Universal amplitude ratios and the interfacial tension near consolute points of binary liquid mixtures

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The densities of the coexisting phases and the capillary length have been measured to obtain the interfacial tension (σ) near the consolute temperatures T_c of the three binary liquid mixtures: triethylamine + water, triethylamine + heavy water, and methanol + cyclohexane. Our data are combined with data from the literature to test predictions for three temperature-independent "universal" ratios: $U_1^+ = \sigma(\xi^+)^2/(k_B T_c)$ and $Y^{(\pm)} = \sigma(\alpha t^2 C_s^{\pm}/k_B)^{-2/3}/(k_B T_0)$. [Here ξ^+ is the correlation length, $C_s^{\pm}$ is the singular part of the heat capacity per unit volume, $\alpha = 0.11$ is the exponent characterizing the specific heat divergence, and $t \equiv (T - T_c)/T_c$]. Near T_c, the new experimental values of $Y^{(+)}$ range from 5.5–5.8 in agreement with the value 5.6 obtained by Moldover [Phys. Rev. **31**, 1022 (1985)] in a review of earlier experiments. However, the experimental values of $Y^{(+)}$ are inconsistent with either the value $Y^{(+)} = 4.4 \pm 0.4$ obtained from a recent simulation of the simple-cubic Ising model or the value $Y^{(+)} = 2.6$–3.0 obtained from a one-loop renormalization group calculation. The experimental values $Y^{(-)} = 3.7$ and $U_1^+ = 0.39$ are also much larger than both the Ising model and the renormalization group values. It is unlikely that the inconsistency between the experimental and the theoretical ratios $Y^{(\pm)}$ and U_1^+ can be explained by systematic errors in the measurements of σ, because diverse techniques for measuring σ have yielded consistent results for a wide variety of fluid systems. A table of the relevant amplitudes for 16 fluid systems is included.

I. INTRODUCTION

The principle of two-scale-factor universality of critical phenomena as stated by Stauffer *et al.*[1] asserts that close enough to the critical temperature T_c within each universality class, the singular part of the free energy per unit volume belonging to a region of volume ξ^d is a universal function of a single variable: $h/|t|^{2-\alpha-\beta}$. [Here ξ is the correlation length, d is the dimensionality of space, $t = (T - T_c)/T_c$, h is the thermodynamic field variable conjugate to the order parameter, and α and β are the usual critical exponents.] The principle of two-scale-factor universality is consistent with renormalization group calculations of the critical behavior of the Landau–Ginsburg–Wilson Hamiltonian. This principle is consistent with our knowledge of three dimensional systems with a scalar order parameter including liquid–vapor systems near critical points,[2] binary liquid mixtures near consolute points,[3] and Ising models.[1,4] Two-scale-factor universality has been confirmed by experiments on the path $h = 0$ (the critical isochore or the critical isopleth). Along this path measurements of the singular part of the specific-heat per unit volume $C_s^{\pm}$ and of the correlation length near T_c are represented by the expressions

$$C_s^{\pm} = k_B \frac{C_0^{\pm}}{\alpha} |t|^{-\alpha}, \quad \xi^{\pm} = \xi_0^{\pm} |t|^{-\nu}. \tag{1}$$

(The superscripts + and − refer to the one-phase and two-phase regions, respectively, and k_B is Boltzmann's constant.) The data for $t > 0$ are consistent with the relation

$$\alpha t^2 C_s^+ (\xi^+)^d / k_B T_c = \text{universal number}. \tag{2}$$

Equation (2) can be restated in the form of a "universal amplitude ratio"

$$(\sigma C_0^+)^{1/d} \xi_0^+ / k_B T_c = \text{universal number} \equiv R_\xi^+. \tag{3}$$

The excellent agreement between experimental and theoretical values of the ratio R_ξ^+ and related ratios was discussed in Refs. 2 and 3.

In addition to the above formulation of the principle of two-scale-factor universality, Stauffer *et al.*, made a second assertion, namely, that the free energy per unit area σ belonging to an interface of area ξ^{d-1} is a universal temperature-independent number. This second assertion applies to states of two-phase coexistence below T_c where it takes the form

$$\sigma(\xi^-)^{d-1}/k_B T_c = \text{universal number} \equiv U_1^-. \tag{4}$$

Measurements of the correlation length in the two-phase region are extremely rare. Thus, to test the second assertion of Stauffer *et al.*, one makes use of the universality of the ratio ξ^+/ξ^- to form the ratio

$$\sigma(\xi^+)^{d-1}/k_B T_c = \text{universal number} \equiv U_1^+. \tag{5}$$

The assertions embodied in Eqs. (2), (4), and (5) imply a useful relationship between σ and C_s which does not include the correlation length

$$\sigma(\alpha t^2 C_s^{\pm}/k_B)^{(1-d)/d}/(k_B T_c) = \text{universal numbers} \equiv Y^{(\pm)}. \tag{6}$$

In a recent publication,[5] one of us (MRM) reviewed the existing literature to test the second assertion of Stauffer *et al.* for three-dimensional fluid systems with a scalar order parameter. The review concluded that the data for a wide variety of fluid systems are consistent with Eqs. (5) and (6);

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TABLE I. Interfacial tension amplitudes and amplitude ratios.

