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# Adsorption and surface complexation of trimesic acid at the $\alpha$ -alumina–electrolyte interface

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## Abstract

Adsorption kinetics, adsorption isotherms and surface complexation of trimesic acid onto  $\alpha$ -alumina surfaces were investigated. Adsorption kinetics of trimesic acid with an initial concentration of 0.5 mM onto  $\alpha$ -alumina surfaces were carried out in batch method in presence of 0.05 mM NaCl<sub>(aq)</sub> at pH 6 and 298.15, 303.15 and 313.15 K. Adsorption isotherms were carried out at 298.15 K, pH 5–9, and 0.05 mM NaCl<sub>(aq)</sub> by varying trimesic acid concentration from 0.01 to 0.6 mM. Three kinetics equations such as pseudo-first-order, pseudo-second-order and Ho equations were used to estimate the kinetics parameters of the adsorption of trimesic acid on the  $\alpha$ -alumina surfaces. Ho equation fits the experimental kinetics data significantly better and the estimated equilibrium concentration is in excellent agreement with the experimental value. The adsorption data were fitted to Freundlich and Langmuir adsorption model and the later best fits the adsorption isotherms. Comparison of adsorption density of trimesic acid with that of benzoic and phthalic acids follows the sequence: benzoic acid < trimesic acid < phthalic acid. The negative activation energy and the Gibbs free energy for adsorption indicate that the adsorption of trimesic acid onto  $\alpha$ -alumina is spontaneous and facile. DRIFT spectroscopic studies reveal that trimesate forms outer-sphere complexes with the surface hydroxyl groups that are generated onto  $\alpha$ -alumina surfaces in the pH range of the study.

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**Keywords:** Adsorption;  $\alpha$ -Alumina; Kinetics; DRIFT; Trimesic acid; Surface complexation

## 1. Introduction

The adsorption of surface-active agents on the metal-oxide or oxy(hydroxide) surfaces has great importance in mineral processing industries, soil remediation, wetting, and dispersion stability [1–3]. Adsorption of simple and well defined benzene carboxylic acids with varying number and position of carboxylic and phenolic groups, mimicking the humic and fulvic acids, on iron and aluminum oxides has reported in the literature [4–6]. Modeling of the adsorption profile of these organic acids showed that the percentage of adsorption increases with the increase of number of carboxylic and phenolic groups taking benzene monocarboxylic acid (i.e., benzoic acid) as the base value. Comparison of adsorption behavior of benzene tricarboxylic acids, namely benzene-1,2,3-tricarboxylic (hemimellitic), benzene-1,2,4-tricarboxylic (trimellitic) and benzene-

1,3,5-tricarboxylic (trimesic) acids, showed that the former two have roughly equivalent and higher adsorption profile than the later [5].

In case of benzene carboxylic acids the adsorption profiles demonstrated that the percentage of adsorption of these acids increases gradually as the number of additional carboxylic group increases in addition to two adjacent carboxylic groups till all the positions in the benzene ring is occupied. For higher adsorption density of benzene carboxylic acids the presence of adjacent carboxylic groups is more important than the number of carboxylic groups as in the case of benzene-1,3,5-tricarboxylic (trimesic) acid.

Adsorption kinetics and detailed adsorption profiles of trimesic acid, to the best of our knowledge, are rare in the literature [4,5,7]. Very recently ‘adsorption-induced self organization’ of trimesic acid on Au (100) and graphite surfaces has been reported [8,9].

The surface charge vis-à-vis the zeta potentials of an adsorbent greatly influence the adsorption profile of an adsorbent as

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functions of pH. For example,  $\alpha$ -alumina, in the present system, has an isoelectric point of 6.7 [10], means the zeta potential of  $\alpha$ -alumina is positive below pH 6.7 and above it is negative. Therefore, the adsorption density of benzene carboxylic acid is expected to decrease with the increase in pH of the medium and salicylate-, benzoate- and phthalate- $\alpha$ -alumina systems showed decrease in adsorption density with increase in pH [10,11].

The complexation of carboxylic acids at the metal-oxide and (oxy)hydroxide-water interface has attracted much attention in geochemical literature due to the importance in fluid-rock system [12]. The extent of adsorption of small aromatic acid onto metal-oxide surfaces and the possible surface complexation through -COOH and -OH groups depend on the functionality and polydispersibility of an acid [13]. Benzoate forms outer-sphere complexes and phthalate forms both inner- and outer-sphere complexes with  $\alpha$ -alumina surfaces depending on the pH of the medium [10]. Salicylate forms inner-sphere complexes at  $\alpha$ -alumina-water interfaces in presence of both mono- and divalent anions of background electrolytes [14,15].

