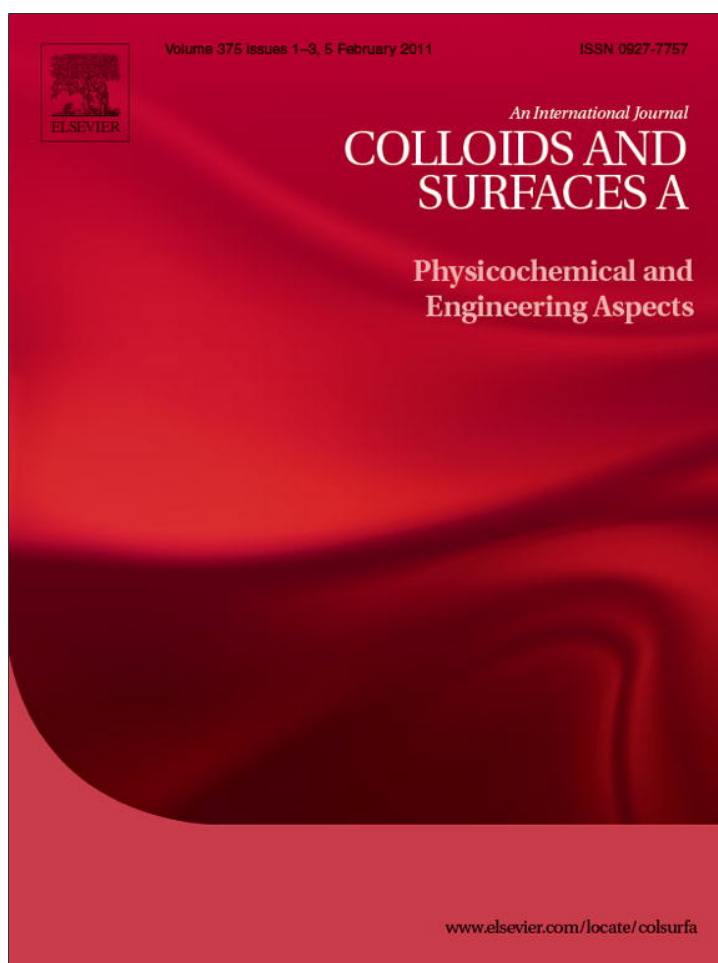


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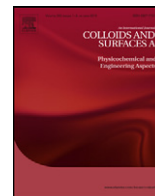
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Influence of functional groups on the adsorption behaviour of substituted benzoic acids at the α -alumina/water interface

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ABSTRACT

Adsorption kinetics of hemimellitic and trimellitic acids at a fixed initial concentration of 0.30 mM onto α -alumina surfaces were carried out in batch method in the presence of 0.05 mM NaCl(aq) at pH 5 and 288.15, 298.15, 303.15, and 313.15 K. The experimental data were significantly better fitted to pseudo-second-order kinetic equation of non-linear form in the entire time duration. The state of equilibration time of benzenetricarboxylic acids at 298.15 K follows the sequence: hemimellitic acid < trimellitic acid < trimesic acid. Adsorption isotherms of hemimellitic and trimellitic acids were carried out at 298.15 K, pH 5–10, and 0.05 mM NaCl(aq) by varying acid concentration. The adsorption data were fitted to Langmuir adsorption model. Adsorption density of benzenetricarboxylic acids follows the sequence: trimesic acid < trimellitic acid < hemimellitic acid. Comparison of the adsorption densities of benzenetricarboxylic acids with dihydroxybenzoic and monohydroxybenzoic acids indicates that (i) in benzenetricarboxylic acids the position and equally the number of –COOH groups, (ii) the two phenolic –OH groups at any two position in the benzene ring of dihydroxybenzoic acids, and (iii) the phenolic –OH groups at *ortho* position in the benzene ring of monohydroxybenzoic acids are the governing parameters for yielding higher adsorption density onto α -alumina surface. Exception is the 2,4-dihydroxybenzoic acid amongst dihydroxybenzoic acids series, which yields highest adsorption density due to *ortho* and *para* position of the phenolic –OH groups. The thermodynamic data indicate that the adsorption process is spontaneous for both the systems. The magnitude of shifting of $\nu_s(-COO^-)$ and $\nu_{as}(-COO^-)$ after adsorption of trimellitic and hemimellitic acids onto α -alumina surface indicate that both acids form outer-sphere surface complexes.

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1. Introduction

Natural organic matter (NOM) consists of simple and well-defined soluble organic (aliphatic and aromatic) acids and very complex organic compounds, e.g., humic and fulvic acids. NOM is ubiquitous in the aquatic ecosystems and their concentration varies from 0.5 to 100 mg/L of organic carbon [1]. NOM undergoes continuous biological, chemical and photochemical transformation [2–6]. The photoreactions of NOM generally produce low molecular weight carboxylic acids and small organic compounds [7–10]. Nevertheless, specific to very complex structured organic acid, the ozonation of fulvic acid produces benzene-polycarboxylic and polyhydroxy-benzene-polycarboxylic acids [6]. These acids with –COOH and –OH groups behave like a surface-active agent but not like a typical surfactant [11]. Note that benzene-polycarboxylic and polyhydroxybenzoic acids adsorbed onto minerals and metal

oxides surfaces and form different surface complexes through –COOH or –OH or both groups that depends on the chemical environment. Nevertheless, the magnitude of adsorption density (amount adsorbed per unit area) onto an adsorbent is governed by the number, types and the position of the functional groups in the benzene ring [12–16]. Specific to the above statement, we note that 2,3,4-trihydroxybenzoic acid has higher adsorption density than the 2-hydroxybenzoic acid [12,16] and benzenhexacarboxylic acid has the higher adsorption density than the phthalic acid [12]. Similarly, *ortho* and *para* substituted benzoic acids produce higher adsorption density than the *meta* substituted benzoic acids [16].

