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Study of fuel oxygenates solubility in aqueous media as a function of temperature and *tert*-butyl alcohol concentration

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Abstract

Methyl *tert*-butyl ether (MTBE) is the most widely used oxygenate in gasoline blending and has become one of the world's most widespread groundwater and surface water pollutants. Alternative oxygenates to MTBE, namely ethyl *tert*-butyl ether (ETBE), *tert*-amyl ether (TAME) and diisopropyl ether (DIPE) have been hardly studied yet. The solubility of these chemicals is a key thermodynamic information for the assessment of the fate and transport of these pollutants. This work reports experimental data of water solubility at the range from 278.15 to 313.15 K and atmospheric pressure of ethers used in fuels (MTBE, ETBE, TAME and DIPE) due to the strong influence of temperature on its trend. From the experimental data, temperature dependent polynomials were fitted, thermodynamic parameters were calculated and theoretical models were used for prediction. Finally, the *tert*-butyl alcohol (TBA) influence in the solubility of MTBE and ETBE in aqueous media was studied.

Keywords: Ethers; Water solubility; Prediction; *tert*-butyl alcohol

1. Introduction

Reliable thermodynamic data of pollutants are highly important from practical and theoretical points of view. Environmental chemistry and engineering need this information for transfer modelling of organic pollutants in the nature, remediation of contaminated soils and surface waters, minimize the presence of hazardous pollutants in aqueous effluents and develop new strategies for cheap and effective cleaning procedures and then, adequate decisions and remediation policies. From a more fundamental point of view, thermodynamics are necessary for the understanding of the complex molecular interactions and mechanisms of solution. The test of existent models and the development of new methods for prediction of these thermodynamic functions, have a particular significance since they are the only way to ensure accurate results.

Oxygenated compounds are added to gasoline in order to improve fuel combustion efficiency and to lower exhaust emissions of CO and hydrocarbons. Examples of these compounds are alcohols (as methanol, ethanol, isopropyl alcohol, isobutyl alcohol and *tert*-butyl alcohol) and ethers (as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and diisopropyl ether (DIPE)) (Deeb et al., 2003). MTBE is the most important fuel oxygenate used worldwide, and from 1998 in USA and 2002 in European Union it was included in monitoring programs of volatile organic compounds (VOC) and it is considered an unique contaminant owed to its ability to move readily throughout various environmental compartments and to its resistance to degradation. On the other hand, MTBE remains in groundwater for a long time after a spill. Other ethers should have a similar behavior into the environment. The contamination of

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water supplies by these kinds of organic chemicals is a problem of increasing concern.

An important gap of thermodynamic data related to these compounds exists into open literature. Only a few authors have developed research on different properties as Arp and Schmidt (2004) (Henry's Law Constant), Krahenbuhl and Gmehling (1994), Toghiani et al. (1996), Arce et al. (1999) and Loras et al. (2002) (vapor pressures). Despite these collections of data, more systematic temperature studies of thermodynamic magnitudes are necessary.

Related with the temperature dependence of water solubility of these kind of fuel oxygenates exist few data in the literature and show a large dispersion. Stephenson (1992) studied the mutual solubility of 16 ethers with water, among them, MTBE and TAME. At the temperature range studied in this work (that usually is the environmental temperatures of water) Stephenson's work only presents six experimental points for MTBE and five experimental points for TAME. Another work in this field was carried out by Fischer et al. (2004). They studied only the water solubility of MTBE at two temperatures. The European Fuel Oxygenates Association (EFOA, 2005) gives also data for MTBE but differ in value and in trend. For ETBE there is a work of Domanska et al. (Domanska et al., 1999) that studies the water solubility at two temperatures and for DIPE Harrison et al. (Harrison and Roquero, 2004) studied it at two temperatures. Other water solubility data is also found in several liquid–liquid equilibria studies (Hellinger and Sandler, 1995; Huttunen et al., 1997; Arce and Blanco, 1998; Fandary et al., 1999; Harrison and Roquero, 2004) and in reviews works (Deeb et al., 2003). Due to the important dispersion of the data into open literature is important to analyze it deeply and improve the quality of the data.

Thus, as a continuation of our scientific work related with the temperature study of physical properties of pollutants and their mixtures (Gonzalez-Olmos and Iglesias, 2007; Iglesias et al., 2007), there are reported the temperature dependence on water solubility at the range 278.15–313.15 K and atmospheric pressure of MTBE, ETBE, TAME and DIPE.

From the experimental data, temperature dependent polynomials were fitted and the corresponding parameters are gathered. Because of the expense of the experimental measurement of such data and current processes design is strongly computer oriented, consideration was also given attention to how accurate theoretical methods work by comparison with the experimental data. The UNIFAC method, that is a group contribution method used to calculate the activity coefficients of species in solution, was used in order to predict the non-ideal temperature dependence of this magnitude at a wide range (Kuramochi et al., 2002). This method is widely used by chemists and chemical engineers for predicting phase equilibria of systems for which no experimental data are available utilizing existing data for similar systems (Reid et al., 1988). The solubility was also calculated applying the thermodynamical relationship of dividing the vapor pressure by the Henry's constant law. This relationship comes from the thermodynamic definition of Henry's law assuming that the solution is sufficiently dilute (Valsaraj, 2000).

Another parameter studied in this work is the influence of TBA concentration, which is a degradation product and an impurity of MTBE and ETBE, on the water solubility of these compounds.

2. Experimental section

2.1. Chemicals

Water was Millipore quality with organic total mass<5 ppb and resistivity 18.2 MΩ cm. MTBE, TAME, DIPE and TBA were of Merck quality with richness better than 99.5 mol%. ETBE that is provided by REPSOL-YPF has a purity higher than 96 mol%. The pure components were stored in sun light protected form and constant humidity and temperature. All products were degassed using ultrasound and dried on molecular sieves (pore diameter of 4 and 5×10^{-10} m from Fluka) before use. Important physico-chemical properties of the investigated compounds are listed in Table 1 many of them measured in our laboratory.

2.2. Experimental determination of water solubility

Four vials (20 ml each) were used to determine the water solubility. Every vial contained a small magnetic stir bar and 10 ml of water. All the vials were filled with 10 ml of water and then were saturated with an excess amount of ether (8 ml). The vials were kept at constant temperature with a Polyscience bath model 9010. Temperature was controlled within $\pm 5 \times 10^{-2}$ K inside the cell, and connected to a controller bath Polyscience model 9010, with a stability of $\pm 10^{-2}$ K. All the solutions were stirred gently for

Table 1
Molecular weight, densities ρ, speed of sound, refractive indices n_D, Henry's constant law K_{iH} and vapour pressure p_i of the pure components at 298.15

Component	MW/g mol^{-1}	ρ/g cm^{-3} (expt)	u/m s^{-1} (expt)	n_D (expt)	K_{iH}/m^3 Pa mol^{-1} (expt)	p_i/kPa[a]
MTBE	88.150	0.734915	1035.89	1.366207	83.50	32.86
ETBE	102.176	0.735327	1034.28	1.373670	135.77	20.29
TAME	102.176	0.765399	1115.55	1.385764	134.04[a]	9.10
DIPE	102.176	0.718160	975.72	1.365115	260.15[a]	19.99
TBA	74.123	0.778522	1116.51	1.384518	1.46[a]	5.60

[a] Arp and Schmidt (2004).