JOURNAL OF COLLOID AND INTERFACE SCIENCE **177,** 150–155 (1996)
Article No. 0015

The Drop Volume Method for Interfacial Tension Determination: An Error Analysis

J. C. EARNSHAW,*[,1] E. G. JOHNSON,* B. J. CARROLL,† AND P. J. DOYLE†

*The Department of Pure and Applied Physics, The Queen's University of Belfast, Belfast BT7 1NN, Northern Ireland; and
†Unilever Research Laboratory, Quarry Road East, Bebington, Merseyside L63 3JW, United Kingdom

Received February 7, 1995; accepted June 7, 1995

An error analysis of the drop volume method of determination of surface or interfacial tension is presented. It is shown that the presence of the empirical correction term may lead to either a decrease or an increase in the final uncertainty of the calculated tension. Recommendations to maximize the precision of measurement are made. It is further shown that the systematic error due to the correction term is less than 0.04%; under the conditions recommended to minimize the statistical uncertainty, the systematic error should be less than half this figure. Tabulations of recommended values of the correction function are given.

Key Words: **interfacial tension; drop volume method; error analysis.**

1. INTRODUCTION

For pure liquids the drop volume method for measuring interfacial or surface tensions (1) is capable of a precision rivalling that of the Wilhelmy plate method, but offers certain advantages over this, notably that only small amounts of the fluids are needed. In favorable circumstances a precision of ± 0.01 mN/m is achievable. This method applies also to surfactant solutions, except when these show significant surface dilatational moduli on the time scale of drop detachment (2).

However, the errors involved in the drop volume method seem not to have been analyzed. Such an analysis is not entirely straightforward, as the technique involves an empirical system-dependent correction, the precision of which is not established. The present paper considers these matters, and offers, for the first time, an analysis of the uncertainties involved in the drop volume technique, both random and systematic.

In the drop volume method, the volume of the drop of liquid which just detached from a cylindrical support of radius r is accurately measured. This volume is a function of the volume V' of the largest drop of liquid that the tip is capable of supporting before detachment occurs, and also of the system dimensions, characterized by the capillary length

$$a = \left(\frac{2\gamma}{\Delta\rho g}\right)^{1/2}, \qquad [1]$$

where $\Delta\rho$ is the operating density difference (i.e., the difference between the densities of the fluid forming the drop and that surrounding the drop), g is the acceleration due to gravity, and γ is the interfacial tension. The relationship between γ and the initial (equilibrium) drop volume V' is given by the Tate equation (3), in which the tension is implicitly treated as a force per unit length:

$$2\pi r\gamma = \Delta\rho g V'. \qquad [2]$$

However, the Tate equation is incorrect when applied to the volume of the detached drop V: first, the drop does not totally leave the tip (as much as 40% may remain attached), second, the boundary tension forces are not generally vertical, and third, there is a pressure difference across the curved interface. Hence an empirically derived correction factor $\phi(r/V^{1/3})$ is introduced (1) to enable the detached drop volume V to be used rather than V':

$$\gamma = \Delta\rho g V / 2\pi r\phi(r/V^{1/3}). \qquad [3]$$

In this paper we analyze the uncertainties involved in the drop volume method. A straightforward error analysis in the next section indicates the role of the correction term. However, this is not susceptible to analytic solution, and so numerical methods are used in Section 3 to estimate the effect the function $\phi(r/V^{1/3})$ has upon the total uncertainty in γ. Finally we consider the systematic errors liable to arise from imperfect knowledge of ϕ.

2. FORMAL CONSIDERATIONS

The tension is a function of three observable quantities: $\Delta\rho$, r, and V. The function contains a functionally unknown

[1] To whom correspondence should be addressed.

0021-9797/96 $12.00

part, but the experimental uncertainties on these observables (written as σ_r, for example) must combine in the usual manner (4),

$$\sigma_\gamma^2 = \left(\frac{\partial\gamma}{\partial\Delta\rho}\right)^2 \sigma_{\Delta\rho}^2 + \left(\frac{\partial\gamma}{\partial r}\right)^2 \sigma_r^2 + \left(\frac{\partial\gamma}{\partial V}\right)^2 \sigma_V^2 + 2\frac{\partial\gamma}{\partial r}\frac{\partial\gamma}{\partial V}\sigma_{rV} + \ldots, \quad [4]$$

where the covariance terms are represented by a single term, for brevity. If the functionally unknown correction term $\phi(r/V^{1/3})$ of Eq. [3] were not necessary, the matter would be trivial. However, the lack of a known analytic representation of this term complicates the issue. We will simplify the analysis below by neglecting the covariance terms; this does not affect any matters of principle, but merely simplifies the algebraic presentation.

