Interfacial Tension in Hydrocarbon Systems

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A high-pressure pendant drop apparatus was used to obtain interfacial tension data for the methane-nonane and butane-decane systems. Methane-nonane data were measured from −30° to 76° F. and from atmospheric to about 1500 p.s.i.a. Butane-decane data were obtained at 40° and 100° F. from 3 to 33 p.s.i.a.. The limiting accuracy of the experimental values appears to be about ±2% of the average interfacial tension measurement.

DESPITE THE VOLUME of material on physical chemistry of surfaces, confusion often results over distinction between two common forms of boundary tension, surface tension, and interfacial tension. To clear this confusion, Hough (*6*) has defined surface tension as a measure of the specific free energy between two phases having the same composition—for example, between a pure liquid and its vapor. In contrast, Hough has defined interfacial tension as a measure of the surface free energy between phases having different composition. According to these definitions, interfacial tension can refer not only to a liquid-liquid interface but also to a gas-liquid surface.

The convention reported by Hough was adopted for the work reported here.

The absorption of gaseous hydrocarbons in liquids is an often-used process in the natural gas and gasoline industry. In spite of its widespread use, the influences of many variables on the absorption phenomenon are poorly understood. Recently, Weber (*18*) carried out an extensive investigation of information on absorption available in the literature. He concluded that the absorption of gaseous components in liquid solutions is controlled and limited by the physical properties of the gases and liquids under consideration. One of the most important physical properties appeared to be surface (or interfacial) tension.

PREVIOUS WORK

Experimental interfacial tension data in the literature have been taken at temperatures and pressures outside the normal operating conditions for natural gas absorbers—for example, Weinaug and Katz (*19*) measured the interfacial tension of mixtures of methane and propane. Recently, interfacial tension data for heavier hydrocarbon mixtures have been measured at temperatures and pressures approaching the critical region. Hough and coworkers (*4, 12, 15, 17*) investigated the methane-butane, methane-pentane, methane-heptane, methane-decane, and ethylene-heptane systems at 100° F. and above.

Since the data described above are not directly applicable to natural gas absorption studies, the experimental work reported in this investigation was undertaken. Primary objectives were the measurement and correlation of interfacial tension at temperatures below ambient.

EXPERIMENTAL METHOD

Adamson (*1*) has written an excellent and extensive review of various methods for measuring surface or interfacial tension. The most commonly used methods he describes are capillary rise, drop weight, ring, maximum bubble pressure, and pendant drop. Adamson also includes advantages and disadvantages of the different techniques.

The pendant drop technique for measuring interfacial tension was chosen for the work reported here. Andreas and coworkers (*2*) and Niederhauser and Bartell (*9*) have cited a list of advantages of the pendant drop method over other methods. The pendant drop method is an absolute method—that is, it has been subjected to a complete mathematical analysis. Thus, pendant drop measurements are free of any empirical correction or adjustment and are directly convertible by analytical means to interfacial tension values. The pendant drop method is easily adapted to measurement under high pressures and wide ranges of temperature. In addition, the photograph of the drop provides a permanent record of the data that can be referred to at any future time.

In the pendant drop method, a drop of liquid is formed at the end of a capillary column and is allowed to hang until stable and all convective motion within the drop has ceased. The drop is then photographed and appropriate measurements are made from the photograph. One such set of measurements is indicated in Figure 1. Interfacial tension is calculated from the measured diameters d_e (maximum or equatorial diameter) and d_s (diameter a distance d_e from the bottom of the drop) through the use of Equation 1

$$\gamma = \frac{g(\rho_L - \rho_V)d_e^2}{H} \tag{1}$$

where

$$1/H = f(S)$$
$$S = d_s/d_e$$

Calculation of interfacial tension from Equation 1 requires a relationship between the shape parameter, H, and the

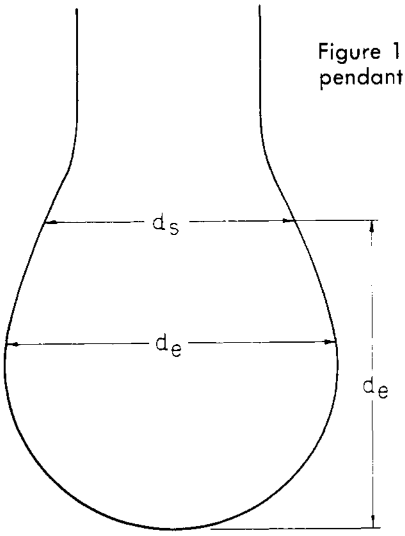

Figure 1. Drop diameters for pendant drop method

shape factor, S. For this work, the relationship between H and S was obtained from tables generated by Fordham (*5*) and Niederhauser and Bartell (*9*). The tabular values were checked independently by computer solution of the analytical relationship between H and S and found to be suitable for this study.

