

RELATION BETWEEN THE ADSORPTION FROM SOLUTIONS
AND THE ADSORPTION OF PURE COMPONENTS
FROM THE GASEOUS PHASE ON SOLID ADSORBENTS

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A relation between the adsorption from solutions on a solid adsorbent and the adsorption of pure substances from the gaseous phase on the same adsorbent has been derived. This relation makes it possible to predict the isotherm of concentration change in dependence on the composition of the solution from the knowledge of adsorption isotherms of pure gaseous components, and it has been verified by comparing the experimental values with the calculated ones in six systems: binary solution of nonpolar organic substances-silica gel. Some assumptions of the proposed method are discussed.

Adsorption forces of the solid adsorbent causing the adsorption of a pure gas are acting also in the adsorption from the liquid phase. It is, therefore, to be expected that some relation is existing between the adsorption from the liquid and from the gas phase. Attempts at finding such a relation are recently found in the literature¹⁻³. In the present paper, the problem will be discussed from the point of view of the thermodynamics of systems in a force field.

THEORETICAL

In measurements of adsorption from solutions on a solid adsorbent, it is the isotherm of concentration change which is determined most frequently. This quantity expresses the difference between the number of moles of the considered substance in the solution before adsorption and in an equilibrium solution, this difference being referred to the mass unit of the adsorbent. The relation between the quantity, Ω , defined in the way described, and the composition of the adsorption layer x_i^o and of the bulk phase x_i^a can be expressed by the equation⁴

$$\Omega = \int_0^1 (x_i^o - x_i^a) Dn^o, \quad (1)$$

where Dn^{ω} denotes the number of moles in a volume element of the adsorption space and the integration is carried out the whole adsorption space which corresponds to the unit mass of the adsorbent.

On the basis of thermodynamic relations valid for equilibrium of the system in a force field, an equation has been derived in one of the previous papers⁴, expressing the interdependence between the composition of the bulk phase, of the adsorbed phase and the adsorption potentials which have been defined as the work necessary for transferring one mole of the considered component from a point where no adsorption forces are acting to the point in the adsorption space

$$\left(\frac{x_1^{\alpha} \gamma_1^{\alpha}}{x_1^{\omega} \gamma_1^{\omega}} \right) \cdot \left(\frac{x_2^{\alpha} \gamma_2^{\alpha}}{x_2^{\omega} \gamma_2^{\omega}} \right)^{-C} = \exp \left(\frac{\Phi_1 - \Phi_2}{RT} \right), \quad (2)$$

where $\gamma_1^{\alpha}, \gamma_2^{\alpha}, \gamma_1^{\omega}, \gamma_2^{\omega}$ are activity coefficients of the component 1 and 2 in the bulk phase and at a given point of the adsorbed phase, $C = V_1/V_2$ is the ratio of molar volumes of the component 1 and 2, and Φ_1, Φ_2 are adsorption potentials of the component 1 and 2 at a given point of the adsorption space. Now some simplifying assumptions are to be introduced so that the equation (2) might be applied to the calculation of the isotherm of concentration change; effects of these assumptions have been already discussed in the previous paper⁵. If the molar volumes of both components do not differ significantly, it is possible to put $C \approx 1$ and to calculate explicitly the mole fraction in the adsorbed phase x_1^{ω} from the equation (2)

$$x_1^{\omega} = \frac{x_1^{\alpha}}{x_1^{\alpha} + (1 - x_1^{\alpha}) Ke^f}, \quad (3)$$

where $K = (\gamma_1^{\omega}/\gamma_2^{\omega})/(\gamma_1^{\alpha}/\gamma_2^{\alpha})$, and $f = (\Phi_1 - \Phi_2)/RT$. Consequently, a relation is obtained for the isotherm of the concentration change

$$\Omega_1 = \int_{\theta} \left[\frac{x_1^{\alpha}}{x_1^{\alpha} + (1 - x_1^{\alpha}) Ke^f} - x_1^{\alpha} \right] Dn^{\omega}. \quad (4)$$

It is assumed usually that the equipotential surfaces of both components are conformal, *i.e.*, that an arbitrary equipotential surface of one component is identical with some equipotential surface of the other component. Further on, for systems the behaviour of which does not differ significantly from the ideal one, an assumption is introduced that the ratio of activity coefficients of both components is the same both in the surface phase and in the bulk phase. In that case, the equation (4) on rearranging assumes the following form

$$\Omega_1 = x_1^\alpha (1 - x_1^\alpha) \int_0^\infty \frac{(1 - e^{\phi}) N}{x_1^\alpha + (1 - x_1^\alpha) e^{\phi}} d\phi. \quad (5)$$

where N is the number of moles in a unit of volume and ϕ denotes the adsorption space.

