Total and partial solubility parameters of supercritical methanol

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Supercritical methanol (above 513 K and 8.1 MPa) is applicable to many processes, including biodiesel production from oils. Its total (Hildebrand) and the partial (Hansen) solubility parameters, the latter pertaining to dispersion, polarity, and hydrogen bonding interactions, are useful quantities, related to the solubilities of various solutes. They have been determined at the relevant thermodynamic states for the applications of supercritical methanol: temperatures in the range 525–675 K and pressures in the range 10–40 MPa.

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1. Introduction

Supercritical methanol has found several applications as a solvent: in biomass processing to produce biodiesel fuels [1,2], in synthetic chemistry, for transesterification [3,4], in supercritical extraction [5], and in supercritical chromatography [6], among others. The solubilities of the required solutes in this solvent are, therefore, key quantities that ought to be known, or else be estimatable from the properties of this solvent and of the solutes. A commonly used method for such an estimation employs the total (Hildebrand) solubility parameters δ_t; the differences between those of the solvent and the solute should not exceed $4\,\text{MPa}^{1/2}$ for appreciable solubility to ensue. A more detailed dealing with this estimation of the solubility is the use of the partial (Hansen) solubility parameters: δ_d for dispersion interactions, δ_p for polar interactions, and δ_{hb} for hydrogen bonding. Such quantities are known for many potential solutes as well as for methanol at ambient conditions, but only δ_t has been reported for supercritical methanol [7], but not the partial ones.

The critical constants of methanol are shown in Table 1.

The Peng–Robinson equation of state (EoS) has been applied to supercritical methanol in order to relate its *PVT* properties to one another [8]. This EoS has the form:

$$P = [RT/(V - b)] - a/[V^2 + 2bV - b^2] \qquad (1)$$

The EoS coefficients are shown in Table 1 and $\alpha = \left[1 + \kappa(1 - T_r^{1/2})\right]^2$, where $T_r = T/T_c$ is the reduced temperature. These parameters permit the calculation of the molar volume V (or the density, $\rho = M/V$, where $M = 0.03204\,\text{kg mol}^{-1}$ is the molar mass of methanol) for the required thermodynamic states defined by T and P.

It is the purpose of this study to provide values for the total and the partial solubility parameters of supercritical methanol at the thermodynamic states relevant to its applications. These states are temperatures in the range $523 \leq T/\text{K} \leq 673$ and pressures in the range $8 \leq P/\text{MPa} \leq 45$.

2. Methods and results

The Peng–Robinson EoS, solved numerically, leads to the following cubic expression for the pressure P in terms of the reduced molar volume $V_r = V/V_c$ and the reduced temperature T_r:

$$P/\text{MPa} = (-874 + 1134\,T_r) + (1771 - 2446\,T_r)\,V_r$$
$$+ (-1340 + 1936\,T_r)\,V_r^2 + (353 - 527\,T_r)\,V_r^2 \qquad (2)$$

Given the values of P and T the value of V can then be readily calculated. Reduced volumes in the range $0.8 \leq V_r \leq 2.0$ and reduced temperatures in the range $1.00 \leq T_r \leq 1.32$ are relevant to the thermodynamic states at which supercritical methanol has been applied.

Methanol cannot be considered a fluid conformal with those where only centric forces between neighboring molecules apply; its acentric coefficient is $\omega = 0.565$. Therefore the extended

Table 1
Literature data concerning methanol.

