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Adsorption of hexane and cyclohexane vapours at the water drop surface

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Abstract: The dependence of the dynamic surface tension of water at the interface with saturated hexane and cyclohexane vapours was measured by the drop profile analysis method. The surface tension for the adsorption layers of cyclohexane at different temperatures was compared with the results reported earlier for the adsorption of hexane and other alkanes from the vapour phase on water drops. It is shown that cyclohexane is adsorbed significantly slower than the adsorption of hexane occurs, and is characterised by a much larger induction time. The error in the drop radius measurements at 40 °C attains 45 µm. The experimental rheologic characteristics of the adsorbed layers are studied and the results are compared with the model developed to describe an adsorption process governed by a kinetic mechanism.

Keywords: water/heptane vapour interface, drop profile analysis tensiometry, dynamic surface tensions, adsorption kinetics

1. Introduction

The adsorption of gaseous hydrocarbons and fluorocarbons from the gas phase at the surface of water drops was studied by various authors. The physical phenomena which accompany the adsorption of alkanes from the gas phase on a water surface were first discussed by Pethica (1996), Lou and Pethica, (1997), Pethica et al. (2003), Ashbaugh and Pethica (2003) and Pethica and Glasser (2005). Interesting properties of such adsorbed alkane layers were determined using X-ray and neutron reflection (Schlossman, 2002; Kwon et al., 2007). It was shown by Kwon et al. (2007) that with the increase of the adsorption layer thickness the adsorption process becomes extremely slow: it needs 200 hours to obtain a 4-5 nm thick layer. Extensive studies were devoted to the concurrent adsorption of alkanes from the gas phase and surfactants (or proteins) from aqueous solution drops (Javadi et al., 2010, Fainerman et al., 2011; Javadi et al., 2011; Krafft et al., 2015; Mucic et al., 2015a,b; Mys et al., 2015; Fainerman et al., 2016a; Miller et al., 2017a,b; Fainerman et al., 2017;). The adsorption of alkanes results in an essential decrease of the surface tension of water or aqueous protein (surfactant) solutions, and often leads to the condensation of the alkane molecules at the surface and the formation of thick films. The influence of temperature on the adsorption behavior of mixed alkane/surfactant layers was studied by Aveyard et al., 1996; Binks et al., 1999, and a packing model for such mixed layer was proposed. The adsorption of fluorocarbon gases on the surface of insoluble adsorbed monolayers was studied by Gerber et al. (2005), Gerber et al. (2006), Krafft and Riess (2007), Nguyen et al. (2011) and Miller et al. (2017b). It was shown in Fainerman et al. (2016a) that the air humidity influences essentially the hexane vapour adsorption and the surface tension of water. The decrease of surface tension in humid air was found to be slower than in dry air. Therefore, due to the quite strong adsorption of alkanes on the water surface this phenomenon could be of practical importance, in

particular, for the environmental monitoring and for the reduction of leakage of harmful hydrocarbons into the ambient air.

In this paper, we study the dependence of the dynamic surface tension of water measured by the drop profile analysis method on the adsorption of hydrocarbons with different structure. In particular, the adsorption of cyclohexane vapours was studied at different temperatures, and the results were compared with those reported earlier for the adsorption of hexane and other alkanes on water drops. It was shown that the measured values of the radius at the drop apex at 40 °C, when compared with the values estimated via the Young-Gauss-Laplace, exhibit errors as large as 50 µm; this phenomenon is caused by the formation of polylayers. It was also shown that the adsorption of cyclohexane occurs essentially slower than that of hexane, and exhibits very large induction times. For example, at 20 °C the cyclohexane induction time is 4200 s, while for hexane, which has an only 20% higher partial saturation pressure, the induction time is less than 10 s. Also, the adsorption of hexane and cyclohexane on the water surface is compared with that on solid surfaces of various nature, as studied in Tarasevich et al. (2009) and Gus'kov et al. (2014), where it was shown that the adsorption of hexane on solid surfaces is more active than that of cyclohexane. The rheologic properties of the adsorbed layers are studied, and the model which assumes a monolayer adsorption governed by a kinetic mechanism is proposed to provide an approximate description of these experimental results.

