Thermodynamic Investigations of Thin Liquid Layers Between Solid Surfaces

III. Benzene Between Differently Polar Fused Silica Surfaces

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Former measurements showed that benzene exhibits a disjoining pressure in extremely thin layers between fused silica plates in a temperature range just above the melting point. An extended theory for evaluating the disjoining pressure and various thermodynamic quantities of the liquid surface zone which displays a molecular long range orientation leads to results which indicate a small structural transition range at about 12—13 °C in bulk benzene. The splitting effect is more pronounced in layers adjacent to fully hydroxylated surfaces since in this case the benzene molecules in the first adsorbed layer are more tightly bound than in the case of surfaces entirely free from hydroxyl groups.

The phenomenon of molecular long range orientation in extremely thin liquid layers is particularly known for water [1, 2]. Former work of the present authors showed that benzene displays a disjoining pressure Π in layers adjacent to fused silica surfaces entirely covered with hydroxyl groups only in a temperature range between the melting point and about 19 °C [3]. Meanwhile we have developed an extended theory which takes account of the surface asperities of the fused silica plates and yields sufficiently precise values for Π [4].

The depth of oriented surface zones of benzene adjacent to quartz surfaces seems not to exceed values of about 500 Å, as was established by measurements of viscous flow carried out by Churaev and coworkers [5] who used capillaries having radii $< 10^{-5}$ cm. Our own measurements of the surface zone viscosity of benzene, which were performed by a new method [6] based on the approach of two differently formed plates, revealed viscous anomalies only for plate distances smaller than 600 Å and a temperature range between the melting point and about 14 °C.

Adsorptional investigations by Deryagin and Zorin [7] also demonstrated the formation of multimolecular benzene layers on highly polished glass plates. Further work in this field stems from Schelrdko and Platikanov [8] and from Zorin [9] who particularly made micropolarization studies of benzene films adsorbed on mercury at saturated or nearly saturated vapour pressure. The most striking evidence was the polymorphism of two different liquid films — one (α) about 70 Å and the other (β) about 210 Å thick — forming on the mercury surface and being in equilibrium with one another and the vapour phase. Bazaron et al. [10], however, who found anomalous shear moduli for thin layers of water, acetic acid, and alcohols, could not detect anomalous boundary properties for benzene.

I. Thermodynamic Considerations

Details of the derivation of a thermodynamic theory of the oriented surface zone are reported in a preceding paper [2]. The results presented in this paper refer to the thermodynamic properties of the molecular layer in the central plane between two solid surfaces having the distance h. Presuming the existence of a molecular long range orientation for plate distances $h < h^+$ the work which must be done

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to squeeze this molecular layer, of thickness $\Delta h \ll h$, into the surrounding bulk liquid was introduced [2] to be $\Delta(\Delta F^{\mathrm{E}}_{\mathrm{m}})_h$, which can be derived from the disjoining pressure, and where "m" refers to molar quantities. These are evaluated by using the density of the bulk since that of the surface zone, which is certainly slightly changed, is unknown hitherto. As long as $\Delta h \ll h$, the thermodynamic quantities of the layer in question have a differential character. When knowing the temperature dependence of $\Delta(\Delta F^{\mathrm{E}}_{\mathrm{m}})_h$, the corresponding differential molar excess entropy is given by

$$\Delta(\Delta S^{\mathrm{E}}_{\mathrm{m}})_h = -\frac{\partial \Delta(\Delta F\ )_h}{\partial T}. \qquad (1)$$

Likewise, a differential molar total excess energy

$$\Delta(\Delta U^{\mathrm{E}}_{\mathrm{m}})_h = \Delta(\Delta F^{\mathrm{E}}_{\mathrm{m}})_h + T\,\Delta(\Delta S^{\mathrm{E}}_{\mathrm{m}})_h \qquad (2)$$

can be evaluated. The temperature derivative of $\Delta(\Delta U^{\mathrm{E}}_{\mathrm{m}})_h$ leads to the differential excess molar heat $\Delta(\Delta C^{\mathrm{E}}_{\mathrm{m}})_h$.