Evanko and Dzombak [12] reported that the adjacent –COOH and phenolic –OH groups and the phenolic –OH group at *ortho* position in the benzene(poly)carboxylic and hydroxybenzoic acids significantly influence the adsorption density onto goethite surface. A similar trend has been observed by Hidber et al. [16]. Guan et al. [13,14] also, based on the adsorption kinetics and surface complexation, reported that (i) the additional carboxylic groups enhance the adsorption, (ii) phenolic –OH group enhances the interaction of carboxylic group and (iii) chelate formation involving carboxylate oxygen and *ortho* phenolic oxygen is important at acidic pH

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and the phenolic –OH groups adjacent to each other are important than the carboxylic groups at alkaline pH for adsorption. In these reports no systematic adsorption isotherms were studied in the presence of any background electrolyte, maintaining adsorption equilibration time, and varying the concentration of acid until the surface of alumina/goethite is saturated. Nevertheless, Guan et al. [14] did not consider 2,4-dihydroxybenzoic acid in their studies. Note that the position of the phenolic –OH groups in dihydroxybenzoic acids (DHBA) significantly influences the electron density of the –COOH group. In that case adsorption density of 2,4-DHBA would be much higher than the other DHBA. Therefore, to understand quantitatively the influence of the number as well as the position of functional groups of an adsorbate, e.g. benzenepoly-carboxylic and hydroxybenzoic acids, the magnitude of adsorption density after the surface saturation from the adsorption isotherms would be the better proposition. For studying adsorption isotherms of an adsorbate-adsorbent system, the equilibration time is the prerequisite, which is different for different systems.

Literature showed that simple and well-defined organic acids mimicking the complex surface-active agents and surfactants are used to understand the dispersion and stability of the dispersed phase of metal oxide/surfactant systems [16,17] and alumina and simple organic acids are taken as model systems. Further simple organic acids are ubiquitous component of the natural eco-system. Therefore, in the scope of adsorption studies of substituted-benzoic acid and of closest relevance to natural process in the aquatic eco-system, we, in this paper, report the adsorption kinetics, isotherms and surface complexation of hemimellitic and trimellitic acids with the α -alumina, taken as a model mineral, surface to understand the influence of functional groups on the adsorption. It is not the subject of a vast literature. We also have shown that such a low concentration of a background electrolyte is sufficient for the ion-specificity in the adsorption isotherm [18]. Finally, we have compared (i) the adsorption density of hemimellitic and trimellitic acids with that of benzoic, phthalic and trimesic acids and the dihydroxybenzoic acids (DHBA), keeping the position of phenolic –OH groups in the benzene ring at per of tricarboxylicbenzoic acids, (ii) the influence of –COOH vs –OH group, and (iii) the position of –OH groups in di- and monohydroxybenzoic acids on the magnitude of adsorption density.

2. Materials and methods

2.1. Materials

α -alumina (>99%, Aldrich, Germany) was washed twice with double-distilled water, dried and finally reactivated at $\sim 700^\circ\text{C}$ for 3 h. α -alumina was kept in a vacuum desiccator and all suspension/solutions were prepared using freshly prepared double-distilled water to minimize $\text{CO}_2(\text{g})$ contamination. Hemimellitic acid (98%, Alpha Aesar, UK), trimellitic acid (99%, Alpha Aesar, UK), salicylic acid (99%, Qualigens, India), *p*-hydroxybenzoic acid (98%, Merck, Germany), sodium hydroxide (>99%, s.d. fine-chem, India), sodium chloride (>99.5%, Merck, India) and HCl (AR grade, NICE Chemicals, India) were used without further purification.

2.2. Adsorption kinetics

Adsorption kinetics of hemimellitic and trimellitic acids onto α -alumina (0.5 g) in a 15 mL suspension were performed at pH 5 and four temperatures in batch method. The temperature was maintained by using temperature controlled refrigerated-shaking-water-bath (SX-10R, Titac, Japan) with an accuracy of $\pm 0.1^\circ$. The

initial concentration of both the acids was 0.30 mM and for NaCl(aq) it was 0.05 mM. The suspension was filtered through a membrane of 0.2 μm pore size at different intervals of time. Both acids being surface-active may sorbed onto the filter-membrane. So, to avoid the uncertainty of the adsorbate concentration in the supernatant liquid few mL (~ 3 mL out of ~ 10 mL) of the filtrate was discarded and the middle fraction was collected for the analysis. The residual concentrations of hemimellitic and trimellitic acids were estimated at absorption maxima, 202.8 and 203.3 nm, respectively by using an UV-visible spectrophotometer (Specord 200, Analytik-jena, Germany). The adsorption density, Γ , of the respective acid onto α -alumina surfaces was estimated by mass balance equation

$$\Gamma = \frac{(C_0 - C_t)V}{ma} \quad (1)$$

where, C_0 is the initial and C_t is the residual concentration at time, t , of an acid in the supernatant liquid in mM, V is the volume of the suspension and m is the mass of α -alumina, respectively. The specific surface area, a , of α -alumina was determined by BET method and was found to be 7.29 m^2/g .

2.3. Adsorption isotherm

Adsorption isotherms of hemimellitic and trimellitic acids onto α -alumina in aqueous medium were studied in the pH range 5–10 at 298.15 K in a screw-capped glass vial by batch method. The adsorption isotherms of each acid were also studied at pH 5 and 288.15, 298.15, 303.15 and 313.15 K for estimating the values of thermodynamic parameters. A suspension of 15 mL containing 0.5 g α -alumina and 0.05 mM NaCl(aq) solution was mixed thoroughly with the help of a vortex mixer. The pH of the suspension was adjusted to a desired value within ± 0.1 unit using either dilute NaOH(aq) or HCl(aq) solution and then allowed to equilibrate for 1 h. The required amount of adsorbate was added and the pH of the suspension was readjusted, whenever required. The suspension was then allowed to equilibrate with continuous stirring in a shaking-water-bath for a fixed duration corresponding to the equilibration time of an adsorbate. After the equilibration time is elapsed, the suspension was then filtered through a membrane of 0.2 μm pore size and the residual concentration of the acid was estimated as indicated in the Section 2.2.

