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Experimental and theoretical description of a technique for the concentration measurement of binary liquids containing nanoparticles



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ABSTRACT

Nanoparticles are known to enhance both the heat and mass transport properties of fluids in which they are suspended resulting in significant interest for many fields, including refrigeration systems whose efficiency is linked to effective heat and mass transport. Within absorption refrigeration the concentration of the binary liquid is a key component in evaluating the performance during operation. Conventional techniques for concentration measurement rely on properties such as the density or electrical conductivity which are changed when nanoparticles are present. In addition to changing the thermophysical properties by adding nanoparticles, the volume fraction of the nanoparticles changes during a mass transfer process which further complicates the concentration measurement. The method presented here is a density based measurement that incorporates the changing volume fraction of the nanoparticles and concentration of the base fluid. Experiments include LiBr and LiCl solutions containing silver and iron-oxide nanoparticles at multiple initial volume fractions and particle sizes. The method developed is extremely robust and useful, as it is possible to determine the concentration of any unknown sample based only on knowledge of the initial concentration of base liquid and nanoparticle volume fraction when the sample is synthesized.

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1. Introduction

Hygroscopic inorganic salts in the form of binary liquids such as lithium bromide and lithium chloride solutions are among the chemical sorbents for applications such as absorption refrigeration, air dehumidification, desiccant cooling, and heat pumps. To enhance thermo-physical and transport properties of binary liquids, the dispersion of nanoparticles in base fluids has been proposed in different applications such as: gas absorption [1], refrigeration systems [2], and direct absorption solar thermal collectors [3]. These nano-sized particles can enhance the thermal conductivity as demonstrated in water based aluminum oxide nanoparticles [4], n-decane oil in binary liquids [5], and carbon nanotubes and aluminum oxide in ammonia water solution [6]. Also, boiling heat transfer is reported to be altered by several nanoparticles such as titania [7], and alumina nanoparticles dispersed in water [8,9]. Moreover, the optical properties are reported to be changed for water and ethylene glycol with dispersion of silver nanospheres and silica-gold core-shell nanoparticles [10], and for optical filters made by nanoparticle suspension [11]. Also, the change of absorption and scattering properties of glycol suspension contains carbon nanoparticles is reported promising for direct solar absorbers [12]. In a study using lithium bromide/water (LiBr/H₂O) binary liquid, the effect of carbon nanotubes and iron nanoparticles on the vapor absorption process was investigated, indicating that the rate of vapor absorption is enhanced by iron nanoparticles and carbon nanotube at the concentration of 0.1 wt.% to the average of 1.9 gs^{-1} and 2.48 gs^{-1} respectively [13]. Additionally, the increased thermal conductivity of a LiBr/H₂O binary mixture due to the stable dispersion of Al₂O₃ nanoparticles has been studied for different concentrations of nanoparticles [14].

In applications dealing with heat and mass transfer, concentration of the binary liquid is among the important parameters for design, performance evaluation, and control of the system. For example in the dehumidification process, the vapor pressure of the desiccant is a function of the concentration such that at higher concentration, the vapor pressure is lower, and consequently the potential for mass transfer would be lower. Also, the inlet concentration of the desiccant has an influence on the dehumidification performance [15]. On the other hand, characterization of fluids containing nanoparticles has a critical role in understanding novel properties of them [16]. Therefore methods of obtaining the concentration based on its correlation with physical properties of

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Nomenclature			
Φ volume fractionCconcentrationVvolume ρ densityuuncertaintya, bexperimental coefficientsPprobability	Subscr np bf w i t	<i>ipts</i> nanoparticle base fluid water initial total	

the pure liquid are most common [17,18]. These properties include: density, viscosity, electrical conductivity [19–21], refractive index, dielectric constant, sound velocity of the fluid, ultrasound, and electromagnetic radiation absorption [17,18, 22–24]. All of the properties mentioned are significantly impacted by the presence of nanoparticles. All of the properties above have been studied in the presence of nanoparticles on the volume fraction, particle size, shape and material [25–28]. Because of this many empirical correlations have been proposed, but a limitation of these correlations is that they require extensive testing and development for each new fluid, particle, and volume fraction utilized.