A schematic diagram of the experimental apparatus is shown in Figure 2. The basic elements are a high-pressure cell, a sample-introduction system, a temperature-control system, and an optical system. Other components include a pressuring system and a liquid-sampling system.

The high-pressure cell was a stainless steel chamber approximately 3 inches in o.d. and 4 inches long. Its internal volume was 14 cc. Each end of the cell was fitted with an optical quartz lens 0.75 inch in diameter. High-pressure connections to the cell were provided for pressuring the cell with gas and for introducing the liquid sample.

The drop-forming apparatus (Figure 3) was used to introduce the liquid sample into the cell. A vernier screw driving a piston with a Viton O-ring seal forced liquid from the reservoir into a 6-inch length of stainless steel capillary having an inside diameter of 0.087 inch. A straight-through ball valve, having an orifice the same size as the capillary, was inserted into the capillary line to separate the liquid reservoir from the cell. A Yale No. 15 stainless steel capillary tip (p. 1863-cm. i.d.) was attached to the pressure fitting inside the cell and was visible from the cell windows. Care was taken to keep the volume of the capillary and sample system as small as possible, so that a minimum amount of hydrocarbon could be used.

The cell was pressured with gas directly from the pressure cylinder. The system pressure was registered on Heise and Marsh pressure gages.

The entire cell and drop-forming assembly were contained in a constant temperature bath capable of maintaining temperatures between −40° and 120° F. The bath was insulated with 1 inch of magnesia packing between the walls and 1 inch of glass wool on the outside. Bath control was provided to 0.1° F. by a Thermistemp Model 63 temperature controller. Heat was supplied with a 300-watt immersion heater. Refrigeration was provided by a locally fabricated compression-type refrigeration unit charged with Freon 22.

The principal components of the optical system were the light source, the camera, and the optical comparator. A Cenco 100-watt high-pressure mercury arc light was placed at one window of the cell and a Nikon Model F 35-mm single-lens reflex camera at the other window. The photograph was recorded on Kodak extreme resolution panchromatic film. To facilitate measurement, photographs of the droplets were projected on a Gaertner 925-AP optical comparator and a Vanguard Model C-11D motion analyzer to obtain approximately 30× magnification.

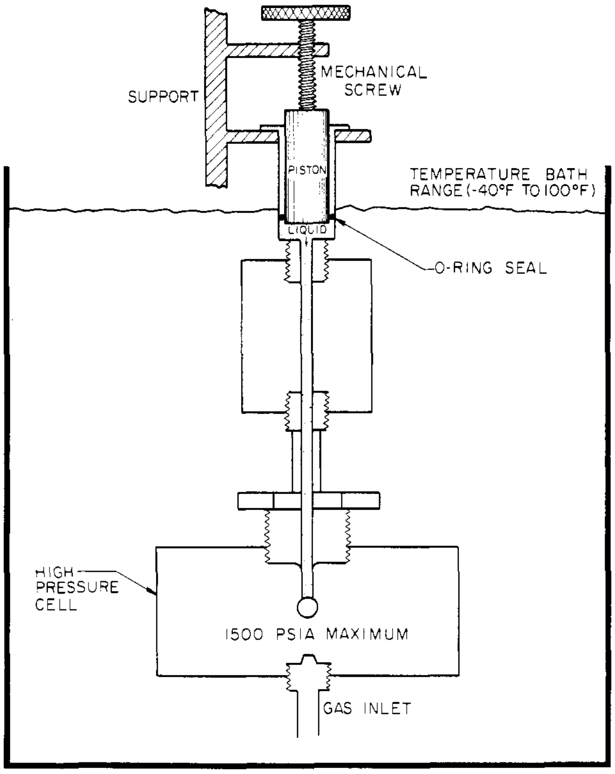

Figure 3. Drop-forming apparatus

The liquid hydrocarbons used in this study were research grade and the hydrocarbon gases were instrument grade, obtained from Phillips Petroleum Co. The specifications on the hydrocarbons were:

	Mole per cent	
Research-grade nonane	99.68	
	0.32	isononanes
Research-grade decane	99.49	
	0.51	isodecanes
Instrument-grade butane	99.55	
	0.40	isobutane
	0.05	propane
Instrument-grade methane	99.29	
	0.60	nitrogen
	20	p.p.m. max. oxygen
	10	p.p.m. max. water