2. Theory

The theoretical model to describe the bilayer adsorption of hydrocarbons from the ambient gaseous phase on drop surfaces was developed in Miller et al. (2017a, 2017b) and Fainerman et al. (2016b). The equation of state for this model reads:

$$-\frac{\Pi\omega}{RT} = \ln(1 - \theta_1) + \ln(1 - \theta_2\theta_1) + a(\theta_1^2 + \theta_2^2). \quad (1)$$

Here R is the gas law constant, T is the temperature, Π is the surface pressure ($\Pi = \gamma_0 - \gamma$), γ and γ_0 are the surface tensions of the solution and the solvent, respectively. The subscripts 1 and 2 refer to the alkane in the first and second adsorption layer, respectively; $\theta_1 = \Gamma_1\omega$ and $\theta_2 = \Gamma_2\omega$ are the corresponding surface coverages by alkane; Γ_1 and Γ_2 are the adsorptions, ω is the molar area of alkane, a is the interaction constant between adsorbed alkane molecules.

For the first layer at the interface with water the adsorption isotherm for the alkane molecules reads:

$$b_1c = \frac{\theta_1}{(1 - \theta_1)} \exp[-2a\theta_1], \quad (2)$$

while for the second layer (the adsorption of alkane from the gaseous phase on the alkane already adsorbed to form the first layer) the adsorption isotherm is:

$$b_2c = \frac{\theta_2}{(\theta_1 - \theta_2)} \exp[-2a\theta_2], \quad (3)$$

In Eqs. (2) and (3) b_1 and b_2 are the alkane adsorption equilibrium constants in the first and second layer, respectively, and c is the alkane concentration in the gaseous phase. It follows from Eq. (3) that the coverage of the second layer cannot exceed that of the first layer.

The adsorption isotherm equation for alkane polylayers (a more realistic model) was derived in Miller et al. (2017b). The adsorption in these additional layers ($2 < j \leq L$) does not affect the equilibrium surface tension, and influences only the kinetics and rheology of the mixed adsorbed layer.

In Fainerman et al. (2016b) and Miller et al. (2017b) a kinetics model of concurrent adsorption of alkanes from the gas phase and surfactants from the aqueous drop bulk on the drop surface was derived. Two mechanisms for the alkane adsorption were considered. For the adsorption of alkanes obeying a diffusion mechanism, the diffusion coefficients were estimated to be by approximately 7 to 8 orders of magnitude lower than the real values. Therefore, a model was applied which assumes kinetic equations for the alkane in the first and second layers. For these layers the adsorption rates are given by:

$$\frac{d\Gamma_1}{dt} = \beta c \left(1 - \frac{\Gamma_1}{\Gamma^{(\infty)}} \right) - \alpha_1 \frac{\Gamma_1}{\Gamma^{(\infty)}}, \quad (4)$$

$$\frac{d\Gamma_2}{dt} = \beta c \left(1 - \frac{\Gamma_2}{\Gamma^{(\infty)}} \right) - \alpha_2 \frac{\Gamma_2}{\Gamma^{(\infty)}}, \quad (5)$$

respectively, where $\Gamma^{(\infty)} = 1/\varpi$, ϖ is the molar area of the adsorbate, $\alpha_1 = \beta/b_1$, $\alpha_2 = \beta/b_2$, and β is the alkane adsorption rate coefficient. In an up-coming work a more rigorous approach will be applied, which involves alkane adsorption kinetics equations for the layers $j > 2$.

