INTERFACIAL TENSION ALONG THE BINODAL CURVE IN THE BENZENE–ETHANOL–WATER AND n-HEXANE–ACETONE–WATER TERNARY SYSTEMS AT 25 °C

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The surface tensions, interfacial tensions and densities of conjugate solutions of compositions lying in the miscibility gap were measured for two ternary systems, viz. benzene–ethanol–water and n-hexane–acetone–water, at 25 °C.

Key words: Interfacial tension; Surface tension; Density; Ternary system.

Interfacial and surface phenomena are of considerable importance in situations involving the transfer of matter across liquid–liquid and liquid–vapour interfaces – in adsorption, diffusion, extraction, catalysis, etc. The effect of surface and interfacial tension on such processes was often neglected, not because it was considered unimportant but because tension data were unavailable. Although interfacial and surface tension data exist in the literature for many two-component liquid–liquid systems, information on three-component systems is scarce and only few papers give interfacial and surface tension data for conjugate phases simultaneously.

In the present paper, interfacial and surface tension values as well as density values are reported for two three-component two-phase systems, viz. benzene–ethanol–water (BEW) and n-hexane–acetone–water (HAW) at 25 °C, with a view to enriching the volume of experimental data in this field of interest.

EXPERIMENTAL

Chemicals

All the chemicals, i.e. benzene and acetone of analytical grade, and n-hexane, n-heptane, and ethanol for UV spectroscopy, were supplied by Lachema Brno, Czech Republic. Prior to measurement, the

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substances were dried on a 4A molecular sieve and rectified on a 60-plate bubble cap column (Jena, Germany). The water content was determined by the Karl Fischer method and was taken into account when calculating the equilibrium phase composition. The normal boiling points, refractive indices at 20 °C and densities at 25 °C of all the substances were measured and compared with published data[1]. Redistilled water was used in all measurements.

Preparation of Solutions

The compositions of the conjugate solutions at the end of the tie lines at 25 °C in the two systems were taken from ref.[2] for BEW and ref.[3] for HAW. All measurements were carried out at 25 ± 0.05 °C in conditions of equilibrium solute distribution between the two phases. The equilibrium condition was established as follows: known amounts of each component in the system were weighed and placed in a flask. The flask was shaken vigorously for a few minutes and the liquid mixture was then stirred using a magnetic stirrer for about 4 h in a constant temperature bath (25 ± 0.05 °C). Subsequently the system was allowed to separate for about 8 h.

Methods of Measurement

Densities of the conjugate phases were measured using a Paar DMA-45 Densimeter at 25 °C (maximum deviation $1 \cdot 10^{-4}$ g cm^{-3}).

The measurements of the interfacial tension between two phases in equilibrium were performed by the capillary rise method[4] and by the drop-volume method. The apparatus used in the latter case has been described previously[5].

A simple but precise capillary tensiometer based on the Czechoslovak patent[6], working on the hanging level principle, was used to determine the surface tension of the organic equilibrium phase. For the equilibrium aqueous phase, the drop-volume method[5] was found to suit better.

All the devices were calibrated by using published data[7] for the benzene–water and n-heptane–water systems for the interfacial tension determination, and the data for water, benzene, toluene, n-hexane, cyclohexane, and methanol were employed in the surface tension measurements.

RESULTS

Phase diagrams for the two systems under study are shown in Figs 1 and 2, respectively. The tie lines chosen for study are numbered in the diagrams; the tie line “0” is located at the base of each diagram (i.e. no ethanol or acetone added). The compositions of the conjugate phases, their densities, surface tensions, and the interfacial tensions between them are presented in Tables I and II.

The plots of the following tensions: interfacial tension σ^{it}, surface tension of the aqueous phase σ^{aq}, and the surface tension of organic phase σ^{org}, denoted generally σ^{k}, against the mole fraction of the solute (ethanol in the case of the BEW system, acetone in case of the HAW system) as given by the compositions at the ends of the tie lines through the points representing the total systems are shown in Figs 3 and 4, respectively. All the plots are smooth curves. The results obtained in this work are compared with those already published. The agreement between the interfacial tensions in the BEW system is very good, whereas the agreement with the HAW data reported in ref.[8]

is rather poor. The values by Murphy et al.[9] are not included in Fig. 4 because the composition of the conjugate phases is not given in the original paper.

