# THE PENDANT DROP METHOD OF SURFACE TENSION MEASUREMENT: EQUATION INTERPOLATING THE SHAPE FACTOR TABLES FOR SEVERAL SELECTED PLANES

### J. Jůza

Institute of Macromolecular Chemistry, Acad. Sci. CR, 16206 Praha 6, Czech Republic

> Received 15 April 1996; final version 7 June 1996

For evaluation of the surface tension by the pendant drop method, the method of selected plane is often preferred to more precise and sophisticated treatments. The several selected planes method, which implies better verification of data, is used only seldom, which is likely due to low accessibility of data for other planes in a suitable form. This article presents equations which express the parameter 1/H with a maximum deviation of  $10^{-4}$ , in terms of the shape parameter  $S_k$  for 5 planes with the distance from drop apex equal to 0.8-1.2 multiple of the equatorial diameter  $d_e$ . The aim of this paper is only to introduce this tool for easier use of the method; the analysis of advantages and disadvantages of using several planes was made prior by several authors.

### 1 Introduction

A frequently used method for measurement of the surface or interfacial tension is the pendant drop method of Andreas et al. [1]. Theoretical fundamentals of this method are explained e.g. by Padday [2], Ambwani and Fort [3], and Hartland and Hartley [4]. The method is based on the fact that the shape of the pendant drop (and of axially symmetrical interfaces generally) in a homogeneous gravitation field can be described by an equation, one form of which is

$$(2 + \beta Z) = \frac{\mathrm{d}\theta}{\mathrm{dS}} + \frac{\sin\theta}{X},\tag{1}$$

where Z, S, X,  $\theta$  are dimensionless coordinates defined as

$$Z = \frac{z}{b}$$
,  $X = \frac{x}{b}$ ,  $S = \frac{s}{b}$ ,  $\cos \theta = \frac{dX}{dS}$ ,  $\sin \theta = \frac{dZ}{dS}$ , (2)

and  $\beta$  is defined by the equation

$$\beta = \frac{g \, \Delta \rho \, b^2}{\gamma} \,, \tag{3}$$

where b is the radius of curvature at the drop apex, z the axial coordinate of the described point to the drop apex, x the distance of the point from the axis of drop, s the arc length to the point from the drop apex,  $\Delta \rho$  the difference of densities of both phases, g the gravitational acceleration and  $\gamma$  the surface tension.

Determination of  $\beta$  or of some related parameter makes it possible to express the surface or interfacial tension.

The methods of determining this parameter range from the most commonly used method of selected plane which uses only two parameters of drop to the most precise and the most reliable direct fitting of parameters using many points of the profile [5,6].

The method of selected plane is the simplest and the most frequently used way of evaluating the pendant drop. This method requires neither expensive programs nor lengthy software development and the calculation is simple and fast.

The equatorial diameter  $d_e$  of the drop and the diameter  $d_s$  in the plane perpendicular to the axis of symmetry and located at the distance  $d_e$  from the apex are determined [1]. The ratio  $d_s/d_e$  is denoted as S.

The parameter H, which can be used for evaluation instead of  $\beta$ , is defined as follows:

$$H = \frac{\Delta \rho \, g \, d_{\rm e}^2}{\gamma} \,. \tag{4}$$

The tables for conversion of S to H or 1/H are obtained by integration of Eq. (1) for respective values of  $\beta$ . The tables of 1/H calculated by Fordham [7] and Stauffer [8] are listed in reviews [2,3]. The main disadvantage of the method is the possibility of obtaining wrong results without warning when the treatment is applied to drops not conforming to Eq. (1).

The method of several selected planes offers a higher degree of verification of the results than the basic method of single selected plane and its use is not substantially more complicated.

The diameters  $d_k$  in planes at the distance  $k d_e$  from the drop apex are evaluated. The values 1/H are determined from the respective factors  $S_k = d_k/d_e$ . All H values should be the same; if not, the shape of drop is not in hydrodynamical equilibrium or other forces not taken into account in Eq. (1) are effective. In such a case, the determined surface tension is probably not correct [9].

