



Study of binary system glycerine–water and its colloidal samples of silver nanoparticles



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ABSTRACT

Density, refractive index and viscosity of the binary system propane-1,2,3-triol (glycerine)–water in a temperature range of 283.15–363.15 K at atmospheric pressure were measured for all concentration range. Excess molar volumes were calculated from experimental densities and correlated using the Redlich–Kister equation. Also molar refraction and polarizability were calculated from experimental data on density and refractive index. Obtained experimental data can serve as an input for subsequent study of colloidal samples of metal nanoparticles dispersed in glycerine–water system, especially for dynamic light scattering analysis of nanoparticle size and zeta potential. Presented data were compared with those determined previously or obtained by different analysis with a good agreement.

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1. Introduction

System propane-1,2,3-triol (glycerine)–water is widely used for many applications, e.g. as cryoprotectors for preservation of biomaterials used for damping of intracellular ice formation and damage of biological tissues [1–3], the stability of biological molecules is explained precisely by glycerol presence [4]. Glycerine–water is also widely employed in nanotechnology fields, e.g. for preparation of colloidal samples of metal nanoparticles [5,6]. System glycerol–water has got a big advantage especially for preparation of metal nanoparticles with expected usage in medicine, because the glycerol seems to be a promising non-toxic and environmentally friendly liquid [6].

Dispersions of metal nanoparticles (NPs) are studied frequently during the last decades for their unique physical and chemical properties which differ from the “bulk” materials [7] and also for their wide range of applications. They can be used for grafting on different substrates to improve their cytocompatibility or antibacterial properties [6,8], for tumor treatment [9–11], and for many other different applications [5,12].

Colloids of metal NPs can be prepared by variable approaches, e.g. by different reduction syntheses or by sputtering of metals into poly(ethyleneglycol) or into glycerine and subsequent dilution by water for stabilization of these systems [5,6,13–20].

The main advantage of the new approach of preparation of AgNPs by sputtering is in an elimination of several chemicals [21]. That is more ecological way. The traditional chemical preparation (wet methods based on reduction chemical reactions) require usage of many chemicals and additives (e.g. reduction agents, surfactants), which can influence all colloidal system and its final properties such as shapes and size of nanoparticles, stability [22]. Prepared system is necessary to purify and remove an excess of agents. These deficiencies of traditional approaches can be eliminated by our new cathode sputtering method. In addition, in this case of preparation of AgNPs into glycerine has got another important advantage, glycerine serves also for electrostatic stabilization of prepared nanoparticles itself, which eliminate usage of any other stabilizing chemicals.

Glycerine due to its low value of interface tension, low vapor pressure, low toxicity and good biocompatibility is a suitable liquid for preparation of metal NP colloids, in which high nucleation rates are achieved and particles have low dimensions [5,6]. Due to presence of hydrophobic and hydrophilic part of molecules of glycerine it is able to orient itself to the metal nanoparticles and these colloids are quiet stable [23].

In all applications of nanotechnology the size, shape and surface charge (electrokinetic potential, zeta potential) of metal NPs dispersed in solutions play an important role for their stability and applications [5,6,20]. It is necessary to determine these properties precisely. There are several methods for determination of NPs size, e.g. UV–vis spectra measurement, electron microscopies or dynamic light scattering (DLS) [5,6]. DLS is an analytical method commonly used for determination of several properties, as the hydrodynamic size, its distribution and zeta potential of the NP colloids in a liquid medium. DLS is the input data

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intensive and sensitive method. It needs many physico-chemical properties of solution, such as viscosity, refractive index [24]. When we need to study the metal NPs dispersed in system glycerol–water, we need accurate input data. These experimental data are only sporadic in literature and it is necessary for the experimental determination of them for the correct and accurate study of colloidal samples of metal NPs by DLS method.

In this work we studied physico-chemical properties (density, excess molar volume, refractive index and viscosity) of binary systems glycerine–water in all concentration range and temperatures between 283.15 and 363.15 K (283.15, 293.15, 298.15, 303.15, 313.15, 323.15, 333.15, 343.15, 353.15 and 363.15 K) at atmospheric pressure as the important input data for subsequent DLS study of silver nanoparticles (AgNPs) prepared into these binary systems. The size and zeta potential of AgNPs in glycerine–water was studied by DLS. Concurrently, we performed transmission electron microscopy with high resolution (HRTEM) and transmission electron microscopy (TEM) analysis to confirm the accuracy of size AgNPs determined by DLS determination. Experimental data on density and refractive index served also as input data for determination of molar refraction and polarizability as the function of concentration and temperature.

2. Theory

Shape and size of prepared nanoparticles depend on several important factors [5,6,25–27] of (i) sputtering approach, such as sputtering power, discharge voltage, and (ii) physico-chemical properties of liquid medium (liquid substrate) such as density, viscosity, excess molar volume. Many authors also discussed as important the properties for dispersions of metal NPs such as viscosity, concentration, density, excess molar volume and other properties of liquid medium [20,21].

