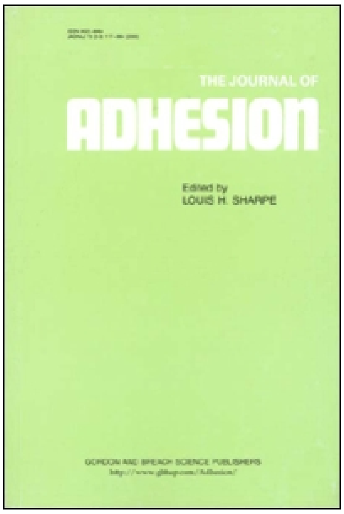

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Adhesion of an Air Bubble to Quartz Surface in Aqueous Solution of Aliphatic Amine Hydrochloride

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Measurements of the force of air bubble detachment from a quartz surface in aqueous solutions of decylamine hydrochloride (DACl), dodecylamine hydrochloride (DDACl) and tetradecylamine hydrochloride (TDACl) were made in the concentration range from 0 to 200 mg/dm^3. At the same time, the instantaneous contact angle for the system quartz-air bubble-aqueous solution of aliphatic amine hydrochloride was photographed at the moment of detachment. Wetting contact angles for the system quartz-air bubble-aqueous solution of DDACl were also measured. On the basis of the measured values of the instantaneous angle and surface tension of the solutions studied, the changes of polar components of surface free energy of quartz/monolayer water film under the influence of adsorption of molecules of aliphatic amine hydrochloride (RACl) from aqueous solution were calculated and compared with the literature data. Using these data, the force of air bubble detachment from the quartz surface in the presence of RACl was also calculated and compared with the measured force, obtaining a good agreement. From the studies and calculations it appears that a little addition of RACl to water considerably changes the stability of the system quartz-air bubble-solution, and that this change is first of all caused by reduction of a polar component of the surface free energy of quartz/monolayer water film as a result of adsorption of RACl molecules in the negative places of such a surface. As a result of RACl adsorption this surface becomes similar to that of paraffin.

KEY WORDS Quartz/amine-air bubble-solution system; adsorption; instantaneous contact angle; detachment force; surface free energy; solution surface tension.

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INTRODUCTION

A selective adhesion of air bubbles to mineral particles is one of the most important elements of the froth flotation process. It depends on the physicochemical properties of a solid surface and the properties of liquids used as flotation reagents. An increase in the force of air bubble adhesion to the surface of polar minerals, in which quartz is included, may be achieved by introducing into the flotation system some organic chemical substances having a long hydrocarbon chain.[1,2] These substances increase the flotation activity of a mineral by being adsorbed from aqueous solution on its surface. The adsorption may be electrostatic, chemical or physical by means of van der Waals' forces. Regardless of the adsorption character the mineral surface is made hydrophobic and the degree of its hydration is decreased and air bubble adhesion to the mineral grain is improved.

Studies of adsorption of *n*-alkanes and alcohols onto a quartz surface made hydrophobic by means of adsorption of dodecylamine hydrochloride and tetradecylamine hydrochloride, carried out by gas chromatography[3] and electrokinetic potential;[4] indicate that such adsorption causes a reduction of the dispersion component of quartz surface free energy to the value comparable with that for paraffin and a reduction of the polar component of quartz surface free energy almost to zero.[3,4]

Measurements of the force of air bubble detachment from the surface of hydrophobic and hydrophilic solids have shown that a very close relation exists between the changes of this force and the changes of the dispersion and polar components of surface free energy of solids under the influence of the liquid film between the air bubble and solid surface.[5–7] The main purpose of this paper is correlation between the changes of the force of air bubble detachment from a quartz surface and the changes of its surface free energy components under the influence of long chain aliphatic amine hydrochlorides. Hence, we carried out measurements of the force of air bubble detachment from a quartz surface in aqueous solutions of decylamine (DACl), dodecylamine (DDACl) and tetradecylamine (TDACl) hydrochlorides in the concentration range from 0 to 200 mg/dm^3, measuring simultaneously the instantaneous contact angle. The wetting contact angle in the system quartz-air bubble-aqueous solution of DDACl as well as the surface tension, using aqueous solutions, were also measured.

