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THE INFLUENCE OF AQUEOUS METHANOL FILM ON THE WETTABILITY OF POLYTETRAFLUOROETHYLENE

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Abstract—Contact angles were measured for polytetrafluoroethylene (PTFE) wetted with aqueous methanol solutions–water drop or diiodomethane drop–air systems as a function of the holding time of the PTFE plate in the measuring chamber filled with a mixture of molecular sieves (4 Å + 5 Å); a theoretical analysis of the equilibrium state of these systems was also made. Using published data, the components of the surface free energy of PTFE for various degrees of the coverage of its surface by water and methanol film were calculated. The contact angles for water and diiodomethane drops settled on PTFE/mixed film (water + methanol) were calculated and compared with the measured values. On the basis of these measurements and calculations, it was found that the contact angle for a water drop depends on the degree of the coverage of the PTFE surface with molecules of methanol, but the contact angle for a diiodomethane drop depends on the degree of a coverage of the PTFE surface with water and methanol molecules. It was shown that the measured contact angles for the studied systems were in the range of the calculated values.

INTRODUCTION

It is usually recognized that a stable film of a liquid may be formed on the surface of a high energy solid when the surface tension of the liquid spreading or adsorbing on the surface of the solid is lower than the surface free energy of this solid. For low energy solids, which include polytetrafluoroethylene (PTFE), films of liquids are unstable and it is supposed that the molecules of liquids adsorbed on the surface of such solids do not change their surface free energies [1–5].

Studies of the wettability of PTFE by aqueous solutions of aliphatic alcohol have shown, however, that the possibility of changes of the surface and interface free energies of PTFE–aqueous alcohol solutions should be taken into account [6–8] in spite of the fact that the surface free energy of PTFE is lower than the surface tension of the aqueous solutions of alcohols [1, 3, 9, 10].

In the previous paper [8], we suggested that the presence of the alcohol films on the surface of PTFE may be responsible for different values of the contact angle measured by two methods viz. the sessile drop and the captive air bubble. Therefore, it seemed interesting to carry out the studies to test the suggestion. For this purpose, measurements of the contact angle for PTFE wetted by the aqueous methanol solution–water drop–air and PTFE wetted by the aqueous methanol solutions–diiodomethane drop–air systems were carried out. A theoretical analysis of the equilibrium state of these systems was also made.

EXPERIMENTAL PROCEDURES

The contact angles were measured by the sessile drop method [11] at 20 ± 0.1°C using a microscope–goniometer system at ×25 magnification. The PTFE was from West Germany.

For these measurements, the PTFE plates were made by the method described earlier [12]; they were cleaned by boiling in aqueous HCl (1:1) and in doubly distilled water. The plates were then cleaned in an ultrasonic bath filled with doubly distilled water for 20 min. Each plate was then immersed in doubly distilled water for 30 min. The PTFE plate was then placed in a thermostated measuring chamber (20 ± 0.1°C) filled with a mixture of molecular sieves (4 Å + 5 Å) and a 2 mm^3 diiodomethane drop was immediately settled on its surface. The contact angle was read several times on both sides of the drop. Then another PTFE plate was placed in the measuring chamber and, after 5 min, a 2 mm^3 diiodomethane drop was settled on its surface and the contact angle was read as before.

This procedure of contact angle measurement was applied for the next PTFE plates but the time between placing the PTFE plate in the chamber and settling the diiodomethane drop on it was extended at fixed intervals (5 min) from 5 min to an hour.

After this time, the contact angle had reached a constant value. Next, contact angle measurements were made for a diiodomethane drop deposited on PTFE plates that had been previously immersed in methanol aqueous solutions at concentrations of 0.01, 0.5, 20 and 100% by weight.

In the same manner, contact angles were measured for a water drop on the surface of the PTFE plates previously wetted by aqueous methanol solutions. Each series of measurements was repeated several times and the measurement error was ±1°.