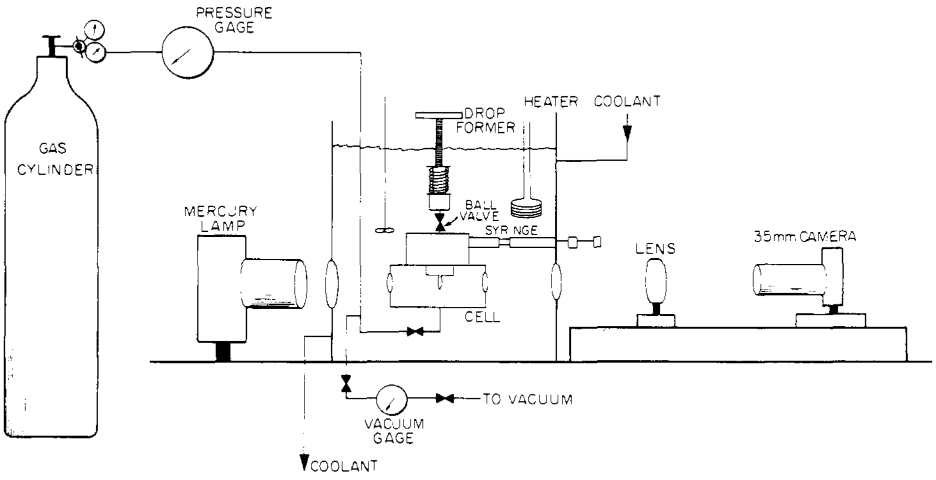

Figure 2. Experimental apparatus

EXPERIMENTAL PROCEDURE

An experimental run consisted of determination of interfacial tension at an isotherm for various pressures.

Before an experimental run, the drop-forming apparatus and the cell were cleaned. An initial ultrasonic cleaning with distilled water was followed with a hydrocarbon liquid wash. The equipment was allowed to drain, and filtered air was passed through for drying.

To start a run, the drop-forming apparatus and the cell were assembled and immersed in the temperature bath. The entire system was made leak-free at a pressure higher than the pressure values for the run. The temperature bath was adjusted to the specified temperature and the entire system brought to temperature equilibrium. The system was evacuated to approximately 5 microns, and the hydrocarbon gas was introduced at a pressure slightly greater than atmospheric. The valve in the capillary was opened, and the piston was withdrawn to the top of the reservoir. The hydrocarbon liquid was injected into the reservoir from a syringe. Every effort was made to use the minimum amount of hydrocarbon liquid, usually not more than 8 drops. The gas was allowed to bubble through the liquid for a few minutes to remove any air that might have entered the cylinder; then the piston was pushed down into the reservoir and the capillary valve was closed. The gas pressure in the cell was raised or lowered to the bubble point pressure required for the desired liquid composition.

After the system had again reached thermal equilibrium, the capillary valve was opened and the mechanical screw used to force a droplet of liquid to the end of the capillary. Liquid mixing was accomplished by continuously exposing new liquid surface to the vapor. Mixing was aided by alternately retracting the piston to suck liquid back into the reservoir and then forcing liquid back down the capillary. Sufficient time, at least 30 minutes, was allowed for the system to reach pressure and mass transfer equilibrium. When convective currents in the undisturbed droplet had damped, at least three photographs were taken. Vibrations were reduced with shock pads and by turning off all motors.

After the photographs were taken, the pressure was raised to the next desired value. The procedure outlined above was repeated.

Extreme care was taken to assure that the drop formed on the end of the capillary was truly stable and quiescent. Considerable error in interfacial tension measurement can be caused by an improperly formed drop on the capillary tip. After the photographs were developed and measurements made, the measurements of each drop were checked against the capillary-tip-size correlation of Niederhauser and Bartell (*9*), to make certain that the droplets met that shape criterion.

An interesting phenomenon was observed as the droplets were formed on the capillary tip. As the gas dissolved in the liquid, the liquid droplet disappeared back up the capillary passage. This movement was partially attributed to mass transfer between the gas and the liquid. When a pendant drop remained on the capillary tip, mass transfer equilibrium between the gas phase and liquid phase was assumed to have been established.

EXPERIMENTAL RESULTS

The first experimental data were taken at ambient temperatures and at 1-atm. pressure for nonane in an air atmosphere and nonane in a methane atmosphere (Table I).

Table II shows the experimental interfacial tension data taken on the methane-nonane system in this investigation. Isotherms were run at 76°, 30°, −10°, and −30° F. at pressures ranging from atmospheric to approximately 1500 p.s.i.a. All data are for saturated liquid mixtures of methane and nonane in equilibrium with the corresponding vapor phase at experimental conditions. Interfacial tension values were generated from phase densities and experimentally determined drop diameters through the use of Equation 1.

Table I. Reliability of Experimental Data

Nonane Surface Tension, Dynes/Cm.	Atmosphere	Source
22.48	Nonane vapor	Jasper (*7*) (linear interpolation between 20° and 30° C.)
Nonane interfacial tension, Dynes/Cm.		
22.39	Dry nitrogen	Jasper (*8*) (linear interpolation)
22.86	Air	This work (77° F. and 1 atm. dry air)
21.98		
22.21		
22.10	Methane	This work (77° F. and 1 atm.)
22.17		
22.05		

Experimental interfacial tension data for the butane-decane binary are presented in Table III. Isotherms were run at 40° and 100° F. from 3 to 34 p.s.i.a. All of the data are for saturated liquid mixtures in equilibrium with the vapor phase. Interfacial tension values were calculated from drop measurements and phase densities by use of Equation 1.

