

Mathematical Determination of the Critical Absolute Hamaker Constant of the Serum (As an Intervening Medium) Which Favours Repulsion in the Human Immunodeficiency Virus (HIV)-Blood Interactions Mechanism

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Abstract - HIV-blood interactions were studied using the Hamaker coefficient approach as a thermodynamic tool in determining the interaction processes. Application was made of the Lifshitz derivation for van der Waals forces as an alternative to the contact angle approach. The methodology involved taking blood samples from twenty HIV-infected persons and from twenty uninfected persons for absorbance measurement using Ultraviolet Visible Spectrophotometer. From the absorbance data the variables (e.g. dielectric constant, etc) required for computations were derived. The Hamaker constants A_{11} , A_{22} , A_{33} and the combined Hamaker coefficients A_{132} were obtained. The value of $A_{132abs} = 0.2587 \times 10^{-21}$ Joule was obtained for HIV-infected blood. A significance of this result is the positive sense of the absolute combined Hamaker coefficient which implies net positive van der Waals forces indicating an attraction between the virus and the lymphocyte. This in effect suggests that infection has occurred thus confirming the role of this principle in HIV-blood interactions. A near zero value for the combined Hamaker coefficient for the uninfected blood samples $A_{131abs} = 0.1026 \times 10^{-21}$ Joule is an indicator that a negative Hamaker coefficient is attainable. To propose a solution to HIV infection, it became necessary to find a way to render the absolute combined Hamaker coefficient A_{132abs} negative. As a first step to this, a mathematical derivation for $A_{33} \geq 0.9763 \times 10^{-21}$ Joule which satisfies this condition for a negative A_{132abs} was obtained. To achieve the condition of the stated A_{33} above with possible additive(s) in form of drugs to the serum as the intervening medium will be the next step.

Index Terms - Absorbance, Dielectric Constant, Hamaker Coefficient, Human Immunodeficiency Virus, Lifshitz formula, Lymphocyte, van der Waal

I. THEORETICAL CONSIDERATIONS

A. Concept of Interfacial Free Energy

THE work done by a force F to move a flat plate along

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another surface by a distance dx is given, for a reversible process, by;

$$\delta w = F dx \quad (1)$$

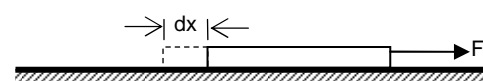


Fig. 1. Schematic Diagramme Showing Application of a Force on a Surface

However, the force F is given by; $F = L\gamma$ Where L is the width of the plate and γ is the surface free energy (interfacial free energy)

Hence; $\delta w = L\gamma dx$

But; $dA = L dx$

Therefore; $\delta w = \gamma dA \quad (2)$

This is the work required to form a new surface of area dA . For pure materials, γ is a function of T only, and the surface is considered a thermodynamic system for which the coordinates are γ , A and T . The unit of γ is Joules. In many processes that involve surface area changes, the concept of interfacial free energy is applicable.

B. The Thermodynamic Approach to Particle-Particle Interaction

The thermodynamic free energy of adhesion of a particle P on a solid S in a liquid L at a separation d_0 [1], is given by;

$$\Delta F_{pls}^{adh}(d_0) = \gamma_{ps} - \gamma_{pl} - \gamma_{sl} \quad (3)$$

Where ΔF^{adh} is the free energy of adhesion, integrated from infinity to the equilibrium separation distance d_0 ; γ_{ps} is the interfacial free energy between P and S ; γ_{pl} is that between P and L and γ_{sl} that between S and L .

For the interaction between the individual components, similar equations can be written also;

$$\Delta F_{ps}^{adh}(d_1) = \gamma_{ps} - \gamma_{pv} - \gamma_{sv} \quad (4)$$

$$\Delta F_{sl}^{adh}(d_1) = \gamma_{sl} - \gamma_{sv} - \gamma_{lv} \quad (5)$$

$$\Delta F_{pl}^{adh}(d_1) = \gamma_{pl} - \gamma_{pv} - \gamma_{lv} \quad (6)$$

For a liquid, the force of cohesion, which is the interaction with itself is described by;

$$\Delta F_{II}^{coh}(d_1) = -2\gamma_{lv} \quad (7)$$

ΔF^{adh} can be determined by several approaches, apart from the above surface free energy approach. The classical work of Hamaker is very appropriate [2].

