COMPARATIVE STUDIES ON THE ADSORPTION EQUILIBRIUM OF LIQUID MIXTURES ON SOLID-LIQUID RESP. LIQUID-GAS INTERFACES

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Concerning the adsorption of liquid mixtures on solid surfaces, up till now many opposite and conflicting theories are sustained. In our opinion one of the main reasons for these contradictions lies in the widespread aim at interpreting liquid adsorption on the basis of certain analogies with vapour adsorption, whereas at the same time there is one fundamental difference between the character of these two types of adsorption: viz. in the case of vapour adsorption the degree of the surface coverage varies with the equilibrium concentration, whereas in that of liquid adsorption the surface is always completely covered and it is but the composition which can vary in the interfacial layer, similarly to liquid-gas interfaces. We investigated, therefore, whether an analogy could be found between these latter two types of adsorption, with the hope that by clearing up the problems related to the adsorption of liquid mixtures this will promote such investigations.

Thermodynamic discussion of unimolecular adsorption

It was previously [1] shown, that in the case of pure physical adsorption of completely miscible liquid pairs on solid surfaces, the interfacial layer can be considered, to a good approximation, as being practically unimolecular and the fact was briefly referred to that in this case thermodynamic relations ought to be valid, identical to those which were given by Hildebrand and others [2] for the adsorption taking place on free liquid surfaces in but one unimolecular layer. For each of the two components one may write accordingly:

$$\ln (f_i x_i) = \frac{(\gamma_i - \gamma)\,\Phi_i}{RT} + \ln (f'_i x'_i)\,; \quad (i = 1, 2) \qquad (1)$$

where $f_i\, x_i = a_i$ is the activity of the respective component in the bulk phase, f_i being its rational activity coefficient which is i unity in its pure state; γ_i resp. γ are the free surface energy excesses characteristic of the pure liquid resp. of the given composition (x'_i) in the interfacial phase; Φ_i is the molar value of surface required by component i(m^2/mmole); $f_i' x_i' = a_i'$ is its activity in the surface layer. The absolute values of γ for the solid-liquid interfacial layer cannot be determined. In the case of wetting liquids (for our investigations only such ones have to be taken into account) γ ought to be negative, the more so with the increasing strength of the adsorptive interaction with the solid surface. Hence, in contradistinction to the free liquid surface, γ does not mean an excess of free energy in the surface layer, but a corresponding deficiency. Equation (1) may also be interpreted by saying that in the interfacial layer the activity coefficient was split into two factors, the real activity coefficient being:

$$f_i^* = f_i' \cdot \exp \frac{(\gamma_i - \gamma)\,\Phi_i}{RT} \tag{2}$$

On the basis of relation (1), the equilibrium mole fraction (x') of the first component in the surface layer, forming from a completely miscible binary liquid pair, can be expressed:

$$x' = \frac{x}{\frac{f_2}{f_1} \cdot \frac{f_1^*}{f_2^*} \cdot (1 - x) + x} \tag{3}$$

where the ratio f_1^*/f_2^* can further be resolved into factors:

$$\frac{f_1^*}{f_2^*} = \frac{f_1'}{f_2'} \cdot \frac{\exp \frac{(\gamma_1 - \gamma)\,\Phi_1}{RT}}{\exp \frac{(\gamma_2 - \gamma)\,\Phi_2}{RT}} = \frac{f_1'}{f_2'} \cdot \exp \frac{\gamma_1 \Phi_1 - \gamma_2 \Phi_2}{RT} \cdot \exp \frac{(\Phi_2 - \Phi_1)\,\gamma}{RT} \tag{4}$$

The factor $\exp \frac{\gamma_1 \Phi_1 - \gamma_2 \Phi_2}{RT}$ is a constant characteristic of the difference in the adsorption potentials of the two components, its magnitude determined by the free molar surface energies for the individual pure materials.

The factor $\exp \frac{(\Phi_2 - \Phi_1)\,\gamma}{RT}$ occurs only when the molar areas of the components are different.

Concerning the adsorption at solid-liquid interfaces, it is well known for a long time that adsorption isotherms and hence the character of the adsorption can be divided in two main groups, according to whether there occurs a change in sign on the isotherm, *i.e.* whether in the whole concentration range it is the same component which is adsorbed more strongly or, depending on composition, the adsorption of one or of the other component is positive.

On the basis of relation (3), together with relation (4), the sign of the adsorption, or otherwise the alternative whether the ratio x'/x is greater or smaller than unity, is determined by the following factors:

1. The difference of the adsorption potentials of the pure components:

$$\exp \frac{\gamma_1 \Phi_1 - \gamma_2 \Phi_2}{RT}$$

2. The ratio of the activity coefficients of the components in the bulk liquid phase:

$$\frac{f_2}{f_1}$$

3. The ratio of the activity coefficients in the surface layer:

$$\frac{f_1'}{f_2'}$$

4. The variation of the free surface energy with the composition, in proportion to the difference of the molar areas:

$$\exp \frac{(\Phi_2 - \Phi_1)\, \gamma}{RT}$$

The condition of a change in sign is that γ should have an extremum value for the corresponding composition. Similarly as in the case of tension equilibrium, an extremum value of the vapour pressure can occur only if the tensions of the two pure components do not differ too much just as the adsorption taking place at the solid surface does not change its sign, *i. e.* the adsorption of one of the components remains positive ($x' > x$) everywhere, when the difference between the adsorption potentials is high enough.

In the case of the difference between the adsorption potentials being small, the variation of f_2/f_1 or of f_1^*/f_2^* can be such that the isotherm changes its sign (adsorption azeotrope). Since at this point $x = x'$, where also the equality $f_i = f_i^*$ has to be satisfied.

According to our investigations, in some cases the course of the isotherms, their changes of sign are decisively determined by the course of the ratio f_2/f_1 [3].

The physical interpretation of the activity coefficients of the components in the surface layer is still an unsolved problem. A preliminary condition for the clarification of the physical background is to determine their magnitude.