2.4. DRIFT spectroscopy

For DRIFT spectroscopic studies 0.5 g of α -alumina was equilibrated for 2 h with 1 mM of an adsorbate in the presence of 0.05 mM NaCl(aq) at different pH 5–10 and 298.15 K following the procedure adopted for the adsorption isotherm. The residue was washed once with double distilled water and dried under vacuum over fused calcium chloride. The DRIFT spectra were recorded with the PerkinElmer FTIR spectrophotometer-2000 using DRIFT attachment (part no. L127-5001). In all cases, the spectra were recorded with 200 scans at a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Adsorption kinetics

Adsorption densities of hemimellitic and trimellitic acids onto α -alumina surfaces as a function of time at pH 5 and 288.15, 298.15, 303.15 and 313.15 K are shown in Fig. 1. For simulating the experimental adsorption kinetic data, the model equations are frequently used. The pseudo-first-order kinetic equation of linear form, $\ln(q_e - q_t) = \ln q_e - k_1 t$ where q_e and q_t are the adsorption density of an adsorbate at the state of equilibrium and time, t , respectively and k_1 is the rate constant, produces a large devi-

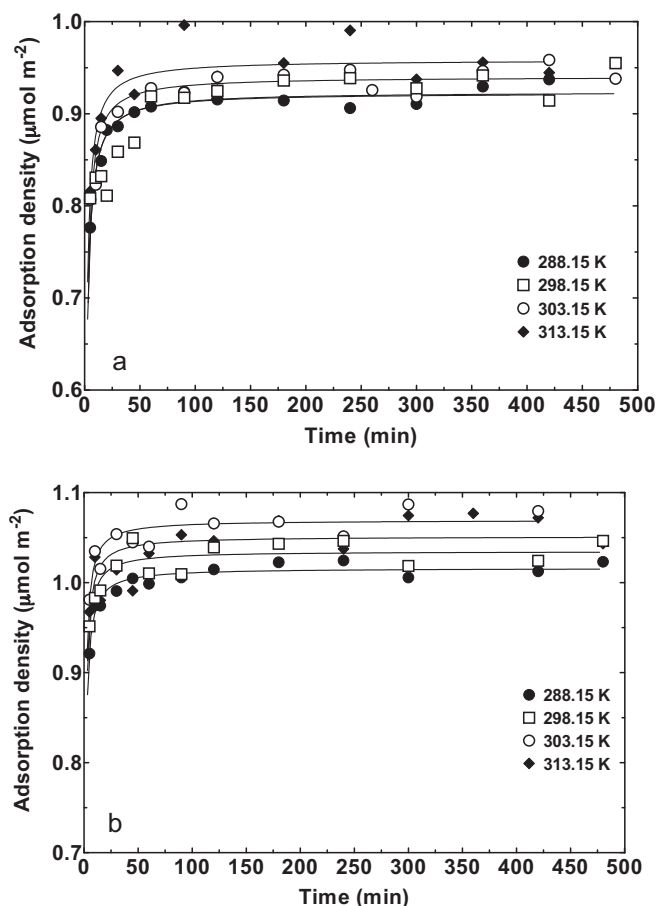


Fig. 1. Effect of temperature on the adsorption density of (a) trimellitic and (b) hemimellitic acids on the α -alumina surfaces: initial concentration of both acids, $C_0 = 0.30$ mM, α -alumina = 0.5 g, NaCl(aq) = 0.05 mM, $V = 15$ mL and pH 5. The reproducibility of data is $\pm 2\%$. The symbols are the experimental data and the lines are calculated from Eq. (2).

ation (up to $\sim 90\%$) in q_e . Regarding the pseudo-second-order kinetic equation of linear form, $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$, where k_2 is the rate constant, many authors have raised question on its applicability for associated statistical errors [19–26]. In contrast, the pseudo-second-order kinetic equation of nonlinear form Eq. (2) [19] is applicable in equilibration region also. Therefore, the experimental data were fitted to pseudo-second-order kinetic equation of nonlinear form and the computed values of the parameters of Eq. (2)

are listed in Table 1.

$$q_t = \frac{q_e^2 k_3 t}{(k_3 q_e t + 1)} \quad (2)$$

where k_3 is the rate constant and the other parameters are defined earlier. The standard deviations (Table 1) show that the Eq. (2) successfully fit the experimental data and the estimated values of q_e are in excellent agreement ($\sim 2\%$ deviation) with the corresponding experimental values (Table 1).

It is apparent from Fig. 1 that the state of equilibrium is attained at 100 min for trimellitic acid and 60 min for hemimellitic acid. For trimelic acid/ α -alumina system the equilibration time was 120 min [25]. In contrast, Guan et al. [13] reported higher equilibration time for the benzenetricarboxylic acids and it is lowest (4 h) in the case of hemimellitic acid. Taking equilibration times of benzoate and phthalate as the base [26] and comparison with the benzenetricarboxylic acids reported in this study at pH 5 and 298.15 K, the sequence of the equilibration time follows: hemimellitic acid < trimellitic acid < trimelic acid < phthalic acid < benzoic acid. These results clearly demonstrate that the lower equilibration time for the benzenetricarboxylic acids in comparison to benzoic acid, are accounted for the presence of higher number of carboxylic groups in the benzene ring and the present findings are in tune with the earlier report [12,26]. Further, the adjacent carboxylic group(s) in the benzene ring is an important characteristic feature for higher adsorption density [12–15,25,26], in that case adsorption density at equilibrium for hemimellitic and trimellitic acids (in both cases at least two $-\text{COOH}$ groups are adjacent) should be nearly of same magnitude. The experimental results from the kinetics run showed that the adsorption density of hemimellitic acid at equilibrium is 8–10% higher than the trimellitic acid and is accounted for the three adjacent carboxylic groups in the benzene ring. We will discuss further this point in the adsorption isotherms section.

3.2. Adsorption isotherms

The variation of the adsorption density of hemimellitic and trimellitic acids with different initial concentrations onto α -alumina surfaces in the presence of 0.05 mM NaCl(aq) at different pH and 298.15 K is shown in Fig. 2. The adsorption densities were fitted to Langmuir equation of the following form:

$$\Gamma = \frac{\Gamma_{\max} C_e}{(K + C_e)} \quad (3)$$

where C_e is the equilibrium concentration of an acid, $K = \frac{1}{K_s}$, K_s is the adsorption coefficient in $\text{dm}^3 \text{mmol}^{-1}$, and Γ and Γ_{\max} are

Table 1
Values of the parameters of Eq. (2) for hemimellitic- and trimellitic acids- α -alumina system at pH 5 and different temperatures*.