RESULTS AND DISCUSSION

The measured values of the contact angle are presented in Figs 1 and 2. These figures show the changes of the contact angle for a water drop (Fig. 1) and a diiodomethane drop (Fig. 2) on the surface of PTFE plates wetted by aqueous solution of methanol at concentrations of 0.01% (curve 1), 0.5% (curve 2), 20% (curve 3) and 100% (curve 4) as a function of the holding time of the PTFE plates in the measuring chamber. Curve 5 in Fig. 2 shows the

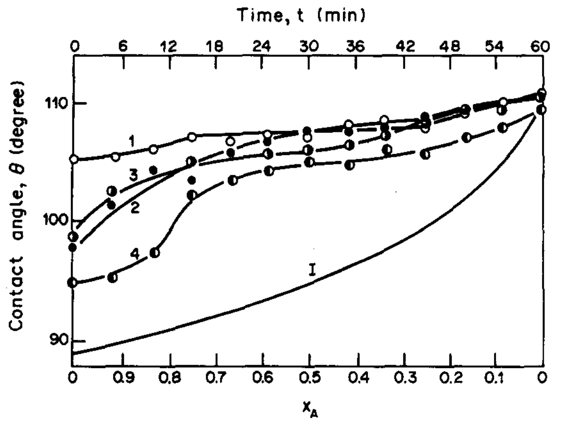

Fig. 1. Dependence of the contact angle (θ_W) in PTFE/mixed film–water drop–air system on the holding time of a PTFE/mixed film plate in the measuring chamber filled with a mixture of molecular sieves (4 Å + 5 Å). PTFE plate wetted with methanol solution at concentrations: 0.01%—curve 1, 0.05%—curve 2, 20%—curve 3 and 100%—curve 4 (top scale). Curve I—θ_W values calculated from equation (3) as a function of the degree of the coverage of PTFE surface by methanol molecules (x_A) (bottom scale).

change of the contact angle for diiodomethane drops on a PTFE surface previously wetted by "clean" water.

Figure 1 shows that the contact angles for a PTFE plate with a mixed film (water + methanol)–water drop–air system increase nonlinearly from the contact angle obtained for a water drop on a "clean" PTFE surface (111°, [10]). The increase of contact angle for each kind of film is different. The largest contact angle change is obtained for the "clean" methanol film (curve 4), and the smallest for the film formed on PTFE surface at 0.01% concentration of methanol (curve 1, Fig. 1).

The greatest changes of the contact angles for all films studied occurred in the interval from 0 to 15 min and constant values of the contact angle were obtained after *ca* 50–60 min of holding PTFE plates in the measuring chamber.

The forms of curves showing the changes of contact angle (θ_D) in PTFE/mixed film (water + methanol)–diiodomethane drop–air system as a function of the holding time of the plates in the measuring chamber (Fig. 2) are different from those shown in Fig. 1.

Figure 2 shows that the contact angle of the PTFE plates covered by a mixed film (water + methanol) [formed at 0.01% (curve 1), 0.5% (curve 2) and 20% (curve 3) concentrations of methanol] increase with increase of the holding time of the plates in the measuring chamber to maximal values and then they decrease to the value found for PTFE–diiodomethane drop–air system (72°, [10]).

For the "clean" water film, the contact angle as a function of time increases nonlinearly (curve 5) to 72°. The contact angles in the system PTFE/"clean" methanol film–diiodomethane drop–air (curve 4) change inversely, i.e. they decrease from 82° to 71.8° as the holding time of the plates in the measuring chamber increases to an hour.

It should be emphasized that the θ_D values are practically constant after *ca* 45 min in the measuring chamber.

In order to explain the changes of the contact angle in the PTFE plate/mixed (water + methanol)–water drop–air and PTFE plate/mixed film (water + methanol)–diiodomethane drop–air systems with the holding time of the plates in the measuring chamber, consider the equilibrium state of these systems on the basis of the Young equation which can be written in the form:

$$\gamma_{\mathrm{sf_l}} - \gamma_{\mathrm{sfL}} = \gamma_{\mathrm{L}} \cos\theta \qquad (1)$$

where $\gamma_{\mathrm{sf_l}}$ is the surface free energy of the PTFE/mixed film (water + methanol) beyond the liquid drop (water or diiodomethane), γ_{sf} is the surface free energy of the PTFE/mixed film (water + methanol) under the liquid drop, γ_{sfL} is the interfacial free energy of the PTFE/mixed film (water + methanol)–liquid (water or diiodomethane, γ_{L} is the surface tension of liquid and θ is the contact angle measured through a liquid phase.

The interfacial free energy of the PTFE/mixed film (water + methanol)–liquid can be expressed as a function of the dispersive and nondispersive intermolecular interaction [1, 13–16].