More selected planes were used e.g. by Roe [9], Wu [10] and Nakajima [11] for five values of k from 0.8 to 1.2, Ramakrishnan et al. [12] used k from 0.75 to 1.5. Roe published the tables [13] for transformation  $S_k$  to 1/H; his cited paper [9] involves one of the tables. A large extent and difficult accessibility of the data may be one of the reasons for rare use of the method.

For convenience, the extensive tables resulting from the integration can be replaced by equations approximating the dependence of 1/H on S. The simplest of them are of the type

$$\frac{1}{H} = k_{\rm e} S^{-k_{\rm m}} \,, \tag{5}$$

where all k are empirical constants. The more precise equations are similar to

$$\frac{1}{H} = k_{\rm e} S^{-k_{\rm m}} + k_3 S^3 + k_2 S^2 + k_1 S + k_0. \tag{6}$$

The equation of type (6) was presented by Misak [14]. He divided the range of S into 5 intervals. For each of them he determined  $k_e$  and  $k_m$  from Eq. (5) and the coefficients  $k_0, \ldots k_3$  from Eq. (6). Similarly, Girault et al. [15] and Hansen et al. [16] found equations for expression of  $\beta$  in terms of S and  $d_e/b$  in terms of  $\beta$ .

## 2 The calculation of tables 1/H vs. S for more selected planes and their expression by equation

The calculation of quantity H from factors  $S_k$  for more selected planes using equations similar to those published [14] for the main selected plane (k = 1) offers an instrument for an easy refinement of computation.

By integration of the Bashforth-Adams equation (1), the parameters 1/H,  $d_e/b$  and all  $d_k/b$  were determined for the set of values  $\beta$  differing by 0.0005. The presented data were calculated using the 4th order Runge-Kutta method with the integration step 0.00025. The integration was stopped on reaching the neck (the minimum of section) of the drop or the last selected plane. The greatest difference from Stauffer's [8] profiles is found for small  $\beta$  and for the part of profile near apex.

It has been found that Eq. (6) is not able to express the results for other planes with a sufficient precision. Using the equation

$$\ln\left(\frac{1}{H}\right) = k_{\rm ex} \left(\ln S\right)^2 + k_{\rm ep} \ln S + \ln k_{\rm e} \tag{7}$$

as an initial approximation instead of Eq. (5), the equation

$$\frac{1}{H} = k_e S^{k_{ex} \ln S + k_{ep}} + k_3 S^3 + k_2 S^2 + k_1 S + k_0$$
 (8)

is obtained instead of Eq. (6). Equation (8) seems to offer the most satisfactory results of the tested variants. The fitting was analogous to that described by Misak [14] for his equations. The values of coefficients are given in Tables 1-5. The range of intervals was selected so that the maximum relative difference of 1/H does not exceed  $10^{-4}$ . Sometimes, this difference was greater in marginal intervals.

The maximum differences of the interpolation function Eq. (8) from the original 1/H obtained by integration are summarized in Table 6. They occur usually on the borders of subranges and belong to the intervals closer to 0.9-0.95 (i.e. at the end of the interval more distant from these values).

### 3 Comparison with data of other authors

For the main selected plane, the data of both Fordham [7] and Stauffer [8] are available for S = 0.66. Their comparison with our computed values and with values obtained by Eq. (8) using coefficients from Tables 1-5 is given in Table 7.

Table 1. Coefficients of Eq. (8) for So.s.

Interval S	$k_{\rm e}$	kex	Kep	k <sub>3</sub>	$k_2$	$k_1$	<b>1</b> 40
0.82 - 0.83	1791452.8	533.85850	170.55837	-81676.15812	202187.89690	-166836.27680	45888.22973
0.83 - 0.84	189.07578	272.52455	72.730022	-19963.60152	50019.79936	-41775.38186	11629.85610
0.84 - 0.85	7.1549709	165.45945	35.285687	-6944.66848	17609.43832	-14883.84379	4193.34232
0.85 - 0.87	1.1496269	95.066407	12.600013	-2158.91585	5571.60176	-4792.82331	1374.26272
0.87 - 0.895	0.47873040	50.357240	0.089787883	-567.76534	1503.51828	-1327.11835	390.45562
0.895 - 0.93	0.35255000	25.498893	-5.4176608	-165.99710	454.58851	-414.93772	126.23908
0.93-0.97	0.32002037	6.8474560	-8.0901766	-102.84970	293.25377	-278.69176	88.27639
0.97 - 0.99	0.30845061	-32.343947	-10.455428	-475.69091	1398.86173	-1371.17931	448.00538
0.99-0.999	0.30110729	-333.50440	-15.711260	-11334.69334	33822.93507	-33642.61426	11154.37157

