Prediction of nanofluids properties: the density and the heat capacity

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Abstract. The results given in this report show that the additives of Al₂O₃ nanoparticles lead to increase the density and decrease the heat capacity of isopropanol. Based on the experimental data the excess molar volume and the excess molar heat capacity were calculated. The report suggests new method for predicting the molar volume and molar heat capacity of nanofluids. It is established that the values of the excess thermodynamic functions are determined by the properties and the volume of the structurally oriented layers of the base fluid molecules near the surface of nanoparticles. The heat capacity of the structurally oriented layers of the base fluid is less than the heat capacity of the base fluid for given parameters due to the greater regulation of its structure. It is shown that information on the geometric dimensions of the structured layers of the base fluid near nanoparticles can be obtained from data on the nanofluids density and at ambient temperature – by the dynamic light scattering method. For calculations of the nanofluids heat capacity over a wide range of temperatures a new correlation based on the extended scaling is proposed.

1. Introduction
Numerous publication are devoted to different thermophysical and electrokinetic properties of nanofluids [1–13]. However, only few of them are focused on the influence of nanoparticles on the density and heat capacity of base fluids [4–13]. Nevertheless, experimental data on the value of the excess functions for these properties provide valuable information about the structure of nanofluid and its nature as a function of the temperature and concentration of nanoparticles.

The equations for density and heat capacity of nanofluids calculation proposed in the literature [6,7], are mostly based on the additivity rule. This refers to the additivity in the “gas” model using the volume fractions of nanoparticles in the base fluid. This approach to predicting the thermophysical properties of nanofluids is not thermodynamically justified.

Therefore, the purpose of our study is to develop methods for predicting the density and heat capacity. As initial information, we used data on the density and heat capacity of a model nanofluid consisting of isopropyl alcohol and alumina oxide nanoparticles Al₂O₃ [14,15]. Selecting of this object of study was due to high stability of colloidal solutions of isopropanol/Al₂O₃ nanoparticles. Samples of nanofluids were prepared by diluting of the concentrated nanofluid (702129 Aldrich, 20±1% by weight. Al₂O₃- 50 nm) with pure isopropyl alcohol (CAS 67-63-0, W292907 Aldrich, purity 99.7%). For investigation of the heat capacity the following nanoparticles concentrations have been prepared - 2.01, 5.11 and 9.96 wt% - (1.19, 3.07 and 6.08 mol % correspondingly). The density measurements
have been performed for following nanoparticles concentrations 0.92, 1.81, 4.01 and 6.65 wt % - (0.54, 1.08, 2.40 and 4.03 mol % correspondingly).

The results on the density and heat capacity of nanofluids of isopropyl alcohol/Al₂O₃ nanoparticles [14,15] are shown in figures 1 and 2.

![Figure 1. Temperature dependences of the density of isopropanol/nanoparticles solutions Al₂O₃ [14].](image)

![Figure 2. Temperature dependence of the heat capacity of isopropanol/nanoparticles solutions Al₂O₃ [15].](image)

From Figures 1 and 2 follow that the presence of nanoparticles in isopropyl alcohol causes the density increase and isobaric heat capacity decrease.

2. “Four-phase” model for predicting the density and heat capacity of nanofluids.

Nanoparticles affect the density and heat capacity of isopropyl alcohol by several factors. The first one is the presence of nanoparticles themselves, which have a higher density and lower heat capacity than the base fluid. However, the difference in the properties of Al₂O₃ nanoparticles and the base fluid does not explain the excess thermodynamic functions (see equations (1) and (2)).

