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METROLOGICAL ANALYSIS OF DIFFERENT TECHNIQUES FOR MEASURING INTERFACE TENSION BETWEEN TWO FLUIDS BASED ON SPINNING DROP METHOD

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Abstract. *The spinning drop method foundations of measuring interface tension between two immiscible liquids are considered. Different techniques of the spinning drop method and their metrology evaluation are compared. The dimensionless parameters of spinning drop are calculated using the fourth-order Runge–Kutta procedure and they are approximated by the seventh-order polynomial dependence. The relative errors of the different techniques and the approximate dependence are obtained.*

Keywords: interface tension, spinning drop method, metrology, error analysis

METROLOGICZNA ANALIZA RÓŻNYCH TECHNIK POMIARU NAPIĘCIA POWIERZCHNIOWEGO NA GRANICY FAZ POMIĘDZY DWOMA PŁYNAMI NA BAZIE METODY WIRUJĄCEJ KROPLI

Streszczenie. *W artykule rozpatrywane podstawy metody wirującej kropli do pomiaru napięcia powierzchniowego na granicy faz między dwoma nie mieszającymi się cieczami. Porównano różne techniki realizacji tej metody i oceniono ich właściwości metrologiczne. Wykorzystując metodę numeryczną Rungego-Kutty 4 rzędu obliczono bezwymiarowe parametry wirującej kropli i aproksymowano za pomocą wielomianu 7 stopnia. Obliczono błąd względny różnych technik oraz proponowanej przybliżonej zależności.*

Słowa kluczowe: napięcie powierzchniowe, metoda wirującej kropli, metrologia, analiza błędów

Introduction

Interface tension (IT) at the interface of two insoluble liquids is a significant parameter of the technological processes where surface characteristics at the interface are essential. This is especially important in the oil production methods with the help of reservoir pressure maintenance using surfactants (SAA) [3]. It should also be noted that IT can vary in the range of 0.01÷20 mN/m.

Table 1. Tabular data of dependence $V^* = f\left(R/x_0\right)$ [5]

R/X_0	r^*	R/X_0	r^*
1.0	0	0.3198	1.2520
0.9997	0.1	0.3122	1.2530
0.9980	0.2	0.3038	1.2540
0.9932	0.3	0.2945	1.2550
0.9840	0.4	0.2837	1.2560
0.9687	0.5	0.2708	1.2570
0.9459	0.6	1.2543	1.2580
0.9140	0.7	0.2297	1.2590
0.8710	0.8	0.2262	1.2591
0.8148	0.9	0.2225	1.2592
0.7415	1.0	0.2183	1.2593
0.6432	1.1	0.2136	1.2594
0.4928	1.2	0.2081	1.2595
0.3332	1.2500	0.2016	1.2596
0.3268	1.2510	0.1932	1.2597

Measurement of such IT values is usually carried out with the help of the devices that implement the spinning drop method (SD) [5]. The essence of the SD method consists in the following: a horizontally placed glass tube is filled with such a heavier fluid under study as aqueous surfactant solution; after that a drop of such a lighter fluid under investigation as oil is injected into this fluid; then the tube is revolved around its horizontal axis with a certain angular velocity ω. Both the appropriate SD dimensions (for example, its largest diameter, length, and volume) and the density difference of the interfacial fluids are measured depending on the selected techniques for determining IT; the IT values σ [4, 6–8] are calculated with the help of the corresponding dependencies [4, 6–8].

Among such dependencies, regardless of the date when their authors published them, the following are wide spread now B. Vonnegut's dependence [1]:

$$\sigma = \Delta\rho\omega^2 R^3 / 4 \tag{1}$$

where $\Delta\rho = \rho_1 - \rho_2$ – density difference between the heavier and lighter fluids respectively, R – the largest SD radius. H. Princen's dependence [4]:

$$\frac{x_0}{r} = \frac{2}{3}\frac{cr^3+1}{\left(cr^3\right)^{1/3}}, \tag{2}$$

where x_0 – half of the SD length; $r = \sqrt[3]{3V/(4\pi)}$ – sphere radius of the lighter fluid with the volume V that is injected into the tube with the heavier fluid; $c = \Delta\rho\omega^2/(4\sigma)$ – a characteristic parameter that is used to calculate the IT σ on the basis of the H. Princen's dependence. J. Slattery's dependence [6]:

$$\sigma = \left(R/r^*\right)^3 \Delta\rho\omega^2 / 2, \tag{3}$$

where r^* – dimensionless parameter which is determined on the basis of the appropriate J. Slattery's table [6] depending on the ratio R/x_0 (table 1). S. Torza's dependence [7]:

$$\sigma = \pi^{-3/2}\Delta\rho\omega^2\left(V/x_0\right)^{3/2}/4. \tag{4}$$

It should be noted that B. Vonnegut recommends to use dependence (1) provided that $x_0/R > 4$ [3]. H. Princen suggests to utilize dependence (2) on the condition that $x_0/R > 3,645$ [4]. Dependence (3), as J. Slattery [6] notes, has a method error of less than 0.4% provided that $x_0/R > 4$. S. Torza recommends to use dependence (4) for $cr^3 > 100$ [7] that corresponds to relation $x_0/R > 67$.

Taking into account the abovementioned, it is necessary to evaluate the method errors of the suggested techniques to calculate IT σ with the help of the SD method and develop recommendations for their elimination.

1. Theoretical Part

Let us conduct theoretical calculation of the SD geometrical dimensions in order to evaluate method errors of the abovementioned techniques.

Let us consider the horizontal rotating tube, inside of which there is fluid 2 with higher density ρ_2 and a drop of fluid 3 with lesser density ρ_1 (Fig. 1). Let the pressure on the y axis inside the drop (pt. O) be equal to P_{O1} and outside the drop – P_{O2}. At the same time, we neglect the gravitational force, which allows us to suggest that the rotation axes of the tube 1 and drop 3 coincide.

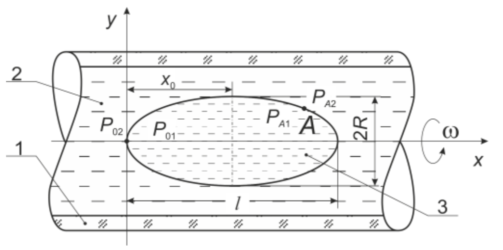

Fig. 1. Rotating tube with investigated heavier and lighter fluids

Then the pressure P_{A1} inside the drop in pt. A is as the following:

$$P_{A1} = P_{O1} + \rho_1 y^2 \omega^2 / 2, \tag{5}$$

where y – distance from pt. A to the x axis.

Correspondingly, the pressure outside the drop in pt. A is as follows:

$$P_{A2} = P_{O2} + \rho_2 y^2 \omega^2 / 2. \tag{6}$$

Hence, the pressure difference along the interface of two fluids in pt. A is as the following:

$$P_{A1} - P_{A2} = P_{O1} - P_{O2} - \Delta\rho y^2 \omega^2 / 2. \tag{7}$$

In case there is gravitational force, the drop rotation axis shifts in relation to the tube rotation axis by the value which is equal to $y^* \approx R^2 \Delta\rho g / (\eta\omega)$ [7], where g – gravitational acceleration, η – dynamic viscosity of the heavier fluid. However, the SD form doesn't change therewith.

On the other hand the pressure difference along the interface in pt. A will be as follows:

$$P_{A1} - P_{A2} = \sigma(1/R_1 + 1/R_2), \tag{8}$$

where R_1 i R_2 – curvature radii of the drop surface in pt. A in the plane of fig. 1 and in the plane that is perpendicular to the plane of Fig. 1 respectively [2].

Besides, the pressure difference ΔP_0 along the interface on the level of the horizontal rotation x axis in pt. O will be as the following [1]:

$$P_{O1} - P_{O2} = \Delta P_0 = 2\sigma / R_0, \tag{9}$$

where R_0 – curvature radius of the SD interface surface in pt. O (Fig. 1).

Then, when we take into account dependencies (8) and (9), dependence (7) will be as the following:

$$\sigma(1/R_1 + 1/R_2) = 2\sigma / R_0 - \Delta\rho y^2 \omega^2 / 2. \tag{10}$$

Equation (10) is a strict equation that describes the SD surface form in relation to σ, $\Delta\rho$ and ω when there is no gravitation.

