

THERMODYNAMIC INVESTIGATION OF THE INTERFACIAL PROPERTIES OF LIQUID MIXTURES

ACTIVITY COEFFICIENTS IN THE INTERFACIAL PHASE

By

L. GY. NAGY

Department for Physical Chemistry, Polytechnical University, Budapest
(Received December 19, 1962)

Thermodynamic investigations of the adsorption of liquid mixtures discuss almost entirely the equilibrium on free liquid surfaces (liquid gas interfaces), discuss the free surface adsorption on a well elaborated theory.

Therefore, in our research work on the solid surface adsorption of liquid mixtures determining the deciding factors of the properties of the interfacial phase, we began the comparative studies on the adsorption equilibrium of liquid mixtures on solid-liquid resp. liquid-gas interfaces.

The adsorption on the liquid-gas and that on the solid-liquid interfaces have namely a very important common property, that is why the research of the analogy can be permitted. Both adsorptions are namely essentially of displacing character, i.e. to enrich the component 1 on the surface, a part of component 2 is to be displaced from the interfacial layer.

In a generally accepted manner after GIBBS [1] the specific adsorption can be determined so, that the adsorbed quantity on the unity of surface or of mass is understood as the excess compared with the interior of the mixture.

Counting with mole fractions

$$\chi_x = H^0(x^0 - x) = W(x' - x) = (n'_1 + n'_2)(x' - x) \quad (1)$$

where

χ_x (mmole/g) = specific adsorption of the component 1

H^0 (mmole/g) = total molenumber of the liquid mixture pro g. ads

x^0, x = initial i.e. equilibrium mole fraction of the component 1

x' = mole fraction of the component 1 in the interfacial phase

W (mmole/g) = $n'_1 + n'_2$ = quantity of the components in the interfacial phase.

The positive results of the determinations of specific surface areas with the adsorptions of liquid mixtures show [2] that in case of pure physical adsorption of completely miscible liquid pairs the interfacial layer can be regarded approximatively as a monomolecular one.

In this case for the adsorption equilibrium the following relation can be written:

$$n'_1 \Phi_1 + n'_2 \Phi_2 = F \quad (2)$$

where Φ_1 and Φ_2 are the molar areas (m^2/mmole) of the components and F is the specific surface area of the adsorbent.

From relations 1 and 2 knowing the specific surface area of the adsorbent and molar areas of the components, the composition can be counted in the interfacial phase:

$$x' = \frac{Fx + \Phi_2 Z}{F + (\Phi_2 - \Phi_1) Z} \quad (3)$$

If it is correct and possible to suppose a monomolecular interfacial layer — the test results on surface areas determination show this — then for the adsorption equilibrium on solid-liquid interfaces the same thermodynamic relations must be correct, which were stated by HILDEBRAND [3] and others [4] for the free surface adsorption supposing a monomolecular layer.

In equilibrium the chemical potentials being identical ($\mu_i = \mu'_i$), for the two components the following relations can be written:

$$\ln f_1 x = \frac{(\gamma_1 - \gamma) \Phi_1}{RT} + \ln f'_1 x' \quad (4/a)$$

$$\ln f_2 (1 - x) = \frac{(\gamma_2 - \gamma) \Phi_2}{RT} + \ln f'_2 (1 - x') \quad (4/b)$$

where μ_i , μ'_i are the chemical potentials of the i -th component in liquid phase and in interfacial one; f_1 , f_2 are the activity coefficients of the components in the interior of the liquid phase (f = rational activity coefficient, equal to unit for the pure liquid state; $x = 1$, $f_1 = 1$).

γ_1 , γ_2 are the surface free energy excesses of the pure materials, γ that of the mixture with given x equilibrium composition in the interfacial phase.

f'_1 , f'_2 are the activity coefficients of the components in the interfacial phase.

The usage of rational activity coefficients made it necessary to introduce the right side first members of the relations (4). The $\frac{(\gamma_i - \gamma) \Phi_i}{RT}$ formula result a reference state changing according to the composition, where $a' = f'x'$ is the activity in the interfacial phase in case of such a hypothetic reference state when the surface tension of the pure liquid is not the real one, but is as great, as that of the mixture [3].

The absolute values of solid-liquid interfacial γ -s cannot be determined (in contrast with the free liquid surface), but on the results got measuring heat of wetting [5] γ must be negative in case of wetting liquid pairs (the

change in the energy of exothermic processes is taken with negative sign). In contrast with the free liquid surface γ means decrease of the free energy on solid-liquid interface.

The investigation of activity coefficients of the interfacial phase, their calculation with relations (4) is possible, if the other factors, inclusive the values of γ and x' , are known.

The value x' can be calculated with relation (3) and in the case of the adsorption on solid-liquid interfaces, γ can be calculated using the measured specific adsorption (χ) and the Gibbs' definition of the adsorption:

$$\frac{\chi}{1-x} = - \frac{F}{RT} \frac{d\gamma}{d \ln a_1} \quad (5)$$

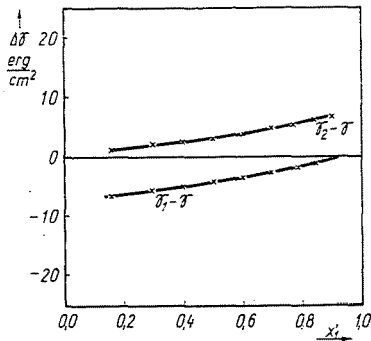


Fig. 1. Variation of the free surface energy of mixture dichlore ethane (1,2)-benzene at silica gel adsorbent

