

A Generalized Equation for Surface Tension from the Triple Point to the Critical Point

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A three-parameter generalized equation is proposed for surface tension from the triple point to the critical point. This equation not only fits the data well but also is good for interpolation between the normal boiling point and the critical point. This equation is also good for extrapolation to the triple point. This equation has been tested using the surface tension of water from the triple point to the critical point. The constants of this equation obtained using orthobaric surface tensions are given for a number of compounds. The isobaric surface tensions determined at a pressure of 1 atm do not differ significantly from the orthobaric surface tensions. Such data also have been used in obtaining equations from the triple to the critical point.

KEY WORDS: alcohols; alkanes; isobaric surface tension; orthobaric surface tension; water.

1. INTRODUCTION

In our continuing search for new equations from the triple point to the critical point for various properties of liquids, we have found that the property of surface tension has received very little attention. The data on surface tension are usually limited to low temperatures only. Since the surface tension is zero at the critical point, a good equation should be able to fill the data from the low temperatures to the critical point. The most commonly used equations for the surface tension are therefore reviewed

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below. The famous equation of Van der Waals [1] for the surface tension is the following:²

$$\gamma = AX^n \quad (1)$$

where the exponent n has the value of 1.25 for most liquids [2].

The Van der Waals equation may also be written as follows:

$$\gamma = k(T_c - T)^n \quad (2)$$

where $k = A/T_c^n$. k has a value of 2.12 for most liquids.

Recently Vargaftik et al. [3] determined the surface tension of water from the triple point to the critical point and correlated their data with temperature using the following equation:

$$\gamma = \sum_{i=1}^9 a_i(T_c - T)^i \quad (3)$$

Subsequently, Vargaftik et al. [4] have fitted the values approved by the International Association for the Properties of Steam to the following equation:

$$\gamma = BX^\mu(1 + bX) \quad (4)$$

where $B = 0.2358 \text{ N} \cdot \text{m}^{-1}$, $b = -0.625$, and $\mu = 1.256$.

Straub et al. [5] investigated the following equation:

$$\gamma = BX^\mu(1 + bX)^c \quad (5)$$

but did not find it helpful to include an additional constant c .

For most compounds the data on surface tension are limited to temperatures below the normal boiling point [6] and are usually expressed by means of a two-constant equation:

$$\gamma = a + bT \quad (6)$$

Since the surface tension at the critical point is zero and since the critical temperature can be estimated [7-12] in many cases with reasonable accuracy, we thought it would be worthwhile to investigate Eq. (4) further to see whether it could be generalized and used for interpolation between the low-temperature data and the critical point. With this goal in mind we propose the following equations:

$$\gamma = aX^{5/4} + bX^{9/4} \quad (7)$$

$$\gamma = aX^{5/4} + bX^{9/4} + cX^{13/4} \quad (8)$$

² Explanation of symbols and associated units is given under Nomenclature, at the end of the paper.

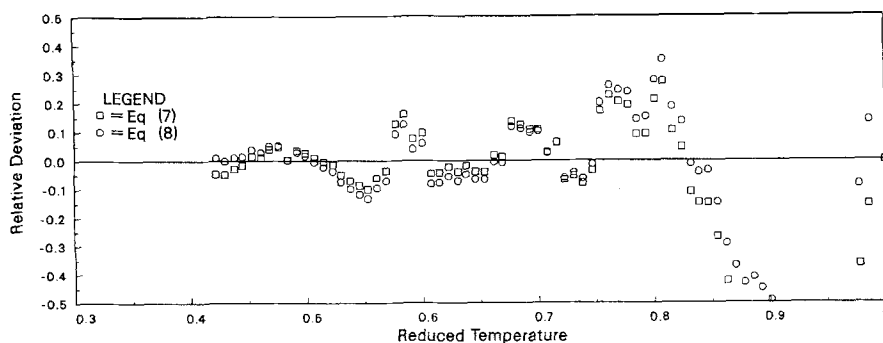


Fig. 1. Plot of relative deviation in surface tension of water versus reduced temperature. The results of the first regression with 83 data points.

