Analysis of Effective Hygroscopic Growths, Kelvin Effects and Water Activities of Maritime Aerosols Using Volume Mix Ratio

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Abstract - *In this paper the effective hygroscopic growths of atmospheric aerosols and effective radii using microphysical properties of atmospheric aerosols are extracted from Optical Properties of Aerosols and Cloud (OPAC) at seven relative humidity (50%,70%,80%,90%,95%,98% and 99%).The microphysical properties extracted were radii of the individual aerosols and the volume mix ratios as functions of relative humidity (RH). The effective hygroscopic growths and effective radii were parameterized and the modified Kholer equation was used to determine water activities, kelvin effects and humidification factors. It was observed that the data fitted the models very well. The results shows that the growth factor and effective radii increases with increase in RH and are more pronounced at 90-99% RHs, the water activities is more dominant than the kelvin effect in all types of models.*

Key Words: Hygroscopic growths, Relative humidity, Kelvin Effect, Humidification factor, Water activity.

1. INTRODUCTION

Aerosols in the atmosphere comprised of numerous and diverse components originating from both natural and anthropogenic activities. The interactions between aerosols and water vapor play a vital role in determining their effect on the environment. The chemical and physical characteristics of aerosols are diverse and attempting to comprehend such variability within hygroscopic model is complex. Aerosol may exist in a solid or liquid form or combination of two over a wide range of ambient conditions in both sub and super saturated humid environment [1].

Chemical compositions of aerosol particles released from natural and anthropogenic sources are not homogeneous either locally or globally, hence characteristics such as hygroscopicity, Kelvin effect and water activity are significantly different from one particle to another, controlling the particle's ability to form cloud droplets and affect particles size [2]. The size dependence, which is due to the surface tension of the solution–air interface, is known as the Kelvin effect [3] is of central importance to cloud drop activation, and as the equilibrium radius is a key property of an atmospheric aerosol particle, affecting its light-scattering behavior, dry deposition, and Kelvin effect can also play an important role in other atmospheric processes [4].

The composition of a solution determines its water activity (a_w) and surface tension (σ_s) [4]. The equation that is often used to describe both hygroscopic growth of aerosol particles and their activation to cloud droplets is the Kohler equation. This equation is divided into two as: (1) the Kelvin effect; this is responsible for the increase in equilibrium water vapor pressure over a curved surface, and is directly proportional to the effective surface tension as a result of the solution–air interface. For an aqueous solution drop with given concentration, the equilibrium fractional relative humidity increases with decreasing drop radius; and (2) the Raoult effect; this is the reduction in water activity associated with solute dissolution in terms of either effective hygroscopic growth and/or the effective radius of the mixtures at given RHs [3]. Almost every property of atmospheric aerosols is a strong function of Relative Humidity [5]. The main parameter used to characterize the hygroscopicity of the aerosol particles is the aerosol hygroscopic growth factor gf (RH), which is defined as the ratio of the particle diameter at any RH to the particle diameter at RH = 0 % [6]. Studies performed by [7] considered volume, mass and number base ratios, and it was observed that the hygroscopic growths factors increases exponentially with relative humidity at various aerosols types such as Antarctic, arctic, continental, desert, maritime and urban and also found almost all aerosols deliquesces behavior at 99% relative humidity. The urban environment is mostly affected by transportation and heavy industry emissions. For atmospheric aerosols, the range of κ typically varies from as low as ~0.01 for some combustion aerosol particles up to ~1 for sea-salt particles [8].

Table -1: *Compositions of aerosol types [12]*

Model Numbers	Aerosols Models	Aerosols Components	Num Conc. (cm-3)	Rmin(um)	Rmax(um)	Sigma	Rmod(um)
Model 1	Maritime Clean	Waso	1,500.0000	0.0050	20.0000	2.2400	0.0212
		Ssam	20.0000	0.0050	20.0000	2.0300	0.2090
		Sscm	0.0032	0.0050	60.0000	2.0300	1.7500
Model 2	Maritime Polluted	Waso	3,800.0000	0.0050	20.0000	2.2400	0.0212
		Soot	5,180.0000	0.0050	20.0000	2.0000	0.0118
		Ssam	20.0000	0.0050	20.0000	2.0300	0.2090
		Sscm	0.0032	0.0050	60.0000	2.0300	1.7500
Model 3	Maritime Tropical	Waso	590.0000	0.0050	20.0000	2.2400	0.0212
		Ssam	10.0000	0.0050	20.0000	2.0300	0.2090
		Sscm	0.0013	0.0050	60.0000	2.0300	1.7500

[9] showed that HGF values of diesel generated soot particles ranged between 1.01 and 1.02. Furthermore, the spark generated soot particles tend to collapse when exposed to high humidity, thus exhibiting HGF values less than 1.

