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Some thermophysical properties of methanol and aqueous methanol mixtures at sub- and supercritical conditions

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ABSTRACT

Expressions for the composition dependence of the critical constants of mixtures of water and methanol are presented as are expressions of the vapor pressure, the molar enthalpy of vaporization, and the molar volume of methanol along its saturation curve. The internal pressure of saturated methanol is compared with its cohesive energy density, reflecting the diminishing strength of its intermolecular hydrogen bonding as the temperature is increased. Thermophysical properties (molar volumes, isobaric expansibilities, isothermal compressibilities, and internal pressures) of mixtures of methanol and water at subcritical temperatures at saturation and at the fixed pressures of 7 and 20 MPa have been calculated and are presented in a table. The self- and mutual association of water and methanol in their mixtures at sub-critical temperatures is examined.

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1. Introduction

Methanol and its mixtures with water are useful in several processes that take place advantageously at elevated temperatures. Supercritical methanol has been used in biomass processing to produce biodiesel fuels [1,2], in supercritical extraction [3], in supercritical chromatography [4], and in synthetic chemistry for transesterification [5,6] and for dissolution and conversion of cellulose [7]. Mixtures of methanol and water have been used at elevated temperatures or at supercritical conditions to extract organic products from oil shale [8] and peat [9], to desulfurize coal [10], for the methanolysis of soybean oil [11] and the chromatographic purification of the drug naproxen [12]. However, supercritical mixtures of water and methanol are prone to reaction (in a nickel-base alloy vessel) to produce a hydrogen rich gas [13].

It is, therefore, of interest to examine the thermophysical properties of methanol and mixtures of methanol and water under both subcritical and supercritical conditions. The thermodynamic states at which supercritical methanol has been applied are temperatures in the range $523 \leq T/K \leq 673$ and pressures in the range $8 \leq P/\text{MPa} \leq 45$. Subcritical states of interest to such applications as listed above are at temperatures down to 150 K below the critical ones for pure methanol and for its mixtures with water. It is the purpose of this paper to report the available relevant thermophysical properties and examine them critically.

2. Results

The critical constants of methanol and water mixtures were first determined by Marshall and Jones [14]. The following expressions result from their data. The critical temperature dependence on the mole fraction of methanol, x_{MeOH} , is quadratic:

$$T_c/K = 647.6 \pm 0.3 - (200.6 \pm 1.8)x_{\text{MeOH}} + (65.8 \pm 1.8)x_{\text{MeOH}}^2 \quad (1)$$

with a squared correlation coefficient $r_{\text{corr}}^2 = 0.99989$ and a standard error of the fit of 0.8 K. This expression leads to $T_c/K = 512.7$ for pure methanol near that reported in a critical examination of the literature [15], 512.6, somewhat smaller than 514.5 reported in [14]. The critical density of the mixtures was estimated [14] to be linear with the composition. It then follows the expression:

$$\rho_c/\text{kg m}^{-3} = 323.3 - 50.89 x_{\text{MeOH}} \quad (2)$$

with a squared correlation coefficient $r_{\text{corr}}^2 = 0.99961$ and a standard error of the fit of 0.4 kg m^{-3} . This expression leads to $\rho_c/\text{kg m}^{-3} = 272.4$ for pure methanol, agreeing with the entry in [15]. The critical molar volume that results from these data follows the expression:

$$V_c/\text{cm}^3 \text{ mol}^{-1} = 55.7 + 61.8x_{\text{MeOH}} \quad (3)$$

yielding $V_c/\text{cm}^3 \text{ mol}^{-1} = 117.5$ for pure methanol. Less detailed information exists regarding the critical pressure: the values for the pure

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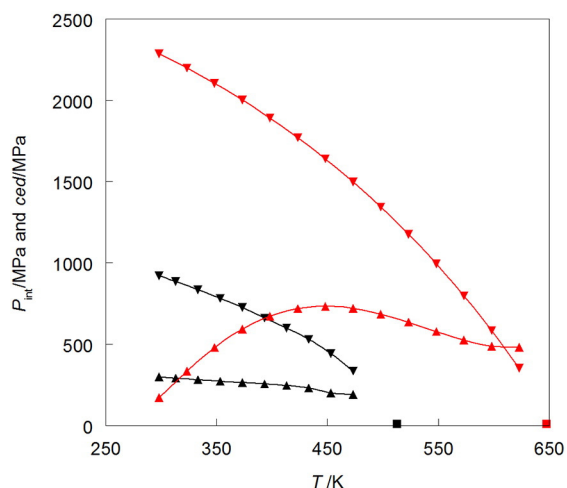


Fig. 1. The internal pressure, P_{int} (upright triangles), cohesive energy density, ced (downward triangles), and critical temperatures (squares) of methanol (black) and water (red) as functions of the temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

components being $P_c/MPa = 22.055$ for water and 8.095 for methanol, but there are only three estimates for intermediate compositions. These are $P_c/MPa = 15.4 \pm 0.4$ [16] or ≈ 15 [17] at $x_{MeOH} = 0.36$, ≤ 13.5 at $x_{MeOH} = 0.5$ [18], and 8.41 at $x_{MeOH} 0.773$ quoted in [18]. These data may be summarized as:

$$P_c/MPa = 22.055 - 23.58x_{MeOH} + 9.34x_{MeOH}^2 \quad (4)$$

with a squared correlation coefficient $r_{corr}^2 = 0.9893$ and a standard error of the fit of 1.0 MPa.

