SURFACE TENSION
OF BINARY SOLUTIONS OF NONELECTROLYTES. VI.*
RELATION BETWEEN THE SURFACE TENSION
OF SOLUTIONS OF NONELECTROLYTES
AND OTHER PROPERTIES OF SOLUTIONS

M.ŠIŠKOVÁ

Department of Physical Chemistry,
Institute of Chemical Technology, Prague 6

A relation has been derived between the adsorption potentials of both components of a binary solution and the composition of equilibrium liquid and vapour phase which has been substituted into an equation expressing the dependence of the surface tension of solutions on composition. Further on, the resulting equation has been simplified by introducing mean adsorption potentials. The relation permits to compute the surface tension of solutions from the behaviour of solutions in the bulk phase and from the surface tension of pure components. A relation is discussed between the surface tension of the solution and the equilibrium behaviour of the system in the liquid and vapour phase and the relations derived are verified by comparing the computed and experimental values where possible.

From the thermodynamic condition of equilibrium in a force field[1] a dependence of the surface tensions of solutions on the solution composition has been derived in the first communication of this series[2]

$$\left(\frac{\delta \sigma_x}{\delta x}\right)_{p,T} = - RT \int_\theta \frac{1 - e^f}{x + (1-x)e^f} e^f \, Dn^\omega , \qquad (1)$$

where σ_x is the surface tension of the solution, x is the mole fraction of the component 1 in the solution, $f = (\varphi_1 - \varphi_2)/RT$, where φ_1 and φ_2 are the adsorption potentials of components 1 and 2 at a given point in the adsorption phase, Dn^ω is the number of moles in the volume element DV^ω of the adsorbed phase and the symbol θ below the integral sign denotes the integration over the whole adsorption space which corresponds to the unit surface. The equation (1) has been derived under assumption that the deviations from the ideal behaviour of the solution in the bulk and in the adsorbed phase are small so that the ratio of activity coefficients $(\gamma_1^\omega/\gamma_2^\omega)/(\gamma_1^\alpha/\gamma_2^\alpha)$ equals approximately one and that similarly the ratio of molar volumes of both components does not differ significantly from one. From this equation it is possible to express the surface tension of the solution as a function of composition of the bulk liquid phase by separating the variables and integrating

---

$$\sigma_x = \sigma_1 - RT \int_1^{x} \left[\int_0^{x} \frac{1 - e^f}{x + (1 - x)\,e^f}\; Dn^{\infty} \right] dx\,, \qquad (2)$$

where σ_1 is the surface tension of the pure component 1. The adsorption potentials Φ_1 and Φ_2 are generally a function of the composition of the solution and of the distance from the boundary between the liquid and vapour phase. In order to apply the equation (2) for the computation of the surface tension of solutions it is necessary to assume some relations concerning both these dependences.

In the paper[3] the adsorption potentials of both components of the solution have been expressed approximately by means of London's relations for intermolecular dispersion forces. In the following a relation will be derived between the surface tension of solutions and the composition of the equilibrium liquid and vapour phase by a similar procedure by which a relation has been derived previously between the surface tension of the pure substance and the vapour tension and the molar volume of the substance in the liquid phase[4].

THEORETICAL

Let us consider a liquid system consisting of two molecular species 1 and 2. Under assumption of central and additive intermolecular forces, the potential energy of one particle inside the solution will be given by the relation

$$E_{1\infty} = \int_V \varphi_{11}(r)\,N_1\,dV + \int_V \varphi_{12}(r)\,N_2\,dV = \int_0^{\infty} \left[\varphi_{11}(r)\,_1N + \varphi_{12}(r)\,N_2 \right] 4\pi r^2\,dr\,, \tag{3}$$

where N_1 and N_2 are number of molecules of the components 1 and 2 in the unit volume, V is the volume of the system, r is the distance between centers of two interacting molecules, and $\varphi_{11}(r)$, $\varphi_{12}(r)$ are functions expressing the dependence of intermolecular potential of two molecules on their distance r. These functions may be expressed by the Lennard–Jones equation[5]

$$\varphi(r) = -\left(A/r^6 + B/r^{12}\right). \tag{4}$$

By neglecting the term expressing the repulsive forces between molecules, and, consequently, by using a model of rigid spheres between which attractive forces are acting, a relation is obtained for the intermolecular energy of one particle in the solution

$$E_{1\infty} = - \int_{d_{11}}^{\infty} A_{11}N_1\,\frac{4\pi r^2}{r^6}\,dr - \int_{d_{12}}^{\infty} A_{12}N_2\,\frac{4\pi r^2}{r^6}\,dr = -\tfrac{4}{3}\pi \left[\frac{A_{11}N_1}{d_{11}^3} + \frac{A_{12}N_2}{d_{12}^3} \right],$$

$$\tag{5}$$

where d_{11}, d_{12} are the least distances to which the centers of two molecules may be approached.

