

# Correlation of Surface and Interfacial Tension of Light Hydrocarbons in the Critical Region

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## ABSTRACT

*Empirical equations for surface tension of propane and normal butane as functions of reduced temperature are obtained from experimental data. Another correlation relating surface tension to enthalpy of vaporization is given for these two compounds. In addition, new parachor numbers are calculated for the normal paraffin hydrocarbons. These numbers are utilized for the calculation of interfacial tension of two-component systems as functions of pressure and temperature, using a modified form of Weinaug-Katz equation. The experimental data for two binary systems are approximated by the correlation. From these results it is found that the interfacial tension in the high-pressure region remains extremely low at large pressure decrements below the critical pressure. Thus, it appears that condensate systems may have flow characteristics almost like single-phase conditions even though the pressure is within the two-phase region.*

*Experimental data have shown that interfacial tension divided by density difference approaches zero as the critical pressure is approached. A calculation of wetting-phase saturations indicates that the saturation gradient at the two-phase contact becomes increasingly abrupt as the critical pressure is approached.*

## DISCUSSION

Prediction of the surface and interfacial tension of the light hydrocarbons and of two-component hydrocarbon mixtures at various temperatures and pressures may be made if other physical properties are known. Extensive experimental work on single-component and binary systems<sup>1</sup> is the basis for the correlations outlined in this paper.

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<sup>1</sup>References given at end of paper.

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Interfacial tension is defined as the specific surface-free energy between two phases of unlike fractional composition, while surface tension is defined as the specific surface-free energy between two phases of the same fractional composition. The usual definitions relating interfacial tension to a liquid-liquid interface and surface tension to a gas-liquid interface are not clearly defined when the critical region is included, and there is no sharp distinction between a gas and a liquid phase.

Interfacial tension is probably the most important single force that makes one-half to one-third of the total oil actually in place in a reservoir rock unrecoverable by conventional gas-drive or waterflood methods. A rough estimate of this figure for the United States is 100 billion bbl. Interfacial tension presently is used by petroleum engineers in the estimation of saturation gradients at the gas-oil contact and at the oil-water contact. The data in this paper should prove useful for estimates of reserves involving gas-oil contacts. Relative permeability undoubtedly is influenced by interfacial tension, for sufficiently small values. These data should be useful in determining how small the values are. In addition, these data should eventually add to our fundamental knowledge of surfaces. At the critical point, all surface excesses approach zero and the thickness becomes very large.

## SINGLE-COMPONENT SYSTEMS

It has been observed<sup>1</sup> that the following relationships are good approximations to the physical properties of propane and n-butane.

For propane,  $\Delta\rho = 0.80 (1 - T/T_c)^{0.326}$ ,  $\gamma = 49.5 (1 - T/T_c)^{1.20}$ ,  $\gamma/\Delta\rho = 61.9 (1 - T/T_c)^{0.874}$ , and  $\gamma = 112.5 \Delta\rho^{3.68}$ .

For n-butane,  $\Delta\rho = 0.86 (1 - T/T_c)^{0.333}$ ,  $\gamma = 52.5 (1 - T/T_c)^{1.22}$ ,  $\gamma/\Delta\rho = 61.0 (1 - T/T_c)^{0.887}$  and  $\gamma = 91.2 \Delta\rho^{3.66}$ .

Guggenheim's<sup>2</sup> values for these constants, not specifically for hydrocarbons, are  $\Delta\rho = C' (1 - T/T_c)^{1/3}$ ,  $\gamma = C'' (1 - T/T_c)^{11/9}$ ,  $\gamma/\Delta\rho = C''' (1 - T/T_c)^{8/9}$ , and  $\gamma = C\Delta\rho^{11/3}$ .

The symbols and units are

$\Delta\rho$  = difference in density of the liquid and vapor phases, gm/cc,  
 $\gamma$  = surface tension, dynes/cm,  
 $T$  = absolute temperature, °R or °K,  
 $T_c$  = critical temperature (absolute), °R or °K, and  
 $C, C', C''$  = constants.