[7] reported that the overestimation due to Kelvin effect is higher for Antarctic and Maritime clean and the errors become more important at higher RH. But for Arctic, Urban and Continental clean, the error is very small, though it becomes higher as from the RHs of 95%, 98% and 99%. For Sahara, the underestimation is more important at higher RHs. From previous

studies the values of water activities in urban aerosols of some substances are saturated sodium chloride solution a_w = 0.97, distilled water a_w = 1.00, [10] typical air indoor a_w = 0.5-0.7 [11] and the highest measured water activity derived from growth factors is typically $a_w \approx 0.9$ [8] and also for kelvin effect k_{eff} =1 for pure water and k_{eff} = 1.15 for sodium chloride [4].

The aim of this paper is to determine the Kelvin effect, water activity and humidification factor, the quantities that depend on and their effect on effective radii and effective hygroscopic growth factor on ten types of atmospheric aerosols extracted from OPAC (table1) at seven relative humidity of 50%, 70%, 80%, 90%, 95%, 98% and 99%. The atmospheric aerosols extracted are Maritime Clean, Maritime pollutant, and Maritime tropical. The microphysical properties extracted are the individual aerosols radii and their volume mix ratios.

2. METHODOLOGY

From table 1.

Where: N_i is the volume concentration, Waso (water soluble), Inso (insoluble), Ssam (sea salt accumulation mode), Sscm (sea salt coagulation mode), Soot (soot, not soluble in water).

The aerosol's hygroscopic growth factor for single particle aerosol given by [6] and [13] modified for the effective growth of the atmosphere aerosol as

$$g_{eff}(s) = \left(\sum_k x_k\, g_k(s) \right)_{1/3} \qquad (1)$$

In this case the information on the hygroscopicity modes was merged into an "over-all" or "bulk" or "effective" hygroscopic growth factor of the mixture.

The effective radius of the mixture was determined using

$$r_{eff} \quad = \quad \left(\sum_k x_k \, r_k^3(s) \right)^{1/3} \tag{2}$$

where the summation is performed over all compounds present in the aerosols particles and x_k represents their respective volume fractions, using the Zdanovskii-Stokes-Robinson relation (ZSR) relation[14],[15].

The Kohler equation combines both Raoult and Kelvin effect.

$$S = k_{eff} a_w \tag{3}$$

It gives the relationship between equilibrium saturation ratio and the size of a solution droplet. In general, the saturation ratio, S, over an aqueous solution droplet can be calculated from [8]

$$S = a_w \, exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right) \tag{4}$$

Table -2: The results of effective hygroscopic growth and effective radii of maritime tropical using equations (1) and (2)

RH%	50	70	80	90	95	98	99
$g_{eff}(s)$	1.592705	1.791564	1.971836	2.356937	2.870684	3.804029	4.729738
r_{eff}	0.744167	0.783386	0.816359	0.875294	0.943518	1.06057	1.186738

Table -3: The results of effective hygroscopic growth and effective radii of maritime polluted using equations (1) and (2)

RH%	50	70	80	90	95	98	99
$g_{eff}(s)$	1.55976	1.755377	1.933246	2.311989	2.819341	3.744269	4.664769
r_{eff}	0.761584	0.804207	0.838052	0.900728	0.969865	1.083629	1.204032

Table -4: The results of effective hygroscopic growth and effective radii of maritime clean using equations (1) and (2)

RH%	50	70	80	90	95	98	99
$g_{eff}(s)$	1.588511	1.787747	1.967489	2.351236	2.864285	3.797478	4.72193
r_{eff}	0.788348	0.830288	0.862174	0.924005	0.9912	1.103281	1.220381

where a_w is the activity of water in solution, ρ_w is the density of water, M_w is the molecular weight of water, $\sigma_{s/a}$ is the surface tension of the solution/air interface, R is the universal gas constant, T is temperature, and D is the diameter of the droplet.

Equation (4) applies over the entire range of relative humidity and solution hygroscopicity. It can thus be used to predict particle water content in the sub saturated (S<1) regime, as well as to predict the conditions for cloud droplet activation [8].