Tables II and III include the measurements of equatorial and plane diameter for each data point. The enlarged measurement of the outside diameter of the capillary (true o.d. 0.221 cm.) is shown to permit ready reduction of the enlarged measurements to true diameters. Measurements taken using the Gaertner Comparator are recorded in centimeters, while those from the Vanguard Analyzer are in inches.

DISCUSSION OF RESULTS

The first experimental data were taken for comparison with literature work on pure nonane. Table I compares the experimental data taken from this work with the data of Jasper (*7, 8*). In general, the data show good agreement, the average value in air being essentially the same as Jasper reports in a dry nitrogen atmosphere. The three experimental points show a total spread of 4% based on the minimum value measured. The deviation from the average value is approximately ±2%. Also shown in Table I are data for nonane in a methane atmosphere at 1-atm. pressure. These data show a slight effect on interfacial tension by the gaseous atmosphere, the values in methane being lower than those for corresponding temperature and pressure in air. The methane data show a total spread of 0.5% based on the minimum value, with an average deviation of approximately ±0.2%.

Measurement errors account for at least part of the spread indicated by the experimental data in Table I. An average value for the maximum diameter of a droplet in this work is approximately 0.25 cm. The Gaertner optical comparator is capable of measurements to 0.0001 cm. With the Gaertner comparator, the diameter of a droplet can be measured to a probable accuracy of 0.002 cm. The probable accuracy of diameter measurements is 0.001 cm. on the Vanguard motion analyzer, which has a capacity for measurement to 0.001 inch on a projected magnified image.

Table II. Experimental Interfacial Tension of Methane-Nonane System

Pressure, P.S.I.A.	d_n, Cm.	d_s, Cm.	d_e, Cm.	Interfacial Tension, Dynes/Cm.	Av. Value
		T = 76° F.			
15 (air)	0.4915	0.5968	0.6992	22.71	22.76
	0.4909	0.5963	0.6987	22.74	
	0.4920	0.5955	0.6992	22.79	
	0.4933	0.5930	0.6985	22.82	
	0.4898	0.5947	0.6970	22.74	
75	0.4983	0.5916	0.6963	21.94	21.77
	0.4983	0.5903	0.6944	21.79	
	0.5020	0.5900	0.6944	21.50	
	0.4958	0.5841	0.5841	21.87	
150	0.4952	0.5831	0.6809	20.63	20.58
	0.4976	0.5844	0.6831	20.62	
	0.4970	0.5850	0.6823	20.50	
	0.4968	0.5843	0.6823	20.58	
300	0.4949	0.5743	0.6650	18.93	18.93
		T = 30° F.			
15 (air)	0.4643	0.5626	0.6704	25.15	25.25
	0.4630	0.5617	0.6702	25.29	
	0.4600	0.5603	0.6670	25.30	
15	0.4698	0.5640	0.6718	24.66	24.37
	0.4618	0.5575	0.6590	24.07	
150	0.4669	0.5553	0.6595	23.47	22.95
	0.4728	0.5610	0.6605	22.44	
300	0.4690	0.5331	0.6215	19.27	19.27
600	0.4573	0.5157	0.5878	16.33	16.28
	0.4564	0.5177	0.5878	16.23	
900	0.4650	0.5077	0.5710	13.68	13.68
	0.4603	0.4900	0.5572	13.69	
1175	0.4623	0.4871	0.5316	10.53	10.48
	0.4590	0.4830	0.5278	10.56	
	0.4558	0.4754	0.5193	10.36	
1315	0.4595	0.4679	0.5065	9.22	9.30
	0.4716	0.4920	0.5261	9.13	
	0.4675	0.4709	0.5137	9.36	
	0.4623	0.4690	0.5115	9.48	
		T = 30° F.			
1475	0.4537	0.4554	0.4885	8.33	8.26
	0.4516	0.4523	0.4846	8.24	
	0.4556	0.4594	0.4903	8.20	
		T = −10° F.			
140	0.4950	0.6161	0.7261	25.32	25.05
	0.4752	0.5745	0.6833	24.94	
	0.4745	0.5781	0.5781	24.89	
310	0.4750	0.5631	0.6555	21.15	21.79
	0.4585	0.5573	0.6522	22.79	
	0.4902	0.5768	0.6757	21.46	
	0.4863	0.5648	0.6672	21.74	
598	0.4960	0.5443	0.6201	16.08	15.91
	0.4938	0.5466	0.6180	15.31	
	0.4925	0.5467	0.6225	15.92	
	0.4919	0.5440	0.6237	16.32	
890	0.4932	0.5275	0.5845	12.27	12.17
	0.4916	0.5281	0.5815	12.02	
	0.4905	0.5241	0.5815	12.32	
	0.4950	0.5315	0.5858	12.06	
1190	0.4938	0.5075	0.5470	9.28	9.27
	0.4941	0.5090	0.5478	9.26	
		T = −30° F.			
147	0.5255	0.6365	0.7531	24.60	24.45
	0.5249	0.6382	0.7520	24.31	
285	0.5220	0.6164	0.7172	21.10	21.73
	0.5298	0.6212	0.7291	21.67	
	0.5111	0.6052	0.7125	22.42	
590	0.5037	0.5507	0.6315	15.99	16.38
	0.4938	0.5538	0.6282	15.99	
	0.4779	0.5452	0.6234	17.17	
1025	0.5191	0.5030	0.5655	10.27	10.41
	0.5167	0.5202	0.5768	10.41	
	0.5224	0.5496	0.6000	10.56	
	0.5156	0.5288	0.5817	10.40	

