

Estimation of Phase Separation in *ETBE*-gasoline Blends

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The objective of this paper is to propose a predictive tool for the estimation of phase separation in ether-gasoline blends. Firstly, water solubility in ETBE-gasoline blends at different temperature was experimentally performed. Based on experimental results, graphical correlations between phase separation and temperature were obtained for two base gasoline oxygenated by 4-15 vol% ETBE. The least-square regression method was involved to demonstrate that the experimental results regarding the water solubility in various ETBE-gasoline blends at various temperatures follows the second order polynomial functions.

Keywords: ETBE (ethyl tert-butyl ether), gasoline, phase separation, predictive tool

A considerable part of environmental air pollution and suspected health hazards arise from motor vehicle emissions [1]. Significantly reduced traffic emissions were achieved by newly developed, formulated fuels. Recent environmental legislative packages have significant effect in the formulation of transportation fuels. In 2003, EU bio-fuels directive (2003/30/EC) mandating the use of biofuels and set a target of 5.75% total bio-fuel share of all consumed gasoline and diesel fuel for transport placed on the market by 2010 [2]. On 2008, the European Commission introduced a legislative package which set target of 10% for the share of bio-fuels in transport. The revised Fuel Quality Directive 2009/30/EC is a part of this legislative package which requires to increase the percentage of oxygenated compounds in fuel from 2.7 weight%, up to a total content of oxygen of 3.5 weight%. Consequently, most of governments announcing commitments to bio-fuel programs as a means to both reduce greenhouse gas emissions and dependence on petroleum-based fuels. There are a variety of biofuels potentially available, but some of them, such as bioethanol and biodiesel are the main biofuels being considered globally [3-5]. Besides bioethanol, many others oxygenated compounds were added to gasoline to improve the combustion efficiency and to reduce the pollution.

The first oxygenated compound used as gasoline additives was methyl *tert*-butyl ether (MTBE) since 1970. This compound was used to increase the number of octane of gasoline, as a replacement of toxic additives such as tetraethyl lead (TEL). In the past, over 85% of gasoline was formulated with MTBE, because of its low price, low vapour pressure, total miscibility with gasoline, medium boiling point and reduction of fuel consumption. Despite of these favorable properties, the main drawbacks of MTBE are its highly solubility in water, its mobility and persistence, and the potential groundwater contaminant [6]. Even at lower concentration level this oxygenated compound make drinking water unpalatable [7]. Besides, MTBE is much more difficult to be degraded than other gasoline components. Therefore, social pressures have propelled other oxygenated compounds. The first solution provided by researchers and accepted by refiners and the users was to revert back to use of ethanol. This has some benefits in reducing water contamination and indicates no significant adverse impacts on public health and environment. Tests of exhaust emissions of vehicles fuelled by gasoline

oxygenated with 10% ethanol have shown a reduction of 4.7-5.8% in carbon monoxide and 5-15.3% total hydrocarbons emissions, as well as a reduction in the emitted levels of nitric oxide [8]. Recent research justified by the addition of ethanol in fuel showed increases in the Reid vapour pressure (RPV) of formulated gasoline, but also alters the distillation curve of fuel. Both properties are dependent upon the content of saturated hydrocarbons, the vapour pressure of the base fuel and ethanol content in the mixture [9, 10]. Hence, additional costly steps are needed to reduce evaporative emissions from ethanol blended gasoline fuels. Furthermore, ethanol blended gasoline fuels will yield high unburned ethanol and acetaldehyde emissions [11, 12] and acetic acid emissions [13]. Another disputed aspect is related to water solubility in ethanol-gasoline blends [14-16].

Tertiary ethers, such as *MTBE* (methyl *tert*-butyl ether), *ETBE* (ethyl *tert*-butyl ether) and *TAME* (tert-amyl methyl ether), present advantages in relation to conventional gasoline: excellent burning characteristics and octane-enhancing gasoline blending compounds, much less unburned hydrocarbons and carbon monoxide. Ethanol-derived ethers can overcome the drawbacks of gasoline with direct ethanol blend. Starting with 2008 the interest for *ETBE* (ethyl *tert*-butyl ether; 2-ethoxy-2-methylpropane) has increased. The *ETBE* is considered as semi-renewable because it can be produced by the etherification of isobutene, from mixture of C4 isomers with bio-ethanol [17, 18]. The production capacity in Europe is approximately 1 million tons *ETBE* per year [1].

