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Research paper

Spectrophotometric analysis of surface free energies of polymer surfaces

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Abstract

This work is focused on the use of a spectrophotometer to determine the surface free energies of polymers. To study the molecular system interaction, there is a need for a simpler method to calculate free energy. The free energy determines the phase interaction of polymer film at different concentrations. One of the simpler methods is the use of a spectrophotometer. The methodology involved taking four polymer samples and dissolving each into different concentrations for absorbance measurement using an ultraviolet spectrophotometer. From the absorbance data, various variables (e.g., dielectric constant, etc.) were derived. This variable (dielectric constant) was also used to determine the haymaker constant of each concentration of each polymer. The surface free energies are determined from the values of the Hamaker constant. The peak values of surface free energies for Polyvinyl alcohol (PVA), Polyethylene glycol (PEG) and Polyacrylamide (PAM) were also obtained from spectrophotometer results and found to be the same, 57.51mJ/m^2. Contact angle measurements on concentration were also obtained. It was found that the contact angle measured on PVA and PEG at different concentrations tends to decrease with an increase in concentration. The results, therefore, show that PVA and PEG surfaces tend to be hydrophilic as concentration increases while PAM and Polyvinyl acetate (PVAC indicate hydrophobic. Surface free energies obtained from the spectrophotometric result and contact angle show little significant difference of about 6.9% and they followed the trend when related with other surface properties.

Keywords: *Polyvinyl Alcohol; Polyacrylamide; Polyethylene Glycol; Polyvinyl Acetate; Surface Free Energy; Absorbance; Spectrophotometer; Hamaker Constant.*

1. Introduction

Surface energy is an important concept in the study of materials science and engineering. For example, surface tension plays an important role in the sintering of metals, ceramic materials and polymers made from powders. Also, it contributes a lot in the growth of particles dispersed in gases, liquids or solids; and to determine the distribution of size and shapes of solids and liquids in multiphase systems and phase transformations (Readey, 2017). The knowledge of interactions associated with surface free energy is necessary for understanding and modelling of many surfaces and interface processes, which involve such wetting phenomena as preparation of suspensions and emulsions, flotation of minerals, detergency, adhesive joints, painting, drug preparation, etc. (Palencia, 2017). In addition, in biological science, the free surface energy of a solid is used for the thermodynamic description of the adsorption of microorganisms on the surface. From this parameter, information about the mechanism of aggregation, biofouling and biofilms is obtained (Abu-Lail et al, 2006; Liu et al, 2005; Long et al 2006). To carry out the characterization of the surface, there are different techniques which must be selected depending on the objective of characterization. Among the most widely used methods are: for the study of composition, X-ray diffraction, photoelectron spectroscopy, Fourier transform infrared spectroscopy usually by attenuated total reflectance; whereas for the study of morphology, scanning electron microscopy and atomic force microscopy. These methods require relatively expensive equipment, skilled technicians and sophisticated techniques to interpret data. However, measurement of the surface energy of the solid can also provide a good understanding of the surface properties of a solid using relatively a very simple approach. In addition, the surface energy of a solid can be determined from the measurement of the contact angle of one pure liquid drop, or systems of liquids, deposited on that solid (Chen et al., 2016; Lerma et al., 2016). Different works have been performed for membrane systems; however, though these measurements are useful to analyze relative changes of membranes, the information associated with structural characterization of the phase cannot be obtained because a magnitude of porous effects is not considered (Palencia et al 2009; Benitez. et al. 2017).

Polymers with well-defined surface and bulk properties are of interest for the development of technologies. Polymeric materials find a large number of applications because of their unique properties such as low cost, lightweight, abundantly available, easy processability, can be moulded and recycled, excellent chemical resistance, non-corrosive etc (Brandrup et al. 1999; Deshmukh et al, 2003). Adhesion, wettability, printability etc. strongly depend upon surface morphology and chemical composition, the presence of polar/non polar groups on the surface (Deshmukh et al, 2003).