The exponents for propane and n-butane are taken from log-log plots. The last equation may be recognized as the surface tension-density difference relationship leading to Sugden's parachor,<sup>3</sup> with the exponent "3/11" rather than "1/4". That is,

$$P = MC^{3/11} = \frac{M\gamma^{3/11}}{\Delta\rho}$$

where  $P$  = parachor, and

$M$  = molecular weight.

From this modified equation, new values of parachor were calculated for some of the normal paraffin hydrocarbons. Surface-tension and density-difference data for methane, ethane, n-decane and n-eicosane were taken from Rossini,<sup>4</sup> for n-pentane from Sage and Lacey<sup>5</sup> and from Katz,<sup>6</sup> and for propane and n-butane from Sage and Lacey and from experimental work.<sup>1</sup> The values are shown in Table 1. Because the parachor is (ideally) independent of temperature, the values of surface tension and density difference were selected at the temperature at which the best data were obtainable or at the temperature at which the vapor density is negligible if this latter data were not available. Fig. 1 shows a regular increase in the parachor with an increase in molecular size from 3 to 20 carbon atoms. Methane

TABLE 1 — PARACHOR OF NORMAL PARAFFIN HYDROCARBONS

Compound	Carbon Atoms	Temp. (°F)	Density Diff. (gm/cc)	Surf. or Intf. Tens. (dynes/cm)	Parachor
Methane	1	-256	0.4218 <sup>R</sup>	13.7 <sup>R</sup>	77.9
Ethane	2	-238	0.620 <sup>R</sup>	26.34 <sup>R</sup>	118.0
Propane	3	100	0.443 <sup>S</sup>	5.47 5.45 <sup>K</sup>	158.1 158
n-Butane	4	120	0.532 <sup>S</sup>	9.27 9.20	200.5 200
n-Pentane	5	100	0.603 <sup>S</sup>	14.0 <sup>K</sup>	246
n-Decane	10	68	0.730 <sup>R</sup>	23.92 <sup>R</sup>	463
n-Eicosane	20	100	0.7754 <sup>R</sup>	27.2 <sup>R</sup>	899

R=Rossini (Ref. 4); S=Sage and Lacey (Ref. 5); and K=Katz (Ref. 6).

TABLE 2 — ENTHALPY OF VAPORIZATION AT CONSTANT PRESSURE — PROPANE

Temperature (°F)	Enthalpy of Vaporization* (calories/gm-mol)	Surface Tension** (dynes/cm)
100	3271	5.48
130	2878	3.66
160	2366	1.97
190	1660	0.58

\*Sage and Lacey (Ref. 5).

\*\*Current paper.

and ethane appear to diverge slightly from this pattern. Some of this divergence is probably caused by the measurement of surface tension against air rather than its own vapor, and by the neglect of the vapor density.

A correlation suggested by Magari<sup>7</sup> relates the enthalpy of vaporization at constant pressure to the surface tension. Tables 2 and 3 and Figs. 2 and 3 express this relation for propane and for n-butane. The straight-line relationship on log-log paper appears to deviate slightly as the critical point is approached.

## TWO-COMPONENT SYSTEMS

Prediction of interfacial tension in two-component systems is much more difficult than in the single-component systems because of the added composition variable. The correlation suggested by Weinaug and Katz<sup>8</sup> has been used with the new exponent and slightly modified for use with molal volumes rather than specific gravity. The relation is

$$\gamma = \left\{ \frac{1}{62.43} \left[ P_1 (x_1/V_x - y_1/V_y) + P_2 (x_2/V_x - y_2/V_y) \right] \right\}^k$$

