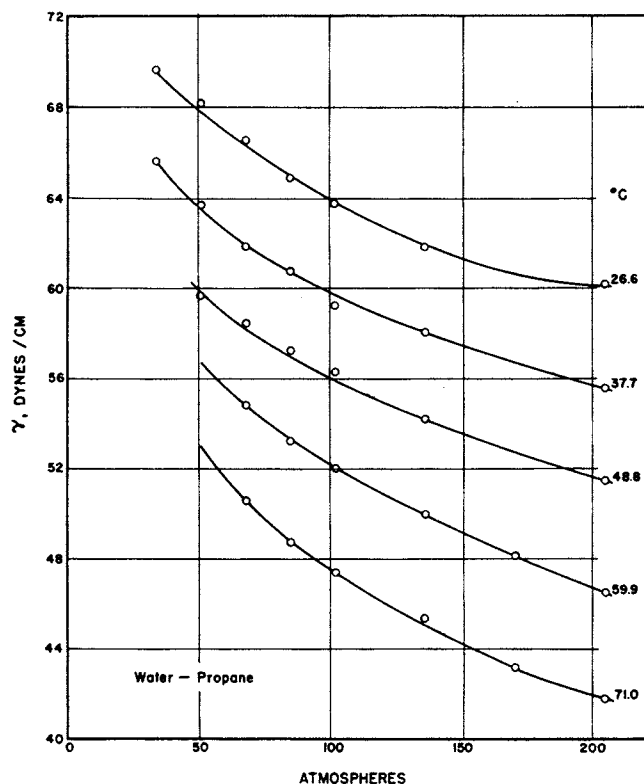


FIG. 6—INTERFACIAL TENSIONS FOR THE WATER-PROPANE SYSTEM.

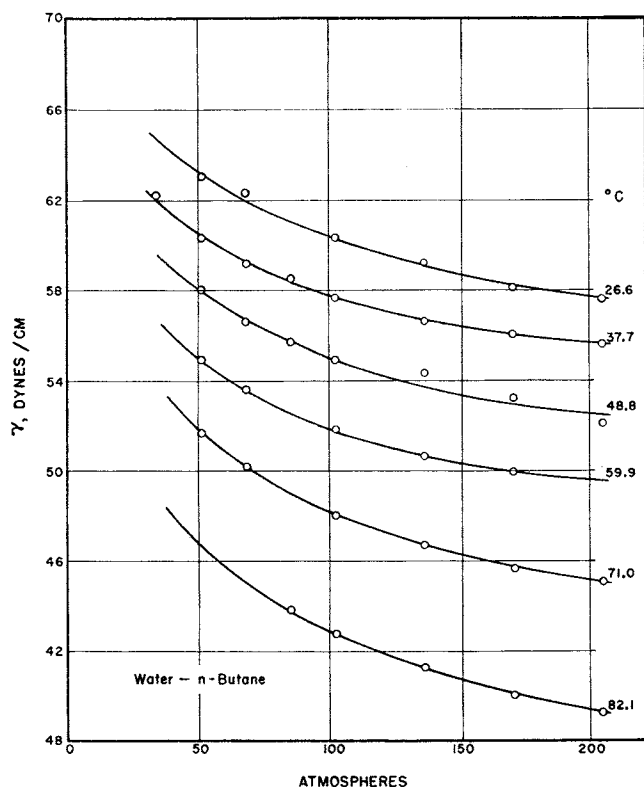


FIG. 7 — INTERFACIAL TENSIONS FOR THE WATER-N-BUTANE SYSTEM.

two reservoirs to the pump were also filled with the separator oil. Reservoir 3 was subsequently connected to the assembly cell. Reservoir 1 was filled with the hydrocarbon to be tested. In the case of n-butane and propane, the cylinder was connected to the reservoir. Extreme care was taken to exclude all air from the system. After being filled, Reservoir 1 was connected to the cell. The cell was filled with deaerated and distilled water and placed in the water bath.

It was considered desirable to make a temperature correlation curve to find how fast heat is transferred from the water bath to the inside of the cell. Thus, with a thermometer inside the cell and another in the water bath, the bath was heated to a predetermined temperature. It was found that thermal equilibrium was established in less than 15 minutes in all cases.