In this paper our main aim is to study the adsorption kinetics, adsorption isotherms and influence of  $\text{NaCl}_{(\text{aq})}$  on the adsorption of trimesic acid at the alumina-electrolyte interface and compare the adsorption profile with benzoic and phthalic acids. As expected the adsorption density of trimesic acid at the  $\alpha$ -alumina-electrolyte interface would be less than that of phthalic acid but more than benzoic acid since none of the carboxylic groups are adjacent in the trimesic acid. We have also studied the possible surface complexation of trimesic acid onto  $\alpha$ -alumina surface.

## 2. Materials and methods

### 2.1. Materials

$\alpha$ -Alumina (>99%, Aldrich, Germany) was washed twice with double-distilled water, dried and finally reactivated at  $\sim 700^\circ\text{C}$  for 3 h. Trimesic acid (>99%, Lancaster, UK), 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 trimesic acid onto  $\alpha$ -alumina (0.5 g) in a 15 mL suspension were performed at pH 6 and three temperatures in batch method. The concentration of trimesic acid and  $\text{NaCl}_{(\text{aq})}$  was 0.5 and 0.05 mM, respectively. The suspension was filtered through a membrane of 0.2  $\mu\text{m}$  pore size at different intervals of time. The residual concentration of trimesic acid was estimated at absorption maxima,  $\lambda_{\text{max}} = 282\text{ nm}$  using UV-visible spectrophotometer (Specord 200, Analytik Zena, Germany). The absorption maximum of a very dilute solution of trimesic acid having pH 2.94 was found at 282 nm. For estimating the concentration of trimesic acid in a supernatant liquid, the pH of the supernatant liquid was adjusted at pH 2.94 with dilute HCl solution and the concentration corresponding to

optical density at  $\lambda_{\text{max}} = 282\text{ nm}$  was calculated after accounting the dilution factor. The adsorption density of trimesic acid (amount adsorbed per unit surface area),  $\Gamma$ , was estimated by mass balance equation

$$\Gamma = (C_0 - C_t)V/ma, \quad (1)$$

where,  $C_0$  is the initial concentration and  $C_t$  is the residual concentration at time,  $t$ , of trimesic acid in the supernatant liquid in  $\text{mmol dm}^{-3}$ ,  $V$  is the volume of the suspension and  $m$  is the mass, respectively. The specific surface area,  $a$ , of  $\alpha$ -alumina was determined by BET method and was found to be  $7.29\text{ m}^2/\text{g}$ .

### 2.3. Adsorption isotherms

Adsorption of trimesic acid onto  $\alpha$ -alumina was carried out at 298.15, 303.15 and 313.15 K in a screw-capped glass tube in batch method. A suspension of 15 mL containing 0.5 g  $\alpha$ -alumina and 0.05 mM  $\text{NaCl}_{(\text{aq})}$  solution was mixed thoroughly with the help of a vortex mixer. The pH of the suspension was adjusted to a desired value within  $\pm 0.1$  unit using either dilute NaOH or HCl solution and then allowed to equilibrate for 1 h. The required amount of trimesic acid was added and the pH of the suspension was readjusted, if necessary. The initial concentration of trimesic acid was varied from 0.01 to 0.6 mM. The suspension was then allowed to equilibrate for 2 h with intermittent mixing. After the reaction period, the suspension was then filtered through a membrane of 0.2  $\mu\text{m}$  pore size and residual concentration was estimated as indicated in the previous section.

### 2.4. DRIFT spectroscopy

For DRIFT spectroscopic studies 0.5 g  $\alpha$ -alumina was equilibrated for 2 h with 0.5 mM trimesic acid in presence of 0.05 mM  $\text{NaCl}_{(\text{aq})}$  at different pH 5–9 and 298.15 K. The suspension was centrifuged at 12,500 rpm for 15 min and the residue was once washed with double-distilled water and dried under vacuum over fused calcium chloride. The DRIFT spectra with a resolution of  $4\text{ cm}^{-1}$  were recorded with 200 scanning using DRIFT attachment (Part No. L127-5001, Perkin-Elmer) with a Perkin-Elmer FTIR spectrophotometer-2000 and KBr as the background.

