Heat Transfer Fluids Based on Amino-Functionalized Silica Dispersed in 1,2-Propylene Glycol and in 50-50 Aqueous 1,2-Propylene Glycol

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Abstract: 1,2-propylene glycol and its 50-50 w/w mixture with water were used to prepare heat transfer fluids based on amino-functionalized silica. On top of pH-neutral dispersions (no reagents added except for the solvent and the particles), dispersions acidified with acetic acid and with HCl were used to enhance the positive electric charge of silica particles. The colloidal particles had a positive zeta potential >40 mV and showed apparent particle radii of 70 nm, and these properties remained unchanged on heating up to 80 °C for up to 28 days.

Keywords: zeta potential; particle size; electrophoresis; nanofluids

1. Introduction

Ethylene glycol (EG) is used in heat transfer fluids due to its low freezing point and high boiling point. Moreover, it is not flammable, moderately toxic, and inexpensive. This is why EG and its mixtures with water are attractive alternatives to water as components of heat transfer nanofluids [1]. The advantages and disadvantages of dispersions over pure solvents as heat transfer fluids were discussed in [1] and in other excellent reviews, and will not be detailed here. Dispersions have higher thermal conductivity than pure solvents, and high thermal conductivity is much desired in heat transfer fluids, but they are also more viscous, which is an adverse effect.

Increasingly higher requirements regarding product safety inspire research toward less toxic alternatives of common heat transfer fluids. 1,2-propylene glycol (PG) is much less toxic than EG [2], and this may be the reason for the application of PG rather than EG, when toxicity matters, including in heat transfer fluids. PG (1,2-propylene glycol) has an isomer, 1,3-propylene glycol, which has similar, but not identical physical properties, and it is also considered as a component of heat transfer fluids [3]. Many publications [4] describe heat transfer fluids based on propylene glycol, but they do not specify which isomer is used. The name propylene glycol (without specification of the isomer) is commonly used for 1,2-propylene glycol (rather than the 1,3-isomer), and we assume that the 1,2-isomer is used when the isomer is not explicitly specified. This study is focused on 1,2-propylene glycol. PG is miscible with water, and the physical properties of PG–water mixtures relevant to this study are reported in Table 1.

At the same glycol concentrations, the viscosities in Table 1 are higher than the viscosities of aqueous ethylene glycol by a factor of 2 [8]. In this respect, aqueous EG is superior to aqueous PG as a component of heat transfer fluids, because less viscous fluids are preferred. EG is also more efficient than PG in terms of the elevation of boiling point and the depression of freezing point at a constant volume concentration of glycol [9]. Therefore, EG and its mixtures with water are more frequently studied as components of heat transfer fluids than similar systems with PG. Nevertheless, several studies involving PG can be found in the literature; these systems are summarized in Table 2.
Table 1. Physical properties of PG–water mixtures.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>0</td>
<td>78.8</td>
<td>0.891</td>
<td>1.3331</td>
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<tr>
<td>10</td>
<td>77.53</td>
<td>1.0531</td>
<td>1.3432</td>
</tr>
<tr>
<td>20</td>
<td>75.1</td>
<td>1.8011</td>
<td>1.3544</td>
</tr>
<tr>
<td>30</td>
<td>72.4</td>
<td>2.7481</td>
<td>1.3658</td>
</tr>
<tr>
<td>40</td>
<td>64.6</td>
<td>3.9785</td>
<td>1.377</td>
</tr>
<tr>
<td>50</td>
<td>58.8</td>
<td>5.6284</td>
<td>1.3878</td>
</tr>
<tr>
<td>60</td>
<td>55.5</td>
<td>7.9308</td>
<td>1.398</td>
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<tr>
<td>70</td>
<td>47.7</td>
<td>11.3144</td>
<td>1.4075</td>
</tr>
<tr>
<td>80</td>
<td>42.6</td>
<td>16.6447</td>
<td>1.4162</td>
</tr>
<tr>
<td>90</td>
<td>36.6</td>
<td>25.9109</td>
<td>1.4241</td>
</tr>
<tr>
<td>100</td>
<td>30.2</td>
<td>44.6335</td>
<td>1.4316</td>
</tr>
</tbody>
</table>

Table 2. Compositions of PG-based systems considered as heat transfer fluids.

