

# Influence Nanotube to Exchange Specific heat capacity and density Power Oils and Water Solutions

**Safarov M.M., Najmudinov Sh.Z., Aminov Sh.A., Zaripova M.A., Tagoev S.A., Sharifov D.A., Zoirov H.A., Zaripov J.A., Anaqulov M.M., Nazirov Sh.M., Abdulloev B.K., Boboeva A.H.**

Tajik technical University after named M.S.Osimi, 734043, Rajabovikh 10, Dushanbe, Tajikistan

E-mail: [mahmad1@list.ru](mailto:mahmad1@list.ru); [sharofiddin@mail.ru](mailto:sharofiddin@mail.ru); [shamsulo@list.ru](mailto:shamsulo@list.ru); [mohirai69@list.ru](mailto:mohirai69@list.ru); [safovuddin@list.ru](mailto:safovuddin@list.ru);

## Abstract

Experimental investigation of the C,P,V,T properties in the power oils-water system with the different composition (x) 0.121, 0.200, 0.256, 0.301 and 0.345 and molar fraction (m.f.) H<sub>2</sub>O were made with a high-temperature adiabatic calorimeter. The mixtures with 0.256 and 0.615 m.f. H<sub>2</sub>O were studied over the wide range of densities ( $\rho$ ) from 208.6 to 399.6 kg m<sup>-3</sup> and from 191.4 to 416.7 kg m<sup>-3</sup> respectively. For the description of some of the thermodynamic properties of the n-hexane-water binary system, the equation of state proposed by Jin et al. was used. Thermal conductivity of oils measured at laboratory is necessary for solving many geophysical problems. However, combination of the experimental study with theoretical methods, allowing one to calculate the thermal conductivity of oils and nanotubes from their composition, gives new possibilities for using the laboratory data. This enables one to reconstruct the investigations materials inner structure, namely, to find the thermal conductivity of mineral skeleton, porosity, and crack shape, i.e., the parameters that mainly control the nanotubes and oils thermal conductivity. It is important that porosity and crack geometry govern other physical properties of measuring systems (electrical conductivity and thermal conductivity). This fact gives a potentiality to find interrelations between various physical properties based on the structural parameters derived from thermal conductivity data. In order to reconstruct the structural parameters using experimental data, it is necessary to find a theoretical formula relating the parameters with measured thermal conductivity.

**Keywords:** thermal conductivity, isochoric heat capacity, nanotube, density, binary systems, oils, water solutions.

## I. Introduction

Investigation of the thermodynamic properties of binary systems is of wide interest, but experimental data are limited or even absent. The n-hexane-water system has been studied (Brenner [1]; De Loos et al.[2]; Tian Yiling et al.[3]; Victorov et al.[4]), but most of the investigation have taken place at high water concentrations at pressures above 20 MPa. In our work, we tried to measure the C, P,V,T properties. (C, isochoric heat capacity; V, volume; T, temperature) in the uninvestigated range of the state parameters and to explain some properties using the crossover equation of state. However, the systems is a micro inhomogeneous carbon consisting of various mineral grains, pores, and cracks filled with various fluids and gases (so-called, inhomogeneities). The inhomogeneities have different thermal conductivity. In this case, the thermal conductivity becomes a coordinate-dependent tensorial function, and temperature gradient at each point of such a carbon depends on the thermal conductivity distribution over the nanotube volume. In the case of spherical inclusions, the figure demonstrates that the Hashin-Shtrikman bounds are also very different for carbon having contrasting components.

The averaged value of bounds and Likhteneker method gives underestimated thermal conductivity. The classical self-consistent method (CSM) produces overestimated thermal conductivity for spherical inclusions. However, taking the aspect ratio of cracks in sandstone equal to 0.15 (typical of sandstones), we obtain good agreement with experimental data. These results point to the fact that inclusion shape markedly affects the effective thermal conductivity of sedimentary tubs and should be taken into account in theoretical modeling.

The theoretical model is also applicable for calculating other physical properties. For elasticity, the calculation formula of the CSM is given by Shermergor (1977), which allows one to compute the elasticity tensor and elastic wave velocities for a micro inhomogeneous carbon and medium. For measurements thermal conductivity are methods monotony regime.