After the bath temperature had reached the desired value, Reservoirs 1 and 2 were raised or lowered until a drop of the hydrocarbon of satisfactory size was formed as shown on the screen. Valve D was then kept slightly open and pressure was applied. Valves B and C were adjusted to keep the size of the drop approximately constant. Valve A was always kept closed after Reservoir 1 had been filled with the hydrocarbon. In the case of propane and butane it was necessary to pressure the cell above the vapor pressures at the start. When the pressure had reached the desired value, the projector lamp was turned off and a film holder was inserted in the camera. Two minutes were allowed between the application of the pressure and the time of exposing the film so that the drop would reach equilibrium. The films were then developed and read by means of millimeter paper.

The degree of magnification was determined from the

size of the tip, which was measured with a micrometer. The tip was ground with emery cloth occasionally, hence the diameter was re-determined when necessary.

Runs were made at the following temperatures: 26.6, 37.7, 48.8, 59.9, 71 and 82.1° C and at the following pressures: 34, 51, 68, 102, 136, 170, and 204 atmospheres. The pressure gauge was calibrated against a dead weight tester before being used and was found satisfactory in the pressure range used in this study.

REMARKS ON THE TECHNIQUE

One of the most important features of all high pressure cells where visual study is necessary is the design of the window. The design used in this study followed the one discussed by Poulter⁵ and used by others.^{1,7} The feature of this design is the fact that the glass is self-sealed against the metal seat. Although the method has been recommended by some investigators, the writers do not find it highly satisfactory. Leakage in various amounts has been noticed even at high pressures. It might be argued that this is due to the fact that either one or both surfaces (glass or metal) are not optically flat. However, the degree of optical flatness of the glass and seats was measured and they were found flat to less than one-half wave length of visible light. Aside from leakage, the windows operated satisfactorily under the pressure and temperature range of this study. No fracture or break of the windows has been noticed.

Some difficulty was experienced at the higher temperatures with moisture condensing on the camera lens. A method of drying or ventilation of the space between the cell window and the lens would circumvent this trouble.

CALCULATION AND DISCUSSION OF RESULTS

The interfacial tensions for the various systems were calculated by means of Equation (1). The "shape factor" S

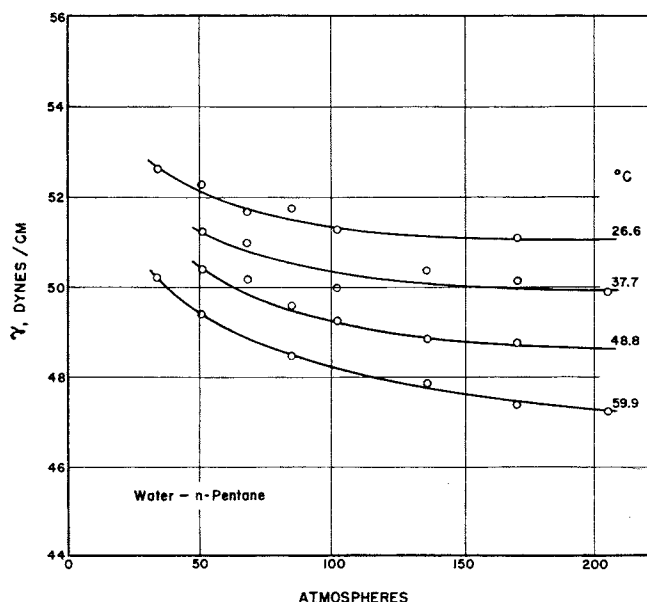


FIG. 8 — INTERFACIAL TENSIONS FOR THE WATER-N-PENTANE SYSTEM.

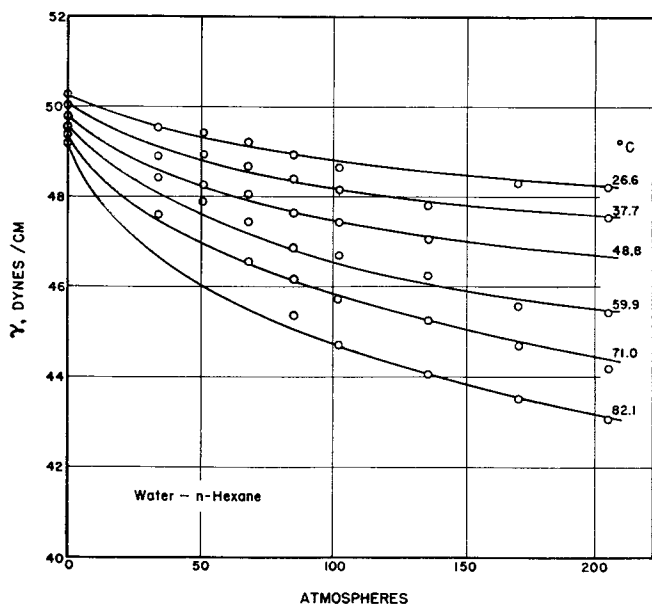


FIG. 9 — INTERFACIAL TENSIONS FOR THE WATER-N-HEXANE SYSTEM.