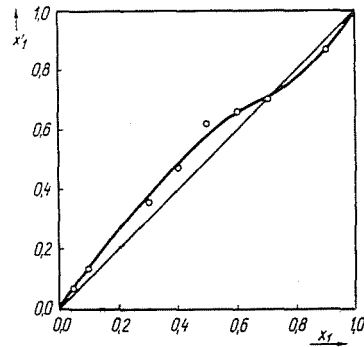


Fig. 2. Diagram of the free surface adsorption equilibrium of acetic acid-benzene

The values $(\gamma_2 - \gamma)$ and $(\gamma_1 - \gamma)$ can be calculated by graphical integration of relation (5) and so the numerical values of the activity coefficients f'_1 and f'_2 can be given from the relations (4) (Fig. 1).

$$(\gamma_1 - \gamma) \Phi_1 = \frac{2,3 RT \Phi_1}{F} \int_{a_1=1}^a \frac{\chi}{1-x} d \lg a_1 \quad (6/a)$$

$$(\gamma_2 - \gamma) \Phi_2 = \frac{2,3 RT \Phi_2}{F} \int_{a_2=1}^a - \frac{\chi}{x} d \lg a_2 \quad (6/b)$$

$$f'_1 = \frac{x \cdot f_1}{x'} \exp \left(- \frac{(\gamma_1 - \gamma) \Phi_1}{RT} \right) \quad (7/a)$$

$$f'_2 = \frac{(1-x) f_2}{1-x'} \exp \left(- \frac{(\gamma_2 - \gamma) \Phi_2}{RT} \right) \quad (7/b)$$

In connection with the solid-liquid adsorption it is well known that the adsorption can have throughout the same sign ($x' > x$) and can change the sign, i.e. in some concentration range one component enriches on the surface and later the other ($x' \cong x$).

Newer investigations showed, that isotherms with change in sign can be found, at free liquid surface adsorption too [6]. On ground of relation (5) the condition of the change in sign, too, can be given: it is the extremum value of γ at x concentration, where the change in sign takes place, i.e. where $\gamma = \pm 0$.

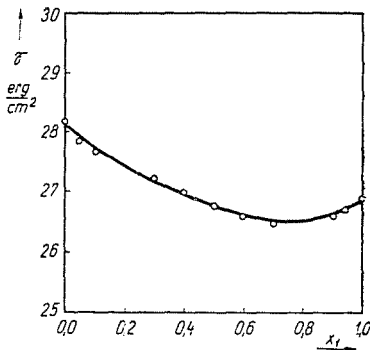


Fig. 3. Variation of surface tension of the mixture acetic acid-benzene

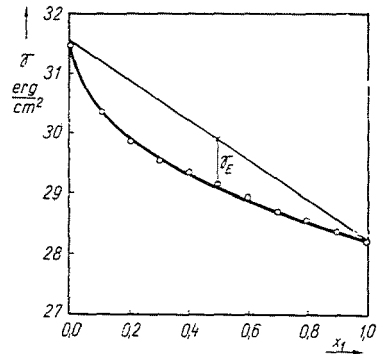


Fig. 4. Variation of the surface tension of the benzene(1)-dichlorethane(2) with the concentration (free liquid surface adsorption)

The experimental data show that as the tension equilibrium relations of the mixtures, γ has an extremum value, if the surface tensions of the pure components are not too different and the mixture is not an ideal one (Fig. 2, 3).

On ground of equation (4) it follows from this that the character of the adsorption, at the isotherms with change in sign, is determined by the course and the relation of the activity coefficients of the liquid and interfacial phase.

The further investigation of the factors determining the adsorption properties is hindered by the fact that the interfacial activity coefficient has not yet got any physical interpretation.

In connection with the physical interpretation of f' the question can be put, how much formal the relations (4) are in this form and would not be better to write the relation (4) (in case of rational activity coefficients) in form

$$x f_1 = x' f_1^* \quad (8/a)$$

$$(1 - x) f_2 = (1 - x') f_2^* \quad (8/b)$$

i.e. to introduce the following activity coefficients

$$f_1^* = f_1' \cdot \exp \frac{(\gamma_1 - \gamma) \Phi_1}{RT} \quad (9/a)$$

$$f_2^* = f_2' \cdot \exp \frac{(\gamma_2 - \gamma) \Phi_2}{RT} \quad (9/b)$$

The interpretation of f' in connection with free liquid surface adsorption was discussed in the literature very much. The most important consequence of these studies has been that f' is an explainable factor [7] (at free liquid surface adsorption) and not a formal one in the equation (4). On ground of these results we examined the explaining possibilities of the activity coefficients in the solid-liquid interface.

At the thermodynamical investigation of the adsorption on the free surface PRIGOGIN, DEFAY and others [7] explained the interfacial activity coefficients as follows:

With the method used for the regular mixtures a relation was established between f' and the change of the energy at substitutions (so called substitutional mixtures).

$$f_1' = \exp (q' x_2'^2 + q'' x_2^2) \quad (10)$$

The molecules in the interfacial phase are in contact with their interfacial neighbours (x'), on one side with the solution (x) and one part of it with the gas phase, too.

Being $f_1 = \exp qx_2^2$, the activity coefficient in the liquid phase, where q is proportional with the change of the energy at substitutions, at the ratio of the contact surface parts at the different phases [7, 11]

$$q' = 0.5 q \quad q'' = 0.25 q$$

or

$$q' = \frac{8}{26} q \quad q'' = \frac{9}{26} q.$$

Ignoring the interaction between the interfacial phase and the liquid phase in the first approximation we can count with $q' = \frac{17}{26} \cdot q$ value [11].

We may suppose that this interpretation of the f' activity coefficient can be applied without any insistence at the solid-liquid adsorption, too.

The dependence of f' from x' and x can give some answer to the question, how case $x' = \text{constant}$ is possible, if x changes. The product $x \cdot f$ (if the

change of f is big enough) changes only slightly in a certain concentration range, and this change can be compensated by $q'' \cdot x_2^2$ in the interfacial phase (at least in principle) and so the nearly constant interfacial composition as supposition cannot be regarded as absurd.