Fluids	M (g/mol)	ρ_c (kg/m^3)	T_c (K)	B_0	a_0^2 (mm^2)	σ_0 (mN/m)	ξ_0^+ (nm)	A_0^-	A_0^+	Y^-	Y^+	U_1^+
TEA + W	24.47	926	291.6	0.420[e]	38.8[e]	148.0[e]	0.10	...	6.61	...	5.66	0.368
TEA + HW	26.02	999	287.8	0.543[e]	26.6[e]	141.6[e]	...	11.20	6.40	3.82	5.55	
ME + CY	57.60	751	318	0.001 98[e]	1150[e]	16.8[e]	0.324[d]	1.37	0.65	3.42	5.62	0.402
IBA + W	25.70	993	299.0	...	...	11.6	0.362	...	0.12	...	6.17	0.368
CY + AN	...	...	302.7	...	...	31.5	0.245	...	...	...	...	0.452
NE + 3MP	80.62	792	299.6	...	...	33	0.216	5.54	3.20	3.39	4.89	0.372
6 polymer solutions	10^4–10^6	...	...	...	...	0.8–7.1	1.4–0.5	...	...	...	...	0.33–0.49
^{3}He	3.016	41.45	3.31	...	...	0.263[c]	...	2.00	1.02	3.86	6.05	...
^{4}He	4.003	69.60	5.19	...	...	0.633[c]	...	3.25	1.62	3.66	5.83	...
Ar	39.944	535	150.73	1.47	4.06	31.35	0.137	9.26	4.94	3.70	5.63	0.283
Xe	131.3	1110	289.73	1.42	2.96	45.69	0.184	9.19	4.80	3.83	5.91	0.387
SF_6	146.07	730	318.69	1.74	3.84	47.85	0.188	15.02	8.12	3.73	5.63	0.384
CO_2	44.01	467.8	304.13	1.60	9.52	70.05	0.153	13.30	7.05	3.76	5.73	0.391
H_2O	18.02	323	647.07	1.980	34.72	218	...	14.23	7.57	3.71	5.65	...
C_2H_4	28.05	214	282.35	1.544	13.90	45.1	...	11.13	5.92	3.66	5.57	...
C_2H_6	32.10	206.5	305.33	1.57	14.42	45.95	0.180	11.09	6.02	3.87	5.82	0.354
C_4H_{10}	58.13	226	407.84	1.641	12.71	46.2	...	13.18	7.01	3.63	5.53	...
Median value for fluids										3.71	5.65	0.386
sc Ising model[a]						$1.2k_BT_c/a^2$	0.478a		2.6–3.1	4.0–4.8		0.25–0.29
bcc Ising model[a]						$1.43k_BT_c/a^2$	0.445a		2.6–3.1	4.0–4.8		0.27–0.30
Renormalization group[b]									1.5–1.8	2.3–2.9		0.18–0.21

[a] Reference 4.
[b] References 6, 28–30.
[c] Reference 35.
[d] References 33 and 34.
[e] This work.

however, the experimental values for the universal numbers U_1^+ and $Y^{(\pm)}$ are inconsistent with the theoretical values obtained from either a renormalization-group calculation[6,7] or from Monte Carlo simulations[4,8] of Ising models. Essentially this same conclusion was reached by Gielen *et al.*[9] at about the same time.

The primary objective of this work is to explore further the conflict between the experimental and theoretical values of U_1^+ and $Y^{(\pm)}$. Because there is no conflict for $R_\xi^+ \equiv (U_1^+/Y^+)^{1/2}$ we were led to search for systematic errors in the measurement of σ. We have measured the interfacial tension near the consolute points of three binary liquid mixtures. The experimental methods we have used differ from those used in earlier experiments; thus, they are subject to different systematic errors. Our results are summarized in the top three lines of Table I and they are combined with data from the literature to obtain new estimates for the universal amplitude ratios $Y^{(\pm)}$ and U_1^+. The new experimental values of $Y^{(\pm)}$ and U_1^+ are in agreement with the older experimental values. Thus, the conflict with the theoretical values is confirmed by our new data.

In the remainder of this Introduction, we state briefly our motives for selecting experimental techniques and mixtures. Then, in Sec. II we specify the notation and the values we assume for the critical exponents. Section III is a thorough description of our experimental procedures and observations. Section IV contains a description of our results and a comparison with other data for the same mixtures. Section V contrasts the theoretical values of $Y^{(\pm)}$ and U_1^+ with the experimental values from our measurements and from other fluid systems.

The conflict between the experimental and the theoretical ratios involving σ prompted us to use a method (the pendant drop method) for measuring σ which is not commonly used near consolute points, on the chance that we would uncover unrecognized sources of systematic error in the more common techniques. Many techniques for measuring σ balance surface forces with gravitational forces. These techniques require separate measurements of the difference between the densities of the coexisting phases ($\Delta\rho$) and the capillary length **a** defined by the expression

$$\mathbf{a}^2 \equiv 2\sigma/(\Delta\rho g), \tag{7}$$

where $g = 9.81$ m/s^2 is the acceleration due to gravity. It is unlikely that the measurements of $\Delta\rho$ are systematically in error because other universal amplitude ratios involving measurements of $\Delta\rho$ are in agreement with theory.[2,3] Thus one is led to question measurements of the capillary length near consolute points. Often the measurements of the capillary length use the capillary rise method. This method makes few demands on the quality of the optical system used and it can have very high resolution, even near T_c, if a small capillary is used. However, it is difficult to ensure that a mixture in a small capillary has the same composition as the mixture

in bulk. This problem becomes more acute near T_c as the time required for equilibration increases. Furthermore, wetting layers might be quite important in a very small capillary. These problems associated with a confined geometry are avoided by the pendant drop method, which we have used. However, the pendant drop method requires accurate imaging and is sensitive to vibration. We have found that the two methods yield consistent results, although they are subject to different kinds of systematic errors. We note that various capillary wave methods for measuring σ have been used near consolute points. These methods require models for the hydrodynamics of the interface and also require careful definition of the optical systems used. They also yield results which are consistent with other techniques.

The binary system methanol + cyclohexane (ME + CY) was chosen for this study because earlier estimates of $Y^{(\pm)}$ for ME + CY appeared to contradict universality. Indeed, the estimates of $Y^{(\pm)}$ for ME + CY in Ref. 5 based on the measurements of σ in Ref. 10 were five times larger than other experimental values of $Y^{(\pm)}$. The present measurements of σ lead to values of $Y^{(\pm)}$ which are consistent with the values for other fluids. The new values of σ are more accurate than the older ones, primarily because they are based on direct measurements of the densities of the coexisting phases. The earlier measurements of σ were based on estimates of densities obtained by linear interpolation between the densities of the pure components.[10] The interpolation caused a large *fractional* error in $\Delta\rho$ because the densities of the pure components are nearly identical in the temperature range of interest.

The binary system triethylamine + heavy water (TEA + HW) was chosen for this study because of the availability[11] of very accurate heat capacity measurements which have been analyzed using modern values for the critical exponent α. For this mixture, we obtained accurate values for $Y^{(\pm)}$ without introducing the uncertainties that occur when published data are reanalyzed.

The binary system triethylamine + water (TEA + W) is useful because there are published heat capacity data[12] which have been reanalyzed by the original authors,[11] and published data[13] for the capillary length and the densities of the coexisting phases. From the perspective of the experimentalist, TEA + W is quite different from TEA + HW. At the same reduced temperature, $\Delta\rho$ for TEA + HW is 40% greater than $\Delta\rho$ for TEA + W and the pendant drops are correspondingly smaller.