Correlation of Surface and Interfacial Tensions

Various methods of plotting the surface and interfacial tensions were applied in attempts to achieve a linear relation, but none of them was fully successful over the entire concentration range.

Surface tension was correlated with the mole fraction of solute (i.e. ethanol or acetone) along a line drawn from the apex of the three-component diagram through the

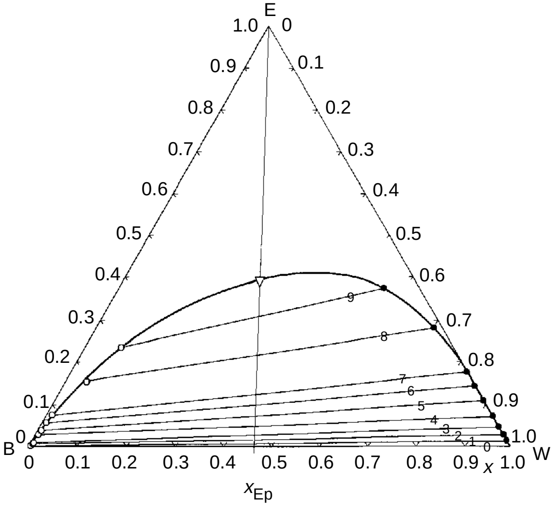

FIG. 1
Phase diagram for the benzene (B)–ethanol (E)–water (W) system at 25 °C (ref.[2]); ❍ organic phase; ● aqueous phase; ∇ plait point; x_{Ep} mole fraction of ethanol along the line drawn from the apex of the triangle through the plait point

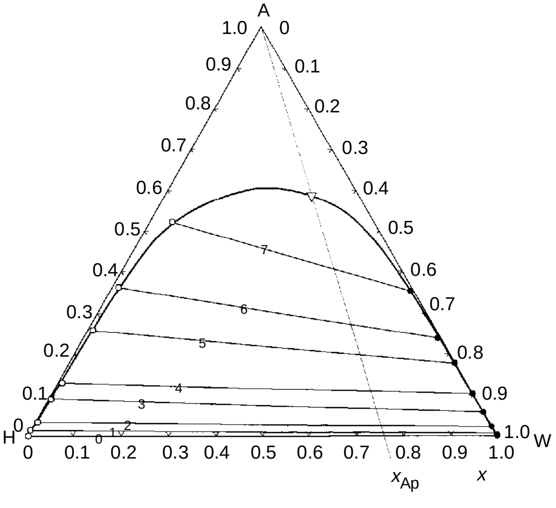

FIG. 2
Phase diagram for the n-hexane (H)–acetone (A)–water (W) system at 25 °C (ref.[3]); ❍ organic phase; ● aqueous phase; ∇ plait point; x_{Ap} mole fraction of acetone along the line drawn from the apex of the triangle through the plait point

plait point (see x_{Ep} and x_{Ap}, Figs 1 and 2, respectively). The shapes of the dependences are very similar to those in Figs 3 and 4. The surface tension of the *organic phases* changes very little with x_p. The dependence is linear in both cases:

TABLE I

Composition given as mole fractions of benzene (x_B) and ethanol (x_E), density (ρ), surface tension σ and interfacial tension, σ^{it}, in the benzene–ethanol–water system at 25 °C (superscripts aq and org refer to the aqueous and organic phase, respectively)