To calculate the dilational viscoelasticity modulus assuming small oscillations of the surface area A with the amplitude ΔA , an approximation was used which accounts for the alkane adsorption in a single layer according to the kinetic equation (4). This leads to the expression for the viscoelastic modulus existing in equilibrium between the subsurface layer with the concentration c_{eq} and the first adsorbed layer, $bc_{eq} = \theta_1/(1-\theta_1)$:

$$E = -E_0 \frac{\Delta \ln \Gamma}{\Delta \ln A} \approx E_0 \left[1 + \frac{\alpha \varpi}{i\omega} (1 + bc_0) \right]^{-1} = E_0 \frac{1}{1 - i \frac{\Omega}{\omega}} = E_0 \left\{ \frac{1}{1 + \left[\frac{\Omega}{\omega} \right]^2} + i \frac{\frac{\Omega}{\omega}}{1 + \left[\frac{\Omega}{\omega} \right]^2} \right\}, \quad (6)$$

where c_0 is the adsorptive concentration, ω is the frequency of surface oscillations,

$$\Omega = \alpha \varpi (1 + bc_0), \quad (7)$$

$$\Pi = -\frac{RT}{\varpi} \ln(1 - \theta_1) = -\frac{RT}{\varpi} \ln(1 - \Gamma \varpi), \quad (8)$$

$$E_0 = \frac{\Delta \Pi}{\Delta \ln \Gamma} = \Gamma \frac{d\Pi}{d\Gamma} = \frac{RT}{\varpi} \frac{\theta_1}{1 - \theta_1}, \quad (9)$$

where $\Gamma = \Gamma_1$ is the total adsorption for the single layer model.

A multilayer rheologic model which assumes a non-diffusional kinetics of alkane adsorption is presently under development.

3. Experimental

The procedure to measure the surface tension using the drop profile analysis method in hexane and cyclohexane vapours is similar to that described earlier in Fainerman et al. (2011) and Miller et al. (2017a). The experiments were performed with the tensiometers PAT-1 and PAT-2P (SINTERFACE Technologies, Germany), the operation principles of which are described in detail by Zholob et al. (2011). The value of surface tension in these instruments is determined by comparing (fitting) the experimentally measured drop profile with that theoretically predicted from the Young-Gauss-Laplace equation. The fitting procedure provides also the values of average error (standard deviation expressed in μm) between the predicted and measured drop profiles corresponding to the calculated surface tension.

The temperature of the measuring cell with a volume of 30 cm³ was kept at 20, 25, 30 and 40 °C, respectively. An amount of 2 cm³ of hexane or cyclohexane was placed at the bottom of the measuring cell. To saturate the air in the cell by water vapour a vessel containing 2 cm³ of water was additionally placed into the cell. The air in the cell was saturated by hexane or cyclohexane and water vapours during 500 s before the drop formation. Also experiments with harmonic oscillations of the drop surface were performed. In these experiments the oscillation frequency was varied in the range of 0.2 to 0.005 Hz, with an oscillation amplitude of $\pm 6\%$.

The hexane (C₆H₁₄) and cyclohexane (C₆H₁₂) were purchased from Fluka. The solutions were prepared using Milli-Q water. The surface tension of water was 72.0 \pm 0.2 mN m⁻¹ at 25 °C over a time interval of up to 30000 s.

4. Results and discussion

Figure 1 illustrates the dynamic surface tension of water in the atmosphere with vapours of cyclohexane and different alkanes at 25 °C. It is seen that the equilibrium surface tension at the interface with alkanes is within the range of 51-54 mN m⁻¹, while for the cyclohexane this value is essentially higher: 57.5 mN m⁻¹ as compared with 51.5 mN m⁻¹ for hexane. The differences between these hydrocarbons become even more evident when the dynamic surface tension is considered: for cyclohexane, the adsorption process proceeds much slower than for the alkanes. This phenomenon is unrelated with the concentration of hydrocarbons in the gaseous phase. For the studied alkanes, the equilibrium concentration at 25 °C is 0.8, 2.6, 8.1 and 26 mol m⁻³ for octane, heptane, hexane and pentane, respectively; these values were recalculated from the corresponding partial pressures P (expressed in Pa) taken from literature, via the relation $c = P/RT$. With increasing temperature, the concentration and partial pressure of alkane in air become higher; therefore, the adsorption rate increases in the series of octane to pentane. For cyclohexane, the equilibrium concentration in the gaseous phase at 25 °C is 5.4 mol m⁻³, which is quite similar to that of hexane. It is seen that for cyclohexane the induction time is very large: for 25 °C this time is 2800 s, while for hexane, with its partial saturated vapour pressure quite close to that of cyclohexane, the induction time is less than 10 s. This difference is attributable to the particularities of the structure of the studied compounds (decrease of the interaction energy between cyclohexane and water molecules, presumably due to the differences in the hydrogen bonding character).