<table>
<thead>
<tr>
<th>% PG by Mass</th>
<th>Particles</th>
<th>Dispersant</th>
<th>Methods 1</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>SiO₂</td>
<td>various</td>
<td>Z</td>
<td>[10]</td>
</tr>
<tr>
<td>100</td>
<td>TiO₂</td>
<td>various</td>
<td>Z</td>
<td>[11]</td>
</tr>
<tr>
<td>100</td>
<td>Multiwall CNTs</td>
<td>various</td>
<td>V, T, H</td>
<td>[12]</td>
</tr>
<tr>
<td>100</td>
<td>SiO₂ + TiO₂</td>
<td>none</td>
<td>V, T, Z</td>
<td>[13]</td>
</tr>
<tr>
<td>100</td>
<td>CeO₂</td>
<td>none</td>
<td>V, T</td>
<td>[14]</td>
</tr>
<tr>
<td>30</td>
<td>SiC</td>
<td>none</td>
<td>V, T, H</td>
<td>[15]</td>
</tr>
<tr>
<td>50, 75, 100</td>
<td>graphene</td>
<td>none</td>
<td>V, T, H</td>
<td>[16]</td>
</tr>
</tbody>
</table>

1 V = viscosity, T = thermal conductivity, H = specific heat capacity, Z = zeta potential.

Several older studies of heat transfer fluids based on PG are summarized in [9]. All solid materials used in the studies cited in Table 2 show a pH-dependent surface charging in water as well as in polar and semi-polar organic solvents [17]. The particles are positively charged in acidic media and negatively charged in basic media. The acidity in water can be easily determined by pH measurements. The pH can also be defined and measured in nonaqueous and mixed solvents [18], but the procedure is complicated and tedious. Therefore, many authors, including the authors of the present paper, prefer the analytical concentration of acid or base as a measure of the acidity of the system. Ionic surfactants such as sodium dodecyl sulfate and cetyltrimethylammonium bromide are often used in heat transfer fluids to enhance the absolute value of the ζ potential of solid particles and thus their stability against coagulation and sedimentation in PG-based nanofluids (Table 2) and nanofluids based on other solvents. We argue that similar effects (enhancement of the absolute value of ζ potential) can be achieved by the functionalization of the surface by acidic or basic groups [8]. The acidity of the solution substantially affects the ζ potential and thus the stability of the dispersion. This study is similar to our previous study [19] except that we used PG rather than EG. We were especially interested in the effect of aging at elevated temperatures on the ζ potential and particle size in PG-based heat transfer fluids.

2. Materials and Methods

The same lot of amino-functionalized silica was used as in [19]; more details on the recipe and characterization of the particles can be found there. The amino-functionalized silica was obtained from commercial fumed silica (Sigma Aldrich, Saint Louis, MO, USA) using a recipe from [20]. Briefly, 10 g of silica was heated at 85 °C in a solution of 20 g of 3-aminopropyltriethoxysilane (APTES, Thermo Fisher Scientific, Waltham, MA, USA) in 700 mL of toluene for 24 h. The particles were separated by centrifugation, washed three times with ethanol, and dried at 105 °C.

The BET-specific surface area of functionalized silica was 169 m²/g [19], and its isoelectric point was at pH 10 [19]. The other reagents were analytical-grade from POCh (Lublin, Poland). Malvern Zetasizer ZEN 3600 (Malvern, Malvern, UK) was used to measure the
electrophoretic mobility, particle size, and conductivity. The conductivity reported in this study was measured in solutions w/o particles. The conversion of electrophoretic mobility into the ζ potential is a problem. The physical properties of PG from Table 1 and the Smoluchowski equation \( \mu = \varepsilon \zeta / \eta \), where \( \mu \) is the electrophoretic mobility, and \( \varepsilon \) and \( \eta \) are the dielectric constant and viscosity of the solvent, were used to calculate the ζ potential. The Smoluchowski equation provides a good approximation for large particles and high ionic strength, but it substantially underestimates the ζ potential in the systems of interest. On the other hand, the Huckel equation, \( \mu = \frac{2}{3} \varepsilon \zeta / \eta \), provides a good approximation for small particles and low ionic strength; however, it probably overestimates the ζ potential in the systems of interest. The following solvents were studied:

- 100% PG;
- 100% PG + 75 μL of 35–38% HCl per 150 g of PG;
- 100% PG + 750 μL of glacial acetic acid per 150 g of PG;
- 50% PG + 75 μL of 35–38% HCl per 150 g of 50% PG;
- 50% PG + 750 μL of glacial acetic acid per 150 g of 50% PG.