Tie line no.	Aqueous phase				Organic phase				σ^{it} mN m^{-1}
	x_B^{aq}	x_E^{aq}	ρ^{aq} g cm^{-3}	σ^{aq} mN m^{-1}	x_B^{org}	x_E^{org}	ρ^{org} g cm^{-3}	σ^{org} mN m^{-1}	
0	0.00040	0.00000	0.9969	62.4	0.99700	0.00000	0.8734	28.17	34.1
1	0.00044	0.01462	0.9908	56.3	0.99401	0.00253	0.8731	28.11	29.4
2	0.00051	0.02787	0.9849	51.8	0.98869	0.00657	0.8728	28.07	23.5
3	0.00057	0.04709	0.9779	46.3	0.98432	0.01009	0.8726	28.03	17.2
4	0.00068	0.07160	0.9704	40.5	0.96514	0.02855	0.8720	27.93	13.2
5	0.00139	0.10801	0.9612	34.2	0.95595	0.03742	0.8710	27.91	9.1
6	0.00147	0.14424	0.9499	30.0	0.93715	0.05485	0.8696	27.74	6.1
7	0.00284	0.17660	0.9388	27.6	0.91378	0.07435	0.8683	27.60	3.9
8	0.01956	0.27832	0.8999	25.7	0.80395	0.15332	0.8634	26.93	1.2
9	0.07493	0.37493	0.8752	26.1	0.69126	0.23252	0.8601	26.20	0.4

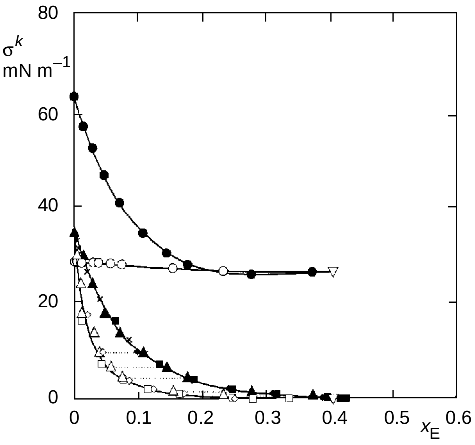

FIG. 3

Dependence of the surface and interfacial tensions in the benzene–ethanol–water system on the mole fraction of ethanol; ❍ surface tension of organic phase, σ^{org}; ● surface tension of aqueous phase, σ^{aq}; Δ interfacial tension, σ^{it}, vs the mole fraction of ethanol in organic phase, x_E; ▲ interfacial tension, σ^{it}, vs the mole fraction of ethanol in aqueous phase, x_E; ∇ plait point; · · · · connecting lines; ❐, ■ data of Patterson and Ross[10] (full symbol – aqueous phase, open symbol – organic phase); ✧, ◆ data of Sada et al.[11] (full symbol – aqueous phase, open symbol – organic phase); × data of Bartell and Davis[12] (only the aqueous phase composition is given)

BEW system

$$\sigma^{org} = 17.81 + 0.70\, x_{Ep} \;, \tag{1}$$

HAW system

$$\sigma^{org} = 28.24 - 6.19\, x_{Ap} \;. \tag{2}$$

TABLE II
Composition given as mole fractions of n-hexane (x_H) and acetone (x_A), density (ρ), surface tension (σ) and interfacial tension (σ^{it}) in the n-hexane–acetone–water system at 25 °C (superscript aq and org refers to the aqueous and organic phase, respectively

Tie line no.	Aqueous phase				Organic phase				σ^{it} mN m^{-1}
	x_H^{aq}	x_A^{aq}	ρ^{aq} g cm^{-3}	σ^{aq} mN m^{-1}	x_H^{org}	x_A^{org}	ρ^{org} g cm^{-3}	σ^{org} mN m^{-1}	
0	$2.78\ .\ 10^{-6}$	0.00000	0.9970	70.76	0.99940	0.00000	0.6549	17.84	49.7
1	0	0.00200	0.9948	62.77	0.99090	0.00910	0.6550	17.89	36.9
2	0	0.02400	0.9866	50.89	0.96590	0.03410	0.6558	17.90	28.4
3	0.00090	0.05910	0.9721	41.18	0.90570	0.09200	0.6582	17.83	19.0
4	0.00040	0.10320	0.9588	35.00	0.86220	0.13180	0.6608	17.83	13.0
5	0.00220	0.17730	0.9312	31.29	0.72950	0.25680	0.6688	17.87	6.9
6	0.00690	0.23860	0.9127	27.57	0.63500	0.36500	0.6766	17.93	4.4
7	0.00761	0.35556	0.8761	23.54	0.43000	0.52500	0.7005	18.21	1.3