From Eq. [3] we have the differentials

$$\frac{\partial\gamma}{\partial\Delta\rho} = \frac{gV}{2\pi r\phi} \quad [5]$$

$$\frac{\partial\gamma}{\partial r} = -\frac{\Delta gV}{2\pi r^2\phi(r/V^{1/3})} - \frac{\Delta\rho g V^{2/3}\phi'(r/V^{1/3})}{2\pi r\phi^2(r/V^{1/3})} \quad [6]$$

$$\frac{\partial\gamma}{\partial V} = \frac{\Delta\rho g}{2\pi r\phi(r/V^{1/3})} + \frac{\Delta\rho g\phi'(r/V^{1/3})}{6\pi V^{1/3}\phi^2(r/V^{1/3})}. \quad [7]$$

Substituting into Eq. [4] and rearranging somewhat, we find

$$\left(\frac{\sigma_\gamma}{\gamma}\right)^2 = \left(\frac{\sigma_{\Delta\rho}}{\Delta\rho}\right)^2 + \left(\frac{\sigma_r}{r}\right)^2\left[1 + \frac{r}{V^{1/3}}\frac{\phi'}{\phi}\right]^2 + \left(\frac{\sigma_V}{V}\right)^2\left[1 + \frac{r}{3V^{1/3}}\frac{\phi'}{\phi}\right]^2, \quad [8]$$

where the argument of the correction function is suppressed for clarity. The influence of this function upon the uncertainty in γ is given by the terms in square brackets.

The problem thus reduces to establishing ϕ and its derivative. In the absence of any functional form for this function, we turn to numerical considerations.

3. NUMERICAL ANALYSIS

The correction term is based upon published tabulations of carefully measured data for fluids of known properties (1, 5). Unfortunately, the data, while close to a cubic, depart significantly from that form (1). Various attempts have been made to determine an appropriate functional form for ϕ. The curves fitted by Strenge (6) and by Lando and Oakley (7) both show systematic deviations from the empirical values (with coefficients of variation, C_v, of 0.42 and 0.22%, respectively). Wilkinson and Kidwell (8) applied regression analysis to limited sections of the data; for the region $0.65 \leqslant r/V^{1/3} \leqslant 0.95$ a regression analysis on 24 points gave a C_v of 0.065% (with a random scatter) for a quadratic fit. Despite these attempts the most precise variation of ϕ with $r/V^{1/3}$ derives from a rather careful manual interpolation of these data (9), which is tabulated in Table 1. However, this procedure does not readily lend itself to either numerical differentiation or statistical analysis, so we have followed a different procedure.

We have fitted the published data with a cubic spline, defined on a series of *knots* across the range of $r/V^{1/3}$. The spline function is a piecewise cubic function, whose value and first two derivatives are continuous functions across the range, the knots being points at which the third derivative of the spline can change discontinuously. Thus the location and number of the knots within the range of the spline permits control over the smoothness of the spline. (This summary of spline approximation is necessarily brief; fuller accounts may be found in (10).)

We have used a computer routine (11) which automatically adjusts the position and number of the knots interior to the range of the data so as to achieve a specified goodness of fit (judged by the sum of square residuals). This procedure is necessary as the uncertainties on the published ϕ data are unknown (1, 5). The fit is refined to the point where any further reduction in the sum of squares causes a sudden increase in the number of interior knots, corresponding to overfitting the data. In practice this refinement is quite unambiguous. The routine provides estimates of ϕ and ϕ' across the range of $r/V^{1/3}$ (covering 0.308–1.353 (1) and 0.064–0.453 (5)).

