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R. Gonzalez-Olmos[a]; M. Iglesias[b]
[a] Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, España [b] PF&PT Research Team, Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Santiago de Compostela, España

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R. Gonzalez-Olmos[1] and M. Iglesias[2]
[1]Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, España
[2]PF&PT Research Team, Department of Chemical Engineering, School of Engineering, University of Santiago de Compostela, Santiago de Compostela, España

Abstract: The thermodynamics of the mass transfer process of fuel oxygenates (MTBE and ETBE) from aqueous phase to air by batch air stripping (BAS) has been studied in this work. This study analyzes the influence of the aeration flow and the temperature. The Mackay approach was used in order to calculate the Henry's law constant for each operational condition and they were compared with those obtained by static methods. The thermodynamics functions of the process, aqueous free excess enthalpy of solution ($\mathrm{H}_{\mathrm{iw}}^{\mathrm{E}}$) and enthalpy of air-water transfer ($\Delta_{\mathrm{wa}}H_i$) for both compounds were calculated and compared with literature values. Finally the effect of the cosolvency of tert butyl alcohol (TBA) was analyzed.

Keywords: Aeration, ETBE, Henry's law constant, MTBE, thermodynamics and cosolvency

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Address correspondence to R. Gonzalez-Olmos, Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Química, Universitat Rovira i Virgili, Avinguda Països Catalans 26, Campus Sescelades, Tarragona 43007, España. Fax: +34-977-559667. E-mail: rafael.gonzalez@urv.net

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 environment, solve the 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 models and the development of new methods for prediction of these thermodynamic functions, have a particular significance because 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 (TBA)) and ethers (as methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), and diisopropyl ether (DIPE)) (1–3). 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 VOC's and it is considered a unique contaminant owing to its ability to move readily throughout various environmental compartments and to its resistance to degradation (4). Other ethers used as fuel oxygenate, whose use is increasing, such as ETBE is expected to have a similar behavior. For all these reasons the contamination of water supplies by these kinds of organic chemicals is a problem of increasing concern.

Their physico-chemical properties (high solubility and low Henry's law constant and low octanol water partition coefficient (5)) make them difficult for their treatment with conventional water cleaning technologies, including air stripping, advanced oxidation processes (AOP), and carbon adsorption (6–9). The several process variables that are involved in these techniques strongly affect their efficiency. One of the typical parameters that can vary more often is the temperature since usually these processes are carried out at environmental conditions. So the efficiency of these processes can be different in summer or in winter. For this reason it is important to improve the knowledge of the temperature dependence of the physico-chemical properties that can affect the cleaning processes. Some temperature dependences of physico-chemical properties of these compounds are found in literature. Arp and Schmidt obtained Henry's Law Constant for these ethers by a static method (10). Gonzalez-Olmos et al. (11,12) studied the temperature dependence of water solubility, the density, and the speed of sound. Krahenbuhl and Gmehling report vapor pressure for ethers (13). Vapor pressure is also published with vapor-liquid equilibria data for binary and/or ternary mixtures containing ethers as in the works of Toghiani et al. (14), Arce et al. (15), and Loras et al. (16). Marsh et al. review the state-of-the-art of the thermodynamics involving these kinds of compounds (17). However, few and poor systematic studies of the temperature dependencies and the thermodynamics of aeration of fuel oxygenates are found in the literature.

In contrast, there exists several isothermal works that analyze the effectiveness of aeration or stripping (always in a continuous process) to remove ethers (especially MTBE) from water. Sutherland et al. (7) examined the treatment of MTBE using air stripping, advanced oxidation techniques, and GAC adsorption in a pilot plant. The work concluded that at high flow rates air stripping tends to be the most adequate treatment in terms of economy and efficiency. At lower rates, all the techniques were competitive and the process selection could be based on other factors. Similar results were obtained by Baus et al. (9). These works conclude saying that stripping is an effective technique but it could be expensive. The reasons are the need of high air flow consumption to achieve the recommended concentration levels and the need of a post-treatment in order to capture the fuel oxygenate in the exhaust air, which increases the operational costs. Ramakrishnan et al. (18) studied the performance of the combination of air stripping with off gas treatment based on adsorption. High removal efficiency was achieved and mass transfer coefficients were obtained. On the other hand Wilhem et al. (8). apply air stripping to remove MTBE from a river. They analyzed the process from an economical point of view and conclude that to remove high concentrations of MTBE could be noncost-effective. Thomson et al. (19) apply the technique in a field site with permeable barriers to remove MTBE from groundwater. Finally Bass et al. (20) studying the effect of using heated air in the stripping tower in order to improve the efficiency to remove MTBE and they found that the efficiency was increased considerably. Finally, there is no work in the literature that studies the aeration/stripping of ETBE.