2. RESULTS AND DISCUSSION

Our results indicate that the three-constant Eq. (8) fits the data much better than the two-constant Eq. (7). We have illustrated this with respect to water in Fig. 1 and in Table I. The surface tension data used for water are from Vargaftik et al. [3] from the triple point to the critical point. Although the improvement is not very significant with respect to water, Eq. (8) is the preferred one in most cases and, particularly, in the case of alcohols. In cases when Eq. (8) is slightly superior to Eq. (7), we have found that both the equations satisfy the following three criteria:

- (1) $A[\text{Eq. 7}] \approx A[\text{Eq. 8}]$
- (2) $\gamma_m[\text{Eq. 7}] \approx \gamma_m[\text{Eq. 8}]$
- (3) $\gamma_f[\text{Eq. 7}] \approx \gamma_f[\text{Eq. 8}]$

where γ_m and γ_f are the surface tensions at the melting point and at a reduced temperature of 0.9, respectively. Normally surface tensions are available over a limited range of temperatures close to the normal boiling

Table I. Values of the Constants of Eqs. (7) and (8) for the Surface Tension of Water

Eq. No.	$T_t(\text{K})$	$T_c(\text{K})$	A	B	C	SD	Av. dev.
(7)	273.16	647.126	233.442454	-144.124989		0.051	0.041
(8)	273.16	647.126	232.713514	-140.186450	-4.890098	0.049	0.039

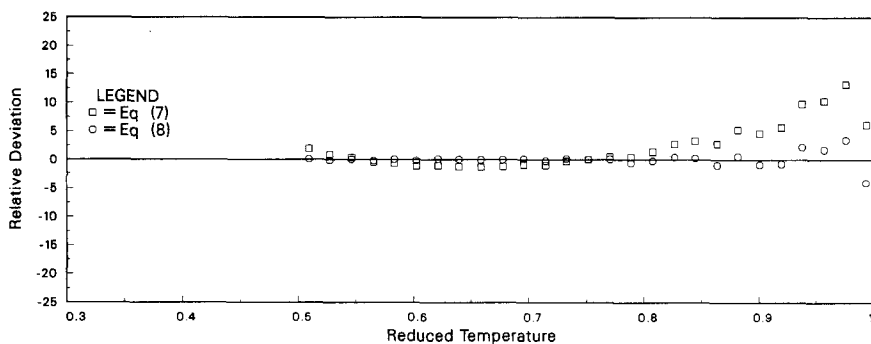


Fig. 2. Plot of relative deviation in surface tension of 1-propanol versus reduced temperature. The results of the first regression with 28 data points.

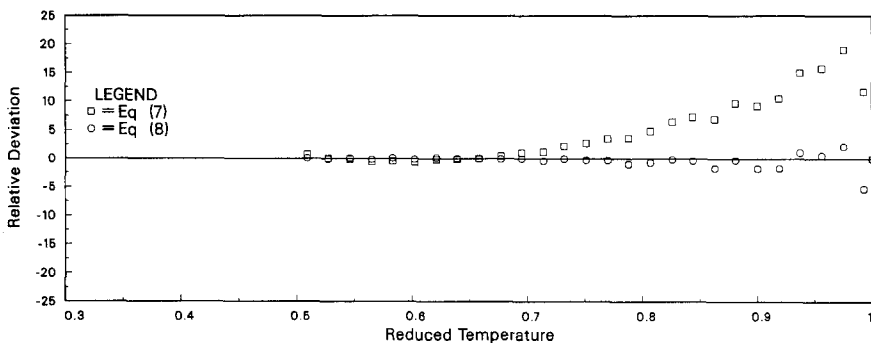


Fig. 3. Plot of relative deviation in surface tension of 1-propanol versus reduced temperature. The results of the second regression with 12 data points.