Expressing the interfacial free energy γ_{sfL} as a function of the geometric mean of the free energy components [1, 13–16], we may write:

$$\gamma_{\mathrm{sfL}} = \gamma_{\mathrm{sf}} + \gamma_{\mathrm{L}} - 2(\gamma^{\mathrm{d}}_{\mathrm{sf}}/\gamma^{\mathrm{d}}_{\mathrm{L}})^{1/2} - 2(\gamma^{\mathrm{n}}_{\mathrm{sf}}\gamma^{\mathrm{n}}_{\mathrm{L}})^{1/2} \qquad (2)$$

where $\gamma^{\mathrm{d}}_{\mathrm{sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{sf}}$ are the dispersion and nondispersion components of the surface free energy of PTFE covered with a mixed film (water + methanol) (γ_{sf}), respectively, and $\gamma^{\mathrm{d}}_{\mathrm{L}}$ and $\gamma^{\mathrm{n}}_{\mathrm{L}}$ are the dispersion and

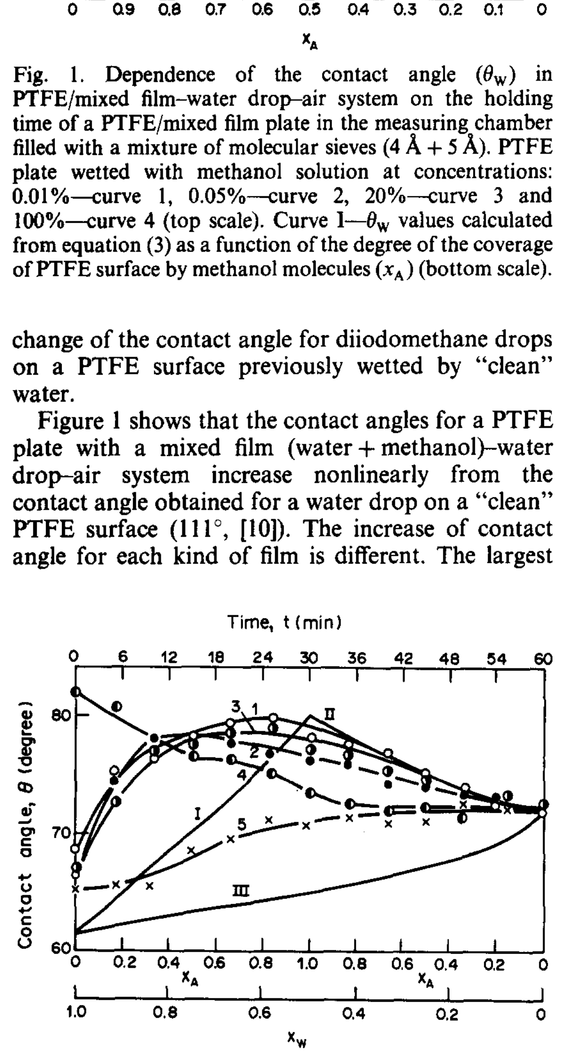

Fig. 2. Dependence of the contact angle (θ_D) in PTFE/mixed film–diiodomethane drop–air system on the holding time of a PTFE/mixed film plate in the measuring chamber filled with a mixture of molecular sieves (4 Å + 5 Å). PTFE plate wetted with methanol solution at concentrations: 0.01%—curve 1, 0.5%—curve 2, 20%—curve 3 and 100%—curve 4, 0% curve—5 (top scale). The changes of the contact angle values calculated for the PTFE/film–diiodomethane drop–air system as a function of the degree of the coverage of PTFE surfaces by methanol molecules—curve I for $\gamma_{\mathrm{sf}} = \gamma_{\mathrm{L}}$ (first left bottom scale), curve II for γ_{sf} in the range from γ_{S} to γ_{A} (first right bottom scale), and curve III by water molecules as a function x_A for γ_{sf} in the range from γ_{S} to γ_{W} (second bottom scale).

nondispersion components of the surface tension of the liquid, respectively.