Equation	Parameters	288.15 K	298.15 K	303.15 K	313.15 K
Hemimellitic acid Pseudo-second-order kinetics (non-linear form)	k_3 ($\text{m}^2/\mu\text{mol min}$)	1.90 ± 0.16	2.05 ± 0.35	2.01 ± 0.37	1.96 ± 0.54
	q_e ($\mu\text{mol m}^{-2}$) (estimated)	1.02 ± 0.01	1.03 ± 0.01	1.07 ± 0.01	1.05 ± 0.01
	S.D.	0.01	0.01	0.02	0.02
	q_e ($\mu\text{mol m}^{-2}$) (experimental)	1.01	1.04	1.05	1.06
Trimellitic acid Pseudo-second-order kinetics (non-linear form)	k_3 ($\text{m}^2/\mu\text{mol min}$)	1.06 ± 0.08	1.04 ± 0.23	1.09 ± 0.01	1.08 ± 0.01
	q_e ($\mu\text{mol m}^{-2}$) (estimated)	0.923 ± 0.003	0.922 ± 0.010	0.940 ± 0.124	0.960 ± 0.181
	S.D.	0.010	0.031	0.015	0.022
	q_e ($\mu\text{mol m}^{-2}$) (experimental)	0.926	0.940	0.956	0.965

* S.D. (standard deviation) = $\left[\frac{\sum (q_{\text{obs}} - q_{\text{cal}})^2}{n-2} \right]^{1/2}$.

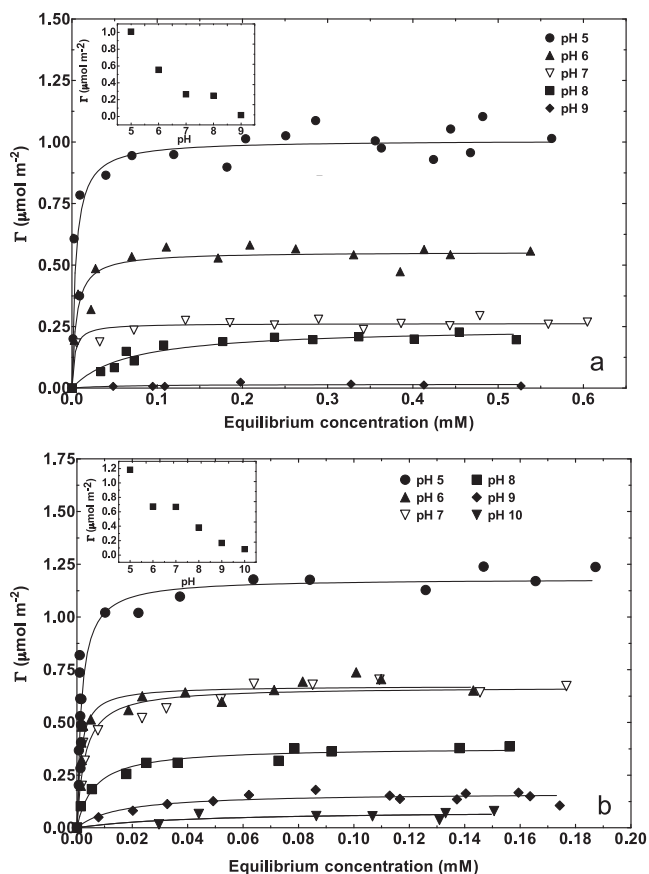


Fig. 2. Adsorption isotherms of (a) trimellitic and (b) hemimellitic acids onto α -alumina at different pH: NaCl(aq)=0.05 mM, α -alumina=0.5 g, $V=15$ mL and $T=298.15$ K. The reproducibility of data is $\pm 5\%$. The symbols are the experimental data and the lines are calculated from Eq. (3). Inset: Γ (maximum adsorption density) vs. pH of the corresponding acids.

the adsorption densities of an acid in $\mu\text{mol m}^{-2}$ at equilibrium and after saturation of α -alumina surfaces, respectively.

The estimated values of the parameters of Eq. (3) for hemimellitic- and trimellitic- α -alumina systems are listed in Table 2. The appearance of near perfect plateau region in the adsorption isotherms indicates monolayer adsorption and the Eq. (3) provides theoretical equilibration concentration, Γ_{max} , at surface saturation. The decrease in adsorption density of an adsorbate with the increase of pH of the suspension is due to the decrease of the surface charge [24–26].

The Γ_{max} vs. pH plots of both the systems are shown in Fig. 2 (Inset). It is apparent that Γ_{max} decreases with the increase in pH and the trend is comparable in the pH range 5–10 with the literature [16]. Such a decrease in adsorption density of hemimellitic and trimellitic acids with pH is not surprising and is linked with the zeta potential of α -alumina. The isoelectric point (IEP) of α -alumina is at pH 6.7, which was slightly lowered in the presence of 0.5 mM

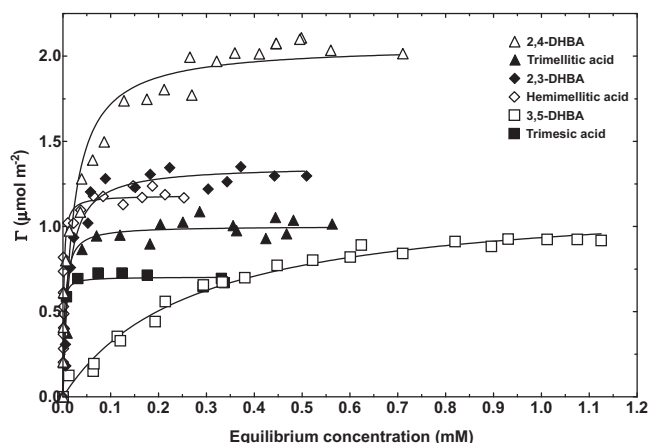


Fig. 3. Adsorption isotherm of benzenetricarboxylic acids onto α -alumina surface at pH 5 and 298.15 K. For comparison adsorption densities of trimesic acid [25], 2,3-, 2,4- and 3,5-DHBA [27] onto α -alumina under similar experimental conditions are added. The reproducibility of data is $\pm 5\%$. The symbols are the experimental data and the lines are calculated from Eq. (3).