II. Experimental

The apparatus for the determination of the disjoining pressure Π is described in detail in a previous paper [11]. The main parts of the experimental set-up are two highly polished ($\lambda/20$) fused silica plates facing each other and being planar and spherically formed, respectively, the latter having a curvature radius of 100 cm. Both plates can be immersed into the liquid under investigation. The spherically formed plate is fastened to a balance system and can be approached to the planar one by a definite force ${}^{k}K$. The plate distance h is determinable by an inductive displacement transducer which is connected to a strain gauge measuring bridge. The variation of h with ${}^{k}K$ can be registered by an xy-recorder. The evaluation of the disjoining pressure [4] is based on the formula

$$\Pi(\xi) = C\,e^{-n\xi} \qquad (3)$$

in which C and n are parameters which must be calculated by the extended theory developed by us; ξ is any distance in the planar/spherical system.

Sufficiently pure, dust and gas free benzene was prepared by distillation from a Merck product (purissimum). To be sure that the measurements were performed with fused silica surfaces entirely covered with hydroxyl groups the plates were exposed to a moist atmosphere some months before and between the measurements, respectively [3]. Fused silica surfaces free from hydroxyl groups were prepared by baking out the plates at about 850 °C for one hour.

III. Benzene Adsorbed on a Silica Surface

By ir-investigations KISELEV and coworkers [12] found that the adsorption of benzene vapour on silica gel with a surface entirely covered with hydroxyl groups (i. e. about 5 OH-groups [13] per 100 Å^2) is appreciably greater than on a surface partially freed from hydroxyl groups. The larger adsorption is ascribed to the formation of hydrogen bonds between the superficial hydroxyls of silica and the π-electrons of the adsorbed benzene molecules [14].

If the surface is dehydrated, the benzene molecules can approach the bulk silica gel to a larger extent, but, nevertheless, the adsorption energy will be smaller since no specific interaction is possible. Some authors [15], for instance, noted that the extraplanar deformational CH-vibration of the benzene molecule lying at about 678 cm^{-1} for a surface covered with OH-groups approaches that of gaseous benzene (671 cm^{-1}) as the hydroxyl groups are removed from the surface by thermal treatment in vacuo. Careful considerations by KISELEV and LYGIN [16] concerning the adsorption entropy of benzene at superficial hydroxyl groups of silica at high coverages support the assumption that the benzene molecules lie flat on the surface, performing hindered translational and rotational motions, the latter referring especially to the axis perpendicular to the ring. Comparable results are reported by WHALEN [27] and MICHEL [18].

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Immersion heats of silica gel in benzene were measured by LU and LAMA[19]; they found a value of about 98 erg/cm² which is larger than the value for a comparable non-aromatic liquid, e.g. cyclohexane (46 erg/cm²).

IV. Experimental Results

The parameters C and n of Eq. (3) which determine the disjoining pressure Π were calculated for benzene between fully hydroxylated and dehydrated fused silica surfaces, respectively (Tab. 1).

(a) fully hydroxylated surfaces			(b) dehydrated surfaces		
t [°C]	C [dyne/cm²]	n [cm⁻¹]	t [°C]	C [dyne/cm²]	n [cm⁻¹]
6.0	$1.9 \cdot 10^6$	$7.3 \cdot 10^5$	5.5	$7.1 \cdot 10^5$	$8.1 \cdot 10^5$
8.5	$2.2 \cdot 10^6$	$9.9 \cdot 10^5$	8.9	$5.0 \cdot 10^5$	$6.6 \cdot 10^5$
11.9	$2.4 \cdot 10^6$	$1.1 \cdot 10^6$	11.0	$5.0 \cdot 10^5$	$5.8 \cdot 10^5$
14.5	$2.6 \cdot 10^6$	$2.0 \cdot 10^6$	14.0	$5.6 \cdot 10^5$	$7.2 \cdot 10^5$

Table 1. Parameters C and n for benzene.

