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## RELATION BETWEEN ADSORPTION FROM BINARY SOLUTIONS AND ADSORPTION OF PURE GASEOUS COMPONENTS ON THE SAME ADSORBENT. THE EFFECT OF THE BULK LIQUID PHASE

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*Dedicated to Professor E. Hála on the occasion of his 60th birthday.*

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The thermodynamic consistency test proposed by Sircar and Myers was employed to show the effect of the bulk liquid phase on the adsorption from solutions on a solid adsorbent. This effect can invalidate the prediction of the isotherm of the concentration change in a solution from experimental adsorption isotherms of pure components adsorbed from the gaseous phase on the same adsorbent.

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In our earlier work<sup>1</sup> we have derived a relation which enables to calculate the isotherm of the concentration change in dependence on the composition of the solution from adsorption isotherms of pure gaseous components on the assumption that the adsorption potentials,  $\Phi_1$  and  $\Phi_2$ , which are equal to the work necessary to transfer 1 mol of component 1 resp. 2 from the solution to its interfacial layer, are equal to the adsorption potentials  $\Phi'_1$  and  $\Phi'_2$ , which correspond to the adsorption of pure components from the gaseous phase and which are consequently equal to the work necessary to transfer one mol of molecules from the pure gaseous phase to the adsorbent surface.

In our work we want to discuss the relation between adsorption of pure components from the gaseous phase and adsorption from a solution from the point of view of the thermodynamic consistency test as proposed by Sircar and Myers<sup>2-4</sup>. These authors started from the assumption that the integration of the Gibbs-Duhem equation for a condensed phase

$$n_1^{\circ} d\mu_1^{\circ} + n_2^{\circ} d\mu_2^{\circ} + n_A d\mu_A = 0 \quad (1)$$

forms after three steps a closed cycle.  $n_1^{\circ}$ ,  $n_2^{\circ}$  are the mass amounts of mol of component 1 and 2 in the adsorbed phase,  $n_A$  is the mass amount of the adsorbent,  $\mu_1^{\circ}$ ,  $\mu_2^{\circ}$  are chemical potentials of component 1 and 2 in the adsorbed phase and  $\mu_A$  is the chemical potential of the adsorbent. The first step of the closed path considered by the authors is the adsorption of pure gaseous component 2 from zero pressure up to the

saturated vapour pressure, during the second step the component 1 is added to the adsorbent and adsorbate immersed in the liquid component 2 and its mole fraction changes from zero to unity and the third step is desorption of pure gaseous component 1. By connecting relations corresponding to these three steps, the authors derived the following thermodynamic consistency test:

$$\int_0^{P_2^0} \frac{n_2^0}{P} dP - \int_0^{P_1^0} \frac{n_1^0}{P} dP + \int_0^1 \frac{\Omega}{\gamma_1 x_1 x_2} d(\gamma_1 x_1) = 0, \quad (2)$$

where  $P_1^0$ ,  $P_2^0$  are saturated vapour pressures of components 1 and 2,  $x_1$ ,  $x_2$  are mole fractions in the solution and  $\gamma_1$  is the activity coefficient. The quantity  $\Omega$  is the difference between mass amounts of component 1 in the solution before the adsorption and in the equilibrium solution, resp.; it is related to unit mass of the adsorbent.

### THEORETICAL

Now let us consider relation (2) from the point of view of the thermodynamics of a system in a force field and employ relations derived earlier<sup>5</sup> for the adsorption from the gaseous phase and from the solution. The first two terms in Eq. (2) can then be expressed as:

$$\int_0^{P_1^0} \frac{n_1^0}{P} dP = \int_0^{\text{sat}} \int_0^{\theta} \frac{d\Phi'_1}{RT} Dn_1^0 = \frac{1}{RT} \int_0^{\text{sat}} \int_0^{\theta} d\Phi'_1 Dn_1^0 = \frac{1}{RT} \int_0^{\theta} \Phi'_1 Dn_1^0, \quad (3)$$

where  $\Phi'_i$  is the adsorption potential of component  $i$  at a definite point of the adsorption space of the solid adsorbent,  $Dn_i^0$  is the mass amount adsorbed in an infinitesimal layer and related to unit mass of the adsorbent and the symbol  $\theta$  below the integral sign denotes integration over the whole adsorption space at the saturated vapour pressure of the adsorbed substance.

