# VOLUMETRIC PROPERTIES OF ETHANOL-WATER MIXTURES UNDER HIGH PRESSURE[#]

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## Abstract

Densities of ethanol-water mixtures have been measured using a vibrating tube densimeter and a different arrangement high-pressure experimental set up. Measurements were carried out at 298,15 K in a pressure range from 0.1 MPa to 5 MPa.

Partial molar volumes, excess molar volumes and coefficients of isothermal compressibility were calculated. The molar volumes of alcohol and it′s partial molar volumes in mixtures with water are found to decrease monotonously with increasing pressure. Excess molar volumes are negative at all pressures. The numerical P-V relations at each composition are correlated satisfactorily as a function of pressure by the Hayward equation.

## Introduction

As alcohol molecules strongly affect water structure, water solutions of alcohol show definite anomalies in various physical properties. In order to understand these anomalies phenomenally and theoretically, it is necessary to measure the accurate pressure-volume –temperature relations of pure alcohol and of binary mixtures of alcohol with water in a wide range of temperature and pressure.

A different experimental set up is used for these measurements, as reported in literature and only some will be mentioned here. Kubota, et al.[1] have determined volumetric behavior of $C_1 - C_4$ alcohol and their water mixtures in the temperature range from 283.15 to 348.15 K at pressures up to 350 MPa with modified an Adams piezometer and a high-pressure burette method. A bellows volumometer was used for the high-pressure measurements of thermodynamic properties 2-methyl-2-propanol+water mixtures.[2] In others studies, as for PVT properties of 1,1,1-trifluoroethane, density measurements were performed by a vibrating tube densimeter.[3]

The current paper reports density measurements for ethanol-water mixtures at 298.15 K in the pressure range from 0.1 MPa to 5 MPa with a vibrating tube densimeter

in our experimental set up. As there have been studies of the pressure volumetric properties of aqueous alcohol solutions reported in the literature, this system would appeared a suitable choice in assessment of the performance of our arrangement.

## Experimental

A schematic diagram of the experimental arrangement is shown in Figure 1. A stainless steel vibrating tube densimeter (4; Anton Paar DMA 512,Graz, Austria) was connected to the electronic unit (5; DMA 60, Anton Par, Graz, Austria). DMA involves a system which excites the U-tube at constant amplitude and a quartz clock, measuring the time corresponding to a fixed number of periods. The U-tube was housed in a brass housing enclosed in a steel heat exchanger. Two tubes connected the heat exchanger with an external temperature controlled circulating bath (6; Hetto). Temperature control of the cell was $\pm 5 \cdot 10^{-3}$ K. The degassed sample was introduced in the tube with a stainless steel syringe (3), where the piston seperates the sample from the used nitrogen (1) for pressurizing. The pressure was adjusted by the controller valve (2) to stable values, indicated on the pressure controller (PI).
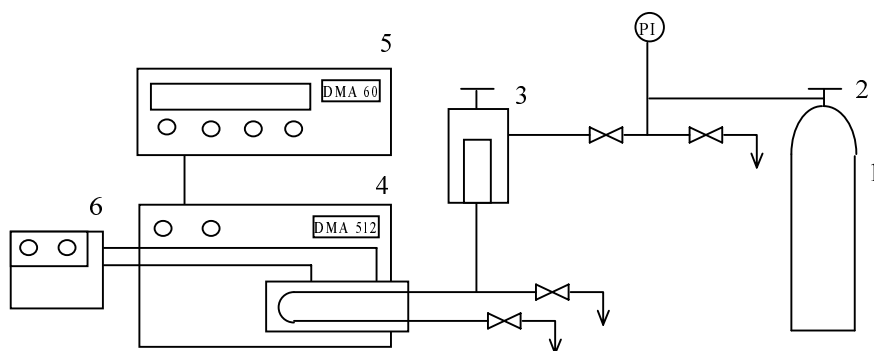


Figure 1: Schematic diagram of the experimental arrangement

The density $\rho$, of any liquid relative to the density of pure water $\rho_w$, is given by

$$\rho = K \cdot \left( \tau^2 - \tau_w^2 \right) + \rho_w ,\qquad\qquad (1)$$

where *K* is the characteristic of the oscillator, $\tau^2$ and $\tau^2_w$ are vibration periods of the tube, filled with liquid and with water, respectively. At each pressure the densimeter was calibrated with nitrogen and water.