Because the equatorial diameter (d_e) and the selected plane diameter (d_s) enter into the interfacial tension calculations, both directly as shown in Equation 1 and indirectly through the relationship between $1/H$ and S, the effect of an error in measurement is multiplied by approximately five in its effect on the interfacial tension. Thus, the limiting accuracy of the experimental measurements of this work appears to be about ±2% of the average interfacial tension measurement. The experimental data shown in Table I fairly well reflect the reproducibility and accuracy of the experimental apparatus and techniques used in this work.

Liquid and vapor densities for experimental methane-nonane interfacial tension data were taken from the work of Shipman and Kohn (*14*). The only experimental density and composition data available in the literature on the methane-nonane system are those reported by Shipman and Kohn, and Savvina (*13*). Savvina reports only liquid-phase compositions as a function of temperature and pressure, while Shipman and Kohn report phase compositions and phase volumes (or densities). In general, liquid-phase compositions from these sources are in good agreement. Under the conditions of this work, the equilibrium constant for nonane never exceeds 0.01. For this reason, the gas phase may be assumed to be essentially pure methane for density calculations. Gas-phase densities calculated from

Table III. Experimental Butane-Decane Interfacial Tension

P, P.S.I.A.	d_n, Inches	d_s, Inches	d_e, Inches	Interfacial Tension Dynes/Cm.	Av. Value
		T = 100° F.			
9	3.911	4.455	5.243	20.08	20.06
	3.900	4.462	5.240	20.05	
	3.839	4.353	5.139	20.19	
	3.858	4.390	5.159	19.90	
24	3.945	4.376	5.066	16.82	16.92
	3.954	4.275	5.014	16.98	
	3.951	4.358	5.066	16.96	
34	3.648	3.904	4.559	15.51	15.73
	3.658	3.843	4.503	15.96	
		T = 40° F.			
3[a]	0.5200	0.6045	0.7093	21.35	21.32
	0.5073	0.5924	0.6933	21.21	
	0.5216	0.5955	0.7051	21.40	

[a] All diameters of T = 40° F., P = 3.6 p.s.i.a. are in centimeters.

methane compressibility factors agree well with the vapor densities reported by Shipman and Kohn.

Liquid densities for the butane-decane points at 100° F. were interpolated from the liquid density data of Reamer, Sage, and Lacey (*12*). The corresponding vapor densities were calculated from the Benedict-Webb-Rubin equation of state (*3*). Vapor densities calculated from butane compressibility factors were in good agreement with the BWR densities. The butane-decane liquid density at 40° F. was calculated from the Rackett saturated-liquid density equation (*11*). The Rackett correlation was found to be the most accurate method for calculation of liquid density in this and other work. The corresponding bubble point pressure at 40° F. was calculated from Raoult's law on the basis of the low value of the butane vapor pressure. The vapor density was calculated from the BWR equation.

Figures 4, 5, and 6 show three different plots of the data presented in Table II. Figures 4 and 5, at first glance, show anomalies in interfacial tension values. This is because there are two counteracting effects in the data. The interfacial tension values should be higher as colder temperatures are reached. At the colder temperatures the solubility of methane increases, tending to lower the interfacial tension. These two effects are separated in Figure 6. From Figure 6 at a given methane concentration in the liquid phase, the interfacial tension increases as the temperature decreases. This is the effect one would expect, but is not clearly shown graphically by either Figure 4 or 5.