Density measurements of a colloidal dispersion of nanoparticles are accurately predicted with the Hamilton-Crosser mixing model [29] which requires knowledge of particle volume fraction and liquid density (for a binary liquid this is concentration dependent). Initially, this empirical equation was used for Al₂O₃ and TiO₂ nanoparticles dispersed in water at room temperature [29]. It is further verified for many types of nanoparticles in mixture of water and ethylene glycol at different concentrations [30]. The most common technique for measuring the concentration of binary liquids is based upon the density [24,31]. While the density measurement at one condition is straightforward, in a process where mass transfer is occurring, the concentration of the working fluid is changing. This results in the volume fraction of nanoparticles in the suspension also changing, complicating the use of a density measurement for concentration. Therefore the mixing rule by itself, which requires the knowledge of volume fraction of nanoparticles is not sufficient to determine the density. To overcome this problem, we propose a method whereby only the initial concentration of base liquid, initial volume fraction of nanoparticles, and density of the nanoparticles is required a priori. The method developed provides a convenient experimental procedure for determining the concentration of aqueous LiBr and LiCl solutions containing suspensions of nanoparticles in terms of density. This method can be applied for any other liquid and it is independent of operational conditions. Therefore, it provides a simple technique to find the concentration of binary liquids in any mass transfer system.

2. Theoretical approach

The starting point for the new method is the prediction of the density of the fluid composed of the base fluid and nanoparticles using the Hamilton–Crosser mixing model which relates the density of the mixture to the density of the base fluid and nanoparticles and is stated in Eq. (1) [29].

$$\rho = \phi_{np}\rho_{np} + (1 - \phi_{np})\rho_{bf} \tag{1}$$

where φ_{np} represents the volume fraction of nanoparticles, ρ_{np} and ρ_{bf} are the density of nanoparticles and base fluid respectively. Depending on the type of binary fluid, the density is related to

the concentration via an empirically derived relationship. For simplicity and due to the range of concentrations used here, we utilized a linear relationship between concentration and density as shown in Eq. (2).

$$\rho_{bf} = aC + b \tag{2}$$

where a, and b are empirical coefficients obtained for a given binary liquid and C is concentration. Eq. (1) is not sufficient to determine the density of a mixture after a mass transfer operation primarily due to the change in the nanoparticle volume fraction. To find the density of nanoparticle suspension independent from changing parameters in a mass transfer operation, we define the nanoparticle volume fraction using Eq. (3).

$$\phi_{np,i} = \frac{V_{np}}{(V_{np} + V_{bf,i})} \tag{3}$$

where $V_{bf,i}$ and V_{np} represent the initial volume of the base fluid and volume of the nanoparticles respectively and $\Phi_{np,i}$ is the initial nanoparticle volume fraction (or the nanoparticle volume fraction at the time of synthesis or mixing into the base fluid). Assuming a stable dispersion, the nanoparticle volume fraction after a mass transfer operation that results in a change in concentration of the base fluid can be found using Eq. (4).

$$\phi_{np} = \frac{V_{np}}{(V_{np} + V_{bf})} \tag{4}$$

where V_{bf} is volume of the base fluid after changing the concentration. The concentration of the salt after a mass transfer operation is given in Eq. (5).

$$C = \frac{C_i m_{bf,i}}{(m_{bf,i} + m_w)} \tag{5}$$

where $m_{bf,t}$ is total mass of the base fluid, C_i is initial concentration of the salt in binary liquid (again as defined at the time of adding nanoparticles), and m_w is mass of the water resulting from the change in concentration in an aqueous binary liquid. Using Eq. (5) one can solve for m_w and the resulting volume from the density of water. With the knowledge that the volume of the base fluid after a change in concentration would be the sum of the initial volume of the base fluid and the resulting volume from the water used in changing the concentration, the total volume of the base fluid, V_{bf} , is found according to the Eq. (6).

$$V_{bf} = \left(\frac{1}{\phi_{np,i}} - 1\right) \left[1 + \frac{\rho_{bf,i}(C_i - C)}{C\rho_w}\right] V_{np}$$
(6)

By substituting equation (6) into Eq. (4), the nanoparticle volume fraction after a change in concentration is found:

$$\phi_{np} = \frac{C\rho_w \phi_{np,i}}{[C\rho_w + (1 - \phi_{np,i})(C_i - C)\rho_{bf,i}]}$$
(7)

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