



Monomer fraction data of dilute alcohol/acetone systems measured with transmission Fourier transform infrared spectroscopy



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ABSTRACT

New monomer fraction data (fraction of non-hydrogen bonded molecules) of dilute ($x_{\text{solute}} < 0.016$) C_1 to C_3 alcohol-in-acetone and dilute acetone-in-alcohol systems were collected via Fourier transform infrared (FTIR) spectroscopy. Monomer fraction data may be used to improve regression parameters within the Statistical Associating Fluid Theory (SAFT) modeling framework. For very dilute ($x_{\text{alcohol}} < 0.003$) alcohol-in-acetone mixtures, it was found that 2-propanol had the highest monomer fractions and methanol the lowest. As the alcohol mole fraction increased ($x_{\text{alcohol}} > 0.003$), methanol maintained the lowest monomer fraction ($X_{\text{mon,MeOH}} = 0.01$ at $x_{\text{MeOH}} = 0.0086$), with ethanol, 1-propanol and 2-propanol approaching similar monomer fraction values, i.e., $X_{\text{mon,alcohol}} \rightarrow 0.06$. For dilute acetone in alcohol, and especially for methanol and ethanol, there was a pronounced trend towards acetone monomer fractions of 1 at infinite dilution. The acetone monomer fractions decreased according to an exponential decay function to values of ± 0.3 for acetone dissolved in methanol and ± 0.1 for the other alcohols investigated. Acetone monomer fractions, therefore, tended to decrease as alcohol chain-length increased, showing that acetone could more easily penetrate the hydrogen bond network of the solvent when the solvent/solvent hydrogen bonds were weaker. For dilute acetone in 2-propanol, a previously unrecorded monomer peak was observed and quantified.

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1. Introduction

Several sources advocate that monomer fraction data obtained from spectroscopy measurements could improve the regression of parameters within the Statistical Associating Fluid Theory (SAFT) framework [1]. There are, however, little data available in the open literature. Those data which have been published consist mostly of binary alcohol/hydrocarbon mixtures with a few pure fluid sets available for water and selected alcohols [2–4].

Von Solms et al. [5] used measured monomer fraction data for 1-alkanol/ n -alkane binary systems to evaluate the ability of the simplified perturbed chain SAFT (sPC-SAFT) equation of state (EoS) to predict monomer fractions. Kontogeorgis et al. [6] went further by incorporating monomer fraction data into their regression algorithm in order to derive new parameters which provide a more accurate description for a wider range of mixture properties.

Most of the published binary monomer fraction data are for systems containing one associating (usually polar) component dissolved in a non-associating fluid. Monomer fractions are linked

to the concept of the ‘unbounded fraction’, which is incorporated in the association term within the SAFT framework. Although the SAFT EoS is of specific interest for most applications, monomer fraction data have also been used in the evaluation of other hydrogen-bonding/association based formulations such as cubic-plus-association (CPA) [6] and non-random hydrogen-bonding (NRHB) [6,7] models.

It is highly unlikely for acetone to form a classical hydrogen bond, since the relevant $C=O \cdots H-C$ bond is not considered energetically strong enough to be differentiated from other van der Waals forces [8,9]. Acetone can form hydrogen bonds in a mixture (most notably with chloroform, which is also non-associating in its pure form) due to the presence of two lone electron pairs on the oxygen atom of the acetone molecule.

Four alcohols, viz. methanol, ethanol, 1- and 2-propanol, were used in this study. Acetone as a non-self associating component was used. n -Hexane was used for data validation purposes. The chemicals used in this study along with their purities are given in Table 1. The pure component, temperature dependent monomer fraction data are available from literature for methanol, ethanol and 1-propanol [2–4]. Furthermore, several binary data sets used to measure monomer fraction data are also available in the literature (as shown in Table 2), of which most constitute alcohol