CORRELATION OF DATA

Interfacial tension data for pure components are usually correlated by the parachor relationship. The form of the parachor equation varies slightly, but in general it can be expressed as

$$\gamma^k = P/M\,(\rho_L - \rho_V) \tag{2}$$

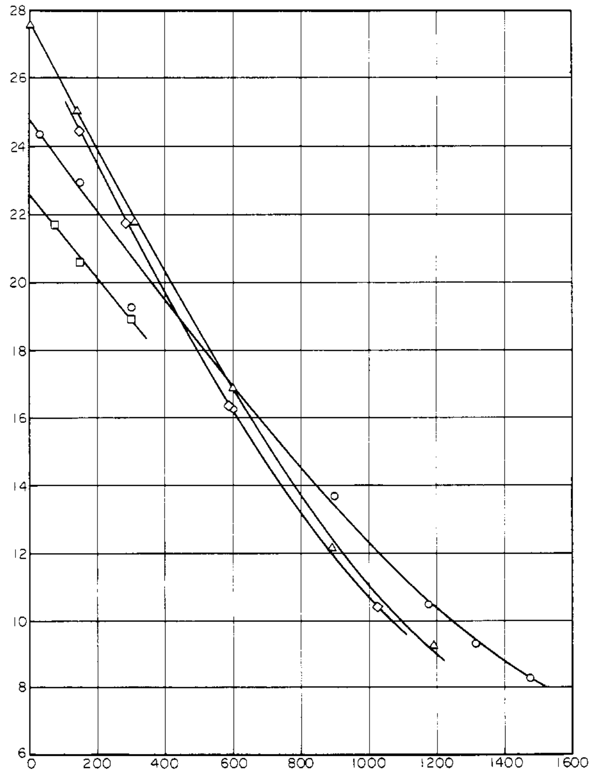

Figure 4. Isothermal surface tension of methane-nonane system

Experimental data

◇ -30° F. ○ 30° F.

△ -10° F. □ 76° F.

Exponent *k* is usually 0.25 as recommended by Sugden (*16*), but some authors assign a slightly different value.

Weinaug and Katz (*19*) and Stegemeier (*15*) have extended the pure component parachor relationship to hydrocarbon mixtures. Katz and Weinaug studied primarily the methane-propane system using the parachor relation in the form

$$\gamma^{1/4} = \sum_{i=1}^{n} P_i\left(\frac{\rho_L}{M_L}x_i - \frac{\rho_V}{M_V}y_i\right) \tag{3}$$

They reported good agreement with experimental data for the methane-propane system. Stegemeier studied the methane-butane, methane-pentane, and methane-decane systems. He preferred a parachor relationship expressed as

$$\gamma^{3/11} = \sum_{i=1}^{n} P_i\left(\frac{\rho_L}{M_L}x_i - \frac{\rho_V}{M_V}y_i\right) \tag{4}$$

Using Equation 4, Stegemeier did not find as good degree of reproducibility of experimental data as Katz and Weinaug did using Equation 3.

Both the Katz and Stegemeier relations were used to calculate the experimental data points measured in this investigation. A summary of these comparisons is shown in Table IV for the methane-nonane system and in Table V for the butane-decane system. For the methane-nonane system, the Katz-Weinaug relation shows maximum deviations of +14% and −2% with an average absolute deviation of 5.5%; the Stegemeier relation shows maximum deviations of +19 and −1.7% with an average absolute deviation of 9.7%. For the butane-decane system the Katz-Weinaug relation shows a maximum deviation of +12.6% with an average absolute deviation of 7.5%; the Stegemeier relation shows a maximum deviation of +11.6% and an average absolute error of 7.1%.

In both the methane-nonane and butane-decane systems nearly all deviations of the calculated surface tension values are positive. The reason for the consistent positive deviations is not immediately obvious. Neither Weinaug and Katz nor Stegemeier described the fitting techniques used

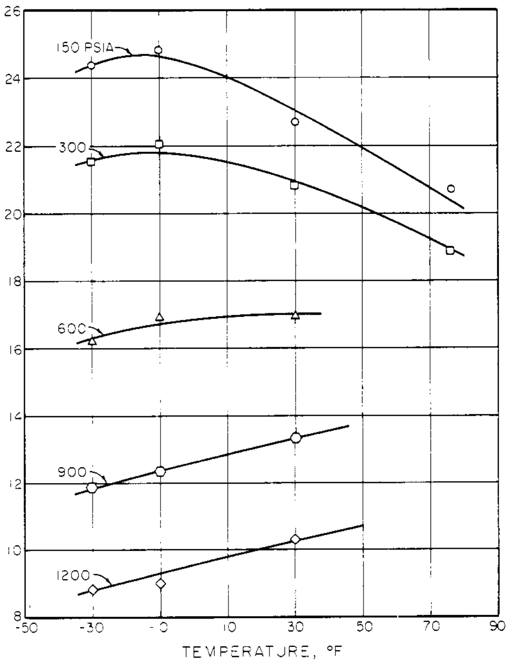

Figure 5. Surface tension of methane-nonane at constant pressure

Smoothed values

Table IV. Comparison of Parachor Correlation of Interfacial Tension Values (Dynes/Cm.) for Methane-Nonane