Introducing equation (2) to equation (1) and assuming that $\gamma_{\mathrm{Sf}_1} \approx \gamma_{\mathrm{Sf}}$ (8), we obtain:

$$\gamma_{\mathrm{L}} \cos\theta = -\gamma_{\mathrm{L}} + 2(\gamma^{\mathrm{d}}_{\mathrm{Sf}}\gamma^{\mathrm{d}}_{\mathrm{L}})^{1/2} + 2(\gamma^{\mathrm{n}}_{\mathrm{Sf}}\gamma^{\mathrm{n}}_{\mathrm{L}})^{1/2}. \quad (3)$$

From equation (3) we can calculate the contact angle for the studied system knowing the values of $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$, $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$, $\gamma^{\mathrm{d}}_{\mathrm{L}}$ and $\gamma^{\mathrm{n}}_{\mathrm{L}}$. The $\gamma^{\mathrm{d}}_{\mathrm{L}}$ and $\gamma^{\mathrm{n}}_{\mathrm{S}}$ values for water and diiodomethane can be found by various methods [1, 10, 17] but the $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ values are not known and their determination for each mixed film (water + methanol) on the surface of the PTFE is very difficult.

Consider four possible cases of the film formation on the PTFE surface by immersion of the PTFE plate in aqueous methanol solutions at concentrations from 0 to 100%.

In the first case, we assume that, on the surface of PTFE, there is mixed water–methanol film and the methanol molecules occupy a fraction x_{A} of this surface. In the second case, the fraction of PTFE surface occupied by the methanol molecules is x_{A} and by water molecules is x_{W} on the assumption that the whole PTFE surface is covered by water and methanol molecules.

The third and the fourth cases refer to "clean" water and methanol film, covering x_{W} and x_{A} fraction of the PTFE surface respectively.

At the present stage of knowledge concerning changes of the surface free energy of a solid caused by a mixed film, it is very difficult to calculate $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ assuming the second case of mixed film formation on the PTFE surface.

For the remaining cases, the calculations of $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ are possible by making some assumptions and approximations.

According to our previous paper [7], we suggest that the surface tension of the aqueous aliphatic alcohol solutions can be calculated from the equation:

$$\gamma_{\mathrm{L}} = \gamma_{\mathrm{W}} - N_{\mathrm{A_S}}(\gamma_{\mathrm{W}} - \gamma_{\mathrm{A}}) \quad (4)$$

where γ_{W} and γ_{A} are the surface tensions of water and alcohol, respectively and $N_{\mathrm{A_S}}$ is the mole fraction of alcohol in the interfacial region solution–air. Corresponding to equation (4), we can write:

$$\gamma^{\mathrm{d}}_{\mathrm{L}} = \gamma^{\mathrm{d}}_{\mathrm{W}} - N_{\mathrm{A_S}}(\gamma^{\mathrm{d}}_{\mathrm{W}} - \gamma^{\mathrm{d}}_{\mathrm{A}}) \quad (5)$$

and

$$\gamma^{\mathrm{n}}_{\mathrm{L}} = \gamma^{\mathrm{n}}_{\mathrm{W}} - N_{\mathrm{A_S}}(\gamma^{\mathrm{n}}_{\mathrm{W}} - \gamma^{\mathrm{n}}_{\mathrm{A}}) \quad (6)$$

where γ^{d} and γ^{n} are the dispersion and nondispersion components of the surface tensions of water (γ_{W}) and alcohol (γ_{A}), respectively.

It is assumed that equations (4), (5) and (6) may be used for the PTFE/mixed film (water + methanol)–air interface and that the surface free energy of the PTFE/mixed film at complete coverage of the PTFE surface by this film tends towards the surface tension of the methanol solution of the given concentration.

Then desorbing the water and methanol molecules from PTFE surface occupied completely by a mixed film, we cause a change of γ_{Sf} from γ_{L} to γ_{S} (γ_{S} is the surface free energy of the PTFE). γ_{Sf} values for a given degree of the coverage of the PTFE surface by the methanol molecules may be calculated from equation (7):

$$\gamma_{\mathrm{Sf}} = \gamma_{\mathrm{W}} - x_{\mathrm{A}}(\gamma_{\mathrm{W}} - \gamma_{\mathrm{A}}) \quad (7)$$

assuming complete coverage of the PTFE surface by the mixed film.