Table 2. Coefficients of Eq. (8) for So.9.

ke kex kep k3 k2 k1   58249804 119.64583 89.483167 -28072.11478 53918.28040 -34519.94034 7   5100.2910 70.920100 46.811007 -9051.10879 17726.62108 -11572.21470 2   19.518159 38.509198 19.951285 -2338.00251 4719.64936 -3175.58038 -3175.58038   1.3823760 20.055606 5.9746092 -522.67397 1102.26575 -774.75596   0.49074291 10.484929 -0.31885445 -111.99730 250.54286 -186.78287   0.34607161 5.4063548 -2.9788620 -24.21100 58.53312 -47.15244   0.31342828 2.1140055 -4.1151543 -9.16969 24.37544 -21.58758   0.30397966 -3.6334200 -4.9395699 -29.80626 85.43510 -81.61766	_	_								
ke kex kep k3 k2   58249804 119.64583 89.483167 -28072.11478 53918.28040 -3   5100.2910 70.920100 46.811007 -9051.10879 17726.62108 -1   19.518159 38.509198 19.951285 -2338.00251 4719.64936 -1   1.3823760 20.055606 5.9746092 -522.67397 1102.26575 -1   0.49074291 10.484929 -0.31885445 -111.99730 250.54286 -2   0.34607161 5.4063548 -2.9788620 -24.21100 58.53312 -2   0.31342828 2.1140055 -4.1151543 -9.16969 24.37544 -2   0.30397966 -3.6334200 -4.9395699 -29.80626 85.43510 -2.6153160	k <sub>0</sub>	7366.77050	2518.10214	712.17229	181.49582	46.40581	12.65668	6.36954	25.98669	419.56923
ke kex kep k3   58249804 119.64583 89.483167 -28072.11478 5   5100.2910 70.920100 46.811007 -9051.10879 1   19.518159 38.509198 19.951285 -2338.00251   1.3823760 20.055606 5.9746092 -522.67397   0.49074291 10.484929 -0.31885445 -111.99730   0.34607161 5.4063548 -2.9788620 -24.21100   0.31342828 2.1140055 -4.1151543 -9.16969   0.30397966 -3.6334200 -4.9395699 -29.80626	k <sub>1</sub>	-34519.94034	-11572.21470	-3175.58038	-774.75596	-186.78287	-47.15244	-21.58758	-81.61766	-1273.10762
ke kex kep   58249804 119.64583 89.483167   5100.2910 70.920100 46.811007   19.518159 38.509198 19.951285   1.3823760 20.055606 5.9746092   0.49074291 10.484929 -0.31885445   0.34607161 5.4063548 -2.9788620   0.31342828 2.1140055 -4.1151543   0.30397966 -3.6334200 -4.9395699	<sup>2</sup> 4	rc.		4719.64936	1102.26575	250.54286	58.53312	24.37544	85.43510	1287.65238
ke kex   58249804 119.64583   5100.2910 70.920100   19.518159 38.509198   1.3823760 20.055606   0.49074291 10.484929   0.34607161 5.4063548   0.31342828 2.1140055   0.30397966 -3.6334200	k <sub>3</sub>	-28072.11478	-9051.10879	-2338.00251	-522.67397	-111.99730	-24.21100	-9.16969	-29.80626	-434.11439
58249804 5100.2910 19.518159 1.3823760 0.49074291 0.34607161 0.31342828 0.30397966 –	kep	89.483167	46.811007	19.951285	5.9746092	-0.31885445	-2.9788620	-4.1151543	-4.9395699	-6.1531194
	¥ex .	119.64583	70.920100	38.509198	20.055606	10.484929	5.4063548	2.1140055	-3.6334200	-34.095653
Interval S 0.635-0.645 0.645-0.66 0.66-0.685 0.685-0.72 0.72-0.77 0.77-0.84 0.84-0.93	ke	58249804	5100.2910	19.518159	1.3823760	0.49074291	0.34607161	0.31342828	0.30397966	0.30007321
	Interval S	0.635 - 0.645	0.645 - 0.66	0.66 - 0.685	0.685 - 0.72	0.72 - 0.77	0.77 - 0.84	0.84 - 0.93	0.93 - 0.98	0.98-0.997