This work is part of a wider study related to theoretical and experimental analysis of thermophysical properties of fuel oxygenates (11,12, 21–24). Thus, as a continuation of our scientific work, we have reported the temperature dependence of Batch Air Stripping (BAS) of ethers spilled in water. BAS experiments of water solutions saturated with MTBE and ETBE were carried out at the aeration 100–400 $\mathrm{ml \cdot min^{-1}}$

range and at 288.15–308.15 K temperature range. The corresponding Henry's law constants were obtained through the dynamics developed by Mackay et al. (25) and were compared with literature values obtained by static methods (10). By the dynamic BAS, small deviations from equilibrium are translated into smaller error in the Henry's coefficient compared to static systems. Different thermodynamics magnitudes were computed and compared with open literature. Finally the effect of the presence of tert-butyl alcohol, one of the most important degradation by-products of these pollutants, in the values of Henry's law was analyzed, a strong dependence in the case of MTBE was found.

EXPERIMENTAL

Chemicals

Water was Millipore quality with organic total mass <5 ppb and resistivity 18.2 MΩ · cm. MTBE and TBA were of Merck quality with richness better than 99.5 mol%. ETBE was provided by REPSOL-YPF with purity higher than 96 mol%. The pure components were stored in sunlight 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. The purity was checked by chromatography and by comparison with literature of density and speed of sound as Table 1 shows.

Table 1. Molecular weight, densities ρ and speed of sound u, of the chemicals at 298.15 K

		$\rho/(g \cdot cm^{-3})$		$u/(m \cdot s^{-1})$	
Chemical	$MW/(g\,mol^{-1})$	Exp.	lit.	Exp.	lit.
MTBE	88.150	0.734915	0.73529[b]	1035.89	1035[e]
ETBE	102.176	0.735327	0.735[c]	1033.33	1034.28[f]
TBA[a]	74.12	0.775212	0.77572[d]	1099.02	1104.8[g]

[a] at 303.15 K.
[b] (26).
[c] (27).
[d] (28).
[e] (29).
[f] (21).
[g] (30).

Batch Air Stripping Experiment

For each temperature a stock solution of water saturated with fuel oxygenates was prepared in order to assure that the initial concentration for each experiment was the same. The stock solutions were obtained by equilibrating the hydrocarbon with water in a separate vessel and the initial concentrations in the aeration experiments correspond to the water solubilities published in our previous work (11). Figure 1 shows a schematic diagram of the apparatus used. The general procedure was to strip the hydrocarbon dissolved in water with compressed air. For each temperature, the column was filled with the corresponding stock solution. Then compressed air was passed through a low-pressure line regulator and an Agilent Flow Tracker 1000 (gas flowmeter). The air was introduced into the thermostatic bath in order to keep its temperature as in the stripping cell. After that, the air was introduced into the bottom of