By graphical integration of relation (5), $(\gamma_1 - \gamma)\,\Phi_1$ and $(\gamma_2 - \gamma)\,\Phi_2$ can be determined [4] from experimental isotherms and thus, on the basis of relation (1) and in the knowledge of x_1', the magnitude and course of f_i' can be given:

$$\frac{\chi}{1-x} = -\frac{1}{RT}\,\frac{F d\gamma}{d \ln a_1} \tag{5}$$

$$\begin{aligned} (\gamma_1 - \gamma)\,\Phi_1 &= \frac{2{,}3\, RT\, \Phi_1}{F} \int_{a_1=1}^{a_1} \frac{\chi}{1-x}\, \mathrm{dlg}\, a_1 \\ (\gamma_2 - \gamma)\,\Phi_2 &= \frac{2{,}3\, RT\, \Phi_2}{F} \int_{a_2=1}^{a_2} -\frac{\chi}{x}\, \mathrm{dlg}\, a_2 \end{aligned} \tag{6}$$

$$f_i' = \frac{a_i}{x_i'} \exp\left[\frac{(\gamma_i - \gamma)\,\Phi_i}{RT}\right] \tag{7}$$

$$f_i^* = \frac{a_i}{x_i'} \tag{8}$$

Knowing the specific adsorption χ (mmole/g), the composition (x_i') in the interfacial phase can be computed$^{(1,3)}$ with the aid of the relations (9) and (10)

$$\chi = (n_1' + n_2')\,(x' - x) \tag{9}$$

$$F = n_1' \Phi_1 + n_2' \Phi_2 \tag{10}$$

$$x' = \frac{Fx + \Phi_2 \chi}{F + (\Phi_2 - \Phi_1)\,\chi} \tag{11}$$

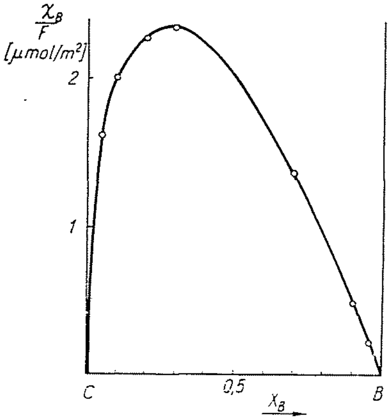

Fig. 1. Adsorption isotherm of the mixture benzene-cyclohexane on carbon black at 25° C

where n_1' and n_2' are the amounts of the two components contained in the surface layer (mmole/g ads) and F is the specific surface area of the adsorbent (m^2/g ads). Data characteristic of the adsorption equilibria in the system benzene-cyklohexane-carbon black are shown in Table I, and Figures 1—4

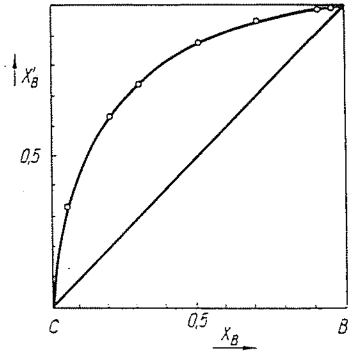

Fig. 2. The variation of composition of the mixture benzene-cyclohexane in the interfacial layer on carbon black (x') as a function of the equilibrium composition of the bulk liquid phase (x_B)

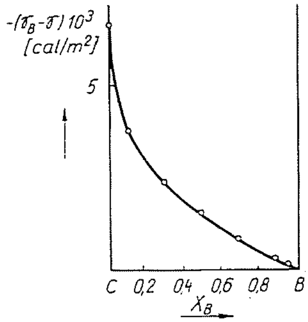

Fig 3. Variation of free surface energy of benzene-cyclohexane on carbon black

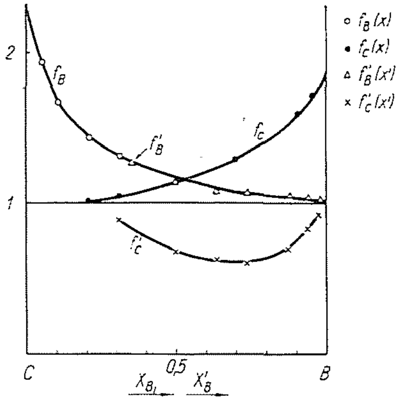

Fig. 4. Activity coefficients of the mixture acetic acid-benzene in the bulk and in the interfacial phases, respectively

For this system no adsorption azeotrope occurs, i. e. along the whole concentration range benzene is enriched only on the surface, γ_i for this component having the more negative value.

Concerning the course of the activity coefficients f_i', the question arises whether the splitting-off of the factor containing γ from the global activity

Table I

Benzene (1)-cyclohexane (2)-carbon black* ($F = 80$ m^2/g)
Benzene (1) ($\Phi_1 = 180$ m/^{2}mmole)

x	f_1	lg a_1	$\frac{\chi}{1-x}$	B_1	$(\gamma_1-\gamma)\,10^3$	x'	f_1^*	f_1'
0.05	1.94	—1.014	0.137	—0.274	—4.66	0.328	0.296	1.25
0.10	1.66	—0.780	0.178	—0.227	—3.86	0.498	0.344	1.12
0.20	1.42	—0.546	0.225	—0.171	—2.90	0.630	0.452	1.09
0.30	1.32	—0.402	0.265	—0.136	—2.31	0.737	0.538	1.09
0.50	1.17	—0.233	0.320	—0.086	—1.462	0.872	0.671	1.04
0.70	1.07	—0.124	0.357	—0.049	—0.832	0.942	0.796	1.02
0.90	1.00	—0.045	0.400	—0.019	—0.323	0.980	0.918	1.01
0.95	1.00	—0.021	0.400	—0.009	—0.153	0.991	0.959	1.00

Cyclohexane (2) ($\Phi_2 = 215$ m^2/mmole)