To throw more light on the concept of Hamaker Constants, use is made of the van der Waals explanation of the derivations of the ideal gas law;

$$PV = RT \quad (8)$$

It was discovered that the kinetic energy of the molecules which strike the container wall is less than that of the bulk molecules. This effect was explained by the fact that the surface molecules are attracted by the bulk molecules (as in fig.2) even when the molecules have no permanent dipoles. It then follows that molecules can attract each other by some kind of cohesive force [3]. These forces have come to be known as van der Waals forces. van der Waals introduced the following corrections to eqn (8);

$$\left[P + \frac{a}{V^2} \right] (V - b) = RT \quad (9)$$

The correction term to the pressure, $\left(\frac{a}{V^2} \right)$ indicates that

the kinetic energy of the molecules which strike the container wall is less than that of the bulk molecules. This signifies the earlier mentioned attraction between the surface molecules and the bulk molecules.

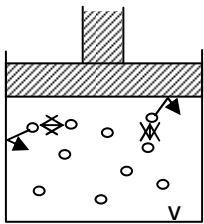


Fig. 2. Attraction of Surface Molecules by Bulk Molecules in a Container of Volume V [4]

After the development of the theory of quantum mechanics, London quantified the van der Waals statement for molecules without a dipole and so molecular attraction forces began to be known as London/van der Waals forces [5]. London stated that the mutual attraction energy, V_A of two molecules in a vacuum can be given by the equation;

$$V_A = -\frac{3}{4} h\nu_0 \left[\frac{\alpha^2}{H^6} \right] = -\left[\frac{\beta_{11}}{H^6} \right] \quad (10)$$

The interaction of two identical molecules of a material 1 is shown in fig.3 below.

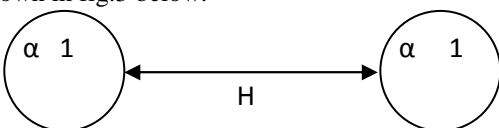


Fig. 3. Interaction of Two Identical Molecules of Materials 1 and Polarizability α , at a Separation H [4]

Hamaker made an essential step in 1937 from the mutual attraction of two molecules. He deduced that assemblies of molecules as in a solid body must attract other assemblies. The interaction energy can be obtained by the summation of all the interaction energies of all molecules present as in fig.4 below.

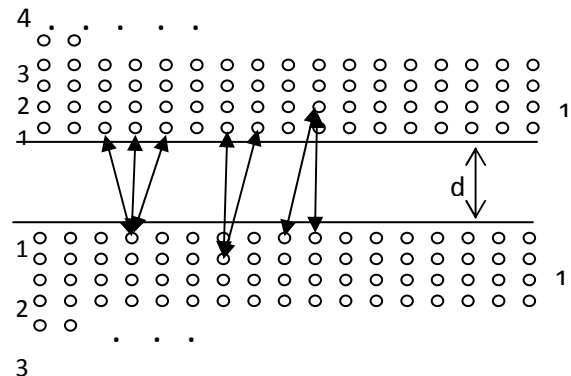


Fig. 4. Interaction of Two Semi-infinite Solid Bodies 1 at a Separation d in Vacuum [4]

This results in a van der Waals pressure, P_{vdw} of attraction between two semi infinite (solid) bodies at a separation distance, d in vacuum;

$$P_{vdw} = \left[\frac{A_{11}}{6\pi d^3} \right] \quad (11)$$

For a sphere of radius, R and a semi-infinite body at a minimum separation distance, d the van der Waals force, F_{vdw} of attraction is given by;

$$F_{vdw} = -\left[\frac{A_{11}R}{6d^2} \right] \quad (12)$$

Where A_{11} is the Hamaker Constant (which is the non-geometrical contribution to the force of attraction, based on molecular properties only)

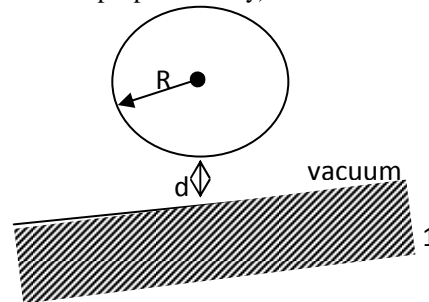


Fig. 5. Interaction of a Sphere of Radius R at a Separation d from a Solid Surface of the same Material 1 in Vacuum [4]

According to Hamaker, the constant A_{11} equals;

$$A_{11} = \pi^2 q_1^2 \beta_{11} \quad (13)$$

Where q_1 is the number of atoms per cm^3 and β_{11} is the London/van der Waals constant for interaction between two molecules. Values for β can be obtained in approximation from the ionization potential of the molecules of interest, and so the Hamaker Constant can be calculated. The corresponding van der Waals force between two condensed

bodies of given geometry can be calculated provided their separation distance is known.