These parameters should not be mixed up with those quoted in a preliminary paper[3] in which a hyperbolic distance dependence is used. For each temperature (±0.2 °C) given in Table 1 the plot of log ^kK vs. h which is a substantial postulate of the extended theory[4] yielded a fairly straight line for sufficiently small values of h, thus fixing n (slope of the line) with only small error. The scatter of the data for C is somewhat greater.

Figure 1 represents the disjoining pressure $\Pi(h)$ in a temperature range just above the melting point for fused silica surfaces (a) covered and (b) free from hydroxyl groups. In case (a) the values of Π, particularly for small distances h, are rather large but fall off at about 15 °C; a shoulder seems to exist at 12 – 13 °C. In case (b) the disjoining pressure has dropped by a factor of about 2, but at 12 – 13 °C a slight maximum appears.

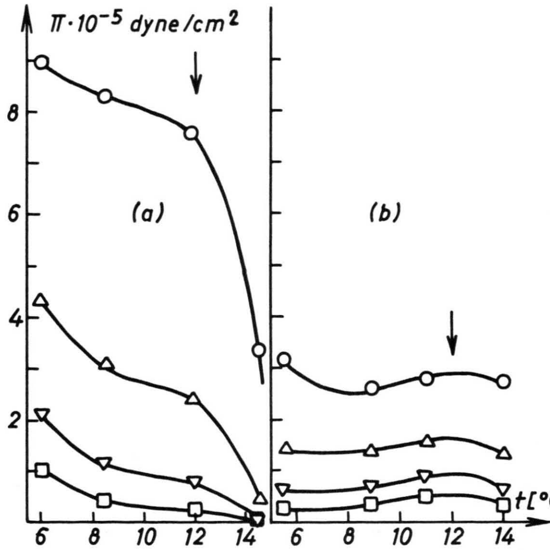

Fig. 1. The variation of the disjoining pressure with temperature between fused silica plates (a) fully hydroxylated, (b) dehydrated: ○ $h = 100$ Å, △ $h = 200$ Å, ▽ $h = 300$ Å, □ $h = 400$ Å. The arrows indicate the center of a possible structural transition range.

Figure 2 shows the temperature dependence of the plate distance h^+ where Π has attained a value of 10^4 dyne/cm². For the largest part of the temperature range in question the surface zone extension in the case (b) exceeds that in the case (a).

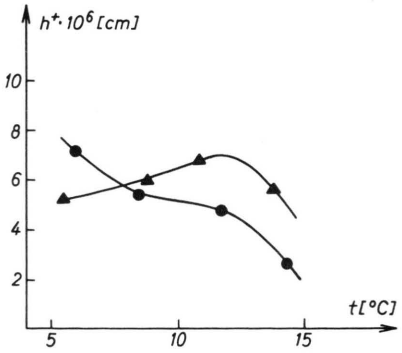

Fig. 2. The variation of h^+ with temperature for fused silica plates; ● fully hydroxylated, ▲ dehydrated.

Figure 3 reflects the temperature dependence of the differential molar excess entropy $\Delta(\Delta S^{\mathrm{E}}_{\mathrm{m}})_h$ for both cases. The benzene layer vicinal to fully hydroxylated surfaces is more ordered than the bulk liquid over the whole temperature range, but for the case of dehydrated surfaces a small temperature range (7 – 12 °C) is prominent in which the benzene layer is less ordered than the bulk.

The differential molar total excess energy $\Delta(\Delta U^{\mathrm{E}}_{\mathrm{m}})_h$ calculated by Eq. (2) is plotted against temperature in Fig. 4. The graph says that in case (a) the mechanical destruction of the surface zone is linked with an endothermic process or, in other words, that the formation of an oriented benzene layer is an exothermic process. In case (b) the

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[19] B. C.-Y. LU and R. F. LAMA, Trans. Faraday Soc. **63**, 727 [1967].