The two sets of data which have been used in the derivation of ϕ here (and in Ref. (9)) appear to be of very unequal precision, although it is not possible to establish uncertainties on either set of data. The two sets appear to be mutually consistent, but the data of Harkins and Brown (1) are considerably less scattered than those of Wilkinson (5). While this is of little consequence to manual interpolation, the eye–brain combination providing a rather good noise filter, objective fitting of the combined data set is not possible, lacking estimates of the errors on the data. We have, therefore, fitted the two sets of data separately. In both cases the fits were constrained to pass through the point $\phi(0) = 1$ (12). The data of Harkins and Brown (1) are so precise that the fitting is seriously affected by inclusion of one or two points which lie off the trend of the data. We have therefore neglected these points, as did Harkins and Brown.

Figure 1 shows the interpolation of ϕ across the established range of $r/V^{1/3}$, for both sets of data. The two fits accord well; the slight differences about $r/V^{1/3} \sim 0.35$ arise from the problems of accurately fitting data points at the

TABLE 1

The Recommended Interpolation of the Correction Function $\phi(r/V^{1/3})$ Tabulated from $r/V^{1/3} = 0.0$ to 1.598 in Steps of 0.002

	$\phi(r/V^{1/3})$									
$r/V^{1/3}$	0.000	0.002	0.004	0.006	0.008	0.010	0.012	0.014	0.016	0.018
0.00	1.00000	0.99800	0.99600	0.99400	0.99200	0.99000	0.98780	0.98580	0.98380	0.98170
0.02	0.97980	0.97770	0.97560	0.97370	0.97170	0.96980	0.96770	0.96560	0.96370	0.96170
0.04	0.95970	0.95770	0.95560	0.95370	0.95170	0.94980	0.94770	0.94560	0.94370	0.94170
0.06	0.93980	0.93780	0.93570	0.93400	0.93180	0.92970	0.92780	0.92580	0.92370	0.92200
0.08	0.91980	0.91780	0.91570	0.91370	0.91180	0.90990	0.90780	0.90570	0.90370	0.90180
0.10	0.89980	0.89780	0.89580	0.89370	0.89150	0.88950	0.88740	0.88570	0.88320	0.88140
0.12	0.87970	0.87770	0.87540	0.87340	0.87180	0.87010	0.86820	0.86630	0.86430	0.86220
0.14	0.86020	0.85860	0.85670	0.85460	0.85250	0.85040	0.84880	0.84710	0.84530	0.84320
0.16	0.84170	0.83960	0.83780	0.83580	0.83420	0.83260	0.83040	0.82870	0.82710	0.82530
0.18	0.82370	0.82180	0.82010	0.81820	0.81680	0.81530	0.81330	0.81130	0.80960	0.80780
0.20	0.80640	0.80460	0.80290	0.80110	0.79970	0.79780	0.79600	0.79440	0.79280	0.79160
0.22	0.78980	0.78800	0.78640	0.78510	0.78380	0.78170	0.78000	0.77860	0.77700	0.77530
0.24	0.77380	0.77230	0.77080	0.76920	0.76770	0.76630	0.76480	0.76320	0.76170	0.76020
0.26	0.75880	0.75730	0.75600	0.75460	0.75290	0.75170	0.75020	0.74870	0.74740	0.74600
0.28	0.74470	0.74320	0.74200	0.74060	0.73960	0.73820	0.73690	0.73570	0.73440	0.73310
0.30	0.73180	0.73060	0.72960	0.72840	0.72720	0.72600	0.72480	0.72370	0.72260	0.72160
0.32	0.72030	0.71920	0.71800	0.71690	0.71590	0.71480	0.71370	0.71270	0.71170	0.71080
0.34	0.70960	0.70860	0.70770	0.70650	0.70560	0.70470	0.70380	0.70280	0.70170	0.70080
0.36	0.69980	0.69890	0.69800	0.69710	0.69620	0.69530	0.69450	0.69360	0.69270	0.69180
0.38	0.69100	0.69020	0.68930	0.68850	0.68760	0.68680	0.68610	0.68540	0.68470	0.68380
