Critical and wetting transitional adsorption behaviour in a liquid system against vapour and other walls

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Abstract
The adsorption of 2, 5 DMP (2, 5-dimethylpyridine) at the free surface of
water (1)–2, 5 DMP (2) liquid mixtures was determined from surface tension
and activity measurements. Two divergences were found: the former was
observed at T_c for the critical isochore and the 2, 5 DMP-rich γ-phase which, at
coexistence, completely wets the surface at T_c, whereas the latter was noticed at
T_w for the water-rich β-phase. These results were compared with those found
under similar conditions for the same liquid system with silica as the wall;
this comparison is quite fruitful because, with silica, the preferentially wetting
phase is the β-phase.

1. Introduction

For a long time, the scientists preoccupied with transition problems, nucleation and critical
effects have paid special attention to adsorption from liquid mixtures [1–6]. Two-liquid
mixtures may present two-phase systems demarcated from single phases by the so-called
coexistence curve terminating at either one (upper or lower) or two (upper and lower)
critical points. As a consequence, adsorption can be affected by a critical behaviour (critical
adsorption), near the critical point, and by nucleation processes that are related to either
the appearance of the two-phase system or prewetting. Prewetting is related to a wetting
transition that, generally, goes from a complete wetting near the critical point to a partial
wetting after the wetting temperature. It is an adsorption process corresponding to the wetting
film nucleation [1].

Besides their interest as regards basic science, such phenomena are of importance in many
applications fields like those of colloids, metallurgy, chemical synthesis in unusual systems
(microdivided systems, supercritical fluids), heterogeneous catalysis and petroleum recovery.
So, in addition to precise elegant laws like the critical divergence of adsorption or the critical
coexistence curve equation [7–9], it is also of great interest to examine the general behaviour
of adsorption in relation to wetting in a phase diagram that is as complete as possible. This
behaviour also allows one to detect possible phenomena that are more minute than critical
behaviours and related divergences like prewetting [10]. Finally, it is of importance for both
purposes to study how the nature of the wall affects these phenomena.

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2. Theoretical aspects: general features of adsorption behaviour related to phase changes and phase diagrams in binary liquid systems

Liquid–liquid demixing in binary mixtures is often characterized by critical points. At these points, the concentrations of liquid phases in equilibrium evolve towards the same value when the critical temperature is raised. This corresponds to an equalization of correlation lengths; and the divergence of the correlation lengths, which is equally observed along the critical isochore, namely at x_{2c}, when temperature is in the monophase region, is moved towards T_c. Correlation length divergence is described by the critical law [5]

$$\xi \sim \xi_0 (T - T_c)^{-\nu} \qquad \text{with } \nu = 0.61. \tag{1}$$

As adsorption—namely the matter content of the heterogeneous zone between the liquid and a wall—is considered as tightly linked to the correlation length in the liquid mixture, it also diverges at T_c, according to the critical law [5, 7–9]

$$\Gamma_{21} \sim (T - T_c)^{-\nu+\beta}. \tag{2}$$

Here, adsorption is taken as the relative adsorption of component 2 with respect to component 1, and is called Γ_{21} [27].

This is not only true along the critical isochore when going to T_c, but also along the coexistence curve, with a marked asymmetry depending on the wetting of every phase against the wall. Close to T_c it is often found that one of the phases, say γ, completely wets the surface and isolates it from the wall. For this phase, denoted by an asterisk, the contact with the wall is effective at each temperature, and the adsorption critical divergence, i.e. adsorption divergence at T_c along the γ-branch of the coexistence curve, is observed.

For the other branch, say β, the contact is in principle only observable if a wetting transition takes place at the temperature T_w while moving away from T_c and for $T \notin [T_c, T_w]$. The value of T_w is very much specific to the adsorption between the β-phase and the wall. It is the only temperature at which adsorption is still observable, and the wetting macroscopic film is already present on the surface. Consequently, the adsorption layer thickness, which is the thickness of the heterogeneous zone in contact with the wall, is the same as that of the wetting film just starting to appear and becomes infinite. So, at T_c, adsorption at the $\gamma-v$ interface (v standing for the vapour phase) also becomes infinite and, thus, diverges [1, 5, 11–13].

This divergence may occur in two different ways: either adsorption progressively takes on very high values—then the wetting transition is of second order—or it very abruptly tends to an infinite value—then the wetting transition is of first order [11, 12]. In fact, such a first-order *wetting transition* has the features of a first-order *phase transition* and thus the system is characterized by a second feature, i.e. prewetting, which is sometimes taken as a *definition of first-order nature for the wetting transition*.

Prewetting is the sign that the γ^*-phase film is going to appear in the surface layer near T_w (at $T \in]T_w, T_c[$) and near the β-branch of the coexistence curve; but, it takes place in the monophase. This is expressed as a surface demixing that induces an adsorption jump on adsorption isotherms like those exhibited by any surface phase change [5, 10, 14, 15]; it goes along with a major alteration in the composition of the surface and a thickening of the adsorption layer. The surface must be enriched in the same component as is the major one of the wetting film. As already stated, at T_c the adsorption layer thickness becomes infinite like the adsorption, and the layer obviously has the same composition as the γ^*-phase at T_w.

Finally, the critical behaviour of the surface tensions of the β- and γ-phases against vapour, $\sigma_{\beta v}$ and $\sigma_{\gamma v}$, has been theoretically described together with the surface tension along the critical isochore $\sigma_{v,\beta\gamma}$ [4, 5]:

$$\sigma_{\beta v} = \sigma_c + A(T - T_c) + B'(T - T_c)^{\mu} \tag{3}$$

$$\sigma_{\gamma v} = \sigma_c + A(T - T_c) + B''(T - T_c)^{\mu} \tag{4}$$

with

$$\sigma_{\beta v} - \sigma_{\gamma v} = (B' - B'')(T - T_c)^{\mu}. \tag{5}$$

At complete wetting,

$$\sigma_{\beta v} - \sigma_{\gamma v} = \sigma_{\beta \gamma}$$

and

$$\sigma_{v,\beta\gamma} = \sigma_c + A(T - T_c) + B(T - T_c)^{\mu} \tag{6}$$

$$\mu = 1.26. \tag{7}$$

Theoretical studies of adsorption along the critical isochore and along the coexistence curve in a binary system model undergoing a wetting transition have been carried out for a solid wall and for vapour [11–13].

A large range of solid-wall potentials have been tested in order to establish general laws for behaviour. However, due to certain aspects of the model, no first-order transition was found [13]. On the contrary, a modelling of the free surfaces has led to first- and second-order wetting transitions, i.e. both possible behaviours, according to the interaction combinations [12]. So, a kind of theoretical guide is available for analysing experimental behaviour. One must emphasize that the surface parameter modelled in [11–13] is the relative adsorption Γ_{21} (or Γ_{12}) which is identical to the experimental parameter discussed in the present paper. When the experimental parameter is the ellipsometric coefficient or a reflectivity datum, there are always some questions arising about the exact relations between these parameters and Γ_{21} (or Γ_{12}). These questions may be fruitful, but the comparison with theory is less direct.

