SURFACE TENSIONS OF TERNARY SYSTEMS

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From the thermodynamic condition of equilibrium in a system in a force field, a relation was derived for calculating surface tensions in three- and multicomponent systems. To check the validity of this relation the surface tension of two ternary systems has beed measured and the experimental values have been compared with the calculated ones.

In the literature, we find a number of relations for calculating surface tensions in binary systems; only a minority of these relations has been extended to ternary or multicomponent mixtures. The majority of the proposed equations does not take into account the difference between the composition of the surface and the bulk phase which is caused by the adsorption at the liquid–vapour interface. The surface tension of the mixture is calculated either as the sum of the products of the surface tensions of pure compounds – or of certain powers of these tensions – and their mole, volume or weight fractions in the bulk phase – as it is with the methods which are purely empirical[1,3] or which start from the definition of the parachor[4–6] – or the calculation of the surface tension of the mixtures is based on the use of pseudocritical properties evaluated in the usual way on the basis of the composition in the bulk phase as with the methods for estimating the surface tensions, based on the theorem of the corresponding states[7,8]. The fact that the composition of the surface layer differs from that of the bulk phase is taken into account only in the relations derived by the methods of classical or statistical thermodynamics[9,10]. However, only few of them have been modified to make possible calculations in the case of ternary or multicomponent mixtures.

In this paper, the relations for calculating the surface tensions of ternary and of multicomponent solutions are derived from the thermodynamic condition of equilibrium in a system in a force field and these relations are verified by comparing the calculated values with the measured surface tensions of two ternary systems.

THEORETICAL

From the thermodynamic condition of equilibrium in a force field[11]

$$\mu_i^\alpha = \mu_i^\omega + \phi_i\,, \tag{1}$$

where μ_i^α and μ_i^ω, resp. denote the chemical potential of the i-th component in the bulk phase and in the surface layer, resp.; ϕ_i is the adsorption potential defined as the work necessary for transferring one mol of molecules from the bulk phase to a certain place in the surface layer, a relation between the composition of the bulk phase (x_i) and that of the surface layer (y_i) was derived[12]:

$$\frac{x_i/y_i}{x_j/y_j} = F_{ij}\,. \tag{2}$$

Under the assumption that there is no appreciable difference between the molar volumes of both pure components, *i.e.* V_i^0 and V_j^0, it is possible to neglect the factor $\exp \int[(V_i^0 - V_j^0)/RT]\,\mathrm{d}P$ (the integral between the limits P^α and P^ω) which differs only slightly from unity and $F_{ij} = \exp(\phi_i - \phi_j)/RT$. Hence we get the following expressions for the mole fractions of the respective components in the surface layer

$$\begin{aligned} y_1 &= x_1/(x_1 + x_2F_{12} + x_3F_{13})\,,\\ y_2 &= x_2/(x_1F_{21} + x_2 + x_3F_{23})\,,\\ y_3 &= x_3/(x_1F_{31} + x_2F_{32} + x_3)\,. \end{aligned} \tag{3}$$

The calculation of the surface tension σ is based on the relation derived in an earlier paper[13]:

$$\sigma = \int_\theta (P^\alpha - P^\omega)\,V^\omega\,\mathrm{D}n^\omega\,, \tag{4}$$

where V^ω stands for the molar volume in a certain place of the surface layer, Dn^ω is the number of moles in the volume element of the surface layer and the symbol $\int_\theta$ denotes the integration over the whole adsorption volume corresponding to the unit surface area.

In the case of a multicomponent system we can write

$$\sigma_{\text{mix}} = \int_\theta \sum_i y_i(P^\alpha - P^\omega)\,\bar{V}_i^\omega\,\mathrm{D}n^\omega\,, \tag{5}$$

where $\bar{V}_i^\omega$ is the partial molar volume of the *i*-th component in a certain position in the surface layer.