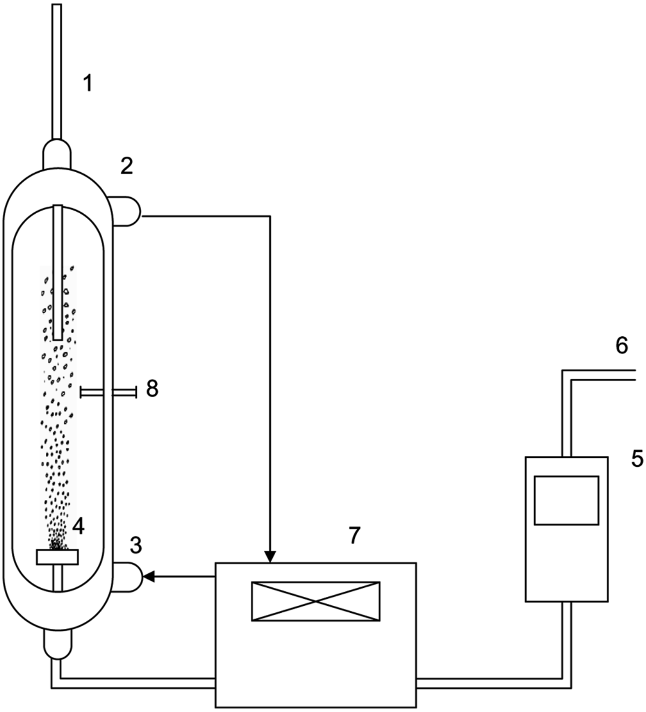


Figure 1. Schematic of BAS experimental setup. Thermometer and polluted water inlet, 1; outlet thermostatic bath, 2; inlet thermostatic bath, 3; fritted glass, 4; gas flowmeter, 5; air inlet, 6; thermostatic bath, 7; Sampling point, 8.

the stripping vessel through a fritted glass disk. The system was maintained at constant temperature ±0.6 K with a Polyscience bath model 9010. The air flow rate was set at 100 to $400 \pm 20\,\mathrm{mL} \cdot \mathrm{min}^{-1}$ range. Flow rates were measured at 5 minutes intervals. The sampling frequency varied from once every 2 minutes to once every 30 minutes, depending on the rate of volatilization. At each sampling, the concentration of the hydrocarbon and time were recorded.

In order to see the influence of the presence of TBA in the aqueous media for both compounds, experiments with different TBA concentration were carried out at 298.15 K and $400\,\mathrm{mL} \cdot \mathrm{min}^{-1}$ of aeration level for both compounds. All the experiments were carried out in triplicate in order to calculate errors.

Analytical Method

The concentration of dissolved hydrocarbon in the water was measured by GC/FID. The GC used was a Hewlett-Packard 6890 operated with Chemstation software. The column was a 30 m capillary column (DB-624, J + W scientific, 0.53 mm, and 3 micron film thickness). The detector was a flame ionization detector (FID). For all measurements, the column temperature was set to 381 K (isotherm) over 4 min. The FID temperature was 523 K and the injector temperature was 453 K. Helium was used as the carrier gas (40 kPa) for all analyses. The flow parameters of other gases were set as fuel gas (hydrogen) $30\,\mathrm{mL} \cdot \mathrm{min}^{-1}$, air $400\,\mathrm{mL} \cdot \mathrm{min}^{-1}$, and make-up (nitrogen) $30\,\mathrm{mL} \cdot \mathrm{min}^{-1}$. Analysis of samples were carried out by taking 2 μL from the aqueous phase (Direct Aqueous Injection) using an Agilent D07-B1086 microsyringe and was automatically injected with an Agilent 7683 series Injector into the GC.

THEORY

Henry's Law Constant

A mathematical description of the stripping process can be readily assembled (25) if it is assumed

1. that the system is isothermal,
2. the liquid phase is well mixed,
3. the vapor behaves ideally,
4. Henry's law is obeyed over the relevant concentration range,
5. the volume of liquid remains constant,

6. the partial pressure of the solute is small compared to the total pressure, and
7. the solute in the exit vapor is in equilibrium with the liquid.

A dynamic mass balance for the solute gives the transfer rate as:

$$-V\left(\frac{dC}{dt}\right) = \left(\frac{PG}{RT}\right) = \left(\frac{K_{iH}GC}{RT}\right) \tag{1}$$

where K_{iH} is the Henry's constant law ($L\,atm\,mol^{-1}$) C is the concentration of ether, G is the gas flow rate ($mL \cdot min^{-1}$), V is the volume of the liquid (mL), R is the universal gas constant, P is the pressure (atm), T is the temperature (K), and t is time (min). This equation can be integrated from initial conditions when $t = 0$ and $C=C_0$ to give:

$$\ln\left(\frac{C}{C_0}\right) = -\left(\frac{K_{iH}G}{VRT}\right) \cdot t \tag{2}$$

A plot of logarithmic concentrations against time should be linear with a slope of $-(K_{iH}G/VRT)$.

