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Calculation of Adsorption Isotherms on Hard Solid Surfaces Using Measurements of Surface Tensions and Contact Angles

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Abstract. The adsorption excess isotherms of binary mixtures adsorbed on hard solids were calculated by means of surface tension and contact angle measurements using the Gibbs adsorption isotherm equation. The calculation procedure is described in detail using the authors' own measurements of mixtures containing ethylene glycol(1)/water(2) on Teflon and poly(vinyl chloride), and water(1)/*n*-propanol(2) on Teflon. On the basis of these results and also from surface tensions and contact angles on hard solids published by other authors, all types of isotherms were found as given for porous adsorbents in the classification of Schay and Nagy. In addition to those, new isotherm types are proposed.

Keywords: adsorption isotherms, surface excess, surface tension, contact angle, hard solid

Introduction

Adsorption excess isotherms of binary mixtures on disperse or porous solids can be successfully applied to characterize the wetting behavior of solid surfaces. Using analytical methods to determine the mole fraction of the preferentially adsorbed component (component 2) before (x_2^0) and after (x_2) adsorption, the adsorption excess amount n_2^σ (the excess is denoted by the upper index σ) related to the solid surface area A can be calculated in the following way:

$$\Gamma_2^\sigma \equiv n_2^\sigma / A = n^0 \left(x_2^0 - x_2\right) / A, \tag{1}$$

where n^0 is the total amount of the two components in the mixture. The absolute adsorption amounts of components Γ_1^s and Γ_2^s (denoted by the upper index s) (Messow et al., 1992) can be calculated by means of several models for the formation of the adsorbed layers (monolayer or multilayers). The measurement of the adsorption excess isotherms at different temperatures allows an estimation of thermodynamic wetting functions such as the specific wetting Gibbs energy and the specific wetting enthalpy or entropy (Messow et al., 1993; Heuchel et al., 1989). The calculated wetting quantities can be directly compared with the wetting quantities obtained by calorimetric methods (Messow et al., 1993).

In the case of adsorption on so-called hard solid surfaces, the surface area of which has a magnitude of only a few cm^2, the surface excess also plays an important role, because all practical problems, such as cleaning those surfaces (Knapikowski et al., 1995), are related to a change in surface excess. But in this case it is impossible to measure the changes of concentrations in the bulk phase according to Eq. (1) usually by analytical methods because of the small surface area. Therefore, another way is proposed to characterize also the wetting behavior of hard solid surfaces: Using the Gibbs adsorption isotherm and the Young equation and measurements of both, surface tensions and contact angles, the adsorption excess can be calculated from these quantities.

In this context we were interested in whether the well-known five isotherm types according to the classification of Schay and Nagy (Nagy et al., 1963), valid for the adsorption on disperse and porous adsorbents, can also be found for the adsorption on hard solid surfaces. To discuss the possible isotherm types also already published results for surface tensions and contact angles are incorporated.

Theory

The so-called Gibbs adsorption isotherm is usually applied the calculation of the surface excess at the interface liquid/gas or liquid/air using the expression

$$\Gamma_2^\sigma = -\frac{1}{RT}\left(\frac{\partial \sigma_{\mathrm{l/g}}}{\partial \ln a_2}\right)_{T,p}, \tag{2}$$

where $\sigma_{\mathrm{l/g}}$ denotes the surface tension of the interface liquid/gas, a_2 the bulk activity of the second component, R the gas constant, T the absolute equilibrium temperature and Γ_2^σ the surface excess of the second component at the interface expressed e.g., in μmol/m^2. It is noted that Eq. (2) is valid only for dilute solutions.

The Gibbs Duhem equation for a binary liquid mixture adsorbed on a solid over the whole range of the mole fraction is given by

$$S^\sigma dT - V^\sigma dp + A d\sigma_{\mathrm{s/l}} + n_1^\sigma d\mu_1 + n_2^\sigma d\mu_2 = 0, \tag{3}$$

where S^σ, V^σ, n_1^σ and n_2^σ are the extensive excess values for the entropy, the volume and the adsorbed amounts, respectively. The intensive quantities of this equation are the equilibrium values of temperature T, pressure p, surface tension $\sigma_{\mathrm{s/l}}$ at the interface solid/liquid and the chemical potentials μ_i of the adsorbed components, which can be expressed by the chemical potential of the bulk mixture applying the common thermodynamical equilibrium conditions. Taking into consideration

$$\begin{gathered}(1-x_2)\, d\mu_1 + x_2 d\mu_2 = 0;\\ T = \text{const.};\ p = \text{const.},\end{gathered} \tag{4}$$

$$n_1^\sigma + n_2^\sigma = 0, \tag{5}$$

and using for the bulk phase the well-known expression for the chemical potential introduced by Lewis

$$\mu_i = \mu_{i*}(T, p) + RT \ln a_i; \quad a_i = x_i f_i, \tag{6}$$

where $\mu_{i*}(T, p)$ is the chemical potential of the pure component i, with a_i and f_i denoting its activity and activity coefficients, the general Gibbs adsorption equation can be obtained

$$\Gamma_2^\sigma = -\frac{1-x_2}{RT}\left(\frac{\partial \sigma_{\mathrm{s/l}}}{\partial \ln a_2}\right)_{T,p}, \tag{7}$$

by which the adsorption excess on the solid surface can be calculated from the surface tension solid/liquid. It can easily be transformed into

$$\Gamma_2^\sigma = -\frac{x_2(1-x_2)}{RT}\frac{(\partial \sigma_{\mathrm{s/l}}/\partial x_2)_{T,p}}{[1 + x_2(\partial \ln f_2/\partial x_2)_{T,p}]}. \tag{8}$$