Complete experimental studies of the behaviour of adsorption in binary systems undergoing both critical point and wetting transitions are scarce. Indeed, attention has been focused either on critical adsorption or on prewetting in systems like methanol–cyclo-hexane [16], metal mixtures [17] and water–dimethylpyridine mixtures [18]. Frequently, these investigations have been carried out by ellipsometry. For water–2, 5 DMP mixtures against a silica wall, our studies included adsorption behaviour along the coexistence curve [19]; their results will be described below.

3. The system

The investigations reported here were focused on free interfaces, i.e. in contact with vapour for the water–2, 5 DMP mixture. The adsorption along the critical isochore as well as the coexistence curve around the lower critical point were studied first. Then, the temperatures around the expected T_w were explored. In the following, we will use the symbol T_w when we are speaking about wetting transitions in general, T_w^{α} when the wall is specifically silica and T_w^{v} when the wall is vapour.

3.1. Phase equilibria

The system phase diagram is shown as figure 1. The liquid–vapour curve, or boiling curve, and the crystallization curve are shown above and below the miscibility loop [20] which characterizes the liquid–liquid demixing into two phases: water-rich β and 2, 5 DMP-rich γ. This crystallization curve for dilute solutions corresponds to pure water crystallization [21]. For the same range of concentrations, vapour along the boiling curve is water-rich, since pure water has a lower boiling point (100 °C) than pure 2, 5 DMP (175 °C). Given the temperature
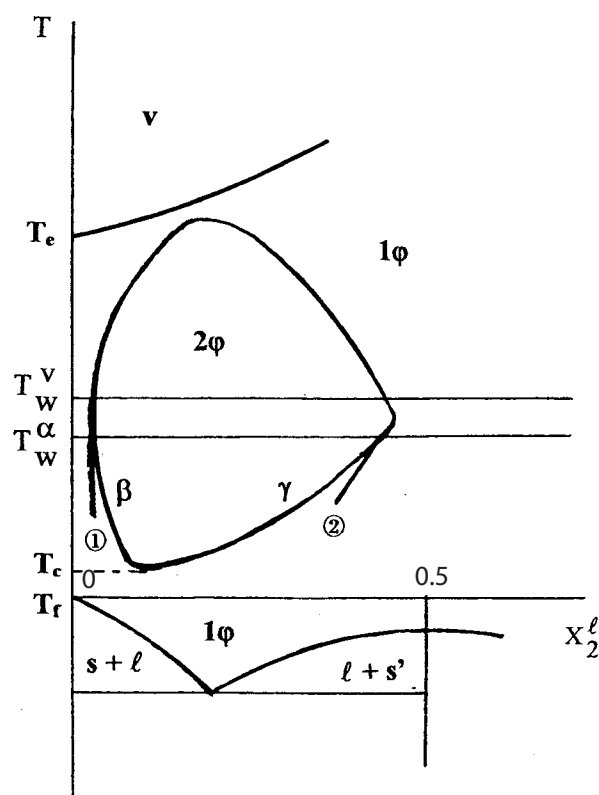
Figure 1. The bulk phase diagram for the water (1)–2, 5 DMP (2) system: x_2 is the mole fraction of 2, 5 DMP; ℓ stands for liquid, v for vapour, s and s' for two different solid phases (s is pure ice), 1φ is a single liquid phase, 2φ is a two-liquid-phase equilibrium (one phase is named β and the other γ); T_e and T_f are the boiling point and the fusion point of pure water respectively; T_c is the critical temperature for the 2φ system; T_w^{α} and T_w^{v} are the wetting temperatures for the two-liquid-phase system against silica and vapour, respectively [20, 21]. Curve 1 is the hypothetical prewetting line against vapour; it should start at T_w^{v} tangentially to the coexistence curve; curve 2 is the already established prewetting line against silica [18, 19], starting at T_w^{α}. Curve 2 is close to the γ-branch because γ is the non-wetting phase against silica. Curve 1 is expected near the β-branch because β is the non-wetting phase against vapour. $T_c = 13.1$ °C; $T_w^{\alpha} = 46$ °C; $T_w^{v} = 50 - 55$ °C; $T_e = 100$ °C; $T_f = 0$ °C. The figure is just a pictorial representation of the different physical behaviours. Scales are not exact.

scale at which the present study was performed, it is worth considering the closeness of phase changes other than simple liquid–liquid separation. The lower liquid–liquid critical point is at 13.1 °C [20].

3.2. Critical surface tensions

We have previously studied the critical behaviour of surface tensions [22, 23]. Values at coexistence were then determined by a short extrapolation to coexistence of the surface tension isotherms on both sides of the miscibility gap:

$$\sigma_{\beta v} = 40.798 - 0.240(T - T_c) + 0.0581(T - T_c)^{1.26} \qquad (8)$$

$$\sigma_{\gamma v} = 40.798 - 0.240(T - T_c) + 0.0398(T - T_c)^{1.26} \tag{9}$$
$$\sigma_{v,\beta\gamma} = 40.798 - 0.240(T - T_c) - 0.0108(T - T_c)^{1.26}. \tag{10}$$

These relations are good for temperature between 3 and 35 °C, namely between 3 and 13.1 °C for equation (10) and between 13.1 and 35 °C for equations (8) and (9). In addition, the tension between β and γ is

$$\sigma_{\beta\gamma} = 0.0183(T - T_c)^{1.26}. \tag{11}$$

3.3. Wetting, wetting transition

Equations (6) and (7) immediately show that $\sigma_{v\gamma} < \sigma_{v\beta}$ close to T_c and far above. This means that γ will be, against vapour, the preferentially wetting phase that we usually call γ^*, the asterisk showing that, with this wall, γ is the preferentially wetting phase. The reverse situation is observed against a silica wall [24]; then, the asterisk is put on β, giving β^*, β being the preferentially wetting phase with this wall.

Comparing equations (6), (7) and (9) shows that

$$\sigma_{\beta v} - \sigma_{\gamma v} = \sigma_{\beta\gamma} \tag{12}$$

which means that there is complete wetting of β by γ^* close to T_c, in contact with vapour.

Other unpublished results [25] have shown that wetting against vapour was complete up to $T = 50$ °C and partial above 55 °C, the exact T_w^v being still unknown. Beside the general adsorption behaviour, the order of the wetting transition should be considered to interpret experiments.

3.4. Chemical potentials, activities

These parameters had been previously measured through the values of vapour pressure and composition at numerous mole fractions and temperatures [26].