$1-x$	f_2	lg a_2	$-\frac{\chi}{x}$	B_2	$(\gamma_2-\gamma)\,10^3$	$(1-x')$	f_2^*	f_2'
0.05	1.69	—1.076	—0.02	0.376	6.39	0.009	9.44	0.923
0.10	1.58	—0.801	—0.04	0.367	6.23	0.020	8.78	0.910
0.30	1.27	—0.419	—0.16	0.331	5.62	0.058	6.36	0.818
0.50	1.12	—0.252	—0.32	0.301	5.11	0.128	4.29	0.668
0.70	1.03	—0.142	—0.62	0.248	4.22	0.263	2.73	0.587
0.80	1.01	—0.092	—0.90	0.210	3.57	0.370	2.18	0.594
0.90	1.00	—0.046	—1.60	0.162	2.75	0.502	1.74	0.650
0.95	1.00	—0.022	—2.60	0.110	1.87	0.672	1.41	0.885

$$B_i = \frac{(\gamma_i - \gamma)\,F}{2.3\,RT}; \quad B_1 - B_2 = \frac{(\gamma_1 - \gamma_2)\,F}{2.3\,RT} = -0.38; \quad f_i^* = \frac{a_i}{x_i'}$$

$$f_i' = f_i^* \exp\left(-\frac{(\gamma_i - \gamma)\cdot\Phi_i}{RT}\right): \quad \gamma_1 - \gamma_2 = -6.5.10^3 \text{ cal/m}^2$$

* The values x' are taken from literature [6]

coefficient f_1^* of the adsorption phase does not represent but a purely formal procedure, or else if it has a real physical meaning on the effect of interactions between the liquid molecules which are strongly affected by the force field of the solid surface.

It follows from equation (5) that the free surface energy excess γ assumes an extremum value where the isotherm changes its sign ($\chi = 0$). As it has

Table II

Acetic acid-benzene-charcoal ($F = 620$ m²/g)*
Acetic acid (1) ($\Phi_i = 120$ m²/mmole)

x	f_1	$\lg a_1$	$\frac{\chi}{1-x}$	B_1	x'	f_1^*	f_1'	$(\gamma_1-\gamma)\,10^4$
0.05	3.20	—0.796	1.11	—0.20	0.326	0.49	0.54	—4.4
0.1	2.82	—0.550	1.26	+0.10	0.386	0.73	0.69	2.2
0.3	2.20	—0.180	0.93	0.52	0.461	1.43	1.13	12.0
0.4	1.98	—0.101	0.42	0.59	0.463	1.71	1.31	13.0
0.5	1.71	—0.068	—0.30	0.60	0.465	1.84	1.39	13.3
0.6	1.50	—0.046	—1.40	0.59	0.470	1.92	1.48	13.0
0.7	1.32	—0.034	—3.17	0.52	0.475	1.95	1.56	11.2
0.9	1.06	—0.020	—10.6	0.21	0.571	1.67	1.52	4.7
0.95	1.02	—0.014	—24.4	0.10	0.673	1.44	1.37	2.2

Benzene (2) ($\Phi_2 = 180$ m²/mmole)

$1-x$	f_2	$\lg a_2$	$-\frac{\chi}{x}$	B_2	$(1-x')$	f_2^*	f_2'	$(\gamma_2-\gamma)\,10^4$
0.05	2.70	—0.869	1.28	0.56	0.327	0.41	0.28	12.3
0.1	2.41	—0.618	1.57	0.68	0.429	0.56	0.35	14.8
0.3	1.72	—0.287	1.36	0.97	0.525	0.98	0.51	21.3
0.4	1.50	—0.221	0.93	1.04	0.530	1.14	0.56	23.0
0.5	1.35	—0.170	0.30	1.06	0.535	1.26	0.62	23.3
0.6	1.22	—0.135	—0.62	1.05	0.537	1.36	0.67	23.0
0.7	1.14	—0.098	—2.16	1.01	0.539	1.48	0.75	22.2
0.9	1.03	—0.033	—11.3	0.56	0.614	1.51	1.03	12.0
0.95	1.01	—0.017	—21.2	0.26	0.674	1.41	1.18	5.7

$$B_i = \frac{(\gamma_i-\gamma)\,F}{2.3\,RT}\;;\quad B_1 - B_2 = \frac{(\gamma_1-\gamma_2)\,F}{2.3\,RT} = 0.46;\quad \gamma_1-\gamma_2 = -1.01.10^3\ \text{cal/m}^2$$

$$f_i^* = \frac{a_i}{x_i'}\;:\; f_i' = f_i^*\exp\left(-\frac{(\gamma_i-\gamma)\,\Phi_i}{RT}\right)$$

* The values f_i and Φ_i are taken from literature [6, 7].

already been mentioned, a change of sign can take place only when $\Delta\gamma_i$, the difference of the free surface energies of the pure components is small.

In view of relation (1) having been originally proposed for the adsorption on the free surface of liquids, it may be expected, that also in this latter case adsorption isotherms with changing sign should occur, but hitherto no investigations carried out from this point of view are to be found in literature.

Table III*

Acetic acid(1)-benzene(2), free liquid surface, at 25° C

x_1	f_1	lg a_1	$\gamma \cdot 10^{4}$* cal/m²	$d\gamma/d\lg a \cdot 10^{4}$ cal/m²	$\chi \cdot 10^{4}$ mmole/m²
		—	67.47		—
0.05	3.20	—0.795	66.68	—1.4	+1.00
0.1	2.82	—0.550	66.20	—2.0	+1.32
0.3	2.20	—0.180	65.08	—5.8	+2.98
0.4	1.98	—0.100	64.55	—11.0	+4.85
0.5	1.71	—0.068	64.00	—21.5	+7.90
0.6	1.50	—0.046	63.47	—15.0	+4.6
0.7	1.32	—0.034	63.23	—1.25	+0.27
0.9	1.06	—0.020	63.47	+29.5	—2.17

x_1	f_1	x_1'	f_1^*	f_1'	f_2	$1-x_1'$	f_2^*	f_2'
0.05	3.20	0.066	2.42	2.55	1.01	0.934	1.02	1.00
0.1	2.82	0.124	2.26	2.35	1.03	0.876	1.06	1.03
0.3	2.20	0.348	2.02	1.92	1.14	0.652	1.22	1.17
0.4	1.98	0.471	1.68	1.69	1.22	0.529	1.38	1.34
0.5	1.71	0.613	1.39	1.38	1.35	0.487	1.38	1.36
0.6	1.50	0.664	1.33	1.30	1.50	0.336	1.78	1.81
0.7	1.32	0.701	1.32	1.29	1.72	0.299	1.73	1.76
0.9	1.06	0.875	1.09	1.07	2.41	0.125	1.92	2.02
0.95	1.02	0.928	1.04	1.03	2.70	0.072	1.88	2.01

$$f_i^* = \frac{a_i}{x_i'}$$

* The surface tension values are taken from the curve drawn through the experimental points.