Equations (7) and (8) are valid for the whole range of the mole fraction x_2 and take into consideration the real mixture properties, if the activity coefficient f_2 is known. But the surface tension solid/liquid cannot be measured directly. So, for further calculations, the well-known Young equation is applied

$$\sigma \equiv \sigma_{\mathrm{s/l}} = \sigma_{\mathrm{s/g}} - \sigma_{\mathrm{l/g}} \cos\theta, \tag{9}$$

where $\sigma_{\mathrm{s/g}}$ and $\sigma_{\mathrm{l/g}}$ are the surface tensions for the interfaces solid/gas and liquid/gas, respectively, and θ is the contact angle. The surface tension $\sigma_{\mathrm{s/g}}$ is independent of the mole fraction x_2 of the liquid mixture. Therefore, the substitution of Eq. (9) into Eq. (8) yields

$$\Gamma_2^\sigma = -\frac{x_2(1-x_2)}{RT}\frac{[\partial(-\sigma_{\mathrm{l/g}}\cos\theta)/\partial x_2]_{T,p}}{[1 + x_2(\partial \ln f_2/\partial x_2)_{T,p}]}. \tag{10}$$

The negative expression of $\sigma_{\mathrm{l/g}}\cos\theta$ is usually known as the wetting Gibbs energy[1]

$$\Delta_{\mathrm{wett}} G = -\sigma_{\mathrm{l/g}} \cos\theta. \tag{11}$$

Then Eq. (10) can be rewritten more simply

$$\Gamma_2^\sigma = -\frac{x_2(1-x_2)}{RT}\frac{(\partial \Delta_{\mathrm{wett}} G/\partial x_2)_{T,p}}{[1 + x_2(\partial \ln f_2/\partial x_2)_{T,p}]}. \tag{12}$$

In the following, the surface tension for the interface liquid/gas is denoted by the symbol σ. The evaluation of the adsorption excess isotherms from Eqs. (10) or (12) is very sensitive, on the one hand, to experimental errors of surface tension σ and contact angle θ, which may be caused by the differentiation process in the nominator of Eq. (10), and on the other hand, to the bulk phase properties of the applied mixtures expressed by the denominator of Eqs. (10) and (12). The natural logarithms of the activity coefficients were calculated using the UNIFAC method (Fredenslund et al., 1977). For the computation of Eq. (12) these values were approximated by the Redlich-Kister polynomial

$$\ln f_2 = (1-x_2)^2 \sum_{k\geq 1} C_k (2x_2 k - 1)(2x_2 - 1)^{k-2}. \quad (13)$$

To describe both, the experimental results of the surface tensions liquid/gas and the contact angles as functions of the mole fraction x_2, the following four mathematical expressions are proposed

$$\text{A: } y = (1-x_2)\, y_{1*} + x_2 y_{2*} + A(1-x_2)\, \exp(-Bx_2) + Cx_2\{1 - \exp[-D(1-x_2)]\} \quad (14)$$

$$\text{B: } y = (1-x_2)\, y_{1*} + x_2 y_{2*} + x_2(1-x_2) \times (a + bx_2 + c\sqrt{x_2}\ln x_2) \quad (15)$$

$$\text{C: } y = (1-x_2)\, y_{1*} + x_2 y_{2*} + x_2(1-x_2)\, \frac{\alpha}{x_2+\beta} \quad (16)$$

$$\text{D: } y = (1-x_2)\, y_{1*} + x_2 y_{2*} + x_2(1-x_2) \times \sum_{j=1}^{m} E_j (2x_2 - 1)^{j-1}. \quad (17)$$

Therefore one can put either σ or $\cos\theta$ for $y \cdot y_{1*}$ and y_{2*} are the values for the pure components 1 and 2. These proposed expressions were chosen because they are, perhaps with the exception of Eq. (17), uniquely suited to smooth the experimental data with a minimum of extreme values, which is very important because extreme values (maximum or minimum) produce a change of sign in the adsorption isotherm, as is obvious from the numerator of Eq. (10). Moreover, all the above mathematical expressions fulfill the condition that the gradient $\partial y/\partial x_2$ is finite at $x_2 \to 0$ and $x_2 \to 1$, respectively. This condition is also required to solve Eq. (10). The choice of one of the proposed four expressions will depend on the experimental system chosen.

Experimental

Contact angles were determined by the measuring system G40 made by KRUESS GmbH, Hamburg. The basic unit is a goniometer equipped with a 100 μl syringe connected to a micrometer dosing unit, a beamsplitter, a video camera, frame grabber, PC and additional b/w-monitor. The contact angle of 8 droplets of each mixture was determined by drop profile analysis. The average value showed a reproducibility of $\pm 2.5^\circ$. The surfaces were cleaned with acetone and subsequently treated in an ultrasonic bath.