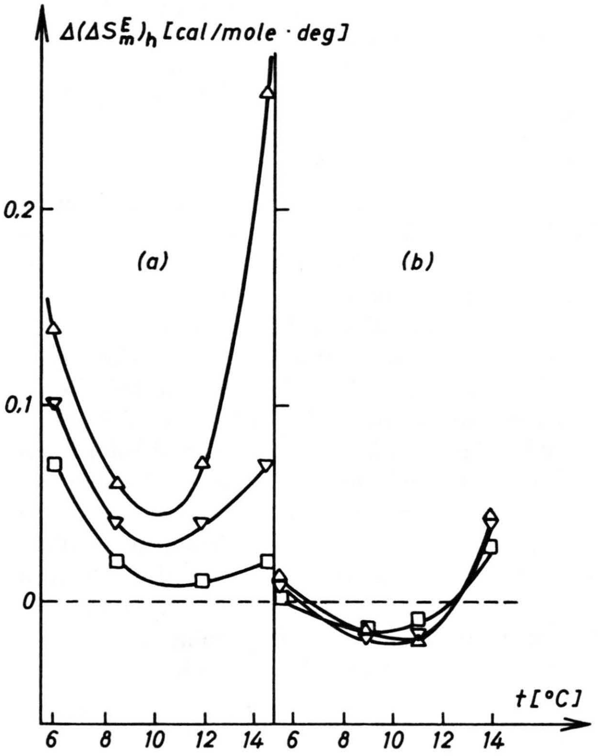

Fig. 3. The variation of the differential molar excess entropy with temperature between fused silica plates (a) fully hydroxylated, (b) dehydrated: △ $h = 200$ Å, ▽ $h = 300$ Å, □ $h = 400$ Å.

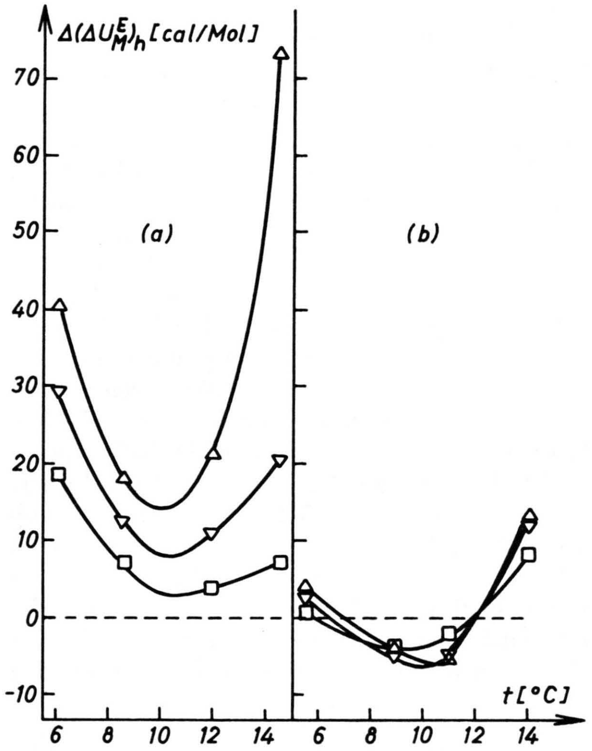

Fig. 4. The variation of the differential molar total excess energy with temperature between fused silica plates (a) fully hydroxylated, (b) dehydrated: △ $h = 200$ Å, ▽ $h = 300$ Å, □ $h = 400$ Å.

reverse is valid for a small limited temperature range. The differential molar excess heats are quoted in Table 2 for $t = 12$ °C.

	$h = 100$ Å	$h = 200$ Å	$h = 300$ Å
case (a)	29	12	3
case (b)	3	5	4

Table 2. Differential molar excess heats $\Delta(\Delta C^{\mathrm{E}}_{\mathrm{v,m}})_h$ [cal/mole deg] for different plate distances at 12 °C.