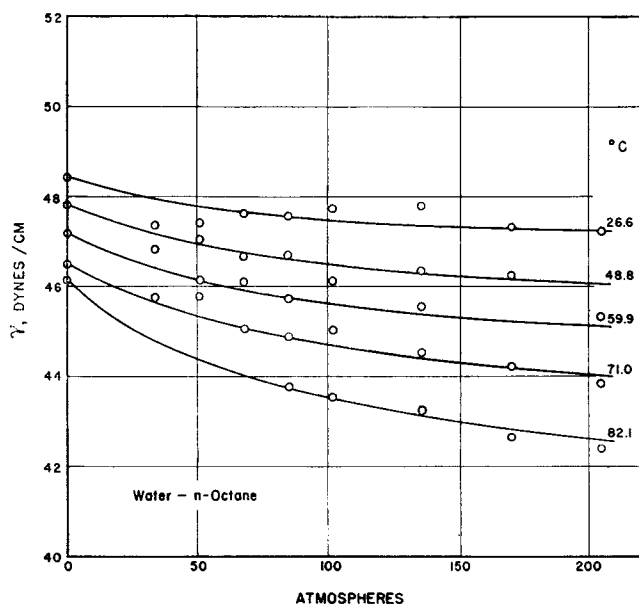


FIG. 10 — INTERFACIAL TENSIONS FOR THE WATER-N-OCTANE SYSTEM.

was determined from measurements on the film and the corresponding value of H taken from the tables of Niederhauser and Bartell.⁴ The densities at the various pressures and temperatures have been obtained from the literature. The densities of benzene, n-pentane, n-hexane, n-octane, and iso-octane were taken from the data of Bridgman.⁹ The density of water was taken from the tables of Smith and Keyes.⁹ The density of propane is from Sage, Schaffsma, and Lacey¹⁰ and that of n-butane from Olds, Reamer, Sage and Lacey.¹¹

Since there may have been a slight difference in the degree of hydrocarbon purity of the materials heavier than butane, as compared with the samples used by Bridgman, accurate density determinations were made at room conditions with a pycnometer. Although the difference between the samples of this investigation and those of Bridgman were small, a correction factor based on relative densities at the same pressure and temperature was applied.

Since the chief impurities in the sample are most likely to be hydrocarbons of slightly higher or lower molecular weights, the effect of such an impurity on the interfacial tensions was tested in the case of n-octane. A solution containing 99 per cent n-octane and one per cent n-hexane was prepared and the interfacial tensions determined at 48.8° C (one of the temperatures previously used) and the pressures previously used. The densities were determined by assuming the same coefficients as those of n-octane. That is, the density of the mixture was taken as 0.999 times the density of the n-octane, at all pressures and temperatures involved. The interfacial tension values were found to be the same as for pure n-octane within the limits of error.

Interfacial tension values as found by Equation (1) are shown by the circles in Fig. 5 to 11. The trends are shown by the curves drawn. It is apparent that the rate of decrease with pressure becomes less as the pressure is increased. Cross plots of interfacial tension against temperature at constant pressure (not reproduced here) show that the rate of decrease with temperature in most cases becomes greater as the temperature is increased.

The average deviation of the points from the smooth curves is about a tenth of a dyne, a few of the points being

off by several tenths. The amount of deviation from the curves is an indication of the degree of reproducibility. Absolute values could be in error somewhat more, as errors of 0.1 per cent in the densities of the heavier liquids would give errors of one to two per cent in the interfacial tensions calculated by using these densities.

For the sake of comparison, the data of Michaels and Hauser are shown for benzene at 23.25° C on Fig. 5. The agreement with the data of the present investigation is seen to be quite close.