Suitable adhesive properties of the polymer compositions can be achieved using appropriate materials, and introducing plastic additives, which cause the modification, particularly effective in the area of the surface layer properties (Harding, 1997; Dalet et al., 1999; Bouhanks et al., 2016). Use of the polymer composition with a surface layer of reduced adsorption causes a reduction in the adhesion of impurities, and particles of foreign matter during transportation and handling. Modification of the polymer composition also relates to the manufacture of porous material, which will reduce the density of the material, and thereby the costs of its production (Żenkiewicz, 2000; Pocius, 2012; Myshkin et al., 2014).

1.1. Absorbance measurement

There are two existing light sources within a UV-VIS spectrophotometer – one for each (UV and visible light) spectrum. The usual light source used to generate visible light is the tungsten-halogen lamp emitting 200-340 nm wavelengths (Gore, 2000). The UV source can be either a high-pressure hydrogen lamp or a deuterium lamp, the latter of which is the one found in the lab. When measuring absorbance at the UV spectrum, the other lamp has to be turned off. The same goes when measuring visible light absorbance. This is to prevent interference of unnecessary wavelengths in the incident light on the sample. The light source is monochromatic, the purpose of which is to filter light and select a specific wavelength by using either a prism or a diffraction grating. After the monochromatic is a series of lenses, slits, mirrors, and filters that act as an optical system to concentrate, increase spectral purity of, and direct monochromatic light towards the sample chamber with cuvettes containing solutions to be tested. In the laboratory, the sample chamber is equipped with multiple slots to allow for continuous measurements of several sample replicates at a particular wavelength. However, since the instrument has only a single beam, every time the wavelength has to be changed a blank reading must precede any sample reading. Concerning cuvettes, which contain sample solutions, there are three kinds available for use today. The first is made of glass and is often utilized for reading absorbance at wavelengths greater than 340 nm due to its undesirable absorption of UV light. The second is made of fused silica or quartz and is the one used in the experiment. It can be utilized in absorbance measurement throughout the UV-VIS spectrum (200 nm to 800 nm) because of its high grade of transparency. The last class is disposable cuvettes, the material of which can vary. One example is made of polymethacrylate and is used only for measurement at 280 nm to 800nm.

The light-sensitive detector follows the sample chamber, it measures the intensity of light transmitted from the cuvettes and passes the information to a meter that records and displays the value to the operator on an LCD screen. Two kinds are of use in UV/VIS spectrophotometers today – the phototube and the photomultiplier tube. The phototube or photocell functions by generating an electric current. When a photon hits the cathode of the cell, an electron is ejected from the cathode and directed to the anode. This flow of electrons produces a current, the magnitude of which is proportional to the energy of the photon. The more sensitive photomultiplier tube relies on Planck’s Photoelectric Effect. Photons hitting the tube’s photosensitive surface eject primary electrons, which then collide with another surface and release secondary electrons. These secondary electrons hit several other surfaces and eject more secondary electrons, which eventually get caught by an anode and produce an electric current. Absorbance measurements are carried out in analytical chemistry very often since the absorbance of a sample is proportional to the concentration of the absorbing species in the sample. Absorbance is also proportional to the thickness of the cuvette, but under standard conditions, it is invariably equal to 1 cm. Because the absorbance of a sample is proportional to the number of absorbing molecules in the light beam (e.g., their molar concentration in the cuvette), the value of A can be recalculated to the concentration with the help of the coefficient of "molar absorptivity" (molar absorbance, ε). Molar absorptivity is defined as the optical density of a 1M solution placed in a cuvette of 1 cm optical length. In this way, the expression for the molar concentration of a chemical compound runs as follows: $c = A/\varepsilon$. Most compounds have tabulated values of their molar absorptivity, which facilitates the precise determination of their concentrations.