In order to assure that the vapor and liquid phases are in equilibrium at the top of the column, a liquid depth of 40 cm was used in this work. Mackay et al. (25). found that for the case of benzene with a length of 38.5 cm in their column the equilibrium achieved was >99%. As they mentioned, for molecules with a lower Henry's constant law, as it is the case of MTBE and ETBE, the equilibrium will be reached faster.

An alternative way to express K_{iH} is by using the dimensionless γ_{iw}^{∞} value. This conversion is done following Eq. (3) (31).

$$K_{iH} = \frac{p_i}{C_{iw}} = p_i^{*}\gamma_{iw}^{\infty}\,\overline{V_w} \tag{3}$$

where C_{iw} is the molar water solubility ($mol \cdot L^{-1}$), γ_{iw}^{∞}, is the activity coefficient of the compound i in water at infinite dilution, $\overline{V_w}$ is the molar volume of water ($L \cdot mol^{-1}$), and p_i^{*} is the vapor pressure at the corresponding temperature (atm).

In order to see how important is the presence of TBA in the BAS process a ratio of Henry's law constant has been defined by the following equation:

$$R_H = \frac{K_{\dim iH'}}{K_{\dim iH}} \tag{4}$$

where $K_{\mathrm{dim\ iH'}}$ is the dimensionless Henry's constant law at a determined molar fraction of TBA and $K_{\mathrm{dim\ iH}}$ is the dimensionless Henry's constant law with no presence of TBA. To obtain the dimensionless Henry's constant law it is necessary to divide K_{iH} by the universal gas constant and temperature.

Thermodynamics of Water-Air Transfer

The temperature dependence of K_{iH} can be related to the enthalpy of vaporization ($\Delta_{\mathrm{vap}}H_i$), the aqueous free excess enthalpy of solution (H^E_{iw}), and the enthalpy of water-air transfer ($\Delta_{\mathrm{wa}}H_i$), through the following equations (32).

$$\ln K_{\mathrm{dim\ iH}} = \frac{-\Delta_{\mathrm{wa}}H_i}{RT} + B \qquad (5)$$

$$\Delta_{\mathrm{wa}}H_i = \Delta_{\mathrm{vap}}H_i - H^E_{\mathrm{iw}} \qquad (6)$$

Using Eq. (5) and the values reported in Table 2, $\Delta_{\mathrm{wa}}H_i$ and the constant B were determined for both ethers. As literature values for the $\Delta_{\mathrm{vap}}H_i$ of these compounds were available (33), the H^E_{iw} could easily be calculated using Eq. (6).

Table 2. Comparison of the dimensionless Henry's constant law, enthalpy of air-water transfer ($\Delta_{\mathrm{wa}}H_i$) and its temperature dependence constant (B) with literature for MTBE and ETBE

T	This work	(10)	(34)	(35)	(36)	(37)
MTBE						
288.15	0.0201 ± 0.0001	0.0210	0.0177	0.016		0.0405
298.15	0.0324 ± 0.0003	0.0330	0.0292	0.031	0.022	0.0513
308.15	0.0594 ± 0.0008	0.0600				
$\Delta_{\mathrm{wa}}H_i/(\mathrm{kJ \cdot mol^{-1}})$	39.9	41.9	35.42	55.25	61.08	23.39
B	12.72	12.6	10.74	18.9	21.0	6.55

T	This work	(10)	(38)
ETBE			
288.15	0.0217 ± 0.0007	0.0299	
298.15	0.0570 ± 0.0047	0.0670	0.0972
308.15	0.1093 ± 0.0074	0.1179	
$\Delta_{\mathrm{wa}}H_i/(\mathrm{kJ \cdot mol^{-1}})$	59.7	52.4	
B	21.14	18.1	

RESULTS AND DISCUSSION

Analysis of Aeration of Ethers

The removal of ethers by aeration can be observed in Fig. 2a for MTBE and in Fig. 2b for ETBE. The best performances are achieved in both cases with high temperatures and high aeration rates. In the case of MTBE it can be observed that at 308.15 K with an aeration rate of $400\,\mathrm{mL}\cdot\mathrm{min}^{-1}$ the concentration of ether is reduced to 99.4% in 30 minutes. In the case of more usual water temperature as 288.15 with the same aeration rate a reduction of 99.6% is achieved in 90 minutes. So the influence of the temperature is high. In the case of ETBE the volatilization rates are higher. In the optimum case ($Q = 400\,\mathrm{mL}\cdot\mathrm{min}^{-1}$ and $T = 308.15\,\mathrm{K}$) a 99.6% of reduction is achieved in 20 minutes while with a temperature of 288.15 K and a air rate of $400\,\mathrm{mL}\cdot\mathrm{min}^{-1}$ a 99.4% of reduction is obtained in 60 minutes.