Plotting the slopes of the iso-thermal curves against the

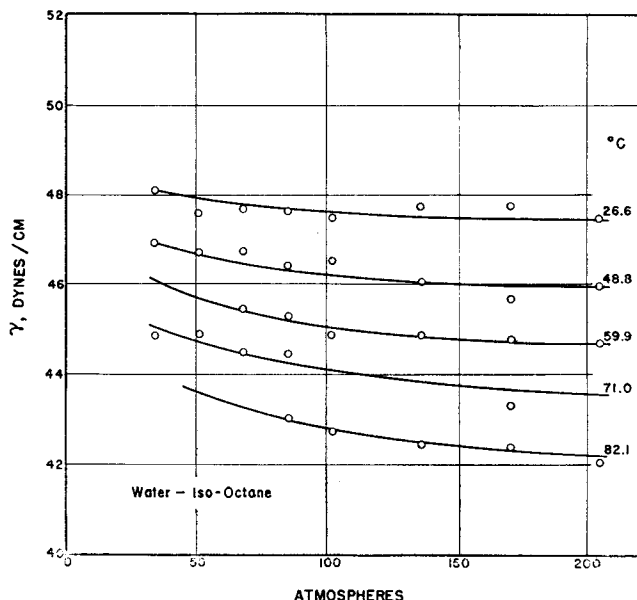


FIG. 11 — INTERFACIAL TENSIONS FOR THE WATER-I-OCTANE SYSTEM.

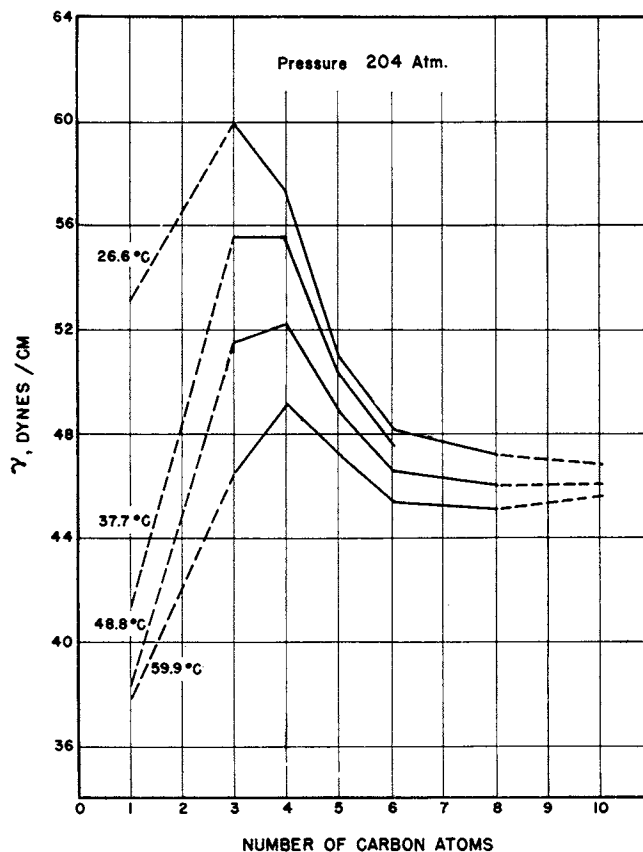
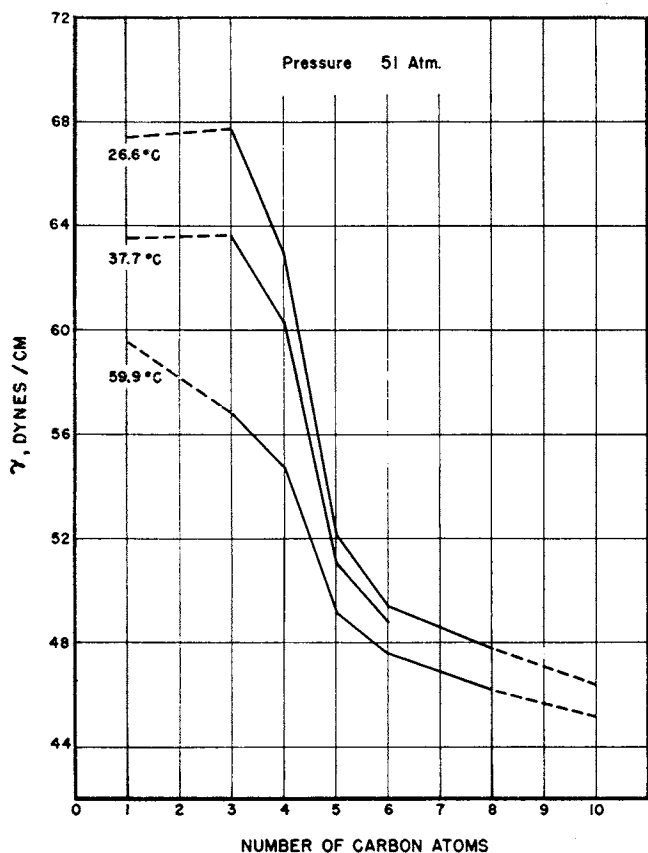


FIG. 12 — EFFECT OF MOLECULAR WEIGHT ON INTERFACIAL TENSIONS FOR NORMAL HYDROCARBONS AT 51 ATM.