EXPERIMENTAL

Measurements of air bubble detachment force from a quartz grain surface in aqueous solutions of DACl, DDACl and TDACl were carried out, using the method described elsewhere.[8,9] In this method the value of the detachment force is read out from the deviation of a calibrated quartz rod (which is placed under a microscope fitted with a photographic camera) at the moment of disruption of the grain-air bubble system. The quartz rod was calibrated by hanging on its end a known weight and reading out its deviation by using a cathetometer. A quartz grain was prepared from Brazilian quartz by pulling off cylindrical rods 0.01666 cm in diameter, which was then melted with the end of the calibrated quartz rod and cut off at about 0.1 cm in length. The quartz grain-quartz rod aggregate was placed for 2.5 hours in a glass vessel filled with doubly distilled water. After this time the quartz grain was contacted with the air bubble (0.4046 cm in diameter) which was formed at the top of the capillaries by means of a micrometer screw and then the detachment force was measured. It was found earlier that the most stable contact of the air bubble with the quartz grain in water is obtained after 2.5 hours stay of the quartz grain in water.[5]

Next, the quartz grain-quartz rod aggregate was removed from water and placed in another glass vessel filled with amine hydrochloride solution of a given concentration. After about 1 hour the detachment force was measured as in pure water. The same procedure was repeated several times for all studied solutions of DACl, DDACl and TDACl in the range of from 0 to 200 mg/dm^3.

Every quartz grain-air bubble system was simultaneously photographed with a Practina Fx camera at the moment of disruption and the contact angle was read out from the pictures. All measurements of the detachment force were carried out at 20°C ± 0.1°C, and the measurement error was $\pm 0.5 \times 10^{-2}$ mN.

Measurements of the wetting contact angle in the system quartz-air bubble-aqueous solution of DDACl at 20°C were made by the captive air bubble method. The contact angle was measured using a microscope-goniometer system at a magnification of 25. The quartz plates employed in the measurements were cut off from quartz cuvettes. The procedure of their preparation was described elsewhere.[10] The plate prepared for measurements was immersed in a cuvette filled with doubly distilled water and the cuvette with the quartz plate was placed in the measuring chamber for 2.5 h. After this time an air bubble 2 mm^3 in volume, impressed from a special capillary was contacted with the quartz plate and the contact angle was measured on both sides of the air bubble. Next, the plate was removed from the cuvette, dried in a hot air stream and dipped into the cuvette filled with aqueous DDACl solution of a lesser concentration and after one hour the contact angle was measured in a manner similar to the above. The same procedure of contact angle measurements was used for all concentrations of the studied solution, and the measurement error was ±1°.

Amine hydrochlorides used for measurements of the detachment force and wetting contact angle were obtained in our laboratory from appropriate amines produced by Koch-Ligth Laboratories Ltd (England) which were recrystallized several times. Measurements of the surface tension of the solutions studies were conduced at 20°C ± 0.1°C using the volume-weight method. The pH of RACl solutions was not controlled but was measured after measurements of detachment force or contact angle. It was never less than 5.5.

RESULTS AND DISCUSSION

The values obtained from the measurements of the force F_0 of air bubble detachment from a quartz grain in aqueous solution of DACl, DDACl and TDACl depending on amine hydrochloride concentration c are shown in Figure 1; the values of instantaneous contact angle for the system quartz-air bubble-aqueous solution of aliphatic amine hydrochloride and the values of the wetting contact angle for the system quartz-air bubble-aqueous solution of DDACl, as well as those of the surface tension of the above mentioned aqueous solution of amine hydrochloride (RACl) are presented in Table I.

In Figure 1, curve 1 refers to decylamine hydrochloride, curve 2

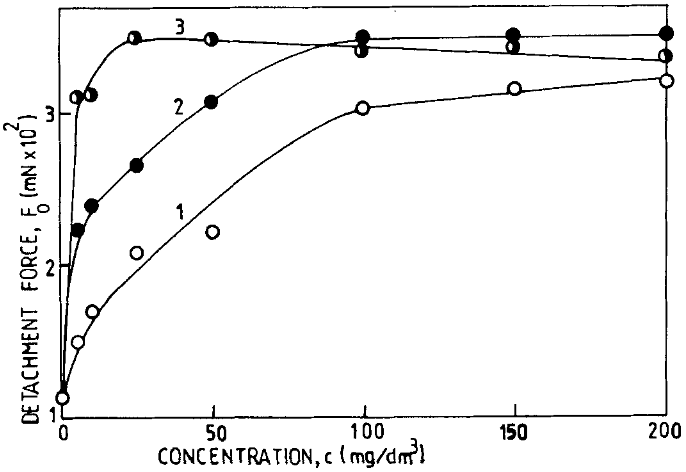

FIGURE 1 Effect of decylamine hydrochloride (curve 1), dodecylamine hydrochloride (curve 2) and tetradecylamine hydrochloride (curve 3) concentration in water on the force of air bubble detachment from a quartz surface.