Accordingly, to calculate the isotherm of concentration change, it is necessary to know the adsorption potentials Φ_1 and Φ_2 . In the case of adsorption from binary solutions on a solid adsorbent, these potentials are equal to the work necessary for transferring one mole of the component 1 or 2 from the solution into the surface layer where two force fields are acting: on the one hand the force field of the solid adsorbent and on the other hand the force field of surrounding molecules which generally differs from that inside the bulk phase.

If a relation is to be determined between the adsorption from the solution and the adsorption of pure components from the gas phase on the same adsorbent, it is necessary to find out a relation which exists between the adsorption potentials Φ_1, Φ_2 such as they have been just defined and the potentials Φ'_1, Φ'_2 which can be determined from the adsorption isotherms of pure substances.

First of all, a relation between the adsorption from the solutions and from the equilibrium vapour phase on the same adsorbent will be considered. In the first case, the layer adsorbed on the surface of the solid adsorbent is in contact with the liquid phase, in the second case it is in contact with the vapour phase. The difference between the adsorption potentials Φ_1, Φ_2 and the potentials Φ'_1, Φ'_2 acting in the adsorption from the vapour phase will be affected partly by the magnitude of the ratio of the adsorption volume to the surface area of phase boundary adsorbed solution-bulk phase, partly by the difference between the force interaction of molecules of the same and of the different kind. In the case of a microporous adsorbent, where the pore diameter is equal to a few multiples of molecular diameters of the substances adsorbed, or in the case of an adsorbent with bottle-shaped pores, the pores will be filled up completely in the adsorption both from the liquid and from the vapour phase, and the number of molecules which are situated on the boundary between the adsorbed and the bulk phase will be small as compared with the total number of adsorbed molecules. In this case, the difference between the adsorption potentials, acting on the boundary adsorbent-solution and on the boundary solid adsorbent-equilibrium gas phase, will be small as well. If, on the contrary, the adsorbent will be a macroporous one, or if it will have a plane surface (from the point of view of molecular dimensions), then the adsorption layer, usually only a few molecular diameters in thickness (from one to three), may be affected by the properties of the bulk phase rather considerably.

Since in the adsorption from solutions the difference of potentials of both components plays a role, the difference of $\Phi_1 - \Phi_2$ in the case of adsorption from the

liquid phase also will be the same as the difference of $\Phi_1'' - \Phi_2''$ for the adsorption from the vapour phase, if the intermolecular forces between the like and unlike particles will be approximately equal. In this case, the effect of the liquid phase on both kinds of molecules in the surface layer will be the same, and the adsorption on the surface of a solid adsorbent will not be affected by the presence of the liquid phase.

A similar situation will be found on comparing the adsorption potentials Φ_1, Φ_2 , and Φ_1', Φ_2' computed from the adsorption isotherms of pure gases. The potentials Φ_1'', Φ_2'' are equal to the work which is necessary for transferring one mole of the substance from the pure gas into the surface layer. Here again, a molecule in the surface layer is affected partly by the force field of the adsorbent, partly by the force field of the remaining molecules in the adsorbed layer which, in this case, all are of the same kind as the molecule considered. Since the interaction of molecules in the gas phase at low pressures is small, the main difference between the potentials Φ_1, Φ_2' and Φ_1'', Φ_2'' consists in that — in the case of adsorption from the pure gas phase — the molecules in the adsorbed layer are of the same kind. Therefore, the potentials Φ_1, Φ_2 may be put equal to the potentials Φ_1', Φ_2' under assumption that the intermolecular forces between the particles 1 and 2 are approximately equal to those between the molecules of the same kind.