For combination of two different materials 1 and 2 in approximation:

$$B_{12} \approx \sqrt{\beta_{11}\beta_{22}} \quad (14)$$

$$\text{Thus; } A_{12} = \sqrt{A_{11}A_{22}} \quad (15)$$

For a combination of three materials when the gap between 1 and 2 is filled with a medium 3, from Hamaker's calculations;

$$A_{131} = A_{11} + A_{33} - 2A_{13} \quad (16)$$

$$\text{Also; } A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (17)$$

Rewriting these equations will give;

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \quad (18)$$

And;

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{12}} - \sqrt{A_{33}}) \quad (19)$$

Equation (19) shows that, for a three-component system involving three different materials, 1, 2 and 3, A_{132} can become negative;

$$A_{132} < 0 \quad (20)$$

$$\text{When; } \sqrt{A_{11}} > \sqrt{A_{33}} \text{ and } \sqrt{A_{22}} < \sqrt{A_{33}} \quad (21)$$

$$\text{Or; } \sqrt{A_{11}} < \sqrt{A_{33}} < \sqrt{A_{22}} \quad (22)$$

Hamaker's approach to the interaction between condensed bodies from molecular properties called microscopic approach has limitations. This is true against the backdrop of its neglect of the screening effect of the molecules which are on the surface of two interacting bodies as regards the underlying molecules. Therefore, Hamaker's approach is regarded as an over simplification.

Langbein has shown that as a consequence of the screening effect, in the interaction between two flat plates at a separation distance d , the predominant contribution to the interaction by van der Waals forces comes from those parts of the interacting bodies, which are in a layer of a thickness equal to the separation distance d between the two plates [6].

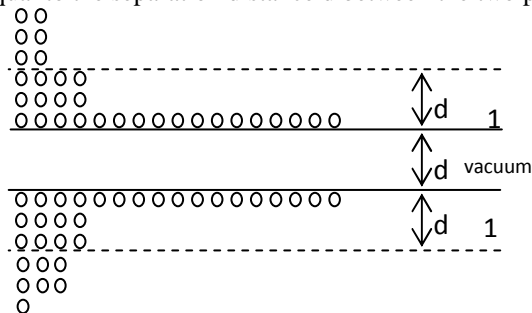


Fig. 6. Schematic Demonstration of the Screening Effect for the Interaction of Two Solid Bodies 1, at a Separation d , in Vacuum [4]

This demonstrates the importance of surface layers like the outer membrane of a cell, or the presence of an adsorbed layer on the overall interaction between two materials at short separations. It also demonstrates the need for the characterization of the surface of a body into its adhesional behaviour.

The limitations of Hamaker's approach led Lifshitz et al to develop an alternative derivation of van der Waals forces between solid bodies [7]. The interaction between solids on the basis of their macroscopic properties considers the screening and other effects in their calculations. Thus the Hamaker Constant A_{132} becomes;

$$A_{132} = \frac{3}{4} \pi \int_0^\infty \left[\frac{\epsilon_1(i\zeta) - \epsilon_3(i\zeta)}{\epsilon_1(i\zeta) + \epsilon_3(i\zeta)} \right] \left[\frac{\epsilon_2(i\zeta) - \epsilon_3(i\zeta)}{\epsilon_2(i\zeta) + \epsilon_3(i\zeta)} \right] d\zeta \quad (23)$$

Where, $\epsilon_1(i\zeta)$ is the dielectric constant of material, j along the imaginary, i frequency axis ($i\zeta$) which can be obtained from the imaginary part $\epsilon_1''(\omega)$ of the dielectric constant $\epsilon_1(\omega)$.