Replacing  $\Omega$  in the third term of Eq. (2) by the following earlier derived expression<sup>5,6</sup>, we obtain

$$\Omega = x_1(1 - x_1) \int_0^{\theta} \frac{1 - e^f}{x_1 + (1 - x_1)e^f} Dn^0, \quad (4)$$

where  $f = (\Phi_1 - \Phi_2)/RT$ ;  $\Phi_1$  and  $\Phi_2$  are the adsorption potentials, which are sums of potentials due to the force field of the solid adsorbent,  $\Phi'_1$  and  $\Phi'_2$ , and to the force field of the solution,  $\Phi''_1$  and  $\Phi''_2$ :

$$\Phi_1 = \Phi'_1 + \Phi''_1 \quad \Phi_2 = \Phi'_2 + \Phi''_2. \quad (5)$$

Eq. (4) was derived on the assumption that the solutions either behave ideally or that their behaviour is identical in the bulk phase and in the interface.

The third term in Eq. (2) is then given by:

$$\begin{aligned} \int_0^1 \frac{\Omega}{x_1(1-x_1)} dx_1 &= \int_0^1 \int_0^1 \frac{1-e^f}{x_1+(1-x_1)e^f} Dn^\omega dx_1 = \\ &= \int_0^1 \int_0^1 \frac{1-e^f}{x_1+(1-x_1)e^f} dx_1 Dn^\omega. \end{aligned} \quad (6)$$

If  $f$  does not depend on  $x$ , the integration can be performed to yield:

$$\int_0^1 \int_0^1 \frac{1-e^f}{x_1+(1-x_1)e^f} dx_1 Dn^\omega = - \int_0^1 f Dn^\omega = - \int_0^1 \frac{\Phi_1 - \Phi_2}{RT} Dn^\omega. \quad (7)$$

By connecting Eqs (2), (3), (5), (6), (7) we obtain:

$$- \int_0^1 \frac{\Phi'_2}{RT} Dn^\omega + \int_0^1 \frac{\Phi'_1}{RT} Dn^\omega - \int_0^1 \left( \frac{\Phi'_1 + \Phi''_1}{RT} - \frac{\Phi'_2 + \Phi''_2}{RT} \right) Dn^\omega = 0. \quad (8)$$

This equation is valid only if the difference between the adsorption potentials ( $\Phi''_1 - \Phi''_2$ ), which represents the effect of the liquid phase, is small in comparison with the difference between the adsorption potentials of the solid adsorbent:

$$|\Phi''_1 - \Phi''_2| \ll |\Phi'_1 - \Phi'_2|. \quad (9)$$

The thermodynamic consistency test expressed by Eq. (2) is then satisfied only in the case when the adsorption from the liquid phase and the adsorption from the equilibrium vapour phase are identical. The deviation of the left-hand side of Eq. (2) from zero,  $\Delta$ , will represent the effect of the force field of the solution on the adsorption from the liquid phase. The following expression is then obtained for  $\Delta$  from relation (8):

$$\Delta = - \int_0^1 \frac{\Phi''_1 - \Phi''_2}{RT} Dn^\omega. \quad (10)$$

The effect of a solution on adsorption from the liquid phase can be evaluated from the composition dependence of the surface tension of a binary solution. For this dependence, the following relation was derived<sup>7</sup> from the thermodynamic condition of equilibrium in a force field

$$\sigma_x = \sigma_1 - RT \int_1^x \int_{\theta''} \frac{1 - e^{f''}}{x_1 + (1 - x_1)e^{f''}} Dn^{\omega} dx_1, \quad (11)$$

where  $\sigma_x$  is the surface tension of the solution with the mole fraction  $x_1$ ,  $\sigma_1$  is the surface tension of pure component 1, the symbol  $\theta''$  below the integral sign denotes integration over the whole adsorption space related to unit area of the interface and  $f'' = (\Phi_1'' - \Phi_2'')/RT$ . If  $f''$  does not depend on the composition of the solution, Eq. (11) can be integrated to yield:

$$\sigma_x - \sigma_1 = -RT \int_{\theta''} \ln [x_1 + (1 - x_1)e^{f''}] Dn^{\omega} \quad (12)$$

and for  $x_1 = 0$

$$\sigma_2 - \sigma_1 = -RT \int_{\theta''} \frac{\Phi_1'' - \Phi_2''}{RT} Dn^{\omega}. \quad (13)$$

In this case, the deviation from the validity region of the thermodynamic consistency test would be directly proportional to the difference between the surface tensions of both pure components:

$$A = A(\sigma_2 - \sigma_1)/RT, \quad (14)$$

where  $A$  is the magnitude of the interface separating the adsorbed layer and the bulk phase. However, the assumption that the adsorption potentials  $\Phi_1''$ ,  $\Phi_2''$  do not depend on composition is in the case of the adsorption at the solution-vapour interface very little justified and, as it has been found by a comparison between calculated values and experiment<sup>8,9</sup>, it is satisfied at least approximately only exceptionally. Simultaneously, the value of quantity  $A$ , which is not identical with the magnitude of the adsorbent surface, is not known and for porous adsorbents it cannot be easily estimated. Consequently, the effect of the liquid phase on the adsorption on a solid adsorbent can rather be estimated than calculated from experimental dependences of the surface tension on the solution composition. If a linear dependence of the surface tension on the solution composition means that both components are present in the same amounts in the interface and in the bulk phase, then the magnitude of the deviation from this linear course can be considered as an approximate measure of the concentration change in the interface; if the surface tension of the solution is lower than the linear combination of the surface tensions of both components, the concentration of the component with the lower surface tension in the interface is higher; the opposite case is encountered exceptionally.