As it has been mentioned above, it is possible to compute the adsorption potentials Φ_1', Φ_2' from the corresponding adsorption isotherms measured. From the thermodynamic condition of equilibrium in a force field⁶, a relation is obtained for the adsorption potential of the pure component

$$\Phi'(\varphi) = G^\alpha - G^\omega = RT \ln(f^\alpha/f^\omega), \quad (6)$$

where G^α and G^ω are molar free enthalpies of the pure component in the bulk and surface phase, and the f^α and f^ω are corresponding fugacities. If both the equilibrium pressure, p , at which the adsorption is measured, and the pressure of saturated vapours, p^0 , are so low, that it is possible to assume the values of fugacity coefficients as approximating to one, it is possible to write

$$\Phi'(\varphi) = RT \ln(p/p^0), \quad \varphi = a/\varrho \quad (7)$$

where a is the adsorbed amount referred to the unit mass of adsorbent, and ϱ is the density in the adsorbed phase which is usually put equal to the density in the liquid phase at the same temperature.

If the adsorption potentials Φ_1', Φ_2' , calculated in this way, are put equal to the potentials Φ_1, Φ_2 in the equation (5), it is possible to predict the whole isotherm of concentration change on the basis of the knowledge of adsorption isotherms of pure components from the gas phase on the same adsorbent.

TABLE I

Adsorption of Pure Gaseous Substances on Silica Gel at 20°C
 p Equilibrium pressure (Torr), a amount adsorbed (mg/g).

Benzene		Toluene		Chlorobenzene		Tetrachloromethane	
p	a	p	a	p	a	p	a
Adsorption							
0-00	4-24	0-16	10-69	0-00	9-46	0-022	3-87
0-003	4-57	0-41	19-07	0-003	9-51	0-066	4-83
0-02	4-89	0-80	26-89	0-30	22-07	0-35	7-04
0-20	7-94	1-12	32-18	0-40	22-94	0-95	9-38
0-64	10-44	1-86	44-97	0-52	26-63	1-30	11-32
1-44	15-11	2-67	54-45	0-72	32-50	1-88	12-69
2-12	18-69	4-15	67-33	0-86	39-24	2-98	15-17
3-50	24-12	5-62	79-58	1-20	46-20	7-02	25-93
5-64	31-40	7-47	94-02	1-79	64-46	9-33	31-60
8-55	40-10	8-58	104-71	2-35	80-98	13-54	42-22
12-83	50-32	9-74	119-81	2-89	96-96	16-62	51-30
23-67	71-92	11-00	138-99	3-50	118-92	21-49	65-80
38-73	115-7	13-03	182-74	4-34	155-44	24-66	77-10
41-87	130-2	14-33	223-74	4-98	198-16	31-18	100-7
49-06	173-9	15-72	289-76	5-45	237-07	36-46	123-7
55-07	236-3	17-32	408-58	5-97	281-5	40-23	141-9
60-02	331-0	17-80	470-97	6-34	335-2	47-69	190-0
70-47	442-3	19-69	534-89	6-76	397-5	53-10	238-2
73-22	470-0	20-56	535-99	7-18	502-0	56-41	268-8
75-45	472-8	21-04	535-99	7-66	577-0	62-72	368-5
		21-67	536-88	8-35	592-0	69-60	530-0
		21-86	538-09	8-66	592-5	78-93	934-6
				9-02	596-4	83-02	979-5
						85-00	982-0
						87-44	982-0
						89-75	984-0

EXPERIMENTAL AND RESULTS

To verify the derived relations between the adsorption from solutions and the adsorption of pure components from the gas phase, the Ω -isotherms were computed for the following six systems: benzene-chlorobenzene-silica gel, toluene-chlorobenzene-silica gel, benzene-tetrachloromethane-silica gel, toluene-tetrachloromethane-silica gel, chlorobenzene-tetrachloromethane-silica gel, and benzene-toluene-silica gel. With these systems, the isotherms of concentration change have been measured in the whole concentration range⁷. On the same silica gel, the adsorption isotherms

TABLE I
(Continued)

