Practical Method for Estimating Surface Tensions of Solutions

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Introduction

The surface tension of solutions has a great effect on the efficiency of gas-liquid contact in unit operations such as distillation, absorption and extraction, so it is desired to establish a simple and practical method for calculating the surface tension of solutions. Recently, Meissner and Michaels[1] presented a method of calculating surface tension of mixtures of organic liquids, which is based on the additivity of Sugden's parachor, but this method is not available for solutions composed of organic solute and a highly polar solvent such as water.

Prigogine and Marechal[2] and one of the present authors[3] developed independently a statistical mechanical theory of the surface tension of a solution of rod-like molecules and derived a relationship between the concentration of the solute in the surface layer and that in the bulk phase. Although the statistical mechanical method gives the most rigorous approach to the present problem, the expression for the surface tension obtained by this method takes a somewhat complicated form which is undesirable for practical purposes.

In this paper, we propose a simple semi-empirical method for calculating the surface tension of solutions, and this method is based on the assumption of the additivity of the parachor in the *surface layer*, not in the *bulk*, and is available for the solutions composed of liquids differing widely in polarity.

Additivity of Sugden's Parachor

Sugden's parachor, (P), can be practically written as follows:

$$(P)=V\cdot\gamma^{1/4}, \tag{1}$$

where V is the molecular volume and γ is the surface tension of liquids. The parachor is independent of temperature and shows an additivity with respect to atoms or atomic groups constituting the molecule, in spite of a wide variety of intramolecular or intermolecular forces; the strength of the intermolecular force decreases, in general, with increasing temperature or with decreasing density, even in the same liquid. These facts suggest that the parachor will practically depend only on the atomic or molecular composition of the system. We may, therefore, write the parachor, (P), of the mixture of liquids A and B in the following form:

$$(P)=V\cdot\gamma^{1/4}=(1-x_b)(P)_A+x_b(P)_B, \tag{2}$$

with

$$(P)_A=V_A\cdot\gamma_A{}^{1/4} \text{ and } (P)_B=V_B\cdot\gamma_B{}^{1/4}. \tag{3}$$

Here $(P)_A$ and $(P)_B$ are the parachors, V_A and V_B the molecular volumes, and γ_A and γ_B the surface tensions of liquids A and B, respectively. x_b is the molar fraction of B in the bulk phase, and V is the mean molecular volume of the mixture. These relationships are essentially equivalent to those of Hammick and Andrew,[4] and of Meissner and Michaels.[1]

However in the case of the solutions showing an appreciable effect of adsorption such as aqueous solutions of organic substances, it seems to be more reasonable to assume the additivity of the parachor in the surface, for the parachor is essentially a quantity concerning the surface. The defect of M.-M. 's method mentioned already originates in the neglect of the effect of adsorption of the solute molecules on the surface, as has been pointed out by M. and M. themselves.[5]

According to the assumption mentioned above we obtain at once

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[1] H.P. Meissner and A.S. Michaels, *Ind. Eng. Chem.*, **41**, 2782 (1949).

[2] I. Prigogine and J. Marechal, *J. Colloid Sci.*, **7**, 122 (1952).

[3] M. Kurata, *Busseiron Kenkyu Researches on Chem. Phys.*), No. **56**, **60** (1952), (in Japanese). This paper will be published in English in near future.

[4] D.L. Hammick and L.W. Andrew, *J. Chem. Soc.*, (London) 1929, 754.

[5] M.-M. proposed another empirical method for calculating the surface tension of aqueous solutions, but it is not adequate for practical purposes.

$$V_s \cdot \gamma^{1/4} = (1-x_s)(P)_A + x_s(P)_B, \qquad (4)$$

instead of Eq. (2). Here V_s is the mean molecular volume and x_s the molar fraction of B, both in the surface layer. If the volume change on mixing is ignored, we can put

$$V_s = (1-x_s)V_A + x_s \cdot V_B. \qquad (5)$$

Combining Eq. (4) with Eq. (5), and using the volume fraction of B-molecule in the surface, v_s, we obtain

$$\gamma = \{(1-v_s)\gamma_A{}^{1/4} + v_s \cdot \gamma_B{}^{1/4}\}^4. \qquad (6)$$

This equation enables us to calculate the surface tension of the mixture in terms of the bulk concentration, x_b, provided that the relation of v_s to x_b is known.