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Nomenclature

AcO	Acetone
A.U.	Absorbance units
ATR	Attenuated total reflectance
CPA	Cubic-plus-association
Di	Dimer fraction
EqS	Equation of state
EtOH	Ethanol
FTIR	Fourier transform infrared
IR	Infrared
MCT	Mercury cadmium telluride
MeOH	Methanol
Mo	Monomer fraction
NRHB	Non-random hydrogen-bonding
Po	Polymer/oligomer fraction
SAFT	Statistical associating fluid theory
sPC-SAFT	Simplified perturbed-chain SAFT
1PrOH	1-Propanol
2B	Association scheme within SAFT framework
2C	Association scheme within SAFT framework
2PrOH	2-Propanol
A—B	Single covalent bond between molecules A and B
A=B	Double covalent bond between molecules A and B
A···B	Hydrogen bond between molecules A and B
$A'(\tilde{\nu})$	Calculated absorbance at wavenumber $\tilde{\nu}$ [A.U.]
A'_{\max}	Maximum absorbance i.e., the height of the fitted peak
A	Integrated area of the absorbance peak [A.U./cm]
a	Lorentzian peak width
b	Gaussian peak width
C	Peak concentration [mol/dm ³]
\tilde{c}_A	Stoichiometric alcohol concentration [mol/dm ³]
c_i	Concentration calculated from a thermodynamic model [mol/dm ³]
d	Cell pathlength through the sample [cm]
i	is designated as monomer, dimer and polymer or data points of an isothermal concentration series
$\frac{K}{\alpha}$	Equilibrium constants
$\tilde{\nu}_{\max}$	Absorption coefficient
$\tilde{\nu}_{\max}$	Wavenumber at center of the fitted peak [cm ⁻¹]
$X_{\text{mon},i}$	Monomer fraction if species i
x_i	Mole fraction of species i

diluted in *n*-alkanes. For alcohol/alkane systems, data sources show that monomer fraction values at infinite dilution tend to one as the solute concentration tends to zero [7]. Conversely, an exponential decrease (similar to a natural decay function) in monomer fraction is seen as the solute concentration increases [5,7]. This trend is consistent with both the theoretical explanation given in Section 2.1 and thermodynamic models such as sPC-SAFT, CPA and NRHB.

Table 2 shows that only one of the previously measured systems contains an alcohol/acetone mixture. While Max and Chapados [17] did not explicitly calculate methanol monomer fractions, they did provide interesting insights into the forming of hydrogen-bonding complexes. Using spectral factor analysis, they determined that 45.6% of acetone molecules appeared as monomers in a dilute solution (0.3 mol%) with methanol. However, no literature data could be found for very dilute ($x_{\text{AcO}} < 0.003$) acetone in

Table 1

Materials used, their purity, H₂O impurity and suppliers.

	% purity ^a	% H ₂ O impurity ^a	Company
Methanol	99.9	<0.02	Sigma-Aldrich
Ethanol	99.8	<0.2	Sigma-Aldrich
1-Propanol	99.9	<0.05	Sigma-Aldrich
2-Propanol	99.9	<0.05	Sigma-Aldrich
Acetone	99.8	<0.2	Fluka
<i>n</i> -Hexane	99.0	<0.01	Sigma-Aldrich

^a All purities and impurities reported on a mass basis.

alcohol mixtures. Table 2 also shows that the ethanol/hexane system is one of the few systems for which multiple data sources are available [5,7]. Therefore, it served as a useful benchmark system in this work for verification of equipment performance and validation of experimental procedures (see Section 4.1). The objective of this work was to add to the current body of monomer fraction data by measuring new monomer fraction data for binary alcohol/acetone mixtures. Data sets were collected for dilute alcohol-in-acetone systems, as well as for dilute acetone-in-alcohol systems, each time in order to calculate the monomer fractions of the relevant diluted components. Fourier transform infrared (FTIR) spectroscopy was used for these measurements, since it has a long history as the most common method for identifying hydrogen bonds [8] and, therefore, monomer fractions (see Section 2.1). In this method, an IR beam interacts with a given sample and the frequencies of the constituent atom vibrations are determined through an energy absorption process. Monomer, dimer and polymer molecules vibrate at different frequencies [7], making it possible to detect them with FTIR.

2. FTIR peak curve fitting

2.1. Identification of alcohol and acetone bonds

Within an alcohol/acetone mixture, two types of hydrogen bonds can be formed viz. alcohol/alcohol (O—H···O) and alcohol/acetone (O—H···O=C) (refer to “Nomenclature” for a description of how the various chemical bonds are presented). Therefore, an alcohol/acetone system represents a complex mixture whereby both fluids exhibit strong polar and hydrogen-bonding interactions.

The O—H bond is of specific interest for evaluating interactions involving alcohol, while the C=O bond is used to characterize the hydrogen bond profile of acetone. The stretch band of all O—H

Table 2

Literature data of binary systems used for measuring monomer fractions of the solute.

Solute	Solvent	Conditions	Reference
Methanol	Hexane	Ambient	[28]
Acetone	Methanol	300.3 K	[17]
Propanol	Heptane	288–328 K	[4]
Pentanol	Hexane	298 K, 308 K	[29]
Hexanol			
Methanol	Hexane	Ambient (298 K)	[7]
Ethanol			
Pentanol	Hexane	298–313 K	
Propanol			
Hexanol			
Ethanol	Heptane	300.3 K	[5]
Propanol			
Methanol	Hexane		
Ethanol			
Propanol			
Pentanol			
Hexanol			

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