The starting point of our further investigations was the criterion that γ has to assume an extremum value at the point of the changing sign. We searched for mixtures with an extremum value on their surface tension curves and chose the mixture acetic acid-benzene for a thorough examination. The slightness in the difference between the surface tensions of these two components corroborates our statement, showing this as one of the conditions to be fulfilled for the sign to change (extremum value of the surface tension).

Table II shows the course of the activity coefficients in the system acetic acid-benzene-charcoal, whereas table III contains our determinations of the

Table IV

Ethanol-benzene, free liquid surface, at 25° C*

x_1	a_1	$\lg a_1$	$\gamma \cdot 10^4$ cal/m²	$d\gamma/d\lg a_1 \cdot 10^4$ cal/m²	$\chi \cdot 10^4$ mmole/m²
0.254	0.597	—0.224	61.0	—14.0	0.77
0.298	0.629	—0.201	60.5	—20.0	1.05
0.335	0.660	—0.181	60.0	—46.0	2.26
0.362	0.673	—0.172	59.65	—57.0	2.66
0.630	0.755	—0.122	56.6	—60.0	1.63
0.836	0.861	—0.065	53.6	—55.0	0.66

x_1	f_1	x_1'	f_1^*	f_1'	f_2	$1-x_1'$	f_2^*	f_2'
0.254	2.35	0.376	1.59	1.07	1.27	0.624	1.52	1.33
0.298	2.11	0.457	1.38	1.66	1.33	0.543	1.72	1.49
0.335	1.97	0.653	1.01	1.225	1.38	0.347	2.65	2.26
0.362	1.86	0.725	0.93	1.12	1.42	0.275	3.29	2.27
0.630	1.20	0.841	0.90	1.02	2.16	0.159	5.04	3.87
0.836	1.03	0.919	0.94	1.00	3.06	0.081	6.20	4.34

* The values γ and f_i are taken from literature [6, 8].

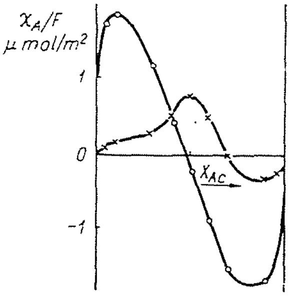

Fig. 5. Adsorption isotherm of the acetic acid-benzene mixture on charcoal and on the free liquid surface at 25° C. o = charcoal (620m²/g); × = free surface

dependence on concentrations of the surface tension of the mixture acetic acid-benzene, of the free liquid surface adsorption isotherm and of the course of the activity coefficients in the free liquid interfacial layer. As regards the course of f_i^*, the following should be kept in mind

$f_i^* < f_i$ in the range $x'_i > x_i$

$f_i^* = f_i$ at the point $x'_i = x_i$ (azeotrope)

$f_i^* > f_i$ in the range $x'_i < x_i$

Figures 5—9 show the adsorptive behaviour of the mixture acetic acid-benzene on charcoal and on the free surface, respectively. Contrary to the adsorption of solid surfaces on the free surface the course of the f'_i-s does not differ in its character from that of the f_i-s.

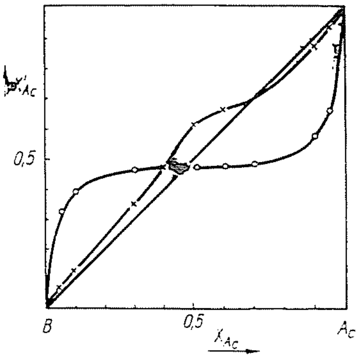

Fig. 6. Equilibrium diagram of the acetic acid-benzene mixture at 25° C. o = charcoal (620 m²/g); × = free surface

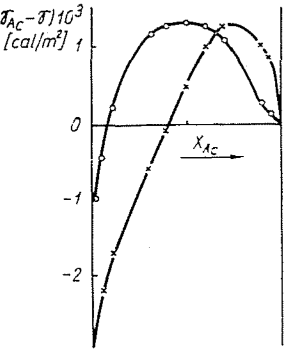

Fig. 7. Free surface energy excess of the acetic acid-benzene mixture on charcoal and on free surface. o = charcoal (620 m²/g); × = free surface

In Table IV, data characteristic of the adsorption on the free liquid surface of ethanol-benzene mixtures, whereas in Tables V and VI those on charcoal from the same system, and comparative data of these two kinds of adsorption isotherms are to be found (Figures 10—14).