## 3. Results and discussion

### 3.1. Adsorption kinetics

The amount of trimesic acid adsorbed per unit surface area of  $\alpha$ -alumina as function of time at three temperatures is shown in Fig. 1. It is apparent from the plots that the state of equilibration is attained in 2 h within the temperature range. Comparison of adsorption kinetics of benzoate and phthalate at 298.15 K [10] with trimesic acid for the same adsorbent showed that the adsorption density varies in the sequence: benzoic acid < trimesic acid < phthalic acid. It implies that the increase of number

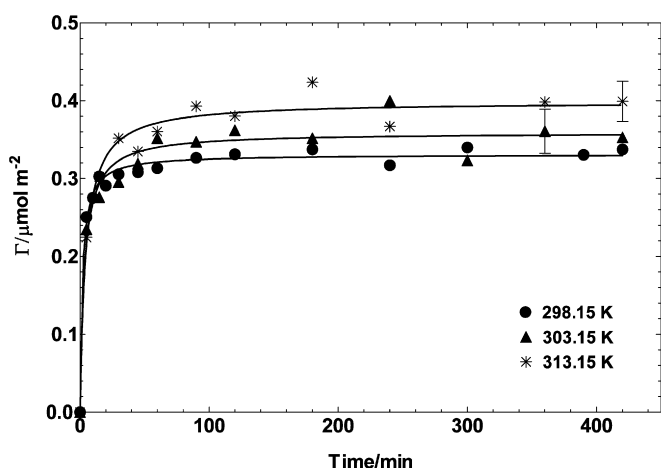


Fig. 1. Effect of temperature on the adsorption of trimesic acid on the  $\alpha$ -alumina surfaces at a fixed initial concentration of trimesic acid:  $C_0 = 0.5$  mM,  $\alpha$ -alumina = 0.5 g,  $\text{NaCl}_{(\text{aq})} = 0.05$  mM,  $V = 15$  mL, and pH 6. The data points represent triplicate adsorption experiments.

of carboxylic group in the benzene ring enhances the adsorption density [5], but the magnitude of the adsorption density is higher when the two carboxylic groups are adjacent to each other, as in the case of phthalic acid [10]. Nevertheless, the equilibration time at 298.15 K follows the sequence: trimesic acid < phthalic acid < benzoic acid. The lower equilibration time for trimesic acid– $\alpha$ -alumina system is accounted for the presence of higher number of carboxylic groups in the benzene ring. To proof this observation we need adsorption kinetics of a series of benzene carboxylic acids with increasing number of carboxylic groups in the benzene ring [5] and are being carried out.

The pseudo-first-order kinetics 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 trimesic acid at the state of equilibrium and time,  $t$ , respectively and  $k_1$  is the rate constant, reproduces the value of  $q_e$  with large deviation (up to ~90%), which was also encountered for many systems and the reasons for such deviations are discussed by many authors [15–21]. Regarding the pseudo-second-order kinetics equation of linear form,  $t/q_t = 1/k_2 q_e^2 + t/q_e$ , where  $k_2$  is the rate constant, many authors have raised question on its applicability for the associated statistical errors [19,20]. Both these kinetics equations of linear form are applicable to kinetics data till the system approaches the equilibration. In contrast, the nonlinear form of the pseudo-second-order kinetics equation is applicable in equilibration region also. One such kinetics equation is the Ho equation [20]

$$q_t = q_e^2 k_3 t / (k_3 q_e t + 1), \quad (2)$$

where  $k_3$  is the rate constant and all the statistical errors associated with the linear form of pseudo-second-order kinetics equation are minimized in nonlinear form.

The values of the  $k_i$  and  $q_e$  parameters for all the three kinetics equations are presented in Table 1. The pseudo-first-order and pseudo-second-order kinetics equations of linear form reproduce the  $q_e$  values with higher percentage of deviation (~2–71%, Table 1). On the other hand, the Ho equation fits the

Table 1

Values of rate constants and equilibrium concentrations for trimesic acid– $\alpha$ -alumina system at pH 6