## II. Experimental

The isochoric heat capacity and P-V-T properties for the binary system n-hexane-water were investigated with the Amirkhanov adiabatic calorimeter (Amirkhanov et al [5]). The investigations were carried out in two stages: firstly we measured, the isochoric with careful stirring of the substance investigation, and then we

determined the temperature dependence on pressure on the isochoric with an immovable calorimeter. The pressure was measured with the freight-piston manometers MT-60 and MP-600. The error in determination of the isochoric heat capacity was 1 -1.5%, density, 0.1%, pressure, 0.09%. Data are presented in Tables 1-3.

Only for the composition with 0.256 m.f. H<sub>2</sub>O do the two jumps become one, indicating the crossing of the singular point. It was suggested that the experiments should be carried out on the critical isochors with different concentrations of water and n hexane. The isochoric heat capacity is defined on the critical isochoric for the composition with 0.256 m.f. of H<sub>2</sub>O and described by the usual scaling relations.

$$C_{v,x} = C^{\pm} / \tau^{-\alpha} + C_0 \quad (1)$$

where  $\tau = (T-T_0)/T$ ,  $C^{\pm}$  are the critical amplitudes, and  $C_0$  the regular part of the isochoric heat capacity. The exponent  $\alpha^{\pm} = 0.101 \pm 0.009$  for the heterogeneous state and  $\alpha = 0.106 \pm 0.008$  for the homogeneous state [5].

The line connecting the first heat capacity  $C_{v,x}$  jumps on the isochors for different compositions the is the curve of the liquid – liquid phase equilibrium. The line connecting the first heat capacity jumps on the isochors is the curve of the liquid - gas phase equilibrium.

According to the classification by Van Konynendurg and Scott [6], the diagram of state for the n-hexane-water system is of type III which means that the critical point are not realized (except in the region where the upper branch of the critical liquid-gas phase equilibrium).

Although we obtained the jumps of the isochoric heat capacity for the liquid- gas state for the composition 0.345 and 0.615 m/f/ H<sub>2</sub>O, they are not critical. But we connected the temperature values corresponding to these jumps with a dotted line and referred to this line as the curve of the liquid-gas phase equilibrium.

So in the region with a low concentration of water the line of liquid-gas critical points (curve 1) is between the critical point of pure n-hexane and the upper end critical point, where the liquid – liquid phase equilibrium (curve 2) and liquid – gas phase equilibrium lines (curve 3) meet, which is the limiting point of the three phase equilibrium.

For the description of some thermodynamic properties of the n-hexane-water binary system, we used the crossover equation of state proposed by Jin at al. [7]. The equation of state incorporates the crossover from singular asymptotic behavior at the critical point to regular behavior far away from the critical point and is based on the crossover function introducing the six-term Landau expansion for the Helmholtz free energy density [7]. Parameters characterizing the individual properties of then system and entering into the equation of state were calculated on the basis of literature data [8.9] for pure n-hexane and water, and the relevant P,V,T and x experimental investigations. The dependences of the critical parameters on concentration were approximated by polynomials and spline function. We used the following values of critical parameters for the pure components: for n-hexane,  $T_c = 507.20$  K,  $P_c = 3.025$  MPa,  $\rho_c = 233.5$  kg m<sup>-3</sup> [8]; and for water,  $T_c = 647.067$  K,  $P_c = 22.064$  MPa,  $\rho_c = 322.788$  kg m<sup>-3</sup> [9].

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The experimental data for pressure for  $x=0.256$  and  $0.615$  for  $0.39, 0.50, 0.60, 0.70$  (data from [3]) m.f. water and for the isochoric heat capacity for  $x=0.256$  were compared with the calculated values. In the region where there is a break in the critical line, we used critical parameters corresponding to the dotted line in [3]. The crossover equation of state gives us the opportunity to describe the thermodynamic properties of the binary n-hexane-water mixture in the range of densities  $0.5\rho_c < \rho < 1.7\rho_c$  (at  $T=T_c$ ) and in the temperature range  $0.95T_c < T < 1.30T_c$  (at  $\rho=\rho_c$ ).