In Figure 10 the adsorption isotherms of the system ethanol-benzene, measured on two types of charcoal and on the free liquid surface, are illustrated. On the solid surface, there appears an adsorption azeotrope, whereas on the

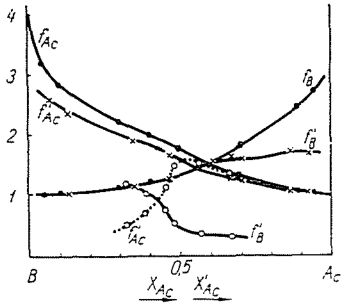

Fig. 8. Activity coefficients of the acetic acid-benzene mixture in bulk and interfacial phases, respectively. ● $f_{Ac}(x) : f_B(x)$; ○ $f_{Ac}(x'): f_B(x')$: on charcoal; × $f_{Ac}(x'); f_B(x')$: free surface

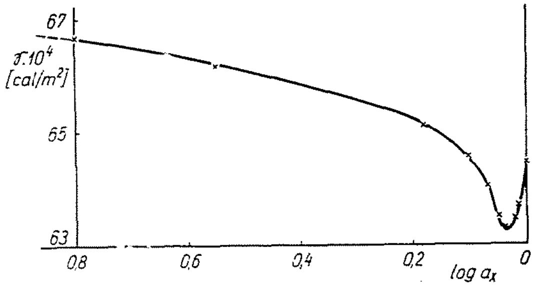

Fig. 9. γ — lg a diagram of the acetic acid-benzene mixture for the determination of surface concentrations

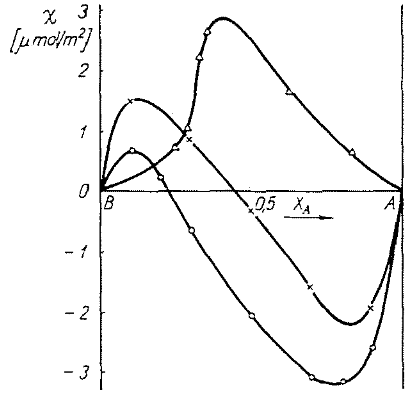

Fig. 10. Adsorption isotherms of the ethyl alcohol-benzene mixture on charcoal and on free liquid surface, at 25° C, respectively. ○ = charcoal, 615 m²/g; × = charcoal, 620 m²/g; △ = free surface (8)

free surface it is always the alcohol which is enriched (hence, from the point of view of the type of isotherm, this latter ought to be compared to the system benzene-cyclohexane-charcoal). It can be seen from the curves f_i, shown in Figures 13—14, that on the free surface the values f_i do not greatly differ from the corresponding values f_i, whereas on the solid surfaces the respective courses are considerably different and are not even the same for the two types of charcoal. This seems to strengthen our assumption that the resolution of the activity coefficients is not a mere formalism.

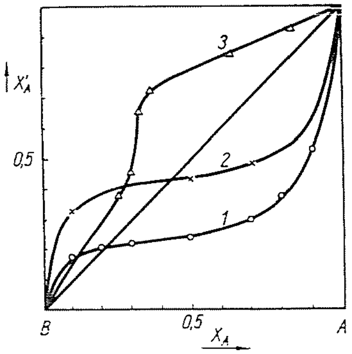

Fig. 11. Adsorption equilibrium diagram of the ethyl alcohol-benzene mixture at 25° C. ○ = charcoal, 615 m²/g (6); × = charcoal, 620 m²/g; △ = free surface

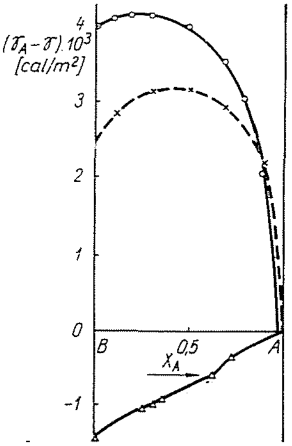

Fig. 12. The variation of the free surface energy of the ethyl alcohol-benzene mixture, as a function of equilibrium concentrations. ○ = charcoal (615 m²/g) (6); × = charcoal (620 m²/g); △ = free surface (8)

Table V

Ethanol(1)-benzene(2)-charcoal (620 m²/g)
Ethanol(1) ($\Phi_1 = 120$ m²/mmole)

x	f_1	$\log a_1$	$\frac{\chi}{1-x}$	B_1	$(\gamma_1-\gamma)\,10^3$	x'	f_1^*	f_1'
0.10	4.97	—0.303	1.02	1.28	2.81	0.331	1.50	0.85
0.30	2.10	—0.201	0.714	1.40	3.08	0.411	1.53	0.86
0.50	1.45	—0.140	—0.4	1.40	3.08	0.432	1.68	0.89
0.70	1.12	—0.106	—3.24	1.30	2.85	0.482	1.66	0.92
0.90	1.02	—0.037	—12.0	1.00	2.20	0.620	1.48	0.95

Benzene(2) ($\Phi_2 = 180$ m²/mmole)

$1-x$	f_2	$\log a_2$	$-\frac{\chi}{x}$	B_2	$(\gamma_2-\gamma)\,10^3$	$1-x'$	f_2^*	f_2'
0.10	3.66	—0.436	1.33	—0.17	—0.373	0.380	0.96	1.08
0.30	2.43	—0.137	1.38	0.14	0.308	0.518	1.41	1.29
0.50	1.74	—0.060	0.4	0.22	0.483	0.568	1.53	1.33
0.70	1.33	—0.034	—1.66	0.23	0.505	0.589	1.58	1.36
0.90	1.08	—0.012	—9.2	0.12	0.264	0.669	1.45	1.34

$$B_i = \exp\frac{(\gamma_i - \gamma)\,F}{2.3\,RT}$$

$$B_1 - B_2 = \frac{(\gamma_1 - \gamma_2)\,F}{2.3\,RT} = 1.1$$

$$\gamma_1 - \gamma_2 = 2.5\cdot 10^{-3}\ \mathrm{cal/m^2}$$

$$f_i^* = \frac{a_i}{x_i'}$$

$$f_i' = f_i^*\cdot\exp - \frac{(\gamma_i - \gamma)\,\Phi_i}{RT}$$

In Table VII, surface tension values taken from earlier literature [5] are quoted for some binary liquid mixtures, whose surface adsorption isotherms show a reversal of sign. Although the reliability of these data may be questioned, as it can be safely stated that there exist completely miscible liquid pairs, for which the free surface adsorption reverses its sign.