The thermodynamic plausibility of the constant interfacial composition is a great result from practical point of view too. The determination of the specific surface areas from the liquid mixture adsorption isotherms is based namely on the supposition of the constant surface composition [2]. The correctness of the supposition could not be explained on a thermodynamic base until now.

The aim of the thermodynamic investigations of the free liquid surface adsorption was generally that for the relation $\gamma - x$ a formula, could be given with that is generally to be applied.

Between the measured and computed results of the concentration relations of the surface tensions there were generally differences, but they could be explained by the uncertainty of the measurements and the roughness of the mathematic approaching; objection of principal significance or problem has not been brought up.

The interfacial composition of completely miscible binary liquid mixtures can be given by the contracted relations (4) too.

$$\frac{x \cdot f_1}{(1-x)f_2} \cdot \frac{(1-x')f_2'}{x'f_1'} = \exp \frac{\gamma_1 \Phi_1 - \gamma_2 \Phi_2}{RT} \exp \frac{(\Phi_2 - \Phi_1)\gamma}{RT} \quad (11)$$

Introducing the following abbreviations:

1. $\exp \frac{\gamma_1 \Phi_1 - \gamma_2 \Phi_2}{RT} = A$; it is a constant, characteristic only for the given mixture pairs and the adsorbent, proportional with the difference of the adsorptive potentials.

2. $\exp \frac{(\Phi_2 - \Phi_1)\gamma}{RT} = k_x$; a factor arising because of the different place requirements of the components, we have

$$x' = \frac{x}{A \cdot k_x \cdot \frac{f_2}{f_1} \cdot \frac{f_1'}{f_2'} (1-x) + x} \quad (12)$$

We investigated the interfacial activity coefficients of the 1,2 dichloro ethane-benzene, regarded as an ideal mixture, in case of free liquid surface and solid-liquid adsorptions.

Surface activity coefficients were calculated from isotherms with different adsorbents and it was found that $1 > f' > 0.9$, the f' -s have a well

defined course in each case. Relating about ideal mixture, the deviation of the interfacial activity coefficients from unit could not be explained properly, therefore the free liquid surface adsorption was examined, where the disturbing effect of the solid surface can be omitted. According the results, at the

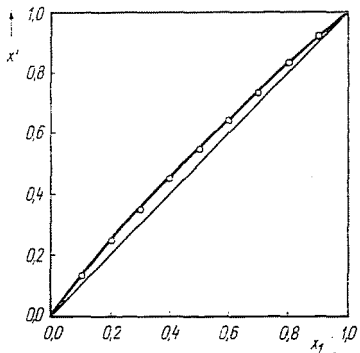


Fig. 5. Equilibrium diagram of the free liquid surface adsorption of benzene(1)-dichloro ethane(2) ($(x'_1 - \mu)$)

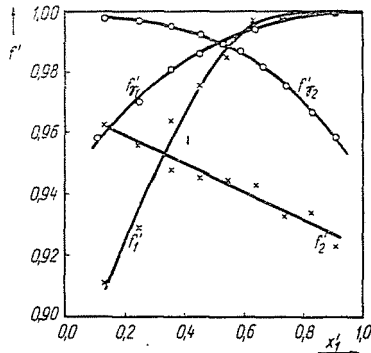


Fig. 6. Variation of the liquid-gas interfacial activity coefficients of the mixture benzene(1)-dichloro-ethane(1,2) (2) with the composition

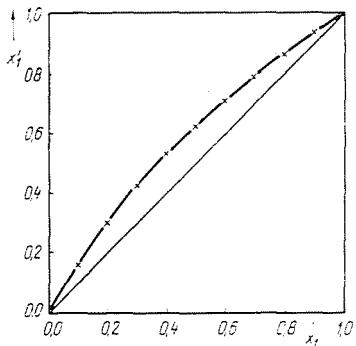


Fig. 7. Equilibrium diagram of the adsorption of dichloro ethane (1,2)(1)-benzene(2)-silica gel system

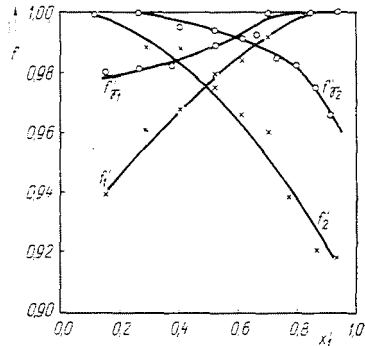


Fig. 8. Variation of surface activity coefficients of the dichloro ethane (1,2)(1)benzene(2)-silica gel system, with the composition

1,2 dichloro ethane-benzene mixture the free surface activity coefficients have a similar course, as on the solid interface (Fig. 4—8).

At an ideal mixture from relation (10) — according to the present theories — f' must be 1 in the whole composition range.

It must be mentioned that literature data [4, 7] can be found about studies of the free surface adsorption of 1,2 dichloro ethane-benzene, the differences between the calculated surface tensions and the measured ones was not so great as to look for its reasons.

The explanation of the difference of f' from the unit can be given applying the theory of the regular solutions according to the character of the interfacial phenomenon.

It can be supposed that the chemical potential change at the substitution in the surface phase takes place not only, because the A—A and B—B interaction is not equal to A—B, but because the surface energy relations, change too and this change has not been taken in notice in form of activity coefficient.

Introducing an f'_γ factor the fact is taken in notice that the interfacial energy relations always differ from the simple summarizing, i.e. there, too, the so called excess function can be deduced as it was with the function of the free energy, and free enthalpy resp.[8].

$$\gamma - (\gamma_1 x_1 + \gamma_2 x_2) = \gamma_e \quad (13)$$

where f'_γ gives the change of the excess surface free energy (γ_e) because of the substitution (Fig. 4).

