THERMOPHYSICAL PROPERTIES

OF MATERIALS

Phase Equilibrium and PVT-Properties
of 0.7223H₂O + 0.1242 n-C₆H₁₄ + 0.1535 n-C₃H₇OH
Ternary System

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Abstract—The results are given of experimental investigation of the PVT-properties and liquid–liquid and liquid–vapor phase equilibria of 0.7223 H₂O + 0.1242 n-C₆H₁₄ + 0.1535 n-C₃H₇OH ternary system along six different isochores. The measurements are performed by the constant-volume piezometer technique in the range of temperature from 309.26 to 678.82 K, density from 81.0 to 485.0 kg/m³, and pressure up to 60 MPa. The behavior of the system in the vicinity of the liquid–liquid and liquid–vapor critical points is treated using the scaling equations. The PVT-properties are described by the Peng–Robinson equation.

INTRODUCTION

Most frequently encountered in nature and in practice are multicomponent, including ternary, systems which exhibit the basic properties of multicomponent systems. Ternary systems, whose composition includes hydrocarbons and polar components such as water and alcohols, are extensively used in oil and petrochemical industries, power generation, chemical technologies, fuel industry, and so on. A knowledge of the parameters of liquid–liquid and liquid–vapor phase equilibria in binary and multicomponent systems is necessary for designing separation and extraction processes; because of the complex pattern of phase diagrams of such mixtures, these systems are of scientific interest from the standpoint, among other things, of checking various molecular-statistical models.

We have experimentally investigated the thermal properties and liquid–liquid and liquid–vapor phase equilibria of 0.7223 H₂O + 0.1242 n-C₆H₁₄ + 0.1535 n-C₃H₇OH ternary system (concentration is given in mole fractions). The measurements were performed in the range of temperature from 309.26 to 678.82 K, density from 81.0 to 485.0 kg/m³, and pressure up to 60 MPa. The data on phase equilibrium in the water–n-hexane–n-propyl alcohol, which are available in the literature, relate largely to close-to-room temperatures [1–4]. In the widest range of parameters of state, the C₆–PVT properties of the 0.3950 (by weight) H₂O + 0.2789 n-C₆H₁₄ + 0.3261 n-C₃H₇OH mixture were investigated in [5], and the PVT-properties of the mixture of 0.3265 H₂O + 0.4778 n-C₆H₁₄ + 0.1957 n-C₃H₇OH – in [6].

Of binary systems making up the water–n-hexane–n-propanol ternary system, most fully investigated is the binary separating n-hexane–water mixture [7–10]. The line of liquid–liquid phase equilibrium continues to the azeotropic point with the parameters T = 495.3 K, P = 5.28 MPa and ρ = 260.01 kg/m³ at x_w = 0.257 mass fraction, and then the temperature hardly changes up to the concentration x_w = 0.966 mass fraction. It is known [11–13] for binary mixtures of n-propanol–water and n-propanol–n-hexane that their components are fairly well soluble in one another in a wide range of parameters of state. Proceeding from the foregoing, we can regard the ternary water–n-hexane–n-propanol mixture as a quasibinary system. The water–n-propanol–n-hexane sys-
tem is solutropic: at low concentrations, the alcohol is more soluble in the water layer, and at high concentrations – in the hydrocarbon layer. On the solubility curve, it shows up as the reversal of sign.

**EXPERIMENTAL SETUP**

Phase equilibrium was studied using the results of investigation of the $PVT$-data. A constant-volume piezometer was used for measurements [14].

The main component of the experimental setup (Fig. 1) is a cylindrical pipe $I$ of $12$Kh$18$N$10$T (chrome-nickel-titanium) stainless steel with the inside diameter of 8.721 mm. For a better equalization of temperature, a massive copper block $4$ was hot-pressed onto the pipe; holes for thermocouple junctions and thermistors were drilled in the ends and middle part of the block. The temperature of the system was maintained automatically by three VRT-3 thermoregulators within 0.01 K. The pressure was registered by a diaphragm cell $2$ with a sensitivity of 0.005 MPa mounted on one end of the pipe and measured by a standard indicating pressure gage up to 1 MPa; above that pressure, an MP-600 deadweight pressure gage with an accuracy of 0.05% was used. The piezometer volume, determined by calibration against water, was $21.160 \pm 0.025$ cm$^3$. For the agitation of the mixture being investigated, a cylindrical weight $6$ with conic ends of stainless steel was placed into the piezometer. Corrections were made in order to take into account the variation of the piezometer volume with temperature and pressure. The entire system was set on half-axles and could turn freely through $180^\circ$. A heater $9$ was wound on the half-axles in order to compensate for heat transfer; the power of this heater was adjusted in accordance with the readings of a differential thermocouple. The piezometer was filled under vacuum via valve $3$ on the piezometer end. The stop valve had two autonomous outlets for producing vacuum in the piezometer and filling it with liquid; these outlets had the form of capillaries of stainless steel. The vacuum outlet was communicated with a pump, and the filling capillary provided with a plug was sunk into a pycnometer with the liquid being investigated. The filling outlet was initially closed, and the system was evacuated by a vacuum pump. Then the vacuum outlet was closed, and the filling outlet was opened. In so doing, the solution flowed completely from the pycnometer to the piezometer. A furnace $5$ was set on the pycnometer and provided for the heating of the pycnometer to $70–80 \ ^\circ\mathrm{C}$ when the entire liquid passed over to the pycnometer. After that, the filling outlet was closed. In order to make sure that all of the liquid was drawn into the piezometer, the

![Fig. 1. The setup for measuring the $PVT$-data: (1) pipe (12Kh18N10T steel), (2) diaphragm null cell, (3) stop valve, (4) massive copper block, (5) three-section furnace, (6) falling weight, (7) hold-up electromagnet, (8) inductance coils, (9) heater.](image-url)