A closer examination of the liquid pairs quoted in Table VII reveals that the two conditions for the occurrence of isotherms with changing sign are the same as in the case of the adsorption on solid-liquid interfaces: *i. e.* an only small difference of the surface tensions of the pure components and

Table VI

Ethanol — benzene

Charcoal (615 m²/g)			Charcoal (620 m²/g)			Liquid surface		
X_A	χ_A	χ_A/F	X_A	χ_A	χ_A/F	X_A	γ_A	γ_A/F
0.1	0.39	0.63	0.1	0.92	1.48	0.0	6.52	—1.47
0.2	0.152	0.248	—	—	—	0.255	6.10	—1.05
0.3	—0.40	—.065	0.3	0.50	0.807	0.30	6.05	—1.00
0.5	—1.26	—2.05	0.5	—0.20	—0.323	0.335	6.00	—0.95
0.7	—1.88	—3.06	0.7	—0.77	—1.56	0.36	5.96	—0.91
0.8	—1.94	—3.16	—	—	—	0.63	5.66	—0.61
0.9	—1.58	—2.57	0.9	—1.2	—1.94	1.00	5.05	0.0

$* \chi = \frac{\text{mmole}}{\text{g} \cdot \text{ads}}$

$F = \text{m}^2/\text{g} \cdot \text{ads}$

a rather considerable deviation from the ideal behaviour. Thus, for instance, the difference of the surface tensions of benzene and toluene is small ($\Delta\gamma_{1,2} = 0.35$ erg/cm²), but their mixture can be considered as practically an ideal one, therefore, the surface tension has no extremum value.

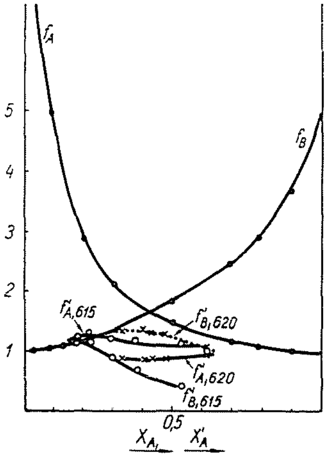

Fig. 13. Activity coefficients of the ethyl alcohol-benzene mixture in bulk phase and in solid-liquid interface, respectively. ● $= f_i(x)$; ○ = 615 m²/g; × = 620 m²/g: $f'_i(x')$ charcoal

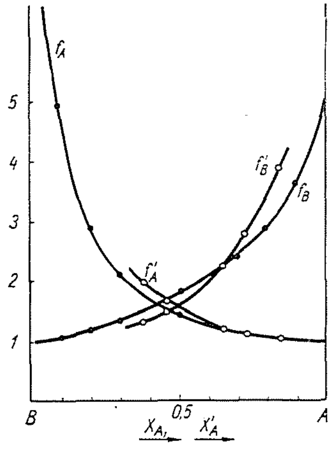

Fig. 14. Activity coefficients of the ethyl alcohol-benzene mixture in bulk phase and on free surface, respectively. ● $= f_i(x)$; ○ $= f'_i(x')$ free surface

Table VII*

Mixture	t C°	γ_o	γ_m	x_{1m}	Note
Carbon tetrachlorid (1) Chloroform (2)	18	27.00 27.33	26.92	0.5	
Carbon tetrachlorid (1) Acetic acid (2)	18	27.00 28.08	26.26	0.5	
Ethylene dichloride (1) Carbon disulfide (2)	18	32.66 32.24	30.63	0.5	
Chloroform (1) Acetic acid (2)	18	27.33 28.08	26.62	0.4	
Acetone (1) Methanol (2)	30	22.34 21.81	22.55	0.4	maximum?
Ethylene bromide (1) Acetic acid (2)	78	25.90 21.81	21.68	0.1	
Chloro benzene (1) Ethylene bromide (2)	13	34.43 40.16	34.29	0.1	
Ethyl iodide (1) Acetic acid (2)	18	28.08 28.83	26.69	0.4	
Toluene (1) Acetic acid (2)	18	29.21 27.57	27.50	0.3	
Ethyl iodide (1) Benzene (2)	18	28.83 28.94	28.61	0.5	
i-Amyl alcohol (1) Ethyl acetate (2)	18	24.29 24.22	24.13	0.8	

* γ_0 = surface tension of pure liquid,
γ_m = extremum value of the surface tension,
x_{1m} = mole fraction at the extremum value.

Method for the determination of the adsorption of free liquid surfaces

The investigation of the properties of the free liquid surface phase was carried out by measuring the surface tension, using the drop weight method [9].

A sketch of the modified stalagmometer used is shown in Figure 15. Electrolytic gas is developed from the sodium hydroxide solution contained in vessel *A*. The uniformity of the current is ensured by a stabilized power supply as well as by a high resistance, in series with the cell. By the pressure of the uniformly developing electrolytic gas, the liquid to be investigated flows from reservoir *B* into the tempered stalagmometer *C*, and drops out from there into the weighing vessel *D*. Into the latter a certain initial amount from the liquid to be measured has to be introduced in order to ensure equilibrium of the drop with its own vapour. The vapour space is conveniently shut off by the upper bubble vessel also filled with the liquid to be measured.

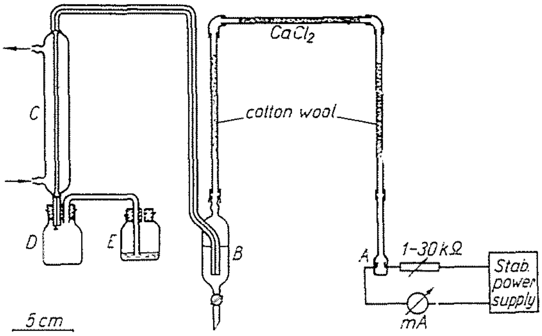

Fig. 15. Stalagmometer for measuring surface tension using the drop weight method

The lower capillary end of the stalagmometer is shaped according to the usual prescriptions, outer diameter 7.0 mm, bore diameter 0.78 mm.

The sensibility resp. accuracy of the drop weight method depends on the following factors:

1. thermostating,
2. number of drops to be weighed,
3. speed and uniformity of dripping,
4. eventual concentration change due to evaporation and
5. purity of vessels and of the material itself.

