On the Diffuse Structure of the Toluene – Water Interface

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Abstract

The electric density profile along the normal to the phase interface between aromatic hydrocarbon toluene and water has been studied by X-ray reflectometry using synchrotron radiation. According to the experimental data, the width of the interface under normal conditions is $(5.7 \pm 0.2)$ Å. This value is much larger than a theoretical value of $(3.9 \pm 0.1)$ Å predicted by the theory of capillary waves with an interphase tension of $(36.0 \pm 0.1)$ mN/m. The observed broadening of the interface is attributed to its own diffuse near-surface structure with a width no less than 4 Å, which is about the value previously discussed for high-molecular-weight n-alkane – water and 1,2-dichloroethane – water interfaces.

Two forms of the transverse structure of the oil – water interface that imply its fundamentally different molecular structures, which affect, e.g., the rates of interphase ion exchange or chemical reactions, are widely discussed [1-4]. This is either an interface with a clear molecular structure with the width determined only by roughness caused by capillary waves or an interface with a diffuse structure at which mixing of phases occurs at a molecular level in a layer with a thickness up to several molecular dimensions. In this work, the first measurement of the reflection coefficient from the interface between water and aromatic hydrocarbon toluene (C₇H₈), which is considered as a model when studying, e.g., adsorption of asphaltenes [5], is reported. The found value of the interface width under normal conditions is significantly different from the prediction of the theory of capillary waves, which is unambiguously determined by the interphase tension $\gamma$ and temperature $T$. The observed smearing of the interface is attributed to its own near-surface structure, e.g., a phase mixing region with the width $\geq 4$ Å.

The planar toluene – water interface oriented by the gravitational force was studied in a thermostated stainless steel cell ($T \approx 298$K) with X-ray transparent windows made from polyethylene glycolterephthalate using the method described in [6]. Aromatic hydrocarbon toluene (C₇H₈, density $\approx 0.86$ g/cm³ 298 , boiling temperature $T_b \approx 384$) was purchased from Sigma-Aldrich and was purified by multiple filtration in a chromatographic column [7]. Toluene and water hardly mix under normal conditions.

The surface tension of the pure interface $\gamma$ was measured by the Wilhelmy plate method directly in the experimental cell and was $\gamma = 36.0 \pm 0.1$ mN/m, which is in good agreement with the data reported in [8-10]. About 100 mL of deionized water with pH $\approx 7$ (Barnstead, NanoPureUV) was used as the upper bulk phase. About 50 mL of toluene was used as the upper bulk phase. Before the measurements of the reflection coefficient $R$, the sample was annealed and was aged for several hours [11].

The transverse structure of the toluene – water interface was studied by X-ray reflectometry in the X19C beamline of the National Synchrotron Light Source. This beamline allows the study of both the surface of solids and liquids and hidden liquid – liquid interfaces [12-16]. A focused monochromatic beam with an intensity of $\approx 10^{11}$ photons/s and a photon energy of $E = 15$ keV (wavelength $\lambda = 0.825 \pm 0.002$ Å) was used in the experiments. This beamline was previously used to study phase transitions in adsorption layers of fatty alcohols and acids at the (saturated hydrocarbonwater) interface [11, 17].

Figure 1 illustrates the kinematics of the surface scattering at the interface, where $\alpha$ is the glancing angle and $\beta$ is the angle between the interface plane and the direction to the detector in the plane of incidence $yz$. In the reflectometry experiment ($\alpha = \beta$), X-rays pass through the oil phase and are reflected from the near-surface structure at the interface. In this case, the scattering vector $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s$, where $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and scattered beam in the direction of the observation point, respectively, is strictly perpendicular to the surface along the $Oz$ axis, i.e., in the direction opposite to the gravitational force. The measurement of the reflection coefficient $R$ as a function of...
where $\sigma_{cw}$ is the capillary width squared, $\sigma_w$ is the rms deviation of the interface from the nominal position $z = 0$. The estimate of the integral characteristic of the spectrum of capillary waves for the isotropic surface of the liquid or the capillary width squared $\sigma_{cw}^2$ is determined by the range of surface spatial frequencies covered in the experiment [23-25]:

$$\sigma_{cw}^2 = \frac{k_BT}{2\pi \gamma} \ln \left( \frac{Q_{max}}{Q_{min}} \right). \quad (3)$$

Here, $Q_{max} = 2\pi/a$ is the short-wave-length limit of the spectrum ($a \approx 10 \text{ Å}$ is the intermolecular distance in order of magnitude) and is the long-wave-length limit, where $\Delta\beta \approx 4 \cdot 10^{-4} \text{ rad}$ is the angular resolution of the detector in the experiment and $q_{cw}^{min} \approx 0.25 \text{ Å}^{-1}$. Consequently, Eq. (3) for the toluene – water interface in this experiment gives $\sigma_{cw} = 3.9 \pm 0.1 \text{ Å}$. 