to dodecylamine hydrochloride and curve 3 to tetradecylamine hydrochloride, respectively.

It appears from Figure 1 that the F_0 values increase as c of RACl increases. For DACl and DDACl (curves 1 and 2) the main increase lies in the range of c from 0 to 100 mg/dm^3. In the range from 100 to 200 mg/dm^3 the detachment force does not significantly change. In the case of TDACl (curve 3) a significant increase of F_0 value is observed in the concentration range from 0 to 25 mg/dm^3. Above $c = 25$ mg/dm^3 the detachment force F_0 slightly decreases up to $c = 200$ mg/dm^3.

It is very characteristic that the slope of curves 2 and 3 in Figure 1 is similar to the slope of the curves showing the change of DDACl and TDACl adsorption from aqueous solution on a polar solid surface as a function of the concentration.[11] Adsorption of RNH_3^+ onto polar-negative sites of the quartz surface eliminates polar interactions of water molecules with quartz, which facilitates the formation of a stable system quartz-air bubble-solution.[12,13]

The stability of a three-phase system, according to the previous studies of air bubble adhesion to hydrophobic and hydrophylic solid

TABLE I

The measured values of instantaneous contact angle for the system quartz-air bubble-solution, the values of surface tension of the studied RACl solutions and the values of the polar component of surface free energy quartz/film (water + RACl) calculated from Eq. (6).

RACl concentration mg/dm^3	Decylamine hydrochloride				Dodecylamine hydrochloride					Tetradecylamine hydrochloride			
	γ_L mJ/m^2	γ_L^p mJ/m^2	θ_1 degree	γ_{Qf}^p mJ/m^2 Eq. (6)	γ_L mJ/m^2	γ_L^p mJ/m^2	θ_1 degree	θ degree	γ_{Qf}^p mJ/m^2 Eq. (6)	γ_L mJ/m^2	γ_L^p mJ/m^2	θ_1 degree	γ_{Qf}^p mJ/m^2 Eq. (6)
0	72.80	51.00	20.6	91.30	72.80	51.00	20.6	22.3	91.30	72.80	51.00	20.6	91.30
5	72.48	50.68	25.0	40.86–37.58	72.60	50.80	38.9	37.7	33.05–30.10	72.40	50.60	55.1	21.96–19.57
10	72.00	50.20	30.5	37.60–34.29	71.12	50.32	42.1	42.0	30.60–27.75–	72.00	50.20	60.5	18.11–15.93
25	71.92	50.12	36.8	33.82–30.83	71.90	50.00	48.0	49.3	26.42–23.77	70.90	49.10	77.2	7.93–6.50
50	71.50	49.70	39.0	32.12–29.19	71.42	49.62	60.0	59.1	18.12–15.94	69.86	48.06	83.0	5.07–3.93
100	71.32	49.52	58.2	19.25–16.99	70.80	49.00	77.1	78.0	7.85–6.51	67.81	46.01	85.1	3.83–2.80
150	71.00	49.20	62.4 63.5	16.40–14.28	70.41	48.61	79.0	79.2	6.92–5.59	66.15	44.35	84.5	3.62–2.63
200	70.90	49.10		15.62–13.58	69.80	48.00	82.0	81.0	5.45–4.27	64.54	42.74	86.0	2.80–1.93

$r_k = 0.0833$ cm; $R = 0.2023$ cm; $\gamma_L^d = 21.8$ mN/m; $\pi e_{\max} = 48.2$ mJ/m^2; $\gamma_S^d = [25.5; 29.7]$ mJ/m^2

surfaces[5,6] can be expressed by the equation:

$$F_0 = 2\pi r_k \gamma_L \left(\sin \theta_1 - \frac{r_k}{R}\right) \tag{1}$$

where: γ_L—the surface tension of water aqueous solution, θ_1—the instantaneous contact angle, r_k—the contact plane radius, R—the radius of the air bubble.