Spectrophotometers measure absorbance in the regions of UV (200 –400 nm) and visible light (400 –800 nm). Any real instrument has a limited range of accurately measured absorbance. A good instrument (including Varian Cary 50) can detect A in the region of 0.001 –3 (99.9% −0.1% Transmittance). The major parameters that determine accuracy are signal-to-noise ratio and isolation from stray light. The first characteristic is important for the measurement of a very low absorbance because noise (i.e. spontaneous fluctuations in the intensity of the source light) hinders the evaluation of a very small difference in absorbance. Likewise, stray light (which is not intended to be in the optical system) will mask a very high absorbance where almost no light passes through the sample inside the cuvette compartment. Quite often the absorbance spectrum provides important information about the structure of a molecule and its interactions with other compounds. This particularly concerns the corrin containing metallo-organic ligands, where stretching of coordination bonds and oxidation–reduction of metal ions causes a remarkable response in the system of conjugated π-bonds in the surrounding corrin ring. Among interesting examples include the prediction of histidine-cobalt coordination in the complex between aqua-cobalamin and transcobalamin, deduced from the obtained absorbance spectrum.

It is the objective of the present work, in general, to determine the surface free energy of different polymers using spectrophotometric data (absorbance) and compare them to those of contact angle. To achieve the objective, solutions of four different polymers will be prepared at ten different concentrations each and cast in a glass slide to dry naturally. The absorbance of the forty samples will be taken at different wavelengths from the spectrophotometer.

2. Methodology

2.1. Major considerations

The approach in this study was to collect some commonly used polymers that are soluble in water and dissolve each in water. The film of the solutions was produced on a glass slide. Spectrophotometric techniques were then used to determine the absorbance characteristics and then the surface free energies. These polymers were considered at different concentrations.

2.2. Samples collection

The four polymers are:

a) Polyvinyl alcohol (PVA); A colourless, water-soluble synthetic resin employed principally in the treating of textiles and paper. PVA is unique among polymers (chemical compounds made up of large, multiple-unit molecules) in that is not built up in polymerization reactions from single-unit precursor molecules known as monomers.
b) Polyacrylamide; Polyacrylamide, is an acrylic resin that has the unique property of being soluble in water. It is employed in the treatment of industrial and municipal wastewater.
c) Polyethylene glycol (PEG); Polyethylene glycol (PEG) is a polyether compound with many applications from industrial manufacturing to medicine.

d) Polyvinyl acetate (PVAC); Polyvinyl acetate PVAC poly (ethenyl ethanoate) is a rubbery synthetic polymer with the molecular formula $(C_4H_6O_2)_n$ and structural formula

2.3. Samples preparation

Four samples of different polymers were obtained. Each Sample of the polymers was dissolved in water at ten different concentrations, starting with 20 gdm^{-3} to 110 gdm^{-3}, at 10 gdm^{-3} intervals. The mass of the samples was measured with a weighing balance

2.4. Slides preparation

A microscopic glass slide of dimension; 25.4 mm × 76.2 mm × 1.2 mm, was used for the test surfaces, and a dropper was used to drop each of the samples' concentration on the glass slide to ensure even distribution of each sample Concentration on the slides. The samples were then allowed to dry under the sun and carefully covered with a slip.

2.5. Spectrophotometer measurements

The requisite thermodynamic parameters were obtained from the Visible MetaSpecAE1405031Pro Spectrophotometer at the laboratory of the Department of Mechanical Engineering, Nnamdi Azikiwe University, Awka. Absorbance data obtained was used for the quantification of the relevant information on the interacting systems. Absorbance measurements were made over a range of wavelengths between 340 and 540A alongside their corresponding transmittance values. The Hamaker constant was calculated using equation (1);