0.40	0.68300	0.68225	0.68145	0.68070	0.68005	0.67925	0.67860	0.67800	0.67740	0.67665
0.42	0.67600	0.67535	0.67480	0.67420	0.67355	0.67290	0.67230	0.67165	0.67105	0.67040
0.44	0.66985	0.66920	0.66865	0.66795	0.66740	0.66670	0.66600	0.66525	0.66470	0.66410
0.46	0.66335	0.66280	0.66220	0.66165	0.66090	0.66030	0.65980	0.65915	0.65860	0.65790
0.48	0.65725	0.65670	0.65610	0.65555	0.65500	0.65440	0.65385	0.65320	0.65270	0.65210
0.50	0.65150	0.65090	0.65010	0.64945	0.64885	0.64825	0.64765	0.64710	0.64650	0.64590
0.52	0.64535	0.64480	0.64420	0.64365	0.64300	0.64240	0.64185	0.64125	0.64065	0.64010
0.54	0.63950	0.63895	0.63835	0.63780	0.63725	0.63670	0.63620	0.63560	0.63505	0.63455
0.56	0.63400	0.63345	0.63300	0.63250	0.63205	0.63155	0.63105	0.63060	0.63015	0.62965
0.58	0.62920	0.62875	0.62835	0.62790	0.62745	0.62705	0.62665	0.62625	0.62585	0.62545
0.60	0.62510	0.62470	0.62430	0.62395	0.62360	0.62325	0.62285	0.62250	0.62225	0.62190
0.62	0.62155	0.62120	0.62090	0.62060	0.62025	0.62000	0.61970	0.61940	0.61910	0.61885
0.64	0.61855	0.61830	0.61795	0.61765	0.61740	0.61705	0.61670	0.61635	0.61605	0.61580
0.66	0.61550	0.61515	0.61490	0.61455	0.61425	0.61400	0.61360	0.61335	0.61300	0.61270
0.68	0.61240	0.61205	0.61180	0.61150	0.61115	0.61085	0.61055	0.61025	0.60995	0.60965
0.70	0.60935	0.60905	0.60880	0.60850	0.60815	0.60790	0.60765	0.60745	0.60715	0.60690
0.72	0.60660	0.60635	0.60610	0.60590	0.60560	0.60540	0.60515	0.60495	0.60470	0.60450
0.74	0.60425	0.60405	0.60390	0.60365	0.60345	0.60325	0.60300	0.60285	0.60265	0.60250
0.76	0.60235	0.60220	0.60205	0.60190	0.60180	0.60165	0.60145	0.60135	0.60120	0.60110
0.78	0.60095	0.60085	0.60070	0.60060	0.60050	0.60045	0.60035	0.60025	0.60015	0.60005
0.80	0.60000	0.59995	0.59990	0.59985	0.59980	0.59970	0.59965	0.59960	0.59955	0.59950
0.82	0.59945	0.59940	0.59935	0.59930	0.59925	0.59920	0.59920	0.59915	0.59915	0.59910
0.84	0.59910	0.59910	0.59905	0.59905	0.59905	0.59905	0.59900	0.59900	0.59900	0.59900
0.86	0.59905	0.59905	0.59905	0.59905	0.59905	0.59910	0.59910	0.59915	0.59915	0.59920
0.88	0.59925	0.59930	0.59935	0.59940	0.59945	0.59950	0.59955	0.59965	0.59970	0.59980
0.90	0.59985	0.59995	0.60000	0.60010	0.60020	0.60035	0.60050	0.60060	0.60070	0.60085
0.92	0.60100	0.60115	0.60125	0.60140	0.60155	0.60170	0.60180	0.60200	0.60210	0.60230
0.94	0.60240	0.60260	0.60275	0.60290	0.60310	0.60330	0.60350	0.60370	0.60395	0.60415
0.96	0.60440	0.60460	0.60485	0.60505	0.60530	0.60550	0.60580	0.60605	0.60635	0.60655
0.98	0.60685	0.60705	0.60730	0.60750	0.60775	0.60800	0.60825	0.60850	0.60880	0.60915
1.00	0.60950	0.60985	0.61010	0.61045	0.61080	0.61110	0.61145	0.61180	0.61210	0.61245
1.02	0.61280	0.61310	0.61345	0.61385	0.61415	0.61455	0.61490	0.61520	0.61555	0.61590
1.04	0.61620	0.61655	0.61695	0.61730	0.61765	0.61800	0.61840	0.61875	0.61910	0.61950
1.06	0.61980	0.62015	0.62055	0.62095	0.62135	0.62170	0.62210	0.62250	0.62290	0.62330
1.08	0.62365	0.62415	0.62455	0.62495	0.62535	0.62580	0.62620	0.62660	0.62705	0.62750
1.10	0.62800	0.62845	0.62895	0.62940	0.62985	0.63035	0.63085	0.63130	0.63175	0.63230
1.12	0.63275	0.63325	0.63375	0.63420	0.63480	0.63535	0.63590	0.63640	0.63695	0.63745