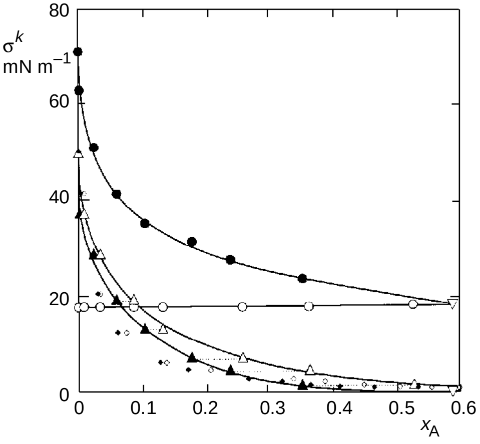

FIG. 4
Dependence of the surface and interfacial tensions in the n-hexane–acetone–water system on the mole fraction of acetone; ❍ surface tension of organic phase, σ^{org}; ● surface tension of aqueous phase, σ^{aq}; Δ interfacial tension, σ^{it}, vs the mole fraction of acetone in organic phase, x_A; ▲ interfacial tension, σ^{it}, vs the mole fraction of acetone in aqueous phase, x_A; ∇ plait point; · · · · connecting lines; ✧, ◆ data of Paul and de Chazal[8] (full symbol – aqueous phase, open symbol – organic phase)

The surface tension of the organic phase in the HAW system increases slightly with increasing concentration of acetone, whereas in the BEW system it decreases slightly with increasing concentration of the third component, ethanol; the changes in the surface tension, however, are within the experimental error limits. Hence, neither acetone nor ethanol appears positively to be adsorbed in the solvent–air interface.

The surface tension of the *aqueous phase* decreases rapidly with solute concentration in both cases. Its plot against x_p gave smooth curves for both ternary systems. No linear dependence between σ^{aq} or its logarithm on x_p was observed.

Inspired by the Szyszkowski equation, the correlation between the $\sigma^{aq}/\sigma_0^{aq}$ ratio and the ln x_p value was tested (σ_0^{aq} refers to the surface tensions in the binary systems, where no solute – acetone or ethanol – is present). The plots are shown in Figs 5 and 6.

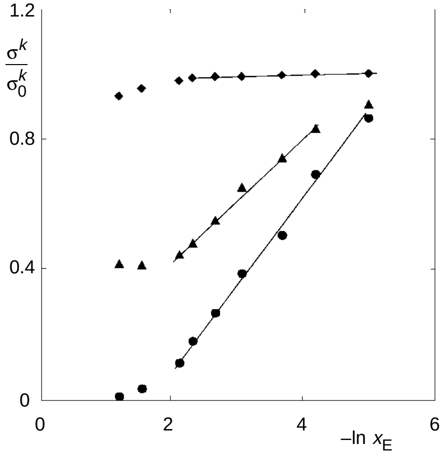

FIG. 5
BEW system – correlation in the sense of the Szyszkowski equation; ● interfacial tensions σ^{it}, —— Eq. (*9*); ▲ surface tensions of aqueous solutions σ^{aq}, —— Eq. (*3*); ◆ surface tensions of organic solutions σ^{org}, —— Eq. (*4*)

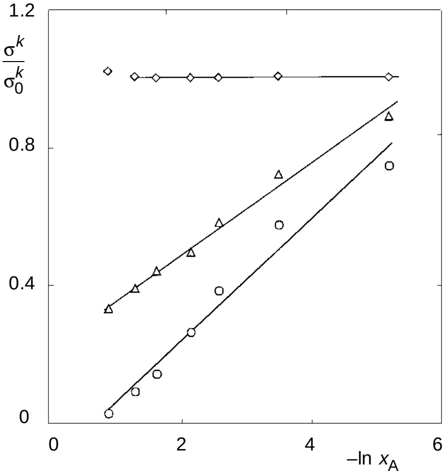

FIG. 6
HAW system – correlation in the sense of the Szyszkowski equation; ❍ interfacial tensions σ^{it}, —— Eq. (*10*); Δ surface tensions of aqueous solutions σ^{aq}, —— Eq. (*5*); ✧ surface tensions of organic solutions σ^{org}, —— Eq. (*6*)