The value of A_{11} could be obtained from the relation;

$$A_{11} = 2.5 \left[\frac{\epsilon_{10} - 1}{\epsilon_{10} + 1} \right]^2 = 2.5 \left[\frac{n_1^2 - 1}{n_1^2 + 1} \right]^2 \quad (24)$$

Where ϵ_{10} is the dielectric constant and n_1 the refractive index of the polymer at zero frequency, both being bulk material properties which can easily be obtained.

C. Relationship between Hamaker Coefficients and Free Energy of Adhesion ΔF^{adh}

For all given combinations, it is possible to express ΔF^{adh} in terms of van der Waals energies. For instance, for a flat plate/flat plate geometry;

$$\Delta F_{12}^{adh}(d_1) = - \left[\frac{A_{12}}{12\pi d_1^2} \right] \quad (25)$$

$$\Delta F_{132}^{adh}(d_0) = - \left[\frac{A_{12}}{12\pi d_0^2} \right] \quad (26)$$

For the four given combinations i.e. eqns (4) to (7) the equilibrium separation distances, however, are not necessarily the same. When a gap is a vacuum, the equilibrium separation d_1 probably is but when the gap contains a liquid, a different separation distance d_0 may be expected. As a result of this the following becomes true;

$$\left[\frac{A_{132}}{d_0} \right] = \left[\frac{A_{12} - A_{13} - A_{23} + A_{33}}{d_1^2} \right] \quad (27)$$

A detailed study of van der Waals forces revealed that in the case of a three-component system, the corresponding Hamaker Constant A_{132} could attain a negative value given the conditions stated below.

$$A_{11} < A_{33} < A_{22} \text{ or } A_{11} > A_{33} > A_{22} \quad (28)$$

Where; A_{11} , A_{22} and A_{33} are the individual Hamaker Constants of components 1, 2 and 3 respectively.

The implication of this is that two adhering bodies 1 and 2 of different composition will separate spontaneously upon immersion in a liquid 3 provided the conditions given by eqn (28) are fulfilled.

II. MATHEMATICAL MODEL FOR THE INTERACTIONS MECHANISM

The mutual attraction energy, V_A of two molecules in a vacuum is given by;

$$V_A = -\frac{3}{4}hv_0 \left[\frac{\alpha^2}{H^6} \right] = -\left[\frac{\beta_{11}}{H^6} \right] \quad (29)$$

Where; h = Planck's constant
 v_0 = characteristic frequency of the molecule
 α = polarizability of the molecule
H = their separation distance

The assemblies of molecules as in a solid body have interaction energy as the summation of all the interaction energies of all the molecules present and the van der Waals pressure, P_{vdw} as follows;

$$P_{vdw} = \left[\frac{A_{11}}{6\pi d^3} \right] \quad (30)$$

For a sphere of radius, R and a semi-infinite body at a maximum separation distance, d the van der Waals force of attraction, F_{vdw} is given as;

$$F_{vdw} = \left[\frac{A_{11}R}{6d^2} \right] \quad (31)$$

Where A_{11} = Hamaker constant

$$A_{11} = \pi^2 q_1^2 \beta_{11} \quad (32)$$

Where; q_1 = number of atoms per cm^3

β_{11} = London-van der Waals constant

Given two dissimilar condensed bodies of given geometry with a separation distance, d, the corresponding van der Waals force between them can be determined. For the system under study, the interacting bodies are the lymphocytes, 1 and the virus, 2.

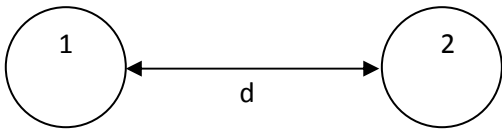


Fig. 7. Interaction of Two Un-identical Molecules of Lymphocyte 1 and Virus (HIV) 2, at a Separation d

The van der Waals force between the lymphocyte, 1 and the virus, 2 is given by the relations;

$$F_{vdw} = -\left[\frac{A_{12}R_{12}}{6d^2} \right] \quad (33)$$

Where $A_{11} = \pi^2 q_1^2 \beta_{11}$ = Hamaker constant for lymphocyte

$A_{22} = \pi^2 q_2^2 \beta_{22}$ = Hamaker constant for the virus (HIV)

$A_{12} = \pi^2 q_{12}^2 \beta_{12}$ = Hamaker constant for both materials (i.e. lymphocyte and the virus)