The choice of solvents was based on our previous study with EG [19], which indicated that dispersions of amino-functionalized silica in these solvents are likely to show high and stable-in-time ζ potential and low and stable-in-time apparent particle size. Acid addition improves the stability of dispersion, but acidic dispersions may also accelerate the corrosion of metals. Nanofluids were prepared by the dispersion of 45 mg of amino-functionalized silica in 150 mL of solvent using an ultrasonic bath. The dispersions were aged for 1 month at 40, 60, and 80 °C. Aliquots of dispersion were collected after different times and allowed to cool down to room temperature; then, the electrophoretic mobility and particle size were measured at 25 °C. The particle size reported in this study (and in most other papers reporting the particle size obtained by means of Malvern Zetasizer and similar instruments) was calculated using a model (uniform spherical particles) that was not necessarily relevant to the studied system. Therefore, the apparent particle size reported below does not represent the actual size of the particles. The model used in the interpretation of the results obtained by dynamic light scattering and its limitations are explained in the user manual of Malvern Zetasizer and in handbooks of colloid chemistry; therefore, they will not be discussed here.

Malvern Zetasizer was also used to measure the electric conductance of dispersions and solutions w/o solid particles.

3. Results and Discussion

3.1. IEP in Aqueous Dispersion

The ζ potential values of the amino-functionalized silica [19] and of the original fumed silica dispersed in aqueous 10⁻³ M NaCl as a function of pH are presented in Figure 1.

Figure 1 shows a substantial shift in the IEP from 3 to 10 due to amino-functionalization. The IEP obtained in this study for the original silica is similar to the IEP reported for the same material by the present authors [21] and others [22]. The IEP of amino-functionalized silica from [19] presented in Figure 1 is high as compared with the IEPs of other amino-functionalized silicas reported by the present authors [8] and others [23–27].

3.2. Dissociation of Hydrochloric and Acetic Acid in PG and 50% Aqueous PG

HCl is a strong acid, and CH₃COOH is a weak acid in water. Due to low dielectric constants of PG and aqueous PG (Table 1), lower degrees of dissociation of electrolytes are expected in these solvents than in water. The dissociation degree of hydrochloric and acetic acid in PG and 50% aqueous PG was estimated from the conductance of their solutions. The electric conductance of HCl solutions in 50% EG and 50% PG is presented in Figure 2.
Figure 1. The ζ potential of the original fumed silica and the amino-functionalized silica dispersed in aqueous $10^{-3}$ M NaCl.

Figure 2. Electric conductance of HCl solutions in 50% EG and 50% PG.

The highest HCl concentration in Figure 2 is equal to the HCl concentration in the nanofluids studied in this paper. Rectilinear dependence between conductance and concentration indicates that HCl is a strong acid in 50% EG and 50% PG, at least in the concentration range studied here. In contrast with the results shown in Figure 2, the graphs showing conductance vs. concentration for HCl in 100% glycols, and especially for acetic acid in 50 and 100% glycols, are not linear, indicating incomplete dissociation.

3.3. Visual Observation of Dispersions

The original dispersions were uniformly turbid and colorless. The dispersions were also uniformly turbid and colorless after aging for 1 month at 40 and 60 °C, except that a yellow deposit was observed in one sample (100% PG, no acid added). The appearance of dispersions after 1 month of aging at 80 °C is shown in Figure 3. A yellow deposit was observed in all dispersions, and the dispersions became pale yellow with 50% PG but not with 100% PG. These results are similar to those previously observed with EG and aqueous EG [18].
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3.4. Electrokinetic Potential in Aged Dispersions

The electrokinetic potential in aged nanofluids is presented in Figures 4–8.

![Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG acidified with HCl at various temperatures (in °C).](image1)

**Figure 4.** Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG acidified with HCl at various temperatures (in °C).

![Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG (no acid added) at various temperatures (in °C).](image2)

**Figure 5.** Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG acidified with acetic acid at various temperatures (in °C).
Figure 5. Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG acidified with acetic acid at various temperatures (in °C).