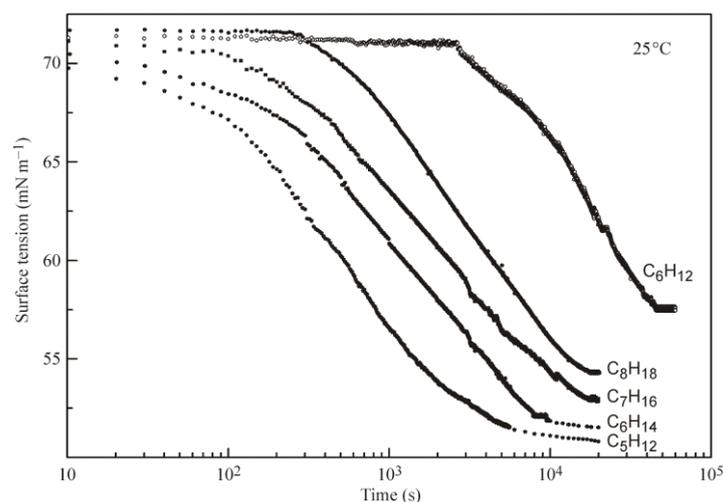


Fig. 1. Dynamic surface tension of water in vapours of cyclohexane and different alkanes at 25 °C

Table 1. Model parameters for cyclohexane vapours at different temperatures assuming a bilayer adsorption on the surface of a water drop

Temperature, °C	c , mol/m ³	b_1/b_2 , m ³ /mol	ω , 10 ⁵ m ² /mol	β , 10 ⁻¹⁰ m/s
20	4.3	0.15/0.14	2.0	0.19
25	5.4	0.22/0.21	2.1	0.35
30	6.8	0.19/0.16	1.9	0.47
40	9.4	0.18/0.16	1.7	1.4

In Figure 2 the dynamic surface tension of water in hexane vapour is compared with that in cyclohexane vapour at 20, 25 and 30 °C. The results obtained at 40 °C are shown in Fig. 3 and are discussed further below. It is seen from Fig. 2 that the adsorption of hexane at all temperatures proceeds more rapidly than that of cyclohexane. The values calculated for cyclohexane using Eqs. (1) - (5) with parameters listed in Table 1, and shown in Fig. 2 by solid lines agree well with the experimental data. It should be noted that the values of the adsorption equilibrium coefficients b_1 and

b_2 (shown before and after the slash in the corresponding column of the table) are quite similar to each other; also, the differences between these values for different temperatures (related to the concentration increase) are rather small. On the contrary, the adsorption rate coefficients β become noticeably higher with increasing temperature.

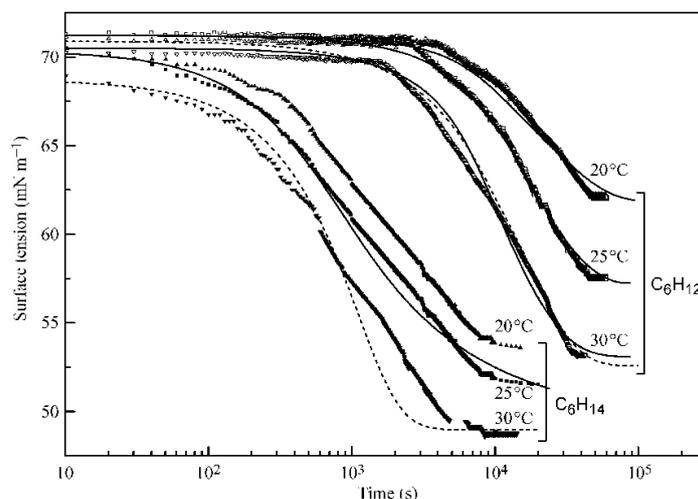


Fig. 2. Dynamic surface tension of water at the interface with hexane and cyclohexane vapours at 20, 25 and 30 °C. Points - experimental data; solid lines - results calculated from Eqs. (1) - (5) with parameters listed in Table 1; dashed lines - results calculated using a single layer model at 30 °C with parameters listed in Table 2