Another factor, which can distort considerably the effect of the liquid phase, is the porous structure of the adsorbent. In the case of the surface tension we deal

with planar surfaces, whereas for the adsorption on solid substances the surface curvature is considerable and in some micropores, whose radius does not exceed a few multiples of the radius of an adsorbed molecule, the effect of the bulk liquid phase cannot manifest itself at all.

In order to establish the effect of the liquid phase on adsorption from solutions on a solid adsorbent, we calculated values of  $\Delta$  for a whole series of systems with known experimental adsorption isotherms of pure components from the gaseous phase on a solid adsorbent, isotherms of the concentration change from binary solutions on the same adsorbent and the surface tension in dependence on the solution composition.

Adsorption isotherms from the gaseous phase on silica gel and active carbon were measured at 20° and 40°C for the following substances: benzene, toluene, chlorobenzene, tetrachloromethane and cyclohexane<sup>1,10,11</sup>. Isotherms of the concentration change from binary solutions on these two adsorbents have also been determined for these substances<sup>6,10,11</sup>. Concentration dependences of the surface tension in all of these solutions have also been measured either by the drop-weight method<sup>8</sup> or by the modified capillary elevation method<sup>12</sup>. Values of the surface tension in the benzene-cyclohexane system as measured by the drop method, which have not been published so far, are reported below in the experimental part.

## EXPERIMENTAL

The surface tension in the benzene-cyclohexane system was measured by the drop-weight method<sup>8</sup> in the whole concentration range at 20°C.

*Materials.* Benzene, c.p. (Lachema) and cyclohexane, c.p. (Lachema), were rectified on a 40-plate bubble-cap column (Jena); their purity was checked by measuring the boiling point and density.

*The apparatus employed and method* have been outlined in our earlier work<sup>8</sup>. Solutions of a suitable concentration were prepared by weighing of the pure components. We used a ground-in thick-wall capillary of an O.D. of 0.74 cm. The temperature was maintained by a water thermostat at 20°C with a  $\pm 0.05^\circ\text{C}$  accuracy. Each measurement was repeated 2–3 times. The error of one measurement did not exceed 0.2%. The surface tension was calculated from the relation

$$\sigma_x = \sigma_A(m_x/m_A)(F_A/F_x), \quad (15)$$

where  $\sigma_x$  is the surface tension of the solution investigated,  $\sigma_A$  is the surface tension of a reference substance,  $m_x$ ,  $m_A$  are the masses of ten drops of the solution investigated and the reference substance, resp., and  $F_A$  and  $F_x$  are correction factors from tables<sup>13</sup>. We employed both pure components of the solution, benzene and cyclohexane, as reference substances and the difference in calculated surface tensions of solutions did not exceed experimental error. The results of our measurements are in Table I.

TABLE I

Surface Tension  $\sigma \cdot 10^{-3}$  ( $J \cdot m^{-2}$ ) in the Benzene(1)–Cyclohexane(2) System at 20°C

$x_1$	$\sigma$	$x_1$	$\sigma$	$x_1$	$\sigma$
0.000	25.04	0.412	25.78	0.777	27.27
0.123	25.19	0.506	26.02	0.871	27.87
0.216	25.38	0.641	26.60	0.909	28.15
0.322	25.56	0.710	26.94	1.000	28.89

TABLE II

The Calculation of the Deviation from the Thermodynamic Consistency Test according to Eq. (16)

$$I_1 = \int_0^{P_0} \frac{n_2^0}{P} dP; \quad I_2 = \int_0^{P_0} \frac{n_1^0}{P} dP; \quad I_3 = \int_0^1 \frac{\Omega}{x_1^2 x_2^2} dx_1^2$$