Method for Calculating the Concentration of Solute in the Surface of a Solution

For the solutions of rod-like molecule B consisting of P segments, Prigogine[2] and one of the authors[3] derived statistically the following relation between the volume fraction of the solute molecule B in the bulk, v_b, and that in surface, v_s; i.e.

$$\{(1-v_b)^P \cdot v_s\}/\{(1-v_s)^P \cdot v_b\} = \exp\{P(\gamma_A - \gamma_B)/NkT\} \qquad (7)$$

where N is the number of lattice points, or the number of the solvent molecule A, per unit area, k is the Boltzmann constant and T is the absolute temperature.

This relation can also be derived by considering a kind of chemical equilibrium between two states of the molecular arrangements; one of which is composed of P solvent molecules located in the surface layer and a solute molecule located in the bulk, and the other of which is composed of P solvent molecules in the bulk and a solute molecule in the surface, i.e.

$$P \cdot \mathrm{A}_{\text{surface}} + \mathrm{B}_{\text{bulk}} \rightleftarrows P \cdot \mathrm{A}_{\text{bulk}} + \mathrm{B}_{\text{surface}}. \qquad (8)$$

The surface tension is the increase of the free energy per unit area due to shifting molecules from the bulk phase to the surface layer; then, γ_A/N or γ_B/N represents this increase of the free energy per molecule A or segment of B. As a molecule of B has P segments, $P(\gamma_B - \gamma_A)/N$ represents the increase of the free energy with the change in Eq. (8), from left to right, and we have for the equilibrium condition Eq. (7), which enables us to estimate the surface composition of the solution v_s in terms of v_b.[6]

Comparison with Experimental Data

If we denote by n_A and n_B the numbers of molecules per unit area of liquids A and B, respectively, the number of lattice points N is given by

$$N = n_A = Pn_B \qquad (9)$$

according to the definition. Using this relation, we can write Eq. (7) as follows:

$$\log_{10}\left(\frac{1-v_s}{v_s}\right) + (P-1)\cdot\log_{10}(1-v_s)$$
$$= \log_{10}\left(\frac{1-v_b}{v_b}\right) + (P-1)\cdot\log_{10}(1-v_b) + Q$$

with (10a)

$$Q \equiv \frac{P}{2.303\,kT}\left(\frac{\gamma_B}{Pn_B} - \frac{\gamma_A}{n_A}\right). \qquad (10b)$$

In the estimation of Q, we adopt for n_A and n_B the values

$$n_A = (N/V_A)^{2/3} \text{ and } n_B = (N/V_B)^{2/3} \qquad (11)$$

where N is the Avogadro number. For the value of P the following assumptions were made:

1) Aqueous solutions of fatty acids and alcohols,

P=Carbon Number. (12a)

2) Aqueous solutions of ketones,[7]

P=(Carbon Number)−1. (12b)

3) Aqueous solutions of halogen derivatives of fatty acids, e.g. homologue of monochloro acetic acid,

$$P = \begin{pmatrix}\text{Carbon}\\ \text{Number}\end{pmatrix} \cdot \left\{\frac{\text{Mol. Vol. of the Substance}}{\text{Mol. Vol. of the Corresponding Fatty Acid}}\right\}. \qquad (12c)$$

4) Solutions composed of organic solute

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6) We assume in this paper that B molecules orientate parallel to the surface (the parallel type), then all of P segments of an adsorbed B molecule occupy the lattice points located in the surface layer. On the other hand, if B molecules do not orientate parallel to the surface (the vertical type), only one end-segment of an adsorbed B molecule occupies the lattice point located in the surface layer, and we obtain

$$\{(1-v_b)\cdot v_s\}/\{(1-v_s)\cdot v_b\} = \exp\{(\gamma_A - \gamma_B)/NkT\} \qquad (7')$$

instead of Eq. (7). When $(\gamma_A - \gamma_B)$ is so large in comparison with NkT that v_s becomes much larger than v_b and the adsorption of B molecules contributes an appreciable effect on surface tension, we can safely ignore the adsorption of the vertical type in comparison with that of the parallel type at high dilutions. At high concentrations, both of the Eqs. (7) and (7′) reduce to a common expression,

$$(1-v_b)/(1-v_s) = \exp\{(\gamma_A - \gamma_B)/NkT\} \qquad (7'')$$

so we can again ignore the effect of the vertical type adsorption.