Figure 6. Evolution of ζ potential in dispersions of amino-functionalized silica in 100% PG (no acid added) at various temperatures (in °C).

Figure 7. Evolution of ζ potential in dispersions of amino-functionalized silica in 50% PG acidified with HCl at various temperatures (in °C).

Figure 8. Evolution of ζ potential in dispersions of amino-functionalized silica in 50% PG acidified with acetic acid at various temperatures (in °C).

Almost all data points in Figures 4–8 are above 40 mV (Smoluchowski), which corresponds to 60 mV (Huckel). According to a common rule of thumb, such a high value of the ζ potential is sufficient to stabilize the dispersion against coagulation and sedimentation. The values of the ζ potential in Figures 4–8 are similar to those reported in our previous study with EG [19], and with 50% PG acidified with acetic acid, the ζ potential is even higher (on average) by about 10 mV than the analogous result obtained with EG [19]. The values of the ζ potential obtained in 50% PG, and especially in 100% PG, are more scattered than the analogous ζ potentials obtained with EG [19] due to the higher viscosity and lower dielectric constant of PG than of EG and 50% PG compared to those of 50% EG (Table 1). A typical scatter of electrophoretic mobility of $10^{-9}$ m$^2$V$^{-1}$s$^{-1}$, which produces ±1.3 mV in water, results in ±10 mV in 50% PG and ±160 mV in 100% PG, so in some sense, the results obtained with 100% PG are surprisingly consistent. Less scattered electrophoretic mobilities in 100% PG than in water may be due to the slower Brownian motion of particles in more viscous fluids.

3.5. Particle Size in Aged Dispersions

As we discussed previously [8,10,19], ζ potentials give only a rough estimate of dispersion stability, and the apparent particle size is more closely related to the rate of aggregation and sedimentation of particles than the ζ potential. We found [19] that the amino-functionalized silica studied at various conditions showed the minimum apparent hydrodynamic radius of about 60–70 nm. This range is assumed to reflect the behavior of primary particles, while higher apparent particle radii represent aggregates. Indeed, the particles dispersed in water at a low ionic strength and at high absolute values of ζ potentials had apparent radii of about 60–70 nm, but they had substantially higher apparent radii at a high ionic strength and low absolute values of ζ potentials, according to the aforementioned rule of thumb and the well-established correlations observed in various materials [22]. The apparent radii of amino-functionalized silica in dispersions in PG and in 50% PG aged at 40, 60 and 80 °C up to 1 month are presented in Figures 9–13.
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![Figure 9](https://example.com/figure9.png)

**Figure 9.** Evolution of apparent hydrodynamic radius in dispersions of amino-functionalized silica in 100% PG acidified with HCl at various temperatures (in °C).

The apparent radii of particles of amino-functionalized silica presented in Figures 9–13 are surprisingly consistent. Most data points fall in the range of 60–80 nm, suggesting primary particles. There are no apparent trends in time; that is, the difference in apparent radii of particles observed for different aging times is due to the random scatter of results rather than to systematic trends. For example, a few outstanding points in Figure 11 can hardly reflect any real process (we rather expect that the properties at 60 °C should be somewhere between the properties at 40 and 80 °C). Again, the results obtained with PG and presented here are similar to the results previously reported for EG [19]. The properties
of dispersions acidified with HCl on the one hand and with acetic acid on the other were very similar.

![Figure 9](image9.png)

**Figure 9.** Evolution of apparent hydrodynamic radius in dispersions of amino-functionalized silica in 100% PG acidified with HCl at various temperatures (in °C).

![Figure 10](image10.png)

**Figure 10.** Evolution of apparent hydrodynamic radius in dispersions of amino-functionalized silica in 100% PG acidified with acetic acid at various temperatures (in °C).

![Figure 11](image11.png)

**Figure 11.** Evolution of apparent hydrodynamic radius in dispersions of amino-functionalized silica in 100% PG (no acid added) at various temperatures (in °C).

![Figure 12](image12.png)

**Figure 12.** Evolution of apparent hydrodynamic radius in dispersions of amino-functionalized silica in 50% PG acidified with HCl at various temperatures (in °C).

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