Surface tension values of mixtures of water and ethylene glycol or *n*-propanol, respectively, were determined by the maximum bubble pressure tensiometer BP MKII, also made by KRUESS GmbH. A glass capillary of 0.205 mm in diameter was immersed exactly 10 mm into the mixture to be measured. Surface tension was registered as a function of the continuously changing bubble formation rate or surface age, respectively. The capillary was connected to a very sensitive pressure sensor. The bubble frequency was varied within a range of 0.1–20 bubbles per second.

Freshly distilled water, ethylene glycol p.a. made by Roth and *n*-propanol for chromatography made by Merck were used.

Results

The liquid mixtures water/*n*-propanol, water/ethylene glycol, tetralin/*n*-octane, decalin/*n*-hexane and ethylene glycol/*n*-propanol and the hard adsorbents Teflon, poly(vinyl chloride), paraffin and polyethylene were used.

Figure 1 shows the natural logarithm of the activity coefficients (Fig. 1(a)), the activities (Fig. 1(b)) and the denominator of Eqs. (10) and (12) (Fig. 1(c)) for the second component, respectively, in dependence on the mole fraction x_2 for the five liquid mixtures considered. In Table 1 the Redlich-Kister coefficients according to Eq. (13) are summarized. With the exception of ethylene glycol/*n*-propanol, all mixtures show a positive deviation from Raoult's law. The adsorption excess isotherms can be calculated including the activity coefficients (the so-called real isotherms) and excluding them (the so-called ideal isotherms). In the case of a positive deviation from Raoult's law the real isotherms are higher than the ideal ones. For ethylene glycol/*n*-propanol the reverse is the case. The mixture decalin/*n*-hexane shows nearly ideal behavior and the denominators in Eqs. (10) and (12) are approximately equal one (see also Fig. 1(c)).

The surface tensions of water/ethylen glycol obtained by using the bubble pressure tensiometer are represented in Fig. 2 at 25°C. The bubble frequency was one bubble per second. These measurements were carried out when necessary to clarify the differences

Table 1. Parameters of Eq. (13).

Mixture	Water(1)/ n-propanol(2)	Water(1)/ ethylene glycol(2)	Tetralin(1)/ n-octane(2)	Decalin(1)/ n-hexane(2)	Ethylen glycol(1)/ n-propanol(2)
C1	1.63490E+0	5.34028E−1	4.42123E−1	9.91610E−2	−1.51783E+0
C2	−4.10000E−1	−2.42931E−1	−2.69340E−2	1.65980E−2	7.81224E−1
C3	1.36651E−1	1.53107E−1	1.98800E−3	2.34580E−3	−4.18386E−1
C4	−1.68882E−1				1.00531E−1
C5	3.69321E−1				−2.44566E−1
C6					3.97945E−1

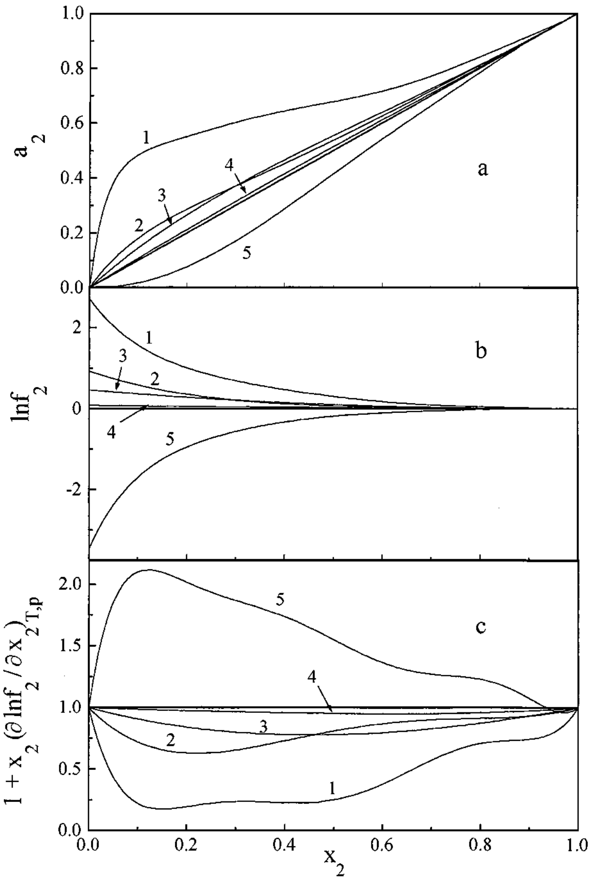

Figure 1. Activities (a), natural logarithm of the activity coefficients (b) and the function $1 + x_2(\partial \ln f_2/\partial x_2)_{T,p}$ (c) for the second component of the considered mixtures in dependence on the mole fraction x_2. 1: water/n-propanol; 2: water/ethylene glycol; 3: tetralin/n-octane; 4: decalin/n-hexane; 5: ethylene glycol/ n-propanol.