Table II. Values of the Constants of Eqs. (7) and (8) for the Surface Tension of 1-Propanol

Eq. No.	T_i (K)	T_c (K)	A	B	C	SD	Av. dev.
Results of 1st regression with 28 data points							
(7)	147.00	536.78	97.6922	-74.9949		0.219	0.184
(8)	147.00	536.78	108.3998	-142.3177	97.2580	0.037	0.030
Results of 2nd regression with 12 data points							
(7)	147.00	536.78	92.7520	-63.4801		0.027	0.035
(8)	147.00	536.78	109.9511	-149.7664	106.0728	0.022	0.034

point. When the above three criteria are satisfied, then the results predicted by Eq. (8) are fairly reliable. For many compounds tested, this has been the case. In the case of alcohols, however, Eq. (8) has been found to be vastly superior to Eq. (7) and the three criteria are not usually met. This has been illustrated with respect to 1-propanol in Figs. 2 and 3 and in Table II. The surface tension data are from Efremov [13]. The results in Table II for the first regression show that the first criterion is not met. Equation (7) extrapolates to a very low value for γ_m . The expected value for γ_m may usually be obtained by linear extrapolation of the low-temperature data to the melting point. The value of γ_m obtained through linear extrapolation is $36.5 \text{ dyne} \cdot \text{cm}^{-1}$. Equation (8) leads to a value of $37.8 \text{ dyne} \cdot \text{cm}^{-1}$, while Eq. (7) gives $29.0 \text{ dyne} \cdot \text{cm}^{-1}$, which is too low. Criterion 3 is met, however, since the data extend all the way to the critical point.

The efficacy of Eq. (8) in determining γ_f is illustrated in Fig. 3. The relative deviations plotted in Fig. 3 are obtained using the surface tension data of 1-propanol only up to the normal boiling point and then one data point at the critical point. In this regression Eq. (8) predicts satisfactorily the surface tensions between the normal boiling point and the critical point. Equation (7) fails to interpolate well. Thus Eq. (8) is superior to Eq. (7) for both extrapolation and interpolation.

There are, however, several instances, in which the behavior of Eq. (7) is quite normal but that of Eq. (8) is abnormal with respect to interpolation to the melting point. The problem, however, could be corrected by fixing the values of γ_m and γ_f . When these two data points are also used in the regression, Eq. (8) behaves normally and is better than Eq. (7).

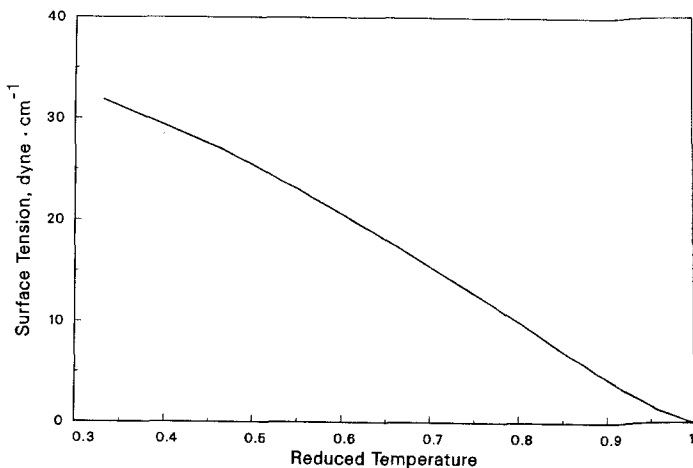


Fig. 4. Plot of surface tension of 1-pentanol versus reduced temperature.