Extensive segments of the plots are linear and can be represented by the following relations:

BEW system

$$\frac{\sigma^{aq}}{\sigma_0^{aq}} = 0.0522 - 0.1886 \ln x_{Ep} \quad (\sigma_0^{aq} = 62.4 \text{ mN m}^{-1}) \ , \tag{3}$$

$$\frac{\sigma^{org}}{\sigma_0^{org}} = 0.9774 - 4.435 \ . \ 10^{-4} \ln x_{Ep} \quad (\sigma_0^{org} = 28.17 \text{ mN m}^{-1}) \ , \tag{4}$$

HAW system

$$\frac{\sigma^{aq}}{\sigma_0^{aq}} = 0.1898 - 0.1491 \ln x_{Ap} \quad (\sigma_0^{aq} = 70.76 \text{ mN m}^{-1}) \ , \tag{5}$$

$$\frac{\sigma^{org}}{\sigma_0^{org}} = 1.0018 - 1.420 \ . \ 10^{-4} \ln x_{Ap} \quad (\sigma_0^{org} = 17.84 \text{ mN m}^{-1}) \ . \tag{6}$$

The interfacial tension is lowered by the presence of the third component in both cases. The logarithm of the interfacial tension can be expressed as a linear function of x_p (see Fig. 7):

BEW system

$$\ln \sigma^{it} = 3.4317 - 16.8751 \, x_{Ep} \ , \tag{7}$$

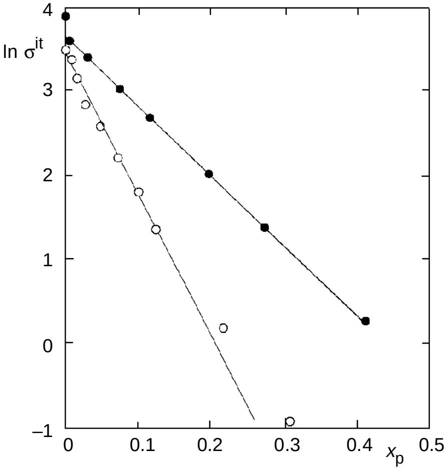

FIG. 7
Correlation of the interfacial tension, σ^{it}, with the mole fraction of solute, x_p, (ethanol or acetone) along the line drawn from the triangle apex through the plait point; ● BEW system, —— Eq. (*7*); ❍ HAW system, —— Eq. (*8*)

HAW system

$$\ln \sigma^{it} = 3.6612 - 8.3687\, x_{Ap} \quad . \tag{8}$$

The correlation in the sense of the Szyszkowski equation (see Figs 5 and 6) is expressed by the relations

BEW system

$$\frac{\sigma^{it}}{\sigma_0^{it}} = -0.4216 - 0.2600 \ln x_{Ep} \quad (\sigma_0^{it} = 34.1 \text{ mN m}^{-1}) \quad , \tag{9}$$

HAW system

$$\frac{\sigma^{it}}{\sigma_0^{it}} = -0.1270 - 0.1800 \ln x_{Ap} \quad (\sigma_0^{it} = 49.7 \text{ mN m}^{-1}) \quad . \tag{10}$$

Figures 5 through 7 show that the experimental data are very well fitted by the above equations over a relatively wide concentration range.