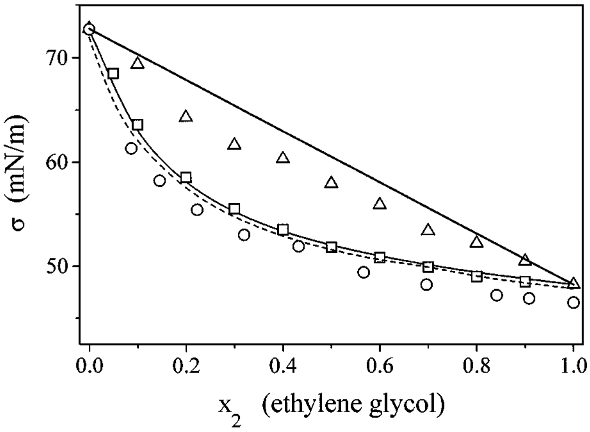

Figure 2. Experimental surface tensions of water/ethylene glycol. △: data by Janczuk (Janczuk et al., 1989); □: data by Dörfler (Dörfler, 1979); ○: the authors' own data; solid line: data by Hoke (Hoke et al., 1991) at 293 K; dashed line: data by Hoke (Hoke et al., 1991) at 298 K.

between experimental data at 20°C obtained by (Janczuk et al., 1989) and (Dörfler, 1979). Using the data recently published by Hoke (Hoke et al., 1991) concerning surface tensions of water/ethylene glycol in dependence on the temperature (see the solid and the dashed line in Fig. 2), a decision can be made in favor of data showing considerable deviations from the ideal behavior. Therefore, Hoke's data were applied for the following calculations. In the case of a water/n-propanol mixture, the data given in the literature for surface tensions and contact angles on teflon (Li et al., 1993 and Knapikowski et al., 1994) were not sufficient for the best possible description by one of Eqs. (14)–(17). Therefore, own measurements were carried out with a bubble frequency of one bubble per second. A variation of the bubble frequency from 0.1 to 10 bubbles per second leads to an increase of the surface tension within the mixture of only 0.2 to 0.3 mN/m. These results and the data from other publications are represented in Fig. 3. Our own measured contact angles of a water/ethylene glycol mixture on Teflon, on poly(vinyl chloride) and of water/n-propanol on Teflon are put together in Table 2. The surface tensions of tetralin/n-octane, decalin/n-hexane and ethylene

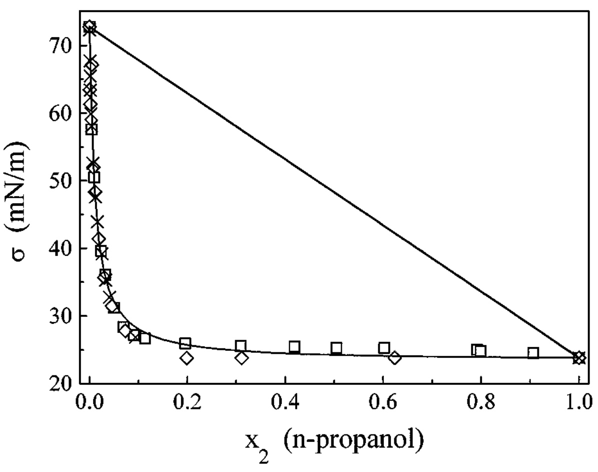

Figure 3. Experimental surface tensions of water/*n*-propanol. □: the authors' own data; ◊ data from Knapikowski (Knapikowski et al., 1994); ×: data by Li (Li et al., 1993); solid line: data approximated by Eq. (16).

glycol/*n*-propanol mixtures were taken over from Li (Li et al., 1993). The surface tension data for all systems were approximated by Eqs. (14)–(17), parameters of which are summarized in Table 3, together with their root mean squares (rms). The contact angles for water/ethylene glycol on paraffin and poyethylene and tetralin/*n*-octane, decalin/*n*-hexane and ethylene glycol/*n*-propanol on Teflon, respectively, were taken over from Janczuk and Li (Janczuk et al., 1989, Li et al., 1993). The parameters of Eqs. (14)–(17) for describing the cosinus of all contact angle data and the corresponding rms are put together in Tables 4 and 5. Our decision on any of the proposed equations can be seen from the subsequent figures. Here it should be noted that the decision for the best possible description of surface tensions and contact angles by these equations was influenced not only by a minimum of rms but also by the smoothness of the experimental data with a minimum of extreme values.

In the following, the attempt will be made to assign the adsorption isotherms for eight adsorption systems to the isotherm types I to V of the classification proposed by Schay and Nagy (Nagy et al., 1963). In the figures the experimental values of the surface tensions and the contact angles are summarized together with the curves obtained by one of Eqs. (14)–(17), the wetting enthalpies calculated from them and the adsorption isotherms evaluated by means of Eq. (12) including or

Table 2. Measured contact angles in degree in dependence on the mole fraction of the second component.

x_2	Water(1)/ethylene glycol(2) adsorbed on Teflon	Water(1)/ethylene glycol(2) adsorbed on PVC	x_2	Water(1)/*n*-propanol(2) adsorbed on Teflon
0.000	110.0	93.4	0.00000	110.0
0.087	107.4	77.3	0.00144	112.5
0.145	106.2	73.9	0.00493	110.7
0.223		76.1	0.00971	102.5
0.276	101.9	69.7	0.02376	91.1
0.319	99.8	65.8	0.03224	84.6
0.387	101.1	62.1	0.05028	72.2
0.432	100.7	60.3	0.06972	62.3
0.581		58.3	0.09057	58.2
0.566	96.1	59.7	0.11330	54.0
0.696	91.6	60.8	0.19560	47.9
0.841	91.2	60.1	0.30980	47.0
0.800	90.2	57.8	0.41180	47.3
0.908	85.1	59.4	0.50790	42.3
1.000	85.0	70.7	0.60200	41.7
			0.71860	43.8
			0.79930	41.6
			0.90650	40.9
			1.00000	38.9

Table 3. Parameters of Eqs. (14)–(17) describing the surface tensions of different mixtures in dependence on the mole fraction of the second component.