4. Experiments

4.1. Adsorption

Adsorption at the free interfaces was determined using the Gibbs isotherm formula, namely

$$\Gamma_{21} = -\left(\frac{\partial \sigma}{\partial \mu_2}\right)_T \tag{13}$$

where σ is the surface tension of the mixture of components 1 and 2, here water and 2, 5 DMP, respectively, at the temperature T and mole fraction x_2, and μ_2 is the chemical potential of component 2 at the same T and x_2 as above:

$$\mu_2 = \mu_2^{\ominus,x} + RT \ln f_2 x_2 = \mu_2^{\ominus,x} + RT \ln a_2 \tag{14}$$

where $\mu_2^{\ominus,x}$ is the standard chemical potential, f_2 is the activity coefficient of component 2 at the mole fraction x_2 and temperature T, $a_2 = f_2 x_2$ is the activity of component 2 at the same T and x_2. Finally,

$$\Gamma_{21} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln f_2 x_2}\right)_T = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln a_2}\right)_T. \tag{15}$$

Γ_{21} can be calculated numerically or graphically from isotherms such as $\sigma = \sigma(\ln f_2 x_2) = \sigma(\ln a_2)$. Γ_{21} is the relative adsorption of component 2 with respect to 1. In molecular terms,
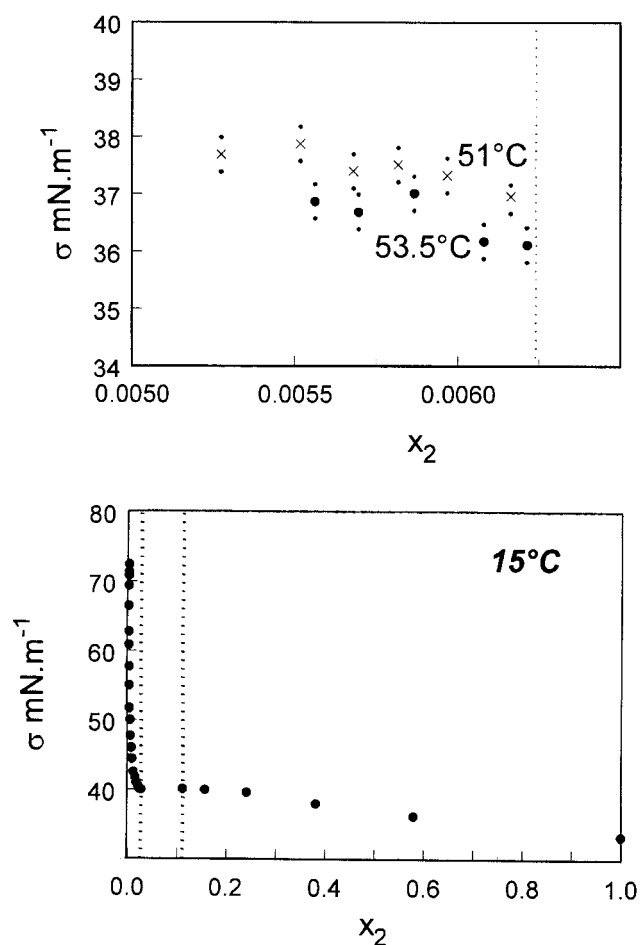
Figure 2. Surface tensions: at 5 and 10 °C on both sides of x_{2c}; at 15 °C on both sides of coexistence and close to β; at two temperatures close to (51 °C) and above (53.3 °C) T_w. The signs T_c and T_w indicate where these temperatures come in between the temperatures where isotherms have been determined.

with ρ_i being the density profiles of species i and z a coordinate perpendicular to the surface, Γ_{21} is equal to

$$\Gamma_{21} = \int_0^\infty [\rho_2(z) - \rho_2(\infty)] \, \mathrm{d}z - \frac{x_2}{x_1} \int_0^\infty [\rho_1(z) - \rho_1(\infty)] \, \mathrm{d}z \qquad (16)$$

or

$$\Gamma_{21} = \Gamma_2 - \frac{x_2}{x_1}\Gamma_1 \qquad (17)$$

where Γ_2 and Γ_1 defined by the integrals in equation (16) are the Gibbs excesses [27].

Surface tensions were measured by the Wilhelmy method using a LAUDA TE1 C tensiometer. The precautions to be taken have been described elsewhere [22, 24]. The precision
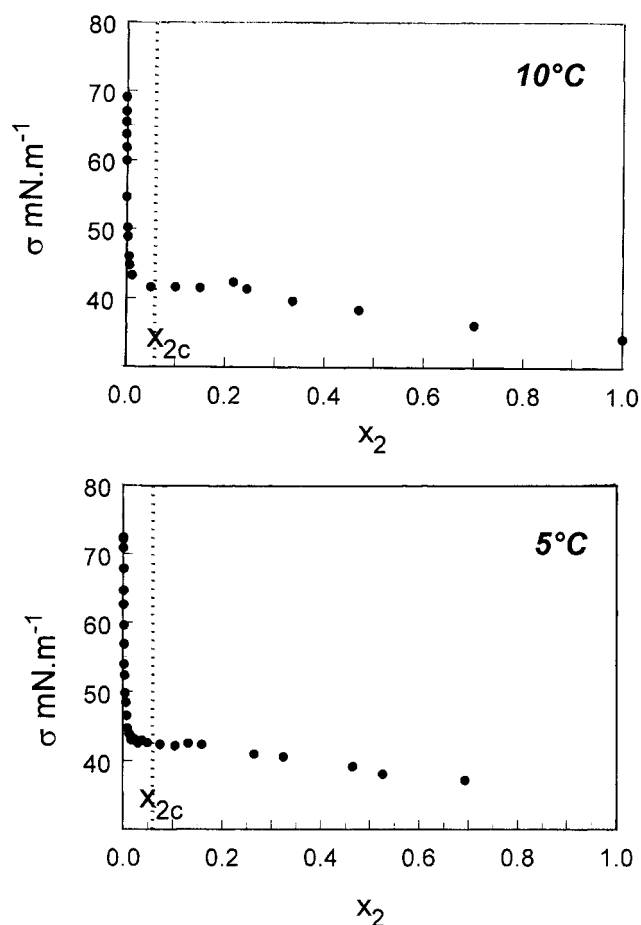
Figure 2. (Continued)

was around ± 0.2 mN m^{-1}. Along the critical isochore the method that we used was strictly the one previously described. To get values at coexistence, measurements above T_c were carried out at four or five different concentrations all very close to demixing, and then the data obtained were extrapolated to coexistence.

$\sigma = f(x_2)$ isotherms such as the ones in figure 2 were then converted through activity data already determined [26] into $\sigma = f(\ln a_2)$ isotherms (not shown). From the $\sigma = f(\ln a_2)$ isotherms, Γ_{21} was then calculated though formula (15). Values at coexistence were obtained by a short extrapolation.