\[ \Delta V = V_{nf} - V_{add} = V_{nf} - \left[ V_{np}x_{np} + V_{bf}\left(1 - x_{np}\right)\right] \] (1)

where \( \Delta V \) – excessive molar volume, \( cm^3 mol^{-1} \); \( V_{nf} \) - experimentally determined molar volume of solutions of isopropyl alcohol/Al₂O₃ nanoparticles, \( cm^3 mol^{-1} \); \( V_{add} \) – molar volume calculated by additivity, \( cm^3 mol^{-1} \); \( V_{np} \) – molar volume of the nanoparticle material taken equal to the molar volume of aluminum oxide in \( \alpha \)-modification at 20 °C [8], \( cm^3 mol^{-1} \); \( x_{np} \) – mole fraction of the nanoparticles substance in the nanofluid, \( mol\ mol^{-1} \);

\[ \Delta C_p^{ex} = C_{p}^{nf} - C_{p}^{add} = C_{p}^{nf} - \left[ C_{p}^{np}x_{np} + C_{p}^{bf}\left(1 - x_{np}\right)\right] \] (2)

where \( \Delta C_p^{ex} \) – excessive heat capacity of nanofluid, \( J\ mol^{-1} K^{-1} \); \( C_{p}^{nf} \) – heat capacity of nanofluid, \( J\ mol^{-1} K^{-1} \); \( C_{p}^{add} \) – heat capacity calculated by additivity, \( J\ mol^{-1} K^{-1} \); \( C_{p}^{np} \) – heat capacity of nanoparticle material (Al₂O₃), \( J\ mol^{-1} K^{-1} \); \( C_{p}^{bf} \) – heat capacity of the dispersion medium (base fluid – isopropyl alcohol) in the nanofluid, \( J\ mol^{-1} K^{-1} \).

The main reason of the excess thermodynamic functions is the structuring of the base fluid near the nanoparticles in a colloidal solution. The results of the analysis of the temperature and concentration dependences of the excess thermodynamic functions are shown in figure 3 and 4.

Results show the low dependence of the excess molar volume of the sample nanofluids on temperature and the nonlinear character of dependence of the excess functions on nanoparticles concentration. These effects are explained by the dependence of the volumes, density and heat capacity of the structured phases of the base fluid near nanoparticles on thermodynamic parameters.
Since any structuring of the liquid phase reduces the heat capacity, the excess heat capacity has a negative value.

**Figure 3.** Concentration dependence of the excess molar volume of isopropanol solutions/Al\(_2\)O\(_3\).

**Figure 4.** Temperature dependence of the excess heat capacity for isopropanol solutions / Al\(_2\)O\(_3\) nanoparticles.

Taking into account the aforementioned, we propose to consider the nanofluid as a thermodynamic system, which consists of:

- **base fluid** – dispersion medium with thermophysical properties which correspond to the properties of pure substance at the same temperature (layer 4 in figure 5);
- **nanoparticles** – dispersed phase with thermophysical properties which, in the first approximation, corresponds to the properties of the material of nanoparticles (layer 1 in figure 5);
- **surface adsorption phase** [16] – layer of the adsorbed on the surface of a nanoparticle molecules of the base fluid with thermophysical properties that differ from the properties of the dispersion medium. According to the physical concepts presented in the monograph [17], in first approximation, the density and heat capacity of this surface adsorption phase can be assumed to be equal to the properties of the dispersion medium at the melting point (layer 2 in figure 5);
- **diffusive layer** – transition layer between the base fluid (liquid phase) and the adsorption phase. The behavior of the substance in the diffuse layer can be considered as a “diffusive phase transition” and the properties of the base substance near the nanoparticles continuously change (layer in figure 5).

In the presented model, we assume that in conditions of multilayer adsorption the micelles that are formed around the nanoparticles have a fairly spherical shape. Taking these provisions into account, our "four-phase" model for predicting the density and heat capacity of nanofluids is shown in figure 5.