Quantity	Value	Reference
Critical constants		
Critical temperature, T_c/K	512.64	[7]
Critical pressure, P_c/MPa	8.09	[7]
Critical density, ρ_c/kg m^{-3}	272	[7]
Critical volume, V_c/m^3 mol^{-1}	1.178×10^{-4}	[7]
Peng–Robinson parameters		
$a/(RT_c^2/P_c)\alpha$	0.457235	[8]
$b/(RT_c/P_c)$	0.077796	[8]
Acentric factor, ω	0.565	[8]
κ	$0.37464 + 1.54226\omega + 0.26992\omega^2$	[8]
Partial (Hansen) solubility parameters at the reference temperature, 298.15 K		
Dispersion, $\delta_{d\ ref}$/MPa$^{1/2}$	15.1 or 14.7	[9] or [10]
Polarity, $\delta_{p\ ref}$/MPa$^{1/2}$	12.3	[9,10]
Hydrogen bonding, $\delta_{hb\ ref}$/MPa$^{1/2}$	22.3	[9,10]

Table 2
The mean number of hydrogen bonds per methanol molecule, n_{hb}, in supercritical methanol at different thermodynamic states.

T/K	ρ/kg m^{-3}	V/m^3 mol^{-1}	Ref.	V_r	n_{hb}
526	633	0.0507	19	0.430	0.961
623	365	0.0878	21	0.745	0.50
523	348	0.0921	21	0.782	0.51
523	348	0.0507	18	0.430	0.369
623	260	0.1232	21	1.045	0.34
623	260	0.1232	18	1.045	0.154
723	250	0.1282	21	1.088	0.25
723	200	0.1602	21	1.360	0.20
523	164	0.1844	20	1.565	0.303

expression reported by the present author (Eq. (19) in [7]) for the total solubility coefficient needs to be used for its calculation:

$$\delta_t/\text{MPa}^{1/2} = 2.95(c/0.4278)^{1/2}(Pc/\text{MPa})^{1/2}[1 + \kappa(1 - T_r^{1/2})]T_r^{1/4}\rho_r \tag{3}$$

The parameters have the following values: $c = 0.45724$ and κ from Table 1 for the Peng–Robinson EoS applicable to supercritical methanol [8]. Hence the working expression for the (Hildebrand) total solubility parameter of supercritical methanol is:

$$\delta_t/\text{MPa}^{1/2} = 8.67[1 + 1.160(1 - T_r^{1/2})]T_r^{1/4}\rho_r \tag{4}$$

The two terms that involve the reduced temperature operate in opposite directions, causing only a mild dependence on T_r, but the total solubility parameter δ_t is directly proportional to the reduced density $\rho_r = 1/V_r$. At T/K = 525, 625, and 725 ($T_r = 1.024$, 1.219, and 1.414) the resulting values of δ_t at $\rho_r = 1.00$ are 8.48, 7.04, and 5.76 MPa$^{1/2}$ respectively.

The (Hansen) partial solubility parameters for methanol at the reference state of $T_{ref} = 298.15$ K and $P_{ref} = 0.1$ MPa are shown in Table 1. For $\delta_{d\ ref}$/MPa$^{1/2}$ the mean value, 14.9 from the two sources is taken here, the contribution of this term being relatively small. The relationship between the total and the partial solubility parameters is: $\delta_d^2 + \delta_p^2 + \delta_{hb}^2 = \delta_t^2$. It holds quite well for the reference state: $14.9^2 + 12.3^2 + 22.3^2 = 871$ compared to $\delta_t^2 = 882$ MPa [11].

The dispersion partial solubility parameter of supercritical methanol is obtained from the expression suggested by Williams et al. [12], traceable to Hildebrand and Scott [13]:

$$\delta_d/\delta_{d\ ref} = (V_{ref}/V)^{5/4} \tag{5}$$

where $V_{ref} = 0.04070$ m^3 mol^{-1} is the molar volume of methanol at the reference state and V pertains to the supercritical methanol.

The polar partial solubility parameter of supercritical methanol is obtained from the expression traceable to Stefanis et al. [14] (their Eq. (6) reads $\delta_p = \text{const}/V^{1/2}$):

$$\delta_p/\delta_{p\ ref} = (V_{ref}/V)^{1/2} \tag{6}$$

These two expressions provide the dependence of δ_d and δ_p on the temperature and the pressure indirectly via the corresponding dependencies of the molar volume of the supercritical methanol, Eq. (2). The larger the temperature and the smaller the pressure the larger then is the molar volume which is in the denominators of Eqs. (5) and (6) and these partial solubility parameters diminish accordingly.