V. Discussion

Disjoining pressures calculated on the basis of long range dispersion forces [20] should only lead to values of about 100 dyne/cm^2 and should exhibit a distance dependence proportional to h^{-3}. ZORIN [9] in calculating the disjoining pressure from the results obtained by multimolecular adsorption of benzene found Π to be approximately proportional to h^{-1}. The data by Zorin, to be sure, refer to a liquid/liquid interface and, moreover, to room temperature where we could not detect any wedging effect because of the restricted sensitivity of our apparatus. In the present work the distance dependence of Π cannot be simply expressed by a negative power of h since we used an exponential function [Eq. (3)]. But trying to make a crude approximation for $100\,\text{Å} \leqq h \leqq 200\,\text{Å}$ the distance dependence of Π was found to be proportional to powers of h more positive than -3. This is in agreement with the statement of some authors [21] that the distance dependence of intermolecular interactions, commonly known to be proportional to h^{-6}, changes to a power of h between -3.5 and -6 if extended

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systems of π-electrons, e. g. aromatic rings, lying parallel to each other are taken into account.

On the basis of systematic studies of the packing effect of macroscopic models done by KAST and STUART[22] benzene molecules, particularly in the vicinity of a solid surface, should show orientational randomization only about the axis perpendicular to the plane of the aromatic ring. VAN DER WAALS forces support the tendency of parallel orientation, particularly of the axes of greatest polarizability[23].

Considering surfaces covered with hydroxyl groups we might assume the aromatic rings to be mainly oriented parallel to the silica surface. Molecules of the second layer should approach the first layer to a larger extent than in the bulk. Thus a model of the surface zone can be constructed where the molecules in the following layers are also oriented parallel to the surface, but to an extent getting smaller with increasing depth. The main feature of this model might be the appearance of a rotational hindering in the surface zone which gives rise to an excess free energy and to a disjoining pressure, respectively[3].

Quantitative calculations concerning this subject were made by DE BOER[24] who found that position (a) (Fig. 5) of the rings having a distance of 3.5 Å leads to an attraction energy three times weaker than position (b). The latter case might be important for the origin of the free excess energy, especially when taking account of the additional interaction via the aromatic π-electrons[21].

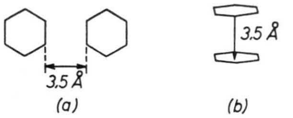

Fig. 5. The position of two adjacent benzene molecules (a) lying in the same plane, (b) lying in parallel planes.

The piling up of oriented molecular layers vicinal to the solid surface can be regarded as a special solvation effect. This seems to be more pronouced the less the solid substratum is curved. WHALEN[17] reported that benzene molecules in layers adjacent to small quartz particles ($<10^{-4}$ cm) show only a rotational hindering, but adjacent to greater particles even an additional translational hindering. This notable influence of particle size is also reflected by immersion heats[17].

All experimental data obtained refer to differences in thermodynamic properties between the surface zone and the bulk. Own results got for numerous organic liquids[25] have established the view that a long range cooperative molecular packing effect in the vicinity of a solid surface is only possible if the surface is actually able to decouple the bulk liquid structure via the first adsorbed layer. This effect should be favoured by not too large molecular interactions in the bulk and strong adsorptional forces in the first layer which, on their part, cause the rotational and translational restriction in question. The latter condition seems to be fulfilled for silica surfaces covered with hydroxyl groups. Dehydrated surfaces induce only a minor effect for a small temperature range about 12 – 13 °C.

After KATZOFF[26] (x-ray diffraction) crystalline benzene exhibits a lattice in which the arrangement of the benzene rings is T-shaped. Recent investigations by some authors[27] confirmed this arrangement in its main features also for the liquid phase at room temperature. In respect to the molecular mobility of benzene ANDREW[28] quotes a rotational transition concerning the axis perpendicular to the ring already for the crystalline state. Rotation around the other two principal axes should be possible not before the melting point is reached[29].