The results for ETBE are better because, as it is shown below, it has higher Henry's constant law. The ethyl group of ETBE gives a character less polar comparing to MTBE that has a methyl group that is shorter. Despite the fact that MTBE is more volatile than ETBE, when it is in aqueous media it builds up a hydrogen bond faster than ETBE due to its lower steric hindrance and higher polarity. For this reason the hydrophobicity of MTBE is lower than of ETBE.

The temperature increases the molecular dynamics and facilitates the transfer of ether molecules from the aqueous phase to the air phase. In addition, as Gonzalez-Olmos et al. (11) showed, the hydrophilicity of both compounds decreases with temperature. The influence of aeration rates is clearly better at higher values due to the fact that the resistance of the mass transfer is lowered.

Henry's Constant Law

Henry's constant law at different temperature was obtained (see Table 2) by the dynamic approach developed by Mackay. The values obtained at different aeration rates were very similar which demonstrates the independence of the method from this variable. The highest values were for ETBE and for both compounds the values increase with temperature in the studied range. The temperature dependence is usually expressed with Eq. (9). In Fig. 3 the linear plots of this equation are shown with the correlation coefficient and the experimental error. The values of $\Delta_{wa}H_i$ and the constant B for both compounds are gathered in Table 2. The results were compared with values obtained by other authors that

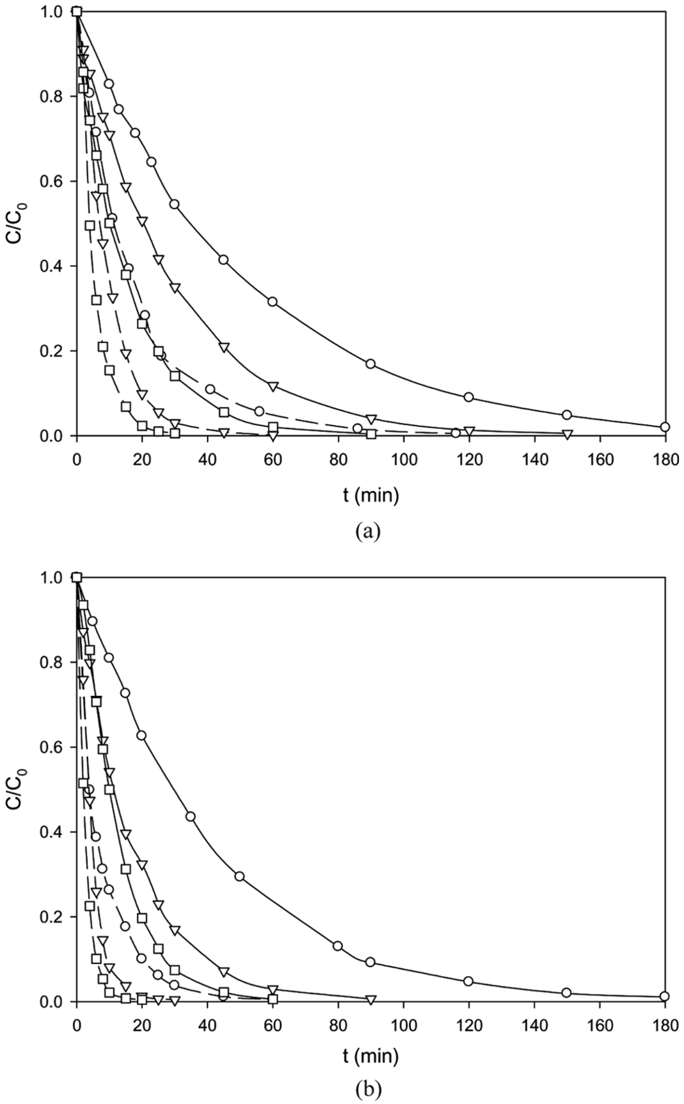


Figure 2. Removal of fuel oxygenates by BAS at 288.15 K (continuous line) and 308.15 k (dashed line) and at aeration rates of 100 mL · min^{-1} (○), 250 mL · min^{-1} (▽) and 400 mL · min^{-1} (□). a) MTBE and b) ETBE.

