

Capillary-Constant Correlations for Some New Refrigerants

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This paper presents a method of evaluating the capillary constant of some new refrigerants, namely HFCs 32, 125, 134, 134a, 143a, and 152a; HCFCs 123, 123a, 124, 141b, and 142b in the liquid-vapor coexistence regions except within 2 K from the critical point. The correlation is of the form $a^2 = a_0^2(1 - T_r)^{0.92}$ where a_0^2 is obtained through the saturated-liquid density data. The calculated results show that the correlation is able to predict experimental data within 4% with a maximum absolute deviation less than 9%. A procedure to calculate the surface tension without the saturated vapor density data is also presented.

KEY WORDS: capillary constant; refrigerants; surface tension.

1. INTRODUCTION

Over recent years there has been a thrust to redesign heat-transfer equipment for applications involving refrigeration, heat pumping and air conditioning in view of the need for adopting ozone benign working fluids. Among the fluids, HFCs 32, 134, 134a, 143a, and 152a; and HCFCs 123, 123a, 124, 125, 141b, and 142b are quite prominent. Some of these fluids and their mixtures are also being proposed as coolants for electronic equipment. The capillary constant is an important thermophysical property of fluids, particularly in the design of evaporators and in determining the flow regime for microchannel flows through calculation of confinement number. The surface tension can be calculated directly from the capillary constant

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if the saturation-phase density data are available. Fortunately, experimental data on the capillary constant of those fluids are available in the literature although an apparent scatter among different sources is observed. The purpose of this article is to provide a method of evaluating the capillary constant from a knowledge of saturated-liquid density data and, hence, of calculating the surface tension.

2. DEVELOPMENT OF CORRELATION

The development of the correlation is primarily based on the procedure presented earlier [1], where it was shown that the capillary constant can be represented by the equation:

$$a^2 = a_0^2(1 - T_r)^{0.92} \quad (1)$$

with

$$a_0^2 = 2(T_r \rho_{fr})_{\max}^{1+\beta} k T_c (N/M)^{2/3} / (g \rho_0^{1/3}) \quad (2)$$

In the above equations T is the temperature, ρ is the density, M is the molecular mass, k is the Boltzmann constant, N is the Avogadro number, and g is the acceleration of gravity. The subscripts r , f , c , and 0 refer to the reduced state, saturated-liquid, critical point, and extrapolated value at 0 K, respectively. $1 + \beta$ is the ratio of T_c to the temperature at which the product $T(\rho_f - \rho_g)$ is a maximum where ρ_g is the saturated-vapor density. The reduced properties are calculated as $\rho_{fr} = \rho_f / \rho_c$ and $T_r = T / T_c$. The physical basis is as follows: for all fluids $T_r \rho_{fr}$ goes through a maximum at a particular temperature (T^*) which is typically 0.8 to $0.82 T_c$ and the magnitude of this maximum characterizes the nature of the fluid [2]. The power (0.92) in Eq. (1) is the value determined from the temperature dependence of experimental capillary-constant data for various fluids including cryogenic liquids, hydrocarbons, and refrigerants. Thus, an evaluation of the capillary constant primarily requires a knowledge of saturated-liquid densities particularly in the region from $0.8 T_c$ to $0.85 T_c$ and a fit of the data from which the value of ρ_0 can be extrapolated to 0 K. The extrapolation is sensitive to the range of temperatures over which saturated-liquid density data are available. Invariably, experimental liquid density measurements cover a fairly wide range of the fluid-phase coexistence region and investigators provide an equation that fits their data. Table I lists the relevant data for the fluids studied here and the source for the saturation data in this study. The average value of β for the liquids considered here is about 0.31. When Eq. (2) was used with the family of fluids here, it was observed that the errors were somewhat large