T, ° F.	P, P.S.I.A.	Av. Exp.	Katz		Stegemeier		Modified Katz	
-30	147	24.45	26.10	+7	26.55	+8.7	25.20	+3
	285	21.73	23.54	+8.3	24.18	+11.2	22.71	+4.5
	590	16.38	18.45	+12	19.42	+18.5	17.75	+8
	1025	10.41	11.04	+6	12.33	+18.5	10.50	+1
-10	140	25.05	25.32	+1	25.84	+3	24.43	-2.5
	310	21.79	22.64	+4	23.37	+7	21.82	+0.1
	598	15.91	18.23	+14	19.22	+18	17.53	+10.0
	890	12.16	13.92	+14	15.11	+19	13.32	+9.5
	1190	9.27	9.94	+7	11.23	+18	9.43	+1.7
30	15 (air)	25.25						
	15	24.37	25.05	+3	24.80	+1.7	24.19	-0.74
	150	22.95	23.27	+1	23.19	+1	22.43	+2.3
	300	19.27	21.24	+10	21.36	+11	20.45	+6.1
	600	16.28	17.37	+7	17.84	+9.6	16.67	+2.4
	900	13.68	14.05	+3	14.75	+7.8	13.43	-1.8
	1175	10.48	10.94	+4	11.81	+12.6	10.38	-1
	1315	9.30	9.54	+3	10.46	+12.5	9.01	-3.1
	1475	8.26	8.33	+1	9.29	+12.5	7.84	-5.1
75	15 (air)	22.76						
	75	21.77	21.34	-2	21.41	-1.7	20.59	-5.4
	150	20.58	20.58	0	20.73	+0.73	19.86	-3.5
	300	18.93	19.06	+1	19.34	+2.2	18.36	-3
Max. deviation, %				+14		+19		+10
Av. deviation, %				5.5		9.7		3.74

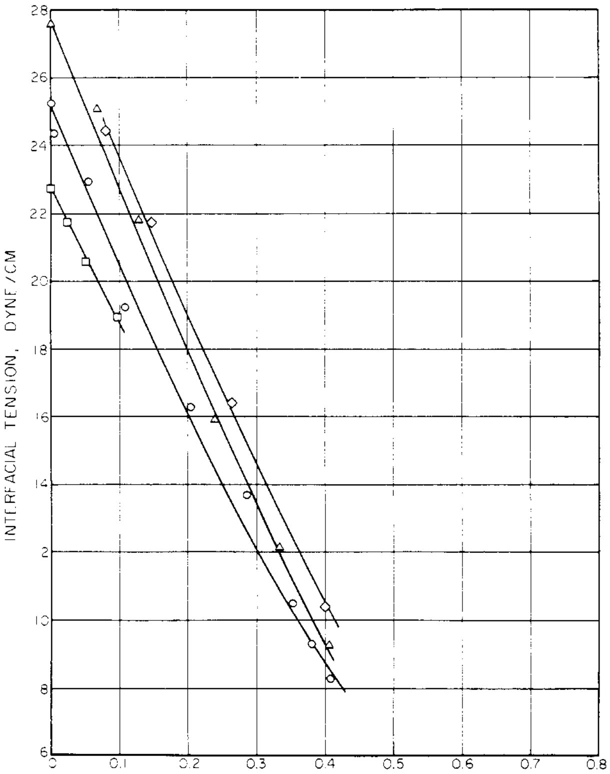

Figure 6. Surface tension–composition diagram for methane-nonane system

Experimental data

◇ -30° F. ○ 30° F.

△ -10° F. □ 76° F.

Table V. Comparison of Parachor Correlation of Interfacial Tension Values (Dynes/Cm.) for Butane-Decane System

T, ° F.	P, P.S.I.A.	Interfacial Tension Av. Exp.	Interfacial Tension Katz	Interfacial Tension Stegemeier	Per Cent Error Katz	Per Cent Error Stegemeier
100	9	20.06	21.13	21.18	+5.3	+5.6
	24	16.92	18.54	18.47	+9.9	+9.1
	34	15.73	16.08	16.00	+2.2	+2.0
40	3.6	21.32	24.02	23.80	+12.6	+11.6
		Maximum error, %			+12.6	+11.6
		Average absolute error, %			7.5	7.1

Table VI. Comparison of Parachor Values

	Methane	Butane	Nonane
Weinaug-Katz	77.9	189.9	391.0
Stegemeier-Hough	77.9	200.5	423.0
Modified Weinaug-Katz	81.0		387.6

to develop their parachor values. A properly derived parachor should give a good fit to the data with both positive and negative errors.

