Measurement of density and determination of partial molar volume

The paper is an evaluation report on the partial molar volume, surface tension, and viscosity data of the cyclohexane-benzene binary system, a mixture of nonelectrolyte liquids. Based on many studies, the benzene-cyclohexane system is a well-established as a test system for excess molar volumes measurement devices. This excess molar volume is directly related with the partial molar volume that will be discussed later.

The students assumed that there is no significant difference between the changes in concentration and the viscosity of the system. It is also hypothesized that there is no significant difference between the changes in concentration and the surface tension of the liquid. Furthermore, it is to prove that the data of the partial molar volume of the system is acceptable that there is a significant difference between the observed and expected value of the partial molar volumes of the system. The study aims to create a partial molar volume versus the mole fraction of benzene graph, to determine the partial molar volume of benzene-cyclohexane system at different concentrations using density measurement, and to compare it to a standard value predetermined by another experimental report.

The study also sought to determine the effects of concentration of the binary system to its surface tension and to its viscosity, to determine the effect of bulk solute concentration on the surface tension of aqueous solution, and to evaluate graphically the parameters of the Gibbs isotherm. Most thermodynamic variables fall into two types. Those representing extensive properties of a phase are proportional to the amount of the phase such as V, E, H, S, A, G, while those representing intensive properties are independent of the amount of phase like p and T. Among intensive variables in

thermodynamics are partial molar quantities defined by the equationwhere Q is any extensive quantities mentioned. So for the partial molar volume the equation isThe bar over the symbol indicates partial molar quantities.

The partial volume in the equation above can be thought of in several ways. It is the incremental volume obtained by adding a small amount of component i to the mixture while holding other components as constants. Another way is that it is the incremental volume obtained by adding one mole of component i to an infinite sample of the mixture. The partial molar volume is not necessarily the same as the volume of one mole of the pure component. The volume of a solution is dependent on its temperature and pressure and the amount of each component used to form the mixture.

For a binary system held at constant temperature and pressure, it can be written as its differential volume upon addition of removal or either component asSubstituting equation 1. 2 to equation 1. 3 will yieldand integrating the differential equation 1. 4 yields an expression which allows us to determine the solution's volume from the partial molar volumes of its componentsThe volumes given in the equations above are the partial molar volumes which are not necessarily equal to the molar volumes of the pure components.

Thus, equation 1. 5 suggests that volumes may not be additive. That is, if one liter of component A is to be mixed with one liter of component B, the final volume would not be likely two liters. This is because water molecules interact with ethanol molecules differently than they interact with other water molecules. The success of the experiment depends greatly upon the

care with which the computations are carried out. The density (?) of every solution was computed to within an accuracy of at least one part per thousand using the equationwhile the moles of each component were computed asAnother thermodynamic property studied in the experiment is the surface tension of the liquid.

Liquids tend to adopt shapes that minimize their surface area, for then the maximum numbers of molecules are in the bulk and hence surrounded by and interacting with neighbors. Droplets of liquids therefore tend to be spherical, because a sphere is the shape with the smallest surface-to-volume ratio. However, there are may be other forces present that compete against the tendency to form this ideal shape and, in particular, gravity may flatten these spheres into puddles or ocean. The molecules at the surface of a liquid are subjected to an unbalanced force of molecular attraction as the molecules of the liquid tend to pull those at the surface inward while the vapor does not have as strong an attraction. This unbalance causes liquids to tend to maintain a minimum surface area. The magnitude of this force is called the surface tension.

The symbol for surface tension is ?. Conventionally, the tension between the liquid and the atmosphere is called surface tension while the tension between one liquid and another is called interfacial tension. The surface tension is depend in the ideal solution on the concentration and temperature which shown by Williard Gibbs thus the following equation is named Gibbs Isotherm (constant temperature)where ? is the surface tension in dynes/cm, C is the bulk solute concentration moles/cm^3, and u is the surface concentration moles/cm^2, R is gas constant and T is constant or particularly

as the room temperature. The method used in the experiment is static method wherein the use of equipment called Du Nouy Tensiometer was shown, which consists of a platinum-iridium ring supported by a stirrup attached to the beam of a torsion balance. The ring is placed at the interface of two liquids or at the surface of a liquid with air. It is then pulled upward until it breaks free of the liquid and moves into the second liquid or into the air.