TABLE 1—*Continued*

	$\phi(r/V^{1/3})$									
$r/V^{1/3}$	0.000	0.002	0.004	0.006	0.008	0.010	0.012	0.014	0.016	0.018
1.14	0.63800	0.63855	0.63910	0.63960	0.64015	0.64070	0.64140	0.64200	0.64255	0.64310
1.16	0.64370	0.64430	0.64485	0.64540	0.64600	0.64650	0.64710	0.64770	0.64825	0.64885
1.18	0.64935	0.64990	0.65050	0.65100	0.65145	0.65190	0.65235	0.65260	0.65300	0.65340
1.20	0.65365	0.65395	0.65425	0.65450	0.65465	0.65495	0.65505	0.65515	0.65525	0.65530
1.22	0.65530	0.65530	0.65520	0.65515	0.65505	0.65495	0.65475	0.65455	0.65435	0.65415
1.24	0.65390	0.65365	0.65335	0.65305	0.65270	0.65240	0.65205	0.65170	0.65135	0.65090
1.26	0.65055	0.65005	0.64960	0.64915	0.64865	0.64815	0.64765	0.64715	0.64660	0.64605
1.28	0.64550	0.64500	0.64445	0.64390	0.64330	0.64270	0.64215	0.64155	0.64095	0.64035
1.30	0.63970	0.63910	0.63850	0.63785	0.63725	0.63660	0.63585	0.63515	0.63450	0.63385
1.32	0.63315	0.63245	0.63180	0.63110	0.63040	0.62975	0.62900	0.62830	0.62760	0.62695
1.34	0.62620	0.62555	0.62485	0.62410	0.62340	0.62265	0.62190	0.62120	0.62050	0.61965
1.36	0.61895	0.61805	0.61740	0.61655	0.61580	0.61500	0.61420	0.61345	0.61270	0.61195
1.38	0.61115	0.61030	0.60950	0.60870	0.60800	0.60715	0.60640	0.60560	0.60490	0.60410
1.40	0.60325	0.60260	0.60180	0.60100	0.60020	0.59950	0.59875	0.59795	0.59720	0.59640
1.42	0.59560	0.59490	0.59405	0.59330	0.59250	0.59165	0.59095	0.59015	0.58940	0.58865
1.44	0.58790	0.58715	0.58645	0.58570	0.58500	0.58435	0.58360	0.58290	0.58220	0.58150
1.46	0.58080	0.58010	0.57940	0.57870	0.57800	0.57730	0.57660	0.57590	0.57515	0.57450
1.48	0.57380	0.57310	0.57245	0.57175	0.57115	0.57045	0.56985	0.56920	0.56850	0.56785
1.50	0.56715	0.56650	0.56585	0.56515	0.56455	0.56395	0.56320	0.56250	0.56185	0.56115
1.52	0.56050	0.55985	0.55910	0.55845	0.55780	0.55705	0.55635	0.55570	0.55505	0.55445
1.54	0.55380	0.55315	0.55255	0.55200	0.55135	0.55065	0.55000	0.54935	0.54865	0.54800
1.56	0.54735	0.54670	0.54605	0.54540	0.54485	0.54415	0.54350	0.54290	0.54235	0.54165
1.58	0.54105	0.54045	0.53990	0.53930	0.53865	0.53800	0.53745	0.53685	0.53625	0.53565

extremes of the two ranges covered. These differences must obviously affect the corresponding derivatives, shown in Fig. 2: the slight differences in the region where the two data sets overlap arise from these extremal values of $r/V^{1/3}$. Estimates of both ϕ and ϕ' from the fits to the separate data sets agree excellently with the best manual interpolation (9) and its derivative apart from at the ends of the ranges of the two data sets, giving us confidence in our fitting procedure. Despite these discrepancies, the main point of present concern is clear: the derivative ϕ' changes sign within the range of tabulated values of $r/V^{1/3}$.