Applying the theory of the regular solutions (8):

$$w_\gamma = \left(\gamma_{x=0.5} - \frac{\gamma_1 + \gamma_2}{2} \right) \Phi_{12}; \quad \Phi_{12} = \frac{\Phi_1 + \Phi_2}{2} \quad (14)$$

$$f'_{\gamma_1} = \exp \cdot \frac{w_\gamma}{RT} x_2'^2 = \exp \cdot q_\gamma x_2'^2 \quad (15)$$

$$f'_1 = f'_{q_1} \cdot f'_{\gamma_1} = \exp (q' x_2'^2 + q'' x_3'^2) \cdot \exp \cdot q_\gamma x_2'^2. \quad (16)$$

A good agreement was found in the course and quantity of f' and f'_γ calculated on the mentioned way at free surface adsorption with dichloro ethane(1,2)-benzene where in this form only $f'_q = 1$, but $f'_\gamma \neq 1$.

The agreement is a good one, too, in case of the solid surface adsorption at dichloro ethane (1,2)-benzene mixture (taking in account the rather approaching character of the formulas).

According to the experiences q_γ is always negative and so f'_γ , too, is less than one ($f' < 1$).

There is a possibility of determining q_γ in case of solid adsorption, too. $(\gamma_1 - \gamma)$ and $(\gamma_2 - \gamma)$ at $x = 0.5$ can be determined from graphical integration of $\frac{Z}{1-x} - \lg a_1$ and $-\frac{Z}{x} - \lg a_2$.

$$w_\gamma = - \frac{(\gamma_1 - \gamma) + (\gamma_2 - \gamma)}{2} \Phi_{12} = \left(\gamma - \frac{\gamma_1 + \gamma_2}{2} \right) \Phi_{12} \quad (17)$$

Principally it would be more correct to use instead of relations (14) and (17) the relation which takes in consideration the different molar areas ($x = 0.5$):

$$w_\gamma = \gamma\Phi_{1,2} - \frac{\gamma_1\Phi_1 + \gamma_2\Phi_2}{2} \tag{18}$$

but at adsorption on solid surface the absolute values of γ -s cannot be determined and therefore as a first approximation we must calculate with relation 17.

The result of measurements with dichloro ethane (1,2)-benzene mixture are shown on Tables I—III.

Table I
Benzene (1) — Ethylene dichlorid (2) — free liquid surface (25° C)

x_1	f_1	$\ln a_1$	γ erg/cm ²	$\frac{\gamma_1 - \gamma}{\text{erg/cm}^2}$	$\frac{z}{1-x}$ $\mu\text{mol/cm}^2$	$\frac{\gamma}{\mu\text{mol/cm}^2}$	f_1'	x_1'
0.1	1	-2.3	30.4	-2.2	0.202	0.182	0.910	0.129
0.2	1	-1.61	29.9	-1.7	0.338	0.270	0.928	0.244
0.3	1	-1.20	29.6	-1.4	0.390	0.273	0.963	0.345
0.4	1	-0.915	29.35	-1.15	0.454	0.272	0.975	0.446
0.5	1	-0.692	29.15	-0.95	0.506	0.253	0.985	0.544
0.6	1	-0.51	29.0	-0.8	0.55	0.220	0.997	0.638
0.7	1	-0.356	28.75	-0.55	0.58	0.174	0.998	0.730
0.8	1	-0.223	28.58	-0.38	0.636	0.127	1.007	0.822
0.9	1	-0.105	28.40	-0.2	0.710	0.071	1.000	0.913

$$\gamma_1 = 28.2 \text{ erg/cm}^2 \quad \Phi_1 = 0.18 \text{ m}^2/\mu\text{mol}$$

$$\gamma_2 = 31.5 \text{ erg/cm}^2 \quad \Phi_2 = 0.157 \text{ m}^2/\mu\text{mol}$$

x_2	f_2	$\frac{\gamma_2 - \gamma}{\text{erg/cm}^2}$	f_2'	x_2'
0.9	1	1.1	0.963	0.871
0.8	1	1.6	0.956	0.756
0.7	1	1.9	0.947	0.655
0.6	1	2.15	0.945	0.554
0.5	1	2.35	0.944	0.456
0.4	1	2.5	0.943	0.362
0.3	1	2.75	0.933	0.270
0.2	1	2.92	0.933	0.178
0.1	1	3.1	0.922	0.087

Table II

Benzene (1) — Ethylene dichlorid (2) — free liquid surface

x_1	f_1	f_{γ_1}	f_2	f_{γ_2}
0.1	0.910	0.964	0.963	0.999
0.2	0.928	0.973	0.956	0.997
0.3	0.963	0.980	0.947	0.994
0.4	0.975	0.985	0.45	0.990
0.5	0.985	0.990	0.944	0.986
0.6	0.997	0.994	0.943	0.980
0.7	0.998	0.997	0.933	0.975
0.8	1.007	0.999	0.933	0.968
0.9	1.000	1.000	0.922	0.961

$$W_{\gamma} = -1.18 \cdot 10^3 \text{ erg}/\mu\text{mol}; \quad q_{\gamma} = -0.05$$

At ethyl alcohol-benzene, ethyl alcohol-water and acetic acid-benzene mixtures we investigated the courses of interfacial activity coefficients, i.e. how the relation $f' = f'_q \cdot f'_\gamma$ can be applied at these nonideal mixtures. The results of measurements and calculations are shown on Tables IV—IX and Fig. 9—16.

At choosing the mixtures our further investigations with solid-liquid mixture adsorption were taken in account (e.g. ethyl alcohol-benzene, Fig. 9—11).