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

Where the refractive index n was obtained by employing the mathematical relation in equation (2);

$$n = \left[\frac{1 - R^{\frac{1}{2}}}{1 + R^{\frac{1}{2}}}\right] \quad (2)$$

Given that

$$A + R + T = 1 \quad (3)$$

Where A, R, and T are the absorbance, reflectance, and transmittance of the samples respectively.
The surface free energy of the polymer surfaces at different concentrations was determined using Lifshitz expression as given in equation (4);

$$\Delta F_{11}^{coh}(d_0) = -2\gamma_s \quad (4)$$

Where the relation between the hamaker constant and force of cohesion ΔF_{11}^{coh} is given by equation (5);

$$A_{ij} = -12\pi r_0^2 \Delta F_{ij}(d_0) \quad (5)$$

Substituting equation (4) into (5);

$$\gamma_{ij} = -\frac{A_{ii}}{12\pi r_0^2} \quad (6)$$

Where the minimum distance $d_0$between the same particles in a liquid is given as;
d_0 =1.82Angstrom

3. Results and discussion

3.1. Absorbance data

The values of absorbance of each polymer sample measured at different concentrations were obtained.
The following features were observed

- Each polymer sample exhibits a maximum in its absorbance at different concentrations.
- The graph for each polymer sample has a different peak absorbance value at different concentration
- Each polymer exhibits the highest peak absorbance at a particular concentration and wavelength
- The wavelength at which the maxima occurred is not affected by the concentration of the polymer
- Table 1 gives the highest peak absorbance values for each polymer and the concentration at which it occurred.
- On the whole, the peak absorbance values for the different concentrations on PVA range from 0.148 to 0.368, on PEG they range from 0.159 to 0.590, on PAM they range from 0,287 to 0.990, and on PVAC they range from 0,012 to 0.052. All these falls within the visible range of ultraviolet radiation which is 340-540A

Table 1: Data for the Highest Peak Absorbance for the Polymers

Polymer	PVA	PEG	PAM	PVAC
Highest peak absorbance	0.368	0.590	0.990	0.052
Concentration	40	100	80	70
Wavelength	480	420	420	338

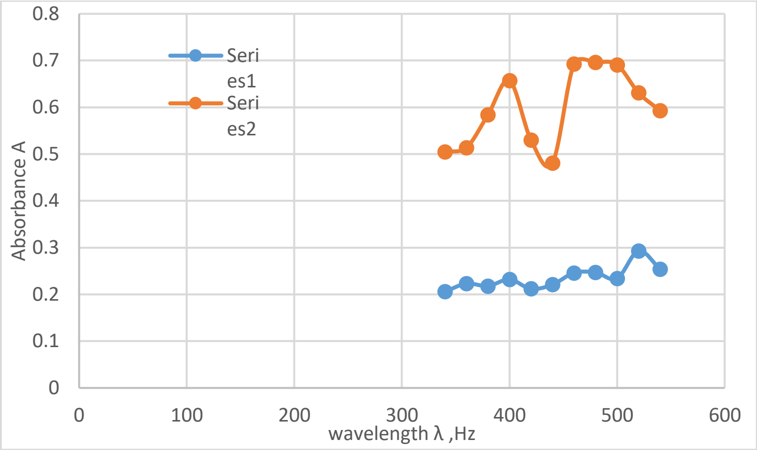

Fig. 1: Summary Graph of Absorbance vs. Wavelength for Highest and Lowest Concentration (PVA).