NaCl(aq) [18,24]. The surface charge of α -alumina at IEP > 6.7 is negative, which causes decrease in adsorption density. Hidber et al. [16] has reported excellent results on the variation of adsorption density of substituted benzoic acids with pH and correlated with the dynamic electrophoretic mobility of alumina particle under similar experimental conditions. For example, the adsorption density of hemimellitic acid onto alumina decreases with the increase in pH of the suspension. Nevertheless, the dynamic electrophoretic mobility vs. pH plot indicates that the IEP shifted from ~ 9.3 to ~ 4.2 with higher negative surface charge at IEP $> \sim 4.2$. As a result adsorption density of hemimellitic acid onto alumina decreases. A similar inference may also be drawn for the present adsorption density trend with pH (Fig. 2a and b, Inset).

3.3. Examination of numbers and position of functional groups, and $-\text{COOH}$ vs. $-\text{OH}$ on the adsorption density at pH 5 and 298.15 K

Fig. 3 provides the quantitative information concerning the adsorption density at saturation obtained from the adsorption isotherms of hemimellitic and trimellitic acids at pH 5 and 298.15 K. For comparison of the influence of the $-\text{COOH}$ and $-\text{OH}$ groups according to their position in the benzene ring, we added the adsorption isotherms of trimesic acid [25] and 2,3-, 2,4- and 3,5-DHBA [27].

First, to understand the importance of the number of similar type of functional groups in the benzene ring, we consider the adsorption densities of benzoic acid [26], phthalic acid [26] and hemimellitic acid (present study) (benzenemo-, di- and tricarboxylic acid series) onto the α -alumina surfaces and on comparison the magnitude of adsorption density follows: benzoic acid $<$ phthalic acid $<$ hemimellitic acid. Similarly, Gocmez studied

Table 2
Values of the parameter of Eq. (3) as a function of pH for adsorption of hemimellitic and trimellitic acid onto α -alumina surface at 298.15 K.

Hemimellitic acid/ α -alumina				Trimellitic acid/ α -alumina			
pH	Γ_{max} ($\mu\text{mol m}^{-2}$)	K_s ($\text{dm}^3 \text{mmol}^{-1}$)	S.D.	pH	Γ_{max} ($\mu\text{mol m}^{-2}$)	K_s ($\text{dm}^3 \text{mmol}^{-1}$)	S.D.
5	1.18 ± 0.05	625 ± 112	0.144	5	1.01 ± 0.03	230 ± 62	0.108
6	0.673 ± 0.023	726 ± 141	0.064	6	0.554 ± 0.017	195 ± 50	0.051
7	0.668 ± 0.022	350 ± 67	0.052	7	0.263 ± 0.007	316 ± 115	0.022
8	0.382 ± 0.012	160 ± 31	0.022	8	0.247 ± 0.015	15.1 ± 3.2	0.019
9	0.167 ± 0.013	65.8 ± 27.2	0.021	9	0.016 ± 0.006	17.3 ± 7.5	0.006
10	0.082 ± 0.030	24.2 ± 15.4	0.017				

the adsorption of benzoic and mono-, di- and trihydroxybenzoic acids and sequence of the magnitude of amount adsorbed follows: benzoic acid < 2-hydroxybenzoic acid < 2,3-dihydroxybenzoic acid < 2,3,4-trihydroxybenzoic acid [17]. It is interesting to note that in both categories of adsorbates the adsorption density increases with the increase in number of functional groups and when they are adjacent. The increase in amount absorbed of (poly)hydroxybenzoic acids was due to the increase in interaction energy [17], which increases with the increase in number of same type of functional groups in benzene ring provided they are adjacent. Therefore, a similar explanation may be applicable in the present system. It is clear that the increase in number of similar type of functional groups and when they are adjacent in the benzene ring is found to be governing factor for increasing of adsorption density.

Second, we consider the benzenetricarboxylic acid: to our surprise the magnitude of Γ_{\max} for hemimellitic acid is ~ 1.7 times and trimellitic acid ~ 1.4 more than the trimesic acid (Fig. 3). Similarly, Γ_{\max} of hemimellitic acid is ~ 1.1 times more than trimellitic acid and the adsorption density sequence follows: trimesic acid < trimellitic acid < hemimellitic acid. Note that in hemimellitic acid all the three $-\text{COOH}$ groups are adjacent (at 1,2,3 position) in the benzene ring. On the other hand, in trimellitic acid only two $-\text{COOH}$ groups are adjacent to each other (at 1 and 2 position) and in trimesic acid none of the $-\text{COOH}$ groups are adjacent in the benzene ring. Therefore, for a series of benzenepolycarboxylic acids having same number of carboxylic groups, the position of the functional groups is also an important factor for the higher magnitude of the adsorption density.

Third, we compare the adsorption densities of benzenetricarboxylic acids with DHBA, where two carboxylic groups are replaced by $-\text{OH}$ groups. Therefore, we can quantitatively compare hemimellitic acid with 2,3-DHBA, trimellitic with 2,4-DHBA and trimesic with 3,5-DHBA. It is interesting to note that DHBA, reported in this paper, have higher adsorption densities at saturation than that of corresponding benzenetricarboxylic acids (Fig. 3). The magnitude of difference in adsorption density between 2,4-DHBA and trimellitic is much higher (~ 2.1 times) than for 2,3-DHBA and hemimellitic acid (~ 1.2 times) and 3,5-DHBA and trimesic acid (~ 1.7 times). As observed in the case of benzenetricarboxylic acids, the adsorption density sequence in DHBA (noting structural symmetry with benzenetricarboxylic acids) should have been: 3,5-DHBA < 2,4-DHBA < 2,3-DHBA but the experimental results showed 3,5-DHBA < 2,3-DHBA < 2,4-DHBA. The higher adsorption density in 2,4-DHBA is may be due to the increase in electron density of the carboxylic group by resonating effect of lone pair of electrons of phenolic oxygen at *ortho* and *para* position. In that case, in 2,3-DHBA two $-\text{OH}$ groups are at 2 and 3 positions, respectively in the benzene ring and the lone pair of electrons of phenolic oxygen at *meta* position cannot increase the electron density of the carboxylic group. Although the first $\text{p}K_a$ of a series of DHBA were correlated with the sequence of adsorption densities [14] but failed to explain in the case of 2,4-DHBA. Further, comparison of the adsorption densities at surface saturation of phthalic and salicylic acids onto alumina at pH 5 and 298.15 K [24,26] also support the importance of the phenolic $-\text{OH}$ group for higher adsorption density, since it can increase the electron density of the carboxylic group. Similarly, the adsorption density of *p*-hydroxybenzoic acid is higher than the salicylic acid on the α -alumina surface [28] and also of the salicylate is higher than the benzoate onto hematite surface [29]. Therefore, we conclude that in contrast to carboxylic groups, the phenolic $-\text{OH}$ groups in DHBA at any two positions in the benzene ring are the governing factor for the higher adsorption density. But phenolic $-\text{OH}$ groups in DHBA at *ortho* and *para* positions yield higher adsorption density.