Since in our studies dealing with the force of air bubble detachment from a quartz surface in the presence of RACl constant values of r_k and R were used, therefore, according to Eq. (1), the changes of F_0 as a function c (Fig. 1) can be determined on the basis of the measured values of γ_L and θ_1. The measurements of instantaneous contact angle θ_1 at the moment of air bubble detachment from hydrophobic and hydrophilic solids in water, and aqueous solutions of organic substances, pointed out that θ_1 values are close to those of wetting contact angle for a given system,[5,6,14] which is confirmed by the data presented in Table I. From the Table it appears that the wetting contact angle values for the system quartz-air bubble-aqueous DDACl solution of a given concentration are close to those of the instantaneous contact angle at the moment of disruption of this system ($\theta_1 \approx \theta$). Thus the value θ_1 can be linked with the magnitude of the surface free energy of quartz and of the solution and the free energy of the quartz-solution interface by employing the Young equation. Hence,

$$\gamma_L \cos \theta_1 = \gamma_{Qf} - \gamma_{QfL} - \pi e \tag{2}$$

where: γ_{Qf}—the surface free energy of quartz covered by a highly oriented, rigid mixed film (water + RACl), γ_{QfL}—the interfacial free energy quartz/highly oriented, rigid mixed film (water + RACl)—solution, πe is the reduction of γ_{Qf} by adsorbed molecules of water and RACl on the highly oriented rigid mixed film (water + RACl).

Taking into account that[15]:

$$\gamma_{QfL} = \gamma_{Qf} + \gamma_L - f(\gamma_{Qf}, \gamma_L) \tag{3}$$

and expressing $f(\gamma_{Qf}, \gamma_L)$ by the geometric mean of dispersion and polar interfacial interactions,[16–21] Eq. (2) may be written as:

$$\gamma_L \cos \theta_1 = -\gamma_L + 2(\gamma_{Qf}^d \gamma_L^d)^{1/2} + 2(\gamma_{Qf}^p \gamma_L^p)^{1/2} - \pi e \tag{4}$$

where γ_{Qf}^d and γ_{Qf}^p are the dispersion and polar components of γ_{Qf}, respectively.

However, it should be stated that Eq. (4) gives only an approximate relationship between θ_1 and the components of surface free energy resulting from various kinds of intermolecular interactions. The geometric mean approach to the dispersion interactions between phase 1 and 2 (according to Fowkes treatment[16]) is the more correct the more similar in size are the volumes and the ionization potentials of the phase 1 and 2 molecules. In the case of polar interactions between phase 1 and 2 the term $2(\gamma_1^p\gamma_2^p)^{1/2}$ is correct if the interactions deal only with dipole–dipole interactions and the distance between dipoles r_{12} is the geometric mean of r_{11} and r_{22} of the pure phases, since the interaction energy between two dipoles is; $-\mu_1^2\mu_2^2/3kTr_{12}^6$ (where μ is the dipole moment, k Boltzmann's constant and T absolute temperature).

In the light of these facts we think that for the systems studied the term $2(\gamma_{Qf}^d\gamma_L^d)^{1/2}$ is rather correct, but the term $2(\gamma_{Qf}^p\gamma_L^p)^{1/2}$ may be a rough approximation, since in these systems the polar interactions result not only from dipole-dipole interactions. We recognize that donor-acceptor interactions may be also present in these systems.

Taking into account that, in the systems tested in this paper, the concentration of RACl is very low, the donor-acceptor interactions cannot be dominant interactions between the quartz surface covered by mixed film (water + RACl) and RACl solution.

Because of lack of the possibility of exact expression of donor-acceptor interaction we think that the approximations made in this paper may be useful for predicting some surface phenomena.

Introducing Eq. (4) into Eq. (1) and assuming that the instantaneous contact angle is close to the equilibrium contact angle, we obtain:

$$F_0 = 2\pi r_k \gamma_L \times \left[\left(1-\left(\frac{-\gamma_L + 2(\gamma_{Qf}^d\gamma_L^d)^{1/2} + 2(\gamma_{Qf}^p\gamma_L^p)^{1/2} - \pi e}{\gamma_L}\right)^2\right)^{1/2} - \frac{r_k}{R}\right] \tag{5}$$

Eq. (5) presents approximate relationship between the force of air bubble detachment from the quartz surface covered by a mixed film (water + RACl) and the dispersion and polar components of the free energy of such a surface and for RACl solution (at low concentrations).