4.2. Temperature

Temperature was regulated by a LAUDA thermoregulator feeding a double-wall glass cell that contained the solution and was closed by a lid. The stability was $\pm 0.05\,^{\circ}$C or even better. The thus-thermoregulated cell and the tensiometer were in a closed thermoregulated chest whose temperature was identical to that of the inner cell at $\pm 1\,^{\circ}$C.
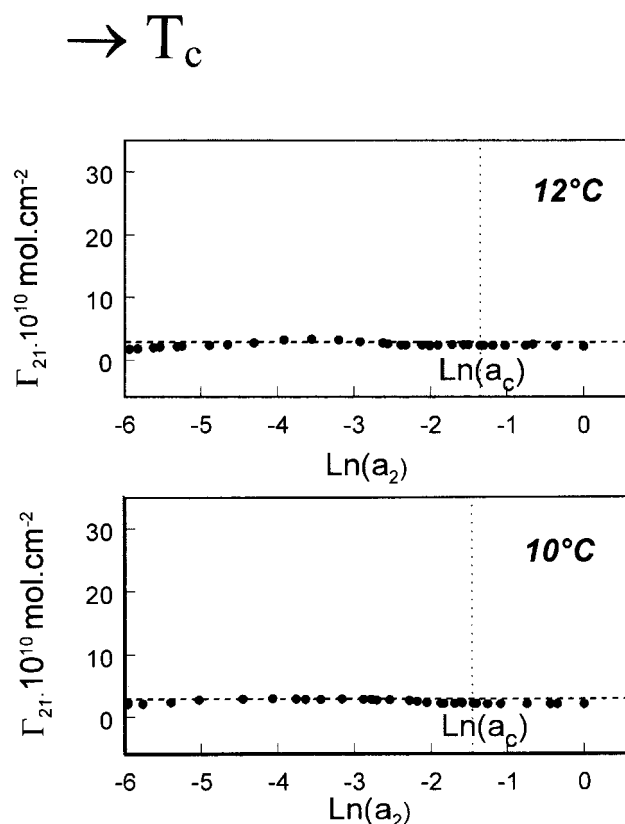
Figure 3. Adsorption isotherms. (a) Adsorption behaviour with concentration and temperature: at 10 and 12 °C; at 20 °C on both sides of coexistence; and at several temperatures below and above T_w^v. The abscissae are $\ln a_2$ where a_2 is the activity according to [26] and equation (14). At coexistence, $\ln a_2$ is the same for both β- and γ-phases. So the miscibility gap in such a representation is reduced to one dot: $x_{2\beta} \neq x_{2\gamma}$, but $\ln a_{2\beta} = \ln a_{2\gamma} = \ln a_D$. $\ln a_D$ is shown by a dotted line ($a_D = a_{2\beta} = a_{2\gamma}$ is the activity of component 2 at coexistence, i.e. for demixing). On either side of the dotted line, adsorption evolution is different. The extrapolation of the curves to the dotted line gives two adsorption values: Γ_{21}^{β} for the extrapolation of the left-hand-side curve and Γ_{21}^{γ} for the right-hand-side curve. Γ_{21}^{β} and Γ_{21}^{γ} are adsorptions at coexistence for a given temperature. Collecting the values extrapolated at several temperatures leads to figure 4(a). Saturation of the surface by a monolayer of flat 2, 5 DMP molecules, whose area was estimated elsewhere [18] as 57.1 Å^2, corresponds to $\Gamma_{21} = 2.91 \times 10^{-10}$ mol cm^{-2} and is shown by a horizontal line in each diagram. (b) 3D representation. This figure, obtained from data from (a) by a system of interpolation, is a pictorial rather than an exact representation of the phenomena. The adsorption divergence at T_c and x_{2c}, only shown in the experimental data by a tendency, is indicated in the figure by a vertical dashed line; the divergence at T_w^v appears as a peak on the dilute β-side. The β- and γ^*-sides are separated by a fault due to the bulk phase discontinuity. The β-side is characterized by a sort of cliff due to the approach of the wetting transition and to the wetting γ^*-like film nucleation. Thick lines show the adsorption behaviour at coexistence against vapour; see also figure 4(a).

4.3. Chemicals

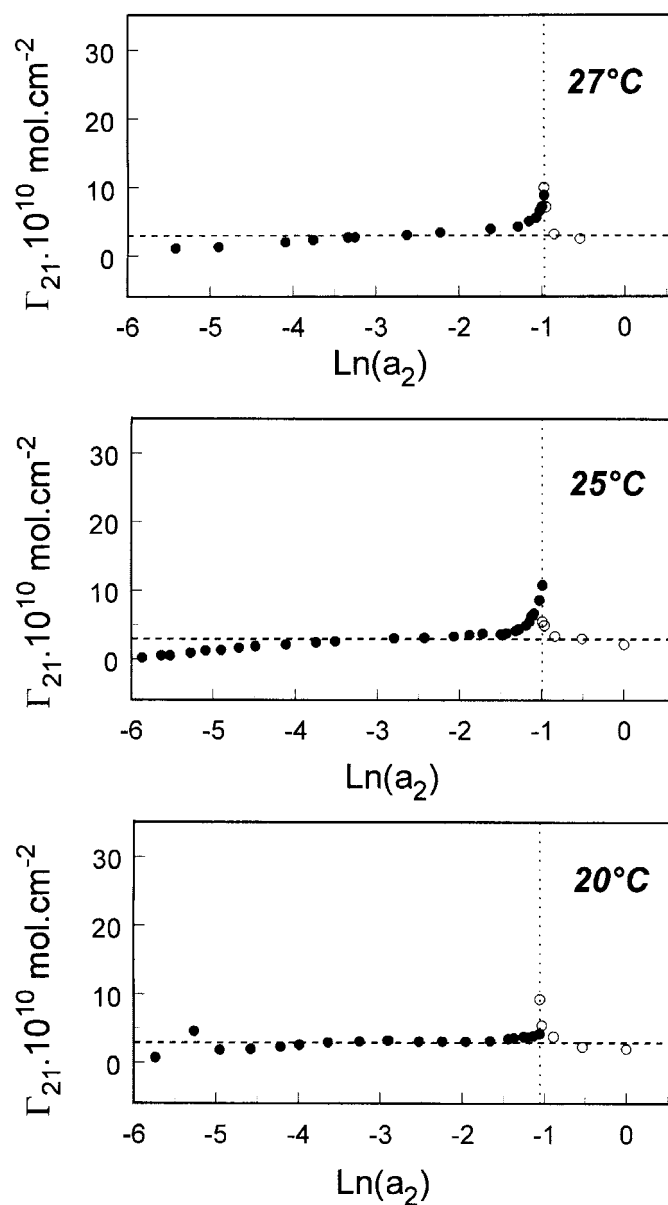The preparation of water and the 2, 5 DMP as well as the washing were performed as previously described [22].