In the first distorted wave Born approximation, the reflection coefficient has the form [26, 27]

$$R(q_z) = R_F(q_z) \exp \left( -\sigma_z^2 q_z^2 - q_c^2 \right), \quad (4)$$

where

$$R_F(q_z) = \left( \frac{q_z - \sqrt{q_z^2 - q_c^2}}{q_z + \sqrt{q_z^2 - q_c^2}} \right)^2, \quad (5)$$

is the Fresnel function and $q_c = (4\pi/\lambda) \sin \alpha_c$.

In Fig. 2, the solid line is the one-parameter model (1) with the fitting parameter $\sigma = 5.7 \pm 0.2 \text{ Å}$ in (4), the dashed line is the Fresnel function (5), and the dotted line is the calculation by Eq. (4) with $\sigma = \sigma_{cw}$.

Thus, according to the experimental data, the electron density profile (1) for the toluene-water interface has the width $\sigma = 5.7 \pm 0.2 \text{ Å}$, which is much larger than the value $\sigma_{cw} = 3.9 \pm 0.1 \text{ Å}$ calculated within the theory of capillary waves for the measured interphase tension ($36.0 \pm 0.1 \text{ mN/m}$). This new and quite surprising experimental result indicates the existence of the structure of the interface with the width no less than $\sigma_0 = \sqrt{\sigma^2 - \sigma_{cw}^2} \approx 4.2 \text{ Å}$, i.e., no less than the radius of the benzene ring of a toluene molecule ($\sim 4 \text{ Å}$).

The previous reflectometry data indicated the absence of any diffuse layer in the near-surface structure of the n-hexane – water, nitrobenzene – water, and 2-heptanone – water interfaces [28-30]. However, the studies of the n-alkane – water and silica hydrosol – air interfaces demonstrated that their interphase width can be described only with the inclusion of contributions both from capillary waves and from their own structure [3, 31]. In the former case, the width of their own structure is determined by two physically significant parameters of the system - the radius of inertia of a hydrocarbon molecule and the bulk correlation length [32, 33]. The latter parameter specifies, e.g., the width of the n-docosane – water interface [6]. In the considered case, the observed width of the diffuse phase mixing region ($\geq 4 \text{ Å}$) has the same order of magnitude as the width previously discussed for the n-hexadecane – water and 1,2-dichloroethane – water interfaces [3, 4].

To summarize, this study of the interface between aromatic hydrocarbon and water, as well as our previous reports on phase transitions at saturated hydrocarbon-water interfaces, has demonstrated new experimental capabilities.
provided by X-ray scattering methods with synchrotron radiation for revealing the essence of processes occurring at phase interfaces in water – oil emulsions in the presence of impurity surfactants (asphaltenes, naphthenic acids, etc.), which affect the efficiency of oil technological processes [34-36].