The correlation of the interfacial tension with the mutual solubility of the components was also examined. The latter was expressed by the relative change in the tie line length, $\Delta l/l_0 = (l_0 - l)/l_0$, where l is the length of the tie line in question and l_0 is the length of the tie line "0". The plot of ln σ^{it} against $\Delta l/l_0$ is linear for the HAW system nearly over the full concentration range, whereas for the BEW system the linear segment is limited (see Fig. 8). Nevertheless, the points departing from the straight line pertain to σ^{it} values near the plait point, which are in the order of experimental error. The following equations fit the relation between σ^{it} and $\Delta l/l_0$:

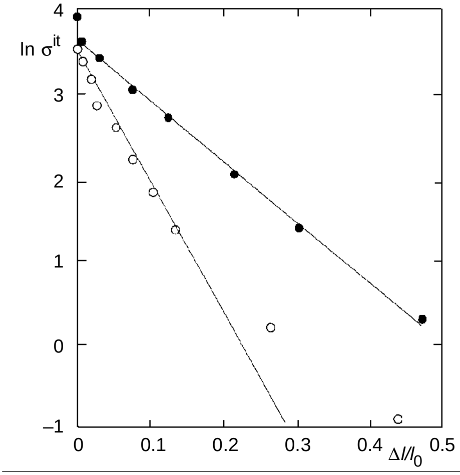

FIG. 8
Correlation of the interfacial tension, σ^{it}, with the relative change in the tie line, $\Delta l/l_0$; ● BEW system, —— Eq. (*11*); ❍ HAW system, —— Eq. (*12*)

BEW system

$$\ln \sigma^{\mathrm{it}} = 3.4962 - 15.5473 \frac{\Delta l}{l_0} \ , \qquad (11)$$

HAW system

$$\ln \sigma^{\mathrm{it}} = 3.6173 - 7.2685 \frac{\Delta l}{l_0} \ . \qquad (12)$$

The ranges of applicability of equations are shown in Figs 5 through 8.

The approach proposed by Paul and de Chazal[13] is based on a treatment of the interfacial region as one of finite thickness. By assuming that the interface concentration gradient is a linear function of thickness, a correlation is obtained between the interfacial tension and the reciprocal solubility of two bulk phases in contact. The presence of a third solute raises the increasing of the interface thickness, lowering the interfacial tension. The interface thickness is expressed in terms of mutual solubility as follows:

BEW system

$$h = \frac{x_{\mathrm{B}}^{\mathrm{aq}} + x_{\mathrm{W}}^{\mathrm{org}} + x_{\mathrm{E}}^{\mathrm{aq}} - 1}{\ln\,(x_{\mathrm{B}}^{\mathrm{aq}} + x_{\mathrm{W}}^{\mathrm{org}} + x_{\mathrm{E}}^{\mathrm{aq}})} \ , \qquad (13)$$

HAW system

$$h = \frac{x_{\mathrm{H}}^{\mathrm{aq}} + x_{\mathrm{W}}^{\mathrm{org}} + x_{\mathrm{A}}^{\mathrm{aq}} - 1}{\ln\,(x_{\mathrm{H}}^{\mathrm{aq}} + x_{\mathrm{W}}^{\mathrm{org}} + x_{\mathrm{A}}^{\mathrm{aq}})} \ , \qquad (14)$$

where x_j^k is the mole fraction of component j (where H stands for n-hexane, W for water, A for acetone, B for benzene) in phase k (k = aq for the aqueous phase, org for the organic phase). Authors[14] suggest a linear relation between $\ln \sigma^{\mathrm{it}}$ and $\ln (1/h)$. A linear plot of this type, however, was obtained neither for the HAW system nor for the BEW system. Over a certain concentration range (up to $1/h \approx 4$) the dependence of σ^{it} vs $1/h$ can be represented by a straight line (Fig. 9), which is common to both of the systems under study, viz.

$$\sigma^{\mathrm{it}} = -14.108 + 10.704 \frac{1}{h} \ . \qquad (15)$$

The fact that the dependences of the interfacial tension on the interfacial layer thickness nearly coincide suggests that the mechanism of lowering the interfacial tension decreases in the presence of the third component is very similar in the two systems. Nevertheless, comparison of the experimental values with those calculated from Eq.

(*15*) (see Tables I and II) demonstrates that this type of correlation fails to give reliable values not only at low concentrations of the third component (E or A) but also in the vicinity of the plait point.