Trimesic acid	Parameters	298.15 K	303.15 K	313.15 K
Pseudo-first-order kinetics	$k_1$ ( $\text{min}^{-1}$ )	0.0417	0.0298	0.0385
	$q_e$ ( $\mu\text{mol m}^{-2}$ ) (estimated)	0.0949	0.1386	0.1653
	S.D.	0.2070	0.1744	0.1858
Pseudo-second-order kinetics	$k_2$ ( $\text{min}^{-1} \text{mol}^{-1} \text{dm}^3$ )	1.1365	0.4794	0.4965
	$q_e$ ( $\mu\text{mol m}^{-2}$ ) (estimated)	0.3355	0.3744	0.3992
	S.D.	0.0129	0.0242	0.0154
Ho equation	$k_3$ ( $\text{m}^2/\mu\text{mol min}$ )	1.6660	0.8315	0.5789
	$q_e$ ( $\mu\text{mol m}^{-2}$ ) (estimated)	0.3309	0.3590	0.3984
	S.D.	0.0085	0.0228	0.0203
Experimental	$q_e$ ( $\mu\text{mol m}^{-2}$ )	0.3280	0.3566	0.3816

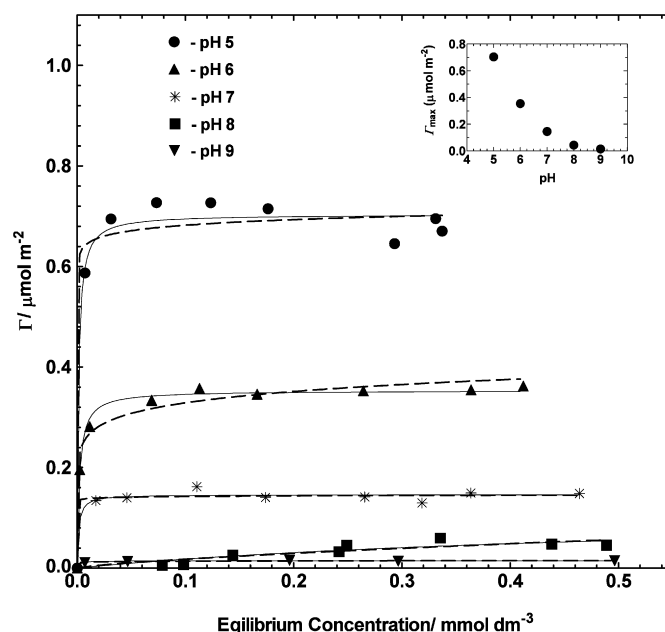


Fig. 2. Adsorption isotherms of trimesic acid onto  $\alpha$ -alumina at different pH, fixed concentration of  $\text{NaCl}_{(\text{aq})} = 0.05$  mM,  $\alpha$ -alumina = 0.5 g,  $V = 15$  mL and at 298.15 K. In the inset  $\Gamma_{\text{max}}$  versus pH is shown. The data points represent triplicate adsorption experiments. The broken lines indicate the Freundlich isotherms (Eq. (3)) and continuous lines indicate Langmuir isotherms (Eq. (4)), respectively.

experimental kinetics data significantly better, as indicated by the standard deviation (Table 1), in the entire time duration than the pseudo-second-order kinetics equation of linear form. The estimated values of  $q_e$  by using Ho equation are in excellent agreement with the corresponding experimental values (Table 1).

### 3.2. Adsorption isotherm

The variation of the adsorption density of trimesic acid with different initial concentrations (0.01 to 0.6 mM) onto the  $\alpha$ -alumina at different pH, 0.05 mM  $\text{NaCl}_{(\text{aq})}$ , and 298.15 K is depicted in Fig. 2. The adsorption isotherms for trimesic acid on the  $\alpha$ -alumina surfaces at three different temperatures and pH 6

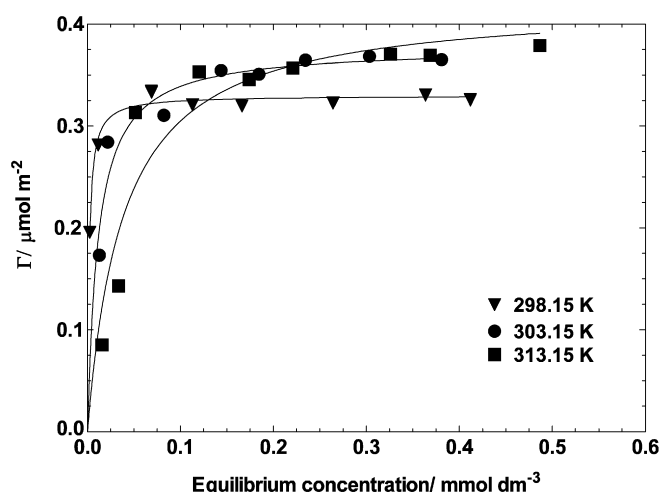


Fig. 3. Adsorption isotherm of trimesic acid onto the  $\alpha$ -alumina surfaces at 298.15 K (inverted triangles), 303.15 K (circles), and 313.15 K (squares).  $\alpha$ -alumina = 0.5 g,  $\text{NaCl}_{(\text{aq})}$  = 0.05 mM,  $V$  = 15 mL, pH 6.