Contrary to the evidence for dipolar liquids which exhibit a disjoining pressure only in a small temperature range about 30 – 40° above the melting point benzene displays a disjoining pressure already just above the melting point. The abnormality in the temperature range about 12 – 13 °C might be explained by the occurence of a structural transition in the bulk as is evident in the case of all dipolar liquids investigated hitherto[25].

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Indeed, deviations in some physical properties of bulk benzene were found at about these temperatures by some authors. Visvosity data reported by DAVIES and MATHESON [29] exhibit an anomaly at about 12 – 13 °C indicating an increase of the activation energy of flow for the lower temperature side. URAZOVSKII et al. [30] found a "kink" at about 20 °C for the same case. After CHETAEV [31] the surface tension displays an anomalous behaviour above the melting point (but <13 °C). BORNEAS and BABUTIA [32] report anomalies in the "rotokinetic" effect of benzene at about 17 °C.

Additional evidence was given by the present authors. The altered boundary viscosity of benzene showed extrema at about 12 °C for the case of fused silica surface free from OH-groups [6]. The thermal anomaly obtained for the surface zone is also present in a solution of 1-nitro-3,5-diaminobenzene ($5.42 \cdot 10^{-4}$ m) in benzene as could be confirmed by spectroscopic investigations [33]. The solute seems to create a solvation shell which bears some resemblance to the larger oriented surface zone.

Results of BOSS and STEJSKAL [34] who measured the pressure dependence of the rotational correlation time τ_R of benzene by nmr-technique support the view that the structural transition should refer to the onset of rotation around one of the principal molecular C_2-axes. Taking mixtures of n-heptane and benzene which display a positive excess volume and thus favour molecular rotational and translational movements in the bulk we found strikingly large disjoining pressures which reached the value of $2 \cdot 10^6$ dyne/cm² at a molar fraction of benzene of 0.7 at $h = 200$ Å and $t = 6$ °C [33].

Therefore, it seems at least reasonable to assume the existence of a structural – possibly rotational – transition range at about 12 – 13 °C. In the graphs of Figs. 3 and 4 one has to note that $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h$ as well as $\Delta(\Delta U_{\mathrm{m}}^{\mathrm{E}})_h$ increase again at the higher temperature side of the minimum value. The effect should occur when the surface zone excess energy gets steeply larger by onset of molecular rotation in the bulk, whereas the disjoining pressure grows smaller by thermal randomization in the surface zone.

The fact that the temperature range for the appearance of a disjoining pressure and the surface zone extension into the bulk liquid, respectively, is somewhat larger in the case of dehydrated silica surfaces might be due to a denser molecular packing in the first adsorbed layer. The specific interaction of benzene molecules with surface hydroxyls obviously excludes the formation of a closely packed layer since the surface hydroxyls are distributed more or less statistically over the whole surface, whereas GALKIN et al. [15] consider each benzene molecule adsorbed on a hydrated surface to cover several surface hydroxyls.

VI. Conclusional Remarks

The results of our work present clear evidence for the occurence of a long range orientation in boundary layers of benzene. It must be emphasized that this effect is strongly dependent on the nature of the solid surfaces contacted. Moreover, the long range orientation is only detectable in a small temperature range which is termed "pre-freezing region" (UBBELOHDE [35]). The experimentally found extension of the surface zone does not contradict the findings of other authors. By means of the disjoining pressure we cannot make any distinction between the existence of a multimolecular α-phase and a β-phase as ZORIN [9] did.

The calculations show that the entropy term in Eq. (2) plays the most decisive role, but, nevertheless, the absolute values of $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h$ are very small. $\Delta(\Delta U_{\mathrm{m}}^{\mathrm{E}})_h$ is likewise rather small and does not reach the energy scale for one degree of freedom, viz. of free rotational motion around one axis (≈ 300 cal/mole). The motion around the axis in question might not strongly be restricted in the surface zone and/or there prevails some rotational hindering in the bulk.

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