Mixture	Water(1)/ *n*-propanol(2)	Water(1)/ ethylene glycol(2)	Tetralin(1)/ *n*-octane(2)	Decalin(1)/ *n*-hexane(2)	Ethylene glycol(1)/ *n*-propanol(2)
A	−4.41080E+1	−1.42618E+1	−5.83640E+0	−2.83423E+0	−1.54921E+1
B	6.35058E+1	8.45865E+0	6.38732E+0	1.21592E+0	5.99170E+0
C	−2.00004E+2	−2.28313E+1	−7.16161E+0	−1.34728E+0	−2.02686E−1
D	1.19120E−2	2.64426E−1	6.52254E−1	−3.07763E−1	1.26259E+1
rms	5.17842E+0	2.03467E−1	1.43171E−1	2.41966E−1	1.12787E+0
a	−2.75879E+3	−3.10082E+2	−8.52605E+1	1.34475E+1	−1.84697E+2
b	2.68126E+3	2.93526E+2	7.68264E+1	−1.37663E+1	1.75406E+2
c	−2.73172E+3	−2.62961E+2	−6.38273E+1	1.83494E+1	−1.34375E+2
rms	1.56765E+1	8.94375E−2	1.26476E−1	1.65351E−1	1.60212E+0
α	−4.91174E+1	−2.22531E+1	−1.21985E+1	−3.93685E+0	−2.11800E+1
β	1.11557E−2	1.53563E−1	2.96913E−1	1.34474E+0	1.98515E−1
rms	3.70524E+0	3.68987E−2	1.46907E−1	2.45467E−1	1.30547E+0
E_1	−8.11776E+1	−3.40650E+1	−1.52411E+1	−2.50169E+0	−2.94398E+1
E_2	9.97565E+1	2.65834E+1	8.24297E+0	1.02117E+0	2.41221E+1
E_3	−5.92484E+2	−1.99217E+1	−7.67458E+0	2.15134E+0	−2.31182E+1
E_4	−1.27600E+2	1.04602E+1	8.47245E+0		1.19581E+1
E_5	2.25859E+3	−9.29040E+0			
E_6	5.99530E+2	2.04953E+1			
E_7	−2.73013E+3	−1.43952E+1			
rms	1.28585E+1	1.99378E−2	1.58970E−1	1.71685E−1	1.10446E+0

excluding the activity coefficients in its denominator, respectively.

The first system, water(1)/ethylene glycol(2), adsorbed on Teflon is characterized by contact angles larger than 90° up to a mole fraction of $x_2 = 0.8$ (see Fig. 4(b)). Therefore $\Delta_{\text{wett}}G$ is positive up to this mole fraction (Fig. 4(c)). The negative gradient of this curve produces the symmetrical ideal adsorption isotherm from type I, represented by a dashed line in Fig. 4(d). The consideration of the activity coefficient in Eq. (12) leads to a more asymmetrical behavior of the real adsorption isotherm (the solid line in Fig. 4(d)), which is greater than the ideal curve due to the positive deviation from Raoult's law for the water/ethylene glycol mixture (cf. Fig. 1(c)) and can be assigned more to the type II. From this mixture, ethylene glycol is preferentially adsorbed in the whole mole fraction range. This is in accordance with the linear decrease of the contact angles shown in Fig. 4(b). The high value of 110° means that Teflon is more difficult to be wetted by water than by ethylene glycol with an contact angle of 85°.

The minimum in $\Delta_{\text{wett}}G$ for water(1)/ethylene glycol(2) adsorbed on poly(vinyl chloride) (see Fig. 5(c)) leads to a change in the sign of the adsorption isotherms of Fig. 5(d) and therefore to the appearance of a so-called "adsorption azeotrope". At this point, the mixture wets the solid in the best possible manner. This isotherm can be assigned to type V.

The $\Delta_{\text{wett}}G$ curves of tetralin(1)/*n*-octane(2) adsorbed on Teflon (Fig. 6(c)), of water(1)/ethylene glycol(2) on paraffin (Fig. 7(c)) and of decaline(1)/*n*-hexane(2) on Teflon (Fig. 8(c)), respectively, produce the adsorption excess isotherms shown in Figs. 6(d)–8(d). They are examples of type II showing asymmetrical behavior, of type III showing asymmetrical behavior and, additionally, with a longer section of constant slope and, finally, of type IV showing a change of sign in the adsorption isotherm and also having a section of constant slope.

Furthermore, new types of adsorption excess isotherms were found that are not included in the above mentioned classification by Schay and Nagy, as was the case with the adsorption of binary liquid mixtures

Table 4. Parameters of Eqs. (14)–(17) describing the cosinus of the contact angles of different mixtures on Teflon in dependence on the mole fraction of the second component.