Further on, the molecules in the vicinity of the surface will be considered. For the intermolecular energy of the particle of the component 1 which is not surrounded by other molecules equally from all sides, a relation is obtained

$$E_{1S} = \int_{d_{11}}^{s} \varphi_{11}(r) N_1 \cdot 2\pi r^2 \, dr + \int_{d_{12}}^{s} \varphi_{12}(r) N_2 \cdot 2\pi r^2 \, dr +$$

$$+ \int_{s}^{\infty} \left[\varphi_{11}(r) N_1 + \varphi_{12}(r) N_2 \right] (2\pi r^2 + 2\pi rs) \, dr =$$

$$= \frac{\pi}{6s^3} (A_{11}N_1 + A_{12}N_2) - \frac{4\pi}{3} \left(\frac{A_{11}N_1}{d_{11}^3} + \frac{A_{12}N_2}{d_{12}^3} \right), \quad (6)$$

if the center of this particle is at a greater distance from the surface than its diameter, *i.e.* $s > d$. For a molecule the center of which is nearer to the surface than its diameter, *i.e.* $s < d$ the following relation is obtained

$$E_{1S} = \int_{d_{11}}^{\infty} \varphi_{11}(r) N_1 (2\pi r^2 + 2\pi rs) \, dr + \int_{d_{12}}^{\infty} \varphi_{12}(r) N_2 (2\pi r^2 + 2\pi rs) \, dr =$$

$$= \frac{2\pi}{3} \left(\frac{A_{11}N_1}{d_{11}^3} + \frac{A_{12}N_2}{d_{12}^3} \right) - \frac{\pi s}{2} \left(\frac{A_{11}N_1}{d_{11}^4} + \frac{A_{12}N_2}{d_{12}^4} \right). \quad (7)$$

Similar relations are valid for the second component of the solution.

Let us denote the intermolecular attraction energy of one mole of the component 1 and 2 inside the liquid phase as $\varphi_{1\infty}$ and $\varphi_{2\infty}$ and at a distance s from the surface as φ_{1S} and φ_{2S}

$$\varphi_{1\infty} = N_A E_{1\infty}, \quad (8)$$

$$\varphi_{2\infty} = N_A E_{2\infty}, \quad (9)$$

$$\varphi_{1S} = N_A E_{1S}, \quad (10)$$

$$\varphi_{2S} = N_A E_{2S}. \quad (11)$$

The adsorption potential which has been defined as the work necessary for transferring one mole of considered molecules from the point where the force field of surface forces is not acting to the point at the potential φ is given by the relations

$$\varphi_1 = \varphi_{1S} - \varphi_{1\infty}, \qquad \varphi_2 = \varphi_{2S} - \varphi_{2\infty}. \quad (12),(13)$$

The relations derived above are substituted into these equations for φ_{1S}, φ_{2S}, $\varphi_{1\infty}$, $\varphi_{2\infty}$. The ratios of s/d_{11}, s/d_{12}, s/d_{22} which express the multiples of molecular diameters are denoted in the following by a single symbol β. The adsorption potentials of molecules of the components 1 and 2 will then be given as functions of the distance of centers of these molecules from the surface expressed in terms of multiples of molecular diameter β by the relations

$$\varphi_1 = -\varphi_{1\infty}/8\beta^3 \, , \tag{14}$$

$$\varphi_2 = -\varphi_{2\infty}/8\beta^3 \, , \tag{15}$$

for molecules the center of which is at a greater distance from the phase boundary than the diameter $(\beta > 1)$, and by

$$\varphi_1 = \left(-\frac{1}{2} + \frac{3\beta}{8}\right)\varphi_{1\infty} \, , \tag{16}$$

$$\varphi_2 = \left(-\frac{1}{2} + \frac{3\beta}{8}\right)\varphi_{2\infty} \, , \tag{17}$$

for molecules the center of which is nearer to the surface than their diameter $(\beta < 1)$.

In order to apply these expressions of adsorption potentials of components 1 and 2 for computing the dependences of surface tensions of solutions on composition, it is necessary to find convenient relations for the calculation of $\varphi_{1\infty}$ and $\varphi_{2\infty}$. Let us begin with the condition of equilibrium in the force field

$$\mu_i^{\alpha} = \mu_i^{\omega} + \varphi_i \, ,$$

where μ_i^{α} and μ_i^{ω} are chemical potentials of the i-th component at a point where the force field is not acting and at a point where a force field of potential φ_i is acting.

If it is considered that in the solution each molecule is found in the force field of action of all other molecules, then the quantity $\varphi_{1\infty}$ may be expressed by the relation

$$\varphi_{1\infty} = \mu_1 - \mu_1^* = RT \ln\left[\frac{f_1^0 \gamma_1 V(1)}{RT}\right] \tag{18}$$

and similarly

$$\varphi_{2\infty} = \mu_2 - \mu_2^* = RT \ln\left[\frac{f_2^0 \gamma_2 V(1)}{RT}\right] , \tag{19}$$

where μ_1, μ_2, μ_1^* and μ_2^* are chemical potentials of the component 1 and 2 in the solu-

tion and in a hypothetical state of an ideal gas which at the considered temperature would assume the same volume as the solution, f_1^0 and f_2^0 are fugacities of pure liquid components 1 and 2, γ_1 and γ_2 are activity coefficients of the components 1 and 2 in the solution, and $V(1)$ is the molar volume of the solution.