It is interesting to compare the results shown in Fig. 2 with the data reported in Tarasevich et al., 2009; Gus'kov et al., 2014. The gas chromatographic studies of adsorption of *n*-hexane and cyclohexane on samples of kaolinite and hydromica (Tarasevich et al., 2009) have revealed a geometric inhomogeneity of the surface of these sorbents and showed differences in their adsorption mechanisms. It was found that the adsorption of *n*-hexane on the studied adsorbents is localised (with the loss of all three translation degrees of freedom); while cyclohexane is adsorbed in a less localised way, retaining the vibrational degrees of freedom. From the data obtained in (Tarasevich et al., 2009) the Henry constants and adsorption heats at low surface coverages were estimated; these characteristics indicate the strength of bonding of the adsorbate molecules with the solid surface. It was shown that both the Henry constant and the adsorption heat are essentially higher for hexane than for cyclohexane; this conclusion obviously agrees with the behaviour illustrated in Fig. 2.

The thermodynamic characteristics of adsorption of various organic molecules on a polymeric sorbent were studied in Gus'kov et al., 2014. It was shown, in particular, that hexane exhibits 20 % larger absolute values of the adsorption enthalpy, and 10 % larger values of the adsorption entropy than cyclohexane. This was attributed to larger conformational flexibility of the hexane molecule which is capable for bonding to the surface by all its carbon atoms.

Table 2. Model parameters of hexane and cyclohexane for a single layer adsorption on the surface of a water drop

Alkanes	c , mol/m ³	b , m ³ /mol	ω , 10 ⁵ m ² /mol	β , 10 ⁻¹⁰ m/s
Hexane, 30 °C	9.3	0.88	2.4	6.1
Cyclohexane, 30 °C	6.8	0.79	2.26	0.53
Cyclohexane, 25 °C	5.4	0.61	2.25	0.48

The results obtained by the calculations based on a single layer model with the parameters listed in Table 2 for 30 °C are shown in Fig. 2 by dashed curves; these values were used to calculate the rheologic characteristics. For cyclohexane, the agreement with the experimental dynamic curve is seen to be quite good, while for hexane (especially in the long time range) the discrepancy is quite essential;

it could be supposed that for this adsorbate a multilayer model is more appropriate. It is seen from Table 2 that for hexane the β value is by one order of magnitude higher than that for cyclohexane.

Note that for temperatures of 30 °C and below, the error (i.e. the standard deviation) related to the calculation of the drop radius in the apex via the Young-Gauss-Laplace equation is lower than 1 μm . At the same time, this error becomes essentially higher at 40 °C for both hydrocarbons studied: it is seen from Fig. 3 that the calculation error becomes as high as 45 μm . At 2000 s for cyclohexane the distortion of the drop profile becomes visible as a light band in the lower part of the drop. This band becomes more distinct after 3000 s. In this time range the fitting error is 24 μm , while at the time when the surface tension starts to decrease rapidly (ca. 2000 s) the error is only about 1 μm . It is seen from the snapshot shown in Fig. 4 that at times above 5000 s the distortions of drop shape become even more distinct.