Starting from the pressure dependence of the chemical potential of the i-th component in the liquid phase

$$\mu_i^\omega(x_i^\omega, P^\omega) - \mu_i(x_i^\omega, P^\alpha) = \int_{P^\alpha}^{P^\omega} \bar{V}_i^\omega \, dP \approx \bar{V}_i^\omega(P^\omega - P^\alpha) \tag{6}$$

and from the dependence of this potential on composition

$$\mu_i(x_i^\omega, P^\alpha) - \mu_i^\alpha(x_i^\alpha, P^\alpha) = RT \ln\left(a_i^\omega / a_i^\alpha\right) \tag{7}$$

we obtain the expression

$$\bar{V}_i^\omega(P^\alpha - P^\omega) = \mu_i^\alpha - \mu_i^\omega + RT \ln\left(a_i^\omega / a_i^\alpha\right) = \mu_i^{0\alpha} - \mu_i^{0\omega} = \phi_i^0 \tag{8}$$

which we insert into Eq. (*5*) for the calculation of the surface tension

$$\sigma_{\mathrm{mix}} = \int_\theta \sum_i y_i \phi_i^0 \, \mathrm{D}n^\omega \, . \tag{9}$$

In one of the earlier papers[14], a relation for calculating the surface tension of pure compounds was derived:

$$\sigma_i^0 = \int_\theta \phi_i^0 \, \mathrm{D}n^\omega \, . \tag{10}$$

Therefore, by combining Eqs. (*8*) and (*9*) we get an approximate relation for the surface tension of the mixture:

$$\sigma_{\mathrm{mix}} = \sum_i y_i \sigma_i \, . \tag{11}$$

In the case of a ternary system, we insert from Eqs. (*3*) the expressions for y_i into this relation and we get the following equation for calculating the surface tension of ternary solutions:

$$\sigma_{\mathrm{mix}} = \frac{x_1\sigma_1}{x_1 + x_2F_{12} + x_3F_{13}} + \frac{x_2\sigma_2}{x_1F_{21} + x_2 + x_3F_{23}} + \frac{x_3\sigma_3}{x_1F_{31} + x_2F_{32} + x_3} =$$

$$= \frac{x_1\sigma_1}{x_1 + x_2F_{12} + x_3F_{13}} + \frac{x_2F_{12}\sigma_2}{x_1 + x_2F_{12} + x_3F_{23}F_{12}} + \frac{x_3F_{13}\sigma_3}{x_1 + x_2(F_{13}/F_{23}) + x_3F_{13}} \, . \tag{12}$$

This equation contains three constants, *i.e.* F_{12}, F_{13}, and F_{22} which can be calculated from the measured values of surface tensions of pure compounds and of binary systems; for the latter ones, we express the surface tensions σ_{ij} by a relation similar to that used for the ternary solutions:

$$\sigma^{ij} = \frac{x_i \sigma_i}{x_i + x_j F_{ij}} + \frac{x_j F_{ij} \sigma_j}{x_i + x_j F_{ij}} . \qquad (13)$$

From here we get the following relations for the above-mentioned constants:

$$F_{12} = \frac{x_1}{x_1 - 1} \cdot \frac{\sigma_1 - \sigma^{12}}{\sigma_2 - \sigma^{12}} ,$$

$$F_{13} = \frac{x_1}{x_1 - 1} \cdot \frac{\sigma_1 - \sigma^{13}}{\sigma_3 - \sigma^{13}} ,$$

$$F_{23} = \frac{x_2}{x_2 - 1} \cdot \frac{\sigma_2 - \sigma^{23}}{\sigma_3 - \sigma^{23}} . \qquad (14)$$

To verify the relation *(12)*, the surface tensions of two ternary systems were measured: benzene–cyclohexane–chlorobenzene and toluene–cyclohexane–chlorobenzene at 20°C in the whole concentration range. At the same time, the surface tensions of the respective binary subsystems were measured using the same apparatus. The measured values have been compared with the calculated ones.