Table I. Refrigerant Properties

Refrigerant	T_c (K)	ρ_c ($\text{kg} \cdot \text{m}^{-3}$)	M	ρ_0 ($\text{kg} \cdot \text{m}^{-3}$)	$(T_r \rho_{fr})_{\max}$	$1 + \beta$	σ (nm)
HFC-32 [3] ^a	351.35	427	52.02	1842.8	1.9184	1.313	0.3912
HFC-125 [3]	339.33	571	120.02	2190.5	1.8612	1.304	0.4760
HFC-134 [4]	391.80	535	102.03	2125.7	1.8575	1.301	0.4618
HFC-134a [5]	374.22	514	102.03	1912.3	1.8709	1.308	0.4655
HFC-143a [6]	345.89	446	84.04	1628.2	1.8160	1.305	0.4620
HFC-152a [7]	386.41	368	66.05	1511.4	1.8879	1.309	0.4479
HCFC-123 [8]	456.74	552	152.93	2056.3	1.8458	1.305	0.5236
HCFC-123a [4]	461.60	550	152.93	2164.6	1.8510	1.303	0.5243
HCFC-124 [9]	395.62	560	136.47	2007.2	1.8447	1.301	0.5018
HCFC-141b [10]	477.30	461	116.95	1638.2	1.8234	1.311	0.5106
HCFC-142b [11]	410.29	446	100.49	1747.5	1.8448	1.305	0.4888

^a Numbers within [] show references for the source of data for saturation properties.

(to the extent of 12%) in the case of HFCs 32, 134, and 152a. Consequently, an adjustable multiplying factor (n) was used for the power, $1 + \beta$, for all the fluids such that the experimental data are fitted with least squares criteria being satisfied. The form of Eq. (1) would then be as follows:

$$a^2 = [2(T_r \rho_{fr})_{\max}^{n(1+\beta)} k T_c (N/M)^{2/3} / (g \rho_0^{1/3})] (1 - T_r)^{0.92} \quad (3)$$

The index of 0.92 for the term describing the temperature dependence in Eq. (1) is retained to be the same as in the earlier case [1] as it appears to be applicable for the HFCs and HCFCs considered here, for which justification is provided in the next section. Further, the value of the calculated a^2 is relatively less sensitive to the index 0.92 than to the constant, a_0^2 .

The surface tension can be calculated from the following equation.

$$\gamma = \gamma_0 (1 - T_r)^{1.244} \quad (4)$$

where

$$\gamma_0 = a_0^2 g \rho_0 / 2 \quad (5)$$

Thus, the surface tension can be evaluated without direct access to the saturated-vapor density data. This is advantageous because experimental saturated-vapor densities seldom cover as wide a range as the saturated-liquid phase. In Eq. (4) the power 1.244 is retained to be the same as in the case of other refrigerants [1].

3. RESULTS AND DISCUSSION

Table II lists the values of the multiplier n and the values of a_0^2 and γ_0 for all the refrigerants studied here along with the sources of experimental data. The value of n is optimized so as to obtain the least sum of squares of deviations between the calculated and the experimental a^2 values. It can be seen that the value of n is around unity except in the case of a few HFCs mentioned above and HCFC 123a. This deviation can be attributed to the fact that these fluids are more polar than the other methane and ethane family refrigerants. In the case of HCFC-123a and HFC-134, the index n is based on a single source of experimental data.

The capillary constant can be non-dimensionalized for the corresponding-states treatment as follows:

$$a^{2*} = a^2 g / (\sigma R T^*) \quad (6)$$

where σ is a length parameter calculated according to the procedure given in Ref. 2,

$$\sigma = 2^{-1/6} (M / \rho_f^* N)^{1/3} \quad (7)$$

with ρ_f^* being the saturated-liquid density at temperature T^* and R is the universal gas constant ($= Nk/M$). a^{2*} is plotted against $(1 - T_r)$ for all 11 fluids in Fig. 1 where the distinction between individual fluids is not shown. A linear relation is observed on the logarithmic plot from which the power of the $(1 - T_r)$ term was found to be 0.92. This value is in complete agreement with that used in Eq. (1). It also compares well with values given by

Table II. Correlation Constants and Results

Refrigerant	n	a_0^2 (mm ²)	γ_0 mN · m ⁻¹	Average error (%)	Experimental source of data
HFC-32	0.853	8.57	77.45	3.7	[12-14]
HFC-125	1.040	5.01	53.81	2.1	[12, 14, 15]
HFC-134	1.094	6.76	70.50	1.3	[16]
HFC-134a	0.977	6.18	57.92	2.3	[17-20]
HFC-143a	0.971	6.55	52.34	2.1	[18, 21, 22]
HFC-152a	0.917	8.87	65.78	2.6	[14, 16]
HCFC-123	1.016	5.68	57.31	1.0	[17, 20]
HCFC-123a	1.073	5.93	62.93	1.5	[16]
HCFC-124	1.021	5.36	52.76	2.4	[14, 21]
HCFC-141b	0.998	7.46	59.95	1.8	[14, 16]
HCFC-142b	1.005	7.06	60.55	1.8	[14, 16]