Table 2

Values of the parameter of Freundlich and Langmuir models (Eqs. (3) and (4)) as a function of pH for adsorption of trimesic acid on  $\alpha$ -alumina

pH	Freundlich model			Langmuir model		
	$K_f$	$n$	S.D.	$\Gamma_{\text{max}}$ ( $\mu\text{mol m}^{-2}$ )	$K_s$	S.D.
5	0.7196	0.0233	0.0424	0.7035	777.0	0.0339
6	0.4098	0.0956	0.0197	0.3530	464.9	0.0106
7	0.1467	0.0126	0.0106	0.1456	792.4	0.0102
8	0.0939	0.7219	0.0111	0.0436	70.9	0.0091
9	0.0158	0.0573	0.0009	0.0147	478.5	0.0008

for estimation of thermodynamic parameters are also shown in Fig. 3. The adsorption densities were fitted to both Freundlich and Langmuir equations of the following forms:

$$\Gamma = K_f C_e^n, \quad (3)$$

$$\Gamma = \Gamma_{\text{max}} C_e / (K + C_e), \quad (4)$$

where  $K_f$  is the adsorption capacity,  $n$  the adsorption intensity,  $C_e$  is the equilibrium concentration of trimesic acid,  $K = 1/K_s$ ,  $K_s$  is the adsorption coefficient, and  $\Gamma$  and  $\Gamma_{\text{max}}$  are the adsorption density of trimesic acid in  $\mu\text{mol m}^{-2}$  at equilibrium and after saturation of  $\alpha$ -alumina surfaces, respectively. The values of the parameters of Eqs. (3) and (4) are presented in Table 2. Close look on the adsorption isotherms (Fig. 2) and the standard deviations (Table 2) suggest that the theoretical lines of the Freundlich isotherm equation (Eq. (3)) are little away from the plateau region. On the other hand, the theoretical lines of the Langmuir equation (Eq. (4)) are showing the near perfect plateau region envisaging monolayer adsorption and provides theoretical equilibration concentration, which Freundlich model fails to do. The standard deviations for the Langmuir adsorption model, at all pH, are less than that of Freundlich model. Nevertheless, Kumar et al. [22] have fitted the adsorption data to different adsorption isotherm models including Freundlich and Langmuir. Their results showed that only the Langmuir adsorption isotherm model is applicable to an adsorbate/adsorbent

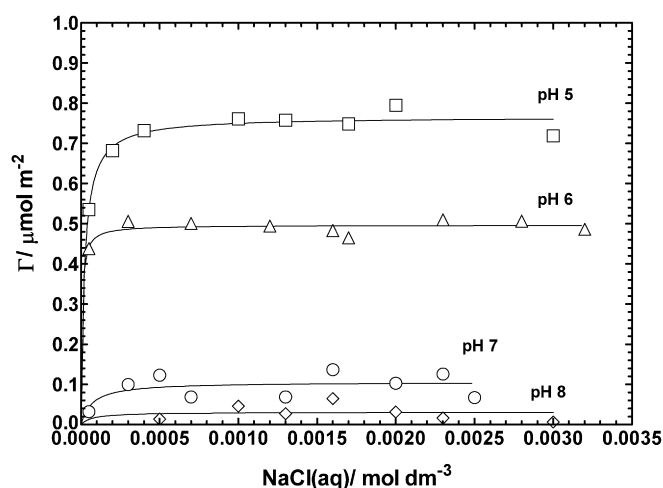


Fig. 4. Variation of adsorption density of trimesic acid on  $\alpha$ -alumina with  $\text{NaCl}_{(\text{aq})}$  concentration at different pH values and at 298.15 K,  $C_0$  = 0.5 mM,  $\alpha$ -alumina = 0.5 g,  $V$  = 15 mL.

system where a perfect plateau is reached (i.e., an equilibration with monolayer adsorption). Nevertheless, Freundlich isotherm model suggest about the heterogeneous surface of  $\alpha$ -alumina and good adsorption affinity for trimesic acid but the adsorption equilibration is not attained. In contrast, the adsorptions of the present system attain equilibration and exhibit a plateau. So, the adsorption isotherms for trimesic acid– $\alpha$ -alumina are Langmuirian in nature.