worked with static methods such Equilibrium Partitioning in Closed Systems (EPICS) or different headspace techniques. The values of this work are very similar to those obtained by Arp et al. (10) by EPICS. There are

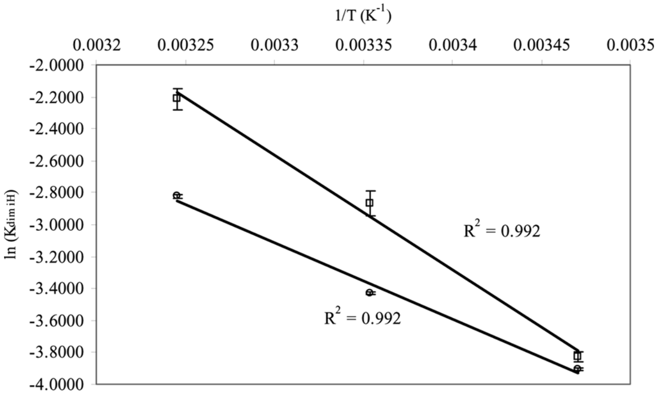


Figure 3. Influence of temperature on Henry's constant law for MTBE (○) and ETBE (□). Solid lines adjusted values with Eq. (5).

little differences with other authors caused probably by the consideration of equilibrium.

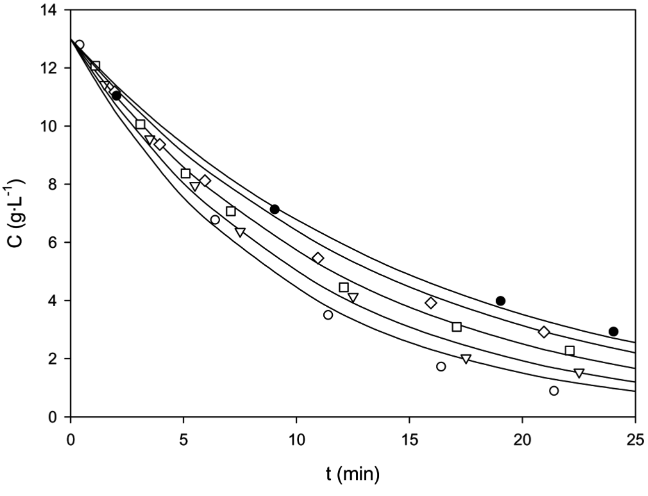
Thermodynamics of BAS of Ethers

The resulting enthalpies were calculated with the experimental data and Eqs. (5) and (6). The activity coefficients at infinite dilution (γ_{iw}^{∞}) were

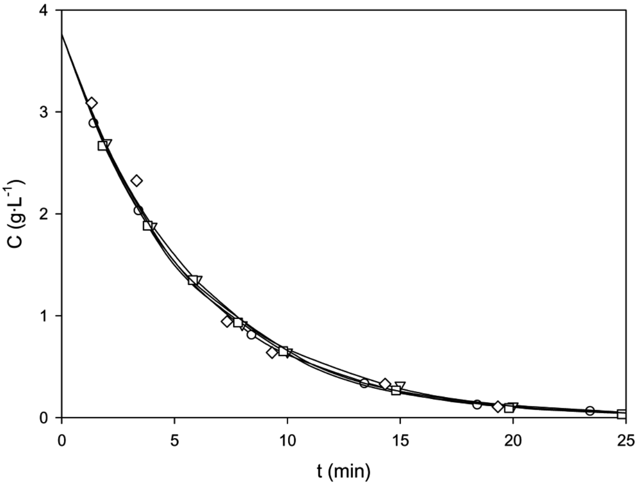
Table 3. Thermodynamic parameters obtained from the BAS process and comparison with open literature