Mixture	Water(1)/ *n*-propanol(2)	Tetralin(1)/ *n*-octane(2)	Decalin(1)/ *n*-hexane(2)	Ethylene glycol(1)/ *n*-propanol(2)
A	1.09850E+0	−2.72753E−1	3.13590E−1	6.33239E−1
B	1.60438E+1	4.44570E−1	3.56009E−1	2.77773E+0
C	1.11938E+1	4.52555E−1	−4.12424E−1	−6.81132E−1
D	−1.91138E−2	8.36950E−1	1.31687E+0	6.89796E−1
rms	1.60933E−1	3.91247E−2	3.78422E−2	4.61220E−2
a	3.64311E+1	−2.43972E+0	4.46379E−1	1.73696E+0
b	−3.56711E+1	2.59953E+0	−8.57037E−1	−1.75738E+0
c	3.38210E+1	−2.80528E+0	6.67716E−1	5.74583E−1
rms	2.29623E−1	2.54281E−2	3.68473E−2	5.20731E−2
α	1.19744E+0	1.85459E+0	−3.48035E+0	4.04227E−1
β	5.11170E−2	8.80997E+0	1.10747E+1	2.27766E−1
rms	2.53962E−1	4.25898E−2	4.63163E−2	5.67272E−2
E_1	2.04219E+0	2.87400E−1	−2.99230E−1	5.33276E−1
E_2	−1.35356E+0	9.59079E−2	−1.47210E−1	−5.77126E−1
E_3	6.32559E−1	−6.07641E−1		3.37620E−1
E_4	−5.45831E+0	−1.05108E−1		
E_5	6.14231E+0			
rms	1.72452E−1	1.22964E−2	3.73329E−2	4.33921E−2

Table 5. Parameters of Eqs. (14)–(17) describing the cosinus of the contact angles of water(1)/ethylene glycol(2) on different hard surfaces in dependence on the mole fraction of the second component.

Adsorbent	Teflon	Poly(vinyl chloride)	Paraffin	Polyethylen
A	3.24062E−1	4.70109E−1	6.54586E−1	7.80101E−1
B	5.83634E−1	7.03327E+0	1.10572E+0	1.11955E+0
C	−3.42436E−1	2.36733E−1	−6.60151E−1	−8.04916E−1
D	5.55087E−1	1.41711E+1	8.48104E−1	1.08809E+0
rms	7.62781E−2	9.23174E−2	3.03200E−2	1.94504E−2
a	6.87892E−1	1.23694E+1	1.49482E−1	2.37510E−2
b	−7.18576E−1	−1.05246E+1	−2.93938E−1	−3.90105E−1
c	6.92976E−1	1.15203E+1	−2.06781E−1	−3.44745E−1
rms	7.56435E−2	1.11434E−1	3.03365E−2	1.88839E−2
α	−1.92959E−3	3.13700E+0	5.58684E+0	−2.06854E−2
β	3.94103E+0	1.48971E+0	7.05581E−2	5.06443E+0
rms	7.74764E−2	1.87546E−1	4.32093E−2	7.75403E−2
E_1	−4.65983E−4	1.38268E+0	9.22884E−2	−6.54330E−3
E_2		−2.78991E−1	−2.36377E−1	−3.44114E−1
E_3		1.43526E+0	6.34615E−2	
rms	7.74742E−2	1.05309E−1	2.98293E−2	1.92831E−2

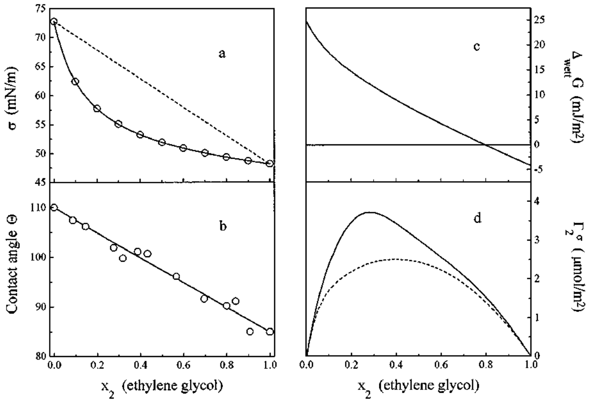

Figure 4. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for water(1)/ethylene glycol(2) on Teflon. Figures (a) and (b): experimental data (○) described by Eq. (17) (solid line), respectively; Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

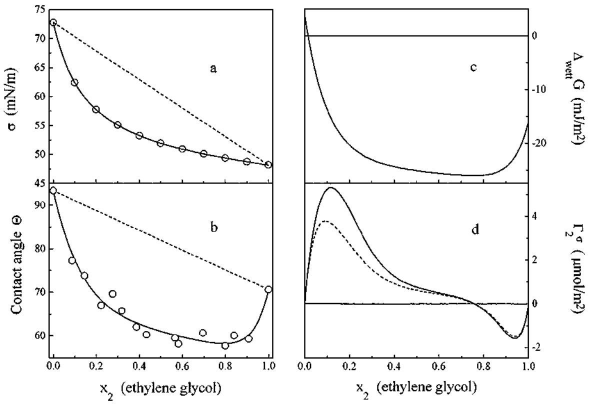

Figure 5. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for water(1)/ethylene glycol(2) on polyvinyl chloride. Figure (a): experimental data (○) described by Eq. (17) (solid line); Fig. (b): experimental data (○) described by Eq. (14) (solid line); Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