7) Cf. Ref. (1), p. 2787. M.-M. have pointed out that the ketones tend to affect the surface tension in a manner characteristic of the acid or alchol containing one less carbon atoms.

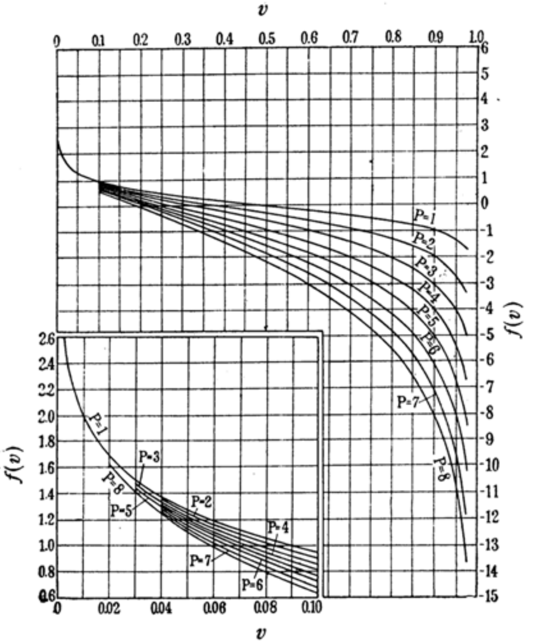
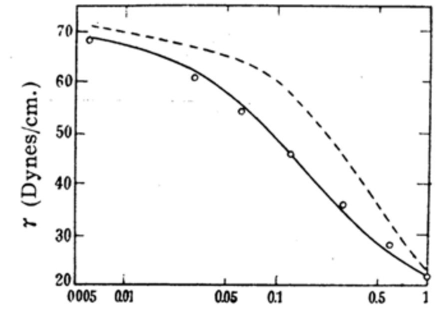


Fig. 1. Curves of $f(v)=\log_{10}(1\text{-}v)/v+(P\text{-}1)\times\log_{10}(1\text{-}v)$ vs. v for some value of P.



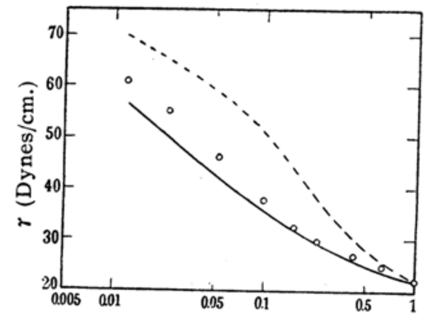
Mole fraction CH_3OH

Fig. 2. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3OH at 30°C.

○ γ_{obs},

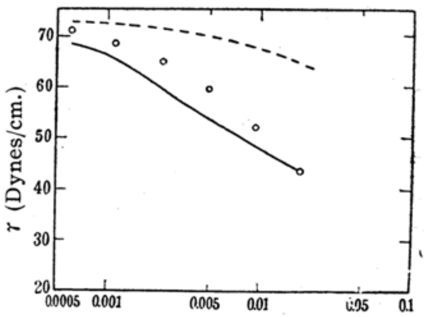
—— γ_{calc} (Present method),

- - - γ_{calc} (M.-M. method).



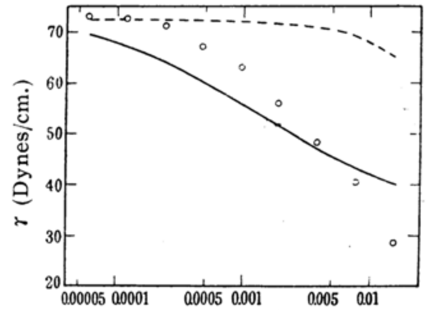
Mole fraction C_2H_5OH

Fig. 3. Comparison between γ_{calc} and γ_{obs} of aqueous solution of C_2H_5OH at 25°C.