II. NOTATION AND EXPONENTS

The principle of two-scale-factor universality leads to universal amplitude ratios when it is applied to data along any locus of thermodynamic states sufficiently near T_0. The extension of this principle to the interfacial tension [Eqs. (4)–(6)] necessarily applies only along the locus of phase coexistence. Along this curve and its smooth extension into one-phase states, the measured quantities of interest are represented by power laws in the reduced temperature t. We use the customary notation for the difference between the densities of the coexisting phases ($\Delta\rho$), the interfacial tension, the capillary length, the molar heat capacity at constant pressure C_p, and the correlation length

$$\begin{aligned}
\Delta\rho &= 2\rho_c B_0(-t)^{\beta}[1+B_1(-t)^{\Delta}+\cdots],\\
\sigma &= \sigma_0(-t)^{\mu}[1+\sigma_1(-t)^{\Delta}+\cdots],\\
\mathbf{a}^2 &= \mathbf{a}_0^2(-t)^{\varphi}[1+\mathbf{a}_1(-t)^{\Delta}\cdots],\\
C_p^{\pm}/R &= A_0^{\pm}|t|^{-\alpha}(1+A_1^{\pm}|t|^{\Delta}+\cdots),\\
\xi^{\pm} &= \xi_0^{\pm}|t|^{-\nu}(1+\xi_1^{\pm}|t|^{\Delta}+\cdots).
\end{aligned} \tag{8}$$

Here, R is the gas constant and ρ_c is the consolute density. The reduced temperature is defined by $t \equiv (T-T_c)/T_c$ for the upper consolute point in the ME + CY mixture and by $t \equiv (T_c - T)/T_c$ for the lower consolute points of the TEA + W and TEA + HW mixtures. The exponent $\Delta \approx 0.5$ is the first symmetric Wegner correction-to-scaling exponent. In terms of the experimental heat capacity amplitudes, Eq. (6) becomes

$$Y^{(\pm)} = \sigma_0 \cdot (\alpha \cdot A_0^{\pm} \cdot \rho_c \cdot N_0/M)^{-2/3}/(k_B T_c),$$

where N_0 is Avogadro's number and M is the molecular weight.

We assume that the critical exponents have the values calculated via the renormalization group,[14,15] namely,

$$\alpha = 0.110, \quad \beta = 0.325, \quad \nu = 0.630, \quad \Delta = 0.5. \tag{9}$$

In three dimensions Widom's scaling law[16] for the interfacial tension gives

$$\mu = 2\nu = 1.26. \tag{10}$$

From the definition of $\mathbf{a}^2$ one obtains

$$\varphi \equiv \mu - \beta = 0.935. \tag{11}$$

III. EXPERIMENTAL MATERIALS AND PROCEDURES

In this section we shall describe the materials used, the method of measurement of the densities of the coexisting phases, and our use of the pendant drop method for measuring the capillary length for the interface between the two liquid phases. We shall also describe the drifts of the consolute temperatures of our samples because this turned out to be the factor which limited our ability to take measurements very close to T_c.

A. Materials

All the chemicals were used as received from their manufacturers. The TEA was designated as "purissima p.a. grade" and the manufacturer[17,18] stated that its purity (as determined by gas chromatography) exceeded 99.5% and that the residue after evaporation was less than 0.003%. The heavy water had been obtained many years ago in sealed glass ampules. The manufacturer[17,19] states that its purity exceeded 99.8%. For the TEA + W mixtures, distilled water was used.

The TEA + W and TEA + HW mixtures were always studied in contact with air; however, precautions were taken to minimize evaporation and the exchange of heavy water vapor for water vapor. Our interfacial tension data will be compared with the constant-pressure specific-heat (C_p) data published by Bloemen *et al.*[11] and Thoen *et al.*[12]. These authors used TEA from the same source we did. The C_p data were obtained with a sealed calorimeter containing stirred

TABLE II. Critical temperatures of various samples.

T_0(° C)	Measurement	Reference
	Triethylamine + heavy water	
14.70, 14.40	$\Delta\rho$	This work
14.68, 14.81	$\mathbf{a}^2$	This work
14.593	C_p	Ref. 11
	Triethlyamine + water	
18.40	$\Delta\rho$	This work
18.28	$\mathbf{a}^2$	This work
18.46	C_p	Ref. 12.
17.80	$\Delta\rho$	Ref. 13
17.57	$\mathbf{a}^2$	Ref. 13
18.323	Phase equilibria	Ref. 24
	cyclohexane + methanol	
45.69, 45.89	$\Delta\rho$	This work
45.62, 45.73	$\mathbf{a}^2$	This work
45.29, 45.68	$\mathbf{a}^2$	Ref. 10
46.14	C_p	Ref. 32
44.826, 44.48	ξ	Ref. 33
45.944	ξ	Ref. 34

liquid samples in contact with their own vapor and a small amount of air. Thus, both the interfacial tension measurements and the C_p measurements used similar materials and followed nearly identical paths in thermodynamic space. The consolute temperatures for various samples are listed in Table II. From the data in the table, it appears that our TEA + W sample closely resembles the sample used by Thoen *et al.*[12] The sample which Derdulla and Rusanow[13] used for interfacial tension measurements appears to differ from these two.

The water content of the methanol we used was stated[20] to be less than 0.01%. The water content of the cyclohexane was stated[21] to be less than 0.02%.

Prior to use with TEA, the silica cells were first cleaned with a chromic acid–potassium permanganate solution. Then, they were rinsed with distilled water, TEA, and then dried. Prior to use with ME + CY solutions, the cells were washed with acetone and then rinsed with methanol and dried several times.

B. Measurement of the density differences

The measurement of the difference between the densities of the coexisting phases is based on Archimedes' Principle. The apparatus is sketched in Fig. 1. A hollow fused silica sinker was weighed when it was immersed in the upper phase and then weighed again when immersed in the lower phase.

The liquid mixture under study was contained in a hollow fused silica cylinder (4 cm in diameter and 24 cm high) which in turn was almost completely immersed in a water bath. The temperature fluctuations of the bath were less than $\pm$ 0.001 K. A primary concern when using this method is to ensure that the rather large volumes of the two liquid phases are in equilibrium. For this reason a circulating pump was made as follows. The silica cylinder was divided into two compartments which communicated via a small hole on the axis and a vertical tube (Fig. 1). In the lower compartment, a magnet encapsulated in silica and held in a stainless steel bearing was used as a centrifugal pump to force the lower phase through the vertical tube so that it flowed through the upper phase. Pumping for several minutes was required to thoroughly mix the two liquid phases. After pumping it was necessary to wait for up to an hour (near T_c) for the droplets made during the mixing process to coalesce and settle.

The hollow silica sinker was almost spherical. It had a volume of 23.771 cm^3 at 21 °C. Lead weights sealed inside the sinker raised its weight to 35.592 g. The sinker was attached to the balance with a 0.13 mm diam stainless steel wire which passed through a small hole in a large Teflon stopper. The hole was sealed with a smaller Teflon stopper except for the brief intervals when the sinker was being weighed.