## Results and Discussion

Determined densities of pure ethanol and it′s mixtures with water agreed well with literature values. Comparison of results with data from Peery′s Chemical Engineer′s Handbook[4] is presented in Table 1.

**Table 1**: Comparison of obtained density at 298.15 K and 0.1 MPa with data in Peery′s Handbook.

| $X_2$ | $\rho$ /g cm$^{-3}$ exp. | $\rho$ /g cm$^{-3}$ lit. |
|---|---|---|
| 0.1499 | 0.94847 | 0.94890 |
| 0.3057 | 0.90325 | 0.90307 |
| 0.4499 | 0.86906 | 0.86912 |
| 0.5993 | 0.84081 | 0.84084 |
| 0.7448 | 0.81823 | 0.81835 |
| 0.8974 | 0.79776 | 0.79791 |
| 1.0000 | 0.78497 | 0.78506 |

Partial molar volumes of ethanol $\overline{V}_2$ are calculated from the corresponding density measurements using the equation :

$$\overline{V}_2 = V_m + (1 - x_2)\left(\frac{\partial V_m}{\partial x_2}\right)_{n_1, P, T} \quad , \tag{2}$$

where $V_m$ is the molar volume of the solution and $x_2$ the molar fraction of ethanol. Results are listed in Table 2.

Excess properties of solutions express the deviation of mixture from the ideal solution behavior. Excess molar volumes $V^E$, which are calculated by using equation,

$$V^E (cm^3\ mol^{-1}) = x_1 \cdot M_1 (\rho^{-1} - \rho_1^{-1}) + x_2 \cdot M_2 (\rho^{-1} - \rho_2^{-1}), \tag{3}$$

are presented in Table 2. In equation (3) $x_1, x_2$ represents the molar fraction of both components, $\rho$ the density of mixture and $\rho_1, \rho_2$ density of pure components, respectively. $M_1$ and $M_2$ are molar masses of component.

**Table 2:** Density (g/dm³), Partial molar volumes (cm³/mol), Excess molar volumes (cm³/mol) and Coefficients of isothermal compressibility ($10^{-4}$ MPa$^{-1}$) for ethanol (2) - water (1) mixtures at 298.15 K at different pressures ( MPa).

| | x₂=0.1499 | | | | | x₂=0.3057 | | | |
|---|---|---|---|---|---|---|---|---|---|
| $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ | $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ |
| 0.1 | 948.473 | 55.425 | -0.732 | 4.623 | 0.1 | 903.254 | 56.902 | -1.049 | 5.862 |
| 1 | 948.859 | 55.388 | -0.726 | 4.453 | 1 | 903.728 | 56.857 | -1.041 | 5.760 |
| 2 | 949.290 | 55.349 | -0.721 | 4.369 | 2 | 904.241 | 56.810 | -1.034 | 5.621 |
| 3 | 949.648 | 55.309 | -0.714 | 4.049 | 3 | 904.730 | 56.766 | -1.026 | 5.445 |
| 4 | 950.076 | 55.272 | -0.709 | 4.022 | 4 | 905.229 | 56.722 | -1.019 | 5.357 |
| 5 | 950.438 | 55.231 | -0.703 | 3.856 | 5 | 905.724 | 56.675 | -1.012 | 5.271 |

| | x₂=0,.4499 | | | | | x₂=0.5993 | | | |
|---|---|---|---|---|---|---|---|---|---|
| $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ | $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ |
| 0.1 | 869.058 | 57.718 | -1.094 | 6.838 | 0.1 | 840.808 | 58.165 | -0.994 | 7.944 |
| 1 | 869.593 | 57.669 | -1.085 | 6.788 | 1 | 841.391 | 58.114 | -0.984 | 7.543 |
| 2 | 870.159 | 57.618 | -1.076 | 6.543 | 2 | 842.055 | 58.057 | -0.978 | 7.467 |
| 3 | 870.723 | 57.571 | -1.069 | 6.421 | 3 | 842.609 | 58.010 | -0.967 | 6.928 |
| 4 | 871.288 | 57.521 | -1.061 | 6.332 | 4 | 843.201 | 57.959 | -0.958 | 6.696 |
| 5 | 871.862 | 57.472 | -1.054 | 6.275 | 5 | 843.762 | 57.915 | -0.948 | 6.442 |