Table III. Constants of Eq. (8) for the Surface Tensions of Various Compounds

Compound	$T_t(K)^a$	$T_c(K)$	A	B	C	SD	Av. dev.
Normal hydrogen	13.95	33.20	6.4906	0.51694	-2.6287	0.009	0.006
Helium-4	0.95	5.30	0.65116	0.09654	-0.38692	0.003	0.003
Neon	24.50	44.50	8.2803	17.3278	-2.7336	0.136	0.069
Argon	83.78	150.69	32.9574	17.1975	-18.4004	0.002	0.002
Krypton	116.55	209.40	12.0211	-156.2650	395.4992	0.256	0.146
Xenon	161.25	289.75	49.1907	13.2643	-10.4283	0.013	0.009
Nitrogen	63.29	126.09	27.5107	5.7440	-3.0719	0.015	0.010
Oxygen	54.35	154.58	38.2261	5.6316	-7.7405	0.021	0.015
Fluorine	53.00	144.30	36.9689	23.9993	-30.0548	0.301	0.192
Chlorine	171.55	416.90	71.0242	21.9901	-22.2131	0.036	0.023
Carbon monoxide	66.15	132.91	35.0998	-9.3076	-1.7393	0.003	0.002
Carbon dioxide	216.55	304.10	75.9675	-5.0913	3.9907	0.009	0.005
Sulfur dioxide	197.65	430.80	101.6572	-20.5010	-5.7962	0.006	0.004
Nitrous oxide	170.85	309.60	78.0454	-1.8982	-33.0621	0.059	0.036
Nitric oxide	112.15	180.00	58.6304	97.8722	-33.6739	0.022	0.013
Hydrogen fluoride	190.15	461.00	25.4706	22.8483	-16.8896	0.051	0.039
Hydrogen bromide	187.15	363.20	74.0521	20.1043	-30.2571	0.012	0.007
Hydrogen selenide	209.15	411.00	121.7175	-118.8804	51.1701	0.056	0.039
Hydrogen telluride	146.35	271.20	88.1547	-82.0460	39.02672	0.279	0.163
Hydrogen disulfide	185.15	572.00	130.1176	-40.6216	4.7716	0.019	0.013
Ammonia	195.45	405.50	104.1403	24.5169	-61.1567	0.099	0.070
Sulfur tetrafluoride	152.15	364.00	79.2098	-23.2043	2.3185	0.002	0.001
Carbonyl chloride	134.95	455.00	76.8219	-13.2836	-2.5768	0.008	0.005
Carbonyl sulfide	135.00	375.10	55.8252	33.3367	-28.7857	0.156	0.112
Nitrosyl chloride	208.65	440.00	133.0218	-101.9320	27.4667	0.056	0.036
Nitryl fluoride	134.15	349.50	59.3349	17.2981	-19.8885	0.017	0.012
Nitrosyl fluoride	139.15	344.20	107.5196	-105.9891	25.3166	0.238	0.149
Methane	90.69	190.55	30.8936	24.9105	-6.8276	0.090	0.058
Ethane	89.89	305.42	53.6025	-7.6050	3.0714	0.055	0.044
Propane	85.47	369.82	55.1756	-7.8600	2.1428	0.033	0.022
Butane	134.86	425.16	55.0822	-2.5019	-3.7758	0.098	0.051
Isobutane	113.54	408.15	50.0587	4.0246	-3.3400	0.118	0.085
Pentane ^b	143.47	469.69	56.2267	-3.7496	-2.9861	0.032	0.025
Hexane	177.83	507.50	52.2937	6.1685	-3.5869	0.065	0.051
Heptane	182.55	540.30	54.1778	-0.75856	3.9897	0.084	0.055
Octane	216.37	568.80	56.5399	-10.4928	8.4723	0.068	0.056
Ethylene	104.00	282.34	53.4828	-13.2207	19.9706	0.152	0.095
Propylene	87.90	364.85	58.6555	-3.7820	-8.8762	0.019	0.011
1-Butene	134.86	425.16	56.3208	1.7620	-3.8580	0.082	0.059
2-Butene	134.24	435.58	53.2909	7.5389	-6.8388	0.073	0.052
2-Methylpropene	132.80	417.90	55.4105	0.30275	1.4928	0.106	0.058
2-Methyl-2-butene	139.38	481.00	60.3193	-9.8480	5.7089	0.217	0.134
Acetylene	192.35	308.33	62.1097	26.0757	-50.9508	0.006	0.004

^a When the triple-point temperature is not available, it is substituted by the melting point.

^b For this compound, the isobaric surface tension data are used.