By substituting these relations into the equations (14), (15), (16) and (17) we obtain

$$\varphi_1 = -\left(1/8\beta^3\right) . \, RT \ln \left[f_1^0 \gamma_1 V(1)/RT \right] , \qquad (20)$$

$$\varphi_2 = -\left(1/8\beta^3\right) . \, RT \ln \left[f_2^0 \gamma_2 V(1)/RT \right] \qquad (21)$$

for $\beta > 1$, and

$$\varphi_1 = \left(-\frac{1}{2} + \frac{3\beta}{8} \right) RT \ln \frac{f_1^0 \gamma_1 V(1)}{RT} , \qquad (22)$$

$$\varphi_2 = \left(-\frac{1}{2} + \frac{3\beta}{8} \right) RT \ln \frac{f_2^0 \gamma_2 V(1)}{RT} , \qquad (23)$$

if $\beta < 1$.

Therefrom the value of the expression e^f which appears in the equation (2), may be expressed as

$$e^f = \left(f_1^0 \gamma_1 / f_2^0 \gamma_2 \right)^{-1/8\beta^3} = F^{\beta > 1} \qquad \text{for} \quad \beta > 1 \qquad (24)$$

and

$$e^f = \left(f_1^0 \gamma_1 / f_2^0 \gamma_2 \right)^{-(1/2)+(3\beta/8)} = F^{\beta < 1} \quad \text{for} \quad \beta < 1 . \qquad (25)$$

Further on, it is necessary to express the quantity Dn^ω in the equation (2)

$$Dn^\omega = \left(\varrho_s/M \right) \sqrt[3]{\left(M\varrho_\infty/N \right)} . \, d\beta , \qquad (26)$$

where ϱ_S is the density of the solution in the surface layer, ϱ_∞ is the density in the bulk phase and M is the molecular weight of the solution. As it has been shown in the previous paper[4],[6], the assumption that the density is constant at all the points of the system, both near the surface and inside the liquid phase, leads to rather great errors in computed surface tensions of pure substances. The far better agreement between measured and calculated values is obtained under assumption that the density is proportional to the intermolecular attraction energy, and that it may be consequently expressed as a function of the distance from the phase boundary

$$\varrho_S/\varrho_\infty = \varphi_S/\varphi_\infty . \qquad (27)$$

Therefrom we obtain

$$\varrho_S = \varrho_\infty \left(1 - \frac{1}{8\beta^3} \right) \qquad \text{for} \quad \beta > 1 , \qquad (28)$$

$$\varrho_s = \varrho_\infty \left(\frac{1}{2} + \frac{3\beta}{8} \right) \qquad \text{for} \quad \beta < 1 . \tag{29}$$

By substituting the relations (24), (25), (26), (28), and (29) into the equation (2), an expression is obtained for calculating the surface tension of solutions in dependence on the composition of the bulk liquid phase

$$\sigma_x = \sigma_1 - RT \int_1^x \frac{\varrho_\infty}{M} \sqrt[3]{\left(\frac{M}{\varrho_\infty N} \right)} \, dx \left[\int_0^1 \frac{1 - F^{\beta < 1}}{x + (1 - x) F^{\beta < 1}} \left(\frac{1}{2} + \frac{3\beta}{8} \right) d\beta + \right.$$

$$\left. + \int_1^\infty \frac{1 - F^{\beta > 1}}{x + (1 - x) F^{\beta > 1}} \left(1 - \frac{1}{8\beta^3} \right) d\beta \right], \tag{30}$$

where $F^{\beta > 1}$ and $F^{\beta < 1}$ are defined by the equations (24) and (25). This equation makes possible to calculate the surface tensions in the whole concentration range if the surface tension of one pure component and the behaviour of both components of the solution in the bulk phase are known. The fugacities of pure components in the liquid phase, f_1^0 and f_2^0, may be substituted at normal pressures and temperatures by the vapour pressures of pure components P_1^0 and P_2^0. The activity coefficients of the components 1 and 2 in the solution, γ_1 and γ_2, may be calculated from the data on equilibrium between the liquid and vapour phase. Assuming the ideal behaviour in the vapour phase we obtain from the relation of equilibrium in the binary system

$$f_1^0 \gamma_1 / f_2^0 \gamma_2 = P_1^0 \gamma_1 / P_2^0 \gamma_2 = y_1 x_2 / y_2 x_1 , \tag{31}$$

where x_1 and x_2 are mole fractions of the components 1 and 2 in the liquid phase, and y_1, y_2 are mole fractions in the equilibrium vapour phase. The validity of this equation is limited only by assumptions that the ratio of activity coefficients of both components in adsorbed and bulk phase, and the ratio of molar volumes of both components are approximately equal one.

