Thermo-physical properties of the nano-binary fluid (acetone–zinc bromide-ZnO) as a low temperature operating fluid for use in an absorption refrigeration machine

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Abstract

The current technical note is an expression for extending aspects of the previous work of Ajib and Karno [1] which related to the thermophysical properties of acetone / ZnBr2. The study covers the thermal conductivity of a solution which appears to be a promising fluid for operating vapour absorption refrigeration (VAR) systems from a low temperature source. It covers also an investigation of acetone / ZnBr2 – ZnO nanofluid including the preparation, stability, structure and properties, a zinc based nanoparticle being chosen in order to reduce chemical interactions. Furthermore, this study illustrates an extension of the log p, T diagram of the acetone zinc bromide up to 1.39 bar. The results show that the thermal conductivity drops with increasing salt concentration. With increasing nanoparticles, the density, viscosity and the thermal conductivity increase, as expected, but the heat capacity drops. Both theoretical and experimentally derived formulae for ZnO nano fluid conductivity from the literature are seen to produce good correspondence to the conductivity measured here, but in the case of the theoretical formula, the influence of particle morphology is seen to be significant. The results indicate that converting the acetone / ZnBr2 to a nanofluid provides a potential improvement of performance of this fluid in the vapour absorption refrigeration system, but that suspension stability is difficult to attain.

1 Introduction

An operating fluid for an absorption refrigeration machine consists of a refrigerant and an absorbent. Both components must have the properties that the refrigerant can be absorbed by cooling water temperatures of 20–40 °C and separable out of the solution again at desorption temperatures higher than 50 °C [1].

Most common working fluids are NH3/H2O and H2O/LiBr. Macriss et al. [2] provided a survey of absorption system fluids; they suggested that there are about 40 refrigerants and around 200 absorbents which can be used in absorption systems. A group of engineers [3] studied the properties (thermal capacity, thermal conductivity, viscosity, surface tension and density) of the NH3/H2O for industrial design of absorption refrigeration systems. In 1996, Xu et al. [4] studied the theoretical analysis of a double effect absorption system using H2O/LiBr as a working fluid. H2O/LiBr is used in many literatures for various purposes described in the following [5–11]. Kim and Machielsen [12] evaluated the air cooled solar half effect absorption cooling system using NH3/H2O, NH3/NaSCN and NH3/LiNO3 and they found that the last solution showed the best results regarding coefficient of performance (CoP). Sencan et al. [13] used an artificial neural network model to analyse the absorption system using H2O/LiCl and H2O/LiBr and they found that the H2O/LiBr has a greater CoP than H2O/LiCl. Grossman et al. [14] simulated the absorption system by computer modelling using different solutions such as H2O/LiBr, NH3/H2O, CH3OH/LiBr-ZnBr2 and they wrote a code for the properties of each solution. In 2008 Ajib and Karno performed two studies [1, 15] related with the properties of acetone zinc bromide...
((\text{CH}_3)_2\text{CO}/\text{ZnBr}_2) and analysis of an absorption refrigeration system, a fluid combination which worked well with a low temperature heat source and it is proposed that it is used in the present research. They experimentally found that the CoP for the single effect absorption refrigeration with acetone/\text{ZnBr}_2 is 0.4 with a heat source under 60 °C. This pair were mentioned in the review of Sun et al. [16] in 2012 as a low temperature working fluid. The acetone has a melting point of 94.6 °C and it can provide sub 0 °C cooling temperature, however, the \text{ZnBr}_2 has a boiling temperature of 650 °C and it is not volatile [17]. In 2016, Hamilton [18] analysed a low temperature waste heat source (80 °C) for an absorption system working with acetone/\text{ZnBr}_2. He stated that the absorption refrigeration system has the ability to provide adequate heat removal at the heat source and the ability to deliver cooling from this low-level energy. One of the ideas to improve the heat transfer in the absorption system is by converting the basefluid (acetone / \text{ZnBr}_2 in our case) to a nanofluid. We consider that since the salt is based on zinc, a suitable nanoparticle to suspend without chemical interaction might be \text{ZnO}.

![Image of a bottle with a clear liquid.](https://via.placeholder.com/150)

The results of our investigation show that the nanoparticles improve the thermophysical properties of the solution and improve the heat transfer in the boiler section of VARS. In the following we illustrate the thermophysical properties of this working solution (acetone/\text{ZnBr}_2 - (\text{ZnO})) and different aspects of this solution, which were not covered by Ajib and Karno [1], such as thermal conductivity. During our test on the VARS we extend the log p, T diagram of the acetone zinc bromide up to 1.39 bar for two cases. The following sections explain the source and preparation of the fluid, and show the properties of the density, viscosity, thermal conductivity, heat capacity and the vapour pressure of the solution.