Silica is completely wet by the lower phase of all three mixtures studied. When the sinker was hung in the upper liquid phase, a film of the lower phase would form on the sinker over a period of hours after the pump was stopped. This film would accumulate as a pendant drop on the bottom of the sinker. A similar drop would adhere to the sinker when it was lifted from the lower phase into the upper phase. We expected that such a drop might cause an error in the measurement of the density of the upper phase on the order of $(\mathbf{a}/R)^3\Delta\rho$ where $\mathbf{a}$ is the capillary length associated with the liquid–liquid interface and R is the radius of the sinker. In this work, $(\mathbf{a}/R)^3\Delta\rho$ becomes as large as 3×10^{-4} g/cm^3 for the TEA + W mixture far from T_c. The data for the density of the upper phase of the TEA + W mixture does have "noise" which becomes as large as 10^{-3} g/cm^3 and might result from wetting films. In future work we intend to use a sinker with a pointed bottom to minimize this effect.

The stainless steel wire is also completely wetted by the lower phase; however, the effects of the lower phase film

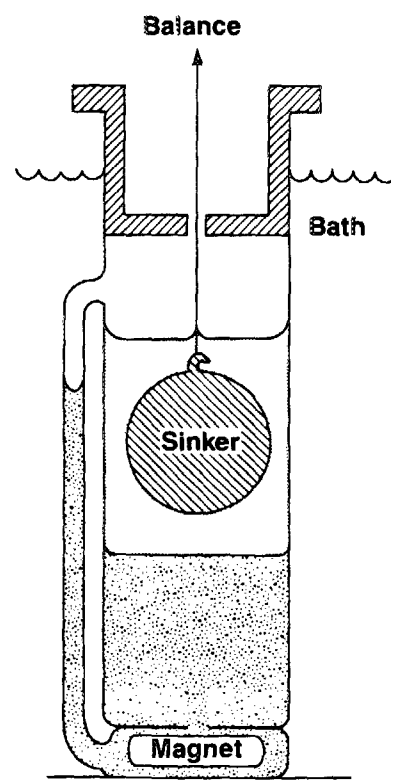

FIG. 1. Cross section of the apparatus for the measurement of the densities of the coexisting phases (not to scale). The magnet in the lower compartment is used for stirring. After stirring, only the lower of the two liquid phases remains in the standpipe.

which forms on the wire are even smaller than the very small effect of the pendant drop on the sinker. Similarly, the effect of the meniscus which forms on the wire when it passes from the upper phase into the lower phase is negligible in ths work.

C. Measurement of the capillary length

The capillary length for the liquid–liquid interface was measured using the pendant drop method. Figure 2 shows a photograph of a pendant drop. We have followed Jennings[22] in measuring the lengths shown in Fig. 2 on photographic negatives to obtain the capillary length. Our primary concerns were to ensure that the liquid phases were in equilibrium and to obtain clear, distortion-free images.

The liquid mixture under study was contained in a flat-windowed quartz spectroscopic cell 2 cm high, 2 cm wide, and 5 cm along the camera's optic axis. This cell was sealed with a Teflon stopper. The cell was totally immersed in a water bath which had flat glass windows to facilitate photography. A Teflon encapsulated magnet was used to mix the liquid phases in this cell.

Pendant drops were made using a syringe which was fastened to the spectroscopic cell. A stainless steel hypodermic needle led from the syringe through the Teflon stopper and into the mixture. The needle was bent so that its tip was close to the cell window nearest to the camera. Pendant drops were obtained by tilting the cell to immerse the needle in the lower phase, loading the syringe, straightening the cell, and finally discharging the syringe.

The pendant drop was illuminated with a low pressure sodium lamp. It was photographed through a 20 mm focal length f/3.5 macro lens. An exposure of 1/125 of a second produced a satisfactory image on an ASA 125 black and white negative. Typically, a magnification of 11 was used. The measurements on the negative were made using a microscope with a calibrated x–y translation stage with a resolution of 0.000 254 cm. The image of the stainless steel needle was used to calibrate the photographic magnification. When the needle was left undisturbed in the upper liquid phase for several hours, a layer of the lower liquid phase slowly formed on the needle and caused difficulties in making reliable measurements of the magnification.

In order to reduce the unwanted vibration of the hypodermic needle and the pendant drops, it was necessary to stop stirring the water bath just before taking the photographs.

The tables provided by Adamson[23] were used to obtain the capillary length from the measurements of d_e and the "shape factor" d_s/d_e. (See Fig. 2.) The scatter in the measurements of the capillary length exceeds the errors which propagate from the imperfect measurements of lengths on the negatives. We have no explanation for this. For the ME + CY mixtures near T_c, the methanol-rich phase spontaneously flowed (very slowly) out of the hypodermic needle. We have no explanation for this either.

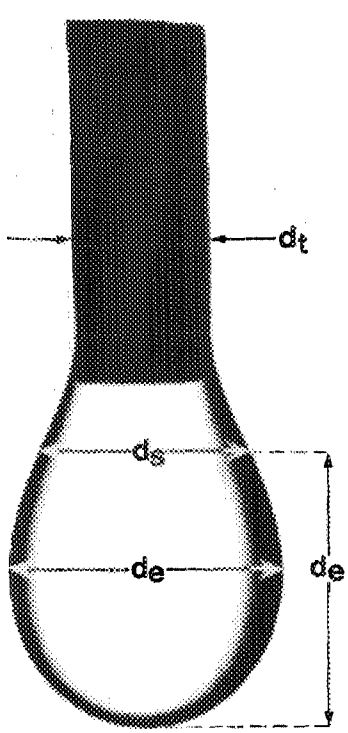

FIG. 2. Photograph of a pendant drop of the water-rich phase hanging from a hypodermic needle immersed in the triethylamine-rich phase. This picture was taken at 22.06 °C where the capillary length is 0.79 mm. A microscope with a calibrated stage is used to measure three lengths on the negative: the diameter of the needle (d_t), the maximum diameter of the drop (d_e), and the diameter of the drop at a distance d_e above the bottom of the drop (d_s). Here, $d_t = 0.361$ mm; $d_e = 0.714$ mm; and $d_s = 0.552$ mm.