The Weinaug-Katz equation, because it gave a better fit to the data than the Stegemeier relation, was used as a basis for deriving new parachor values for methane and nonane. The Weinaug-Katz relationship was fitted by regression analysis to the experimental methane-nonane data. The results of this fitting are shown in Table IV as the modified Katz values. These show a maximum positive deviation of 10% and a maximum negative deviation of 5.4% with an average absolute deviation of 3.74%.

Table VI compares the parachor values derived by Weinaug and Katz, Stegemeier and Hough, and the values obtained from fitting the methane-nonane data of this work. Though differences in the parachor values appear to be small, the modified values give a better fit of the experimental methane-nonane data. Modified parachors were not derived for butane and decane because of the small amount of data.

NOMENCLATURE

d_e = equatorial diameter, cm.
d_n = outside diameter of capillary, cm.
d_s = selected plane diameter, cm.
g = acceleration due to gravity
H = shape-dependent parameter
k = exponent in surface tension equation
M = molecular weight, grams
P = parachor
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Symbols

γ = surface or interfacial tension, dynes/cm.
ρ = density, g./cc.

Subscripts

i = any component
L = liquid phase
V = vapor phase

LITERATURE CITED

(1) Adamson, A.W., "Physical Chemistry of Surfaces," pp. 1–44, Interscience, New York, 1960.
(2) Andreas, J.M., Hauser, E.A., Tucker, W.B., *J. Phys. Chem.* **42**, 1001 (1938).
(3) Benedict, M., Webb, G.M., Rubin, L.C., *Chem. Eng. Progr.* **47**, 419 (1951).
(4) Brauer, E.B., Hough, E.W., *Producers Monthly* **29** (8), 13 (1965).
(5) Fordham, S., *Proc. Roy. Soc. (London)* **194A**, 1 (1948).
(6) Hough, E.W., Wood, B.B., Rzasa, M.J., *J. Phys. Chem.* **56**, 996 (1952).
(7) Jasper, J.J., Kerr, E.R., Gregorich, F., *J. Am. Chem. Soc.* **75**, 5252 (1953).
(8) Jasper, J.J., Kring, E.V., *J. Phys. Chem.* **59**, 1019 (1955).
(9) Niederhauser, D.O., Bartell, F.E., "Report of Progress. Fundamental Research on Occurrence and Recovery of Petroleum," 1948–49, American Petroleum Institute, Baltimore, Md., p. 114, 1950.
(10) Pennington, B.F., Hough, E.W., *Producers Monthly* **29** (7), 4 (1965).
(11) Rackett, H.G., S.M. thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1960.
(12) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **38**, 986 (1946).
(13) Savvina, Y.O., Velikovskii, A.S., *J. Phys. Chem. (USSR)* **30**, 1596 (1956).
(14) Shipman, L.M., Kohn, J.P., J. CHEM. ENG. DATA **11**, 176 (1966).
(15) Stegemeier, G.L., Ph.D. dissertation, University of Texas, Austin, Tex., 1959.
(16) Sugden, S., *J. Chem. Soc.* **858**, 30 (1922).
(17) Warren, H.G., Ph.D. dissertation, Mississippi State University, State College, Miss., 1965.
(18) Weber, J.H., "Absorption Literature Survey," prepared for Natural Gas Processors' Association, Sept. 3, 1964.
(19) Weinaug, C.F., Katz, D.L., *Ind. Eng. Chem.* **35**, 239 (1943).

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The System 2-Isopropoxypropane–2-Propanol–Water

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The vapor-liquid equilibrium data of the ternary system and the related binary systems, including the composition of the azeotropic mixtures and liquid-liquid equilibrium at the boiling point, are reported for 760 mm. of Hg.

A STUDY of the liquid-liquid and vapor-liquid equilibria of the ternary system 2-isopropoxypropane–2-propanol–water has been made. The liquid-liquid equilibrium was studied at 25° C. and at the boiling points of the mixtures, with a constant pressure of 760 mm. of Hg. Since Frère (*4*) published data on the liquid-liquid equilibrium at 25° C. which agree very well with the present measurements, no data about this equilibrium are listed in the present work. This study does not contain new data for the 2-propanol–water system, since other sets of data are available for it (*10*). Miller and Bliss (*8*) reported data for the binary system 2-isopropoxypropane–2-propanol, and Motina and coworkers (*9*) for the ternary system 2-isopropoxypropane–2-propanol–water.

EXPERIMENTAL

Experimental methods for the purification of materials, the determination of the liquid-liquid and vapor-liquid equilibria, and the method employed for the analysis of the samples are published (*12*). Only few remarks must be added.

The purification of 2-isopropoxypropane requires some precautions because of possible peroxidation. This was avoided by distillation under nitrogen atmosphere and keeping the samples in iron vessels.

It was impossible to purify the 2-isopropoxypropane by distillation only. Therefore, the ether was stirred thoroughly with sulfuric acid (about 65 weight %), washed, dried, and distilled.