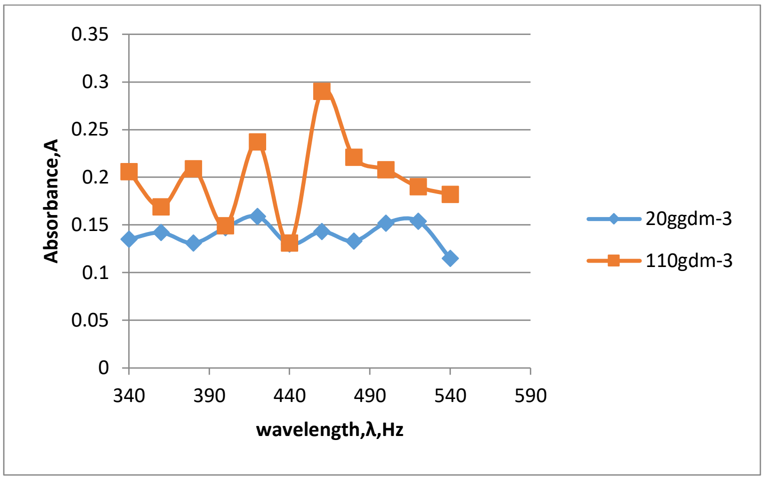

Fig. 2: Summary Graph of Absorbance vs. Wavelength for Highest and Lowest Concentration (PEG).

3.2. Surface free energy

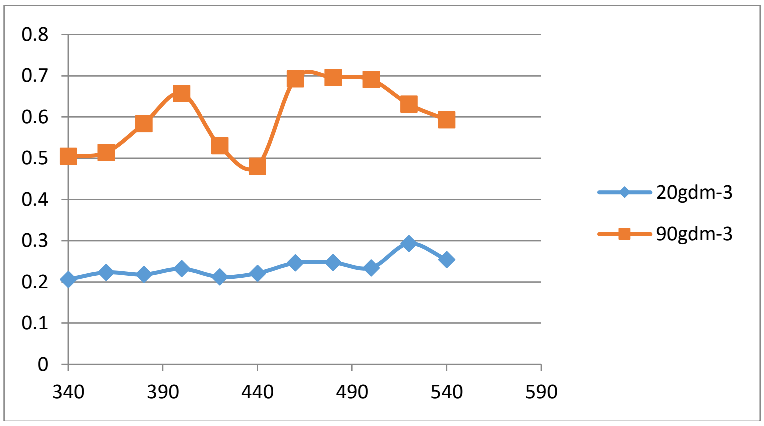

Fig. 3: Summary Graph of Absorbance vs. Wavelength for Highest and Lowest Concentration (PAM).

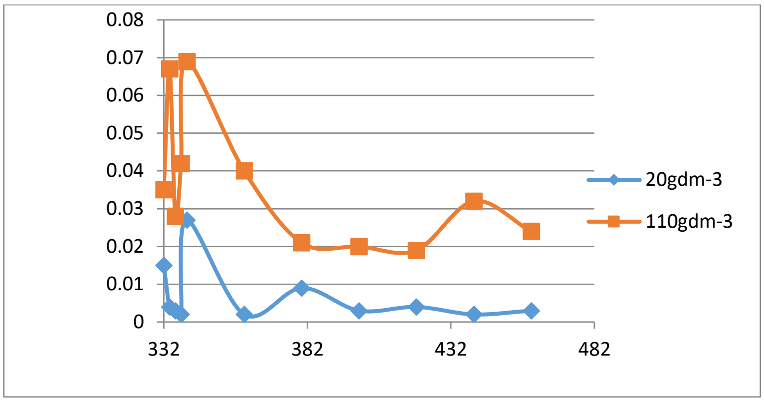

Fig. 4: Summary Graph of Absorbance vs. Wavelength for Highest and Lowest Concentration (PVAC).

The Hamaker constants calculated using the absorbance data are listed in tables 2 to 5 together with the corresponding surface free energies for the polymers.