Table III. (Continued)

Compound	$T_t(\text{K})^a$	$T_c(\text{K})$	A	B	C	SD	Av. dev.
Propyne	170.45	402.38	59.0221	10.7105	-17.9898	0.007	0.005
Cyclopentene ^b	138.07	506.00	68.1927	-3.1949	-0.3066	0.017	0.010
Cyclohexene ^b	169.64	560.48	68.8892	-3.0521	-1.4380	0.030	0.021
Benzene ^b	278.68	562.16	76.6304	-15.7455	15.0819	0.041	0.023
Methanol	175.59	512.64	122.6257	-199.4044	153.3744	0.077	0.053
Ethanol	159.00	513.92	111.4452	-146.0229	89.5703	0.115	0.082
Propanaol	147.00	536.78	107.1238	-133.8128	84.4357	0.047	0.034
Butanol	184.51	563.05	90.0628	-63.9846	9.8636	0.085	0.064
Pentanol	195.0	588.15	83.4602	-46.9235	1.3739	0.108	0.076
Hexanol	229.0	611.00	84.7167	-62.4496	26.8171	0.158	0.118
Heptanol	240.35	633.00	82.3757	-58.1057	25.4571	0.055	0.040
Octanol	258.0	652.50	83.0798	-64.7335	35.2950	0.052	0.039
Nonanol	268.0	671.0	83.5043	-65.2637	35.2271	0.058	0.039
Decanol	280.05	687.00	87.3144	-79.4003	49.0394	0.121	0.074
Dimethyl ether	131.66	400.00	65.9957	-7.1673	-4.2062	0.006	0.004
Ethyl ether	157.0	466.74	61.0417	-6.7908	0.14046	0.043	0.033
Ethyl acetate	190.0	523.30	70.0490	-5.8887	1.5038	0.046	0.035
Acetic acid	290.0	592.70	91.9020	-91.7035	77.5072	0.055	0.044
Boron trifluoride	146.35	260.80	88.1547	-82.0460	39.0267	0.279	0.163
Diborane	104.15	289.80	38.0417	29.7743	-24.2605	0.051	0.035

There are, however, no hard and fast rules for estimating the values of γ_m and γ_f . A typical plot illustrating the behavior of surface tension of 1-pentanol close to the triple point is shown in Fig. 4. It shows that surface tension varies almost linearly with temperature in the low-temperature region. The value of γ_m can therefore be determined by linear extrapolation of the low-temperature data. The value of γ_f may be obtained by averaging the values of γ_f obtained from both the equations. The value of γ_f is, on the average, 3.5 ± 1.0 dyne \cdot cm⁻¹.

Finally, we like to point out that the isobaric surface tensions determined at 1 atm do not seem to deviate appreciably from the orthobaric surface tensions as evidenced from the results reported for normal alkanes [14, 15]. Consequently, such isobaric surface tensions may also be used in developing equations from the triple point to the critical point. Since triple-point temperatures are available only for a few compounds, we have used the normal melting point in the place of the triple point. The constants of Eq. (8) determined using the above procedures are given in Table III for a number of substances. The data used in such determinations come largely from Jasper and co-workers [6, 14, 15], and from Vargaftik [16]. For alcohols, the data are from Efremov [13].

NOMENCLATURE

T_c = Critical temperature, K

T_t = Triple point, K

T_m = Melting point, K

T_r = Reduced temperature, K

$X = (T_c - T)/T_c$

γ = Surface tension, $\text{dyne} \cdot \text{cm}^{-1}$; $10^{-3} \text{N} \cdot \text{m}^{-1}$

γ_m = Surface tension at the melting point

γ_f = Surface tension at $T_r = 0.9$

γ_t = Surface tension at the triple point

Relative deviation = $100[\gamma_{\text{obsd}} - \gamma_{\text{calcd}}]/\gamma_{\text{obsd}}$

Standard deviation = $[\sum (\gamma_{\text{obsd}} - \gamma_{\text{calcd}})^2 / (\text{No. points} - \text{No. parameters})]^{0.5}$

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