Finally, we compare the position of a particular functional group in a benzene ring for the magnitude of the adsorption density. In

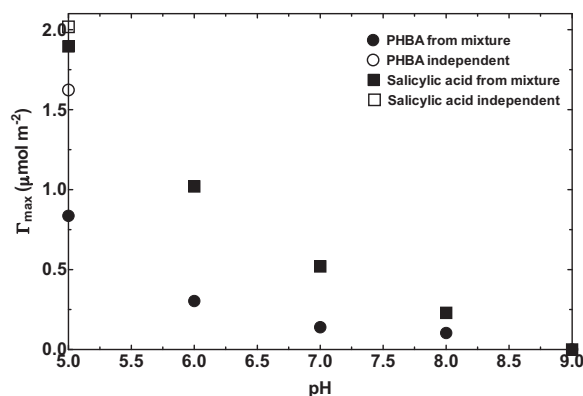


Fig. 4. Variation adsorption densities of salicylic and *p*-hydroxybenzoic (PHBA) acid as a function of pH. Adsorption density of each acid was estimated from their mixtures at different pH and the adsorption densities after surface saturation, Γ_{\max} , are reported.

the preceding paragraph we noted that $-\text{OH}$ group either at *para* or *ortho* or both position of a DHBA (e.g. 2,4-DHBA) is more effective for yielding higher adsorption density. Here we present some experimental adsorption densities of monohydroxybenzoic acids like, salicylic and *p*-hydroxybenzoic acids onto α -alumina as functions of pH obtained from competitive adsorption isotherms at 298.15 K along with their individual adsorption densities [28] and are shown in Fig. 4. Note that the adsorption densities of salicylic acid onto α -alumina surface, either from the mixture or individual, are higher than *p*-hydroxybenzoic acid. Though the lone pair of electrons of phenolic oxygen at *ortho* and *para* positions enhance the electron density of the carboxylic group but the magnitude of increase of electron density by the phenolic oxygen at *ortho* position seems to be comparatively higher. With the above results we conclude that in the case of monohydroxybenzoic acids phenolic $-\text{OH}$ group at *ortho* position yields higher adsorption density.

3.4. Adsorption thermodynamics

The adsorption isotherms for hemimellitic and trimellitic acid on the α -alumina surfaces at four different temperatures and pH 5 for estimation of thermodynamic parameters are shown in Fig. 5.

Note that for estimating the numerical values of the thermodynamic parameter, the units of the adsorption density (mol m^{-2}) and the concentration of acid (mol m^{-3}) were considered. The activation energy, E , for adsorption was calculated by using Arrhenius equation, $k_3 = Ae^{-E/RT}$, where k_3 is the rate constant for adsorption, A the frequency factor, R the gas constant, and T the temperature in Kelvin. The enthalpy, ΔH (kJ mol^{-1}), entropy, ΔS ($\text{kJ mol}^{-1} \text{K}^{-1}$), and Gibbs free energy, ΔG (kJ mol^{-1}), for adsorption were estimated using following equations [30] and are listed in Table 3. The values of k_3 were taken from Table 1.

$$\Delta G = -RT \ln K_s \quad (6)$$

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\ln K_s = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

The numerical values of activation energy, Gibbs free energy and the entropy for adsorption of hemimellitic and trimellitic acids onto α -alumina surface are roughly comparable and suggest that the adsorption of both the acids onto α -alumina is spontaneous. The activation energy of the present systems in contrast to reported values [13] is much smaller, less than 21 kJ mol^{-1} [31], which indicates that the adsorption is primarily controlled by film-diffusion process. The enthalpy values (Table 3) indicate that the adsorption process is endothermic for hemimellitic and

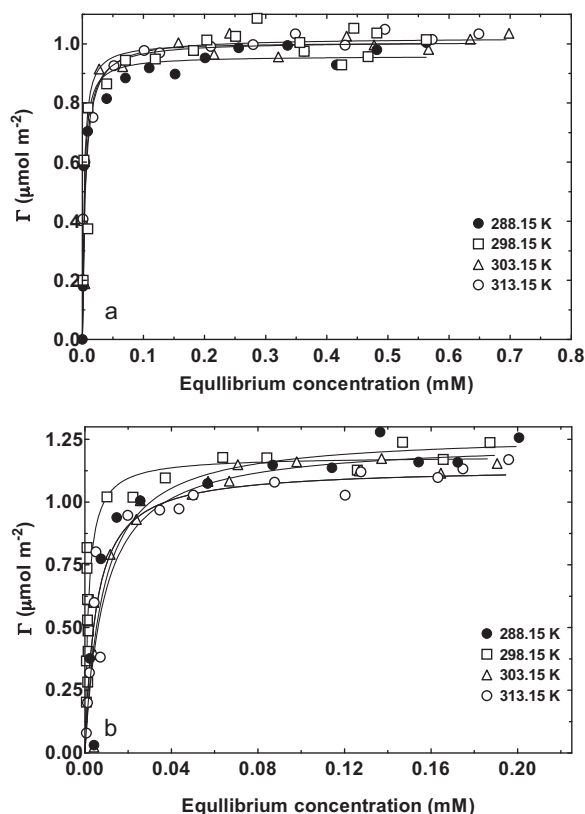


Fig. 5. Adsorption isotherms of (a) trimellitic (b) hemimellitic acid onto the α -alumina surfaces at different temperatures: α -alumina = 0.5 g, NaCl(aq) = 0.05 mM, $V = 15$ mL, pH 5. The reproducibility of data is $\pm 5\%$. The symbols are the experimental data and the lines are calculated from Eq. (3).

exothermic for trimellitic acids. The Gibbs free energy for adsorption indicates that the adsorption process for both the systems is spontaneous.