Since the calculations according to the equation (30) are rather tedious and the integrals on the right hand side are to be solved graphically or numerically, a simplified method of calculating is given in the following.

The adsorption potentials φ_1 and φ_2 which are generally functions of the distance from the boundary of both phases will be substituted by mean potentials $\bar{\varphi}_1$ and $\bar{\varphi}_2$ which are constant in the whole adsorption space. The equation (30) will be simplified to the form

$$\sigma = \sigma_1 - RT \int_1^x \frac{1 - e^{\bar{f}}}{x + (1 - x) e^{\bar{f}}} \, n^\omega \, dx , \tag{32}$$

where $e^{\bar{f}} = \exp \left[(\bar{\varphi}_1 - \bar{\varphi}_2)/RT \right]$ and n^ω is the number of moles of solution in the adsorption space corresponding to the unit surface; this quantity may be considered approximately as constant

independent of the solution composition. In order to eliminate this quantity — its value being unknown — we divide the whole equation by an analogous relation for the difference of surface tensions of pure substances, $\sigma_2 - \sigma_1$, and for the calculation of the surface tension of solution we obtain

$$\sigma_x = \sigma_1 + (\sigma_2 - \sigma_1) \int_1^x \frac{1 - e^{\bar{f}}}{x + (1 - x)\, e^{\bar{f}}} \, dx \bigg/ \int_1^0 \frac{1 - e^{\bar{f}}}{x + (1 - x)\, e^{\bar{f}}} \, dx \,. \tag{33}$$

Now it is necessary to determine the values of φ_1 and φ_2; they will be calculated from the relations

$$\bar{\varphi}_1 = \frac{1}{\lambda} \int_0^\infty \varphi_1(\beta) \, d\beta = \frac{1}{\lambda}\left[\int_0^1 \left(-\frac{1}{2} + \frac{3}{8}\beta\right) \varphi_{1\infty} \, d\beta + \int_1^\infty -\frac{\varphi_{1\infty}}{8\beta^3} \, d\beta \right] = -\frac{0 \cdot 375}{\lambda} \varphi_{1\infty} \tag{34}$$

$$\bar{\varphi}_2 = -\frac{0 \cdot 375}{\lambda} \varphi_{2\infty} \,, \tag{35}$$

where λ is the thickness of the adsorption layer expressed in multiples of molecular diameters. The value of λ is selected in such a way that the deviation between the function expressing the dependence of the adsorption potential on the distance from the surface and the approximate function $\varphi_1 = \text{const.}$ for $\theta < \beta < \lambda$ and $\varphi_1 = 0$ for $\beta > \lambda$ will be minimum. This condition is fulfilled if the sum of areas P_1, P_2 and P_3 in the Fig. 1 is minimum. Since $P_1 + P_2 = P_3$, the condition of the extreme is expressed by the relation $\delta(P_1 + P_2)/\delta\lambda = 0$. The P_1 is given by the expression

$$P_1 = \int_0^\alpha \left(-\tfrac{1}{2} + \tfrac{3}{8}\beta\right) \varphi_{1\infty} \, d\beta - \bar{\varphi}_1 \alpha = -\frac{4}{3}\left(\frac{0 \cdot 375}{\lambda} - \frac{1}{2}\right)^2 \varphi_{1\infty} \,, \tag{36}$$

where the α has been substituted from the relation

$$[-(\tfrac{1}{2}) + (3\alpha/8)] \varphi_{1\infty} = -0 \cdot 375 \varphi_{1\infty}/\lambda \,. \tag{37}$$

The P_2 is given by the equation

$$P_2 = \int_\lambda^\infty (-\varphi_{1\infty}/8\beta^3) \, d\beta = -\varphi_{1\infty}/16\lambda^2 \,. \tag{38}$$

By substituting for P_1 and P_2 into the condition of the extreme, we obtain

$$\frac{\delta(P_1 + P_2)}{\delta\lambda} = \frac{8}{3} \varphi_{1\infty} \frac{0 \cdot 375}{\lambda^2}\left(-\frac{1}{2} + \frac{0 \cdot 375}{\lambda}\right) + \frac{\varphi_{1\infty}}{8\beta^3} = 0 \,. \tag{39}$$

Therefrom $\lambda = 1$.