The error is 3% for the pressure description, as and 6-7% for the isochoric heat capacity description. As well as for other reasons, this is conditioned by the disparity and insufficiency of the literature data, which are used in the determination of system-dependent constants.

Table 2. P-V-T data for the n-hexane-water system with concentration 0.615 mol. fraction of H<sub>2</sub>O

| T/K                            | P/MPa | T/K                            | P/MPa | T/K                            | P/MPa |
|--------------------------------|-------|--------------------------------|-------|--------------------------------|-------|
| $\rho=416.7 \text{ kg m}^{-3}$ |       | $\rho=398.7 \text{ kg m}^{-3}$ |       | $\rho=262.0 \text{ kg m}^{-3}$ |       |
| 465.04                         | 3.087 | 489.00                         | 4.851 | 487.65                         | 4.586 |
| 478.37                         | 4.018 | 491.83                         | 5.194 | 497.15                         | 5.488 |
| 483.30                         | 4.508 | 492.91                         | 5.292 | 512.06                         | 6.958 |
| 489.81                         | 5.194 | 503.85                         | 6.958 | 551.00                         | 11.86 |
| 493.16                         | 5.589 | 509.62                         | 7.938 | 553.52                         | 12.15 |
| 495.64                         | 5.978 | 515.67                         | 8.918 | 546.15                         | 13.52 |
| 498.62                         | 6.468 | 526.47                         | 10.88 | 594.26                         | 16.86 |
| 501.57                         | 6.958 | 536.39                         | 12.84 | 621.65                         | 20.38 |
| 504.35                         | 7.448 | 540.90                         | 13.82 |                                |       |
| 506.95                         | 7.987 | 542.89                         | 14.31 | $\rho=399.6 \text{ kg m}^{-3}$ |       |
| 509.83                         | 8.428 | 543.58                         | 14.50 | 357.15                         | 0.294 |
| 512.43                         | 8.918 | 544.76                         | 14.80 | 417.30                         | 0.980 |
| 517.50                         | 9.898 |                                |       | 441.23                         | 1.764 |
| 522.46                         | 10.88 | $\rho=306.6 \text{ kg m}^{-3}$ |       | 468.25                         | 3.038 |
| 540.94                         | 14.90 | 444.47                         | 2.107 | 470.95                         | 3.234 |
| 559.63                         | 19.70 | 466.08                         | 3.007 | 480.79                         | 3.920 |
| 561.06                         | 20.09 | 496.55                         | 5.390 | 484.55                         | 4.214 |
| 577.30                         | 24.11 | 501.05                         | 5.978 | 491.45                         | 4.802 |
|                                |       | 505.80                         | 6.468 | 492.78                         | 4.949 |
| $\rho=398.7 \text{ kg m}^{-3}$ |       | 509.94                         | 6.958 | 494.88                         | 5.145 |
| 365.29                         | 0.294 | 518.26                         | 7.987 | 497.92                         | 5.390 |
| 389.38                         | 0.588 | 528.75                         | 9.408 | 504.15                         | 5.880 |
| 419.05                         | 1.176 | 535.15                         | 10.39 | 533.36                         | 8.428 |
| 438.86                         | 1.813 | 544.77                         | 11.86 | 559.33                         | 10.58 |
| 447.29                         | 2.156 | 556.75                         | 13.82 |                                |       |
| 457.77                         | 2.646 | $\rho=362.0 \text{ kg m}^{-3}$ |       |                                |       |
| 466.26                         | 3.136 | 414.65                         | 0.980 |                                |       |
| 473.97                         | 3.626 | 450.00                         | 2.156 |                                |       |
| 485.45                         | 4.606 | 473.66                         | 3.479 |                                |       |
| 488.21                         | 4.802 | 482.04                         | 4.106 |                                |       |