Ad 1. Thermostating was better than ±0.05° C. Since the temperature coefficients of the surface tension of water and butyl-alcohol[1] are $\left(\frac{d\gamma}{dt}\right)$: —0.15 and —0.08 dyn cm^{-1} $degree^{-1}$, respectively, the maximal error caused by the temperature uncertainty amounts to ±0.008, resp. ±0.004 dyn/cm, which corresponds to ±0.01% for water and to ±0.02% for butyl-alcohol.

Ad 2—4. Somewhat conflicting requirements are raised by the factors enumerated in items 2—4. In order to get the maximum out of the sensibility of the analytical balance the number of drops ought to be high, at the same time the speed of dripping has to be greatly decreased, or else the kinetic energy at the separation of the drop cannot be neglected. For the diminution of the errors due to evaporation, the measurement has to be carried out, on the other hand, as rapidly as possible. Hence, the optimal measuring conditions had to be established by simultaneous consideration of the above-mentioned factors. The error due to evaporation was eliminated by producing at the very beginning a vapour space of equilibrium composition in the measuring vessel *D*. According to preliminary experiments, a rate of two drops per minute and a total amount of 20 drops proved to be the most favourable conditions.

Ad 5. The substances employed were:

distilled water;
analytically pure benzene (Chinoin), distilled fractionally from over sodium, and crystallized four times fractionally; acetic acid distilled fractionally twice and crystallized four times fractionally.

The reproducibility of the measurements was first examined for water and benzene which are accepted as bases of reference. The pertaining data are contained in Table VIII, where *g* is the weight of 20 drops, in mgs. In order to be able to reproduce the drop weight measurements with such accuracy (of 0.05%), apart from controlling the conditions already described above, the stalagmometer had to be suspended on a rubber strip to adequately prevent the vibration of the pending drop.

The ratio of the two surface tensions (water/benzene) is $2.54_3 \pm 0.1\%$, according to data from literature, whereas from our measurements we have: $2.52_0 \pm 0.07\%$. According to literature, the surface tension of acetic acid at the temperature of 25.0° C lies between 26.9—27.3 erg/cm^2, whereas, as a result of our own measurements we obtained 26.98 ± 0.015 erg/cm^2.

For the computation of absolute values of surface tensions, either the value of the surface tension of water (primary standard) or that of benzene (secondary standard) usually serve as a basis. For aqueous solutions, logically pure water, whereas for organic mixtures, particularly mixtures containing benzene, the surface tension of benzene is considered as the reference basis.

The kind of relation assumed between the surface tension and the drop weight presents, however, a problem of its own. According to the simplest, but only approximative relation, the surface tension is directly proportional to the drop weight at the moment of dripping, this weight being just equal to the surface forces acting at the separation limits (circumference of a circle)

$$2r\,\pi\gamma = g \tag{12}$$

where r = the radius of the contact circle.

Hence

$$\gamma = \frac{1}{2\,r\pi}\cdot g \tag{13}$$

the relation is a linear one, and the proportionality factor is the circumference of the circle. In order to calculate the surface tensions from the drop weight for different substances with the aid of this relation, it has to be assumed that the proportionality factor is independent of the drop's substance, i. e. that the contact circle of the separating drop is identical for any substance. In principle this assumption is not correct, just because of the difference of the surface tensions, the dimensions of the drops, and owing to this fact also the circumferences of the contact circles may differ for different substances. The situation becomes even more complicated because the drop does not break off instantaneously. And so after the breakdown of the above force equilibrium a drop more or less smaller than that corresponding to this equilibrium falls down.

To account for these phenomena, empirical correction factors are generally applied to relation (13).

According to the procedure of Harkins and Brown, which is mostly accepted in literature [11, 12], the weight of the drop ought to be multiplied by a correction factor depending on V/r^3 and this corrected value has to be substituted into relation (13) in order to obtain a correct value for the surface tension (V = the volume of the drop which can be calculated in the knowledge of the specific weight of the liquid; r = the outer radius of the stalagmometer tube end).

According to their measurements the factor suggested by Harkins and Brown is independent of the stalagmometer material and of the liquid, and can be well reproduced.

Table VIII

The dispersion of the drop weight measurements (at 25.0° C)

g_{water}	Δ	Δ^2	$g_{benzene}$	Δ	Δ^2
1870.4	—6.2	38.5	743.5	—0.8	0.64
1875.3	—1.3	1.69	743.0	—1.4	1.96
1878.5	+1.9	3.61	745.0	+0.6	0.36
1878.7	+2.1	4.41	743.9	—0.5	0.25
1873.2	—3.4	11.56	746.8	+2.4	5.76
1877.7	+1.1	1.21	743.8	—0.6	0.36
1878.7	+2.1	4.41	744.8	+0.4	0.16
1777.9	+1.3	1.69			
1879.0	+2.4	5.76			

Mean value: 1876.6 744.4

Standard deviation: ±1.0 = ±0.05%; ±0.4 = ±0.06%

$$\left(\sqrt{\frac{\Delta^2}{n^2}}\right)$$

However, computing our own data of measurements by assuming simple proportionality according to (13), a better agreement with surface tension values, considered as the most reliable ones in literature, was obtained.

In view of the failure of a better and absolutely reliable method, the surface tension values were, therefore, computed in this manner.

It should be noted, that the determination of absolute surface tension values with the precision needed in our case (about ±0.05%) cannot be considered as a solved task, as can be seen by surveying data given in literature. The probable errors of the surface tension values indicated in literature as well as the deviations between different author's values exceed the ±0.05% limit (for acetic acid, for instance, one finds about ±1%). For the satisfactory solution of the problem, we intend to carry out further measurements, not only by the drop weight but also by other methods.

Method adopted for investigating the adsorption on solid-liquid interfaces

As it is known, the determination of the adsorption taking place from liquid mixtures on solid interfaces is carried out by immersing the adsorbent into a solution of known amount (V°, H°) and of known initial composition (c°, x°) and by measuring the final equilibrium composition in the bulk phase (c, x).

The conditions for the reproducibility of the adsorption isotherms of binary mixtures are:

1. Strict absence of any other components in the initial and equilibrium mixtures besides the two in question;
2. Real establishment of adsorption equilibrium;
3. Constancy of temperature;
4. Application of an adequate analytical method.