Table III

Ethylene dichlorid (1) — Benzene (2) — Silica gel (25° C)

x_1	$\frac{\gamma_1 - \gamma}{\text{erg}/\text{cm}^2}$	$-\frac{Z}{1-x}$	$\frac{Z}{\mu\text{mol},\text{m}}$	f'_1	x'_1	γ'_1	$f_{\gamma'_2}$
0.1	-6.4	0.407	0.37	0.940	0.158	0.98	1.00
0.2	-5.48	0.755	0.59	0.961	0.295	0.98	1.00
0.3	-4.64	1.07	0.75	0.968	0.417	0.98	0.99
0.4	-4.18	1.35	0.81	0.975	0.524	0.99	0.99
0.5	-3.14	1.61	0.805	0.948	0.621	0.99	0.99
0.6	-2.44	1.80	0.72	0.992	0.707	0.99	0.98
0.7	-1.79	1.84	0.55	0.998	0.786	1.00	0.98
0.8	-1.17	2.1	0.42	1.000	0.861	1.00	0.97
0.9	-0.58	2.36	0.24	1.000	0.934	1.00	0.96

x_2	$\gamma_2 - \gamma$ erg/cm ²	$-\frac{Z}{x}$ $\mu\text{mol/m}^2$	f_2'	x_2'
0.9	0.94	-0.41	1.00	0.842
0.8	1.82	-0.74	0.988	0.705
0.7	2.64	-1.07	0.988	0.583
0.6	3.43	-1.35	0.979	0.476
0.5	4.18	-1.61	0.966	0.379
0.4	4.85	-1.80	0.960	0.293
0.3	5.52	-1.84	0.938	0.214
0.2	6.24	-2.1	0.920	0.139
0.1	6.75	-2.36	0.918	0.066

$q_\gamma = -0.04$

Table IV
Ethanol (1) — Benzene (2) — free liquid surface (25° C)

x_1	f_1	$\ln a_1$	γ erg/cm ²	$\gamma_1 - \gamma$ erg/cm ²	$\frac{Z}{1-x}$	$\frac{Z}{\mu\text{mol/m}^2}$	f_1'	x_1'
0.1	4.97	-0.70	27.3	-5.4	2.23	2.01	1.56	0.413
0.2	2.87	-0.55	26.4	-4.5	2.77	2.22	1.35	0.529
0.3	2.10	-0.46	25.7	-3.8	3.26	2.28	1.21	0.625
0.4	1.69	-0.39	25.1	-3.2	3.64	2.20	1.12	0.703
0.5	1.45	-0.32	24.5	-2.6	4.0	2.0	1.07	0.767
0.6	1.26	-0.28	24.25	-2.35	4.24	1.7	1.03	0.822
0.7	1.12	-0.24	23.8	-1.9	4.5	1.35	0.985	0.873
0.8	1.05	-0.17	23.35	-1.45	4.8	0.96	0.980	0.920
0.9	1.02	-0.09	22.65	-0.75	5.0	0.5	0.992	0.960

$\gamma_1 = 22.0 \text{ erg/cm}^2$ $\Phi_1 = 0.12 \text{ m}^2/\mu\text{mol}$
 $\gamma_2 = 28.2 \text{ erg/cm}^2$ $\Phi_2 = 0.18 \text{ m}^2/\mu\text{mol}$

x_2	f_2	$\gamma_2 - \gamma$ erg/cm ²	f_2'	x_2'
0.9	1.08	0.9	1.55	0.587
0.8	1.20	1.8	1.79	0.471
0.7	1.33	2.5	2.07	0.375
0.6	1.51	3.1	2.43	0.297
0.5	1.74	3.7	2.92	0.233
0.4	2.05	3.95	3.45	0.178
0.3	2.43	4.4	4.16	0.127
0.2	2.85	4.85	5.01	0.08
0.1	3.66	5.55	6.1	0.04

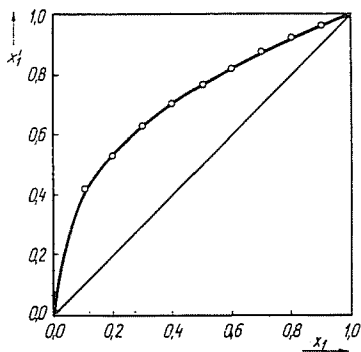


Fig. 9. Equilibrium diagram of the free surface adsorption of the ethanol-benzene

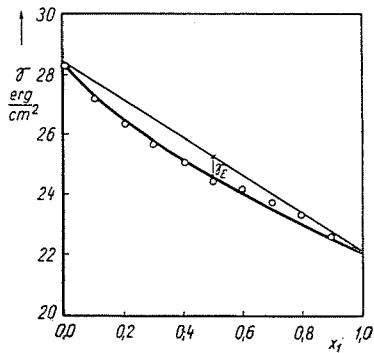


Fig. 10. Variation of surface tension of the mixture ethanol-benzene with the concentration