The effect of the correction term ϕ, which is always positive itself, is thus either to raise or to lower the final uncertainty on γ over different parts of the range (cf. Eq. [8]). To achieve the optimal precision of determination of tension, it is apparent that measurements should be made in such a way that the combination $r/V^{1/3}$ lies in the regime where ϕ' is negative.

The effect of the correction term upon the final uncertainty in γ is expressed in Eq. [8] through the ratio $(r/V^{1/3})(\phi'/\phi)$. Figure 3 shows this ratio as a function of $r/V^{1/3}$ for the fits to both sets of data, and for the manual interpolation already cited. Clearly for $0 < r/V^{1/3} < 0.85$ the final uncertainty in γ is reduced by the effects of the function ϕ. Over part of this range, from about 0.2 to about 0.55, the ratio is below -0.2. In this smaller range, therefore, the influences of σ_r and σ_V in the quadratic composition of uncertainties are reduced to less than 64 and 87% of the values in the absence of ϕ. It is clear that the precision of γ would be maximized by working within this range.

4. SYSTEMATIC ERRORS

The correction term $\phi(r/V^{1/3})$ derives from empirical data. It must itself, therefore, be uncertain to a degree. This entails a systematic error intrinsic to the drop volume method. How significant is this error? We adopt a jackknife approach to this question (13).

The jackknife is a computer-intensive resampling approach to establish the accuracy attending the estimation of some quantity from a limited set of data. Each point in the original data set, of say n members, is discarded in turn, generating n sets of $n - 1$ members which are individually analyzed. The scatter of the n estimates of the statistic of interest (x_i) can be used to estimate the standard error of the mean $\hat{x}$ This is given by

$$\sigma = \sqrt{\frac{n-1}{n}\sum_{i=1}^{n}(x_i - \hat{x})^2}\,. \qquad [9]$$

The factor $(n - 1)$ 'inflates' the estimated standard error to allow for the fact that the n data sets are more similar to each other than truly independent data sets would be (see p. 143 of (13)). Other resampling schemes avoid this inflation of the estimated error (13), but are inappropriate in the

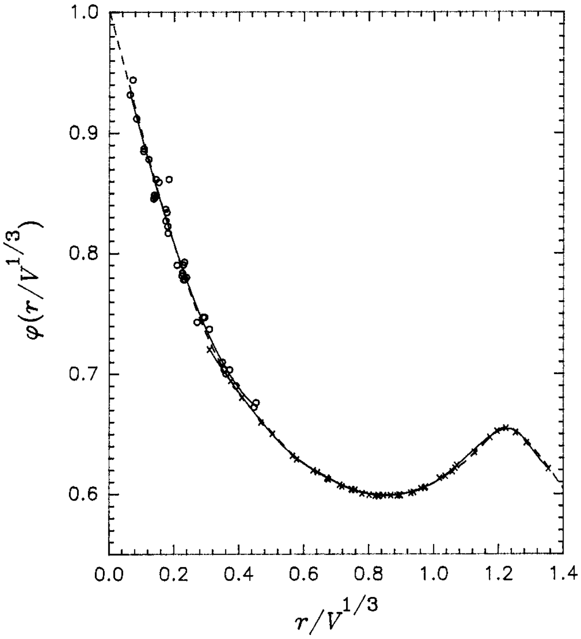

FIG. 1. Cubic spline approximations (solid lines) to the data of Harkins and Brown (1) (×) and Wilkinson (5) (○). Note the greater scatter on the latter data. The broken line represents the manual interpolation of the combined set of data referred to in the text.

present case where the statistic of interest derives from a spline fit to the resampled data. In the present case the analysis involves spline fitting the literature tabulations of ϕ, the statistic of interest being the estimate of ϕ at a given