Since $R_1 = ds / d\varphi$, $R_2 = y / \sin\varphi$, where s – SD profile arc length, φ – angle between the x axis and normal to pt. A on the SD surface [2], (10) will have the following form after corresponding transformations:

$$d\varphi / ds = 2 / R_0 - \omega^2 y^2 \Delta\rho / (2\sigma) - \sin\varphi / y. \tag{11}$$

After introduction of the new variable $a^3 = \sigma / (\Delta\rho\omega^2) = 1/(4c)$ we will see that

$$d\varphi / ds = 2 / R_0 - y^2 / (2a^3) - \sin\varphi / y. \tag{12}$$

Having multiplied both the left and the right parts of (12) by a, we will obtain an equation in a dimensionless form that describes the SD surface:

$$\frac{d\varphi}{d(s/a)} = \frac{2}{R_0/a} - \frac{1}{2}\left(\frac{y}{a}\right)^2 - \frac{\sin\varphi}{y/a}. \tag{13}$$

Other variables, which are included in (13), can be determined with the help of the following dependencies [2]:

$$\frac{d(y/a)}{d(s/a)} = \cos\varphi, \quad \frac{d(V/a^3)}{d(s/a)} = \pi\left(\frac{y}{a}\right)^2 \sin\varphi, \quad \frac{d(x/a)}{d(s/a)} = \sin\varphi. \tag{14}$$

When solving (13) and (14) for different specified values of R_0 / a at the moment when the angle reaches $\varphi = 90°$, we find the corresponding SD geometrical parameters.

The initial boundary conditions are the following:

$$y = x = s = V = \varphi = 0, \;\; 1/R_0 = 1/R_1 = 1/R_2; \tag{15}$$

and the final boundary conditions are as follows:

$$R/a = 4^{1/3}, \;\; R_0/a = 2 \cdot 4^{1/3}/3, \;\; R/R_0 = 3/2. \tag{16}$$

When the final conditions of (16) are reached, there isn't any further increase in the parameters according to (16) and the SD surface becomes strictly cylindrical, i. e. $R_1 = \infty$, $R_2 = R$.

2. Results and Discussion

Some of the results of the SD dimensionless parameters (R/a, a^3/V, x_0/R, l^3/V, R/R_0, R/r, cr^3) calculated using the fourth-order Runge-Kutta method for solving equations (13) and (14) with the account of (15) and (16) for $1{,}0 \le R_0/a \le 2 \cdot 4^{1/3}/3$, $\varphi = 90°$ are provided in table 2, where $l = 2x_0$. It should be noted that the calculation was conducted for 2744 values of the parameter R_0/a with the calculation error of the final values being equal to $2{,}22 \cdot 10^{-16}$.

Table 2 . Results of the SD geometrical parameters calculation

R_0/a	R/a	V/a^3	$l/(2R)$	l^3/V	R/R_0	R/r	cr^3
1,058265	1,585254	83,667883	4,001111	24,398863	1,497974	0,026455	4,993559
1,058267	1,586014	90,016592	4,252025	27,256878	1,498691	0,024601	5,372470
1,058267	1,586504	96,333744	4,502207	30,262971	1,499153	0,022995	5,749497
1,058267	1,586808	102,334273	4,740190	33,268167	1,499439	0,021651	6,107627
1,058267	1,587030	109,126461	5,009843	36,845738	1,499649	0,020306	6,513006
1,058267	1,587143	114,414555	5,219926	39,760317	1,499756	0,019369	6,828616
1,058267	1,587353	138,749310	6,187515	54,629624	1,499954	0,015974	8,280989
1,058267	1,587358	140,300909	6,249233	55,658832	1,499959	0,015797	8,373594
1,058267	1,587373	146,649795	6,501791	59,971459	1,499974	0,015113	8,752515
1,058267	1,587383	152,919518	6,751218	64,390025	1,499983	0,014494	9,126711
1,058267	1,587389	159,141744	6,998768	68,932000	1,499989	0,013927	9,498073
1,058267	1,587393	164,319016	7,204750	72,830305	1,499992	0,013489	9,807069
1,058267	1,587396	172,931969	7,547433	79,555225	1,499996	0,012817	10,321117
1,058267	1,587398	177,396772	7,725076	83,159112	1,499997	0,012494	10,587590
1,058267	1,587399	184,315634	8,000363	88,902753	1,499998	0,012025	11,000529
1,058267	1,587400	190,601190	8,250454	94,288085	1,499999	0,011629	11,375671
1,058267	1,587400	196,981742	8,504326	99,917822	1,499999	0,011252	11,756482
1,058267	1,587400	202,950645	8,741819	105,333027	1,499999	0,010921	12,112724
1,058267	1,587401	210,692803	9,049869	112,571087	1,500000	0,010520	12,574800
1,058267	1,587401	221,870644	9,494620	123,447634	1,500000	0,009990	13,241929