It is interesting to note that trimesic and mellitic acids with their symmetric molecular morphology and the benzenedicarboxylic

acid have the tendency to form self-assembly at the solid–liquid interface [32–35]. Referring to Fig. 2 and very small value of the activation energy ($-36.6 \text{ kJ mol}^{-1}$) of trimesic acid [25] we comment that in addition to adsorption there is a possibility of occurrence of self-assembly of trimesic acids as the carboxylic group is a well-know component for supra-molecule synthesis [36]. If trimesic acid is self-assembled onto α -alumina surface then the surface coverage will be much higher than the surface complexation through $-\text{COO}^-$ onto α -alumina surfaces resulting in lower adsorption density in comparison to hemimellitic and trimellitic acids. Therefore, to understand the adsorption isotherms of a planer and symmetric aromatic organic acids onto an adsorbent, the scanning tunnelling microscopy would be good choice and could evoke explainable molecular architecture and surface complexation onto an adsorbent surface.

4. DRIFT spectroscopy

4.1. Trimellitic acid/ α -alumina system

The characteristics peak frequencies of sodium salt of trimellitic and trimellitic acids adsorbed on α -alumina at different pH are given in Table 4 and in Fig. 6. The peak values are almost good agreement with literature [13,37]. The peak at 1383 and 1573 cm^{-1} corresponds to the symmetric and asymmetric vibration of COO^- of salt of trimellitic acid respectively. The peak at $1283\text{--}1292 \text{ cm}^{-1}$ corresponds to bending vibration of $>\text{C}\text{--}\text{OH}$ stretching and the peak involved at $1486\text{--}1497 \text{ cm}^{-1}$ corresponds to $\text{C}=\text{C}$ ring vibration with low intensity. The peak at 1573 cm^{-1} due to $\nu_{\text{as}}(-\text{COO}^-)$ shifted to higher frequency $\sim 2\text{--}17 \text{ cm}^{-1}$ after adsorption onto α -alumina surface and the peak at 1383 cm^{-1} due to $\nu_{\text{s}}(-\text{COO}^-)$ shifted to lower frequency $\sim 2\text{--}14 \text{ cm}^{-1}$ after adsorption. The peak $\nu_{\text{s}}(-\text{COO}^-)$ disappears at pH 9 and 10. The peak 1131 cm^{-1} assigned for $\delta(\text{C}\text{--}\text{H})$ vibration, shifted to $1104\text{--}1110 \text{ cm}^{-1}$ after adsorption [38,39]. From the shifting of $\nu_{\text{s}}(-\text{COO}^-)$ and $\nu_{\text{as}}(-\text{COO}^-)$ it concludes that hemimellitic acid forms outer-sphere complex with α -alumina surface and similar surface complexation is reported in literature [13].

Table 3

Values of the thermodynamic parameters for adsorption of hemimellitic and trimellitic acids onto α -alumina at pH 5 and different temperatures.

Temperature (K)	E (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS ($\text{kJ mol}^{-1} \text{ K}^{-1}$)
Hemimellitic acid				
288.15	1.1	4.39	-11.5	0.06
298.15			-16.0	0.07
303.15			-11.9	0.05
313.15			-13.7	0.06
Trimellitic acid				
288.15	0.86	-0.69	-14.1	0.05
298.15			-13.5	0.04
303.15			-13.3	0.04
313.15			-15.4	0.05

Table 4

Characteristic peak frequencies of trimellitic acid salt and acid adsorbed on α -alumina at pH 5–10.

Mode	ν (cm^{-1})								
	Trimellitic acid	Trimellitic acid salt	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10	
$\nu_{\text{s}}(-\text{COO}^-)$		1383	1376	1376	1375	1377	1381	1369	
$\nu_{\text{as}}(-\text{COO}^-)$		1573	1576	1578	1575	1577	1580	1590	
$\delta_{\text{C}\text{--}\text{O}}(>\text{C}\text{--}\text{OH})$	1294	1292	1286	1283	1286	1292	1292	1290	
$\nu_{\text{C}=\text{C}}(\text{ring})$	1502	1486	1491	1490	1491	1495	1497		
$\nu_{\text{C}\text{--}\text{C}}(\text{ring})$	1617		1619	1624	1623	1625	1627	1632	
$\nu_{\text{C}=\text{O}}$	1699								
$\delta(\text{C}\text{--}\text{H})$ and ring hydrogen vibration	1071, 1130	1069, 1131	1063, 1107	1062, 1110	1064, 1104	1065, 1108	1065, 1113	1067, 1108	

Table 5
Characteristic peak frequencies of hemimellitic acid adsorbed on α -alumina at pH 5–10.

Mode	ν (cm^{-1})							
	Hemimellitic acid	Hemimellitic acid salt	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
$\nu_s(-\text{COO}^-)$		1389	1379	1379	1378	1383	1389	1386
$\nu_{as}(-\text{COO}^-)$		1585	1573	1571	1570	1575	1572	1571
$\delta_{C-O}(>C-OH)$	1292	1284	1286	1286	1285	1287	1286	1268
$\nu_{C=C}(\text{ring})$	1463	1460	1461	1460	1457	1457	1455	
$\nu_{C-C}(\text{ring})$		1616	1616	1625	1631	1638	1638	1638
$\nu_{C=O}$	1702							
$\delta(C-H)$ and ring hydrogen vibration	1069, 1128	1062	1068, 1108	1067, 1112	1066, 1129	1063, 1102	1060, 1108	1060, 1113