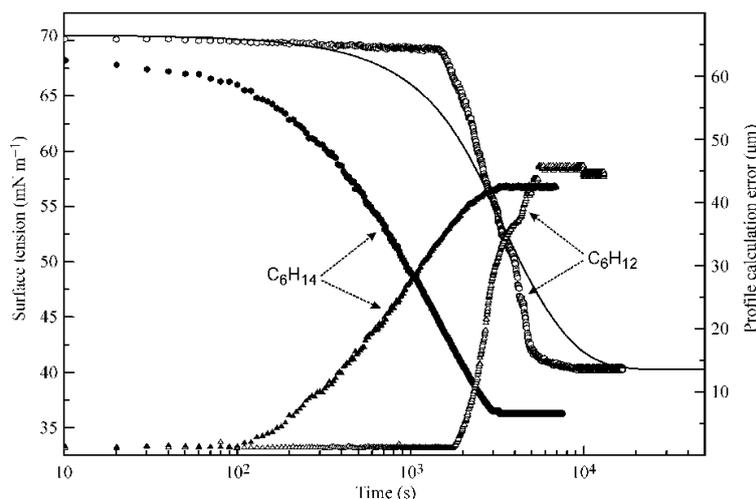


Fig. 3. Dynamic surface tension (hexagons) and profile calculating error (triangles) for cyclohexane (open symbols) and hexane (filled symbols) at 40 °C. Solid curve - calculations with Eqs. (1)-(5) for cyclohexane

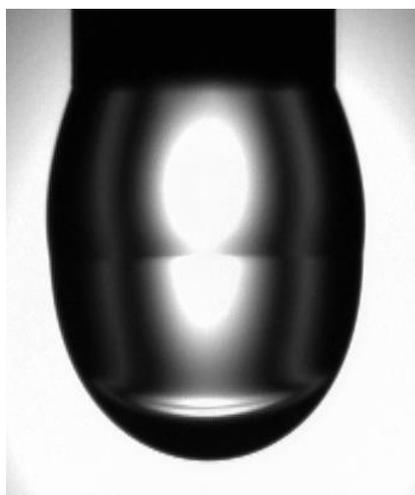


Fig. 4. Snapshot of a water drop at 40 °C and a drop ageing time of 5000 s in cyclohexane vapour

It is seen from Fig. 3 that the agreement between the observed results and the theoretical predictions calculated from the double layer model for cyclohexane is rather poor; this could possibly be attributed to the errors in drop profile calculations and their influence on the calculated surface tensions.

Let us consider now the results obtained for the dilational rheologic characteristics. During the dynamic experiments, at certain surface tension values harmonic oscillations with a frequency of 0.1 Hz were imposed onto the drop surface; the response was then analysed using the Laplace

transformation. The viscoelasticity modulus values for the two hydrocarbons studied here at 30 °C and 25 °C are shown in Figs. 5 and 6, respectively; note that the imaginary component of the modulus was by several orders of magnitude lower than the real component, which was virtually equal to the total modulus value. The variations of frequency within the range of 0.2 to 0.005 Hz had little effect on the viscoelasticity modulus values. It is seen that the values of the modulus taken at the same surface pressure value are higher for the cyclohexane. This result is by no means trivial. Usually the dependence of the viscoelasticity modulus on the surfactant concentration exhibits a maximum. Also, for surfactants with different surface activity the values of the modulus could exhibit different behaviour in the ranges of low and high surface pressure (Fainerman et al., 2009a, 2009b); for example, it was shown in Fainerman et al. (2009b) that for equal low surface pressure the modulus for Triton 165 is higher than that for Triton 100, while for equal high surface pressure values the opposite situation was observed. In this case, the surface activities of the hydrocarbons are quite similar; only the concentrations are slightly different. Therefore, it could be supposed that also the viscoelasticity modulus is mainly determined by the surfactant structure. The theoretical curve for a cyclohexane single layer calculated using the parameters listed in Table 2, similarly to the corresponding dynamic surface tension dependence (dashed line in Fig. 2), exhibits good agreement with the experiment.