Table 2: Hamaker Constant, A_{11}, and Surface Free Energy, γ_s for PVA at Different Concentrations

Concentration	Peak Absorbance	Hamaker Constant	Surface Energy
20	0.159	1.125	44.37
30	0.213	1.269	51.29
40	0.196	1.227	57.51
50	0.349	1.405	57.31
60	0.325	1.400	57.31
70	0.519	1.290	53.67
80	0.485	1.338	56.12
90	0.480	1.344	51.09
100	0.590	1.158	46.83

Table 3: Hamaker Constant, A_{11}, And Surface Free Energy, γ_s For Peg At Different Concentrations

Concentration	Peak Absorbance	Hamaker constant	Surface energy
20	0.293	1.383	46.05
30	0.287	1.377	51.95
40	0.393	1.405	50.23
50	0.420	1.394	57.51
60	0.590	1.158	57.31
70	0.470	1.355	52.81
80	0.690	1.877	54.77
90	0.696	0.859	55.02
100	0.701	0.873	47.40

Table 4: Hamaker Constant, A_{11}, and Surface Free Energy, γ_s for Pam at Different Concentrations

Concentration	Peak Absorbance	Hamaker Constant	Surface Energy
20	0.293	1.383	56.61
30	0.287	1.377	56.37
40	0.393	1.405	57.51
50	0.420	1.394	57.06
60	0.590	1.158	47.40
70	0.470	1.355	55.47
80	0.69O	0.877	35.90
90	0.696	0.859	35.16
100	0	0	0

Table 5: Hamaker Constant, A_{11}, and Surface Free Energy, γ_s for Pvac at Different Concentrations

Concentration	Peak Absorbance	Hamaker Constant	Surface Energy
20	0.027	0.317	12.98
30	0.032	0.361	14.78
40	0.035	0.386	15.80
50	0.047	0.502	20.55
60	0.048	0.509	20.84
70	0.052	0.541	22.15
80	0.042	0.453	18.54
90	0.043	0.461	18.87
100	0.050	0.526	21.53
110	0.069	0.672	27.51

Table 2 to 5 shows the values of the surface free energies γs and Hamaker constants A_{11} for the four polymers at different concentrations. The values of the surface free energies of PVA range from 46.05– 57.51 mJ//m^2, PEG range from 35.16– 57.51 mJ/m^2 PAM range from 35.16– 57.51 mJ/$m^2 PVAC\ range\ from$ 12.98– 27.51 mJ/m^2 . PVA and PEG have the lowest surface free energy at a concentration of 20gdm^3 and 100 gdm^3 and the highest at 50 gdm^3. PAM has the highest surface free energy at a concentration of 40 gdm^3. This shows that polymers are most hydrophobic at the lowest and highest concentration. To obtain the least hydrophobic (most hydrophilic) polymer, there should be a gradual increase in concentration.

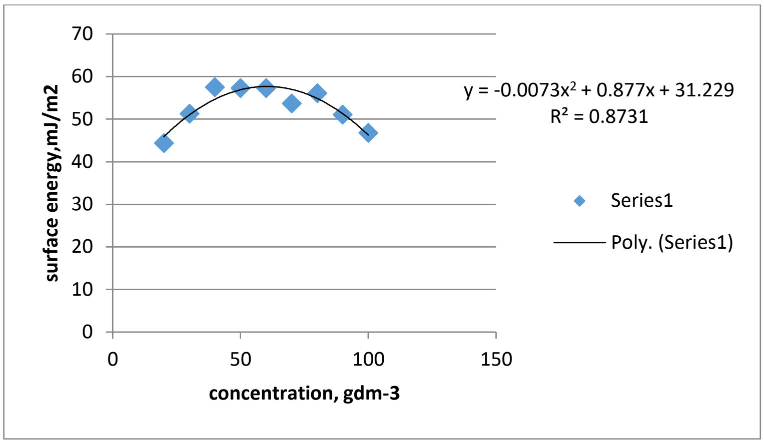

Fig. 5: Graph of Surface Free Energy Against Concentration (Absorbance Values PVA).