The Kohler equation (Eq.3) described by [2] can be modified to multiple components aerosols as

$$\ln S = \frac{A}{r_{eff(s)}} + \frac{B}{1-(g_{eff}(S))^3} \tag{5}$$

$$\ln k_e = \frac{A}{r_{eff(s)}} \qquad or \qquad k_e = \exp\left(\frac{A}{r_{eff(s)}}\right) \tag{6}$$

where k_e is   Kelvin effect

Similarly for

$$\ln a_w = \frac{B}{1-(g_{eff}(s))^3} \quad or \quad a_w = exp\left(\frac{B}{1-(g_{eff}(s))^3}\right) \tag{7}$$

where a_w is water activity, Also from the Eq (5) the parameter B was described as the Raoult term (i.e. solute effect) and A Kelvin term (surface tension) [2].

Humidograms of the ambient aerosols obtained in various atmospheric conditions showed that gf_eff (RH) could as well be fitted well with a γ-law [16],[17]

$$gf_{eff}(RH) = (1-RH)^\gamma \tag{8}$$

The γ known as the humidification factor represents the dependence of aerosol optical properties on RH, which results from the changes in the particles sizes and refractive indices upon humidification. The use of γ has the advantage of describing the hygroscopic behaviour of aerosols in a linear manner over a broad range of RH values. The γ parameter is dimensionless, and it increases with increasing particle water uptake [5].

3. RESULTS AND DISSCUSSIONS

From tables 2, 3, and 4.

Table -3: The results of the regression of equation (5) of the ambient   Relative Humidity, R^2 is coefficient of determination; p-value is the probability of null or Alternative Hypothesis

MODELS	R SQUARE	P-values A	P-values B	Significant
TROPICAL	0.989195	0.077984	3.55E-05	7.5E-05
CLEAN	0.992188	0.033622	4.54E-05	3.92E-05
POLLUTED	0.990155	0.079253	2.81E-05	6.23E-05

From the values of R^2 of table 4 it can be observed that the data fitted the model very well and for the p-values of the coefficient B has highest significant than coefficient A these shows that the water activities have contributed significantly on the tropical and polluted aerosols than kelvin effect and also for clean both the coefficients have the significant on the clean aerosols.
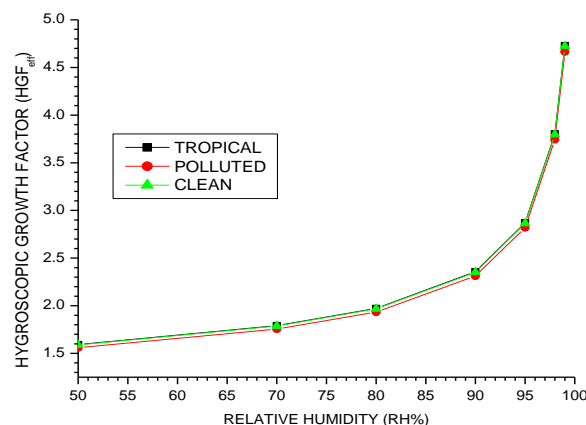

Chart -1: A Graph of Hygroscopic Growth Factor against Relative Humidity (Humidograms) Using Equation (1)

Figure 1 shows that from 50% to 80% are linear increase and from 80% to 99% are nonlinear in aerosols growth factor with relative humidity with relative humidity (RHs). The deliquescence point was observed from 95% to 99%.The highest growth factor was found in tropical aerosols at 99%RH.The growth factor of all aerosols increased with relative humidity as [6] reported and all plot satisfy the power laws. It was also shows it dependency on compositions.
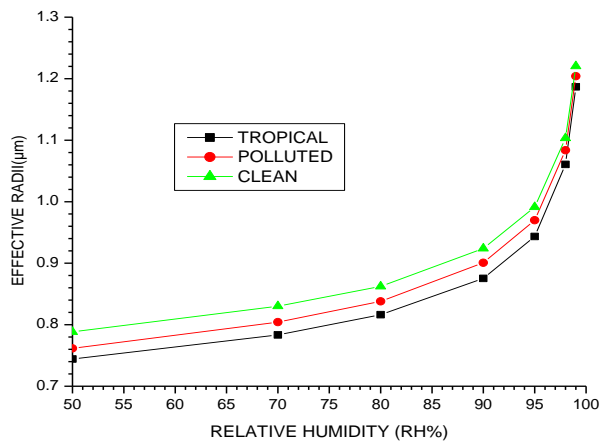

Chart -2: A Graph of Effective Radii versus Relative Humidity Using Equation (2)