Figure 3. (Continued)

5. Results and discussion

5.1. Surface tensions

Most of the surface tension values used in this study have already been published [24]. Figure 2 displays tension isotherms at 5 and 10 °C, then at 15 °C on both sides of coexistence and also around and above T_w^v on the β-side where a special behaviour is expected. This was all the more interesting as none of the values around T_w^v had been determined before.
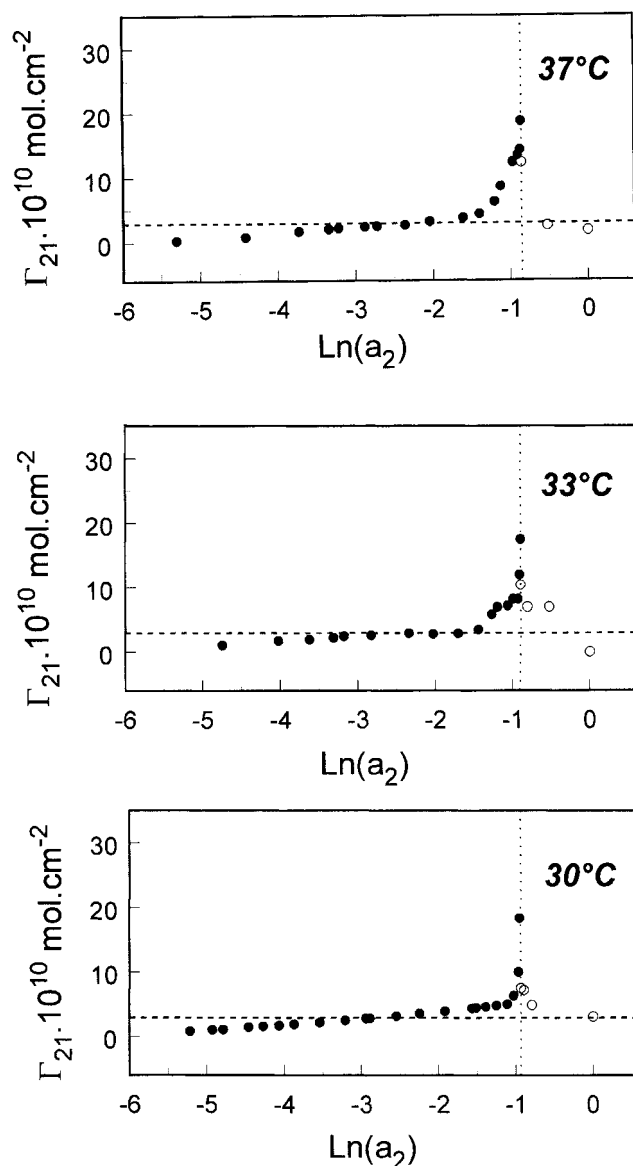
Figure 3. (Continued)

Whatever the temperature and concentration conditions were during the experiment, all of the values found were lower than that of the pure water surface tension. This result was the one expected: indeed, since the pure 2, 5 DMP tension is around 34 mN m^{-1} and lower than the water tension, 2, 5 DMP will preferentially adsorb at the free surface except in the event of interference with more subtle phenomena; σ for the mixtures will be lower than for pure water.

At 5, 10 and even 15 °C, around x_{2c} or close to the miscibility gap, one can notice a flat part on each isotherm (figure 2): it corresponds to the critical behaviour of the surface, whose other manifestations are the critical laws (equations (8)–(10)).
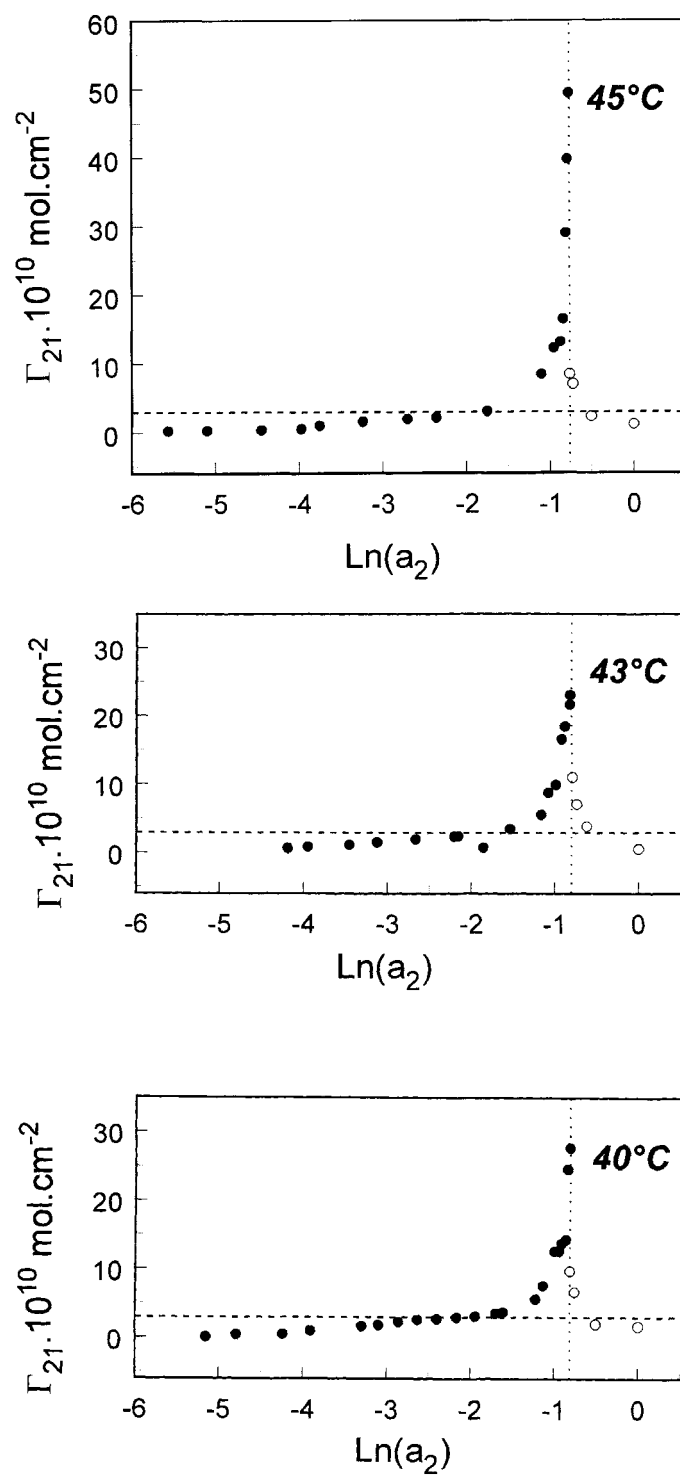
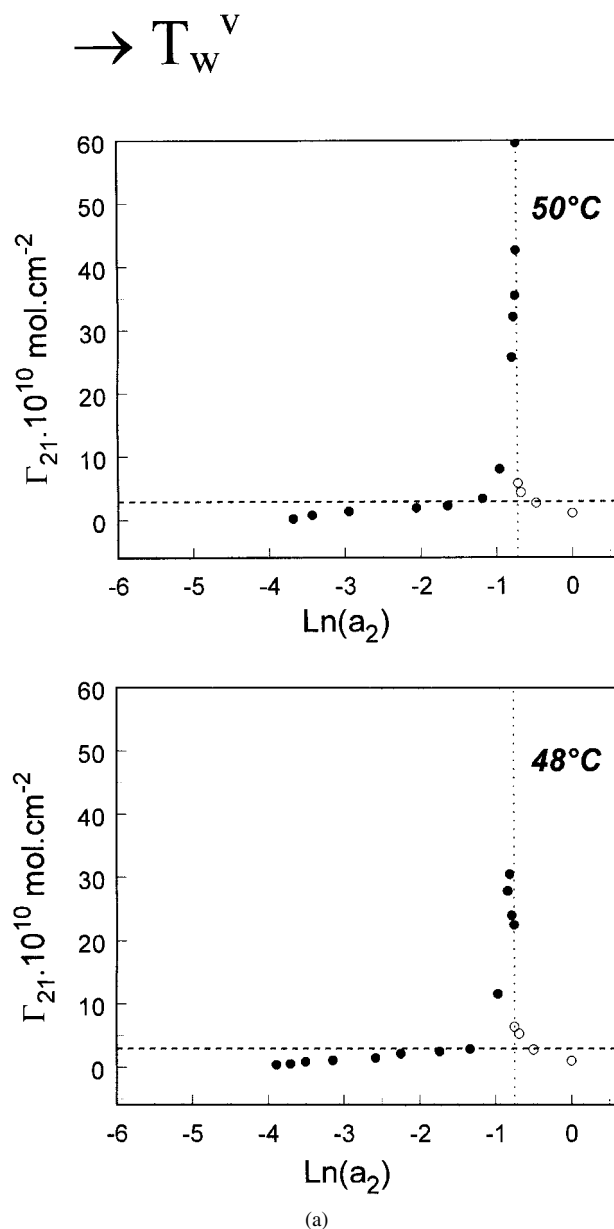**Figure 3.** (Continued)