D. Drifts in T_c

Kohler and Rice[24] report that TEA + W solutions in contact with air, attack Pyrex glass. They observed that T_c for TEA + W solutions decreased as the reaction progressed. In preliminary experiments, we found similar phenomena in a borosilicate glass apparatus. Accordingly, we followed the suggestion of Kohler and Rice in fabricating our apparatus out of fused silica. Nevertheless, we observed a progressive decrease in T_c when the TEA + W and TEA + HW solutions were in the density apparatus. We documented this effect most carefully with the TEA + HW solution. T_c decreased 2.4 mK/day over a 10 day period. The decrease did not seem to depend either on the frequency of density measurements or on the duration of the interval between stirring the sample. We were able to determine T_c with a precision of $\pm$ 1 mK within a few hours and we were able to make measurements of the densities of the coexisting phases at several temperatures in the two phase region in a few hours. Thus the drift in T_c did not degrade the temperature resolution of these data seriously. Data on subsequent days were corrected for the presumed drift in T_c. The drift was verified by redetermining T_c after the conclusion of a series of measurements and then density measurements were repeated at a few temperatures near T_c.

We did not observe drifts in T_c when the TEA + W and TEA + HW samples were in the smaller cell used for the capillary length measurements. We note that this cell was nearly full of liquid and that it was not opened, except for changing samples.

The value of T_c for ME + CY mixtures is extremely sensitive to small additions of water. Tveekrem and Jacobs[25] found that the addition of one part per million (by volume) of water increased T_c by 3.8 mK. We found that T_c for ME + CY samples in our density apparatus drifted less than 1 mK/day when the apparatus was undisturbed; however, it increased 2–5 mK each time a density measurement was

made. This effect limited the temperature resolution of useful data. For this mixture also, the densities of the coexisting phases at temperatures nearest T_c were measured between successive determinations of T_c. We believe that this procedure limited the error in $T_c - T$ to less than 5 mK. We were unable to detect effects of much greater amounts of water on the measurements of the density differences. Two samples whose T_c differed by 0.21 °C had essentially identical values of B_0, the parameter of greater interest in this work. We note that Warren and Webb[10] found almost identical values for the capillary length parameter, a_0, for two ME + CY samples whose T_c differed by 0.39 °C.

IV. EXPERIMENTAL RESULTS

Our experimental results are presented graphically in Figs. 3–8 and analytic representations of some of the data are included in this section. We have not carried out elaborate statistical analyses of our data using a variety of models, ranges of fitting, etc. Figures 3, 4, 6, and 8 convey the precision with which the data can determine the amplitudes B_0 and $\mathbf{a}_0^2$ (from which we determine σ_0). If one assumes the universality of A^+/A^-, U_1^+, and $Y^{(\pm)}$, systematic errors can be estimated by comparing the ratios from diverse systems in Table I, for which the errors of measurement greatly differ. For the reader who is concerned with a particular form of analysis, we have tabulated the data in the appendix.

Figure 3 displays our capillary length data for two samples of TEA + W and one sample of TEA + HW as well as the capillary length data of Derdulla and Rusanow[13] for TEA + W. Near T_c, our TEA + W data are consistent with the relation $\mathbf{a}^2/(-t)^{0.935} = (38.8 \pm 1.1)$ mm^2 and our TEA + HW data are consistent with $\mathbf{a}^2/(-t)^{0.935} = (26.6 \pm 0.8)$ mm^2. The fractional errors in $\mathbf{a}^2$ lead to identical fractional errors in the interfacial tension

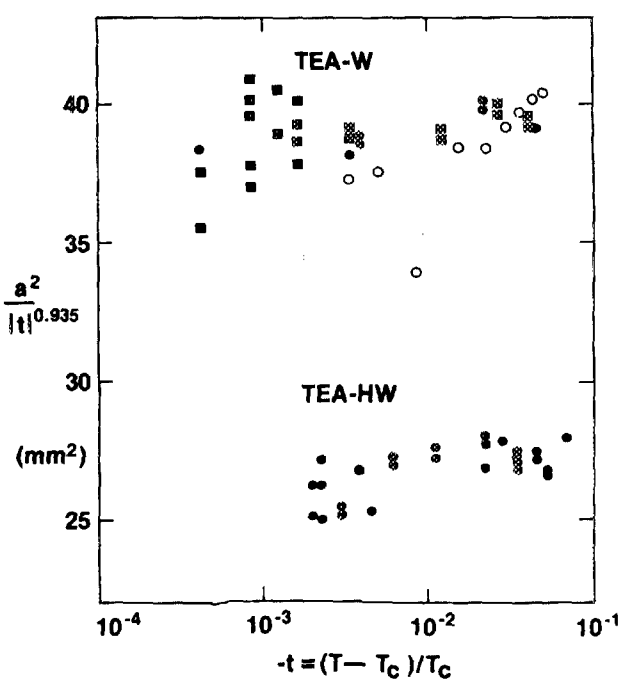

FIG. 3. Scaled capillary length data for mixtures of triethylamine with water or heavy water as a function of the reduced temperature. To the extent that the data fall on a horizontal straight line, they can be represented by the relation: $a^2 = a_0^2[(T - T_c)/T_c]^{0.935}$. Our TEA + W data near $t = 10^{-3}$, ■ and ●, are consistent with $a_0^2 = 38.8 \pm 1.1$ mm^2. Our TEA + HW data, ●, are consistent with $a_0^2 = 26.6 \pm 0.8$ mm. The TEA + W data from Ref. 13 are denoted by open circles. They were fitted for both a_0^2 and T_c. The values $a_0^2 = 38$ mm^2 and $T_c = 17.57$ °C resulted.

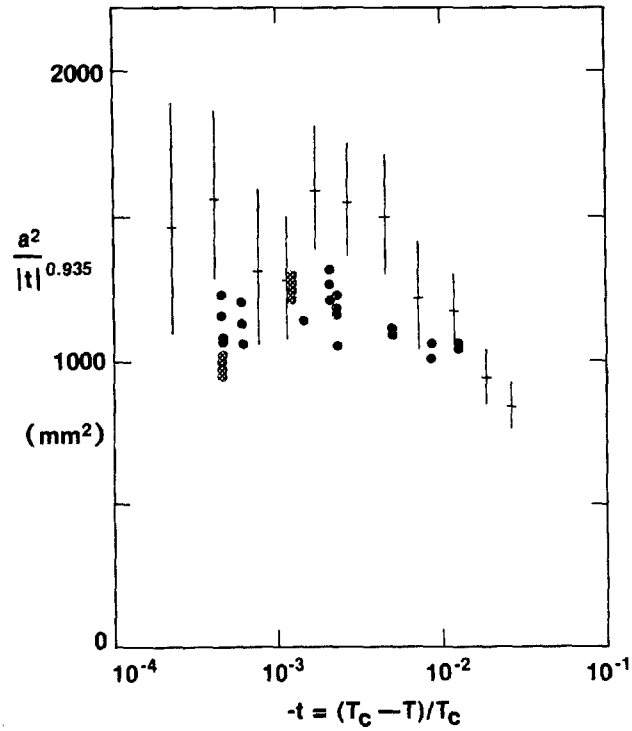

FIG. 4. Scaled capillary length data for methanol + cyclohexane mixtures. Our data, ●, are consistent with $a_0^2 = 1150$ mm^2. One of the two sets of data in Ref. 10 have been replotted as vertical lines.

