

THE (p, ρ, T) and (p_s, ρ_s, T_s) PROPERTIES OF AQUEOUS METHANOL SOLUTIONS

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The (p, ρ, T) and (p_s, ρ_s, T_s) properties of aqueous methanol solutions at temperatures $T=(298.15$ to $473.15)$ K and mole fractions of methanol $x=(0.12324, 0.27263, 0.35989, 0.45751, \text{ and } 0.69221)$ and from the bubble point pressure up to 60 MPa are reported.

The measurements were carried out by using an apparatus, which used a constant volume piezometer. The apparatus enables one to measure the (p, ρ, T) and (p_s, ρ_s, T_s) properties with high accuracy, as well as to perform experimental isotherms, isochores, and isobars. The volume of the piezometer was $350.13 \times 10^{-6} \text{ m}^3$ at room temperature. At these conditions the density of ordinary water is known with high accuracy (0.001-0.003%) from the IAPWS formulation values for ordinary water.

The methanol from "Merck" company (Germany) was used in the experiments. The mass fraction of the methanol was $w \geq 0.998$. Double distilled water was used for the preparation of the solutions. The reliability of the obtained data was verified after each run by a control measurement of volumetric properties of water.

Calculation of deviations for experimental quantities was carried out according to the recommendations of meteorologic services: $\Delta T = \pm 3$ mK for temperature, $\Delta p = \pm 5 \cdot 10^{-2}$ MPa for high pressure, $\Delta p = \pm 5 \cdot 10^{-4}$ MPa for ambient pressure and $\Delta \rho = \pm 3 \cdot 10^{-2} \text{ kg} \cdot \text{m}^{-3}$ for density.

Using standard data fitting programs an equation of state for aqueous methanol solutions was constructed and described below:

$$p = A\rho^2 + B\rho^8 + C\rho^{12}, \quad (1)$$

where: A, B and C are coefficients of Eq. (1) and all functions of temperature and mole fraction in the following form:

$$A = \sum_{i=1}^3 T^i \sum_{j=0}^8 a_{ij} x^j; B = \sum_{i=0}^2 T^i \sum_{j=0}^8 b_{ij} x^j; C = \sum_{i=0}^2 T^i \sum_{j=0}^8 c_{ij} x^j. \quad (2)$$

The a_{ij}, b_{ij} and c_{ij} are the coefficients of the polynomials. The Eq. (1) with Eq. (2) reproduces our experimental values with a ± 0.05 % average deviation.

The excess molar volumes V_m^E of $\{(1-x)\text{H}_2\text{O}+x\text{CH}_3\text{OH}\}$ were calculated from experimental (p, ρ, T) values of solutions using equation (1-2):

$$V_m^E = \{xM_a + (1-x)M_w\} / \rho - xM_a / \rho_a - (1-x)M_w / \rho_w, \quad (1)$$

where: V_m^E is the excess molar volume of solution, M_a and M_w are the molar masses of methanol and water, respectively; and ρ_a and ρ_w are the densities of methanol and water, respectively.