where  $\gamma$  = interfacial tension, dynes/cm,

$P_1$  = parachor of the first component,

$P_2$  = parachor of the second component,

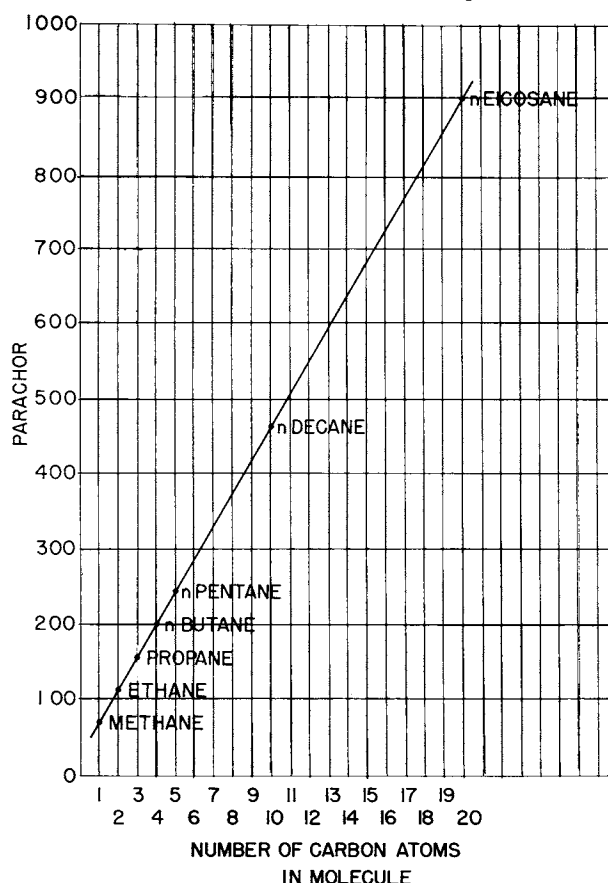


FIG. 1 — PARACHOR, NORMAL PARAFFIN HYDROCARBONS.

TABLE 3 — ENTHALPY OF VAPORIZATION AT  
CONSTANT PRESSURE — NORMAL BUTANE

Temperature (° F)	Enthalpy of Vaporization* (calories/gm-mol)	Surface Tension** (dynes/cm)
100	4816	10.49
130	4566	8.67
160	4266	6.88
190	3912	5.14
220	3498	3.48
250	2980	2.02
280	2307	0.80

\*Sage and Lacey (Ref. 5).

\*\*Current paper.

$x_1, x_2$  = mol fraction in the liquid phase,  
 $y_1, y_2$  = mol fraction in the vapor phase,  
 $V_x, V_y$  = molal volume, cu ft/lb mol, and  
 $k$  = new exponent of the parachor relation  
 $= 11/3$ .

The modified values of the parachor together with the new exponent are used in this equation to predict values of interfacial tension determined experimentally<sup>1</sup> on the methane-normal pentane system and on the methane-normal decane system. These experimental data are summarized on the pressure-temperature plots in Figs. 4 and 5. The boundaries of this region are the vapor-pressure curves for the pure components and the line of critical loci of the various intermediate mixtures. Superposed on these diagrams are the lines of constant interfacial tension. The known data for these iso-interfacial tension lines are the surface-tension data of the pure compounds and the experimental data by the authors, which include a very limited range in comparison to the complete two-phase region. Since the properties of the liquid and the gas at the critical point are identical, the line of

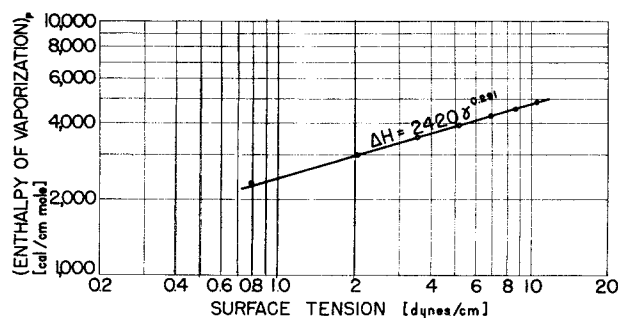


FIG. 2 — ENTHALPY OF VAPORIZATION, PROPANE.

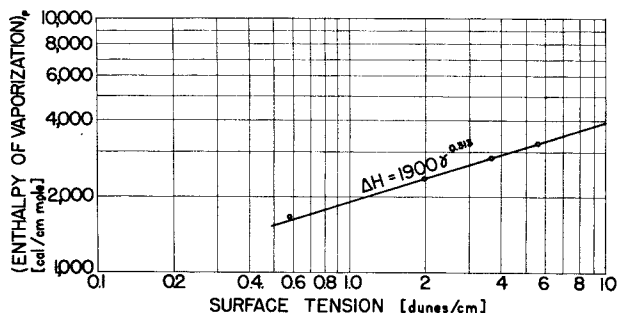


FIG. 3 — ENTHALPY OF VAPORIZATION, NORMAL BUTANE.