Thermophysical properties of liquid methanol at elevated temperatures have been reported by several authors [19–21]. The saturation curve for neat methanol, obtained from the data by Machedo and Streett

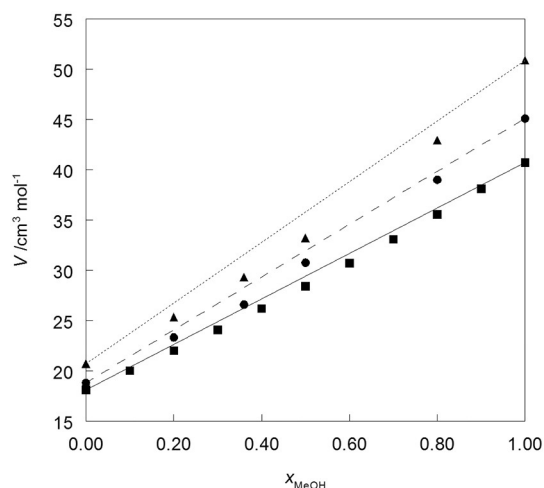


Fig. 2. The molar volume of mixtures of water and methanol at 298.15 K and 0.1 MPa (■ and full line), 373.15 K and saturation pressure (● and dashed line) and at 473.15 K and 7 MPa (▲ and dotted line). The straight lines show the ideal mixing volumes and do not represent experimental points.

[19], follows the expression:

$$\ln(p/MPa) = -(23.98 \pm 0.75) + (0.0897 \pm 0.0038) \times (T/K) - (7.61 \pm 0.48)(T/K)^2 \quad (5)$$

with a squared correlation coefficient $r_{corr}^2 = 0.99917$ and a standard error of the fit of 0.064 , when extended (from $T = 473.15$ K) up to the critical point $T_c = 512.6$ K.

The molar enthalpy of vaporization, $\Delta_v H$, was reported by Machedo and Streett [19] along the saturation curve up to 473.15 K. It follows the expression:

$$\Delta_v H/kJ \text{ mol}^{-1} = 148.62 - 0.9013(T/K) + 0.002534(T/K)^2 - 2.5474 \times 10^{-6}(T/K)^3 \quad (6)$$

Table 1 Molar volumes, isobaric expansibilities, isothermal compressibilities and internal pressures of subcritical mixtures of methanol and water.

T/K	P/MPa	$x_{MeOH} = 0.00$	0.20	0.36	0.50	0.80	$x_{MeOH} = 1.00$
Molar volume, $V/cm^3 \text{ mol}^{-1}$							
323.15	Saturation	18.37	22.45	25.88	29.06	36.58	42.01
373.15	Saturation	18.80	23.31	26.58	30.75	38.99	45.09
423.15	Saturation	19.64			34.54		49.53
473.15	Saturation	20.83			37.78		58.14
373.15	7	18.74	23.37	27.03	30.88	39.16	45.04
423.15	7	19.57	24.53	28.85	32.60	41.37	48.46
473.15	7	20.69	25.36	29.30	33.22	42.93	50.89
373.15	20	18.63	23.33	27.28	30.88	39.15	44.93
423.15	20	19.42	24.50	28.85	32.80	41.87	48.24
473.15	20	20.44	25.52	29.87	33.97	43.56	50.63
Isobaric expansibility, $10^3 \alpha_p/K^{-1}$							
373.15	Saturation	0.750	0.752	1.031	1.130	1.276	1.611
423.15	7	1.003	1.295	1.510	1.675	1.974	2.118
473.15	20	1.251	1.637	1.934	2.145	2.383	2.453
Isothermal compressibility, κ_T/GPa^{-1}							
373.15	Saturation	0.490	0.685	0.887	1.10	1.65	2.28
423.15	7	0.616	0.853	1.092	1.43	2.47	3.47
473.15	20	0.766	1.468	2.08	2.64	3.96	4.92
Internal pressure, P_{int}/MPa							
373.15	saturation	571	510	434	383	289	264
423.15	7	682	635	578	489	331	251
473.15	20	556	508	420	364	265	216

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