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 vis-à-vis the zeta potential of an adsorbent and a good correlation was observed between adsorption density and zeta potential [10,11] and it is again, a similar trend is observed in the case of trimesic acid– $\alpha$ -alumina system. The adsorption density of trimesic acid decreases sharply from pH 5 to 7 and beyond it is roughly gradual (Fig. 2 inset) and is due to the reversal of surface charge of  $\alpha$ -alumina before and after the isoelectric point. From the adsorption isotherms (Fig. 2) it is clear that adsorption density increases with the increase of trimesic acid concentration within the pH range of study and after certain trimesic acid initial concentration ( $\sim 0.15 \text{ mmol dm}^{-3}$ ) the plateau is attained. The comparison of the adsorption density of benzoate and phthalate on the  $\alpha$ -alumina surfaces at pH 6 [10] with that of trimesic acid reveals that benzoate has lower ( $\sim 1.2$  times) and phthalate has higher ( $\sim 5.1$  times) adsorption density and follows the sequence: benzoic acid < trimesic acid < phthalic acid. The higher adsorption density for the later is not only due to the number of carboxylic groups but also due to the presence of the adjacent carboxylic group in the benzene ring [5,10].

### 3.3. Variation of $\text{NaCl}_{(\text{aq})}$ concentration

The adsorption density of trimesic acid onto  $\alpha$ -alumina at 298.15 K with the increase of background electrolyte,  $\text{NaCl}_{(\text{aq})}$ , from 0.05 to 3.0 mM at different pH 5–8 and at a fixed concentration of trimesic acid, 0.5 mM, is shown in Fig. 4. It is interesting to note that the adsorption density of trimesic acid sharply



Table 3

Values of the thermodynamic parameters for adsorption of trimesic acid on  $\alpha$ -alumina at pH 6 and different temperatures

Temperature (K)	$E$ (kJ mol <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )
298.15			-15.8	459.2
303.15	-36.6	-152.8	-11.3	466.7
313.15			-8.5	460.7

increases with the increase of NaCl<sub>(aq)</sub> at pH 5 and 6 and the increase is gradual at pH 7 and 8. The plateau in the adsorption density is reached after  $\sim 0.05$  mM NaCl<sub>(aq)</sub> in the pH range of the study. A similar trend was observed in the case of phthalate- $\alpha$ -alumina system [10]. But for benzoate- $\alpha$ -alumina system no adsorption density was detected beyond isoelectric point (pH 6.7) of  $\alpha$ -alumina [10]. There is no influence of NaCl<sub>(aq)</sub> concentration on adsorption density at pH 8. The results imply that NaCl<sub>(aq)</sub> has no influence on the adsorption density of trimesic acid roughly beyond 0.05 mM NaCl<sub>(aq)</sub> in the pH range of the study. The decrease of maximum adsorption density of trimesic acid with the increase in pH (Fig. 4) of the suspension is due to the fact that the positive surface charge of  $\alpha$ -alumina decreases. The distribution of Cl<sup>-</sup> near the surface of  $\alpha$ -alumina is also increased resulting in decrease in double layer thickness [21]. The notable adsorption density of trimesic acid, in the present study, and phthalate on  $\alpha$ -alumina surfaces beyond isoelectric point (pH 6.7) and in comparison to benzoate- $\alpha$ -alumina system [10] is likely governed by the additional carboxylic groups in the benzene ring.

### 3.4. Thermodynamic parameters

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  $T$  temperature in Kelvin and the estimated values of thermodynamic parameters are presented in Table 3. The negative values of  $E$  and  $\Delta G$  indicate that the adsorption of trimesic acid onto  $\alpha$ -alumina is spontaneous and more facile. A similar negative activation energy for adsorption of Pb(II) on china clay and wollastonite with negative values of enthalpy change has also been reported [23]. The probable explanation for the negative activation energy in the present system, which is not encountered for normal kinetics, is due to the available thermal energies ( $\Delta H = -152.8$  kJ mol<sup>-1</sup>) to overcome the energy barrier. Comparison of the thermodynamic properties for benzoate and phthalate adsorption onto  $\alpha$ -alumina [10] with that of trimesic acid- $\alpha$ -alumina system, we can conclude that the numbers of carboxylic groups in the benzene ring facilitate the adsorption process. Further kinetics and adsorption studies of benzene polycarboxylic acids (e.g., hemimellitic, trimellitic, pyromellitic and mellitic acids) onto  $\alpha$ -alumina, which are being studied, will certainly support our conclusion and nevertheless, with the results in hand the sequence of spontaneity of adsorption follows: benzoate < phthalate < trimesate, which also conforms from the equilibration time (Fig. 1 and Section 3.1).