EXPERIMENTAL

Substances used: benzene (R. G.), toluene for the UV spectroscopy, cyclohexane (R. G.), and chlorobenzene (pure); all these substances, supplied by Lachema, were rectified and their purity was checked by measuring the refractive index n, density ϱ and the boiling point. The measured values and those found in the literature[15] were: benzene $n = 1{\cdot}5015$ (lit. 1·5011), $\varrho = 0{\cdot}8792$ (lit. 0·8789); toluene $n = 1{\cdot}4968$ (lit. 1·4967), $\varrho = 0{\cdot}8667$ (lit. 0·8669); cyclohexane $n = 1{\cdot}4265$ (lit. 1·4263), $\varrho = 0{\cdot}7792$ (lit. 0·7785); chlorobenzene $n = 1{\cdot}5252$ (lit. 1·5246), $\varrho = 1{\cdot}1076$ (lit. 1·1061).

For measuring the surface tension, the method of drop weighing was chosen. The surface tension σ was calculated according to the formula:

$$\sigma = \sigma_s \frac{m F_s}{m_s F} , \qquad (15)$$

where σ_s is the surface tension of the reference substance, m and m_s are the weights of one drop of the measured liquid and of the standard, respectively, F and F_s the corrections for the measured solution and for the reference substance, respectively, which were determined from tables[17] as functions of the drop volume; therefore, it was necessary to know the densities of the measured solutions. The density of several mixtures was determined by Reischauer's pycnometer. The comparison of experimental density with the value calculated according to the Amagat's law showed that the error accompanying the determination of the surface tension according to this law can be neglected. Benzene was used as a reference substance.

For the measurement of the surface tension, an apparatus was used which had been described in a previous communication[16]. The solutions were prepared by weighing. The ternary solutions were prepared by mixing first two more volatile liquids; to these binary solutions different amounts of the third component were then added to cover the whole concentration range. Each measurement was repeated twice or three times. The measured values of the surface tension of individual systems are given in Tables I and II.

DISCUSSION

From the measured surface tensions of binary systems, the values of F_{ij} were calculated according to Eq. (*14*) and then inserted into Eq. (*12*). The values of the surface tension of both ternary systems calculated in this way are compared with the experi-

TABLE I

Surface tension σ (mJ/m^2) at 20°C of binary systems

x_1	σ	x_3	σ
cyclohexane(1)–benzene(2)		cyclohexane(1)–chlorobenzene(3)	
0·0000	28·89	0·0000	25·04
0·0906	28·17	0·2144	26·29
0·2232	27·26	0·4065	27·52
0·3590	26·56	0·5963	29·00
0·5879	25·78	0·8111	31·20
0·7837	25·37	1·0000	33·71
0·8767	25·19		
1·0000	25·04	benzene(2)–chlorobenzene(3)	
		0·0000	28·89
cyclohexane(1)–toluene(2′)		0·2055	29·85
0·0000	28·47	0·3786	30·71
0·2090	27·28	0·5747	31·67
0·4299	26·39	0·7925	32·75
0·6284	25·78	1·0000	33·71
0·7512	25·48		
1·0000	25·04	toluene(2′)–chlorobenzene(3)	
		0·0000	28·47
		0·2319	29·52
		0·4038	30·42
		0·6234	31·57
		0·8165	32·64
		1·0000	33·71

mental data in Table III. The calculated deviations Δ, *i.e.* the differences between the experimental values and calculated ones, are for both ternary systems within the limits of experimental errors, the average deviation being 0·26% in the case of the system benzene–cyclohexane–chlorobenzene, and 0·21% in the case of the toluene–cyclohexane–chlorobenzene system. The maximum deviation is found with the system consisting of 34 mol.% of cyclohexane, 24 mol.% of benzene and 42 mol.% of chlorobenzene: $\Delta = -0{\cdot}61\%$.

As can be seen from the Table, the mutual agreement of the calculated and measured values is very good; therefore, Eq. (*12*) enables us to calculate surface tensions of multicomponent systems only on the basis of experimental values for pure compounds and for the binary systems. On the other hand, however, we must admit that the results found here for two ternary systems do not allow us to draw conclusions of general validity.