Where; $\beta_{12} = \sqrt{\beta_{11}\beta_{22}}$

Thus the Hamaker constant becomes;

$$A_{12} = \sqrt{(\pi^2 q_1^2 \beta_{11})(\pi^2 q_2^2 \beta_{22})} \quad (34)$$

$$A_{12} = \sqrt{A_{11}A_{22}} \quad (35)$$

For a combination of the two dissimilar materials (i.e. lymphocyte 1, and the virus 2) with the gap between them filled with plasma or serum as the medium 3 the combined Hamaker coefficient will be given by;

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \quad (36)$$

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \quad (37)$$

A_{33} = Hamaker constant for serum (plasma)

A_{13} = Hamaker constant for both materials (i.e. lymphocyte and plasma)

A_{23} = Hamaker constant for both materials (i.e. the virus and plasma)

$$A_{132abs} = \frac{3}{4} \pi \hbar \int_0^\infty \left[\frac{\epsilon_1(i\zeta) - \epsilon_3(i\zeta)}{\epsilon_1(i\zeta) + \epsilon_3(i\zeta)} \right] \left[\frac{\epsilon_2(i\zeta) - \epsilon_3(i\zeta)}{\epsilon_2(i\zeta) + \epsilon_3(i\zeta)} \right] d\zeta \quad (38)$$

The mean of all the values of the combined Hamaker coefficient, A_{132} gives an absolute value for the coefficient denoted by A_{132abs} ;

$$A_{132abs} = \frac{\sum_0^N (A_{132})}{N} \quad (39)$$

TABLE 1
COMPARISON OF THE VALUES OF THE HAMAKER CONSTANTS A_{11} , A_{22} , A_{33} AND HAMAKER COEFFICIENTS A_{132} , A_{232} FOR THE INFECTED AND A_{131} FOR THE UNINFECTED BLOOD SAMPLES [8]

Variable ($\times 10^{-21}$ Joule)	Infected Blood		Uninfected Blood	
	Peak Value	Absolute Value	Peak Value	Absolute Value
A_{11}	---	---	1.3899	0.9659
A_{22}	1.4049	0.9868	---	---
A_{33}	0.7052	0.2486	0.9369	0.4388
A_{132}	0.7601	0.2587	---	---
A_{131}	---	---	0.9120	0.1026
A_{232}	0.7514	0.2823	---	---

The table 1 shows the peak and absolute values of Hamaker constants A_{11} for the uninfected blood samples. A_{22} is the Hamaker constant for the virus, here represented by the infected lymphocytes. This is against the backdrop of no known process of isolation of the virus yet. However, it is a very close approximation for the virus owing to the manner of the infection mechanism. The Hamaker constants A_{33} for the plasma reveal greater values for the uninfected samples which invariably indicate a higher surface energy than the infected ones. This could be validated by the surface energy approach using the contact angle method. The higher absolute values of A_{132} and A_{232} as against that of A_{131} , as well as the near zero (i.e. 0.1026×10^{-21} Joule) value of the absolute combined Hamaker coefficient A_{131abs} for the uninfected samples is once again a clear indication of the relevance of the concept in the HIV infection process.

III. DEDUCTIONS FOR THE ABSOLUTE COMBINED HAMAKER COEFFICIENT A_{132ABS}

Applying Lifshitz derivation for van der Waals forces as in eqn (23 or 38); A mean of all the values of the Hamaker coefficients to obtain a single value known as absolute combined Hamaker coefficient A_{132abs} became necessary and was got as;

$$A_{132abs} = 0.2587 \times 10^{-21} \text{Joule}$$

This was done by obtaining a mean of all the values of the Hamaker coefficients for the infected blood over the whole range of wavelength, $\lambda=230$ to 890 Hertz, to obtain a single value of 0.2587×10^{-21} Joule. This value agrees with those obtained by various authors for other biological processes as have earlier been shown in the literature review.