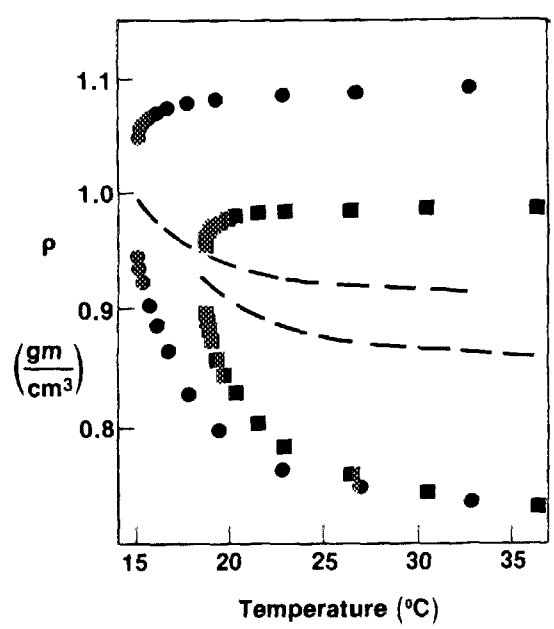

FIG. 5. The densities of the coexisting phases of mixtures of triethylamine with water or heavy water. The average of the densities of the coexisting phases (the rectilinear diameter) is denoted by the dashed line.

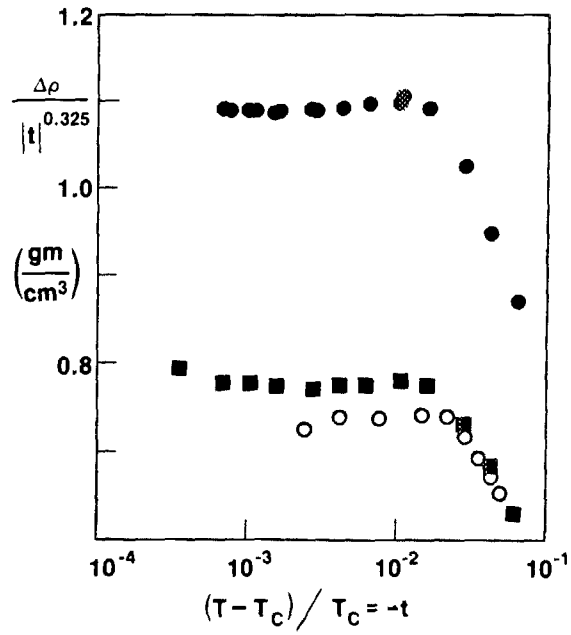

FIG. 6. Scaled density difference data for mixtures of triethylamine with water or heavy water as a function of the reduced temperature. The data from Ref. 13, ○, are plotted with $T_c = 17.8$ °C as reported therein. To the extent that the data fall on a horizontal straight line, they can be represented by the relation $\Delta\rho = B_0[(T-T_c)/T_c]^{0.325}$.

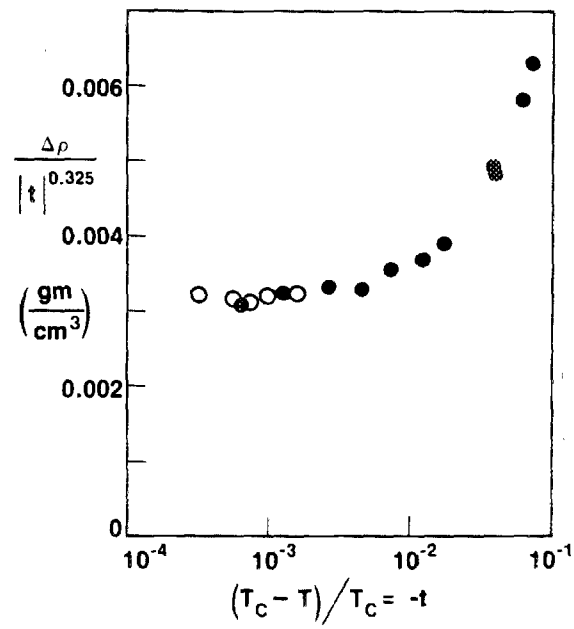

FIG. 8. Scaled density difference data for methanol + cyclohexane mixtures as a function of the reduced temperature. Data for two different samples are shown.

amplitude σ_0 and in the ratios $Y^{(\pm)}$ and U_1^+. the stated errors are standard deviations and make no allowance for possible terms such as $\mathbf{a}_1(-t)^\Delta$ which are expected in the expansion of $\mathbf{a}^2$ about the consolute point. If a_1 were roughly 1, such a term would lead to a systematic error in the determination of $\mathbf{a}_0^2$ which is smaller than 5%.

There is excellent agreement between our pendant drop data and Derdulla and Rusanow's capillary rise data far from T_c ($-t > 0.03$, or equivalently, 19–32 °C). Near T_c, we have fitted Derdulla and Rusanow's data for both $\mathbf{a}_0^2$ and T_c. The value $T_c = 17.57$ °C resulted and was used for Fig. 3. The fitted value $\mathbf{a}_0^2 = 38$ mm^2 is in very good agreement with our value $\mathbf{a}_0^2 = 38.8$ mm^2. Derdulla and Rusanow report the value $T_c = 17.8$ °C which is consistent with their $\Delta\rho$ data for a different sample. If we had used $T_c = 17.8$ °C to plot their data on Fig. 3, $\mathbf{a}^2/(-t)^{0.935}$ would increase dramatically near T_c, attaining the value 50 mm^2 at $-t = 0.003$.