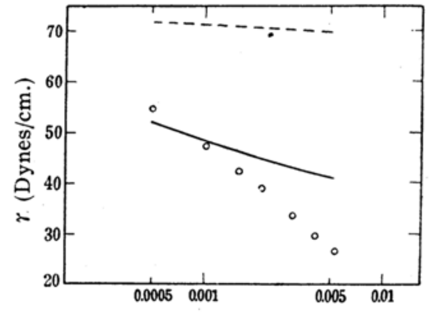
Mole fraction $n\text{-}C_3H_7OH$

Fig. 4. Comparison between γ_{calc} and γ_{obs} of aqueous solution of $n\text{-}C_3H_7OH$ at 15°C.



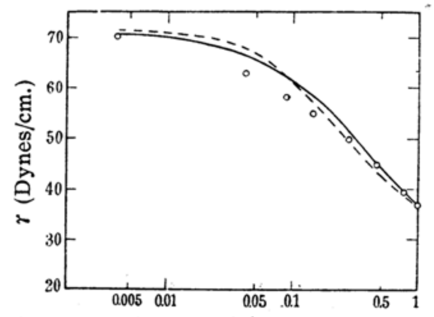
Mole fraction $n\text{-}C_4H_9OH$

Fig. 5. Comparison between γ_{calc} and γ_{obs} of aqueous solution of $n\text{-}C_4H_9OH$ at 15°C.



Mole fraction $iso\text{-}C_5H_{11}OH$

Fig. 6. Comparison between γ_{calc} and γ_{obs} of aqueous solution of $iso\text{-}C_5H_{11}OH$ at 30°C.



Mole fraction HCOOH

Fig. 7. Comparison between γ_{calc} and γ_{obs} of aqueous solution of HCOOH at 30°C.

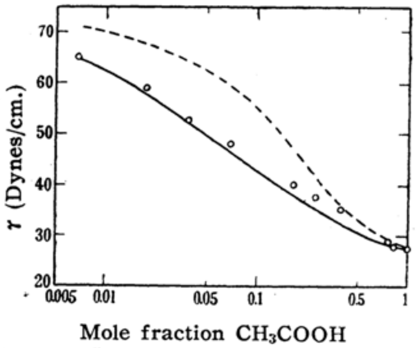


Fig. 8. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3COOH at 25°C.

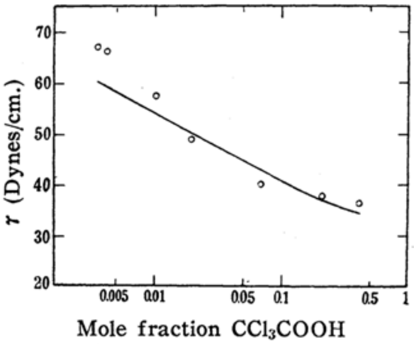


Fig. 9. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CCl_3COOH at 25°C.

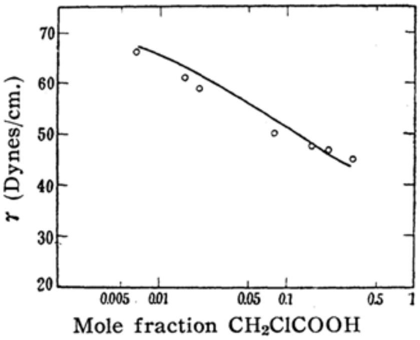


Fig. 10. Comparison between γ_{calc} and γ_{obs} of aqueous solution of $CH_2ClCOOH$ at 25°C.

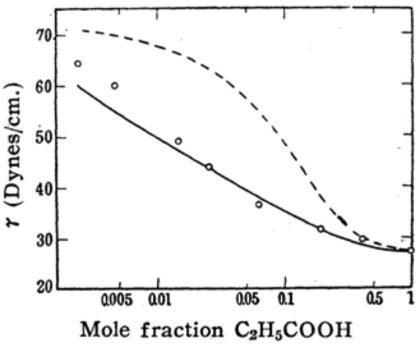


Fig. 11. Comparison between γ_{calc} and γ_{obs} of aqueous solution of C_2H_5COOH at 25°C.