$$\rightarrow \mathrm{T_W}^V$$

Figure 3. (Continued)

5.2. Adsorption

In the following, Γ_{21} stands for Γ_{21}^v, the adsorption at the free surface, except when clearly specified, particularly in the comparison with the adsorption against α (figure 4, later). When necessary, the superscript β or γ is added to make clear in which phase the adsorption is measured or discussed and the superscript $\beta\gamma$ is added for the critical isochore.

Figure 3 shows the adsorption isotherms $\Gamma_{21} = f(\ln a_2)$, where $a_2 = f_2 x_2$ is the activity of component 2 in the mixture; a_2 and μ_2 are related by equation (14). According to (13),
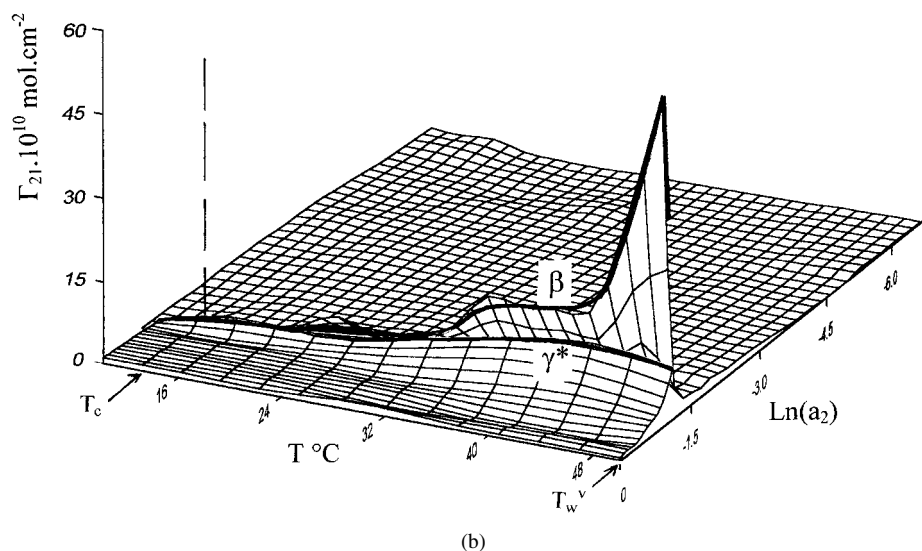
(b)

Figure 3. (Continued)

as the slopes of $\sigma = f(\ln a_2)$ are negative, Γ_{21} is always positive, but it can vary in many different ways because of the critical behaviour of μ_2 or of wetting transition manifestations. In figure 3(a), coexistence is indicated by a vertical axis at the exact value of μ_2 that β and γ^* have in common. As previously [18, 19], a crude model of a monolayer, supposing a flat adsorption of the aromatic rings of the 2, 5 DMP molecules, gives $\Gamma_{21} = 2.7 \times 10^{-10} \, \mathrm{mol \, cm^{-1}}$ at the monolayer. This value is commonly reached rather quickly for the curves on the left of demixing, hardly passed at low temperatures, but strongly exceeded when T_w^v is approached and close to coexistence. Generally speaking, one should note that at low temperatures, and particularly below T_c, Γ_{21} values are low because σ does not vary much with a_2. In addition, there is no clear sign of a critical behaviour except a slight maximum: indeed, in the calculation of the derivative (equation (11)), the great flatness of the σ-curve around x_{2c} is not compensated enough by the also very flat variation of the μ_2-isotherm around x_{2c}. It is likely that Γ_{21} values are low, but calculating Γ_{21} with precision in a zone where σ and μ_2 are both almost constant is tricky. One should also underline that, at the same type of interface, a very similar behaviour was observed in the model used by Tarazona *et al* [11]. However, critical divergence in free surfaces was experimentally observed by means of ellipsometry and neutron reflectivity in an extremely narrow range of temperatures [7–9] *for other systems* and, here, it is likely that divergence will be only observed very, very close to T_c or to x_{2c}.

As illustrated in figure 3(a), when temperature is raised, Γ_{21} increases, *especially on the left of the miscibility gap*—namely the black-dotted curves (leading to β)—while the increasing of values of Γ_{21} is slower for the open-dotted curves on the right of the miscibility gap (leading to γ^*): thus, between the adsorption behaviour on the left-hand side and on the right-hand side of the line representing demixing, there is a noticeable difference which results from the different wetting capabilities of β- and γ^*-phases at coexistence. According to the temperature, $\Gamma_{21}^{v\beta}$ can be 10, 20 or even 30 times the monolayer (whatever the sense of this word is); $\Gamma_{21}^{v\gamma}$ is never more than twice the monolayer.

The general behaviour is summarized in figure 3(b); adsorption divergence at T_c and x_{2c}, only shown in the experimental data by a tendency, is indicated in the figure by a vertical dashed

line; divergence at T_w^v appears as a peak on the dilute β-side. Thick lines show the adsorption behaviour at coexistence against vapour; see also figure 4(a). Figure 3(b) obtained from data from figure 3(a) by a system of interpolation is a pictorial rather than an exact representation of the phenomena.