### 2 Sources of the materials

The materials (acetone, \text{ZnBr}_2 extra pure, and \text{ZnO} nanoparticles (50 nm)) were purchased from Sigma-Aldrich Company Ltd.

### 3 Preparation

There are two methods commonly used for creating nanofluids. The first is a single (one)-step method and the second is a two-step method. The one-step process can prepare uniformly dispersed nanoparticles and the particles can be stably suspended in the base fluid. The two-step method consists of adding dry nanoparticles to the base fluid. Dry nanoparticle powders are preparing by inert gas condensation, chemical vapour deposition, mechanical alloying or other suitable techniques, and the nano-sized particles are then dispersed into a fluid in a second stage to synthesise a nanofluid. Agglomeration of nanoparticles in the two-step method is higher than the case of the one step method, especially in the process of drying, storage, and transportation of nanoparticles. Agglomeration in a nanofluid will have the undesirable effect of decreasing the thermal conductivity. To minimize the nanoparticle aggregations and improve the dispersion behaviour, techniques such as ultrasonic agitation or the addition of surfactants to the fluids are often used [19].

To prepare the binary nanofluid of this study (acetone/\text{ZnBr}_2 - (\text{ZnO})), a basefluid (acetone/\text{ZnBr}_2) is prepared with various mass concentrations (40 wt.% - 65 wt.% with incensements of 5%) of \text{ZnBr}_2 using the two step method. During mixing the refrigerant (acetone) and the absorbent (\text{ZnBr}_2), solution energy is released from the mixture, which is proportional to the amount of the \text{ZnBr}_2 mixed; the temperature of the solution may reach to 65 °C when 65 wt.% of \text{ZnBr}_2 is added to the acetone. This heat generates as a result of breaking bonds between the absorbent molecules and atoms. Stability and Transmission Electron Microscope (TEM) analysis of the nanofluid samples are performed as well as measurements of density, heat capacity, thermal conductivity and viscosity and comparing with data gathered by Ajib and Karno [1] for the same base fluid.

### 4 Zinc oxide (\text{ZnO})(susension stability study)

The first experiment produced an acetone - \text{ZnBr}_2/\text{ZnO} nanofluid with 50 wt.% of \text{ZnBr}_2 and different volume concentrations of \text{ZnO}. The solution samples are put into a sonication bath (38 KHz with ultrasonic effective output of 30 W), model SW1H produced by NICKEL-ELECTRO LTD [20] for 2 h. During sonication, some sedimentation appears with \text{ZnO} particle concentrations of 1 and 1.2 vol.%. Figure 1 shows nanofluid suspensions with different concentrations of \text{ZnO} and different sonication options. For the 0.3 vol.% concentration (bottle number 1), the solution converts to a brown colour because it was left in the ultrasonic bath for 24 h to check the effect of extended sonication. The heat generated through the sonication process converts the solution colour from white to brown. The heat and (or) laboratory light converts the zinc bromide-acetone solution to brown within 24 h in a bright laboratory when it is maintained at 55 °C, and 15 days with light at the lab temperature of 20 °C is also enough to change the colour. This is due to the degradation of zinc bromide forming bromine. The bottle number 2 was prepared without sonication. The other samples were left in the ultrasonic bath for 2 h. The sonication process time has no significant influence on the duration of suspension stability. In the Fig. 1d, by comparing the top part of the bottle 4 with the top part of the bottle 3, it can be seen that the top part of the bottle 4 is clearer than the same region of bottle 3. This is because bottle 4 contains a greater concentration of nanoparticles, and the particles are close to each other and together with the high surface area of
the nanoparticles, they gather and agglomerate to produce bigger agglomerations of particles and consequently faster sedimentation. But in bottle number 3 the particles are separated by relatively large distances between them and they take a longer time to reach each other and agglomerate. From this behaviour it is concluded that the higher concentration of nanofluids sediment completely significantly faster than the dilute nanofluid. Since the duration of stable quiescent fluid suspension is seen here more than 1.5 h (lab. Experiment time), experiments on efficacy of the nano fluid in assisting heat transfer are only reliable for this duration without further intervention to improve stability. Despite this limitation on quiescent fluid, it is expected that the continuous fluid disturbance of boiling in the absorption refrigeration cycle may help to maintain the suspension for longer.

