Thermodynamic Investigations of Thin Liquid Layers Between Solid Surfaces

III. Benzene Between Differently Polar Fused Silica Surfaces

G. PESCHEL and K. H. ADLFINGER

Institut für Physikalische Chemie der Universität Würzburg

(Z. Naturforsch. **26 a**, 716—721 [1971]; received 16 December 1970)

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 °C³. 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 coworkers⁵ who used capillaries having radii $<10^{-5}$ cm. Our own measurements of the surface zone viscosity of benzene, which were performed by a new method⁶ 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 ZORIN⁷ also demonstrated the formation of multi-

molecular benzene layers on highly polished glass plates. Further work in this field stems from SCHELUDKO and PLATIKANOV⁸ and from ZORIN⁹ 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 paper². 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

¹ J. C. HENNIKER, Rev. Mod. Phys. **21**, 322 [1949].

² G. PESCHEL and K. H. ADLFINGER, Z. Naturforsch. **26 a**, 707 [1971].

³ G. PESCHEL and K. H. ADLFINGER, Z. Physik. Chem. (N.F.) **63**, 150 [1969].

⁴ K. H. ADLFINGER and G. PESCHEL, Z. Physik. Chem. (N.F.) **70**, 151 [1970]. — K. H. ADLFINGER, R. SCHNORRER, and G. PESCHEL, Z. Angew. Physik **29**, 136 [1970].

⁵ N. V. CHURAEV, V. D. SOBOLEV, and Z. M. ZORIN, Disc. Faraday Soc., in press.

⁶ G. PESCHEL and K. H. ADLFINGER, Ber. Bunsenges. Physik. Chem. **74**, 351, 933 [1970].

⁷ B. V. DERYAGIN and Z. M. ZORIN, Zh. Fiz. Khim. **29**, 1010, 1755 [1955].

⁸ A. SCHELUDKO and D. PLATIKANOV, Kolloid-Z. **175**, 150 [1961].

⁹ Z. M. ZORIN, Kolloidn. Zh. **25**, 624 [1963]; Research in Surface Forces, Vol. 2, p. 134, ed. B. V. DERYAGIN, Consultants Bureau, New York 1966.

¹⁰ U. B. BAZARON, B. V. DERYAGIN, and A. V. BULGADAEV, Zh. Eksp. Teor. Fiz. **51**, 969 [1966].

to squeeze this molecular layer, of thickness $\Delta h \ll h$, into the surrounding bulk liquid was introduced² to be $\Delta(\Delta F_m^E)_h$, 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 $\Delta(\Delta F_m^E)_h$, the corresponding differential molar excess entropy is given by

$$\Delta(\Delta S_m^E)_h = - \frac{\partial \Delta(\Delta F_m^E)_h}{\partial T}. \quad (1)$$

Likewise, a differential molar total excess energy

$$\Delta(\Delta U_m^E)_h = \Delta(\Delta F_m^E)_h + T \Delta(\Delta S_m^E)_h \quad (2)$$

can be evaluated. The temperature derivative of $\Delta(\Delta U_m^E)_h$ leads to the differential excess molar heat $\Delta(\Delta C_m^E)_h$.

II. Experimental

The apparatus for the determination of the disjoining pressure Π is described in detail in a previous paper¹¹. 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 kK . 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 kK can be registered by an xy -recorder. The evaluation of the disjoining pressure⁴ is based on the formula

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

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, respectively³. 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 coworkers¹² found that the adsorption of benzene vapour on silica gel with a surface entirely covered with hydroxyl groups (i. e. about 5 OH-groups¹³ per 100 Å²) 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 molecules¹⁴.

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 authors¹⁵, 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 LYGIN¹⁶ 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 WHALEN¹⁷ and MICHEL¹⁸.

¹¹ G. PESCHEL, Z. Physik. Chem. (N.F.) **59**, 27 [1968].

¹² A. V. KISELEV, K. G. KRASILNIKOV, and L. N. SOBOLEVA, Dokl. Akad. Nauk SSSR **94**, 85 [1954]. — L. D. BELIAKOVA and A. V. KISELEV, Dokl. Akad. Nauk SSSR **119**, 298 [1958].

¹³ A. A. AGZAMKHODZHAEV, L. T. ZURAVLEV, and A. V. KISELEV, Izv. Akad. Nauk SSSR, Ser. Khim. **1968**, 1186.

¹⁴ A. V. KISELEV and B. A. FROLOV, Kinet. Katal. **3**, 774 [1962].

¹⁵ G. A. GALKIN, A. V. KISELEV, and V. I. LYGIN, Kinet. Katal. **5**, 1040 [1964].

¹⁶ A. V. KISELEV and V. I. LYGIN, Kolloidn. Zh. **23**, 574 [1961].

¹⁷ J. W. WHALEN, J. Phys. Chem. **67**, 2114 [1963].

¹⁸ D. MICHEL, Z. Naturforsch. **23 a**, 339 [1968].

Immersion heats of silica gel in benzene were measured by LU and LAMA¹⁹; 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/cm ²]	n [cm ⁻¹]	t [°C]	C [dyne/cm ²]	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 paper³ in which a hyperbolic distance dependence is used. For each temperature (± 0.2 °C) given in Table 1 the plot of $\log {}^hK$ vs. h which is a substantial postulate of the extended theory⁴ 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.

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).