TABLE II

Surface tension σ (mJ/m^2) at 20°C of ternary systems

Cyclohexane(1)–benzene(2)–chlorobenzene(3)							
$x_1 : x_2 = 0{\cdot}2214$		$x_1 : x_2 = 0{\cdot}6315$		$x_1 : x_2 = 1{\cdot}4322$		$x_1 : x_2 = 3{\cdot}8302$	
x_3	σ	x_3	σ	x_3	σ	x_3	σ
0·0000	27·56	0·0000	26·42	0·0000	25·78	0·0000	25·38
0·1996	28·65	0·1717	27·51	0·2474	27·33	0·2407	26·81
0·3645	29·60	0·4483	29·31	0·4184	28·52	0·4178	28·02
0·5347	30·66	0·5518	30·09	0·6414	30·22	0·6209	29·60
0·7718	32·19	0·7633	31·78	0·7920	31·62	0·8024	31·37
1·0000	33·71	1·0000	33·71	1·0000	33·71	1·0000	33·71

Cyclohexane(1)–toluene(2′)–chlorobenzene(3)							
$x_1 : x_2' = 0{\cdot}2643$		$x_1 : x_2' = 0{\cdot}7665$		$x_1 : x_2' = 1{\cdot}5634$		$x_1 : x_2' = 4{\cdot}0854$	
x_3	σ	x_3	σ	x_3	σ	x_3	σ
0·0000	27·26	0·0000	26·38	0·0000	25·83	0·0000	25·37
0·2154	28·42	0·2041	27·57	0·2049	27·03	0·2073	26·59
0·3945	29·48	0·3912	28·75	0·3994	28·31	0·3993	27·86
0·6032	30·85	0·5770	30·03	0·5958	29·77	0·5958	29·36
0·7977	32·27	0·7950	31·79	0·8039	31·62	0·8023	31·33
1·0000	33·71	1·0000	33·71	1·0000	33·71	1·0000	33·71

TABLE III

Comparison of experimental values of the surface tension in the ternary systems with the values calculated according to Eq. (*12*)

Cyclohexane(1)–benzene(2)–chlorobenzene(3)

x_1	x_2	x_3	σ_{exp}	σ_{calc}	$\Delta\%$
0·1451	0·6553	0·1996	28·62	28·60	−0·171
0·1152	0·5203	0·3645	29·60	29·59	−0·020
0·0843	0·3810	0·5347	30·66	30·68	+0·072
0·0414	0·1868	0·7718	32·19	32·31	+0·360
0·3206	0·5077	0·1717	27·51	27·37	−0·501
0·2136	0·3381	0·4483	29·31	29·19	−0·399
0·1735	0·2747	0·5518	30·09	29·96	−0·442
0·0916	0·1451	0·7633	31·78	31·72	−0·179
0·4432	0·3094	0·2474	27·33	27·19	−0·527
0·3425	0·2391	0·4184	28·52	28·35	−0·614
0·2112	0·1474	0·6414	30·22	30·21	−0·033
0·1225	0·0855	0·7920	31·62	31·59	−0·104
0·4617	0·1205	0·4178	28·02	27·91	−0·399
0·3006	0·0785	0·6209	29·60	29·59	−0·050
0·6021	0·1572	0·2407	26·81	26·74	−0·261
0·1567	0·0409	0·8024	31·37	31·37	0·000
Cyclohexane(1)–toluene(2′)–chlorobenzene(3)					
0·1640	0·6206	0·2154	28·42	28·35	−0·236
0·1258	0·4797	0·3945	29·48	29·40	−0·281
0·0830	0·3138	0·6032	30·85	30·77	−0·269
0·0423	0·1600	0·7977	32·27	32·16	−0·338
0·3453	0·4506	0·2041	27·57	27·45	−0·424
0·2642	0·3446	0·3912	28·75	28·63	−0·424
0·1835	0·2395	0·5770	30·03	28·98	−0·156
0·0890	0·1160	0·7950	31·79	31·78	−0·019
0·4849	0·3102	0·2049	27·03	26·96	−0·244
0·3663	0·2443	0·3994	28·31	28·22	−0·300
0·2465	0·1577	0·5958	29·77	29·73	−0·118
0·1196	0·0765	0·8039	31·62	31·63	+0·019
0·6368	0·1559	0·2073	26·59	26·55	−0·158
0·4826	0·1181	0·3993	27·86	27·82	−0·151
0·3247	0·0805	0·5958	29·36	29·37	+0·037
0·1558	0·0389	0·8023	31·33	31·37	+0·115

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