FIG. 13 — EFFECT OF MOLECULAR WEIGHT ON INTERFACIAL TENSIONS FOR NORMAL HYDROCARBONS AT 204 ATM.

logarithm of the pressure indicated a linear relation. Assuming such a relation, the following empirical equation may be written:

$$\gamma = \gamma_0 - aP + bP \log_{10} P \dots \dots \dots (2)$$

where γ_0 is the interfacial tension at atmospheric pressure and a and b depend on the system and on the temperature. The last term would, of course, not be applicable at pressures less than unity. Values of a and b are given in Table I, when P is in atmospheres.

One would expect some definite trend in the water-oil interfacial tension at a given pressure and temperature with molecular weight for members of a homologous series. Such a trend is indicated in Fig. 12 and 13. Values for normal decane were taken from Michaels and Hauser,⁸ and they appear to fit well into the trend. Values for methane were

taken from Hough, Rzasa, and Wood¹ and were added to the graphs as a matter of interest. Since all temperatures shown are above the critical temperature for methane, the data for methane are not strictly comparable with those for the other members of the series.

ACKNOWLEDGMENT

This paper is a digest of a PhD thesis written by Hassan, with further calculations and correlations based on his data. A portion of the experimental work was supported by The Pennsylvania Grade Crude Oil Association.

Table 1

Constants of Equation 4 ($t' = t - 25$, where $t = ^\circ\text{C}$)

Compound	V_0	a	b
C_3H_8	$74.7 - .3t'$	$.31 + .0016t'$	$.10 + .0006t'$
C_4H_{10}	$68.6 - .23t'$	$.26 + .0025t'$	$.085 + .0011t'$
C_5H_{12}	$54.1 - .06t'$	$.11 + .0008t'$	$.041 + .0002t'$
C_6H_{14}	$50.3 - .027t'$	$.037 + .0014t'$	$.012 + .0005t'$
C_8H_{18}	$48.9 - .05t'$	$.032 + .0006t'$	$.01 + .00027t'$
$\text{C}_{10}\text{H}_{22}$	$49.5 - .07t'$	$.065 + .0003t'$	$.024 + .0001t'$
C_6H_6	$33.3 - .045t'$	$.032 + .0005t'$	$.012 + .0002t'$

REFERENCES

- Hough, E. W., Rzasa, M. J., and Wood, B. B.: "Interfacial Tensions at Reservoir Pressures and Temperatures; Apparatus and Water-Methane System," *Trans. AIME*, (1951), 192, 57.
- Bashforth, F., and Adams, J. C.: "An Attempt to Test the Theories of Capillary Action." University Press, Cambridge, England, (1883).

3. Andreas, J. H., Hauser, E. A., and Tucker, W. B.: "Boundary Tension by Pendent Drops," *Jour. Phys. Chem.* (1938), **42**, 1,001.
4. Niederhauser, D. O., and Bartell, F. E.: "A Corrected Table for the Calculation of Boundary Tensions by the Pendent Drop Method," *Fundamental Research on Occurrence and Recovery of Petroleum*, API, (1948-49), 114.
5. Poulter, T. C.: "A Glass Window Mounting for Withstanding Pressures of 30,000 Atmospheres," *Phys. Rev.*, (1930), **35**, 297.
6. Birdgman, P. W.: "The Volumes of Eighteen Liquids as a Function of Temperature and Pressure," *Proc. Am. Acad. Arts and Science*, (1931), **66**, 185.
7. Hauser, E. A., and Michaels, A. S.: "Interfacial Tension at Elevated Pressures and Temperatures," *Jour. Phys. and Coll. Chem.*, (1948), **52**, 1157.
8. Michaels, A. S., and Hauser, E. A.: "Interfacial Properties of Hydrocarbon Water Systems," *Jour. Phys. and Coll. Chem.* (1951), **55**, 408.
9. Smith, L. B., and Keyes, F. G.: "The Volumes of Unit Mass of Liquid Water," *Proc. Am. Acad. Arts and Science*, (1934), **69**, 285.
10. Sage, B. H., Schaafsma, J. K., and Lacey, W. N.: "Pressure-Volume-Temperature Relations and Thermal Properties of Propane," *Ind. Eng. Chem.*, (1934), **26**, 1218.
11. Olds, R. H., Reamer, H. H., Sage, B. H., and Lacey, W. N.: "Volumetric Behavior of n-Butane," *Ind. Eng. Chem.*, (1944), **36**, 282.