critical loci is also the line of zero interfacial tension; hence, the subsequent iso-interfacial tension lines must roughly parallel this boundary. These data and assumptions allow extrapolation and interpolation to all points within the two-phase region. It is evident from these plots that the interfacial tension of a binary mixture in the temperature range in which the critical pressure is high increases much more slowly with a decrease in pressure than either of the pure components. In the case of the methane-normal pentane system, a pressure drop of 450 psi from the critical pressure is required at 100°F before the interfacial tension reaches 1 dyne/cm. The same increase for the pure components occurs with a pressure drop of about 120 psi. In the methane-normal decane system the effect is even more pronounced, the pressure drop at 100°F being 1,040 psi for a comparable increase in interfacial tension. These facts suggest that interfacial forces may be negligible, as far as flow conditions

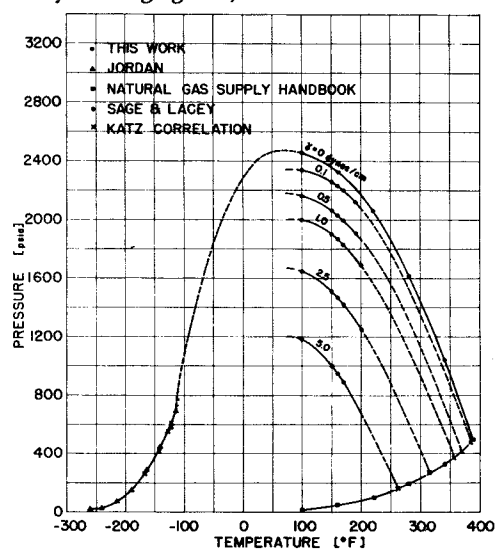


FIG. 4 — METHANE-NORMAL PENTANE.

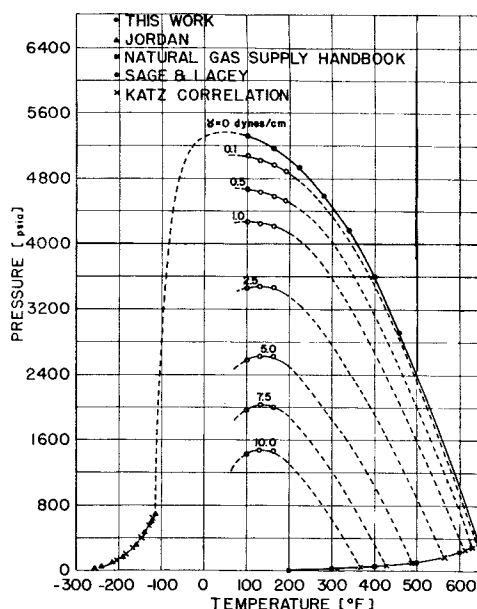


FIG. 5 — METHANE-NORMAL DECANE.

are concerned, for a condensate reservoir for an appreciable portion of the two-phase region.

Prediction of these experimental results from the modified equation of Weinaug and Katz was attempted with the PVT data of Sage and Lacey. A summary of these calculations is given in Table 4.

The equation for binary systems may be generalized to multicomponents systems as follows.

$$\gamma = \left\{ \frac{1}{62.43} \left[ P_1 \left( \frac{x_1}{V_x} - \frac{y_1}{V_y} \right) + P_2 \left( \frac{x_2}{V_x} - \frac{y_2}{V_y} \right) + P_n \left( \frac{x_n}{V_x} - \frac{y_n}{V_y} \right) \right] \right\}^{11/3}$$

This calculation requires a knowledge of the composition of both phases and the molal volume or density of each phase. In the absence of density data, reduced temperature calculations may be used as an approximation to the density. The parachor numbers for each compound of the normal paraffin hydrocarbons from methane to n-eicosane are shown in Fig. 1.

#### SURFACE EXCESS

Excess concentration of methane at the liquid surface for the two-component systems may be approximated from the equation given by Rice.<sup>9</sup>

$$\Gamma_1 = -\rho_N \left( \frac{\partial \gamma}{\partial p} \right)_T$$

where  $\Gamma_1$  = excess of methane in the surface, mol/sq cm,

$\rho_N$  = density of methane, mol/cc,

$p$  = pressure, dynes/sq cm, and

$T$  = temperature, °R or °K.