5.3. Adsorption along the critical isochore and along coexistence

Figure 4(a) shows that, within 0 and 13.1 °C, along the critical isochore, adsorption $\Gamma_{21}^{v,\beta\gamma}$ is weak; it first decreases while T is increasing, which is a bit surprising, then $\Gamma_{21}^{v,\beta\gamma}$ slightly strengthens close to T_c (here, $\beta\gamma$ indicates the critical isochore). Though this last trend is the expected one, since Γ_{21} must be infinite at T_c, one should note that it is weak. So, one should question the calculation method and the prefactor value: did the former introduce some incorrectness in the values or is the latter very weak in the critical law? Both factors may cause problems.

When $T > T_c$ along γ^*, $\Gamma_{21}^{v,\gamma}$ values are higher and tend also to increase while going towards T_c, but the expected divergence is still very damped.

The behaviour of $\Gamma_{21}^{v,\beta}$ along β is very unusual: indeed, when T is between 51 and 60 °C, $\Gamma_{21}^{v,\beta}$ strongly increases concomitantly with T, which is rather surprising. While $\Gamma_{21}^{v,\beta}$ values must be treated with some caution because they were calculated from extrapolated values of a_2, the trend is quite definite and must be explained. For $T < 51$ °C, which is the zone where wetting of β by γ^* is complete, we also plotted values of $\Gamma_{21}^{v,\beta}$, i.e. extrapolated to coexistence, which is not classical. Since wetting is complete, as soon as γ^* appears (coexistence) there is no longer contact between β and v; the values corresponding to this contact do not appear in the statistical treatment [11], which prevents one from extrapolating experimental results. However, under the same conditions, i.e. below T_w^v and for one phase completely wetted by the other, $\sigma_{\beta v}$ is considered and included in a critical development. The argument developed by Widom and co-workers [4] is that there may be a β–v contact as shown by figure 5; the only condition is that γ does not completely wet the vessel wall. At least the β–v interface should be considered as an entity, maybe metastable, that does exist physically and can be observed.

In any case the diagram depicted as figure 4(a) can thus be admitted, at least, as showing the behaviour of $\Gamma_{21}^{v,\beta}$ in the case where the situation displayed in figure 5 is created and if $\Gamma_{21}^{v,\beta}$ can be observed at least temporarily. The short extrapolation of isotherms to coexistence corresponds to this case.

Then, when T is below 51 °C, $\Gamma_{21}^{v,\beta}$ strongly increases concomitantly with T; it probably becomes infinite around 51 °C, which suggests that this value is that of T_w^v. The isotherm at 51 °C, not shown, shows a very high $\Gamma_{21}^{v,\beta}$ and confirms that this temperature is T_w^v.

Passing from 52.5 to 51 °C leads to such a striking change that one should suspect a first-order transition. One way to confirm this could be to examine the $\Gamma_{21}^{v,\beta}$ isotherm at the temperatures just before T_w, which would consist in examining the occurrence of prewetting. The expected shapes are shown on figure 6: the vertical parts correspond to surface demixing, which is followed by a short and low-slope part just before bulk demixing.

A careful examination of figure 3 shows that the isotherms close to bulk demixing (depicted in figure 5) tend to get closer to verticality, but the accuracy of the $\Gamma_{21}^{v,\beta}$ values is insufficient for detecting the two breaks that should define the strictly vertical part. This was observed for the $\Gamma_{21}^{v,\beta}$ isotherm at the contact with silica, because β preferentially wets silica and adsorption was determined rather directly and more accurately. In the kind of study reported here, another method like ellipsometry should be used to observe isotherm shapes precisely.
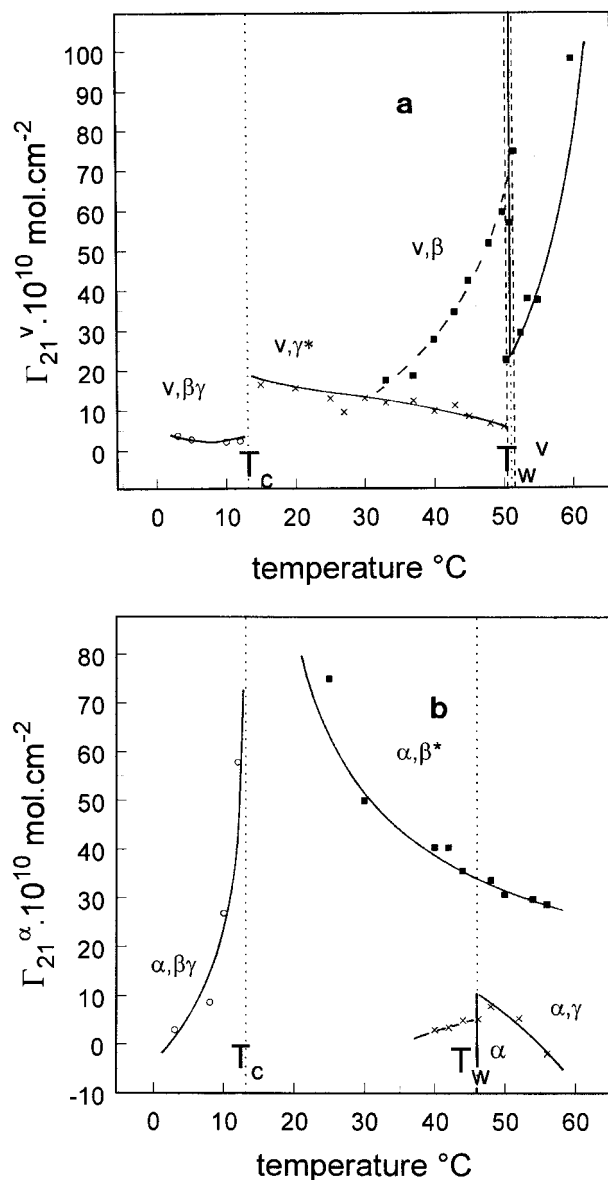
Figure 4. (a) Adsorption versus T in °C: along the critical isochore $(v, \beta\gamma)$ and at coexistence $(\beta-v$ and $\gamma^*-v)$. The asterisk on γ reminds us that, between T_c and T_w, γ is the completely wetting phase between β and v. T_w^v is the wetting transition temperature: above T_w^v, γ^* only partially wets β in contact with v. T_c is the bulk critical temperature. The $\beta-v$ curve is in two parts: above T_w^v (equilibrium values) and below T_w^v (values extrapolated to a metastable $\beta-v$ interface). A first-order transition seems to appear. See also figure 3(b). (b) The corresponding figure for silica contact. The completely wetting phase is now β^*. The critical divergence is clearly seen. The divergence at T_w^α, definitely established elsewhere [18], is to $-\infty$ due to the wetting film nature (water-rich) and to the structure of the experimental parameter Γ_{21}^α. $\Gamma_{21}^{\alpha\gamma}$ at coexistence for $T < T_w^\alpha$ (prewetting-surface-demixing zone) is insensitive to surface demixing, due to the layering (see the text).
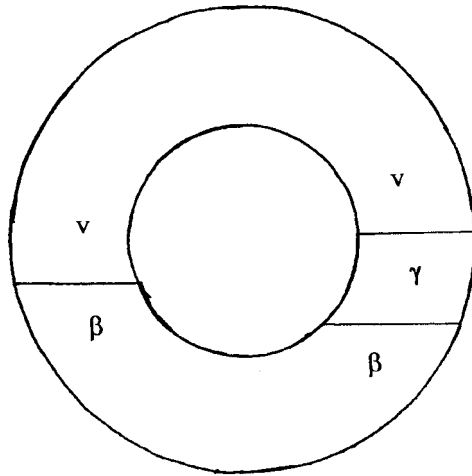
Figure 5. An experimental device showing the physical meaning of the β–v interface at coexistence even when γ^* is completely wetting β.
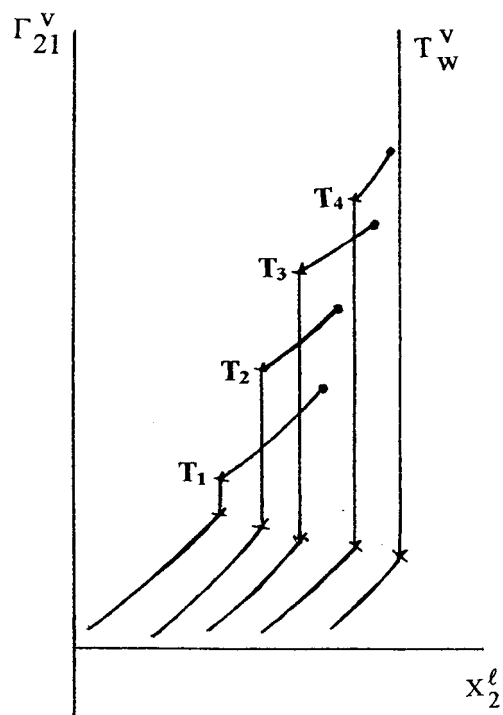
Figure 6. Isotherm shapes expected for prewetting. Surface demixings are seen through the vertical parts. The only temperature at which adsorption merges with the wetting film is T_w^v: Γ_{21}^v diverges.