By substituting this value into the equations (34) and (35) we obtain expressions for the $\bar{\varphi}_1$ and $\bar{\varphi}_2$

$$\bar{\varphi}_1 = -0 \cdot 375 \varphi_{1\infty} \,, \tag{40}$$

$$\bar{\varphi}_2 = -0 \cdot 375 \varphi_{2\infty} \,, \tag{41}$$

and

$$F = \exp\left[(\bar{\varphi}_1 - \bar{\varphi}_2)/RT\right] = (f_1^0 \gamma_1 / f_2^0 \gamma_2)^{-0 \cdot 375} \,. \tag{42}$$

Then, the surface tension of solutions may be computed from the equation

$$\sigma_x = \sigma_1 + (\sigma_2 - \sigma_1) \int_1^x \frac{1-F}{x+(1-x)F}\, dx \bigg/ \int_1^0 \frac{1-F}{x+(1-x)F}\, dx \,. \qquad (43)$$

Here again, only properties of both components in the bulk phase do appear in addition to the surface tensions of pure components. The calculation of the surface tension of solutions according to this equation is rather simpler than according to the equation (30).

DISCUSSION

Now the relation can be discussed between the surface tension of the solution and the equilibrium behaviour of the system in the liquid and vapour phase.

If the system behaves ideally in both phases, *i.e.* it follows the Raoult's law, the following relations are valid

$$\gamma_1 = \gamma_2 = 1 \,, \qquad (44)$$

$$f_1^0 \gamma_1 / f_2^0 \gamma_2 = P_1^0 / P_2^0 \,, \qquad (45)$$

$$\exp\left[(\overline{\varphi}_1 - \overline{\varphi}_2)/RT\right] = (P_1^0/P_2^0)^{-0.375} \,. \qquad (46)$$

The difference of adsorption potentials $\overline{\varphi}_1 - \overline{\varphi}_2$ is in this case constant in the whole concentration range and independent of the solution composition. The equation (43) may be integrated, and an expression is obtained for the calculation of the dependence of surface tension of the solution on composition

$$\sigma_x = \sigma_1 + (\sigma_2 - \sigma_1)\frac{\ln\left[x + (1-x)\left(P_1^0/P_2^0\right)^{-0.375}\right]}{-0.375 \ln\left(P_1^0/P_2^0\right)} \,. \qquad (47)$$
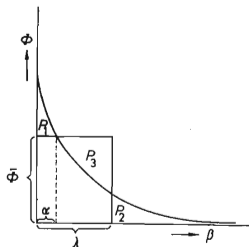

Fig. 1

Dependence of Adsorption Potential on Distance from Phase Boundary

The relation between the dependence of the surface tension on the mol fraction in the liquid phase and the dependence of the vapour phase composition on the composition of the liquid phase for two ideal systems $(P_1^0/P_2^0 = 3/2, P_1^0/P_2^0 = 2)$ is shown in the Fig. 2. In both cases two curves are obtained of the dependence of the surface tension on the composition of the solution: if the surface tension of the component 2 is higher than the surface tension of the component 1, $\sigma_2 - \sigma_1 > 0$, the calculated surface tensions of the solution are always lower than the linear combination of surface tension of both pure components; to the contrary, if $\sigma_2 - \sigma_1 < 0$, the calculated surface tension are higher. With ideal systems the deviation from the diagonal is small in both cases. Of course, only the first case, *i.e.* the higher surface tension of the component 2, corresponds to the relation

$$\sigma_2 - \sigma_1 = - n^\omega RT \int_1^0 \frac{1 - (P_1^0/P_2^0)^{-0.375}}{x + (1-x)(P_1^0/P_2^0)^{-0.375}} \, dx \,, \qquad (48)$$

the solution of which takes the form

$$\sigma_2 - \sigma_1 = 0.375 n^\omega \, RT \ln \left(P_1^0/P_2^0\right) > 0 \,. \qquad (49)$$

The reversed case, *i.e.* $\sigma_1 > \sigma_2$ may appear if the molar volume of the component 2 is rather higher than the molar volume of the component 1 and if the difference between the vapour pressures of both pure components is small. For such a system the relations are not suitable for calculating the surface tensions of solutions derived under assumption that the ratio of molar volumes of both components is approximately equal one.
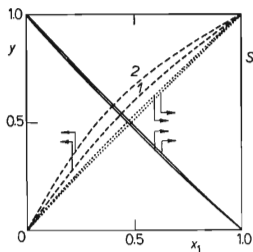

FIG. 2

Dependence of Surface Tension of Solution $[S = (\sigma_x - \sigma_1)/(\sigma_2 - \sigma_1)]$ on Composition of the Solution for Two Ideal Systems: *1* $P_1^0/P_2^0 = 3/2$, *2* $P_1^0/P_2^0 = 2$

$- - -$ mole fraction in equilibrium vapour phase y as function of composition of the liquid phase y, ——— surface tension of solution as function of liquid phase composition for $\sigma_2 > \sigma_1$, ... surface tension of solution as function of the liquid phase composition for $\sigma_2 < \sigma_1$.