Table 4

Characteristics peak frequencies of trimesate and trimesic acid after adsorption on  $\alpha$ -alumina surface at different pH

Mode	$\nu$ (cm <sup>-1</sup> )					
	Trimesate	pH 5	pH 6	pH 7	pH 8	pH 9
$\nu_s(-\text{COO}^-)$	1372	1367	1364	1358	1356	1350
$\nu_{as}(-\text{COO}^-)$	1572	1585	1583	1592	1595	1590
$\nu_{C-O}(>C-OH)$		1194	1194			
$\nu_{C-C}(\text{ring and } -\text{COO}^-)$	1436	1437	1435	1430	1432	1425
$\nu_{C-C}(\text{ring})$	1621	1618	1617			
$\nu_{C=O}(-\text{COO}^-)$		1702	1700			
$\delta(C-H)$ and ring hydrogen vibration	1112	1129	1120	1109	1114	1113

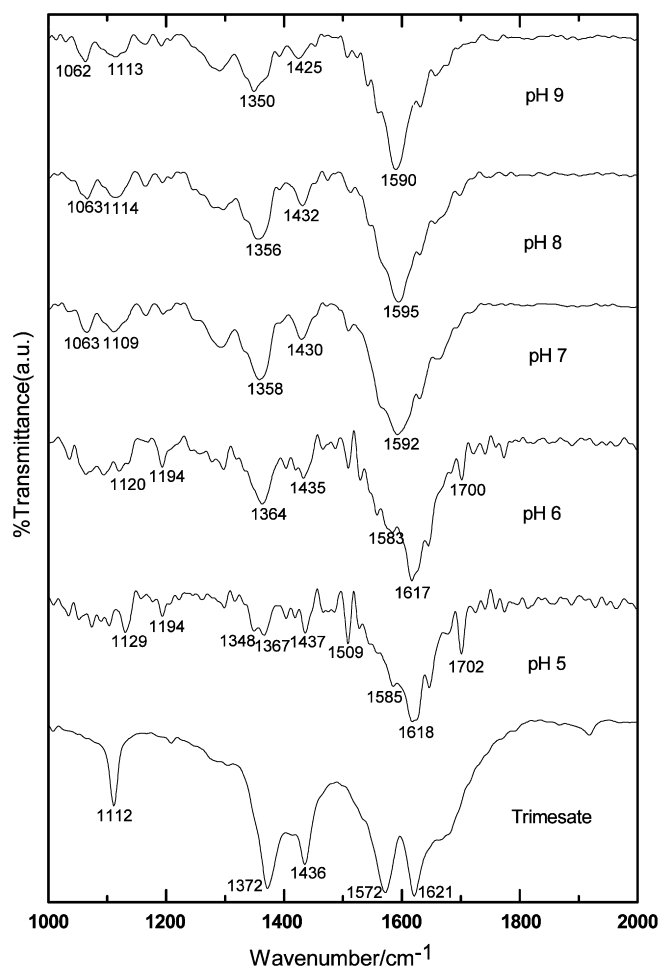


Fig. 5. DRIFT spectra of trimesate and trimesic acid after adsorption on the  $\alpha$ -alumina at pH 5–9 in presence of 0.05 mM NaCl<sub>(aq)</sub>,  $C_0 = 0.5$  mM and at 298.15 K.

### 3.5. DRIFT spectroscopy

The characteristics peaks of sodium salt of trimesic acid (i.e., trimesate) are given in Table 4 and shown in Fig. 5. The peak at 1112 cm<sup>-1</sup> is assigned for  $\delta(C-H)$  and the ring hydrogen vibration, which finally vanishes for benzene-hexacarboxylic (mellitic) acid due to complete substitution of benzene ring by  $-\text{COOH}$  group [24]. Unlike equivalent carboxylate groups, as in the case of phthalate [10], there is no multiple bands appeared