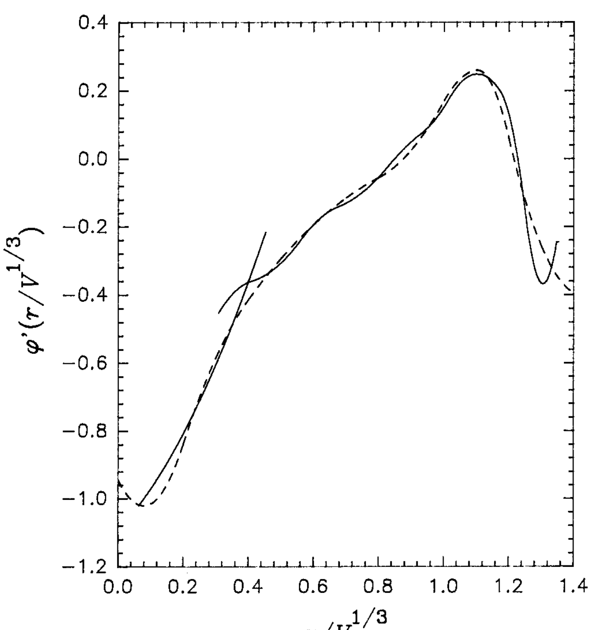

FIG. 2. The first derivatives of the spline fits to $\phi(r/V^{1/3})$ from Fig. 1 (solid lines). The broken line derives from the corresponding line of Fig. 1.

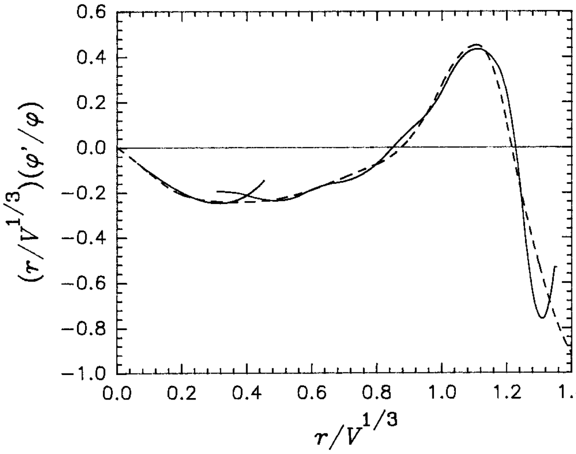

FIG. 3. The ratio $(r/V^{1/3})\,(\phi'/\phi)$ for the fits to the two sets of data (solid lines) and the manual interpolation of the combined data set (broken line). Note that the ratio is negative over part of the range covered.

$r/V^{1/3}$. The above error estimate refers to the precision of ϕ at a single arbitrarily chosen value of the argument of that function. But ϕ must be a smooth function, and so this will overestimate its uncertainty. We compromise by taking the standard deviation of the jackknife values of $\phi(r/V^{1/3})$ as

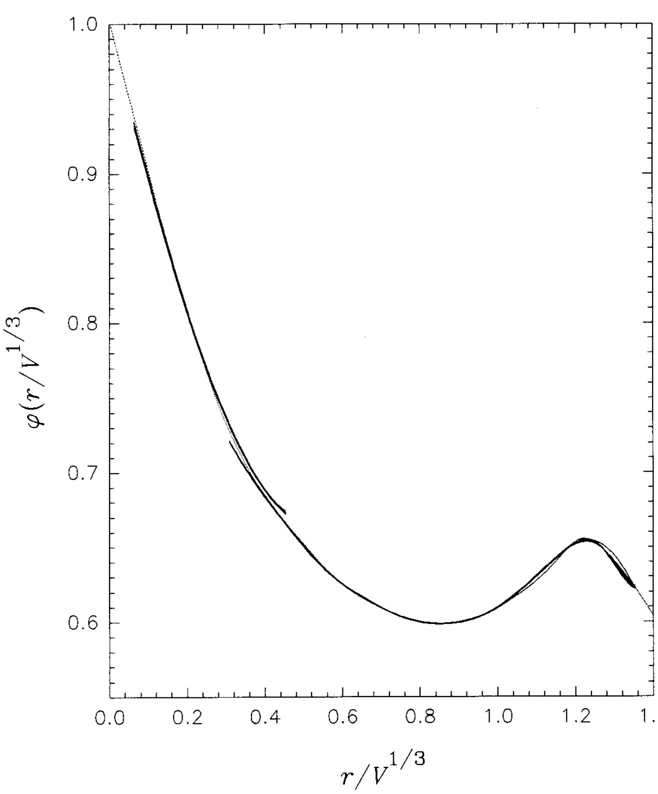

FIG. 4. Cubic spline fits to jackknife data sets derived from the data of Harkins and Brown (1) and Wilkinson (5), together with the manual interpolated variation (broken line). Note the closeness of the fits to the manual interpolation and the rather small scatter on the jackknife fits.

the uncertainty in that function. This estimate, while not very rigorous, does indicate the likely systematic error; the jackknife is, after all, a crude device (13).