If the values of surface tension of ideal solutions calculated according to the equation (47) differ greatly from the experimental values it is possible to assume that some ordering of molecules takes place in the surface layer so that the assumption of ideal behaviour of the solution is not here justified as in the bulk phase, and in the relation for $(\partial\sigma/\partial x)_{p,T}$ the ratio of activity coefficients of both components in the adsorbed phase γ_1^ω and γ_2^ω appears

$$\left(\frac{\partial\sigma}{\partial x}\right)_{p,T} = RT\,n^\omega\,\frac{1 - (\gamma_1^\omega)/(\gamma_2^\omega)/(P_1^0/P_2^0)^{-0\cdot375}}{x + (1-x)\,(\gamma_1^\omega/\gamma_2^\omega)\,(P_1^0/P_2^0)^{-0\cdot375}}\,. \tag{50}$$

If the dependence of the surface tension of the solution on composition has been determined by experiment, it is possible to calculate from this equation the ratio of activity coefficients in the surface phase $\gamma_1^\omega/\gamma_2^\omega$ for different compositions of the solution

$$\frac{\gamma_1^\omega}{\gamma_2^\omega} = \left(\frac{P_1^0}{P_2^0}\right)^{0\cdot375}\frac{n^\omega\,RT - (\partial\sigma/\partial x)_{p,T}\cdot x}{n^\omega\,RT + (\partial\sigma/\partial x)_{p,T}\cdot(1-x)}\,, \tag{51}$$

where the $(\partial\sigma/\partial x)_{p,T}$ will be determined from the experimental dependence σ on x and $n^\omega = \bar\varrho_s\lambda d/M$. The optimum thickness of the layer λd, in which the action of the mean adsorption potential φ is assumed equals to d as has been shown above and the mean density in the surface layer $\bar\varrho_s = 10\varrho_\infty/16$. Therefore, the number of adsorbed moles n^ω may be estimated from the relation

$$n^\omega = 0\cdot625(\bar\varrho_\infty/\overline{M})\sqrt[3]{\overline{M}/(\bar\varrho_\infty N)}\,. \tag{52}$$

From the value of the ratio of activity coefficients $\gamma_1^\omega/\gamma_2^\omega$ calculated in this way it would be possible to draw conclusions as to the ordering of molecules in the surface layer.
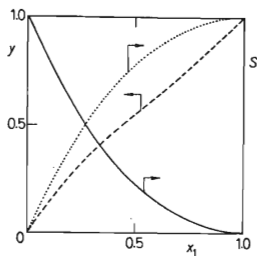

Fig. 3

Dependence of Surface Tension of Solution [$S = (\sigma_x - \sigma_1)/(\sigma_2 - \sigma_1)$] on Solution Composition for Symmetrical System

$---$ mole fraction in the equilibrium vapour phase y as function of the liquid phase composition, $\underline{\quad\quad}$ surface tension of the solution as function of the liquid phase composition for $\sigma_2 > \sigma_1$, $\ldots\ldots$ surface tension of solution as function of the liquid phase composition for $\sigma_2 < \sigma_1$.

If the considered system behaves as a symmetrical one, so that the activity coefficients may be expressed with the symmetrical form of the Margules or Van Laar equation

$$\log \gamma_1 = A x_2^2 , \tag{53}$$

$$\log \gamma_2 = A x_1^2 , \tag{54}$$

then

$$f_1^0 \gamma_1 / f_2^0 \gamma_2 = \left(P_1^0 / P_2^0 \right) \exp\left[2 \cdot 303 A \left(x_2^2 - x_1^2 \right) \right] \tag{55}$$

and

$$\bar{\varphi}_1 - \bar{\varphi}_2 = 0 \cdot 375 \cdot 2 \cdot 303 RT \left[\left(A + \log\left(P_1^0 / P_2^0 \right) + 2 A x_1 \right] . \tag{56}$$

In this case the difference of adsorption potentials is linear function of the liquid phase composition. The form of the dependence of the surface tension on the solution composition of a given symmetrical system is shown in the Fig. 3.

If the system forms an azeotrop then

$$f_1^0 \gamma_{1az} / f_2^0 \gamma_{2az} = x_{2az} y_{1az} / x_{1az} y_{az} = 1 , \tag{57}$$

$$e_{az}^{\bar{f}} = 1 . \tag{58}$$

Thus the integrand of the equation (32) equals zero for $x = x_{az}$, the dependence of the integrand value on x intersects the x axis, and a maximum or minimum appears on the curve of the dependence of the surface tension on composition.

A comparison of $y - x$ dependences for four fundamental types of real binary systems with σ vs x curves calculated according to the equation (43) is shown in the Fig. 4a—c. and d. With real systems, of course, the behaviour is very remote from the ideal one, the use of the equation (43) is not appropriate since an assumption has been made in its derivation that the ratio of activity coefficients of both components in the surface and bulk phase $(\gamma_1^\alpha / \gamma_2^\alpha)/(\gamma_1^\pi / \gamma_2^\pi)$ equals approximately one.