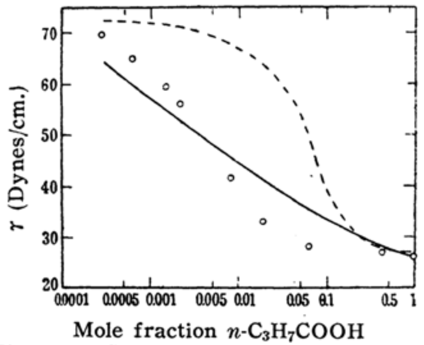


Fig. 12. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_3H_7COOH at 25°C.

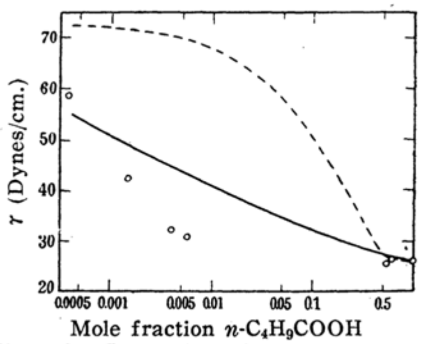


Fig. 13. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_4H_9COOH at 25°C.

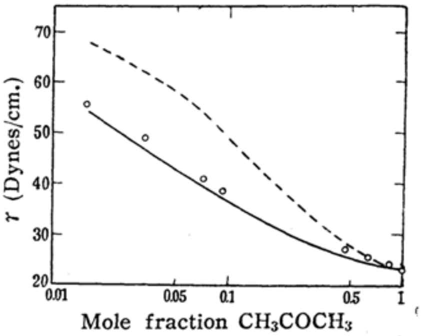


Fig. 14. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3COCH_3 at 25°C.

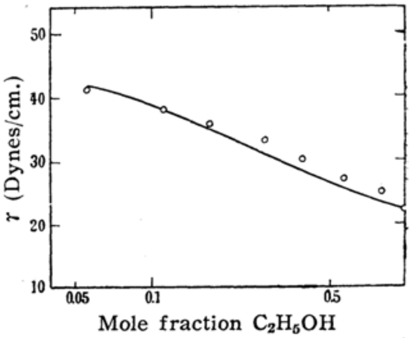


Fig. 15. Comparison between γ_{calc} and γ_{obs} of ethylene glycol solution of C_2H_5OH at 20°C.

and organic polar solvent,[8,9]

$$P = \text{(Mol. Vol. of Solute)}/\text{(Mol. Vol. of Solvent)} \quad (12d)$$

The values of Q thus obtained are listed in Table I.

Fig. 1 shows the curves of $f(v)[\equiv \log_{10}\{(1-v)/v\} + (P-1)\cdot\log_{10}(1-v)]$ vers. v for some values of P. Using this figure, we can easily solve Eq. (10a) graphically. For example, in the case of aqueous solution of CH_3OH at 30°C, $P=1$ and $Q=-0.338$ are obtained from Eqs. (12a) and (10b). If $v_b=0.241$, we get $f(0.241)=0.500$, $f(v_s)=f(0.241)+Q=0.162$, and then $v_s=0.406$ from Fig. 1. The substitution of this value of v_s into Eq. (6) gives us $\gamma=45.9$ dynes/cm, while the observed value of γ is 46.1 dynes/cm. v_s and γ_{calc} of this example are given in Table II with v_b and γ_{obs}.

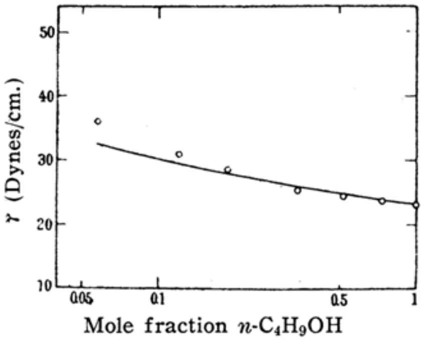


Fig. 16. Comparison between γ_{calc} and γ_{obs} of ethylene glycol solution of n-C_4H_9OH at 20°C.