Table 3. Coefficients of Eq. (8) for Sig.

		TOTAL O.	table of Comments of Eq. (c) for 21.0.	0.10 tot (a) .P.d			
Interval $S$	ke	kex	kep	k3	<b>k</b> 2	k <sub>1</sub>	ko
0.17-0.31	0.31081678	-0.086278355	-2.7023254	-13.95071	10.30398	-2.49619	0.19805
0.30 - 0.45	0.30636442	-0.094871613	-2.7246428	0.38766	-0.44128	0.16613	-0.02068
0.45 - 0.68	0.31156188	-0.063734909	-2.6789763	0.41537	-0.71168	0.40321	-0.07551
0.68 - 0.90	0.31195754	-0.092720991	-2.6863859	-0.44813	1.06637	-0.84260	0.22106
0.90 - 0.983	0.30712046	-1.5619311	-2.9809169	-5.74538	16.23781	-15.29128	4.79808

Table 4. Coefficients of Eq. (8) for S<sub>1.1</sub>.

Interval S	ke	Kex	day	k <sub>3</sub>	k2	k <sub>1</sub>	k <sub>0</sub>
0.06-0.08	1.6030433	0.043380701	-0.15208454	-1341.32950	282.27311	-19.71010	0.45664
0.08 - 0.13	0.85491410	-0.056761738	-0.65372414	-160.97221	50.59168	-5.23625	0.17842
0.13 - 0.20	0.57401485	-0.15265815	-1.0443069	-42.79943	21.22139	-3.47357	0.18765
0.20 - 0.30	0.41622542	-0.27871823	-1.4464670	-14.08741	10.58863	-2.63159	0.21621
0.30 - 0.44	0.33587066	-0.42674255	-1.8022482	-3.22540	3.58964	-1.32194	0.16106
0.44 - 0.75	0.31504207	-0.51197565	-1.9499037	0.07609	-0.13681	0.08090	-0.01572
0.75 - 0.953	0.31658938	-0.49808609	-1.9290368	-0.24018	0.61450	-0.52258	0.14771

Table 5. Coefficients of Eq. (8) for  $S_{1.2}$ .

Interval $S$	ke.	kex	kep	<b>k</b> 3	<b>k</b> 2	$k_1$	, ko
0.10-0.12	103.56308	1.2019976	4.4869062	-6625.95443	2292.46751	-264.28560	10.15218
0.12 - 0.14	2.1585254	0.34129627	0.83653215	-742.15388	289.52312	-37.59979	1.62555
0.14 - 0.19	0.65654048	0.031877859	-0.37693028	-66.92134	33.18430	- 5.45788	0.29773
0.19-0.27	0.45076908	-0.10378254	-0.82836350	-10.66154	7.36263	-1.68453	0.12768
0.27 - 0.40	0.37085833	-0.21965481	-1.1287016	-2.87493	2.88810	-0.95966	0.10546
0.40 - 0.55	0.33605594	-0.33317467	-1.3397591	-0.70394	1.00402	-0.47492	0.07450
0.55 - 0.902	0.32790337	-0.39597877	-1.4180887	0.00490	-0.01070	0.00769	-0.00182

Table 6. Maximum differences of interpolating function (8) from the original data.