From figure 2 it was observed that the highest value of effective radii is that of maritime clean at 99% relative humidity and the lowest value was found in the tropical aerosols at 50% relative humidity and the plot shows a non-linear relation with RH this shows the plot obey the power laws.
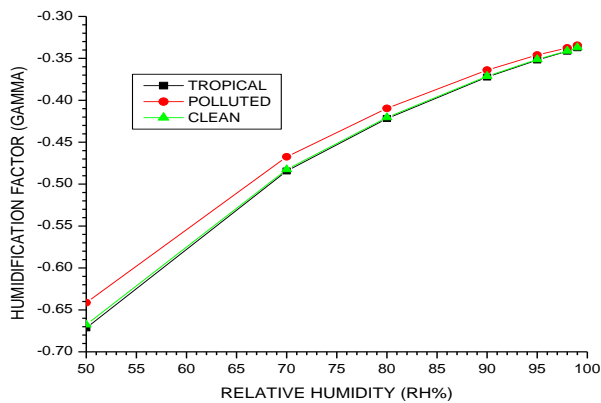

Chart -3: A graph of gamma versus relative humidity using equation (8)

From figure (3) it was observed that the highest value of humidification factor is that of polluted at both 50% and 99% relative humidity this shows that maritime polluted aerosols have highest magnitude of the dependence of aerosols optical properties on RH due to the large concentration of insoluble substances such as soot in the region and for the maritime clean and tropical due the highest concentration of water soluble substance this shows that the lowest optical properties dependence resulting to the changes in particles sizes and refractive indices upon humidification. Studies from [5] for maritime polluted region ranged between -0.625   and -0.125 this result is close to our observation.
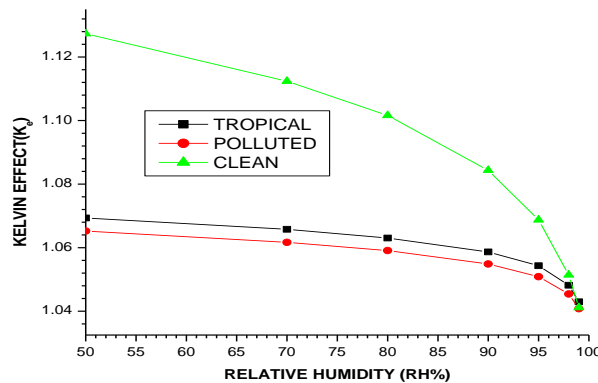
Chart -4: A Graph of Kelvin Effect against Relative Humidity Using Equation (6)

From the figure (4) it can be seen that the highest value of kelvin effect is that of maritime clean 50% RH and almost all aerosols converge at 99% RH. These shows that the kelvin effect has negligible effect at 50% RH but the effect is increased with relative humidity because of the wide gap between water soluble substances that is between clean and tropical aerosols is greater than the small gap between water soluble aerosol that is tropical and water in soluble aerosols that is polluted.
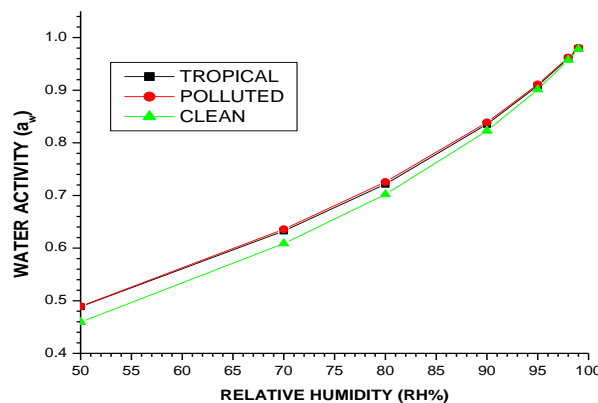

Chart -5: A graph of Water Activity against Relative Humidity Using Equation (7)

From the figure (5) it can be seen that the values of water activities were observed the same at all RH for the tropical and polluted aerosols and the lowest was found in maritime clean at 50% RH and also the plots are non-linear this show the exponential nature of the plot and converge to unity at 99% RH. This also shows that the water activity changes as RH change.

4. CONCLUSIONS

We determined the hygroscopic behavior of atmospheric aerosols using microphysical properties of aerosol data extracted from Optical Properties of Aerosols and Cloud (OPAC) at seven different relative humidity values using volume base ratio. The results shows that the growth factor and effective radii increases with increase in RH and are more pronounced at 90-99% RHs, this indicated that the aerosols in clean ,tropical and polluted are mostly hygroscopic as [6] observed.

We observed that the data fitted the models very well because the values of R^2 and P-values. Finally water activities factor that is Raoult effect is more dominant in all three models (clean, tropical and polluted) than kelvin effect that causes the curvature effect hence the particle aerosols are large in size since the effect of kelvin effect is negligible compare to the Raoult effect.

In conclusion the large the atmospheric aerosols size lead to the direct effect causes scatter and absorption radiation, affect the earth radiation balance in both direct and indirect ways.

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