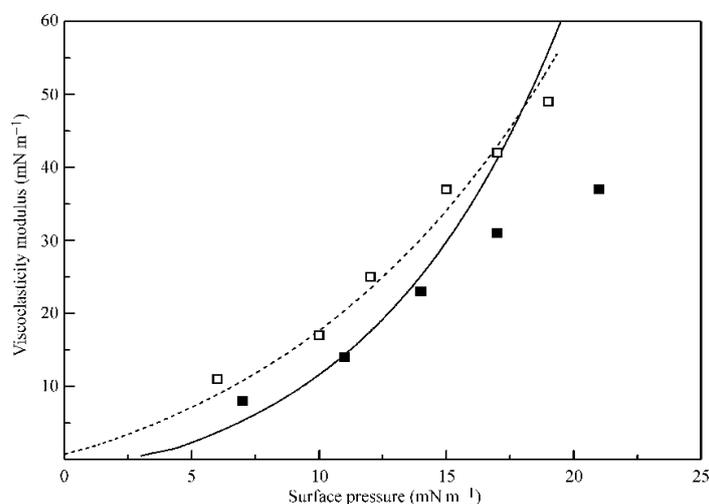


Fig. 5. Dependence of the experimental (points) and theoretical (curves) viscoelasticity modulus for cyclohexane (open squares, dashed curve) and hexane (filled squares, solid curve) on surface pressure at 30 °C for the frequency of 0.1 Hz

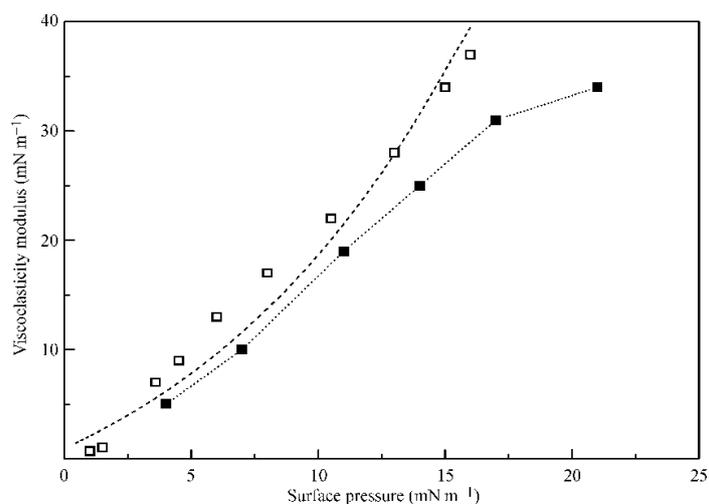


Fig. 6. Dependence of the experimental (open squares) and theoretical (dashed curve) viscoelasticity modulus for cyclohexane, and experimental (filled squares) viscoelasticity modulus for hexane on surface pressure at 25 °C for the frequency of 0.1 Hz; the dotted curve is a guide for the eye

On the contrary, similarly to what is seen from Fig. 2, the theoretical dependence for hexane agrees well with the experimental values of the modulus only in the low surface pressure range. Presumably, a better description of the hexane behaviour could be obtained using a polylayer adsorption model which accounts for the influence of all layers on the surface tension. This model is being developed now and will be presented in future communications.

5. Conclusions

The dependence of the dynamic surface tension of water at the interface with saturated vapours on the structure of adsorbed hydrocarbon molecules is measured by the drop profile analysis method. In particular, the surface tension for the adsorption layers of cyclohexane vapours at different temperatures is studied and compared with the results reported earlier for the adsorption of hexane and other alkanes on water drops. It is shown that cyclohexane is adsorbed significantly slower than the adsorption of hexane occurs, and is characterised by a much larger induction time: at 20 °C the induction time for cyclohexane is 4200 s, while for hexane (having only a 20% higher saturation vapour pressure than cyclohexane) the induction time is less than 10 s. It is shown that errors in the drop radius measurements as compared with the results obtained via the Young-Gauss-Laplace equation at 40 °C attain 45 µm. This phenomenon is ascribed to the formation of polylayers. The data taken from literature are used to compare the processes of the adsorption of hexane and cyclohexane on the water surface with their adsorption on solid surfaces. The rheologic characteristics of the adsorbed layers are studied experimentally, and the results are compared with the model developed to describe a single layer adsorption governed by a kinetic mechanism. For cyclohexane, the theoretical dependencies of the dynamic surface tension and viscoelasticity modulus calculated using this model agree well with the experimental data.

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