Figure 3 reflects the temperature dependence of the differential molar excess entropy $\Delta(\Delta S_m^E)_h$ for

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

Fig. 2. The variation of h^+ with temperature for fused silica plates; $\bullet$ fully hydroxylated, $\blacktriangle$ dehydrated.

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 $\Delta(\Delta U_m^E)_h$ 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

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: $\triangle$ $h = 200$ Å, ∇ $h = 300$ Å, $\square$ $h = 400$ Å.

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

reverse is valid for a small limited temperature range. The differential molar excess heats are quoted in Table 2 for $t = 12^\circ\text{C}$.

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

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

V. Discussion

Disjoining pressures calculated on the basis of long range dispersion forces²⁰ should only lead to values of about 100 dyne/cm² and should exhibit a distance dependence proportional to h^{-3} . ZORIN⁹ in calculating the disjoining pressure from the re-

sults 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 $100 \text{ Å} \leq h \leq 200 \text{ Å}$ 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 authors²¹ 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

²⁰ J. FRENKEL, Kinetic Theory of Liquids, Dover Publications, Inc., New York 1955.

²¹ E. F. HAUGH and J. O. HIRSCHFELDER, J. Chem. Phys. **23**, 1778 [1955]. — C. A. COULSON and P. L. DAVIES, Trans. Faraday Soc. **48**, 777 [1952].

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 STUART²² 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 polarizability²³.

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, respectively³.

Quantitative calculations concerning this subject were made by DE BOER²⁴ 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 -electrons²¹.

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 pronounced the less the solid substratum is curved. WHALEN¹⁷

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 heats¹⁷.

All experimental data obtained refer to differences in thermodynamic properties between the surface zone and the bulk. Own results got for numerous organic liquids²⁵ 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 KATZOFF²⁶ (x-ray diffraction) crystalline benzene exhibits a lattice in which the arrangement of the benzene rings is T-shaped. Recent investigations by some authors²⁷ confirmed this arrangement in its main features also for the liquid phase at room temperature. In respect to the molecular mobility of benzene ANDREW²⁸ 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 reached²⁹.

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 occurrence of a structural transition in the bulk as is evident in the case of all dipolar liquids investigated hitherto²⁵.

²² W. KAST and H. A. STUART, *Phys. Z.* **40**, 714 [1939].

²³ G. BRIEGLEB, *Zwischenmolekulare Kräfte*, F. Enke, Stuttgart 1937.

²⁴ J. H. DE BOER, *Trans. Faraday Soc.* **32**, 10 [1936].

²⁵ K. H. ADLFINGER and G. PESCHEL, *Disc. Faraday Soc.*, in press; presentation at the Disc. Dtsch. Bunsenges., *Molecular Motions in Liquids*, Herrenalb 1970; R. SCHNORRER and G. PESCHEL, being prepared.

²⁶ S. KATZOFF, *J. Chem. Phys.* **2**, 841 [1943].

²⁷ G. ROTH, *Z. Naturforsch.* **18a**, 516 [1963]. — A. H. NARTEN, *J. Chem. Phys.* **48**, 1630 [1968]. — R. L. SCHMIDT and J. H. GOLDSTEIN, *J. Chem. Phys.* **50**, 1494 [1969].

²⁸ E. R. ANDREW, *J. Phys. Chem. Solids* **18**, 9 [1961].

²⁹ D. B. DAVIES and A. J. MATHESON, *J. Chem. Phys.* **45**, 1000 [1966].; *Trans. Faraday Soc.* **63**, 596 [1967]; *Disc. Faraday Soc.* **43**, 216 [1967].

Indeed, deviations in some physical properties of bulk benzene were found at about these temperatures by some authors. Viscosity data reported by DAVIES and MATHESON²⁹ 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 CHETAEV³¹ the surface tension displays an anomalous behaviour above the melting point (but <13 °C). BORNEAS and BABUTIA³² 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-groups⁶. 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 investigations³³. The solute seems to create a solvation shell which bears some resemblance to the larger oriented surface zone.

Results of BOSS and STEJSKAL³⁴ 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 $t = 6$ °C³³.

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 $\Delta(\Delta S_m^E)_h$ as well as $\Delta(\Delta U_m^E)_h$ 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. Concluding Remarks

The results of our work present clear evidence for the occurrence 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" (UBBELOHDE³⁵). 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 ZORIN⁹ did.

The calculations show that the entropy term in Eq. (2) plays the most decisive role, but, nevertheless, the absolute values of $\Delta(\Delta S_m^E)_h$ are very small. $\Delta(\Delta U_m^E)_h$ 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.

The authors wish to thank Prof. Dr. G. BRIEGLER and the Deutsche Forschungsgemeinschaft for support of this work.

³⁰ S. S. URAZOVSKII and P. A. CERNJAVSKII, Tr. Charkov. Politech. Inst. Lenina **26**, 29 [1959].

³¹ P. M. CHETAEV, Zh. Fiz. Khim. **25**, 1454 [1951].

³² M. BORNEAS and I. BABUTIA, Naturwiss. **47**, 373 [1960].

³³ G. PESCHEL, unpublished.

³⁴ B. D. BOSS and E. O. STEJSKAL, J. Chem. Phys. **45**, 81 [1966].

³⁵ A. R. UBBELOHDE, Melting and Crystal Structure, Clarendon Press, Oxford 1965.