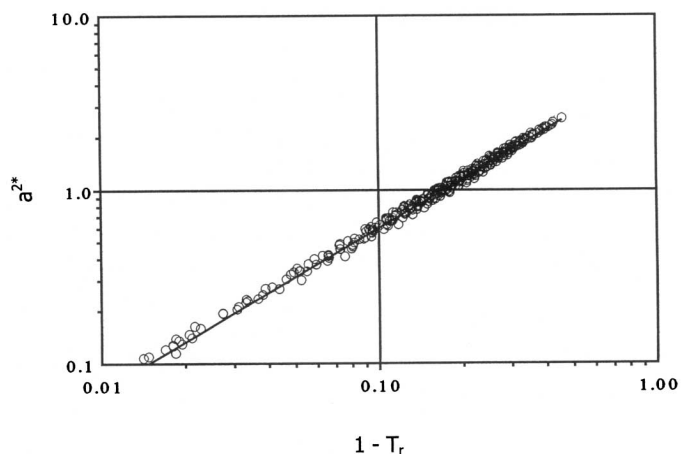


Fig. 1. Temperature dependence of non-dimensional capillary constant for all 11 refrigerants.

other investigators [12, 16, 17, 21]. However, in the case of Eq. (4), the value 1.244 is in variance with those proposed in the literature, namely 1.201 for HFC-32 [13] to 1.26 for HFC-134a [17].

The values of γ_0 as calculated from Eq. (5) agree with the values reported in various publications for the fluids studied here. Invariably one requires data on saturated-fluid phase density difference to calculate the value of γ from the capillary constant, a^2 . Each group of experimentalists uses a source of data of their preference for this purpose, which may be in variance with that used by other groups. Although the saturated-liquid densities from various sources are generally in agreement to within 0.3%, the saturated-vapor densities may differ by as much as 3%, particularly at temperatures away from the critical point. This could cause an additional uncertainty in the reported surface tension value. It is for this reason that the directly measured experimental capillary-constant is correlated in this paper. The empirical Eq. (4) proposed above does not require the fluid phase density difference.

Figures 2 to 12 show the percentage deviations of the experimental results from the calculated values of a^2 for all the refrigerants studied here. The deviation is defined as $(a_{\text{exp}}^2 - a_{\text{cal}}^2)/a_{\text{exp}}^2 \times 100\%$. The differences between temperature scales IPTS-68 and ITS-90 are ignored since they are small in the region of interest. These figures mainly show that no preference can be given to any one particular source of data. It must be reiterated that these figures have been obtained after adjusting the index n to satisfy the least squares criterion. Table II lists the average % deviations observed

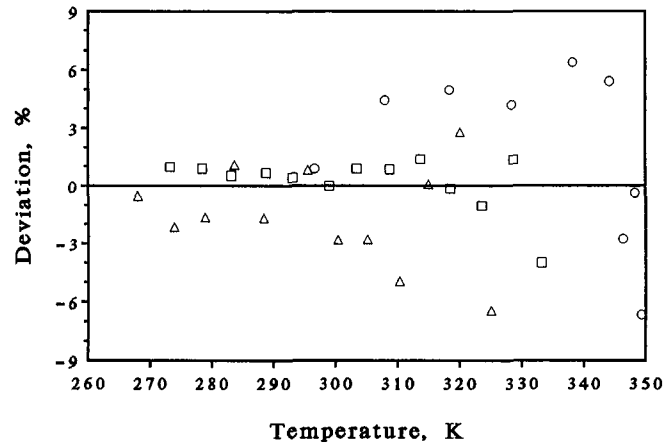


Fig. 2. Percentage deviations of experimental data for capillary constant for HFC-32 measured by Schmidt and Moldover [12] (\circ), Zhu and Lu [13] (\triangle), and Okada and Higashi [14] (\square) from values calculated with Eq. (3).