The verification of the derived relations by comparing the calculated and measured values of surface tensions is hindered by the fact that for the measured systems very few reliable experimental data are available of the liquid–vapour equilibrium at low temperatures. For this reason the σ vs x curves have been calculated first according to the equation (47), *i.e.* under the assumption that the considered systems obeyed the Raoult's law. The vapour pressures of pure components[7] only are necessary for the calculation in this case. The curves calculated in this way for systems measured previously: benzene–chlorobenzene, toluene–chlorobenzene, toluene–tetrachloromethane, chlorobenzene–tetrachloromethane, benzene–toluene, toluene–cyclohexane, chlorobenzene–cyclohexane, and tetrachloromethane–cyclohexane are compared with experimental values in the Fig. 5. A good agreement of measured and calculated values is obtained with the systems of toluene–chlorobenzene and tetra-

chloromethane–chlorobenzene; rather small deviations are found with the systeme of benzene–chlorobenzene, benzene–toluene, and chlorobenzene–cyclohexane. The calculated and measured curves are rather different with the systems of toluene–cyclohexane, toluene–tetrachloromethane, and tetrachloromethane–cyclohexane.

Experimental data on vapour–liquid equilibrium have been found for systems of benzene–chlorobenzene, toluene–tetrachloromethane, benzene–toluene, and tetrachloromethane–cyclohexane[8]. With these systems the dependences of the surface tensions of solutions on composition have been calculated according to the relation (43). Their comparison with measured values is given in the Fig. 5a—d. A good agreement is found again with systems of benzene–chlorobenzene and benzene–toluene.

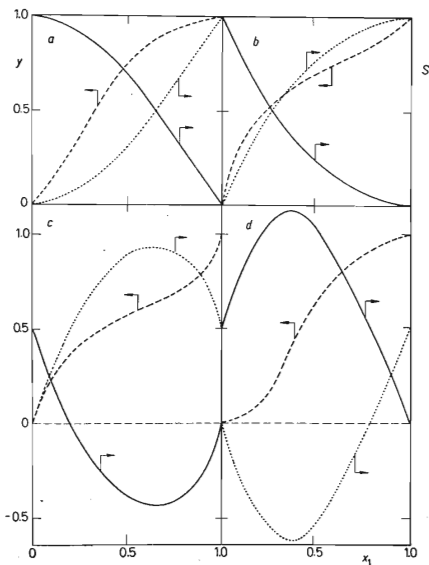Fig. 4

Dependence of Surface Tensions of Solutions ($S = (\sigma_x - \sigma_1)/(\sigma_2 - \sigma_1)$) on Solution Composition for Four Fundamental Types y vs x Curves of Real Binary Systems

— — — mole fraction in the equilibrium vapour phase y as function of the liquid phase composition, ——— surface tension of the solution as function of the liquid phase composition for $\sigma_2 > \sigma_1$, ... surface tension of solution as function of the liquid phase composition for $\sigma_2 < \sigma_1$.

With the system toluene–cyclohexane both the measured and calculated values of surface tensions are lower than the linear combination of surface tensions of pure components, however, the deviations are considerably greater with the measured curve than with the curve calculated under assumption of validity of the Raoult's law. Since no experimental data of vapour–liquid equilibrium are available with this system it is not possible to draw conclusions to what extent these deviations are caused by a different arrangement of molecules, and thus by nonideal behaviour in the surface phase.

With the system toluene–tetrachloromethane the calculation yields both under assumption of ideal behaviour and from the experimental data of vapour–liquid equilibrium a dependence of surface tensions of solutions on composition almost identical which is, however, lower than the linear combination of surface tensions of pure component, whereas the values obtained by the method of capillary rise and by the method of drop weight are higher than the linear combination of the surface tensions of both components. The deviations of measured and calculated values may be here due to a considerably nonideal behaviour in the surface layer; the
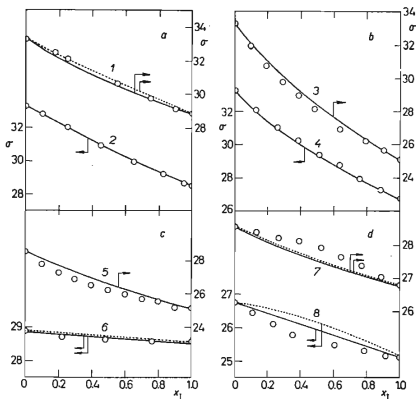

FIG. 5

Comparison of Experimental and Calculated Values of Surface Tension of Solutions
——— Equation (50), ... equation (46) 1 benzene(I)–chlorobenzene(II), 2 toluene(I)–chlorobenzene (II), 3 cyclohexane(I)–chlorobenzene(II), 4 tetrachloromethane(I)–chlorobenzene(II), 5 cyclohexane(I)–toluene(II), 6 toluene(I)–benzene(II), 7 tetrachloromethane(I)–toluene(II), 8 cyclohexane(I)–tetrachloromethane(II).

molecules of the toluene and tetrachloromethane differ from another both by the shape and probably by the intermolecular force field. However, it is necessary to note here that the dependences of surface tension of solutions on composition at different temperatures found for this system in the literature[8] are in a rather good agreement with the calculated values. A similar situation is found with the system benzene–tetrachloromethane which is not given here since the values of surface tensions have not yet been measured by the method of capillary rise, and the method of drop weight does not give reliable results with this system[9]. In this case even the published surface tensions of solutions are generally lower than the linear combination of surface tensions of the pure components; this corresponds to the curve calculated from the liquid–vapour equilibrium data in this system, however, the surface tensions are sometimes higher in agreement with the measured values of ours.