Since the interfacial as well as surface tension values of the conjugate phases were obtained, the possibility of using Antonoff's rule to predict the interfacial tension in the ternary systems was examined. According to Antonoff[11], the interfacial tension for two

TABLE III
Correlation of interfacial tension σ^{it} of conjugate solutions in the benzene–ethanol–water system

Tie line no.	σ^{it}_{exp}, mN m^{-1}	σ^{it}_{calc}, mN m^{-1}			
		Eq. (*7*)	Eq. (*9*)	Eq. (*11*)	Eq. (*15*)
0	34.1	30.9	34.1	33.0	(46.9)
1	29.4	27.5	29.7	27.2	29.4
2	23.5	23.8	22.6	23.3	23.6
3	17.2	20.1	18.2	19.2	19.0
4	13.2	13.9	12.7	13.6	15.4
5	9.1	9.2	9.0	9.4	12.0
6	6.1	5.7	6.1	6.1	9.6
7	3.9	3.9	4.2	3.7	7.8
8	1.2	0.8	–	0.4	3.4
9	0.4	0.2	–	0.0_3	0.4

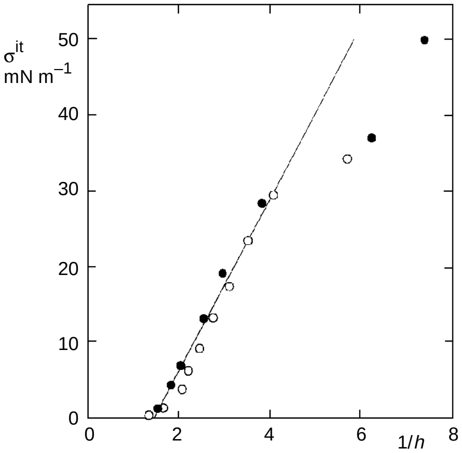

FIG. 9
Correlation of the interfacial tension, σ^{it}, with the interfacial layer thickness, *h*; ● BEW system, ❍ HAW system, —— Eq. (*15*)

saturated liquids in equilibrium is equal to the difference in the surface tensions of the two solutions against air. A comparison of the line obtained by applying Antonoff's rule with the experimental values is shown in Fig. 10. A very good applicability of Antonoff's rule is only observed for the BEW system over a certain range, whereas for the HAW system there is a difference between the Antonoff's plot and the experimental values, amounting to 3–6 mN m^{-1}.

Tables III and IV summarize the results of correlations for interfacial tensions in comparison with the experimental values.

TABLE IV
Correlation of interfacial tension σ^{it} of conjugate solutions in the hexane–acetone–water system

Tie line no.	σ^{it}_{exp}, mN m^{-1}	σ^{it}_{calc}, mN m^{-1}			
		Eq. (*8*)	Eq. (*10*)	Eq. (*12*)	Eq. (*15*)
0	49.7	38.9	49.7	37.2	(65.2)
1	36.9	37.1	39.5	35.9	(52.6)
2	28.4	30.3	25.0	29.9	26.8
3	19.0	20.8	17.0	21.6	17.6
4	13.0	14.9	13.0	15.2	13.0
5	6.9	7.5	8.2	7.8	7.7
6	4.4	4.0	5.3	4.1	5.5
7	1.3	1.3	1.7	1.2	2.1

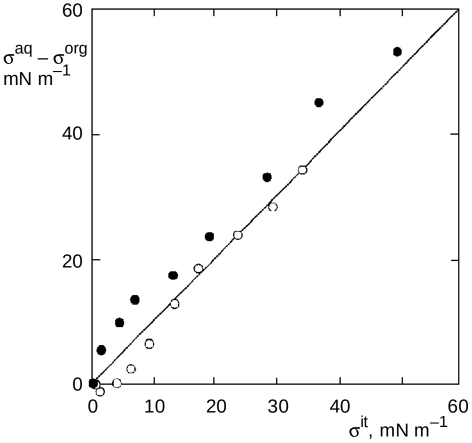

FIG. 10
Antonoff's rule testing; ● BEW system, ○ HAW system, —— $\sigma^{it} = \sigma^{aq} - \sigma^{org}$

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