The hydrogen bonding partial solubility parameter of supercritical methanol is more difficult to estimate. The difference in the molar enthalpies of vaporization of methanol and its non-hydrogen-bonding analog dimethyl ether might be ascribed to the

hydrogen bonding in the former. Then, at 293.15 K this difference, $\Delta\Delta H_V/\text{kJ mol}^{-1} = 37.70 - 18.59 = 19.11$, is also the difference in the cohesive energy. The value for methanol, prorated from the entries at 298.15 K and the boiling point, and that for dimethyl ether are from the compilation of Riddick et al. [11]. The cohesive energy difference is then ascribed to the configurational energy for the hydrogen bonding and divided by the molar volume of methanol at 293.15 K, 0.04050 m^3 mol^{-1}, should yield the cohesive energy density δ_{hb}^2, leading to $\delta_{hb} = 22.7$ MPa$^{1/2}$. This is only ~2.7% smaller than the reference value in Table 1, the small temperature difference probably being unimportant. However, no values can be obtained from this method for the temperatures relevant to supercritical methanol.

Recourse is, therefore, taken for obtaining δ_{hb} of supercritical methanol with the expression suggested by Stefanis et al. [14]:

$$\delta_{hb} = (n_{hb}\varepsilon_{hb}^*)^{1/2}V^{-1/2} \tag{7}$$

This expression requires the mean number of hydrogen bonds per methanol molecule, n_{hb}, and the (negative of the) molar energy per hydrogen bond, ε_{hb}^*. The latter quantity, $\varepsilon_{hb}^* = 19.9$ kJ mol^{-1}, was reported by Gupta and Chandra [16]. Another, much smaller, estimate of $\varepsilon_{hb}^* = 8.5$ kJ mol^{-1} has been suggested by Gómez-Álvarez et al. [17]. The mean numbers of hydrogen bonds per methanol molecule, n_{hb}, at diverse supercritical thermodynamic states have been reported by several authors [18–21] as shown in Table 2, listed at increasing V and V_r values calculated from the reported densities (and for ref. [19] from the reported pressure according to Eq. (2)). The δ_{hb} values resulting from Eq. (7) with the above-mentioned two estimates of ε_{hb}^* are shown in Fig. 1. However, the average (negative of the) molar energy per hydrogen bond in water is only 12.9 kJ mol^{-1} [22], so that the larger value for methanol is unlikely to be correct. Therefore, the expression $\delta_{hb}^*/\text{MPa}^{1/2} = 4.5\ V_r^{-1}$ could be deduced from the lower set of data in Fig. 1 for $\varepsilon_{hb}^* = 8.5$ kJ mol^{-1}.

The values of δ_d, δ_p, and δ_{hb} of supercritical methanol obtained as described above are shown in Table 3 for several thermodynamic states relevant to its applications mentioned above. Also shown there are the values of $[\delta_d^2 + \delta_p^2 + \delta_{hb}^2]^{1/2}$, compared with δ_t, calculated from Eq. (4) that should agree. The partial solubility parameters diminish with increasing temperatures (Fig. 2) and increase with increasing pressures (Fig. 3).

3. Discussion

The discrepancy noted in Table 3 between $[\delta_d^2 + \delta_p^2 + \delta_{hb}^2]^{1/2}$ and δ_t for supercritical methanol may be due to several causes. One cause may be the values of δ_d and of δ_p for methanol at the reference state of ambient conditions [9,10], to which the values for supercritical methanol are proportional, Eq. (6). However, this explanation is unlikely to be true, because the squares of the partial solubility parameters for methanol at ambient conditions add up to the square of the total solubility parameters as noted above.