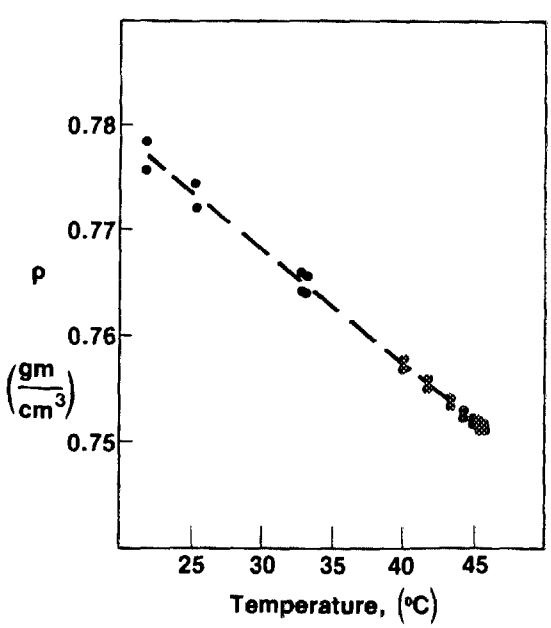

FIG. 7. The densities of the coexisting phases of methanol + cyclohexane mixtures. The average of the densities of the coexisting phases is denoted by the dashed line.

Figure 4 displays our capillary length data for ME + CY as well as one of the two sets of capillary length data for the same mixture obtained by Warren and Webb.[10] Far from T_c, there is excellent agreement between our pendant drop data and the values of $\mathbf{a}^2$ obtained by Warren and Webb from measurements of the shape of the meniscus between the two liquid phases in a wide cubic cell. Near T_c, our values of $\mathbf{a}^2$ average 25% less than Warren and Webb's, a difference which is slightly larger than the combined scatter of the two sets of data. Our data in the range $10^{-3.5} < -t < 10^{-2.5}$ are consistent with $\mathbf{a}^2/(-t)^{0.935} = 1150 \pm 100$ mm^2. The precision of the data do not justify looking for a term such as $a_1(-t)^\Delta$. Again, if a_1 happened to equal 1, such a term would lead to a 3% effect in the temperature range mentioned.

Figure 5 displays the densities of the coexisting phases of the mixtures TEA + W and TEA + HW. The remarkably curved rectilinear diameter of these mixtures is indicated by dashed lines. The volume fractions of the coexisting phases of TEA + W mixtures also show a curved diameter.[24] In Fig. 6 the scaled density differences for the same mixtures are plotted. In the range $10^{-3.3} < -t < 10^{-2}$ our TEA + W

data can be represented by the expressions

$$\Delta\rho/(2\rho_c) = 0.420(-t)^{0.325}[1 - 0.06(-t)^{0.5}],$$
$$\rho_c = 0.9261 \text{ g/cm}^3.$$

In the range $10^{-3.3} < -t < 10^{-2}$ our TEA + HW data can be represented by the expressions

$$\Delta\rho/(2\rho_c) = 0.543(-t)^{0.325}\cdot[1 + 0.12(-t)^{0.5}],$$
$$\rho_c = 0.9988 \text{ g/cm}^3.$$

The scaled $\Delta\rho$ data from Derdulla and Rusanow[13] plotted in Fig. 6 are consistently 2½% smaller than our TEA + W data. The difference between the data sets exceeds plausible errors of measurement and probably reflects differences in the purity of the TEA. This 2½% difference would lead to a 2½% effect in the universal amplitude ratios. In Sec. III, we stressed that our TEA comes from the same source as the TEA used for the heat capacity measurements and correlation length measurements which we use to compute the amplitude ratios.

Figure 7 displays the densities of the coexisting phases of ME + CY mixtures. The nearly perfect match of the coexisting densities is evident along with the very straight rectilinear diameter. (Note that the ordinate is very greatly expanded in comparison with Fig. 5.) In Fig. 8, the scaled density difference data for two samples of the same mixture are displayed. In the range $10^{-3.7} < -t < 10^{-2}$ the $\Delta\rho$ data for ME + CY can be represented by

$$\Delta\rho/(2\rho_c) = 0.002\,10(-t)^{0.325}[1 + 1.98(-t)^{0.5}],$$
$$\rho_c = 0.7507 \text{ g/cm}^3.$$

The entire set of $\Delta\rho$ data spanning the range $0.0003 < -t < 0.075$ can be represented by

$$\Delta\rho/(2\rho_c) = 0.001\,98(-t)^{0.325}[1 + 13(-t)],$$
$$\rho_c = 0.7507 \text{ g/cm}^3.$$

Thus, for the ME + CY system, the leading coefficient in the expansion of $\Delta\rho$ is reasonably insensitive to the range of the fit or the form of the correction terms.

It is interesting to note that the corrections to the leading singularities are much more evident in the $\Delta\rho$ data than in the capillary length data. This is not solely a result of the greater precision of the $\Delta\rho$ data. This same feature appears in the data for pure fluids near the liquid–vapor critical point.[5]

V. COMPARISON OF THEORETICAL AND EXPERIMENTAL AMPLITUDE RATIOS

The renormalization-group (RG) value for U_1^+ in Table I was obtained by multiplying the result $0.0507 < U_1^- < 0.0572$ obtained by Brezin and Feng[6] (and independently by Pant and Jasnow[7]) by the result $(\xi^+/\xi^-)^2 = (1.91)^2$ obtained by Brezin *et al.*[26] The RG value for ξ^+/ξ^- is close to the value $(\xi^+/\xi^-) = 1.96 \pm 0.03$ that was obtained from analysis of high temperature series for several Ising models,[27] and thus it is not likely to be seriously in error.

The RG values for Y^+ were obtained by multiplying the RG values of U_1^+ by the RG values of $(R_\xi^+)^{-2}$ where the ratio (R_ξ^+) is defined in Eq. (3). Bervillier and Godreche[28] give the RG result $R_\xi^+ = 0.2699 \pm 0.0008$. Nicoll and Albright[29] obtained the result $R_\xi^+ = 0.2814 \pm 0.0088$ by an independent RG method. Here, we have naively used both values to compute Y^+, thus enlarging the error assignment for Y^+. The Ising series values given in Ref. 1, $R_\xi^+ = 0.2545$–0.2550, are probably biased by today's standards because they were obtained with the assumption $\alpha = 0.125$.

The RG value for Y^- was obtained from the relation $Y^- = Y^+(A_0^+/A_0^-)^{2/3}$ using the value $(A_0^+/A_0^-) = 0.494$ which Chase and Kaufman[30] recently obtained. Series[31] for the Ising model give $(A_0^+/A_0^-) = 0.51$.

In Table I we have used the Ising model values for Y^+ and U_1^+ obtained recently by Mon and Jasnow.[4] They argued that their simulations on two lattices are more accurate than previous work[8] and that the dominant errors occur in the determination of σ from the simulation.[4]

In Table I, our results are combined with the amplitudes for the heat capacity from Ref. 11 (TEA + W and TEA + HW) and Ref. 32. The latter were recalculated with the exponent $\sigma = 0.11$ as discussed in Ref. 5. For ME + CY the amplitude $\xi_0^+ = 0.324$ nm was obtained independently by two recent measurements.[33,34] The other amplitudes in Table I were taken from Ref. 5 with the exception of the values of σ_0 for ^{3}He and ^{4}He. These were obtained from the new data of Iino, Suzuki, and Ikushima[35] near $-t = 0.005$ using the condition $\mu = 1.26$.