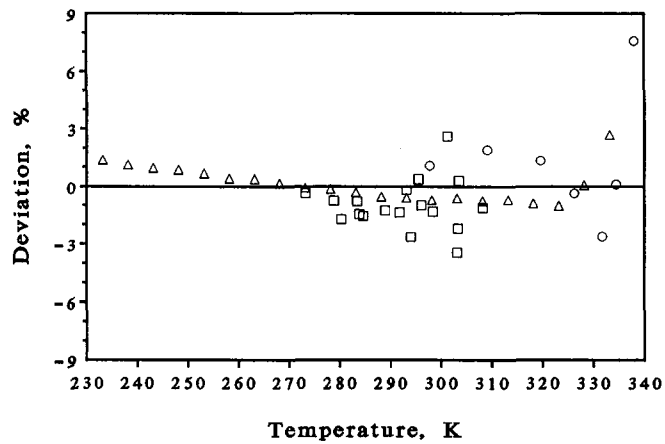


Fig. 3. Percentage deviations of experimental data for capillary constant for HFC-125 measured by Schmidt and Moldover [12] (\circ), Okada and Higashi [14] (\square), and Liu et al. [15] (\triangle) from values calculated with Eq. (3).

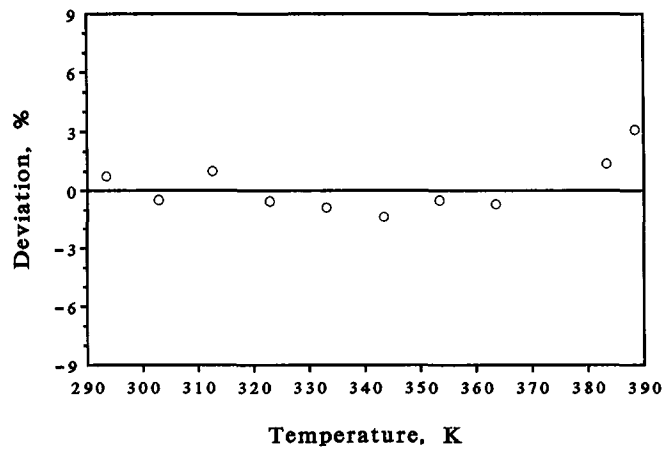


Fig. 4. Percentage deviations of experimental data for capillary constant for HFC-134 measured by Chae et al. [16] (○) from values calculated with Eq. (3).

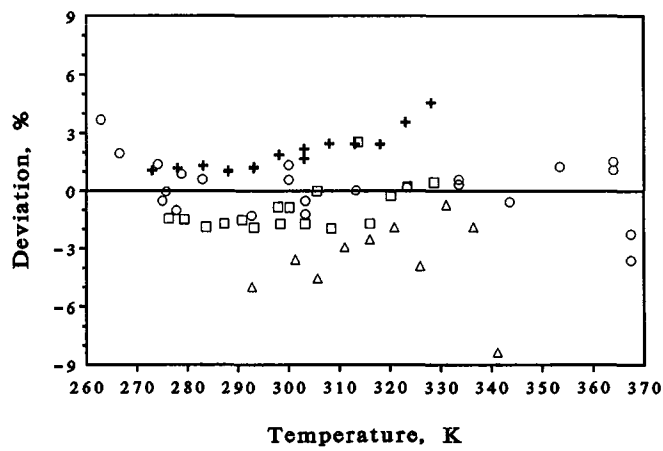


Fig. 5. Percentage deviations of experimental data for capillary constant for HFC-134a measured by Chae et al. [17], Higashi et al. [18] (+), Zhu et al. [19] (△), and Higashi et al. [20] (□) from values calculated with Eq. (3).

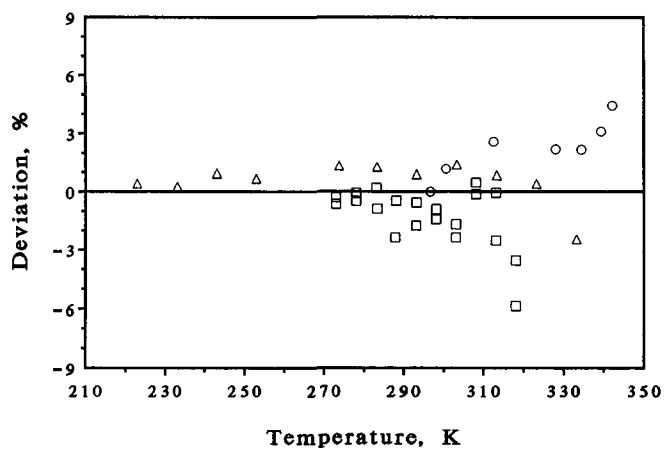


Fig. 6. Percentage deviations of experimental data for capillary constant for HFC-143a measured by Higashi et al. [18] (+), Schmidt et al. [21] (\square), and Heide and Schenk [22] (\triangle) from values calculated with Eq. (3).