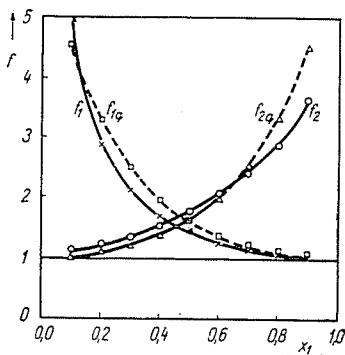


Fig. 11. Free surface activity coefficients of ethanol-benzene

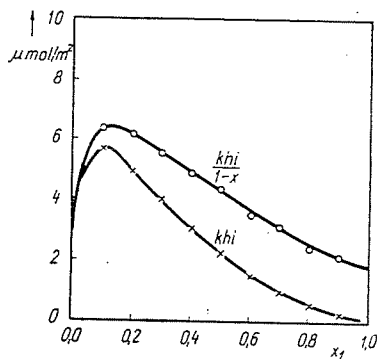


Fig. 12. Isotherm of free surface adsorption of ethanol-water

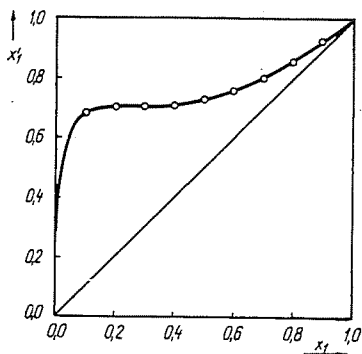


Fig. 13. Equilibrium diagram of free surface adsorption of ethanol-water

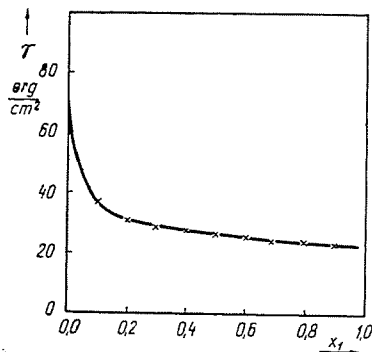


Fig. 14. Variation of surface tension of ethanol-water

Table V
Ethanol (1) — Benzene (2) — free liquid surface*

x_1	f_1^I	f_1^{II}	$f_{\gamma_1}^{III}$	$f_{\gamma_1}^{IV}$	$f_{q_1}^V$	f_2^I	f_2^{II}	$f_{\gamma_2}^{III}$	$f_{\gamma_2}^{IV}$	$f_{q_2}^V$
	I	II	III	IV	V	I	II	III	IV	V
0.1	1.56	1.50	0.987	1.024	1.524	1.55	1.22	0.994	1.26	1.232
0.2	1.35	1.30	0.992	1.028	1.312	1.79	1.40	0.990	1.27	1.409
0.3	1.21	1.18	0.995	1.020	1.186	2.07	1.59	0.986	1.28	1.611
0.4	1.12	1.11	0.997	1.000	1.113	2.43	1.80	0.982	1.32	1.828
0.5	1.07	1.061	0.998	1.001	1.068	2.92	2.01	0.979	1.42	2.056
0.6	1.03	1.038	0.999	0.992	1.039	3.45	2.20	0.976	1.51	2.281
0.7	0.985	1.018	0.999	0.966	1.020	4.16	2.47	0.972	1.64	2.511
0.8	0.980	1.008	1.000	0.972	1.008	5.01	2.74	0.969	1.77	2.819
0.9	0.992	1.002	1.000	0.990	1.002	6.1	2.98	0.967	1.98	3.083

$$W_{\gamma} = -9 \cdot 10^2 \text{ erg}/\mu\text{mol}; q_{\gamma} = -0.036$$

$$* f_i^I = \lg f_i = \lg f_i x_i - \frac{(\gamma_i - \gamma) \Phi_i}{2.3 RT} - \lg x_i$$

$$f_i^{II} = f_{q_i}^V f_{\gamma_i}^{III}$$

$$f_{\gamma_i}^{III} = \exp q_{\gamma} (1 - x_i)^2$$

$$f_{\gamma_i}^{IV} = \frac{f_i^I}{f_{q_i}^V}$$

$$f_{q_i}^V = \exp q' (1 - x_i)^2$$

Table VI
Ethanol (1) — Water (2) — free liquid surface (25° C)

x_1	f_1	$\ln a_1$	$\frac{\gamma}{\text{erg/cm}^2}$	$\frac{\gamma_1 - \gamma}{\text{erg/cm}^2}$	$\frac{\chi}{\mu\text{mol/m}^2}$	χ	f_1^I	$f_{1q_1}^I$	$f_{1q_2}^I$	x_1'
0.1	3.00	-1.203	36.4	-14.4	6.48	5.82	0.875	1.45	1.078	0.69
0.2	2.25	-0.800	29.7	-7.7	6.2	4.95	0.926	1.35	1.073	0.71
0.3	1.77	-0.634	27.6	-5.6	5.55	3.88	0.998	1.27	1.073	0.70
0.4	1.45	-0.545	26.35	-4.5	4.86	2.92	1.023	1.20	1.073	0.70
0.5	1.24	-0.477	25.4	-3.4	4.37	2.18	1.003	1.15	1.059	0.73
0.6	1.13	-0.388	24.6	-2.6	3.52	1.41	1.026	1.09	1.050	0.75
0.7	1.06	-0.298	23.85	-1.85	3.04	0.91	1.015	1.05	1.032	0.80
0.8	1.02	-0.203	23.2	-1.2	2.43	0.49	1.018	1.03	1.018	0.85
0.9	1.00	-0.106	22.6	-0.6	2.02	0.2	1.01	1.01	1.005	0.92

$$f_{1q_1}^I = \exp \cdot q \left(\frac{8}{26} (x_2)^2 + \frac{9}{26} (x_2)^2 \right); \quad q = 1.2$$

$$f_{1q_2}^I = \exp \cdot q \cdot \frac{17}{26} x_1^2$$

x_2	f_i	$\frac{\gamma_2 - \gamma}{\text{erg/cm}^2}$	f'_2	$f'_{2\gamma_1}$	$f'_{2\gamma_2}$	x'_2
0.9	1.01	35.8	1.23	1.19	1.452	0.31
0.8	1.06	43.5	1.04	1.226	1.485	0.29
0.7	1.16	44.6	0.915	1.245	1.469	0.30
0.6	1.28	45.85	0.840	1.282	1.469	0.30
0.5	1.44	46.8	0.834	1.351	1.521	0.27
0.4	1.63	47.6	0.831	1.427	1.556	0.25
0.3	1.86	48.35	0.862	1.552	1.652	0.20
0.2	2.02	49.0	0.821	1.72	1.762	0.15
0.1	2.20	49.6	0.823	1.914	1.950	0.08