Table 3. Heat capacity (C) along isochors for different composition of the n-hexane-water systems: x, mol. fraction of water;  $\rho$ , density

| T/K                            | P/MPa | T/K                            | P/MPa | T/K                            | P/MPa |
|--------------------------------|-------|--------------------------------|-------|--------------------------------|-------|
| $x=0.121 \text{ m.f.}$         |       | $x=0.247 \text{ m.f.}$         |       | $x=0.345 \text{ m.f.}$         |       |
| $\rho=263.4 \text{ kg m}^{-3}$ |       | $\rho=263.8 \text{ kg m}^{-3}$ |       | $\rho=262.9 \text{ kg m}^{-3}$ |       |
| 455.13                         | 3.64  | 493.82                         | 4.08  | 494.41                         | 7.41  |
| 455.33                         | 3.69  | 494.01                         | 4.09  | 494.60                         | 7.79  |
| 455.53                         | 3.84  | 494.39                         | 4.13  | 494.98                         | 5.26  |
| 455.73                         | 3.88  | 494.58                         | 4.18  | 495.17                         | 5.02  |
| 455.93                         | 3.95  | 494.77                         | 4.39  | 503.41                         | 4.67  |
| 456.13                         | 4.15  | 494.96                         | 4.60  | 512.37                         | 4.74  |
| 456.33                         | 3.82  | 495.34                         | 3.38  | 515.60                         | 4.82  |
| 456.53                         | 3.73  | 495.53                         | 3.21  | 515.79                         | 4.79  |
| 456.73                         | 3.60  |                                |       | 515.98                         | 4.73  |
| 456.93                         | 3.57  | $x=0.256 \text{ m.f.}$         |       | 516.17                         | 4.62  |
| 457.13                         | 3.25  | $\rho=299.9 \text{ kg m}^{-3}$ |       | 516.36                         | 4.34  |
| 457.33                         | 3.14  | 493.19                         | 6.02  | 516.55                         | 4.07  |
| 457.53                         | 3.13  | 493.38                         | 6.10  |                                |       |
| 457.73                         | 3.08  | 493.76                         | 6.24  | $x=0.615 \text{ m.f.}$         |       |
| 457.93                         | 3.09  | 494.14                         | 6.62  | $\rho=286.0 \text{ kg m}^{-3}$ |       |
| 499.53                         | 3.86  | 494.33                         | 6.98  | 493.84                         | 6.68  |
| 499.82                         | 3.88  | 494.59                         | 7.72  | 494.03                         | 6.89  |
| 500.10                         | 3.96  | 494.78                         | 5.31  | 494.22                         | 6.95  |
| 500.29                         | 3.99  | 494.97                         | 4.95  | 494.41                         | 7.24  |
| 500.48                         | 4.07  | 495.15                         | 4.67  | 494.60                         | 7.57  |
| 500.68                         | 4.19  | 495.34                         | 4.43  | 494.79                         | 5.92  |
| 500.86                         | 4.27  | 495.53                         | 4.13  | 495.17                         | 4.89  |
| 501.05                         | 4.49  | 495.91                         | 3.84  | 495.36                         | 4.67  |
| 501.24                         | 3.55  | 496.10                         | 3.63  | 495.54                         | 4.62  |
|                                |       | 497.24                         | 3.42  | 495.73                         | 4.55  |
| $x=0.247 \text{ m.f.}$         |       | 497.43                         | 3.36  | 572.10                         | 6.35  |
| $\rho=263.8 \text{ kg m}^{-3}$ |       | 497.62                         | 3.23  | 573.87                         | 6.41  |
| 491.92                         | 5.41  | $x=0.345 \text{ m.f.}$         |       | 574.06                         | 6.06  |
| 492.30                         | 5.62  | $\rho=262.9 \text{ kg m}^{-3}$ |       | 574.25                         | 5.97  |
| 492.49                         | 5.69  | 493.65                         | 6.77  | 574.63                         | 5.67  |
| 492.68                         | 5.79  | 493.84                         | 6.80  | 574.82                         | 5.25  |
| 492.06                         | 4.46  | 494.03                         | 6.93  | 575.00                         | 4.82  |
| 493.25                         | 4.12  | 494.22                         | 7.17  | 575.19                         | 4.54  |

### III. Conclusion

We have reported a systematic series of measurements of the complex thermo-physical properties in the liquids phase and along the phase equilibrium line for samples of the water solutions and powers oils. Comparisons with previous experimental results for the pure components are presented. It is noted that the general behaviour of  $C_v$  saturated-liquid densities is identical for the mixture and pure components. The present experimental results may be used for the equation of state of n-hexane mixtures.

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