| | x₂=0.7448 | | | | | x₂=0.8974 | | | |
|---|---|---|---|---|---|---|---|---|---|
| $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ | $P$ | $\rho$ | $\overline{V_2}$ | $V^E$ | $\kappa_T$ |
| 0.1 | 818.232 | 58.424 | -0.773 | 9.434 | 0,1 | 797.763 | 58.621 | -0.386 | 10.334 |
| 1 | 818.923 | 58.367 | -0.767 | 9.170 | 1 | 798.493 | 58.564 | -0.382 | 9,.917 |
| 2 | 819.616 | 58.311 | -0.761 | 8.492 | 2 | 799.238 | 58.507 | -0.378 | 9.253 |
| 3 | 820.286 | 58.254 | -0.755 | 8.061 | 3 | 799.976 | 58.447 | -0.375 | 8.859 |
| 4 | 820.983 | 58.197 | -0.749 | 7.830 | 4 | 800.708 | 58.390 | -0.371 | 8.539 |
| 5 | 821.633 | 58.148 | -0.743 | 7.522 | 5 | 801.324 | 58.344 | -0.362 | 8.029 |

Composition dependencies of excess molar volumes were correlated by the Redlich – Kister equation:[5]

$$V^E = x_1 \cdot x_2 \cdot \sum_{i=0}^{n} A_i \cdot \left(1 - 2 \cdot x_2\right)^i \tag{4}$$

Values of coefficients $A_i$ are listed in Table 3, together with the standard deviations $\sigma V^E$, defined as

$$\sigma V^E = \sqrt{\dfrac{\sum_{i=1}^{N} \left(V_{eksp}^E - V_{calc}^E\right)_i^2}{N - n}} \quad , \tag{5}$$

where $N$ is the number of data points and $n$ is the number of coefficients.

**Table 3**: Coefficients $A_i$ and standard deviation $\sigma V^E$ of equation (4) at different pressures

| $P$ / MPa | $A_0$ | $A_1$ | $A_2$ | $A_3$ | $\sigma V^E$ |
|---|---|---|---|---|---|
| 0.1 | -4.3046 | -1.0991 | -1.2913 | -0.0976 | 0.0019 |
| 1 | -4.2692 | -1.0910 | -1.2767 | -0.1123 | 0.0026 |
| 2 | -4.2394 | -1.0822 | -1.2577 | -0.1258 | 0.0029 |
| 3 | -4.2051 | -1.0950 | -1.2415 | -0.0737 | 0.0033 |
| 4 | -4.1717 | -1.0894 | -1.2272 | -0.0866 | 0.0045 |
| 5 | -4.1475 | -1.0758 | -1.1487 | -0.1585 | 0.0073 |

As it can be seen in Figure 2, all ethanol solutions have negative excess volumes, implying a reduced free volume in the liquid structure. As the pressure increases, the excess volume becomes less negative, and in a sense, the mixture approaches ideal solution behavior with increasing pressure.
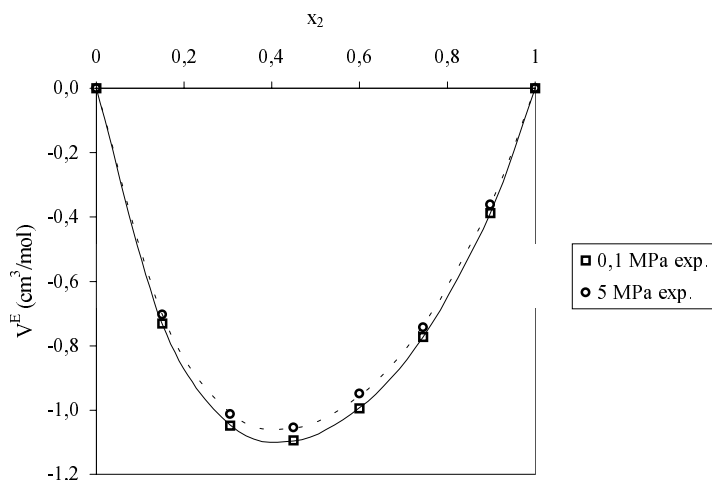
**Figure 2**: Excess molar volumes of ethanol-water mixtures at 0.1 MPa and 5 MPa; T=298.15 K.

To express compressive properties of solution the empirical Hayward[6] equation was used:

$$k = \frac{V_0 \cdot (P - 0{,}1)}{V_0 - V} = \sum_i a_i \cdot P^i \quad, \tag{6}$$

where $k$ is the secant bulk modulus, $P$ the pressure in MPa, $V$ volume at pressure $P$, $V_0$ volume at pressure 0,1 MPa and $a_i$ fitting parameters. In our case linear dependence $k$ versus $P$ reproduces experimental data within minimal average deviations.