	$\Delta_{vap}H_i/(kJ \cdot mol^{-1})$ (34)	$\Delta_{wa}H_i/(kJ \cdot mol^{-1})$	$H_{iw}^{E}/(kJ \cdot mol^{-1})$
MTBE	30	39.9	−9.9
ETBE	33	59.7	−26.7
	γ_{iw}^{∞}		
T/(K)	288.15	298.15	308.15
MTBE			
This work	123	136	170
(10)	128	137	175
(11)	93	121	156
ETBE			
This work	276	387	600
(10)	377	548	648
(11)	291	411	566

calculated with Eq. (3). The values, given in Table 3, are similar to those obtained by Arp et al. (10) by the EPICS method and by Gonzalez-Olmos et al. (11) obtained by water solubility measurements. $\gamma_{\text{iw}}^{\infty}$ for MTBE is



(a)



(b)

Figure 4. Influence of TBA concentration on the fuel oxygenate removal by BAS at 298.15 and 400 mL · min^{-1}. a) MTBE with TBA molar concentrations of 0 (○) 0.0002 (▽), 0.001 (□), 0.003 (◇) and 0.006 (●). b) ETBE with TBA molar concentrations of 0 (○) 0.003 (▽), 0.005 (□), 0.011 (◇). Solid lines values adjusted with Eq. (2).

smaller than for the ETBE by at least a factor of 3, and it changes less with temperature, i.e., the H_{iw}^{E} and $\Delta_{wa}H_i$ is smaller. As reported (10), it appears that the smaller the molecular volume, the smaller γ_{iw}^{∞} and H_{iw}^{E}.

Influence of the Cosolvency of TBA in the Value of Henry's Constant Law

In the last part of the work we analyzed the effect of the cosolvency of TBA, a typical degradation byproduct of MTBE and ETBE, in the value of Henry's constant law. The experiments consisted of carrying out BAS experiments with different initial molar fractions of TBA in the polluted water to observe how the Henry's constant law of both ethers changed with the TBA presence. The TBA cosolvency experiments were carried out at constant temperature (298.15 K) and air mass flow (400 mL · min^{-1}).

The results are gathered in Fig. 4 and Table 4. They show how the presence of TBA has a high effect in the Henry's law constant value for MTBE. With an initial TBA molar fraction in water of 0.006 the value of the constant is 38% lower than without TBA. In the case of ETBE the effect is lower. With a very high presence of TBA (molar fraction = 0.011) the reduction of the constant is only of a 9%. Due to these quantities of TBA (molar fraction = 0.011) are very difficult to find in the environment we can conclude that Henry's constant law of ETBE will not be affected by TBA. Probably, the main reason is because the presence of TBA (which has a very low Henry's constant law) has a

Table 4. Dimensionless Henry's constant law ($K_{dim\,iH}$) of fuel oxygenates at 298.15 K as function of TBA molar fraction and ratio of Henry's constants law (R_H)

x_{TBA}	$K_{dim\,iH}$	R_H
MTBE		
0.0060	0.0201	0.62
0.0030	0.0217	0.67
0.0020	0.0243	0.75
0.0010	0.0261	0.81
0.0002	0.0292	0.90
0.0000	0.0322	1.00
ETBE		
0.0114	0.0478	0.91
0.0047	0.0500	0.95
0.0025	0.0517	0.98
0.0000	0.0527	1.00

stronger influence in Henry's constant law of MTBE is due to the fact that the interactions between these compounds are much higher.

CONCLUSIONS

New experimental data of water-air mass transfer at temperature range of 288.15–308.15 K and an aeration flow rate range of 150–400 mL · min^{-1} for ethers used as fuel oxygenates in gasoline blending were obtained through the dynamic method of Batch Air Stripping. From these data Henry's law constant was computed and compared with those obtained by static methods obtaining a good agreement. Different thermodynamical parameters such us $\Delta_{wa}H_i$ and H_{iw}^E were computed from the experimental data and compared with literature. Furthermore, γ_{iw}^{∞} were obtained at different temperatures for both compounds and compared also with literature. Finally, the influence of the presence of TBA into water was studied for MTBE and ETBE being found to have a strong influence for MTBE.

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