Three surfactant agents were tested in an attempt to improve stability. Samples were prepared with the same concentration of nanoparticles (0.5 vol.%) and by adding 1 wt. % of the surfactants (poly vinyl pyrrolidone (PVP), sodium dodecyl sulphate (SDS) and polyvinyl alcohol (PVA)). As shown in Fig. 2 by comparison with the settling time in Fig. 1, these types of surfactants are initially effective on the sedimentation time of nanoparticles. But after 1 h, the surfactants gather on the top surface of the samples and the particles start to settle. Also, the PVA cannot dissolve in the acetone / ZnBr₂ solution. Therefore, no suitable surfactant was found for this combination in this work.

TEM is the primary technique to verify single particle dimensions and to show the distribution of the particles in the fluid. TEM samples were prepared by casting several drops of the sample solution onto copper-mesh holey-carbon film TEM grids. Holey carbon films provide a carbon support film with a range of relatively small hole sizes, particularly suited for suspensions of nanoparticles. By imaging the samples of ZnO nanoparticles, the structure of them can be illustrated as in Fig. 3, which shows different images, illustrating the ZnO nanoparticles and ZnBr₂ behaviour on the copper grid and the carbon film for the sample acetone / ZnBr₂ based on ZnO. Figure 3 (a) and (b) show random star shapes inside the holes of the carbon film; this is caused by the crystallization of the ZnBr₂ on ZnO particles which form crystal nucleation sites.

![Fig. 1 Sedimentation of different concentration of ZnO nanoparticles in acetone - ZnBr₂.](image)
due to the drying process which must be done in order to conduct the TEM. Figure 3 (c) and (d) show very small grains appear between the holes of the carbon film, which seem to be ZnBr₂ crystals, since these grains only appear when the acetone / ZnBr₂ is used as a base fluid and they do not appear when acetone alone is used as a base fluid.

Fig. 3 Various TEM images of ZnO suspension in the acetone / ZnBr₂ solution on the copper mesh holey carbon film, a & b show the random star shape of the ZnBr₂ crystallization resulting from drying the solution for the TEM process and c & d show how grains appear in the hole of the carbon film.
5 Properties investigation

5.1 Density

The density of acetone / ZnBr₂ with different concentrations of ZnBr₂ measured in this work were significantly different to those measured by Ajib and Karno [1]. When the salt (ZnBr₂) is added and dissolved in the acetone, the volume of the total solution increases.

Table 1 shows the difference between the densities of different concentrations of acetone / ZnBr₂ as found experimentally, from literature and if the volume of acetone does not change when the ZnBr₂ is added. The volumetric flask had a narrow neck, which reduces the error in volume in making up the solution. The fluid level on the flask’s mark may have an error of ±0.5 mm and the diameter of the neck of flask is 10 mm, which make the error on volume ± 0.4% for a 10 ml sample. The results here show that the previous values for density of [1] are consistent with assuming no volume change due to adding the salt to the solvent.

The density of the nanofluid is new in this paper and there is no existing information on properties for it. The density of the nanofluid increases directly with increasing concentration of ZnO nanoparticles, for example, the density increases from 1368 to 1417 kg/m³ by increasing the volume fraction from 0.001 to 0.012. From the Fig. 4 it can be seen that the experimental results are approximately the same as the theoretical density found by the simple mixture idea as in Eq. 1.

\[ \rho_{nf} = (1-\Phi_p)\rho_f + \Phi_p\rho_p \]  

(1)

where the subscripts nf, p and f refer to nanofluid, particles and fluid respectively, \( \rho \) and \( \Phi \) refer to the density and volume fraction respectively.

5.2 Viscosity

The viscosity of the acetone with different concentrations of ZnBr₂ were measured (using hts-VROC Viscometer Rheometer On a Chip produced by RheoSense) and found to be the same as those measured by [1].

The viscosity of the acetone / ZnBr₂ nanofluid with different concentrations of ZnO at 25 °C is measured. The viscosity increased from 3.228 to 4.79 mPa.s with increasing concentration of nanoparticles from 0 to 1.2 vol.% as shown in Fig. 5. The measurement was repeated by the viscometer ten times for each sample. The viscosity of the acetone alone was found to be 0.308 ± 0.007 m Pa.s depending on the equation of uncertainty of the measurement, the maximum uncertainty was 0.4 mPa.s for the acetone / 50 vol.% ZnBr₂ with 1.2 vol.% ZnO as shown in Fig. 5. The Newtonian (i.e like a single-phase liquid) behaviour of the acetone/ZnBr₂ based ZnO nanofluids was observed also.