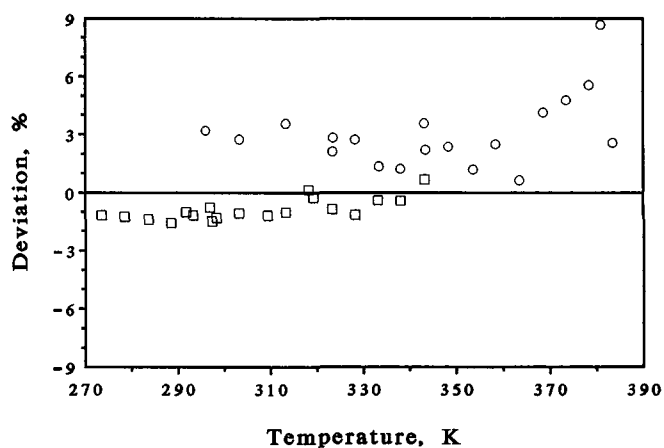


Fig. 7. Percentage deviations of experimental data for capillary constant for HFC-152a measured by Okada and Higashi [14] (\square) and Chae et al. [16] (\circ) from values calculated with Eq. (3).

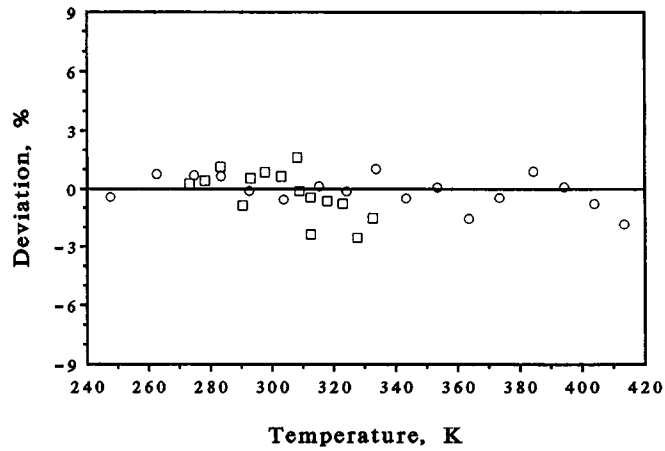


Fig. 8. Percentage deviations of experimental data for capillary constant for HFC-123 measured by Chae et al. [17] (○) and Higashi et al. [20] (□) from values calculated with Eq. (3).

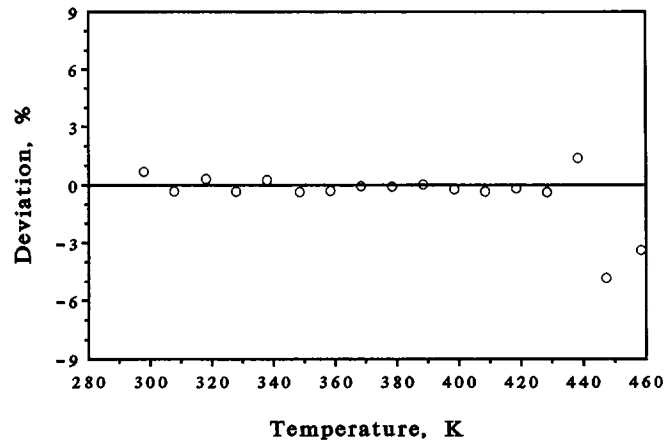


Fig. 9. Percentage deviations of experimental data for capillary constant for HFC-123a measured by Chae et al. [16] (○) from values calculated with Eq. (3).