Finally, two unexpected behaviours should be considered: the increase of adsorption, on the one hand, along $\beta\gamma$ when T is decreasing from T_c and, on the other hand, along β when T is increasing. If one admits the correlation length as the leading parameter, it is worth realizing, first, that a temperature decrease below T_c leads straight to ice demixing from the

liquid mixture (it is, thus, the way in which the lowest phase diagram in figure 1 must be read) and, secondly, that a temperature increase above 60 °C results in boiling, i.e. in the formation of water-rich vapour. In both cases, the closeness of bulk demixing should affect the correlation length and, therefore, the adsorption layer thickness, perhaps in the same way. But getting insight into this point would require the use of a more detailed model that should explain why, in both cases, the surface becomes richer in 2, 5 DMP than the solution: this phenomenon is possible, but has to be explained.

5.4. Comparison with a silica wall

Comparison of the adsorption related to the critical point and wetting can be made from figures 4(a) and 4(b). Bulk liquid mixtures have, of course, the same behaviour in the two cases. However, due to the multiple interactions in the system, the preferentially wetting phase against vapour is the 2, 5 DMP-rich γ-phase (the case of v), whereas against silica (the case of α) it is the water-rich β-phase. In both cases, however, 2, 5 DMP is the preferentially adsorbed component, except at T_w^α for the case of α.

Comparison is judicious around T_c and T_w. Around T_c the two behaviours are very alike: adsorption along the critical isochore and along the preferentially wetting phase, i.e. γ and β for the cases of v and α, respectively, diverges or tends to diverge to $+\infty$. However, in the case of v, we observe a trend to divergence, rather than the divergence itself. It is likely that, in addition to the accuracy problem in the adsorption determination, prefactors are responsible for this behaviour.

Around T_w, against different walls, one should consider β for the case of v, and γ for the case of α: both of them are, indeed, non-wetting phases. On such phases, close to coexistence, a film of the other phase is nucleating: it will be a 2, 5 DMP-rich film in the case of v and a water-rich film in the case of α. Wetting by these films will be complete at T_w^v and at $T < T_w^v$ against vapour, or at T_w^α and $T < T_w^\alpha$. As these films have infinite thickness, an infinite quantity of 2, 5 DMP comes into the surface layer in the case of v (γ-film forming), whereas it is an infinite quantity of water in the case of α (β-film forming). Consequently, at T_w, Γ_{21} adsorption diverges to $+\infty$ in the case of v and to $-\infty$ in the case of α for the non-wetting phase; see formula (17).

When $T_c \ll T < T_w$ one should note on this branch of the curves (figure 4) that adsorption apparently goes to $+\infty$ at T_w^v (the case of v), whereas in the case of α it maintains a rather small value. This seems to be caused by interference between two surface phenomena: layering, i.e. the successive separation of a 'pure' layer of 2, 5 DMP, and wetting transition [28]. The trend to $-\infty$ divergence is clearly noticeable on adsorption isotherms [18, 19]; however, this trend is periodically interrupted by the manifestation of layering which increases adsorption until divergence takes place again.

A layer-by-layer formation of wetting film has been evidenced at contacts with vapour [16] but through kinetic processes. Apparently, in equilibrium data like those here, this does not appear.

6. Conclusions

Ideas currently admitted and tested in several statistical models about adsorption behaviour, for liquid binary systems undergoing liquid–liquid phase demixing around the critical point and along the coexistence curve through a wetting temperature, were verified for the same liquid system against two different walls. Though the critical laws were not determined because of the lack of accuracy and/or low number of data within the area of concern, divergence of

adsorption was observed against both walls on the critical isochore and on the wetting phase for each system at coexistence.

On the non-wetting phase, divergence was also observed at T_w, but to $\pm\infty$ according to the nature of the wall, i.e. according to the nature of the wetting film appearing at T_w. Both transitions seem to be first order, but this was really demonstrated for the silica wall only.

Experimental difficulties are very much dependent on the wall used: classical adsorption determinations are more direct and precise for solid walls; against vapour, the necessary use of the Gibbs isotherm formula for the non-ideal system is far more difficult. In both cases other phenomena interfere with the major trends studied: with the silica wall, the main trouble was due to *surface* demixing, namely layering; but it was manifested essentially around T_w. With the vapour wall, *bulk* demixing, like ice forming and vapour forming, seems to influence both adsorption behaviours in the vicinity of T_c (ice forming) and around T_w (vapour forming).

Though these systems do not exhibit behaviours as simple as those expected from models, they show that the major trends are respected and must be taken into account in every real system possessing a critical point and a wetting transition, whether related or not related to a critical point.

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