We show the multiple estimates of $\phi(r/V^{1/3})$ in Fig. 4. All the spline fits are very close to the best manual interpolation, giving assurance of the satisfactory nature of the present results. The scatter of the fits is really rather small: the error in the interpolated value of ϕ is not large. The fractional standard deviation of these fits to ϕ varies with $r/V^{1/3}$: it is $\leqslant 3 \times 10^{-4}$ over most of the range studied by Harkins and Brown (1), rising to 10^{-3} about $r/V^{1/3} \sim 1.3$. For the data of Wilkinson (5), the corresponding figure is $\leqslant 5 \times 10^{-4}$ over the entire range covered. For $0.3 \leqslant r/V^{1/3} \leqslant 0.85$, the portion of the Harkins and Brown range for which ϕ' is negative, the fractional jackknife error is $\leqslant 2 \times 10^{-4}$. These figures represent our estimate of the systematic error on γ, due to the inherent imprecision of ϕ, expressed as a fraction of γ.

5. CONCLUSIONS

In summary we have presented, for the first time, a detailed error analysis of the drop volume method of determination of surface or interfacial tensions. The principal conclusions are that, due to the effect of the empirical correction term, the uncertainty in the measured tensions can be minimized by making measurements so that $r/V^{1/3} \leqslant 0.85$, where the effect of the correction term is to reduce the effects of the errors in r and V. This recommendation partially reinforces that of Harkins and Brown (1), who suggested that the most accurate results would be obtained between $0.6 \leqslant r/V^{1/3} \leqslant 1.2$, where the slope of the plot of ϕ was not too great. Very small values of r may involve experimental difficulties (14) and should, therefore, be avoided.

We have also considered the possible systematic errors in γ due to the empirical basis of the correction term. It seems unlikely that this systematic error could exceed 0.02%, which is likely to be smaller than the random errors of measurement. We offer the tabulation of the manual interpolation (9) of $\phi(r/V^{1/3})$ given in Table 1 as a recommended variation for use by other workers.

ACKNOWLEDGMENTS

E.G.J. is grateful to DENI and Unilever research for financial support. J. Magorrian is thanked for advice on computing aspects.

REFERENCES

1. Harkins, W. D., and Brown, F. E., *J. Am. Chem. Soc.* **41,** 499 (1919).
2. Carroll, B. J., Doyle, P. J., Donegan, A. C., and Ward, A. J., *J. Chem. Soc. Faraday Trans. 1* **81,** 2975 (1985).
3. Tate, T., *Philos. Mag.* **27,** 176 (1864).
4. See, e.g., Barlow, R. J., ''Statistics.'' Wiley, Chichester, 1989.
5. Wilkinson, M. C., *J. Colloid Interface Sci.* **40,** 14 (1972).
6. Strenge, K. H., *J. Colloid Interface Sci.* **29,** 732 (1969).
7. Lando, J. L., and Oakley, H. T., *J. Colloid Interface Sci.* **25,** 526 (1967).
8. Wilkinson, M. C., and Kidwell, R. L., *J. Colloid Interface Sci.* **35,** 114 (1971).
9. Doyle, P. J., PhD thesis, CNAA, 1991.
10. e.g., de Boor, C., ''A Practical Guide to Splines.'' Springer–Verlag, New York, 1978; Dierckx, P., ''Curve and Surface Fitting with Splines.'' Oxford Univ. Press, Oxford, 1993.
11. Routine E02BEF of the NAG Library, Numerical Algorithms Group, Oxford, OX2 8DR, UK.
12. Harkins, W. D., *in* ''Physical Methods of Inorganic Chemistry'' (A. Weissberger, Ed.), Vol. 1, p. 355. Interscience, New York, 1949.
13. Efron, B., and Tibshirani, R. J., ''An Introduction to the Bootstrap.'' Chapman & Hall, New York, 1993.
14. Kaufman, S., *J. Colloid Interface Sci.* **57,** 399 (1976).