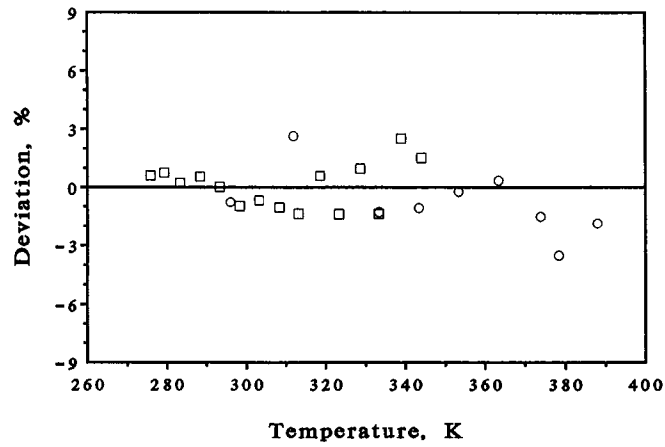


Fig. 10. Percentage deviations of experimental data for capillary constant for HFC-124 measured by Okada and Higashi [14] (□) and Schmidt et al. [21] (○) from values calculated with Eq. (3).

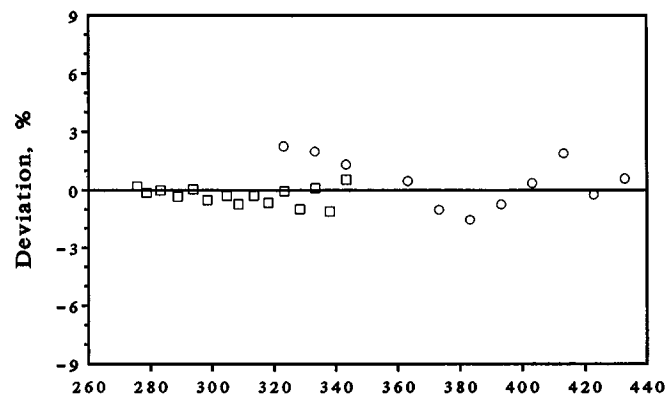


Fig. 11. Percentage deviations of experimental data for capillary constant for HFC-141b measured by Okada and Higashi [14] (□) and Chae et al. [16] (○) from values calculated with Eq. (3).

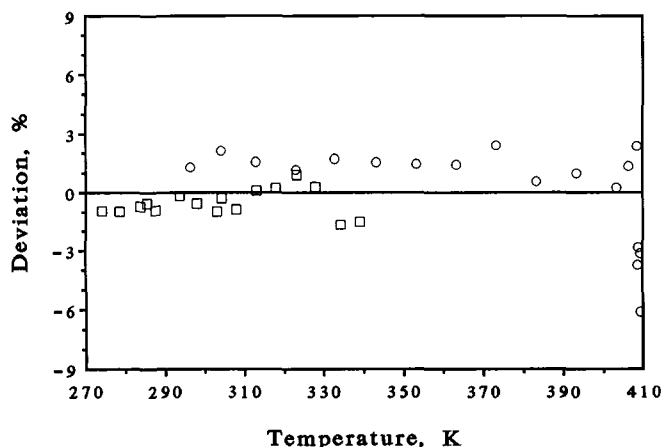


Fig. 12. Percentage deviations of experimental data for capillary constant for HFC-142b measured by Okada and Higashi [14] (□) and Chae et al. [16] (○) from values calculated with Eq. (3).

when Eq. (1) is applied to various sources of data. For this purpose, only data at least 2 K away from the critical point of each fluid were taken. The reason for this cut off is that the % deviations tend to increase near the critical point although the absolute differences are quite small. It is also possible that experimental uncertainties could be larger as the capillary rise near the critical temperature would be very small. No weighting factors were used for any data sources as it was found that all the measurements were made with samples of comparable purity and the experimental techniques have also been the same. A general observation is that the consistency among several sources of data is the best in the case of HCFC-123 and somewhat varied in the case of HFCs, in general.

For the purpose of estimation of the capillary constants of new refrigerants for which capillary constants are not yet obtained but only saturation data are available, Eq. (1) can be used with the index, n , in Eq.(2) set equal to unity.

4. CONCLUSIONS

A correlation has been derived for the calculation of the capillary constant of eleven new refrigerants belonging to the methane and ethane families. These correlations require mainly saturated-liquid density data. The surface tension also can be calculated without explicit use of saturated-vapor data. The correlations, valid over a wide range of saturation temperatures except

within 2 K of the critical point, agree with the experimental results and will be useful in the design of heat-transfer equipment.

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