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References

[1] I. Benjamin, Science (Washington, DC, U. S.) 261, 1558 (1993).
[2] D. J. Henderson and W. Schmickler, J. Chem. Soc., Faraday Trans. 92, 3839 (1996).
[3] D. M. Mitrinovic, A. M. Tikhonov, M. Li, Z. Huang, and M. L. Schlossman, Phys. Rev. Lett. 85, 582 (2000).
[4] D. S. Walker, M. G. Brown, C. L. McFeari, and G. L. Richmond, J. Phys. Chem. B 108, 2111 (2004).
[5] S. Zarkar, V. Pauchard, U. Farooq, A. Couzis, and S. Banerjee, Langmuir 31, 4878 (2015).
[6] A. M. Tikhonov, D. M. Mitriñovíc, M. Li, Z. Huang, and M. L. Schlossman, J. Phys. Chem. B 104, 6336 (2000).
[7] A. Goebel and K. Lunkenheimer, Langmuir 13, 369 (1997).
[8] A. W. Adamson, Physical Chemistry of Surfaces, 3rd ed. (Wiley, New York, 1976).
[9] L. L. Schramm and L. G. Hepler, Can. J. Chem. 72, 1915 (1994).
[10] J. Saien and S. Akbari, J. Chem. Eng. Data 51, 1832 (2006).
[11] A. M. Tikhonov, JETP Lett. 104, 309 (2016).
[12] M. L. Schlossman, D. Synal, Y. Guan, M. Meron, G. Shea-McCarthy, Z. Huang, A. Acero, S. M. Williams, S. A. Rice, and P. J. Viccaro, Rev. Sci. Instrum. 68, 4372 (1997).
[13] F. A. Akin, I. Jang, M. L. Schlossman, S. B. Sinnott, G. Zajac, E. R. Fuoco, M. B. J. Wijesundara, M. Li, A. M. Tikhonov, S. V. Pingali, A. T. Wroble, and L. Hanley, J. Phys. Chem. B 108, 9656 (2004).
[14] A. M. Tikhonov, J. Phys. Chem. B 110, 2746 (2006).
[15] J. Koo, S. Park, S. Satija, A. M. Tikhonov, J. C. Sokolov, M. H. Rafailovich, and T. Koga, J. Colloid Interface Sci. 318, 103 (2008).
[16] A. M. Tikhonov, J. Chem. Phys. 130, 024512 (2009).
[17] A. M. Tikhonov and M. L. Schlossman, J. Phys.:Condens. Matter 19, 375101 (2007).
[18] M. L. Schlossman, M. Li, D. M. Mitrinovic, and A.M. Tikhonov, High Perform. Polym. 12, 551 (2000).
[19] S. V. Pingali, T. Takiue, G. Guangming, A. M. Tikhonov, N. Ikeda, M. Aratono, and M. L. Schlossman, J. Dispersion Technol. 27, 715 (2006).
[20] F. P. Buff, R. A. Lovett, and F. H. Stillinger, Phys. Rev. Lett. 15, 621 (1965).
[21] E. S. Wu and W. W. Webb, Phys. Rev. A 8, 2065 (1973).
[22] J. D. Weeks, J. Chem. Phys. 67, 3106 (1977).
[23] A. Braslau, M. Deutsch, P. S. Pershan, A. H. Weiss, J. Als-Nielsen, and J. Bohr, Phys. Rev. Lett. 54, 114 (1985).
[24] A. Braslau, P. S. Pershan, G. Swislow, B. M. Ocko, and J. Als-Nielsen, Phys. Rev. A 38, 2457 (1988).
[25] D. K. Schwartz, M. L. Schlossman, E. H. Kawamoto, G. J. Kellogg, P. S. Pershan, and B. M. Ocko, Phys. Rev. A 41, 5687 (1990).
[26] L. Nevot and P. Croce, Rev. Phys. Appl. 15, 761 (1980).
[27] S. K. Sinha, E. B. Sirola, S. Garoff, and H. B. Stanley, Phys. Rev. B 38, 2297 (1988).
[28] D. M. Mitrinovic, Z. Zhang, S. M. Williams, Z. Huang, and M. L. Schlossman, J. Phys. Chem. B 103, 1779 (1999).
[29] G. Luo, S. Malkova, S. V. Pingali, D. G. Schultz, B. Lin, M. Meron, T. J. Graber, J. Gebhardt, P. Vanysek, and M. L. Schlossman, Electrochem. Commun. 7, 627 (2005).
[30] G. Luo, S. Malkova, S. V. Pingali, D. G. Schultz, M. L. Schlossman, P. Vanysek, B. Lin, M. Meron, T. Graber, and J. Gebhardt, Faraday Discuss. 129, 23 (2005).
[31] A. M. Tikhonov, V. E. Asadchikov, Yu. O. Volkov, B. S. Roshchin, B. Honkimaki, and M. V. Blanko, JETP Lett. 107, 384 (2018).
[32] G. Avitabile and A. Tuzi, J. Polymer Sci. 21, 2379 (1983).
[33] E. Eisenriegler, J. Chem. Phys. 79, 1052 (1983).
[34] M. L. Schlossman and A. M. Tikhonov, Ann. Rev. Phys. Chem. 59, 153 (2008).
[35] K. Akbarzadeh, A. Hammami, A. Kharrat, D. Zhan, S. Al- lenson, J. Creek, S. Kabir, A. J. Jamaaluddin, A. G. Marshall, R. P. Rodgers, O. C. Mullins, and T. Solbakken, Oilfield Rev. 19 (2), 22 (2007).
[36] O. C. Mullins, Ann. Rev. Anal. Chem. 4, 393 (2011).