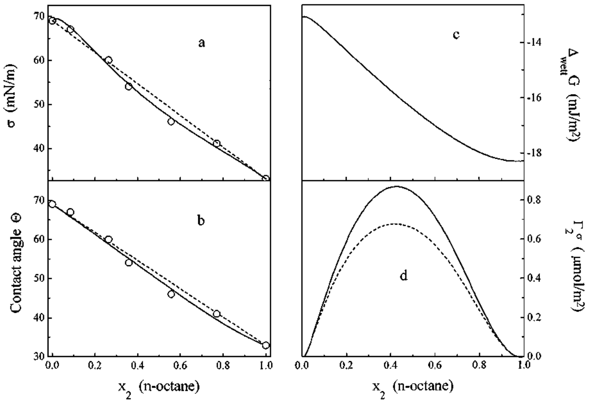

Figure 6. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for tetralin(1)/*n*-octane(2) on Teflon. Figure (a): experimental data (○) described by Eq. (15) (solid line); Fig. (b): experimental data (○) described by Eq. (14) (solid line); Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

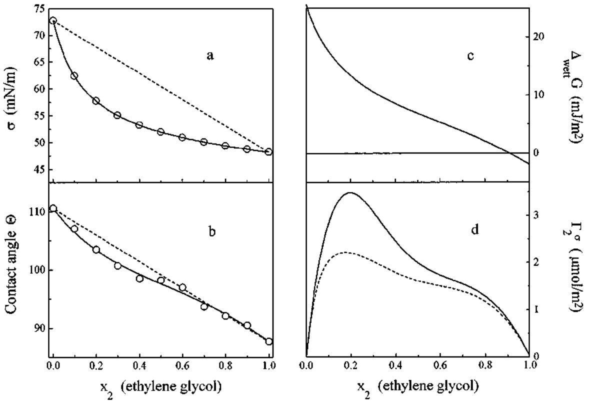

Figure 7. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for water(1)/ethylene glycol(2) on paraffin. Figures (a) and (b): experimental data (○) described by Eq. (17) (solid line), respectively; Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

onto porous adsorbents. The shape of the adsorption excess isotherm of water(1)/ethylene glycol(2) adsorbed on polyethylene (Fig. 9(d)) with two maxima should be defined as type VI, which has also been observed for the system water(1)/ethanol(2) (Everett et al., 1986) and *n*-heptane(1)/*n*-hexanol(2) (Everett, 1978) systems, both adsorbed on graphon. An adsorption excess isotherm with a plateau for ethylene glycol(1)/*n*-propanol(2) on Teflon is shown in Fig. 10(d) and assigned as type VII. Here, the activity coefficient of the second component is smaller than one and so the ideal isotherm (Fig. 10(d)) is greater than the real form. Finally, an adsorption excess isotherm with two "adsorption azeotropes" found for water(1)/*n*-propanol(2) on Teflon (Fig. 11(d)) is defined as type VIII isotherm. The last type could be obtained for the adsorption of ethanol(1)/*n*-hexane

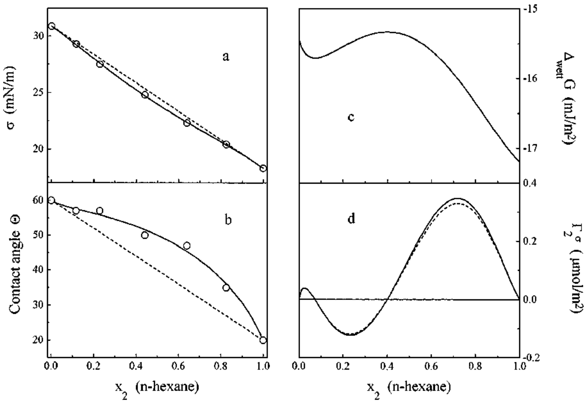

Figure 8. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for decaline(1)/*n*-hexane on Teflon. Figure (a): experimental data (○) described by Eq. (17) (solid line); Fig. (b): experimental data (○) described by Eq. (15) (solid line); Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

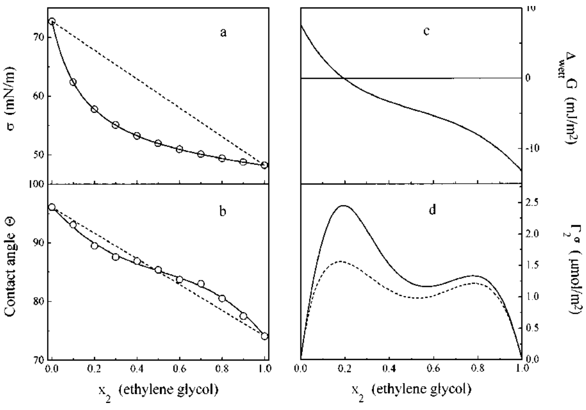

Figure 9. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for water(1)/ethylene glycol(2) on polyethylene. Figure (a): experimental data (○) described by Eq. (17) (solid line); Fig. (b): experimental data (○) described by Eq. (15) (solid line); Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