The force that is just requiring breaking the ring free of the liquid/liquid or liquid/air interface is proportional to the surface tension. Another property of the liquid or solution is the viscosity. The general concept of viscosity is a familiar one. Less mobile liquids such as tar and lubricating oils are said to have greater viscosity than the more mobile liquids such as water and benzene. In general, it may be stated that the flow rate of a liquid is determined by its viscosity.

More precisely, the resistance experienced by one layer of liquid in moving past another layer is called the viscosity. A column of liquid in a circular tube can be considered to be made up of concentric layers, or cylinders of liquid. In moving through the tube, the layer nearest the wall remains stationary if wetting of the surface takes place. Each successive inner layer moves past, on the inside, with a velocity that increases as the centre of the tube is approached.

It is known as streamline flow and is generally characterised by the absence of eddies and turbulence. Hagen and Poiseuille obtained the following equation applicable to the Ostwald procedure, where p is hydrostatic

pressure on the liquid (proportional to the density ?), t is the time of flow in seconds, r is the radius of the tube, l is the length of the capillary in centimetres, and V is the volume of the liquid in cubic centimetres. The equation may be determined experimentally for a given viscometer so that the absolute viscosity can be calculated. The usual procedure is to determine the viscosity relative to a reference substance at a selected temperature.

This is determined as the relative viscosity. Water at 20oC is usually used as the reference liquid. Delta P can be expressed as the product of density of the liquid, gravity and height which varies during measurement yielding to equation 1. 10 and manipulating and simplifying it will yield to equation 1. 11.

where A is a constant for a given viscometer which can be determined through calibration with a liquid of known viscosity and density at a given temperature. MethodologyThe experiment was conducted to determine the properties of Cyclohexane-benzene binary solution. Properties include measurement of density and determination of partial molar volume, determination of surface tension, and measurement of viscosity by capillary flow method. The methods will be discussed separately to understand simultaneously such properties of the liquid mixture: cyclohexane and benzene.

The most common method of measuring partial molar volumes is to measure the dependence of the volume of a solution upon its composition. The observed volume can then be fitted to a function of the composition using MS Excel application and the slope of this function can be determined at any

composition of interest by differentiation. This experiment used equipment and apparatus such as pycnometer, 250-mL beakers, 25-mL graduated cylinders, 10-mL pipet, 2-mL pipet, top-loading balance and aspirator. The pycnometer (see Appendix D, Figure 1) is a glass flask with a close-fitting ground glass stopper with a capillary hole through it.

This fine hole releases a spare liquid after closing a top-filled pycnometer and allows for obtaining a given volume of measured and/or working liquid with a high accuracy. Calibration of the pycnometer to determine its weight and volume was first performed. It was done by filling the pycnometer with water thoroughly without the presence of tiny bubbles. In the calibration, the group acquired the volume of the pycnometer by the difference of mass of pycnometer with and pycnometer without water resulting to the mass of water divided by the density of water with respect to its temperature. Different concentrations of 60cm3 Cyclohexane-benzene mixture were prepared in separate beakers. The pycnometer was filled with the mixture one at a time then covered with the thermometer and glass stopper.

Elimination of the overflowed mixture by wiping the surface of the pycnometer was meticulously finished. The temperature of the weighed mixture was recorded. Using the same principle, the density of the mixture is the change in mass of the pycnometer after sample is contained in it per computed volume of the pycnometer. Same method is applied to all mixture.