Benzene		Toluene		Chlorobenzene		Tetrachloromethane	
<i>p</i>	<i>a</i>	<i>p</i>	<i>a</i>	<i>p</i>	<i>a</i>	<i>p</i>	<i>a</i>
Desorption							
72.45	471.0	20.34	535.55	8.84	593.4	85.87	982.0
64.76	468.2	17.98	520.71	7.92	590.8	78.83	976.5
60.01	454.0	16.05	485.50	6.64	561.9	65.11	662.0
54.21	343.0	14.50	342.50	5.32	328.6	56.91	402.0
48.31	238.5	12.57	231.00	4.60	240.1	47.99	251.5
37.74	147.6	9.52	141.85	3.55	166.8	40.70	181.7
29.41	105.2	7.53	111.54	1.88	85.3	31.36	124.6
23.45	86.25	6.46	98.21	0.88	40.76	26.16	99.6
17.12	65.20	6.09	93.25			17.55	62.5
11.66	50.50	5.77	89.61			15.38	48.7
5.01	30.33	5.51	87.07			13.87	45.4
2.75	21.41	5.34	85.75			11.33	38.6
0.70	10.87	5.09	82.99			8.38	31.6
0.24	7.39	4.63	78.70			6.18	26.08
0.08	5.43	4.28	74.40			2.33	16.28
		3.75	69.44			0.89	8.42
		3.41	64.37			0.28	6.90
		2.23	45.96				

have been measured of pure substances — benzene, toluene, chlorobenzene, and tetrachloromethane — from the gas phase by the vacuum method using the quartz spiral balance with mercury valves. The pressure has been measured with a mercury U-manometer and with a McLeod manometer (the McLeod manometer, used to the measurements of equilibrium vapour pressures, has been kept at a constant temperature of 60°C and the compression ratios have been selected in such a way that no condensation of vapours took place in the compression capillary of the manometer). The sensitivity of spirals amounted to 2 mg/mm, and the precision of the cathetometer reading was ± 0.01 mm. Prior to the measurements, the samples of adsorbents were heated for 8 hours at a temperature of 350°–400°C under a vacuum obtained with a rotatory pump and a mercury diffusion pump. The period of equilibrium establishing in the adsorption and desorption ranged from 2 to 12 hours. The results of these measurements are presented in Table I. A detailed description of the experimental methods used and a discussion of their accuracy are given in previous papers^{7,8}.

From the measured dependences of the amounts of pure substances, adsorbed from the gas phase, on pressure, the adsorption potentials Φ' of benzene, toluene,

chlorobenzene, and tetrachloromethane have been computed according to the equation (7) in dependence on the volume of the adsorbed phase, φ . The dependences are plotted in Fig. 1.

A graphical integration of the curves has been carried out, and the average potentials, Φ' , have been calculated. Further on, it has been found that the dependences determined by experiment can be well expressed by means of an analytical equation

$$-\Phi' = \Phi^{0'}(\varphi_r^{-\frac{1}{2}} - 1), \quad (8)$$

where $\varphi_r = \varphi/\varphi_{\max}$ is the reduced volume, φ_{\max} is the volume of the adsorbed phase, if the equilibrium pressure equals to the pressure of saturated vapors, and $\Phi^{0'}$ is a constant. By plotting $(-\Phi')$ versus $\varphi_r^{-\frac{1}{2}}$, a straight line is obtained (Fig. 2). The values of the constant $\Phi^{0'}$ have been calculated by the method of least squares. The equation (8) represents a type of the so called F-distribution⁹ of adsorption volumes with respect to the potential Φ' .

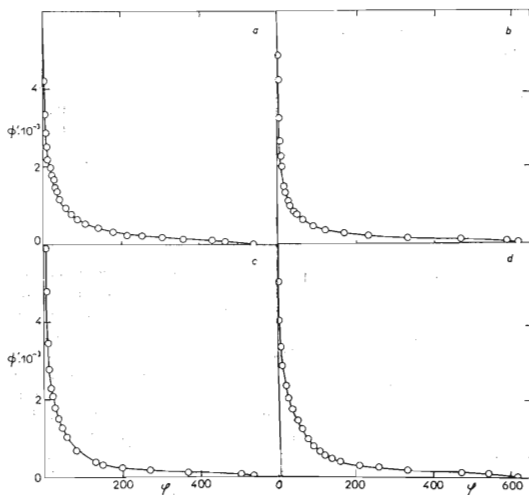


FIG. 1

Dependence of the Adsorption Potential Φ' on the Volume of the Adsorbed Phase, φ
a Chlorobenzene, *b* tetrachloromethane, *c* benzene, *d* toluene.