However, it is difficult to make an exact analysis of the changes of F_0 as a function of c, because we do not know the values of γ^d_{Qf}, γ^p_{Qf}, γ^d_L, γ^p_L and πe for the given RACl concentration. Only some of the measured F_0 values can be compared with these approximately calculated from Eq. (5) using the available literature data.

It is known that a quartz surface in contact with water vapor is easily hydrated, and water molecules form a film[10,22,23] in which the first layer of water near the quartz surface has special properties.[22–24] This layer cannot be removed by physical adsorption,[23] but only a high temperature makes this removal easier. Therefore, there is little probability that an air bubble could contact a "bare" quartz surface. So, in such a case the presence of a water film must be taken into account to consider the detachment force of a air bubble from a quartz surface in water, which was confirmed by Bernett and Zisman.[24] They found that a monolayer of adsorbed water determines the wettability of quartz. Hence, to calculate from Eq. (5) the detachment force ($F_{0(c)}$), the surface free energy of quartz/monolayer film was used (Table I). This force was calculated upon the assumption that $\pi e = \gamma_{Qf} - \gamma_W$, the values of which are listed in Table II. From Table II it is seen that the value of $F_{0(c)}$ calculated from Eq. (5) is only slightly higher than that measured in the system quartz-air bubble-water. So, the model used for calculations seems to be reasonable.

TABLE II

Values of the detachment force of an air bubble from a quartz surface covered by DDACl and TDACl film calculated ($F_{0(c)}$) from Eq. (5), maximum ($F_{0(\max)}$) values measured for aqueous solution of DDACl and TDACl and literature data of γ^d_{Qf} and γ^p_{Qf}.

Statistical monolayers on quartz surface (water + RACl)	γ^d_{Qf} mJ/m^2	γ^p_{Qf} mJ/m^2	Ref.	$F_{0(\max)}$ $\times 10^{-2}$ mN	$F_{0(c)}$ $\times 10^{-2}$ mN
1 (water)	29.7	91.3	6	1.16	1.41
0.265 (DDACl)	28.2	7.14	4	3.50	3.57–3.40
1.0 (TDACl)	25.5	7.7	3	3.50	3.59–3.09
1.06 (DDACl)	26.4	0.0	4	3.50	3.43–3.32

RACl molecules introduced into water are adsorbed on the quartz surface forming a mixed film (water + RACl) which changes the values of γ_{Qf}^{d}, γ_{Qf}^{p} and πe. According to Chibowski *et al.*[4] and Wojcik *et al.*[3] DDACl and TDACl reduce γ_{Qf}^{d} to the surface free energy of paraffin (γ_p)[25,26] and γ_{Qf}^{p} to 0. They determined the components of the surface free energy of quartz covered with RACl film. On the basis of their results F_0 could be calculated (from Eq. (5)) for the system quartz/film (water + RACl)—air bubble-solution (assuming $\gamma_{Qf} \leqslant \gamma_L$, $\pi e \approx 0$)[16] if the values γ_L^d, γ_L^p and γ_L could be determined for the given RACl covering.

The data given in Table I indicate that the changes of γ_L in the studied RACl concentration range in water are as follows: for DACl from 72.8 to 70.9 mN/m, for DDACl from 72.8 to 69.8 mN/m and for TDACl from 72.8 to 64.54 mN/m. Thus, except for TDACl, the changes of γ_L as a function of c are slight. Taking this into account and assuming that the hydrocarbon chain cannot change too much the value of the dispersion component of the surface tension of water (dispersion interactions of aliphatic hydrocarbons are close to water[16]) in the studied range of c, then $\gamma_L^d \approx \gamma_W^d = 21.8$ mN/m[16]. Hence, the value γ_L^p is equal to $\gamma_L - 21.8$ mN/m. Since we do not know what sort of a film (RACl + water) can be formed on a quartz surface at a given RACl concentration in water, the highest and lowest values of γ_L^p for RACl solutions have been used for F_0 calculations (from Eq. (5)). Taking the above mentioned assumptions and approximations as valid, and using some data for DDACl and TDACl from the literature[3,4] (Table II), F_0 has, as an example, calculated (from Eq. (5)) for a 0.265 and a 1.06 monolayer DDACl film and for a 1 monolayer TDACl film on a quartz surface. The calculated values of F_0 are listed in Table II together with the measured maximal ones for DDACl and TDACl.