In turn, the $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ components may be calculated from the equations:

$$\gamma^{\mathrm{d}}_{\mathrm{Sf}} = \gamma^{\mathrm{d}}_{\mathrm{W}} - x_{\mathrm{A}}(\gamma^{\mathrm{d}}_{\mathrm{W}} - \gamma^{\mathrm{d}}_{\mathrm{A}}) \quad (8)$$

and

$$\gamma^{\mathrm{n}}_{\mathrm{Sf}} = \gamma^{\mathrm{n}}_{\mathrm{W}} - x_{\mathrm{A}}(\gamma^{\mathrm{n}}_{\mathrm{W}} - \gamma^{\mathrm{n}}_{\mathrm{A}}). \quad (9)$$

In the case when the PTFE surface is only covered with methanol or water film at degrees of coverage of x_{A} and x_{W}, respectively, γ_{Sf}, $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ values may be calculated from these equations

$$\gamma_{\mathrm{Sf}} = \gamma_{\mathrm{S}} - x_{\mathrm{A}}(\gamma_{\mathrm{S}} - \gamma_{\mathrm{A}}) \quad (10)$$

$$\gamma^{\mathrm{d}}_{\mathrm{Sf}} = \gamma^{\mathrm{d}}_{\mathrm{S}} - x_{\mathrm{A}}(\gamma^{\mathrm{d}}_{\mathrm{S}} - \gamma^{\mathrm{d}}_{\mathrm{A}}) \quad (11)$$

$$\gamma^{\mathrm{n}}_{\mathrm{Sf}} = \gamma^{\mathrm{n}}_{\mathrm{S}} - x_{\mathrm{A}}(\gamma^{\mathrm{n}}_{\mathrm{S}} - \gamma^{\mathrm{n}}_{\mathrm{A}}) \quad (12)$$

$$\gamma_{\mathrm{Sf}} = \gamma_{\mathrm{S}} - x_{\mathrm{W}}(\gamma_{\mathrm{S}} - \gamma_{\mathrm{W}}) \quad (13)$$

$$\gamma^{\mathrm{d}}_{\mathrm{Sf}} = \gamma^{\mathrm{d}}_{\mathrm{S}} - x_{\mathrm{W}}(\gamma^{\mathrm{d}}_{\mathrm{S}} - \gamma^{\mathrm{d}}_{\mathrm{W}}) \quad (14)$$

$$\gamma^{\mathrm{n}}_{\mathrm{Sf}} = \gamma^{\mathrm{n}}_{\mathrm{S}} - x_{\mathrm{W}}(\gamma^{\mathrm{n}}_{\mathrm{S}} - \gamma^{\mathrm{n}}_{\mathrm{W}}). \quad (15)$$

Introducing into these equations $\gamma^{\mathrm{d}}_{\mathrm{S}}$, $\gamma^{\mathrm{n}}_{\mathrm{S}}$, $\gamma^{\mathrm{d}}_{\mathrm{W}}$, $\gamma^{\mathrm{n}}_{\mathrm{W}}$, $\gamma^{\mathrm{d}}_{\mathrm{A}}$, $\gamma^{\mathrm{n}}_{\mathrm{A}}$ and γ_{A} values from the literature [1, 10] and x_{A} and x_{W} values from 0 to 1, we calculated the dispersion and nondispersion components of the surface free energy of PTFE covered with a film (see Table 1).

Next, introducing into equation (3) $\gamma^{\mathrm{d}}_{\mathrm{Sf}}$ and $\gamma^{\mathrm{n}}_{\mathrm{Sf}}$ values and appropriate γ, γ^{d} and γ^{n} values for water and diiodomethane [1, 10], we calculated the contact angles for the PTFE/mixed film (water + methanol)–water drop or diiodomethane drop–air systems; they are plotted in Figs 1 and 2.

Curve I in Fig. 1 represents the dependence of the contact angle calculated for a water drop (θ_{W}) on the PTFE/methanol film surface on the degree of the coverage of the PTFE surface with methanol (x_{A}) (bottom scale).

The changes of the contact angle (θ_{D}) calculated for the PTFE/film–diiodomethane drop–air system are presented in Fig. 2 (curve I, II and III).