After weighing a mixture using top-loading balance, the pycnometer was cleaned by pouring out its content, washing, drying in the oven with minute amount of ethanol. The group was cautious in washing the pycnometer and

kept it uncontaminated before drying since flammable compounds were used. Before the repetition of the steps, the experimenters waited until the high temperature of the pycnometer decreases to room temperature. For the partial molar volume of ethanol-water system, the values for the partial molar volume of benzene, C_6H_6 vs. mole fraction of cyclohexane, C_6H_{12} was plotted.

The data was expected to have a parabolic path. MS Excel was used in determining the most fixed quadratic equation on the data. Tangent lines to the curve through the plotted points were positioned. A measurement of distance of the y-value by means of horizontal lines to the intersection of the tangent line at molar fraction points was obtained. The partial molar volume was then determined by the addition of the initial molar volume of the mixture. Surface tension is a measurement of the cohesive energy present at an interface.

The molecules of a liquid attract each other. The interactions of a molecule in the bulk of a liquid are balanced by an equal attractive force in all directions. Equipment and glassware used in the experiments were Du Noüy tensiometer (see Appendix D, Figure 2), 50-mL volumetric flasks, 1-mL pipets, rubber aspirators. Du Noüy ring method is one technique by which the surface tension of a liquid can be measured. The method involves slowly lifting a ring, made of platinum iridium alloy, from the surface of a liquid.

The force required to raise the ring from the liquid's surface is measured and related to the liquid's surface tension. The group performed three trials of pure water for calibration then obtained its mean value. Calculation for the

surface tension correction factor is equal to the difference of the mean value and literature value of the surface tension. If the difference is positive, it would be subtracted to the measured surface tension of binary solution; otherwise, it would be added. Concentrations were prepared with fixed increments of cyclohexane-benzene solution. The concentration of the solution was obtained by getting the product of the density and volume of benzene divided by the molecular mass of benzene multiplied by volume of solution.

To clearly understand, see Appendix A: Sample computation. Surface tension of cyclohexane-benzene solution was determined by pouring two-thirds of the mixture in the sample flask. The Du Noüy tensiometer automatically measure surface tension in clicking buttons in five steps: Up, Stop, Peak, Down, Stop. Up button was first clicked so the vessel will be raised until the Du Noüy ring break the surface tension of the liquid then stopped followed by Peak then Down until it break again the tension then stopped. The group plotted the natural logarithm of concentration and the surface tension to observe their relationship.

Then, the computation for surface tension using the slope of the line was done. The group last performed the measurement of viscosity of cyclohexane-benzene solution by capillary flow method or Ostwald-Fenske method to be specific. Ostwald-Fenske method made use of the Hagen-Poiseuille equation for the determination of liquid viscosities by measuring the time flow of a given volume liquid through a vertical capillary tube under the influence of gravity. The experimenters performed the measurement of viscosity using Ostwald-Fenske viscometer (see Appendix D, Figure 2), pipet,

rubber suction bulb, volumetric flasks and beakers. The viscometer was filled with 10mL of the pure benzene.

The viscometer was fractionally immersed in the water bath at room temperature. Using suction bulb, the liquid was drawn into the viscometer up to the capillary arm until the feed bulb was filled and the meniscus was above the upper mark. When the liquid was in the upper meniscus, the group recorded the time elapsed from the upper mark to the lower mark. The method was repeated for pure cyclohexane. Mixtures with different concentrations of cyclohexane and benzene were also measured. Fixed increments in addition to the volume were performed to have different concentrations.

The mixtures' concentrations were determined by dividing the volume of cyclohexane and benzene. Ostwald Fenske method was also applied. For the calculation of viscosity, it is important to compute for the area of contact, A, which is constant. It can be determined through calibration with a liquid of known viscosity and density like pure water. In performing these experiments, the group was cautious with every procedure since benzene and cyclohexane are flammable and benzene is carcinogenic.

It is important to be familiar with the compounds first before using the binary compounds like the experimenters did.