It must be noted that this equation was derived with the assumption of a zero surface excess of the other (heavier) component.

Calculation of surface excess from experimental

TABLE 4 — INTERFACIAL TENSION CORRELATION  
(Weinaug and Katz<sup>6</sup>)

Components	Temperature (°F)	Pressure (psia)	Interfacial Tension (dynes/cm)	
			Exper.	Calc.
Methane and n-Pentane	100	600	9.02	9.30
		1250	4.59	4.78
		1750	2.01	2.09
		2250	0.27	0.21
	220	600	4.62*	5.02
		1250	1.98*	2.14
		2000	0.07*	0.05
	340	800	0.37*	0.37
Methane and n-Decane	100	1250	11.3	11.8
		2000	7.35	7.02
		3500	2.40	1.84
		5000	0.16	0.09
	280	1000	9.13*	9.30
		3000	2.31*	2.32
		4500	0.06*	0.02
	460	1000	3.3*	3.95
		2750	0.3*	0.10

\*Extrapolated

values is obtained by using the slope of isotherms of interfacial tension plotted against pressure for both two-component systems. If pressure is expressed in pounds per square inch, interfacial tension in dynes per centimeter and specific volume in cubic feet per pound-mole, a conversion factor must be used in the modified equation.

$$\Gamma_1 = - \frac{14.013 \times 10^{16}}{V_1} \left( \frac{\partial \gamma}{\partial p} \right)_T$$

For example, methane-normal pentane at 100°F and 1,500 psia,

$$\left( \frac{\partial \gamma}{\partial p} \right)_T = -0.00506 \frac{\text{dynes/cm}}{\text{psi}},$$

$V_1 = 3.50$  cu ft/lb mol (methane), and

$\Gamma_1 = 2.03 \times 10^{14}$  mol methane/sq cm.

Results of surface-excess calculations are given in Tables 5 and 6. As the pressure approaches zero, the value of the density term in the surface-excess equation approaches zero and the isothermal change in interfacial tension with pressure remains finite; hence, the surface excess as the pressure approaches zero also approaches zero. See Figs. 6 and 7. As the pressure approaches the critical point of the mixture, the density of methane remains finite; but, according to experimental results, the change in interfacial tension with pressure approaches zero. Therefore, the surface excess again approaches zero as the critical pressure is approached. For intermediate values of pressure, the density term is positive and the slope was found to be negative; hence, the surface excess is positive between zero and the critical pressure, and has at least one

TABLE 5 — SURFACE EXCESS OF METHANE IN THE  
METHANE-NORMAL PENTANE SYSTEM  
(MOLECULES  $\times 10^{-14}$ /SQ CM)

Pressure (psia)	Temperature (°F)				
	100	150	160	170	200
2250	1.38	0.72	0.57	0.42	—
2000	1.90	1.34	1.25	1.17	—
1750	2.09	1.53	1.40	1.36	0.99
1500	2.03	1.50	1.40	1.33	1.03
1250	1.92	1.46	1.35	1.27	0.98
1000	1.66	1.26	1.16	1.08	0.90
800	1.40	1.07	0.98	0.93	0.76
600	1.17	0.82	0.78	0.74	0.60

TABLE 6 — SURFACE EXCESS OF METHANE,  
METHANE-NORMAL DECANE (MOLECULES  $\times 10^{-14}$ /SQ CM)

Pressure (psia)	Temperature (°F)		
	100	130	160
5000	0.98	0.86	0.69
4500	1.42	1.39	1.33
4000	1.74	1.56	1.57
3500	2.03	1.93	1.83
3000	2.34	2.21	2.12
2750	2.45	2.38	2.20
2500	2.54	2.41	2.22
2250	2.54	2.30	2.13
2000	2.44	2.12	1.96
1750	2.29	2.04	1.88
1500	2.00	1.79	1.67
1250	1.66	1.50	1.40

maximum point at some intermediate pressure.