The isotherms of the concentration change have been computed in two ways:

1) The adsorption potentials $\Phi'_1(\varphi)$, $\Phi'_2(\varphi)$ have been replaced by average adsorption potentials Φ_1 , Φ_2 , the values of which are constant in the whole adsorption space. In this case, the equation (5) is simplified to

$$\Omega_1 = \bar{n}^w x_1^\alpha (1 - x_1^\alpha) \left[\frac{1 - e^f}{x_1^\alpha + (1 - x_1^\alpha) e^f} \right], \quad (9)$$

where $f = (\bar{\Phi}'_1 - \bar{\Phi}'_2)/RT$ and \bar{n}^w is the number of moles adsorbed on the unit mass of adsorbent; the \bar{n}^w has been calculated as an average value of the number of adsorbed moles of both pure components from the gas phase. The curves calculated in this way are compared with the experimental values in the Fig. 3.

2) The adsorption potentials $\Phi'_1(\varphi_r)$, $\Phi'_2(\varphi_r)$ have been expressed as functions of the reduced adsorption volume φ_r according to the equation (8) and the Ω -isotherms have been computed by a numerical integration of the relation

$$\Omega_1 = \bar{n}^w x_1^\alpha (1 - x_1^\alpha) \int_0^1 \frac{1 - e^f}{x_1^\alpha + (1 - x_1^\alpha) e^f} d\varphi_r, \quad (10)$$

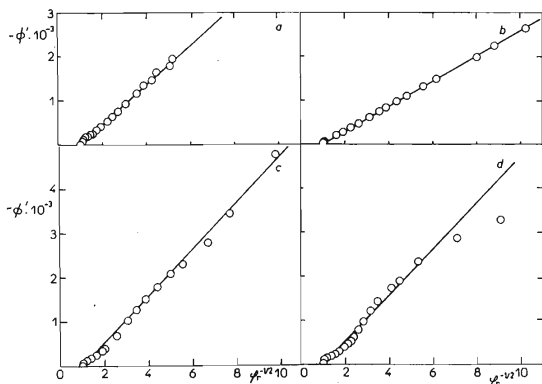


FIG. 2.

Dependence of $(-\Phi')$ on $\varphi_r^{-1/2}$

a Chlorobenzene, *b* tetrachloromethane, *c* benzene, *d* toluene.

where $f = (\Phi_1^{0'} - \Phi_2^{0'}) (\varphi_r^{-1/2} - 1) / RT$ for values of $x_1^a = 0.1, 0.2, 0.3 \dots 0.9$. The value of \bar{n}^w has been determined in the same way as in the first case. The computed curves are presented in the Fig. 4, where the measured values are plotted as well.

DISCUSSION

As it is evident from the figures, there is an agreement between the computed and the experimentally found component adsorbed preferentially in all the six systems studied. That means, the calculated and measured adsorption isotherms have the same sign in all cases, and the adsorption potential determined from the measurements of adsorption isotherms from the gas phase has a higher absolute value for that component which is adsorbed on the silica gel from the solution more strongly.

In the systems benzene-chlorobenzene and toluene-chlorobenzene, even the quantitative agreement between the measured values and the curves calculated according to the equations (9), (10) is very good. In the systems benzene-tetrachloromethane, and chlorobenzene-tetrachloromethane, the curves calculated with the use of the average potential according to the equation (9) are considerably lower than the measured values, whereas, the Ω -isotherm calculated according to the equa-

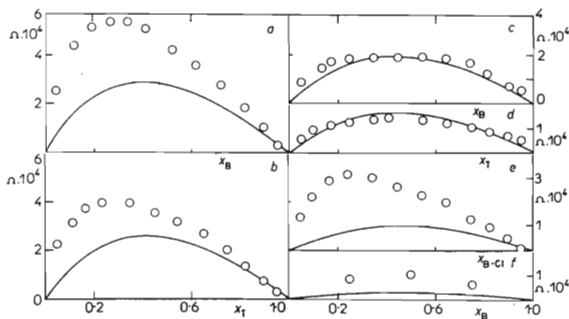


FIG. 3

Comparison of Isotherms of Concentration Change Calculated according to the Equation (9) under Assumption of Average Adsorption Potentials with Experimental Values