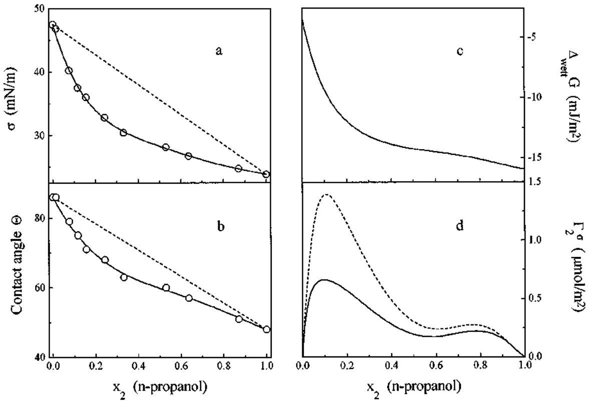

Figure 10. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for ethylene glycol(1)/*n*-propanol(2) on Teflon. Figures (a) and (b): experimental data (○) described by Eq. (17) (solid line), respectively; Fig. d: adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

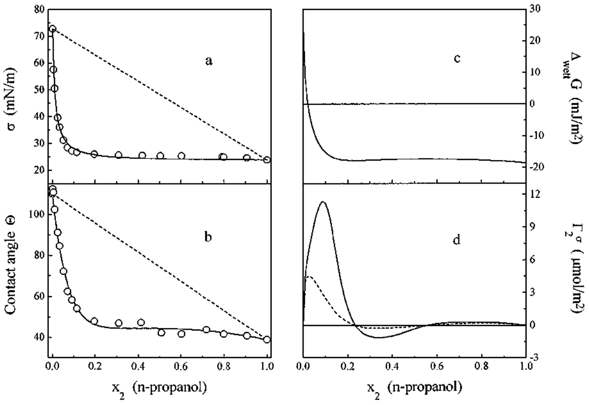

Figure 11. Surface tensions (a), contact angles (b), wetting Gibbs energy (c) and calculated adsorption excess isotherms (d) in dependence on the mole fraction x_2 for water(1)/*n*-propanol(2) on Teflon. Figure (a): experimental data (○) described by Eq. (16) (solid line); Fig. (b): experimental data (○) described by Eq. (14) (solid line); Fig. (d): adsorption isotherms including (the dashed line) and excluding (the solid line) the activity coefficients f_2 of the bulk phase.

(2) on active carbon AS (Kalies et al., 1995). Basically, the qualitative and quantitative behavior of this isotherm is in good agreement with an isotherm obtained by Knapikowski (Knapikowski et al., 1994) from dynamically measured surface tensions and contact angles using the Wilhelmy method. The second adsorption "azeotrope" in Fig. 11 cannot be regarded as a secured result, because even small changes in the curves for the surface tensions and contact angles obtained by the mathematical descriptions of Eqs. (14)–(17) may lead to changes in the isotherm shape, especially in the *n*-propanol enriched concentration range.

Conclusions

If the difference between the surface tensions and the contact angles of the pure components is significant, the component with the smallest surface tension and the smallest contact angle is preferentially adsorbed. If the difference is not significant, a change of sign in the adsorption isotherm (a so-called "azeotrope" behavior) can be observed. In this case, it is the slope of the wetting Gibbs energy $\Delta_{\mathrm{wett}}G$ that makes a clear statement about the preferentially adsorbed component.

Comparable calculations of adsorption excess isotherms for dilute solutions containing surfactants adsorbed on hard solid surfaces will require new formulae instead of Eqs. (14)–(17) (Messow et al., 1998) for the mathematical description of the surface tensions and contact angles involved.

Nomenclature

A	Surface area of the solid	m^2
a_i	Activity of the ith component	—
f_i	Activity coefficient of the ith component	—
G	Gibbs energy	J/mol
$\Delta_{\mathrm{wett}}G$	Wetting Gibbs energy	mJ/m^2
n^0	Total number of moles of both components in the mixture	mol
n_i^σ	Number of moles of the ith adsorbed excess component	mol
p	Pressure	Pa
R	Gas constant	J/mol/K
S^σ	Excess entropy	J/mol/K
T	Temperature	K
V^σ	Excess volume	m^3
x_i^0	Mole fraction of the ith component before adsorption	—
x_i	Mole fraction of the ith component after adsorption	—
Γ_i^σ	Adsorbed excess amount of the ith component related to the surface area A	$\mu mol/m^2$
θ	Contact angle	degree
μ_i	Chemical potential of the ith component in the bulk phase	J/mol
μ_{i*}	Chemical potential of the pure ith component	J/mol
σ	Surface tension	mN/m
$\sigma_{\mathrm{l/g}}$	Surface tension of the interface liquid/gas	mN/m
$\sigma_{\mathrm{s/l}}$	Surface tension of the interface solid/liquid	mN/m
$\sigma_{\mathrm{s/g}}$	Surface tension of the interface solid /gas	mN/m
C_k	The kth coefficient of the Redlich-Kister polynomial	—
A, B, C, D	Parameters of mathematical expressions for describing the surface tensions or the contact angles as function of the mole fraction	—
a, b, c, α, β	Parameters of mathematical expressions for describing the surface tensions or the contact angles as function of the mole fraction	—
E_j	The jth coefficient of a modified Redlich-Kister polynomial for describing the surface tensions or the contact angles as function of the mole fraction	—

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Note

1. $\Delta_{\mathrm{wett}}G$ is positive, if the contact angle lies between 90° and 180°, what is a characteristic for bad wetting. In contrast to this $\Delta_{\mathrm{wett}}G$ is negative, if the contact angle has values between 0° and 90°, what is an evidence for good wetting the solid surface.

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