Fulfilment of the first condition is the most strenuous requirement. It means, namely, that the components forming the mixture should be extremely pure, hence, for instance, completely free from water, and that the adsorbent cannot be allowed to contain any components, impurities, water, which are soluble in the mixture in question. The complete removal of water from the liquid components as well as that of the soluble ash and humidity contents of the adsorbent is a task requiring great and lengthy labour.

The correct choice of the of ratio amounts of liquid and of adsorbent is another decisive condition for the isotherm to be reproducible. The following contradictory requirements have to be satisfied:

a) The polluting effect of the adsorbent should be negligible: high liquid-adsorbent ratios are desirable.

b) The concentration change caused by adsorption should be high, in order to facilitate a more exact determination: this means a small liquid-adsorbent ratio. In the case of a sufficiently great concentration change, for the mixtures benzene-ethylalcohol or acetic acid-benzene, for instance, instead of the interferometer also an immersion refractometer could be conveniently used, because only small amounts are needed and the determinations are quicker and simpler than measurements carried out by interferometer.

In the case of particles having a diameter of 0.3—1.0 mm, the equilibrium of physical adsorption is practically completely established within 8 hours. At the end of the first hour 70—90% of the equilibrium value can be measured.

The temperature dependence of the adsorption of mixtures ethyl alcohol-benzene was examined between 0—40° C on silica and charcoal. The maximum temperature coefficient is $\frac{1}{\chi} \cdot \frac{\Delta \chi}{\Delta t} \cdot 100 = 0.5\%$ on silica and 0.3% on charcoal respectively.

To determine the concentration changes of binary nonelectrolyte or weak electrolyte mixtures, in the majority of cases measurement of the refractive index and especially the interferometric method is the most suitable one. Because of the high sensitivity of the interferometer, in fact, the determination of concentration changes in almost any mixture is possible (with a 10 mm cuvette, a change of $2 \cdot 10^{-6}$, with that of 20 mm, one of $1 \cdot 10^{-6}$ and with the 40 mm cuvette, a change of $5 \cdot 10^{-7}$ can be measured in the refractive index). Determinations of adsorption isotherms by this method, however, become rather cumbersome, and for this reason the possibilities for using other methods have been investigated. One of these is the use of the temperable double prism immersion refractometer. Its sensitivity is $1.5—2 \cdot 10^{-5}$ refractivity units. Though this method requires very careful thermostating owing to the high temperature coefficient, but an amount of 0.1 ml of liquid is sufficient (the volume of the 20 mm cuvette of the interferometer is 6 + 6 ml), and the measurement can quickly be carried out. It is to be noted that also the interferometer has to be tempered and until the temperature is not quite equalized in the cells, the band system is blurred and migrating; the equalization time amounts to 5—10 minutes and depends greatly on the temperature coefficient of the refractivity of the mixture in question. With the immersion refractometer, the temperature of the thermostat is rapidly taken up (in 30—50 second) by the small amount of liquid on the prism.

The use of the immersion refractometer is restricted, but not excluded by its lesser sensitivity. It proved suitable in the case of mixtures for which the difference of the refractivities of the components is great enough, and also the concentration change arising from adsorption is sufficiently great.

In Table IX, the differences in the refractivities of the components of some mixtures as well as the concentration changes (Δx) corresponding to a change of $2 \cdot 10^{-5}$ in the refractivity are contained (i. e. the change which can be detected by the immersion refractometer).

Table IX

Mixture	n_D^{25}	Δn_D^{25}	$\Delta x \cdot 10^4$
Methyl alcohol Benzene	1.32661 1.49793	0.17132	1.16
Ethyl alcohol Benzene	1.35944 1.49793	0.13849	1.44
n-Propyl alcohol Benzene	1.38358 1.49793	0.11435	1.74
Acetic acid Benzene	1.37003 1.49793	0.1279	1.56

Summary

The adsorptive properties of completely miscible binary liquid systems on free liquid and solid-liquid interfaces have been compared. It could be ascertained that in both cases the same two conditions have to be fulfilled for a reversal of the sign of the adsorption: the surface free energies of the pure components have to differ only to a small extent and the mixture must deviate from the ideal behaviour.

Adsorption on the free liquid surface was examined by surface tension measurements using the drop weight method, by a modified stalagmometer. The optimal measuring conditions were chosen taking into account the factors influencing the precision.

The adsorption on solid surfaces can be determined by the concentration changes occurring in the liquid phase. We investigated the conditions to be fulfilled for the mixture adsorption isotherms being reproducible, and also in which cases could the concentration changes be determined by the tempered double prism immersion refractometer, instead of the more complicated interferometric method.

Literature

1. Nagy, L. Gy., Schay, G.: M. Kémiai F., 66, 31 (1960)
2. Hildebrand, J. H., Scott, N. L.: Solubility of Nonelectrolytes (Reinhold, 1955) 406—415
3. Schay, G., Nagy, L. Gy.: J. Chim. Phys. **149** (1961)
4. Gibbs, J. W.: The Collected Works, Vol. I, Thermodynamics N. Y. 1931
5. International Critical Tables, Mc Graw Hill, New York, 1928, vol. IV.
6. Blackburn, A., Kipling, J. J., Tester, D. A.: J. Chem. Soc. 2373 (1957)
7. Landolt, Börnstein, Roth: Tabellen. Springer, Berlin, 1923—36
8. Morgan, L. R., Scarlett, A. J.: J. A. C. S. **39**, 2275 (1917)
9. Partington: An Advanced Treatise on Physical Chemistry. Longman, London 1951. Vol. II. 182. 1.
10. Weissberger: Physical Methods of Organic Chemistry. Interscience, New York, 1949, Part I. Vol. I. 373
11. Weissberger: Technique of Organic Chemistry, Interscience. New York, 1955. Vol. VII.
12. Lange: Handbook of Chemistry. Handbook, Sandusky, Ohio, 1949.

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