An examination of Table I supports our two conclusions: First, the amplitude ratios U_1^+ and $Y^{(\pm)}$ are remarkably consistent for a wide variety of fluid systems, and second, the experimental values are quite different from the Ising model values and the RG values.

Our new data for σ_0 for TEA + W and TEA + HW lead to amplitude ratios in good agreement with those for other fluids, although our data rely on very different measurement techniques. It is also significant that the new data for ME + CY, ^{3}He, and ^{4}He lead to amplitude ratios in much better agreement with the ratios for other fluids than the older data discussed in Ref. 5. (In Ref. 5, $Y^{(\pm)}$ for ME + CY were 500% higher than the median value for other fluids and $Y^{(\pm)}$ were 20% higher for ^{3}He than for other fluids.) We believe that the remaining differences between the experimental and the theoretical amplitude ratios cannot be explained by systematic errors in the experiments.

One may speculate that interfacial tension data with $-t < 10^{-3}$ (the practical limit of our measurements) would reconcile the experimental and theoretical amplitude ratios. In this context, we note that the Ising model simulations[4] are *further* from T_c than the fluid data. The simulations occur in the very narrow temperature range $0.01 < -t < 0.02$ and are carried out on systems with dimensions L in the range $1 < L/\xi < 3$.

ACKNOWLEDGMENTS

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APPENDIX: The density data are quoted to higher precision than their accuracy to preserve the precision of the density differences.

TABLE III. Coexisting densities.

$-10^3 t$	ρ_{upper} (g/cm^3)	ρ_{lower} (g/cm^3)
	ME + CY	
6.39	0.750 795	0.751 077
12.69	0.750 980	0.751 351
13.01	0.751 006	0.751 376
26.42	0.751 426	0.751 906
45.82	0.752 112	0.752 684
74.59	0.753 117	0.753 837
123.0	0.754 804	0.755 679
177.4	0.756 664	0.757 707
394.1	0.763 933	0.765 628
401.3	0.764 135	0.765 826
638.9	0.771 951	0.774 324
749.1	0.775 510	0.778 219
5.68	0.750 997	0.751 275
9.94	0.751 115	0.751 452
3.24	0.750 913	0.751 149
15.94	0.751 338	0.751 733
7.43	0.751 039	0.751 338
	TEA + W	
3.43	0.895 12	0.954 52
6.86	0.887 21	0.959 78
10.29	0.880 09	0.963 15
15.46	0.872 30	0.966 63
27.43	0.858 31	0.971 31
41.14	0.844 44	0.974 47
61.72	0.829 15	0.977 64
102.9	0.804 33	0.980 72
154.3	0.783 09	0.982 59
274.3	0.757 58	0.984 54
411.4	0.743 59	0.985 34
617.2	0.730 90	0.985 39
6.82	0.887 24	0.959 75
	TEA + HW	
7.57	0.942 33	1.047 70
10.97	0.933 24	1.052 28
16.29	0.922 11	1.057 37
28.44	0.902 13	1.064 23
42.33	0.883 92	1.068 64
63.17	0.861 10	1.072 51
104.8	0.826 45	1.077 46
156.9	0.797 61	1.080 65
278.5	0.764 33	1.084 63
417.4	0.749 55	1.087 22
625.7	0.736 00	1.089 58
11.22	0.932 71	1.052 61
7.05	0.943 73	1.046 86
10.28	0.935 08	1.051 61
15.59	0.923 64	1.056 79
26.36	0.905 36	1.063 77
7.57	0.942 16	1.047 73
15.21	0.924 22	1.056 44
101.5	0.829 40	1.077 05

TABLE IV. Capillary length.

$-10^3 t$	$a^2/t^{0.935}$ (mm^2)
ME + CY	
1.24	1207
1.24	1235
1.25	1230
1.24	1281
1.24	1254
2.12	1255
2.12	1307
2.15	1207
2.15	1198
2.13	1259
2.13	1249
4.94	1095
4.94	1101
4.94	1075
4.94	1098
8.52	991
8.52	1045
12.42	1028
12.41	1043
0.61	1054
0.61	1123
0.61	1199
1.47	1128
1.48	1135
0.46	960
0.46	939
0.46	1010
0.46	1057
0.46	989
0.46	939
0.46	769
0.46	1070
0.45	1152
0.45	1224
0.45	1149
0.45	968
0.45	1000
2.36	1219
2.36	1179
2.36	1145
2.36	1156
2.36	1168
2.36	1173
2.36	1162
2.36	1156
2.34	1175
2.34	1158
2.35	1044
2.35	1224
2.35	1216
TEA + W	
0.42	38.3
0.81	39.5
1.22	40.5
1.22	38.9
3.42	38.1
3.42	38.8
3.42	38.8
3.42	38.7
21.24	40.0
21.24	40.0
21.24	39.6

TABLE IV. (*continued*).

-10^3t	$a^2/t^{0.935}$ (mm^2)
TEA + W	
21.24	39.9
44.15	38.9
44.15	39.0
44.15	39.0
44.15	38.9
0.42	35.5
0.42	37.5
0.83	37.7
0.83	36.9
0.83	40.1
0.83	40.9
1.63	38.6
1.63	37.8
1.63	39.1
1.63	40.0
3.37	38.5
3.37	38.6
3.37	38.8
3.37	39.1
12.10	38.9
12.10	38.6
12.10	38.8
12.10	38.7
26.33	39.5
26.33	39.5
26.33	39.9
26.33	39.8
40.14	39.1
40.14	39.2
40.14	39.4
40.14	39.5
TEA + HW	
34.32	26.7
34.32	27.3
34.32	27.0
34.32	27.1
52.31	26.4
52.31	26.6
52.31	26.5
6.10	26.8
6.10	27.2
11.01	27.4
11.00	26.7
22.00	26.7
22.02	27.9
22.02	27.6
27.87	27.7
44.75	27.0
44.75	27.3
68.84	27.8
2.96	25.1
2.96	25.4
3.81	26.7
4.54	25.2
1.98	25.1
1.98	26.1
2.00	26.3
2.24	26.2
2.26	27.1
2.28	24.9

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[18]Fluka AG.
[19]Stuart Oxygen Co.
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