System	$I_1$	$I_2$	$I_3$	$\Delta$
Adsorption on silica gel				
Benzene–chlorobenzene	4.50	4.80	0.92	+0.62
Toluene–chlorobenzene	4.50	4.74	0.68	+0.44
Benzene–tetrachloromethane	3.24	4.80	5.36	+3.80
Toluene–tetrachloromethane	3.24	4.74	4.17	+2.67
Chlorobenzene–tetrachloromethane	3.24	4.50	2.69	+1.43
Benzene–toluene	4.74	4.80	0.295	+0.23
Benzene–cyclohexane	2.46	4.80	2.16	-0.18
Toluene–cyclohexane	2.46	4.74	2.24	-0.04
Chlorobenzene–cyclohexane	2.46	4.50	2.02	-0.02
Tetrachloromethane–cyclohexane	2.46	3.24	0.65	-0.13
Adsorption on active carbon				
Chlorobenzene–benzene	35.97	42.72	4.798	-1.95
Chlorobenzene–toluene	35.16	42.72	2.216	-5.34
Benzene–tetrachloromethane	32.79	35.97	8.004	+4.82
Toluene–tetrachloromethane	32.79	35.16	8.265	+5.90
Chlorobenzene–tetrachloromethane	32.79	42.72	15.106	+5.18
Benzene–toluene	35.16	35.97	1.322	+0.51
Benzene–cyclohexane	28.68	35.97	4.389	-2.90
Toluene–cyclohexane	28.68	35.16	5.320	-1.16
Chlorobenzene–cyclohexane	28.68	42.72	6.06	-7.98
Tetrachloromethane–cyclohexane	28.68	32.79	2.66	-1.48

## DISCUSSION

Values of the first two terms in Eq. (2) were calculated from experimental adsorption isotherms of pure gaseous components and they are given in Table II. Even though all measurements were performed at very low relative pressures, we found during the evaluation of these terms by graphical integration that this region is the source of a considerable uncertainty, especially in the case of active carbon, and that this fact produces a high uncertainty during the evaluation of the integrated area. The third term in Eq. (2) was calculated from experimental isotherms of the concentration change of individual systems (Table II). The deviation from the thermodynamic consistency test,  $\Delta$ , was then calculated from the equation:

$$\Delta = \int_0^{P_2^0} \frac{n_2^0}{P} dP - \int_0^{P_1^0} \frac{n_1^0}{P} dP + \int_0^1 \frac{\Omega}{x_1 x_2} dx_1 \quad (16)$$

and it is also given in Table II. As it is obvious from the reported values, the deviations  $\Delta$  are of the same order as the values of the third term on the right-hand side of Eq. (16), which was calculated from the isotherm of the concentration change by integrating the whole concentration region. Values of the first two integrals on the right-hand side of Eq. (16) are considerably higher, in the case of active carbon almost 10 times, than the third term on the right-hand side and the deviation  $\Delta$ . All these circumstances indicate that values of the deviation  $\Delta$  can be, especially in systems adsorbed on active carbon, loaded with a high error. In spite of this fact we can observe at least qualitative agreement between the sign of the deviation  $\Delta$  and the concentration dependence of the surface tension of solutions. For systems adsorbed on silica gel, positive deviations were found in benzene-chlorobenzene, toluene-chlorobenzene, benzene-tetrachloromethane, toluene-tetrachloromethane, chlorobenzene-tetrachloromethane and benzene-toluene solutions, which means that the experimental adsorption of a preferentially adsorbed component from the solutions is higher than the adsorption calculated from adsorption isotherms of pure gaseous components. This is in accordance with experimental values of the surface tension, since in the above systems the adsorption of this component in the surface layer at the solution-vapour interface is also positive. In the benzene-cyclohexane, toluene-cyclohexane, chlorobenzene-cyclohexane and tetrachloromethane-cyclohexane systems, for which a negative deviation from the thermodynamic consistency test was observed, the adsorption from the liquid phase on silica gel is positive for benzene, toluene, chlorobenzene and tetrachloromethane, whereas the course of the concentration dependence of the surface tension indicates that cyclohexane accumulates in the surface layer. The highest values of  $\Delta$  were found in the benzene-tetrachloromethane and toluene-tetrachloromethane systems, for which the deviation of the concentration dependence of the surface tension from a linear course is also highest.

For systems adsorbed on active carbon, the sign of the deviation  $\Delta$  also agrees with the experimental course of the surface tension. In contrast to silica gel, the adsorption of chlorobenzene on active carbon in the benzene-chlorobenzene and toluene-chlorobenzene systems is positive and since, as it may be deduced from the course of the surface tension, the solution-vapour interface becomes rich on benzene and toluene, the deviation from the thermodynamic consistency test is negative. Values of the deviation  $\Delta$  are considerably higher than for the systems adsorbed on silica gel.

Our results indicate that the deviation from the thermodynamic consistency test is caused by the effect of the adsorption force field of the liquid phase and that this effect on adsorption from solutions on solid adsorbent cannot be in most cases neglected.

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