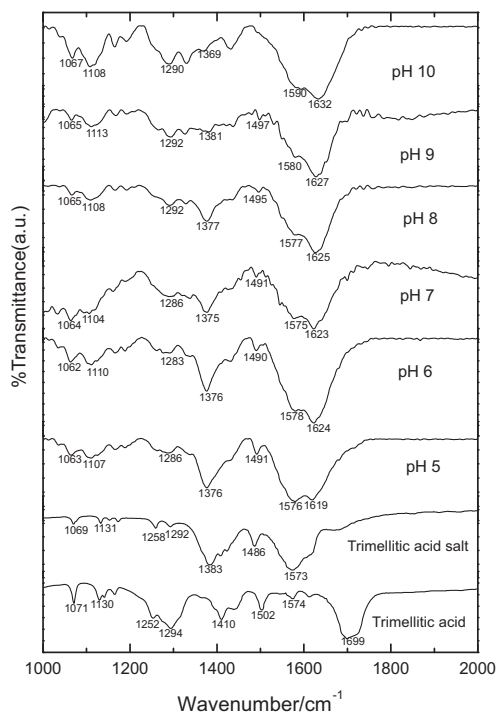


Fig. 6. DRIFT spectra of trimellitic acid adsorbed on α -alumina at pH 5–10: α -alumina = 0.5 g, trimellitic acid = 1 mM, NaCl(aq) = 0.05 mM.

4.2. Hemimellitic acid/ α -alumina system

The characteristic peak of hemimellitic acid and its adsorption onto α -alumina surface at pH 5–10 are shown in Table 5 and Fig. 7. The peaks are good agreement with literature [13]. The peak at 1585 and 1389 cm^{-1} could be attributed to the asymmetric and symmetric stretching vibration of carboxylate group, $\nu_{as}(-\text{COO}^-)$ and $\nu_s(-\text{COO}^-)$ respectively. The peak at 1702 cm^{-1} assigned for $\nu_{C=O}$ of hemimellitic acid. The bands at 1455–1461 cm^{-1} were assigned to stretching vibration of the ring C=C and the peak at 1268–1286 cm^{-1} were assigned to C–OH bending modes of hemimellitic acid after adsorption onto α -alumina surface at pH 5–8, but this peaks disappears at pH 9 and 10. The peak at 1385 cm^{-1} due to $\nu_s(-\text{COO}^-)$ of hemimellitate shifted towards lower frequency by ~ 5 –8 cm^{-1} and the intensity of this peak become decreases at pH 9 and 10. The peak at 1585 cm^{-1} due to $\nu_{as}(-\text{COO}^-)$ shifted towards lower frequency of ~ 10 –15 cm^{-1} . The peak intensity of $\nu_s(-\text{COO}^-)$ become decreases with increase in pH. The peak $\nu_s(-\text{COO}^-)$ become broadens after adsorption in the range of pH 5–8. For inner-sphere surface complexation the peak $\nu_s(-\text{COO}^-)$ should be >40 cm^{-1} [40]. Further, no Al^{3+} was detected in the filtrate by Atomic Adsorption Spectrophotometer. So, depending on the shifting of $\nu_s(-\text{COO}^-)$ it confirms that

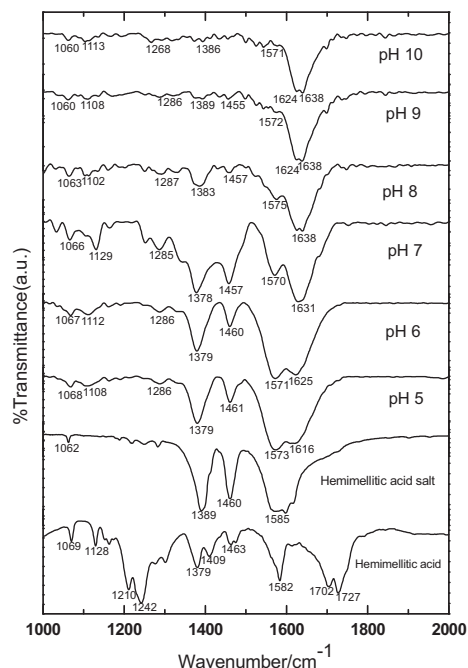


Fig. 7. DRIFT spectra of hemimellitic acid adsorbed on α -alumina: α -alumina = 0.5 g, hemimellitic acid = 1 mM, NaCl(aq) = 0.05 mM.

hemimellitic acid forms outer-sphere complexes with alumina surface and same type of surface complexation is reported in literature [13].

5. Conclusion

The adsorption kinetics and isotherms of hemimellitic acid and trimellitic acids were compared with reported data of benzenemono-, di-, and tricarboxylic acids and mono- and dihydroxybenzoic acids. The magnitude of the adsorption densities of aromatic acids with different functionalities is highly dependent on the number of functional groups and their position in the benzene ring. Specific to adsorption equilibration time, higher the number of same type of functional groups and when they are adjacent in the benzene ring yields lower equilibration time. In the case of benzenemono-, di-, and tricarboxylic acids and in benzenetricarboxylic acids with carboxylic groups adjacent to each other the magnitude of adsorption density depends on the number of functional groups. In contrast to benzenetricarboxylic acids, the corresponding DHBA produce higher adsorption density, the reason is the presence of phenolic –OH groups in the benzene ring. Nevertheless, the results indicate that the phenolic –OH groups in DHBA at any position in the benzene ring rather than the –COOH groups produce higher adsorption densities, the exception is the 2,4-DHBA amongst the DHBA series, where the phenolic–OH

groups at *ortho* and *para* positions are the most important for maximum adsorption density in contrast to adjacent –OH groups (e.g., 2,3-DHBA) as reported by Guan et al. [14]. In monohydroxybenzoic acids the phenolic –OH group at *ortho* position yields higher adsorption density. For benzenepolycarboxylic acids with symmetric structure, like trimesic and mellitic acids in addition to adsorption there may be self-assembly. In that case adsorption isotherms of a simple aromatic organic acid onto an adsorbent in conjunction with the scanning tunnelling microscopy would evoke reasonable explanation to the molecular architecture with additional information. The magnitude of shifting of $\nu_s(-COO^-)$ and $\nu_{as}(-COO^-)$ after adsorption of trimellitic and hemimellitic acids onto α -alumina surface indicate that both acids forms outer-sphere surface complexes.

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