With the system tetrachloromethane–cyclohexane the measured surface tensions of solutions are lower than the linear combination of surface tension of the pure components, whereas the curves calculated both from the vapour pressures of pure components and from experimental data on vapour–liquid equilibrium are higher than the straight line connecting the surface tensions of both components, even though the curve calculated under assumption of validity of the Raoult's law is almost linear. This difference may be due partly to dissimilar properties of molecules and thus to the resulting nonideal behaviour in the surface layer, partly to the fact that the surface tension and vapour pressure of the tetrachloromethane is higher than that of the cyclohexane. This contradicts — as mentioned above — to the equation (48) the solution of which yields higher surface tension of the cyclohexane than that of the tetrachloromethane. The difference of surface tensions of both pure components with a right sign is obtained if their surface tensions are calculated according to the relation

$$ \sigma = -0.2625 \frac{\varrho_\infty}{M} \sqrt[3]{\left(\frac{M}{\varrho_\infty N}\right)} . RT \ln \frac{P°V_1}{RT} , \qquad (59) $$

which has been derived in the previous paper[4]. Here the molar volumes of both components do appear in addition to the vapour pressures. The introduction of the assumption that $V_1/V_2 \approx 1$ results in the change of the sign of $(\sigma_1 - \sigma_2)$, since in this case the molar volumes are rather different, whereas the difference between the vapour pressures is small.

LIST OF SYMBOLS

A_{11}, A_{12}, A_{22}	constant of Lennard–Jones equation in the term expressing attraction intermolecular forces
$\beta = s/d$	
d_{11}, d_{12}, d_{22}	least distance of approach of centers of two molecules

$E_{1\infty}, E_{2\infty}$	intermolecular potential energy of particle in bulk
E_{1S}, E_{2S}	intermolecular potential energy of particle at a distance s from surface
$f = (\varphi_1 - \varphi_2)/RT$	
$\bar{f} = (\overline{\varphi}_1 - \overline{\varphi}_2)/RT$	
f_1^0, f_2^0	fugacity of pure liquid component 1 and 2
$\varphi_{11}, \varphi_{12}, \varphi_{22}$	function expressing the dependence of force interaction between two molecules on their distances
φ_1, φ_2	adsorption potential of component 1 and 2
$\overline{\varphi}_1, \overline{\varphi}_2$	mean adsorption potential of component 1 and 2
$\varphi_{1\infty} = NE_{1\infty}, \varphi_{2\infty} = NE_{2\infty}$	
$\varphi_{1S} = NE_{1S}, \varphi_{2S} = NE_{2S}$	
γ_1, γ_2	activity coefficients in liquid phase
λ	thickness of adsorption layer expressed as multiple of molecular diameters
M	molecular weight
μ_1, μ_2	chemical potential of component 1 and 2 in solution
μ_1^*, μ_2^*	chemical potential of component 1 and 2 in state of ideal gas
μ_1^π, μ_2^π	chemical potential of component 1 and 2 in bulk phase
$\mu_1^\omega, \mu_2^\omega$	chemical potential of component 1 and 2 in adsorbed phase
n^ω	number of adsorbed mol on unit surface
N	Avogadro's constant
N_1, N_2	number of particles of component 1 and 2 in unit volume
P_1^0, P_2^0	vapour pressures of pure components 1 and 2
r	distance between centers of two molecules
R	gas constant
ϱ_∞	density in bulk phase
ϱ_S	density in surface layer
s	distance from phase boundary
σ_1, σ_2	surface tension of pure component 1 and 2
σ_x	surface tension of solution
T	temperature in K
V_1	molar volume in liquid phase
x_1, x_2	mole fraction of component 1 and 2 in liquid phase
y_1, y_2	mole fraction of component 1 and 2 in vapour phase

REFERENCES

1. Erdös E.: Chem. listy *48*, 1287 (1954).
2. Erdös E., Šišková M.: This Journal *31*, 415 (1966).
3. Šišková M., Erdös E.: This Journal *31*, 2318 (1966).
4. Šišková M.: This Journal *35*, 1641 (1970).
5. Hirschfelder J. O., Curtiss C. K. F., Bird R. B.: *Molecular Theory of Gases and Liquids*. Wiley, New York 1954.
6. Erdös E., Šišková M.: This Journal *25*, 1729 (1960).
7. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam 1950.
8. Timmermans J.: *Physico-Chemical Constants of Binary Systems* I, II. Interscience, New York 1950.
9. Šišková M., Šecová V.: This Journal *35*, 2702 (1970).

Translated by E. Erdös.