The occurrence of a maximum, followed by decreasing values of surface excess, is attributed to the increased value of the surface excess of the heavier component. This value is probably small in the low-pressure region, but it becomes large as the pressure becomes large. Thus, it is reasonable to assume that the decrease in the "surface excess", as calculated, is the result of the surface excess of the heavier component's becoming significantly large. The maximum value of the calculated surface excess of the methane-normal pentane system (or the methane-normal decane system) might be associated with the attainment of a monolayer of methane on a solid surface, since extrapolation of these values for the various isotherms gives fairly good agreement of values of surface density<sup>10</sup> of a monolayer of methane on a solid surface at  $-297^{\circ}\text{F}$ .

It appears that surface excess might be useful as a correlating device for interfacial tension, since its values appear to be much more constant for the various systems than interfacial tension itself. For instance, a plot of surface excess divided by density difference appears to give nearly a straight line when plotted against pressure and might possibly yield a finite value at the critical pressure, although in the case of the methane-normal pentane system the value appeared to approach zero very near the critical point.

Experimental data<sup>1</sup> have shown that not only the interfacial tension, but also the interfacial tension

divided by density difference approaches zero as the critical point is approached. The significance of the latter is emphasized by a calculation of wetting-phase saturation of porous media from interfacial-tension data. Plotting saturation gradient vs height, one obtains a very sharp gas-liquid contact as the critical point is approached.<sup>1</sup> This sharp liquid-gas saturation gradient may be a contributing factor to the nonequilibrium conditions found in oil reservoirs by Cupps, Lipstate and Fry.<sup>11</sup>

## SUMMARY

A considerable amount of data has been accumulated on the surface tension of propane and normal butane, especially near their critical temperatures. In addition, the binary systems — methane-normal pentane and methane-normal decane — have been investigated throughout a wide pressure and temperature range, particularly in the region near the critical points. All these data point to the regularity of the pressure and temperature functions of surface and interfacial tension. Of most interest in the data, however, is the persistence of low interfacial tensions with relatively large changes in pressure in the region about the critical points. The importance of this fact to the petroleum engineer lies in its relationship to liquid saturations and flow behavior in an oil reservoir.

A means of predicting interfacial tension for hydrocarbon mixtures from composition and volumetric data appears to fit experimental results very well. Other correlating devices such as reduced temperature relations, enthalpy of vaporization relations, and surface-excess calculations give promise of relating the surface phenomena to better known physical phenomena.

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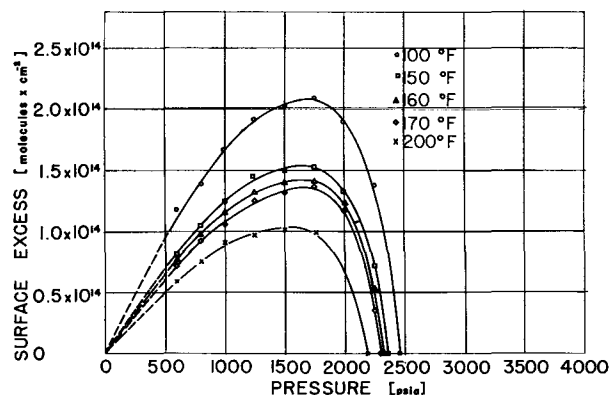


FIG. 6 — SURFACE EXCESS, METHANE-NORMAL PENTANE.

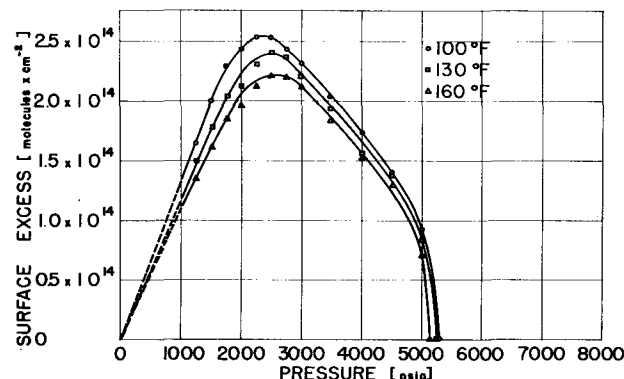


FIG. 7 — SURFACE EXCESS, METHANE-NORMAL DECANE.