IV. DEDUCTIONS FOR THE ABSOLUTE COMBINED NEGATIVE HAMAKER COEFFICIENT

To define the condition where the absolute Hamaker coefficient becomes negative will require employing the relations that express that condition. Hence, recalling eqns (16 to 22), we can derive a state where the Hamaker Coefficient, A_{132} is less than zero. This situation could be possible with the following already stated conditions;

$$A_{132} < 0 \quad (40)$$

$$\text{When; } \sqrt{A_{11}} > \sqrt{A_{33}} \text{ and } \sqrt{A_{22}} < \sqrt{A_{33}} \quad (41)$$

$$\text{Or } \sqrt{A_{11}} < \sqrt{A_{33}} < \sqrt{A_{22}} \quad (42)$$

The mean of all values of A_{11} and A_{22} could be obtained and substituted into the relation below (i.e. eqn (43)) in order to derive a value for A_{33} at which A_{132} is equal to zero in agreement with the earlier stated reasons.

$$A_{132} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right) \left(\sqrt{A_{22}} - \sqrt{A_{33}} \right) \quad (43)$$

Rearranging eqn (43) and making A_{33} subject of the formula

$$\text{we obtain; } A_{33} = \left[\frac{2\sqrt{A_{11}}\sqrt{A_{22}} - A_{132}}{\sqrt{A_{11}} + \sqrt{A_{22}}} \right]^2 \quad (44)$$

Obtaining a mean of the values of A_{11} and A_{22} to give absolute values of the Hamaker constants yielded the values given below;

$$A_{11} = 0.9659 \times 10^{-21} \text{Joule}$$

$$A_{22} = 0.9868 \times 10^{-21} \text{Joule}$$

Thus, plowing these values into eqn (44) and rendering $A_{132} \leq 0$ will give the critical value of A_{33C} that satisfies the condition for the combined Hamaker coefficient to be equal to or less than zero. Hence any value of A_{33} greater than the critical would be the desired value necessary to attain a negative combined Hamaker coefficient.

Hence, the critical absolute Hamaker constant A_{33C} for the plasma (serum) which renders the A_{132} negative is given as;

$$A_{33C} = 0.9763 \times 10^{-21} \text{Joule}$$

Thus for negative combined Hamaker coefficient A_{132} of the infected blood to be attained, the combined Hamaker constant of the serum (plasma) as the intervening medium A_{33} should be of the magnitude;

$$A_{33} \geq 0.9763 \times 10^{-21} \text{Joule}$$

Inserting the above value of A_{33} into eqn (43) would yield a negative value for A_{132} as follows;

$$A_{132} = -0.2809 \times 10^{-25} \text{Joule (when } A_{33} = 0.9763 \times 10^{-21} \text{Joule)}$$

To obtain a value for the combined Hamaker coefficient A_{131} for the uninfected blood the relation of eqns (45) and (46) are employed.

$$A_{131} = A_{11} + A_{33} - 2A_{13} \quad (45)$$

$$A_{131} = \left(\sqrt{A_{11}} - \sqrt{A_{33}} \right)^2 \quad (46)$$

Upon deriving a mean of all values of A_{131} for the twenty uninfected blood samples, an absolute value A_{131abs} was derived as given below;

$$A_{131abs} = 0.1026 \times 10^{-21} \text{Joule}$$

This value is very nearly equal to zero which is a clear indication of the validity of the concept of Hamaker coefficient to the process and progress of human infection with the Human Immunodeficiency Virus (HIV). The near zero value of the A_{131abs} shows the absence of infection in the blood samples thus suggesting the usefulness of the concept of negative Hamaker coefficient in finding a solution to HIV infection. Table 1 shows the comparison of the Hamaker constants and coefficients for the infected and uninfected blood samples.

V. CONCLUSION

This research work reveals that the interactions of the HIV and the lymphocytes could be mathematically modeled and the ensuing mathematics resolved in a bid to find a solution to the infection. The values of the Hamaker coefficients and constants derived are a proof of the relevance of the concept of Hamaker coefficient to the HIV-blood interactions and by extension to other biological and particulate systems. This study equally reveals the possibility of solving for the value of A_{33C} (i.e. a condition of the serum) which would favour the prevalence of a negative combined absolute Hamaker coefficient A_{132abs} . Such a condition in essence would mean repulsion between the virus and the blood cells and could prove the much desired solution to the HIV jinx. A synergy of Engineers, Pharmacists, Doctors, Pharmacologists, Medical laboratory scientists etc may well be needed in interpreting the meaning of the A_{33C} values and the medical, biological and toxicity implications of additives in form of drugs that could yield the required characteristics.

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