The obtained results of the calculation were used to get approximate dependence $a^3/V = f\left(l^3/V\right)$ of the following type:

$$a^3/V = \sum_{i=0}^{7} C_i \left(l^3/V\right)^i, \tag{17}$$

where $C_0 = 0,03227$; $C_1 = -0,001722$; $C_2 = 5,787 \cdot 10^{-5}$; $C_3 = -1,18 \cdot 10^{-6}$; $C_4 = 1,481 \cdot 10^{-8}$; $C_5 = -1,117 \cdot 10^{-10}$; $C_6 = 4,639 \cdot 10^{-13}$; $C_7 = -8,14 \cdot 10^{-16}$.

Then the IT value σ can be calculated in the following way:

$$\sigma = \Delta\rho\omega^2 V \sum_{i=0}^{7} C_i \left(l^3/V\right)^i. \tag{18}$$

Evaluation of the relative method errors δ_m of B. Vonnegut, H. Princen, S. Torza, and J. Slattery's techniques, as well as of approximate dependence (18), was conducted by comparing the results of the IT σ calculation for each of the mentioned techniques with the results of the IT σ_{table} calculation on the basis of the data in table 2:

$$\sigma_m = \left(\sigma - \sigma_{table}\right)/\sigma_{table}. \tag{19}$$

The results of such error calculation are provided in table 3.

Table 3. Evaluation results of the errors σ_m of different techniques for IT σ calculation with the help of the SD method for $4,0 \le l/2R \le 9,5$

$l/2R$	B. Vonnegut	S. Torza	H. Princen	J. Slattery	Dependence (18)
4,0	-0,00405	-0,239	0,07828	$6,61 \cdot 10^{-6}$	$-6,38 \cdot 10^{-5}$
4,5	-0,00169	-0,213	0,05795	$-2,79 \cdot 10^{-6}$	-0,000277
5,0	-0,000702	-0,192	0,04273	$-3,56 \cdot 10^{-6}$	-0,000382
5,5	-0,000260	-0,173	0,03050	$1,79 \cdot 10^{-6}$	$7,34 \cdot 10^{-5}$
6,0	$-9,12 \cdot 10^{-5}$	-0,156	0,02158	$-1,27 \cdot 10^{-6}$	0,000309
6,5	$-5,28 \cdot 10^{-5}$	-0,149	0,01813	$1,21 \cdot 10^{-6}$	$3,84 \cdot 10^{-6}$
7,0	$-2,24 \cdot 10^{-5}$	-0,139	0,01387	$1,42 \cdot 10^{-6}$	-0,000415
7,5	$-8,05 \cdot 10^{-6}$	-0,129	0,01042	$4.08 \cdot 10^{-6}$	$4,70 \cdot 10^{-5}$
8,0	$-3,94 \cdot 10^{-6}$	-0,122	0,00828	$4.07 \cdot 10^{-6}$	0,000414
8,5	$-1,65 \cdot 10^{-6}$	-0,115	0,00644	$-3,25 \cdot 10^{-6}$	-0,000393
9,0	$-7,09 \cdot 10^{-7}$	-0,108	0,00507	$2,73 \cdot 10^{-6}$	0,000151
9,5	$-2,96 \cdot 10^{-7}$	-0,103	0,00397	$-3,41 \cdot 10^{-6}$	$-2,07 \cdot 10^{-5}$

Thus, it can be seen from table 3 that B. Vonnegut, J. Slattery, and H. Princen's techniques, as well as approximate dependence (18), have a small method error in the indicated range of values $l/2R$. However, when implementing B. Vonnegut and J. Slattery's techniques there is a necessity to measure the largest SD radius $2R$, which is significantly influenced by the optical zoom factor Ì of the tube with the fluids under study that can vary in the range from 1.332 to 1.34 [1]. Calculation of a certain Ì value depends on many factors and it can lead to significant additional errors of the obtained results.

Therefore, it is advisable to use the techniques that do not involve measurement of the largest SD diameter $2R$ (S. Torza and H. Princen's techniques and approximate dependence (18)). However, S. Torza and H. Princen's techniques are characterized by significant method errors.

Therefore, it is recommended to use approximate dependence (18) given that modern means for IT σ measurement are equipped with computer aids. This allows to easily develop the appropriate software that would consider dependence (18).

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