Systems: *a* benzene-tetrachloromethane-silica gel, *b* toluene-tetrachloromethane-silica gel, *c* benzene-chlorobenzene-silica gel, *d* toluene-chlorobenzene-silica gel, *e* chlorobenzene-tetrachloromethane-silica gel, *f* benzene-toluene-silica gel. Mole fractions (in equilibrium solutions): x_B benzene, x_T toluene, x_{B-C1} chlorobenzene.

tion (10) reproduces rather well the experimental data in the case of systems benzene-tetrachloromethane and chlorobenzene-tetrachloromethane, and it is higher in the case of the system toluene-tetrachloromethane. In all the cases, the maximum of the calculated Ω -isotherms is shifted towards the middle. The height of the Ω -isotherm depends both on the magnitude of the difference of adsorption potentials and on the number of moles adsorbed, while the position of the maximum of the isotherm of the concentration change is dependent solely on the difference of adsorption potentials of both components. Therefore, the shift of the maximum towards the middle of the concentration axis signifies that this difference determined from the adsorption measurements of pure substances from the gas phase is smaller than in the adsorption from the liquid phase. In the system benzene-toluene, the curves calculated by both methods are significantly lower than the values measured. This system, of course, has been measured to a small extent because of a low accuracy of the analytical method, and the experimental values are not very reliable.

Since the surface area of the silica gel used, calculated from the adsorption isotherms from the gas phase according to the BET equation amounts approximately to $110 \text{ m}^2/\text{g}$, it is probably not a typical microporous adsorbent, where the effect of the liquid phase on the adsorbed layer would be negligible. In the systems benzene-chlorobenzene and toluene-chlorobenzene, the curves of the surface tension measured in dependence on the composition of the solution are almost linear¹⁰.

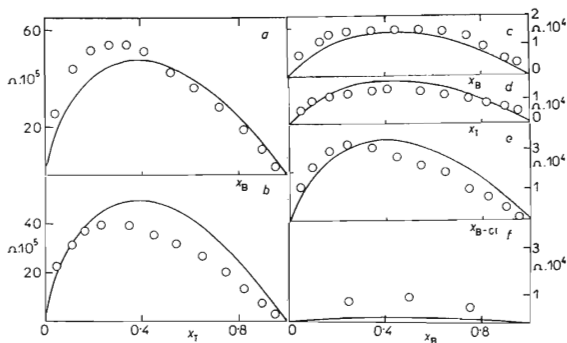


FIG. 4

Comparison of Isotherms of Concentration Change Calculated according to Equation (10) with Experimental Values

The designation is the same as in Fig. 3.

The composition of the surface layer on the boundary liquid-gas, therefore, differs very little from the composition of the bulk phase, so that it is possible to assume that the effect of the liquid phase on the adsorption from the mentioned solutions on the silica gel is negligible. On the other hand in the systems benzene-tetrachloromethane and toluene-tetrachloromethane, it has been found from the measurements of the surface tensions¹⁰ that on the boundary solution-vapour phase a negative adsorption of the tetrachloromethane takes place. That means that the liquid phase is acting on the surface layer in the same sense as the solid adsorbent, so that it can be expected that the difference of adsorption potentials calculated from the adsorption measurements of pure substances from the gas phase will be lower than the difference of the adsorption potentials which plays a role in the adsorption from these solutions on silica gel, and this situation is in agreement with the dependences observed. In the system chlorobenzene-tetrachloromethane, the values of the surface tensions, determined by the capillary rise method and by the drop weight method differ one from another to such a degree¹¹ that even a qualitative estimation of the effect of the liquid phase on the shape and height of the Ω -isotherm is not feasible.

The results obtained as well as the analysis carried out in this paper indicate that the relation between the adsorption from solutions and the adsorption of pure components from the gas phase on a solid adsorbent represents a rather complicated problem in which both the properties of the adsorbent alone and the behaviour of the mixed adsorbate can play a significant role. Consequently, these circumstances can affect the feasibility of predicting the isotherms of concentration change from the knowledge of the adsorption of pure components from the gas phase only.

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