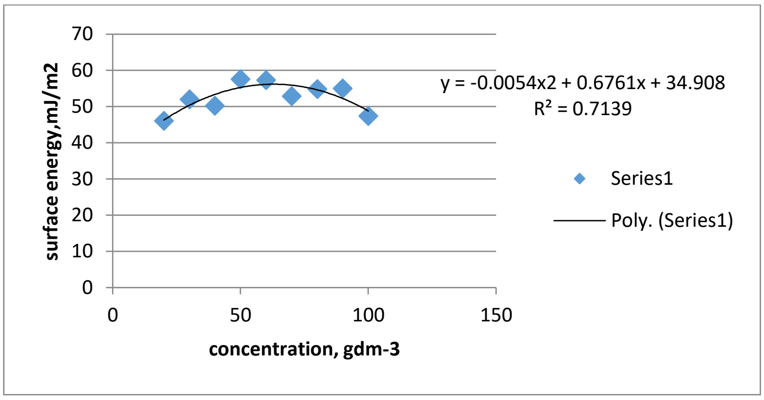

Fig. 6: Graph of Surface Free Energy Against Concentration (Absorbance Values PEG).

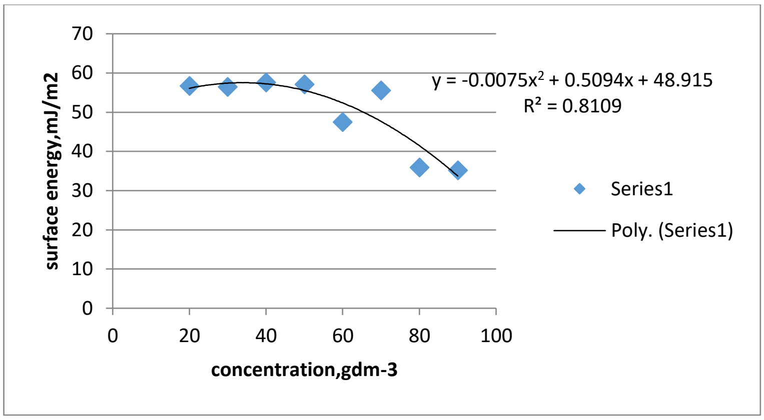

Fig. 7: Graph of Surface Free Energy Against Concentration (Absorbance Values PAM).

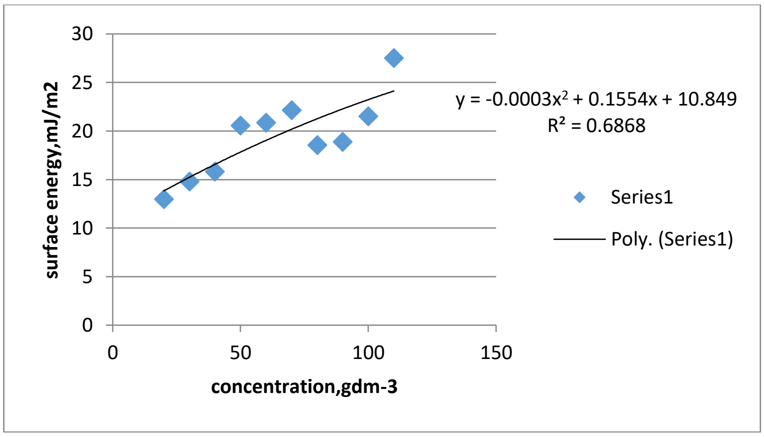

Fig. 8: Graph of Surface Free Energy Against Concentration (Absorbance Values PVAC).

Figures 5 to 8 show that a particular concentration of polymer improves the surface free energy. Therefore, it may suggest that the concentration with the highest surface free energy will be least hydrophobic, i.e., better wetting, and hence more hydrophilic.