Plane	Absolute o	lifference	Relative d	ifference
1 Iulic	value	for $S_k$	value	for $S_k$
0.8	0.00016	0.999	0.0005	0.999
0.8ª)	-0.00017	0.85	-0.00009	0.85
0.9	-0.0004	0.66	-0.0001	0.66
1.0	-0.0019	0.17	0.00006	0.45
1.1	-0.00026	0.08	-0.0001	0.30
1.2	-0.00012	0.14	-0.00008	0.14

 $<sup>^{\</sup>text{a}}$ ) 0.83 < S < 0.99

Table 7. Comparison of data for the main selected plane and S=0.66 with other authors.

Author	1/ <i>H</i>
Fordham [7]	0.93828
Stauffer [8]	0.93803
This work original	0.938026
I his work Eq.(8)	0.938018

Table 8. Comparison of data (1/H) for the plane with subscript 1.2 with data of Roe [9].

Author			$S_{1.5}$	2		
	0.75	0.80	0.85	0.9	0.95	0.99
Roe [9]	0.47719	0.44117	0.40859	0.37909	0.35228	0.33249
$ \begin{array}{c} \textbf{This work} \left\{ \begin{array}{l} \textbf{computed} \\ \textbf{interpolated} \end{array} \right. \end{aligned} $		0.441164 0.441167			beyond	the neck

Table 8 gives the comparison of our data with data of Roe [9] for the selected plane with index 1.2.

The tables show an agreement in at least 4 digits with the values of Stauffer and Roe; this difference is lower than the difference between data of Fordham and Stauffer. Since the 4 decimal places accuracy is considered as fully sufficient for common surface tension measurements [9], it can be stated that both the own 1/H integrated values and the interpolated values are sufficiently consistent with already published data of other authors.

### 4 Conclusion

The interpolating equations expressing 1/H by means of the shape ratio  $S_k$  for 5 selected planes with an accuracy of at least 4 decimal places were found. The values are consistent with the tables of Stauffer and Roe. These equations enable a convenient use of several selected planes in the pendant drop method of boundary tension measurements; the use of more planes enables one to prevent the evaluation of the drop not conforming to the Bashforth-Adams equation (to a theoretical model) and its advantages and disadvantages were already analyzed by other authors [9].

#### References

- [1] Andreas J.M., Hauser E.A., and Tucker W.R.: J. Phys. Chem. 42 (1938) 1001.
- [2] Padday J.F.: in Surface and Colloid Science (Ed. Matijević E.), Wiley-Interscience, New York, 1969, Vol. 1, p. 103.
- [3] Ambwani D.S. and Fort T.: in Surface and Colloid Science (Eds. Good R.J. and Stromberg R.R.), Wiley, New York, 1979, Vol. 11, p. 93.
- [4] Hartland S. and Hartley R.W.: Axisymmetric fluid-liquid interfaces. Elsevier, Amsterdam, 1976.
- [5] Rotenberg Y., Boruvka L., and Neumann A.W.: J. Colloid Interface Sci. 93 (1983) 169.
- [6] Anastasiadis S.H., Chen J.K., Koberstein J.T., Siegel A.F., Sohn J.E., and Emerson J.A.: J. Colloid Interface Sci. 119 (1987) 55.
- [7] Fordham S.: Proc. R. Soc. A (London) Ser. A 194 (1948) 1.
- [8] Stauffer C.E.: J. Phys. Chem. 69 (1965) 1933.
- [9] Roe R.J., Bachetta V.L., and Wong P.M.G.: J. Phys. Chem. 71 (1967) 4190.
- [10] Wu S.: J. Colloid Interface Sci. 31 (1969) 153.
- [11] Nakajima A. and Murakami M.: Polymer 3 (1972) 640.
- [12] Ramakrishnan S., Princz J.F., and Hartland S.: Indian J. Pure Appl. Phys. 15 (1977) 228.
- [13] Roe R.J.: Document No 9668, Congress Library of USA (Complete tables).
- [14] Misak M.D.: J. Colloid Interface Sci. 27 (1968) 141.
- [15] Girault H.H., Schiffrin D.J., and Smith B.D.V.: J. Electroanal. Chem. 137 (1982) 207.
- [16] Hansen F.K. and Rødsrud G.: J. Colloid Interface Sci. 141 (1991) 1.