**Figure 5.** "Four-phase" model for predicting the density and heat capacity of nanofluids.
Our analysis shows that the density of the adsorption layer of isopropanol molecules near the nanoparticles slightly differs from the density of the base fluid at the parameters below the boiling point. Therefore, in calculations of the nanofluids density the contribution of the excess molar volume caused by a diffuse layer of the formed micelles can be neglected. In contrast, the contribution of the heat capacity of the diffuse layer must be taken into account in predicting of the excess heat capacity. Thus, the calculation of the excess molar heat capacity must be calculated by the formula

$$\Delta C_p^{ex} = C_p^{dl} x_{dl} + C_p^{ad} x_{ad} - C_p^{bf} (x_{ad} + x_{dl}),$$

(3)

where $C_p^{ad}$ – heat capacity of the dispersion medium (isopropanol) in the adsorption layer, $J \text{ mol}^{-1} \text{ K}^{-1}$; $x_{ad}$ – mole fraction of the dispersion medium in the adsorption layer near the nanoparticle, $\text{mol mol}^{-1}$; $C_p^{bf}$ – heat capacity of the dispersion medium in the diffuse layer, $J \text{ mol}^{-1} \text{ K}^{-1}$; $x_{dl}$ – mole fraction of the dispersion medium in the diffuse layer, $\text{mol mol}^{-1}$.

**Figure 6.** Dependence of the mole fraction of the adsorbed isopropanol molecules on the surface of nanoparticles $x_{ad}$ on their concentration in the base fluid.

The heat capacity of isopropanol alcohol in the diffusion layer – $C_p^{dl}$ in the proposed prediction model can be calculated as the average value of heat capacities of the base liquid at the melting temperature and at a given temperature of the nanofluid.

The proposed "four-phase" model of nanofluid makes it possible to determine the volume and concentration of the adsorption and diffusive phases of nanofluids. To solve this problem, we used data on the excess thermodynamic functions $\Delta C_p^{ex}$ and $\Delta V$ and information about the average size of nanoparticles. The results of the performed calculations demonstrate figure 6-8.

**Figure 7.** Temperature dependence of isopropanol concentration in the diffuse layer.

**Figure 8.** Concentration dependence of diameters of the adsorption $D_{ad}$ and diffuse $D_{dl}$ isopropanol molecules layers on the surface of $\text{Al}_2\text{O}_3$ nanoparticles; ♦ – the method of spectroturbidimetry at a temperature of 293 K; ■ – the method of dynamic light scattering at a temperature of 293 K; – diameter of the adsorption phase obtained from data on the nanofluids density [14]; ● – data on the diameter of the diffuse layer obtained from the heat capacity data at 293 K [15].
The information in figures 6-8 allows us to formulate several conclusions. First, the mole fraction of the base fluid molecules adsorbed on the surface of nanoparticles intensively increases only at low concentrations of nanoparticles in the base fluid (less than 0.02 mole fraction). The equivalent diameter of the adsorption layer of Al₂O₃ nanoparticles in isopropyl alcohol essentially depends on its composition and insignificantly depends on temperature.

Secondly, the diffusion layer is destroyed due to the kinetic energy of Brownian motion of nanoparticles increase with increasing temperature. This leads to a decrease of both, the diameter of the diffuse layer and its concentration in the nanofluid. It should be mentioned that as the temperature increases the rate of change of the adsorption phase and the diffuse layer decreases. The largest diameters of the adsorption and diffusion layers are observed near the melting point of the nanofluids.

Thirdly, data on the diameter of the adsorption layer of the base fluid on nanoparticles obtained by processing the information about nanofluid of isopropanol/Al₂O₃ nanoparticles are in good agreement with data of the dynamic light scattering measurements [14]. Information on the diameter of the diffusive layer obtained by processing data on the heat capacity of nanofluids satisfactorily agrees with data obtained by spectroturbidimetry method at low concentrations of nanoparticles in isopropanol.

Based on this information it can be concluded that the problem of developing methods for predicting the density and heat capacity of nanofluids reduces to the problem of determining the excess thermodynamic functions \( \Delta C_p^\gamma u \Delta V \). At the same time, the excess thermodynamic functions \( \Delta C_p^\gamma u \Delta V \) can be calculated using experimental data on the density of nanofluids and on the equivalent diameters of nanoparticles. Equivalent sizes of nanoparticles under normal conditions can be easily obtained by dynamic light scattering and by spectroturbidimetry methods.