TABLE I

LIST OF Q OF VARIOUS SYSTEMS

system			
A	B	°C	Q
H_2O	CH_3OH	30	−0.338
H_2O	C_2H_5OH	25	−0.983
H_2O	n–C_3H_7OH	15	−1.662
H_2O	n–C_4H_9OH	20	−2.265
H_2O	i–$C_5H_{11}OH$	30	−2.801
H_2O	$HCOOH$	30	−0.111
H_2O	CH_3COOH	25	−0.857
H_2O	CCl_3COOH	25	−1.497
H_2O	$CHCl_2COOH$	25	−1.054
H_2O	$CH_2ClCOOH$	25	−0.758
H_2O	C_2H_5COOH	25	−1.532
H_2O	n–C_3H_7COOH	25	−2.157
H_2O	n–C_4H_9COOH	25	−2.801
H_2O	CH_3COCH_3	25	−0.868
CH_2OH $\vert$ CH_2OH	C_2H_5OH	20	−0.549
CH_2OH $\vert$ CH_2OH	n–C_4H_9OH	20	−1.396

TABLE II

COMPARISON BETWEEN γ_{calc} AND γ_{obs} OF AQUEOUS SOLUTION OF CH_3OH AT 30°C.

v_b	v_s	γ_{calc} (Dynes/cm.)	γ_{obs} (Dynes/cm.)
0.013	0.028	69.2	68.4
0.063	0.126	62.4	61.0
0.124	0.232	55.7	54.6
0.241	0.406	45.9	46.1
0.460	0.651	34.3	36.1
0.749	0.865	26.1	28.2

The values of γ obtained by the present method, Eq. (6) with Eqs. (10) and (11), are shown in Figures 2 to 16 by solid lines,[10] where the observed values[11,12,13] are plotted by circles and also the calculated values of M.—M. are given by dotted lines for the sake of comparison. Although the agreement of the solid lines with observed data is not entirely excellent, the present method seems to be adequate for most practical purposes, if we take into consideration that the surface tention of the solution given here decreases extremely rapidly with increasing concentration of the solute. In the present method, the values necessary to calculate the surface tension are only four quantities, γ_A, γ_B, V_A and V_B.[14] γ_A and γ_B can be easily calculated, with good accuracy, by using the additivity of the atomic parachor; therefore we can use the present method even when the observed values of these two quantities are absent. This will be one of the merits of our method.

In the case of the mixtures of organic liquids, the difference between γ_A and γ_B are commonly small so that the effect of adsorption can be safely ignored, and then Eq. (2) or the method of M.—M. can be used with sufficient accuracy.

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8) For the sake of convenience we use

$$P = \text{(Carbon Number of Solute)}/\text{(Carbon Number of Solvent)} \quad (12d')$$

instead of Eq. (12d) in the calculations given below. The difference between two values of P obtained by Eqs. (12d) and (12d′) seems to be not appreciable in the examples adopted in this paper.

9) For mixtures of organic liquids, Meissner and Michaels' method can be used with sufficient accuracy, provided that the difference in the polarity of the liquids is not large.

10) On performing calculation, we ignore the volume change on mixing; i.e.

$$V=(1-x_b)V_A+x_bV_B.$$

11) "International Critical Tables", Vol. 4, p. 467 (New York, McGraw-Hill Book Co., Inc., 1926).

12) H. Landolt and R. Börnstein, "Physikalisch-chemische Tabellen", 5th ed., (Berlin, J. Springer, 1928).

13) I. Yamakita and H. Aida, private communication.

14) When the pure solute is in solid state at the temperature in question (e.g. in the case of aqueous solution of CCl_3COOH), we can use the extrapolated values of γ_B and V_B from its liquid state.

Conclusion

We have presented a method for estimating the surface tension of the solutions composed of liquids differing widely in polarity, for which Meissner and Michael's method can not be applied, and have obtained good consistency of the calculated values with observed data. The percentage error, $\{(\gamma_{\text{calc}} - \gamma_{\text{obs}})/\gamma_{\text{obs}}\} \times 100$, is within 10% when $P<5$, and within 20% for large P.

In conclusion, the authors are indebted to Dr. I. Yamakita and Mr. H. Aida of Kyoto University for offering some unpublished data of the surface tension, and also to the Ministry of Education of the Japanese Government for a grant-in-aid.

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