for  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  for trimesate. This may be due to the position of  $-\text{COO}^-$  in the benzene ring. As a result, a single peak for  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  is appeared at 1372 and 1572  $\text{cm}^{-1}$ , respectively. The peak at 1436  $\text{cm}^{-1}$  is assigned to  $\nu_{\text{C-C}}$  (ring and  $-\text{COO}^-$ ) and 1621  $\text{cm}^{-1}$  to  $\nu_{\text{C-C}}$  (ring). The band at  $\sim 1700 \text{ cm}^{-1}$  due to  $\nu_{\text{C=O}}$  is absent for trimesate, which indicates that trimesic acid is fully ionized. Comparison of the recent spectroscopic studies of trimesate and trimesate adsorbed onto aluminum hydroxide [7] and ours, we noted that the characteristic peaks appeared at lower frequency region in the former case. However, after adsorption of trimesic acid onto  $\alpha$ -alumina the peak due to  $\nu_{\text{C=O}}$  is appeared at  $\sim 1700 \text{ cm}^{-1}$  for pH 5 and 6 along with peaks for  $\nu_s(-\text{COO}^-)$  at 1367 and 1364  $\text{cm}^{-1}$  and  $\nu_{\text{as}}(-\text{COO}^-)$  at 1585 and 1583  $\text{cm}^{-1}$  with relatively low intensity, respectively. The intensity of the band due to  $\nu_{\text{C=O}}$  at  $\sim 1700 \text{ cm}^{-1}$  decreases with increasing pH and finally disappeared at pH 7 and above (Fig. 5). It implies that trimesic acid is not fully ionized at pH 5 and 6.

The mode of mixing between  $-\text{COO}^-$  and aromatic ring vibration is highly probable in case of aromatic polycarboxylic acids and the intramolecular vibration and the co-ordination affects the splitting and position of bands of  $-\text{COO}^-$  [17]. This situation is reflected for  $\nu_{\text{as}}(-\text{COO}^-)$  and  $\nu_{\text{C-C}}$  (ligand) at pH 7 and above (Fig. 5). The shifting of  $\nu_{\text{C-C}}$  (1621  $\text{cm}^{-1}$ ) of ligand towards low frequency region on adsorption is also due to the change of  $\pi$  electron density of trimesic acid.

For assigning of the surface complexation of trimesic acid onto  $\alpha$ -alumina surfaces the magnitude of  $\Delta\nu = \nu_{\text{as}} - \nu_s$  is not considered [10,25]. The peak at 1372  $\text{cm}^{-1}$  due to  $\nu_s(-\text{COO}^-)$  of trimesate shifted by  $\sim 5\text{--}22 \text{ cm}^{-1}$  with increasing pH towards low frequency region while the  $\nu_{\text{as}}(-\text{COO}^-)$  shifted by  $\sim 11\text{--}23 \text{ cm}^{-1}$  towards higher frequency region. On the contrary, the  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  for trimesic after adsorption onto aluminum hydroxide do not shift with respect to ligand at corresponding pH [7]. Nevertheless the peak for  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  on adsorption is relatively broadened in comparison to trimesate (Fig. 5). For the inner-sphere surface complexation of trimesic acid with  $\alpha$ -alumina surfaces, the shifting of  $\nu_s(-\text{COO}^-)$  should be  $>40 \text{ cm}^{-1}$  [26]. Within the pH range (5–9) the shifting of  $\nu_s(-\text{COO}^-)$  on adsorption of trimesate onto  $\alpha$ -alumina only  $\leq 22 \text{ cm}^{-1}$ . Therefore, the broadening and the magnitude of shifting of  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  indicate that trimesic acid chemisorbed onto  $\alpha$ -alumina and forms outer-sphere surface complexes with the surface hydroxyl groups that are generated onto  $\alpha$ -alumina surfaces [27] and similar surface complexation is also reported in the literature [7].

#### 4. Summary

The equilibration time for trimesic acid is low (2 h) in comparison to benzoate and phthalate. The presence of higher number of carboxylic groups in the benzene ring of an aromatic carboxylic acid lowers the equilibration time. Adsorption density depends on the number and the adjacent carboxylic groups

in the benzene ring. The Freundlich isotherm model suggests about the heterogeneous surface of  $\alpha$ -alumina and good adsorption affinity for trimesic acid but without equilibration concentration and the Langmuir isotherm model exhibits a plateau for monolayer adsorption. The negative values of activation energy and the Gibbs free energy reveal fast and facile adsorption for trimesic acid onto  $\alpha$ -alumina surfaces. The magnitude of shifting of  $\nu_s(-\text{COO}^-)$  and  $\nu_{\text{as}}(-\text{COO}^-)$  after adsorption of trimesic acid onto  $\alpha$ -alumina surfaces indicates that trimesate forms outer-sphere complexes with the surface hydroxyl groups that are produced onto  $\alpha$ -alumina surface at all pH range of the study.

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