5.3 Specific heat capacity

The heat capacity of the acetone with different concentrations of ZnBr₂ were measured using TA instrument Q10 Differential Scanning Calorimetry (DSC) and found to be the same as those measured by [1]. The previous work did not cover the nanofluid of this solution, the current research reports a part of it. Figure 6 shows that the specific heat capacity is inversely proportional with particles (ZnO)

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**Table 1** Density of different concentrations of acetone / ZnBr₂ as found experimentally, from literature and if the volume of acetone does not change when the ZnBr₂ added

| ZnBr₂ Concentration | Density was reported in [1] (kg/m³) | Density as found by assuming no change in volume (kg/m³) | Experimental density for this work (kg/m³) |
|---------------------|-------------------------------------|-----------------------------------------------------|-----------------------------------------|
| 40%                 | 1293                                | 1317.5                                              | 1164                                    |
| 45%                 | 1420                                | 1437.2                                              | 1228                                    |
| 50%                 | 1581                                | 1581                                                | 1360                                    |
| 55%                 | 1778                                | 1756.6                                              | 1426                                    |
| 60%                 | 2013                                | 1976.2                                              | 1550                                    |
| 65%                 | 2292                                | 2258.6                                              | 1662                                    |

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concentration because the specific heat of these particles is low (0.487 J/g.K) compared with the specific heat of the base fluid (1.14 J/g.K). Figure 6 also shows that the difference between the theoretical results which is found using Eq. 2 and the experimental results increase for a higher volume fraction. Because with a higher concentration, the size of the particles increases due to the agglomerations as mention before. Larger particles size leads to drop the heat capacity, and this is confirmed by some previous works [21, 22]. Equation 2 is a simple mixture method used for thermal analysis of the nanofluid [23, 24],

\[
(\rho_v)_{nf} = (1-\phi)\rho_f c_p f + \rho_p c_p \phi
\]

where \( \rho_v \) is the specific heat capacity of the solution.

### 5.4 Thermal conductivity

The thermal conductivity of the acetone / ZnBr₂ as a base fluid or nanofluid was not studied by Ajib and Karno [1]. In the current study the thermal conductivity of the base fluid and nanofluid with different concentrations of ZnBr₂ in the solution (40–65 wt.%) and different concentration of nanoparticles was measured using the thermal conductivity analyser C-THERM TCI produced by C-THERM TECHNOLOGIES. It was found that the thermal conductivity of the solution decreases from 0.159 to 0.149 W/m.K with increasing concentration of ZnBr₂ from 40 to 65 wt.% as shown in Table 2. The thermal conductivity of the pure acetone and solid ZnBr₂ (salt) were measured separately by the same method and found to be 0.164 and 0.1 W/m.K respectively. The table shows how the thermal conductivity of the salt solution decreases with increasing the concentration of the salt.

The solution of acetone / ZnBr₂ with 50 wt.% ZnBr₂ was converted to a nanofluid with five different concentrations (0.1, 0.3, 0.5, 1, 1.2 vol.%) of ZnO nanoparticles, which has a thermal conductivity of 36 W/m.K as measured. The thermal conductivity of the nanofluid was measured after keeping these samples for 2 h in the sonication bath. The thermal conductivity increases from 0.152 to 0.168 W/m.K when the concentration of the Zinc Oxide nanoparticles increases from 0 to 1.2 vol.%, this means that the thermal conductivity increases by 10.53% as shown in Table 3.

Figure 7 presents the relation between thermal conductivity and volume fraction of ZnO for acetone / 50 wt.% ZnBr₂ based on ZnO. The Figure shows how the experimental results differ with the theoretical model assuming a spherical ZnO nanoparticle structure, which are based on Maxwell (Eq. 3) [25] and the experimental model, which was correlated by the experimental study of Suganthi (Eq. 4) [26] for ZnO nanoparticles suspended in ethylene glycol solution (EG).

| Concentration of ZnBr₂ (wt.%) | Thermal conductivity (W/m.K) |
|-----------------------------|-------------------------------|
| 40                          | 0.1593                        |
| 45                          | 0.1543                        |
| 50                          | 0.1524                        |
| 55                          | 0.1515                        |
| 60                          | 0.1505                        |
| 65                          | 0.1498                        |