From Table II it appears that, in the case of DDACl, covering the quartz surface by a 0.265 static monolayer is quite enough to obtain the maximum stability for the system quartz/film (water + RACl)—air bubble-solution. Furthermore, too much RACl on the quartz surface may have a negative action on the F_0 force. A decrease of the F_0 value is possible at a high concentration of RACl in water, which is partially confirmed by data presented in Figure 1 (TDACl—curve 3).

The convergence of the calculated F_0 values with the maximum values measured indicates that it is reasonable to use in calculations the assumptions and approximations in the absence of more definite data concerning the studied systems.

From the calculations mentioned above it also appears that in the range of RACl concentrations from 0 to 200 mg/dm^3 in water, γ_{Qf}^d changes slightly ($29.7-25.5$ mJ/m^2).[22,25,26] The changes of γ_{Qf}^p and πe have a decisive influence on the course of F_0 being a function of c, but it is very probable that at low concentrations of RACl in water πe is almost equal to zero, which is evident from zeta potential measurements[4] and chromatographic studies.[3] Assuming $\pi e \approx 0$ and taking into account the above mentioned approximations, one can calculate γ_{Qf}^p changes as a function of c on the basis of measurements of instantaneous contact angle for the system quartz/film (water + RACl)-air bubble-solution using the following equation:

$$(\gamma_{Qf}^p)^{1/2} = \frac{\gamma_L(\cos\theta_1 + 1) - 2(\gamma_{Qf}^d \gamma_L^d)^{1/2}}{2(\gamma_L^p)^{1/2}} \tag{6}$$

Using the measured values of γ_L, θ_1 (Table I), $\gamma_L^d = \gamma_W^d =$ 21.8 mN/m, $\gamma_L^p = \gamma_L - 21.8$ mN/m and γ_{Qf}^d in the range from 25.5 to 29.7 mJ/m^2, the values of γ_{Qf}^p were calculated (from Eq. (6)) which are presented in Table I. From Table I it can be seen that when the RACl concentration increases the value of γ_{Qf}^d rapidly decreases.

The influence of individual aliphatic amine hydrochlorides on changes of γ_{Qf}^p is not similar.

Polar interactions with water molecules are blocked most efficiently by TDACl, and practically 80% of the polar component of the surface free energy of quartz covered by a monolayer water film is reduced in the range from 0 to 25 mg/dm^3. The smallest changes of γ_{Qf}^d *vs*. c are observed for aqueous DACl solution. Even at a concentration of DACl of 200 mg/dm^3, γ_{Qf}^d is quite high. Hence, from the data presented above it is evident that the highest hydrophobicity of the quartz surface is achieved for TDACl, and the lowest for DACl. It is very characteristic that maximum values of the detachment force in the case of DDACl and TDACl (Fig. 1) are obtained for the same γ_{Qf}^p value (Table I—$\gamma_{Qf}^p =$ [7.94, 6.51] mJ/m^2: $\gamma_{Qf}^p =$ [7.93, 6.50] mJ/m^2). These values of γ_{Qf}^p for DDACl are obtained at the concentration of 100 mg/dm^3 and are close to the values of γ_{Qf}^{p} determined by Chibowski *et al.*[4] from zeta potential measurements for *n*-alcohols on a quartz surface covered by 0.265 monolayer of DDACl (7.14 mJ/m^2). In the case of TDACl, γ_{Qf}^{p} values from the range 7.93–6.5 mJ/m^2 are close to the minimum values obtained by chromatography for quartz covered by a TDACl monolayer (7.7 mJ/m^2)[3].

From the presented measurements and calculations it appears that the stability of the system quartz/film (water + RACl)-air bubble-aqueous solution of RACl as a function of concentration can change by reduction of the polar interaction of quartz with water molecules. This is caused by adsorption of RACl molecules on the quartz surface to produce a surface similar to a paraffin surface.[25,26]

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