Figure 9 shows that the values of the isobaric mole heat capacity, which is calculated using the characteristic sizes of nanoparticles in the base fluid [14] are in a good agreement with experimental data on the heat capacity of isopropyl alcohol/Al₂O₃ nanoparticles at a temperature of 293 \( K \).

\[ C_p = C_{p0} e^{\gamma \psi(t)}, \quad (4) \]

where \( C_{p0} \) – coefficient depending on the thermodynamic properties of a substance; \( \gamma \) – critical parameter, which has a universal value for different substances - \( \gamma = 1.24 \) [19]; \( \psi(t) \) – crossover function of the reduced temperature – \( t = 1 - \frac{T}{T_c} \); \( T_c \) – critical temperature, \( K \).

Since optical studies are generally performed at environment temperature, the proposed method cannot predict the isobaric heat capacity of nanofluids in a wide range of the state parameters. To solve this problem, we propose to use the method of predicting the thermophysical properties of substances on the boiling line, which is based on the application of the basic principles of extended scaling [18]. According to this method, the heat capacity of various substances on the boiling line can be described by the equation:
In [18] the authors show that the crossover function for non-associated substances has a universal character. For nanofluids, in which the base fluid belongs to the class of associated substances, the function $\psi(t)$ must be determined individually using reference information on the heat capacity on the boiling line.

Thus, in relation to nanofluids in the proposed correlation (4), we have two unknown coefficients: pseudocritical temperature $-\tilde{T}_c$ and coefficient $C_{P0}$, which depends on the concentration of nanoparticles in isopropyl alcohol. The studies [20] show that nanoparticles are not significantly affect the value of the pseudocritical temperature. In addition, colloidal solutions are characterized by low thermal stability. Therefore, we may assume that the value of the pseudocritical temperature is equal to the critical temperature of the base fluid.

The performed study shows that in the range of reduced temperatures $0.055 \leq t_\ast \leq 0.55$ the value of the function $\psi(t)$ for isopropyl alcohol can be calculated from the equation

$$\psi = 1 + 8.272692 t - 8.26809 t^2 + 29.68993 t^3 - 58.8476 t^4 + 62.93494 t^5$$

(5)

The value of the single unknown coefficient $C_{P0}$ in equation (4) for isopropyl alcohol can be determined from the experimental data obtained at a temperature of 293 $K$ or calculated using the "four-phase" heat capacity prediction model. A comparison of the heat capacity values of nanofluids of isopropanol/Al$_2$O$_3$ nanoparticles calculated from equations (4) and (5) is given in figure 10.

![Figure 10. Relative deviations of the experimental values of the specific isobaric heat capacity for the studied nanofluids from the values calculated by the “four-phase” model.](image)

The information in figure 10 confirms the high quality of the data on the heat capacity of nanofluids of isopropanol/Al$_2$O$_3$ nanoparticles calculated from equations (4) and (5) in a wide temperature range.

**Conclusions**

In this paper, it is shown that the values of the excess thermodynamic functions for the molar volume and heat capacity are determined by the effects of structuring of the base fluid near the nanoparticles in the colloidal solution.

A new method for predicting the nanofluids heat capacity based on the application of a "four-phase" model of nanofluids is proposed. In this model, only the density of nanofluids (the diameter of the adsorption layer of molecules on the surface of nanoparticles [14]) and the equivalent diameter of nanoparticles, which can be determined by the method of spectroturbidimetry can be used as initial data.

The proposed equations for predicting the density and isobaric heat capacity on the boiling line have limited range of applicability. Since any colloidal systems are thermally unstable, the equations (4) and (5) can be applied only in the temperature range of the thermal stability for the investigated nanofluids.
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