For stability of prepared colloidal samples the concentration of solution is important [20]. It can be due to the so-called excess molar volume. When mixing liquids which behave as the ideal ones, the total volume is given by a summing up of volume of individual liquids. During mixing of liquids of non-ideal behavior, the total volume can expand or contract due to interactions between molecules of individual components. Both liquids under our study, glycerine and water, have strong H-bonds which result in the dramatic decrease of the total volume during mixing. This volume difference is represented by the excess molar volume. Determination of accurate excess molar volume is relatively easy by calculation from experimentally measured density. Currently density measurements are carried out using the vibrating-tube densimetry technique. Density determination by vibrating densimeter is based on measurement of resonant frequency of the measuring cell, which is presented as a linear relation between density and frequency [28–30]. The excess molar volumes, V_m^E , coincide with the mixing volume $\Delta_{\text{mix}}V$, which is calculated from the experimental densities by a relation [28–30]:

$$V_m^E = \Delta_{\text{mix}}V = V_{\text{ms}} - \sum x_i V_{\text{mi}} = \frac{(x_1 \cdot M_1 + x_2 \cdot M_2)}{\rho} - x_1 \cdot \frac{M_1}{\rho_1} - x_2 \cdot \frac{M_2}{\rho_2} \quad (1)$$

where V_{ms} and V_{mi} stand for the volume of one mol of the real mixture and molar volume of component i , x_1 and x_2 are the mole fraction of glycerine and water, resp., M_1 and M_2 are their molar weights, ρ_1 and ρ_2 are the densities of pure glycerine and water, resp. and ρ is the density of mixture of glycerine and water of relevant concentration (mole fraction). The simplest semi-empirical expression using to correlate experimental data of excess molar volumes is that proposed by Redlich and Kister [31]:

$$V_m^E = x_i \cdot (1-x_i) \cdot [A_1 + A_2 \cdot (1-2 \cdot x_i) + A_3 \cdot (1-2 \cdot x_i)^2 + \dots] \quad (2)$$

where parameters A_1 , A_2 , A_3 , etc. are valid for a single temperature.

Vibrating tube densimeters provide directly density values and the measurement is based on the determination of a resonant frequency of the measuring cell, f . Density of studied liquid, ρ is then calculated by a relation [28–30]:

$$\rho = \frac{a}{f^2} - b \quad (3)$$

where ρ is the density of measured liquid, a and b are calibration constants dependent on temperature. Calibration constants are evaluated from measurements realized by two reference compounds with known density.

Measured values of density, ρ , and refractive index, n , can serve as input data for the following calculation of other physico-chemical properties, such as specific refraction, molar refraction, and polarizability [32,33]. Molar refraction, R_M , can be determined by Eq. (4):

$$\frac{(n^2-1)}{(n^2+2)} = r \cdot \rho = \frac{R_M}{M} \cdot \rho \quad (4)$$

where M is the molar weight of liquid (for binary mixture of two liquids $M = x_1 \cdot M_1 + x_2 \cdot M_2$).

Molar refraction, R_M , can be also determined by usage of the so-called group contribution methods [34–40]. Group contribution methods are based on the “additive principle”. That means any compound can be divided into fragments (usually atoms, bonds or group of atoms). All fragments have a partial value called a contribution. These contributions are calculated from known experimental data. Property of a compound is obtained by a summing up of the values of all contributions present in the molecule. For molar refraction, R_M , it can be determined by the Eq. (5) [34–40]:

$$R_M = \sum \nu_i \cdot R_{M,i} \quad (5)$$

where $R_{M,i}$ are molar refractions of individual fragments of relevant compound and ν_i is a number of its occurrence in the molecule.

Polarizability, α , can be calculated by the Clausius–Mossotti or by the Lorentz–Lorentz relations, Eq. (6) [32,33]:

$$\frac{(n^2-1)}{(n^2+2)} = \left(\frac{4\pi}{3}\right) \cdot \left(\frac{\rho}{M}\right) \cdot N_A \cdot \alpha \quad (6)$$

Shape and size of prepared nanoparticles depend on physico-chemical properties of liquid substrate. An important substrate property is viscosity, which is strongly affected by temperature. The viscosity can play the role for the nanoparticle movement, which can be lower in liquid surrounding of higher viscosity in comparison with lower viscosity. On the other hand, for stability of colloidal system the zeta potential is more important. And it is affected strongly by concentration and viscosity of liquid surrounding. In most of heterogeneous systems consisting of solid material in liquid medium the interface exhibits an electrical charge. This charge plays the important role in stability of these systems and in their behavior [41–43]. When the surface is charged, then it can attract ions of opposite charge (counter-ions) from the liquid. In this way the electrical double layer is created, consisting of two oppositely charged layers. The counter-ions are bonded to the surface either by electrostatic or adsorption forces. Between the surface and volume liquid phase is a potential gradient of the same charge as the surface charge. Potential of volume liquid phase is equal to zero. When the liquid flows along the solid surface, the electrical double layer divides. Inner layer (the solid phase) does not move, and adsorbed or bonded counter ions, while the outer layer flows along. The potential created at this mobile interface is known as electrokinetic potential or zeta potential (ζ -potential). This zeta potential strongly depends on concentration and viscosity of liquid medium. When concentration increase, the created electrical double layer is pressed and surface charge changes

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