$$\Phi_1 = 0.12 \text{ m}^2/\mu\text{mol}$$

$$\gamma_1 = 22.0 \text{ erg/cm}^2$$

$$\Phi_2 = 0.06 \text{ m}^2/\mu\text{mol}$$

$$\gamma_2 = 72.2 \text{ erg/cm}^2$$

$$f'_{2q_1} = \exp \cdot q \cdot \left(\frac{8}{26} x_1^2 + \frac{9}{26} x_1^3 \right)$$

$$f'_{2q_2} = \exp \cdot q \cdot \frac{17}{26} x_1^2$$

Table VII

Ethanol (1) — Water (2) — free liquid surface

$$W\gamma = -1.95 \cdot 10^4 \text{ erg}/\mu\text{mol} \quad q\gamma = -0.79$$

x_1	f_i	f'_i	f'_{γ_1}	f'_{γ_2}	f'_{q_1}	f'_2	f'_2	f'_{γ_2}	f'_{γ_2}	f'_{γ_2}
	I	II	III	IV	V	I	II	III	IV	V
0.1	0.875	0.987	0.927	0.813	1.078	1.23	0.997	0.687	0.848	1.452
0.2	0.926	0.989	0.931	0.863	1.073	1.4	0.995	0.671	0.699	0.485
0.3	0.998	0.989	0.931	0.930	1.073	0.915	0.996	0.679	0.623	1.469
0.4	1.023	0.989	0.931	0.953	1.073	0.840	0.996	0.679	0.572	1.469
0.5	1.003	0.997	0.944	0.948	1.059	0.834	1.000	0.658	0.548	1.521
0.6	1.026	0.999	0.952	0.977	1.050	0.831	1.002	0.641	0.533	1.556
0.7	1.015	1.000	0.969	0.982	1.032	0.862	1.002	6.603	0.520	1.652
0.8	1.018	1.000	0.982	1.000	1.018	0.921	0.997	0.566	0.466	1.762
0.9	1.01	1.000	0.995	1.005	1.005	0.823	0.997	0.512	0.421	1.950

$$f_i I = \lg f_i = \lg f_i x_i - \frac{(\gamma_i - \gamma)\Phi_i}{2.3 RT} - \lg x_i$$

$$f'_i II = f'_{qi} f'_{\gamma_i}$$

$$f'_{\gamma_i} III = \exp \cdot q_\gamma (1 - x_i)^2$$

$$f'_{\gamma_i} IV = \frac{f_i}{f'_{qi}}$$

$$f'_{qi} V = \exp \cdot q \cdot \frac{17}{26} (1 - x_i)^2$$

Table VIII

Acetic acid (1) — Benzene (2) — free liquid surface (25° C)

x_1	f_1	$\ln a_1$	γ erg/cm ²	$\gamma_1 - \gamma$ erg/cm ²	$\frac{Z}{1-x}$	$\frac{Z}{\mu\text{mol/m}^2}$	f_1	f'_{1q_1}	f'_{1q_2}	x'_1
0.05	3.20	-1.83	27.9	-1.02	0.105	0.100	2.55	2.54	2.62	0.66
0.1	2.82	-1.27	27.7	-0.82	0.165	0.132	2.35	2.18	2.34	0.124
0.3	2.20	-0.414	27.5	-0.37	0.426	0.298	1.92	1.67	1.60	0.348
0.4	1.98	-0.23	27.0	-0.12	0.863	0.485	1.69	1.43	1.37	0.471
0.5	1.71	-0.16	26.8	+0.08	1.58	0.790	1.38	1.31	1.30	0.613
0.6	1.50	-0.106	26.6	+0.28	1.15	0.460	1.30	1.17	1.13	0.664
0.7	1.32	-0.078	26.5	+0.38	0.093	0.027	1.29	1.10	1.11	0.701
0.9	1.06	-0.046	26.6	+0.28	2.17	-0.217	1.07	1.03	1.02	0.875
0.95	1.02	-0.032	26.7	+0.18	-3.5	-0.176	1.03	1.01	1.01	0.928

$\Phi_1 = 120\text{m}^2/\text{mmol}$

$f'_{1q_1} = \exp \cdot q \cdot \left(\frac{8}{26} x_2^2 + \frac{9}{26} x_2 \right)$

$\Phi_2 = 180\text{m}^2/\text{mmol}$

$\gamma_1 = 26.88 \text{ erg/cm}^2$

$f'_{1q_2} = \exp \cdot q \cdot \frac{17}{26} \cdot x_2^2$

$\gamma_2 = 23.20 \text{ erg/cm}^2$

$q = 1.7$

x_2	f	$\gamma_2 - \gamma$ erg/cm ²	f_2	f'_{2q_1}	f'_{2q_2}	x'_2
0.95	1.01	0.3	1.005	1.01	1.03	0.934
0.9	1.03	0.5	1.02	1.03	1.04	0.876
0.7	1.14	0.95	1.14	1.12	1.14	0.652
0.6	1.22	1.2	1.27	1.23	1.28	0.529
0.5	1.35	1.4	1.25	1.41	1.52	0.487
0.4	1.50	1.6	1.6	1.56	1.63	0.336
0.3	1.72	1.7	1.53	1.73	1.72	0.299
0.1	2.41	1.6	1.72	2.18	2.34	0.125
0.05	2.70	1.5	1.70	2.54	2.59	0.072

$f'_{2q_1} = \exp \cdot q \cdot \left(\frac{8}{26} x_1^2 + \frac{9}{26} x_1 \right)$