Curve I represents the changes of θ_{D} values for the PTFE surface covered with a mixed water–methanol film as a function of x_{A} (first left bottom scale) for $\gamma_{\mathrm{Sf}} = \gamma_{\mathrm{L}}$. Curve II represents the change of θ_{D} values

Table 1. Values of the dispersion ($\gamma^{\mathrm{d}}_{\mathrm{Sf}}$) and the nondispersion ($\gamma^{\mathrm{n}}_{\mathrm{Sf}}$) components of the surface free energy of PTFE for various degrees of coverage of its surface with water (x_{W}) and methanol (x_{A}) molecules

x_{W}	$\gamma^{\mathrm{d}}_{\mathrm{Sf}}$	$\gamma^{\mathrm{n}}_{\mathrm{Sf}}$	x_{A}	$\gamma^{\mathrm{d}}_{\mathrm{Sf}}$	$\gamma^{\mathrm{n}}_{\mathrm{Sf}}$	x_{A}	$\gamma^{\mathrm{d}}_{\mathrm{Sf}}$	$\gamma^{\mathrm{n}}_{\mathrm{Sf}}$
1.0	21.80	51.00	1.0	15.80	6.81	0.0	21.80	51.00
0.9	21.79	45.91	0.9	16.39	6.13	0.1	21.20	46.58
0.8	21.78	40.81	0.8	16.98	5.46	0.2	20.60	42.16
0.7	21.78	35.72	0.7	17.56	4.79	0.3	20.00	37.74
0.6	21.77	30.62	0.6	18.17	4.11	0.4	19.40	33.32
0.5	21.76	25.53	0.5	18.76	3.43	0.5	18.80	28.91
0.4	21.75	20.43	0.4	19.35	2.75	0.6	18.20	24.49
0.3	21.74	15.33	0.3	19.84	2.08	0.7	17.60	20.07
0.2	21.74	10.24	0.2	20.63	1.40	0.8	17.00	15.65
0.1	21.73	6.00	0.1	21.13	0.73	0.9	16.40	11.23
0.0	21.72	0.05	0.0	21.72	0.05	1.0	15.80	6.81

for the PTFE surface covered with a methanol film as a function of x_A (first right bottom scale) for γ_{Sf} in the range from γ_S to γ_A, and curve III represents the changes of θ_D values for the PTFE surface covered with a water film as a function of x_W for γ_{Sf} in the range from γ_S to γ_W (second bottom scale).

Figure 1 shows that decrease of the degree of the coverage of the PTFE surface with the methanol molecules causes an increase of θ_W from 88.7 to 111°. Comparing the calculated contact angles in the PTFE/mixed film–water drop–air system with those measured, we conclude that all measured θ_W values are in the range of the calculated values, i.e. between 88.7–111°. It should be emphasized that the immersion of the PTFE plate in "clean" methanol causes a decrease of the contact angle only to 95°, when the calculated value of θ_W in this case is 88.7°. Therefore, we conclude that the methanol film on the surface of PTFE is not stable and it is difficult to achieve complete coverage of the surface with methanol.

Changes of the contact angles calculated and measured for the PTFE/mixed film (water + methanol)–water drop–air system are different from those for the PTFE/mixed film–diiodomethane drop–air system, as shown in Figs 1 and 2.

The calculated values of the contact angle (θ_D) in the PTFE/mixed film–diiodomethane drop–air system [(Fig. 2) curve I] increase from 61.4 to 79.9° with increasing x_A in the mixed film from 0 to 1 when $\gamma_{Sf} = \gamma_L$.

For PTFE/"clean" methanol film–diiodomethane drop–air system, the calculated value of θ_D decreases from 79.9 to 72° (value of the contact angle for diiodomethane drop on "clean" PTFE surface [10]) as the degree of the coverage of PTFE surface with methanol (x_A) decreases from 1 to 0 (Fig. 2; curve II).

For the PTFE/water film–diiodomethane drop–air system the calculated values of θ_D increase from 61.4 to 72° (Fig. 2; curve III) with decrease of the degree of the coverage of the PTFE surface with water molecules.

Comparing the calculated and measured values of the contact angle in the PTFE/mixed film–diiodomethane drop–air system, we conclude that the calculated values of θ_D for all the studied systems are in the range of the measured values. The changes of the contact angle measured in the system involving only the "clean" methanol film are similar to the changes of θ_D represented by curve II in Fig. 2, but the changes of θ_D in the PTFE/water film–diiodomethane drop–air system are similar to curve III in Fig. 2.

The calculations indicate the possibility of the appearance of a maximal value of the contact angle in PTFE/mixed film (water + methanol)–diiodomethane drop–air system when the PTFE plate is held in the measuring chamber filled with molecular sieves (4 Å + 5 Å) which cause a decrease of vapour pressures of water and methanol to minimal values.

However, it should be emphasized that these calculations do not explain the influence of all possible parameters on θ_D and θ_W but they indicate a way to achieve this aim.

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