Coefficients of isothermal compressibility, $\kappa_T$, given in Table 2 and Figure 3 were calculated using parameters of the secant bulk modulus fit by equation:

$$\kappa_T = -\left(\frac{1}{(P - 0{,}1) - k}\right) \cdot \left(1 - \frac{(P - 0{,}1)}{k} \cdot \left(\frac{\partial k}{\partial P}\right)_T\right) \tag{7}$$
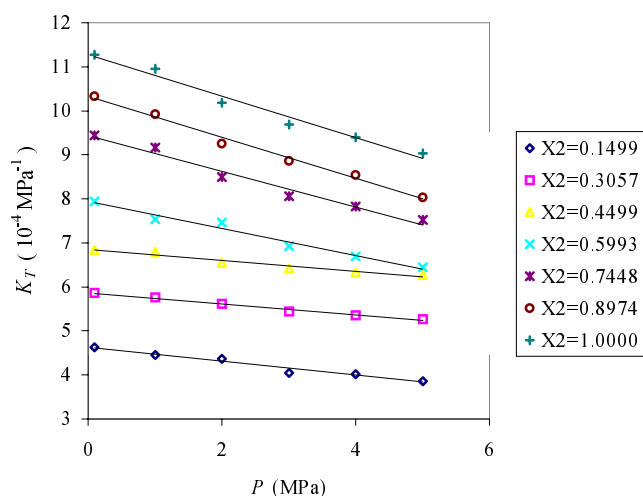
**Figure 3**:  Coefficients of isothermal compressibility for ethanol-water
mixtures at 298.15 K as a function of pressure.

Coefficients of isothermal compressibility for particular mixtures indicate that compressibility decreases with increasing pressure (Fig. 3). Slopes of straight lines are gradually changing from that of water to that of ethanol.

At detached pressure, compressibility increases with increasing molar fraction of alcohol (Fig.4).
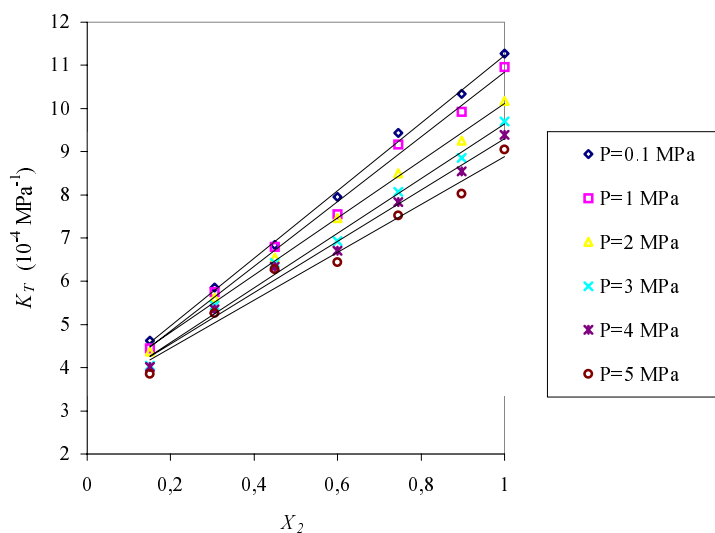


**Figure 4**: Composition dependence of coefficients of isothermal compressibility
for ethanol-water mixtures at 298.15 K.

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A simple explanation for such behavior could be, that the hydrogen-bonded network is gradually disintegrated as concentration of ethanol increases and so the larger compressibility of alcohol becomes dominant.

## References

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## Povzetek

Gostote mešanic etanola z vodo smo izmerili z gostotomerom, ki je bil prirejen za visokotlačne poskuse. Meritve so potekale pri 298,15 K v območju tlakov od 0,1 MPa do 5 MPa.

Iz izmerjenih gostot smo izračunali parcialne molske prostornine, presežne molske prostornine in koeficiente izotermične stisljivosti. Molske prostornine etanola in njegove parcialne molske prostornine v mešanicah z vodo se monotono zmanjšujejo s povečevanjem tlaka. Pri vseh tlakih so presežne molske prostornine negativne. Numerične P-V zveze v odvisnosti od tlaka so za vsako sestavo raztopine podane s Haywardovo enačbo.