$f'_{2q_2} = \exp \cdot q \cdot \frac{17}{26} \cdot x_1^2$

Table IX

Acetic acid (1) — Benzene (2) — free liquid surface

$$W_\gamma = -1.11 \cdot 10^3 \text{ erg/mol}$$

$$q_\gamma = -0.045$$

x_1	f_1^I	f_1^I	$f_{\gamma_1}^I$	$f_{\gamma_1}^I$	$f_{\gamma_1}^I$	f_2^I	$f_{\gamma_2}^I$	$f_{\gamma_2}^I$	$f_{\gamma_2}^I$	$f_{\gamma_2}^I$
	I	II	III	IV	V	I	II	III	IV	V
0.05	2.55	2.52	0.962	0.973	2.62	1.005	1.03	1.000	0.980	1.03
0.1	2.35	2.26	0.966	1.004	2.34	1.02	1.04	0.999	0.980	1.04
0.3	1.92	1.57	0.981	1.20	1.60	1.14	1.14	0.995	1.00	1.14
0.4	1.69	1.35	0.987	1.23	1.37	1.27	1.27	0.990	0.992	1.28
0.5	1.38	1.29	0.990	1.06	1.30	1.25	1.49	0.983	0.823	1.52
0.6	1.30	1.12	0.995	1.15	1.13	1.60	1.60	0.980	0.893	1.63
0.7	1.29	1.11	0.996	1.16	1.10	1.53	1.63	0.978	0.890	1.72
0.9	1.07	1.02	0.999	1.05	1.02	1.72	2.26	0.966	0.735	2.34
0.95	1.03	1.01	1.000	1.02	1.01	1.70	2.49	0.962	0.658	2.59

$$f_i^I = \lg f_i = \lg f_i x_i - \frac{(\gamma_i - \gamma) \phi_i}{2.3 RT} - \lg x_i$$

$$f_i^{II} = f_{qi} f_{\gamma_i}$$

$$f_{\gamma_i}^{III} = \exp \cdot q_\gamma (1 - x_i)^2$$

$$f_{\gamma_i}^{IV} = \frac{f_i}{f_{qi}}$$

$$f_{qi}^V = \exp \cdot q \cdot \frac{17}{26} \cdot (1 - x_i)^2,$$

The free surface adsorption isotherm of the ethanol-water mixture is of type 3; the isotherm can be used to surface determination, too [2] (Fig. 12—15). Its significance is that the graphical evaluation of the free surface

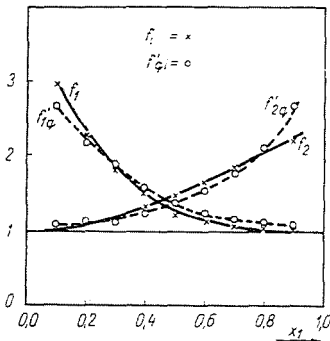


Fig. 15. Free surface activity coefficients of ethanol-water

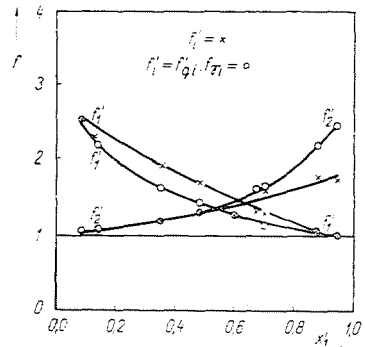


Fig. 16. Free surface activity coefficients of the mixture acetic acid benzene

isotherm after NAGY—SCHAY [2] proves the monomolecular surface layer [9]. At the acetic acid-benzene mixture it is interesting, that its free surface adsorption isotherm, too, has a change in sign.

On ground of these results it can be said that the thermodynamic investigations of free liquid surface adsorption cannot be thought as finished up. The correction of the activity coefficients with f'_i factor seemed to be an effective method in first approaching, it can be a hopeful beginning for further investigations. A further task is to increase the number of the investigated systems to extend the investigations to the solid surface adsorption and to complete the calculating method for f'_i .

Measuring methods

The measuring of the free surface adsorption (surface tension) was done with the modified stalagmometer, with the drop weight method [6].

The adsorption of the liquid mixture on solid surface was determined measuring the change in refractivity [2, 10].

Summary

Determining the activity coefficients of the components of the liquid mixtures in the interfacial phase, also the difference of the surface tension from the additivity was taken in account. The modification of the interpretation of the activity coefficients in the interfacial phase gives a good explanation to the appearance of the interfacial activity coefficients at the free surface and solid surface adsorptions of ideal mixtures.

Literature

1. GIBBS, J. W.: The Collected Works. Vol. I. Thermodynamics N. Y. 1931.
2. NAGY, L. GY., SCHAY, G.: M. Kém. F. **66**, 31 (1960).
3. HILDEBRAND, G. H., SCOTT, N. L.: Solubility of Nonelectrolytes. Reinhold, 1955. 406—415.
4. GUGGENHEIM, F. A.: Mixtures. Oxford, Univ. Press, 1952.
5. SCHAY, G., NAGY, L. GY., SZEKRÉNYESY, T.: M. Kém. F. **66**, 271 (1960).
6. SCHAY, G., NAGY, L. GY., SZEKRÉNYESY, T.: Per. Polytechn. **6**, 91 (1962).
7. SCHUCHOWITZKY, A.: Acta Physicochim. URSS, **176**, 508 (1944).
BELTON, J. W., EVANS, M. G.: Trans. Farad. Soc. **41**, 1 (1945).
DEFAY, R., PRIGOGINE, I.: Trans. Farad. Soc. **46**, 199 (1950).
8. PRIGOGINE, I.: The Molecular Theory of Solutions. North-Holland P. C. Amsterdam.
9. CORNFORD, P. V., KIPLING, J. J., WRIGHT, E. H. M.: Trans. Farad. Soc. **58**, 74 (1962).
10. SCHAY, G., NAGY, L. GY.: Reprint of the lecture on the Congress of the Hungarian Chemical Society, 1962.
11. SCHAY, G.: Acta Chimica Hung. **10**, 281 (1956).

L. GY. NAGY, Budapest, XI., Budafoki u. 8. Hungary.