Table 6: Comparison of Surface Free Energies Obtained from Contact Angle and Absorbance Values in Different Concentration

	PVA		PEG		PAM		PVAC	
Concentration gdm^{-3}	Contact Angle	Absorb.	Contact Angle	Absorb.	Contact Angle	Absorb.	Contact Angle	Absorb.
20	47.65	44.37	48.85	46.05	53.49	56.61	65.80	12.98
30	49.44	51.29	51.21	51.95	55.69	56.37	68.54	14.78
40	53.49	57.51	50.04	50.23	57.28	57.51	69.65	15.80
50	56.22	57.31	52.93	57.51	56.22	57.06	70.14	20.55
60	57.28	57.31	53.49	57.31	50.04	47.40	70.60	20.84
70	55.15	53.67	52.36	52.81	48.85	55.47	70.14	22.15
80	54.60	56.12	52.20	54.77	46.43	35.90	69.39	18.54
90	55.15	51.09	51.55	55.02	42.72	35.16	69.65	18.87
100	54.05	46.83	51.05	47.4	42.16	0	69.12	21.53

Table 6 shows that surface free energies increase with concentration to a maximum and start to decrease as concentration is increased. It is observed that the surface free energies follow the same trend irrespective of the method or parameter used. The values obtained in spectrophotometer data (absorbance) are very close to about 6.9% of that of contact angle except in PVAC due to its colourless nature on the slide. The graphs of Figures 5 to 8 show almost similar behaviour with varying R^2 values. By studying the graphs of the surface free energy plotted against concentration using spectrophotometer data and contact angle value of the polymer one observes that spectrophotometer data can be used to calculate surface free energy. It is observed that the surface free energy increases from zero concentration to a certain level (maximum point). This shows that a higher concentration after the maximum value has been reached will reduce the surface free energy. This is due to the disproportionate decomposition of molecules at higher concentrations (Beer's law of absorption). In PAM; the decrease in surface free energy as absorbance increases is due to the decrease in power of a radiant beam of light. The power of the radiant beam decreases with the distance (thickness) that it travels through on the absorbing medium (Atkins, et al, 2006). The gelatinous nature of PAM caused the thickness of the polymer film on the slide.

Table 7: Surface Free Energies with Concentrations Using Peak Absorbance Values.

Concentration gdm^{-3}	PVA Surface free Energy(γ_{sv})	PEG Surface free Energy(γ_{sv})	PAM Surface free Energy(γ_{sv})	PVAC Surface free Energy(γ_{sv})
20	44.37	46.05	56.61	12.98
30	51.29	51.95	56.37	14.78
40	57.51	50.23	57.51	15.8
50	57.31	57.51	57.06	20.55
60	57.31	57.31	47.4	20.84
70	53.67	52.81	55.47	22.15
80	56.12	54.77	35.9	18.54
90	51.09	55.02	35.16	18.87
100	46.83	47.4		21.53

4. Conclusions

Surface free energy is quantified in terms of the forces acting on a unit length at the solid–vapour interface. Surface free energies tend to increase as concentration increases. That is, as the concentration increases the surface free energy increases until a maximum value is reached and it starts to decrease with an additional increase in concentration. Recall that, at low concentrations there is an attraction between the particles themselves as they dissolve completely. Here the surface energy increases due to strong cohesive forces. But when the concentration increases, the solubility reduces and some of the particles are suspended in a liquid, there is a Van der Waals pull that minimizes the surface area and hence decreases in surface energy. This would then mean that high concentration tends to lower surface energy. The results in Table 4 indicated that surface free energy increases with the absorbance in PVA and PVAC. The table shows that the two polymers are interrelated in properties. PEG shows an increase in surface energy and later decreases after a maximum is reached. The particles of polymers attract themselves at low concentrations irrespective of the value of absorbance. Results have shown that the Hamaker constant increases with the concentration until a maximum is attained and it starts to decrease. This means that the more the particles interact with themselves the more the absorption and high cohesive force. The high value of Hamaker at the absorbance of 0.368 shows the highest cohesive force and lowest at 0.148 for the lowest interaction. The highest value of the Hamaker constant is 1.405x10^{-16} or 0.1405x10^{-21}J. the finding of this research work suggests a thermodynamic criterion for polymer concentration that will make it the least hydrophobic. Every polymer has a concentration at which it exhibits the highest surface free energy.

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