Table 2  Relation of the thermal conductivity with the concentration of the ZnBr₂ in the acetone / ZnBr₂ solution at 24 °C

| ZnO nanoparticles (vol.%) | Thermal conductivity (W/K.m) | Enhancement % |
|--------------------------|------------------------------|---------------|
| 0                        | 0.152                        | –             |
| 0.1                      | 0.153                        | 0.96          |
| 0.3                      | 0.157                        | 2.97          |
| 0.5                      | 0.159                        | 4.79          |
| 1                        | 0.164                        | 8.12          |
| 1.2                      | 0.168                        | 10.53         |

Table 3  Thermal conductivity of the acetone/ZnBr₂ (50 wt.%) - ZnO with increasing the concentration of nanoparticles
\[
knf = \frac{k_p + \left(\frac{3}{\psi} - 1\right) k_f + \left(\frac{3}{\psi} - 1\right) (k_p - k_f) \Phi_p}{k_p + \left(\frac{3}{\psi} - 1\right) k_f - (k_p - k_f) \Phi_p}
\]

(3)

Where \(\psi\) is the ratio of surface area of a sphere with equal volume to the particle, to the surface area of the particle.

\[
k_{nf} = k_f \left(1 + 7.926 \Phi_p\right)
\]

(4)

Where \(k\) is the thermal conductivity of the solution, subscript \(f\) is base fluid and \(p\) is particle.

It is known that ZnO crystals take the form of either a hexagonal prism, or less commonly a cube. A hexagonal prism ZnO crystal is likely, with height 3.3 times the hexagon side length, which fits the description of some nano-crystals lengthening depending on reaction time during manufacture [27] producing a \(\psi\) of 0.365, with conductivity of ZnO as 36 W/mK, Eq. 3 produces an identical result to Eq. 4. In this way the theory of Eq. 3 can be seen to be consistent with eq. 4 when further details of the particle characteristics are taken into account.

Figure 7 shows that the thermal conductivity is proportional to the concentration of nanoparticles. The uncertainty for each case with and without nanoparticles is calculated depending on the uncertainty of measurement equation (half difference between maximum and minimum values). The maximum values of the uncertainty are 0.005 and 0.004 for the cases concentration of ZnO 0.1 vol.%. The conductivity of ZnO in this situation with ZnBr₂ is consistent with the formula develop from the experimental work of Suganthi [26] with ZnO in EG, reflecting the reliability of that experimental correlation. That the theoretical formula, Eq. 3, fits exactly the same line when crystal morphology is taken into account, expresses the likely reliability of the theoretical model also.

### 5.5 Vapour pressure

The plotting of (log p, T) diagram is required to define the solution concentration range of the operating process of the absorption refrigeration machine. Depending on this range, it could determine the necessary heat source temperature to operate the machine depending upon the boundary conditions. Ajib and Karno [1] presented a log p, T diagram up to 1 bar. In the current study, the log p, T diagram for two case (ZnBr₂ = 0 & 50 vol.%) are extended up to 1.39 bar (Shown in Fig. 8). We went up to this pressure because in our experiment it reached the pressure in response to the temperature of the boiler surface and the flow rate of the fluid. The flow rate was set in a range suitable for removing 15 kW thermal energy from a 30 cm square photovoltaic panel in order to provide cooling for the silicon PV cells to enhance their efficiency. The temperature was set by finding the minimum required temperature to ensure steady boiling. Below the temperature of 170 °C the boiler ceased to function because in the configuration appropriate for solar CPV cooling, the area is compact. Therefore, the heat flux must be high, which demands a high temperature gradient. Hence, if this fluid is to be used for VARS with CPV,
with the demand for low temperature operation, then the method of heat transfer must be further considered.

6 Conclusion

This technical note is an extension of the previous work of Ajib and Karno [1] and reports new aspects which were not covered by them such as thermal conductivity of the solution. It covers also a study of acetone / ZnBr₂ – ZnO nanofluid including the preparation, stability, structure and properties. Furthermore, this study shows an extension of the log p, T diagram of the acetone zinc bromide from 1 bar up to 1.39 bar. The density of the base-fluid solution was found to be different from those found by Ajib and Karno [1], and the possible explanation may be a methodology error to calculate the density. It is found that the density increases with increasing the nanoparticles concentration. The viscosity increases with increasing the nanoparticles concentration and the nanofluid shows a Newtonian behaviour. The heat capacity decreases, and the thermal conductivity increases with increasing the concentration of the nanoparticles. The thermal conductivity corresponds well to available formulae from the literature, directly for the prior experimentally formed correlation, but in the case of the theoretically developed formula, only when the particle morphology is considered as intended. It is found that the thermal conductivity of the base fluid drops with increasing the salt concentration in the solution.

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