In the last few years a considerable effort has been developed in the field of properties of the *ETBE* oxygenated gasoline. Recent research indicates that the substitution of gasoline with various *ETBE* proportions has a good influence in volatility properties and in octane increasing of gasoline-ether blending [19].

As a part of an extensive study [10, 15, 19] related to the experimental analysis of mixtures containing oxygenated and gasoline compounds, this paper presents the temperature dependence of the water solubility in different oxygenated gasoline formulated by their substitution with *ETBE*. Two synthetic gasolines with different chemical composition were oxygenated with various proportions of *ETBE* (in range of 4 to 15 vol% *ETBE*). Next, the water solubility in organic phase was tested by Carl-Fisher method, in temperature range of 268 to 303K. Experimental

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Properties	Values and UM		Equipment	Techniques
Hydrocarbons type	B1 gasoline blend	B2 gasoline blend	IROX 2000 Fuel Analyzer	ASTM D1319
Saturates	49.0 vol%	54.6 vol%	Portable Gasoline Analysis with MID-FTIR	
Olefins	12.9 vol%	11.5 vol%		
Aromatics total	38.1 vol%	33.9 vol%		
Reid pressure vapour	56 kPa	63.7 kPa	MINIVAP VPS/VPSH Vapor Pressure Tester	ASTM D6378
Distillation curves:				
- Initial	41.1 °C	41.8 °C	MINIDIS Analyzer	ASTM D86
- E70	33.0 % vol	35.0 % vol	Portable Minidistillation	
- E100	51.5 % vol	53.0 % vol		
- E150	78.0 % vol	78.0 % vol		
- FBP	190.4 °C	195 °C		
Octane numbers:				
-MON	85.0	85.0	IROX 2000 Fuel Analyzer	Correlation to ASTM D2699 and D2700
-RON	95.0	95.5	Portable Gasoline Analysis with MID-FTIR	

Table 1
PHYSICO-CHEMICAL PROPERTIES OF THE TWO SYNTHETIC GASOLINES

results help to achieve new graphical correlations and to propose a simple predictive tool for the estimation of water solubility in ETBE-gasoline blends. The proposed method presented is simply to use and is suitable for rapid estimation of phase separation in the fuel storage tank or in the onboard vehicle fuel tank of the customers. Two examples demonstrate the usefulness of the proposed tools.

Experimental part

First of all, two types of synthetic gasolines were prepared in laboratory and labeled as B1 and B2. The both gasolines were volumetric formulated by blending of three base components: the catalytic cracking gasoline, the catalytic reforming gasoline and an isomerization fraction. Refinery components were supplied by two different local companies. The gasoline mixture labeled as B1 was prepared by 35 vol% catalytic cracking gasoline, 43 vol% catalytic reforming gasoline and 22 vol% isomerization fraction, and gasoline blend labeled as B2 consists of 40 vol% catalytic cracking gasoline, 33 vol% catalytic reforming gasoline and 27 vol% isomerization fraction.

The synthetic gasolines were characterized based on their physicochemical properties: chemical composition, distillation range at atmospheric pressure, Reid pressure vapour, motor octane number (MON) and research octane number (RON). Different experimental techniques and lab equipment were used for this purpose and are listed in table 1 along with physicochemical properties of tested gasolines.

As table 1 indicates, the B1 base gasoline shows a higher fraction of aromatic hydrocarbons, while B2 a higher proportion of saturated hydrocarbons.

The ETBE (provided by Merck Company) was used without any purification as oxygenated compound. The two base gasolines (B1 and B2) received ETBE in the volumetric proportions of 4, 7, 10 and 15% (v/v) and stored in the insulated recipients. Next, in each sample was introduced certain volumes of distilled water and mixed manually. Gasoline and ETBE mixtures were deposited for 30 min into a *Thermo Scientific NESLAB refrigerated circulating bath* at different controlled temperatures (268, 273, 283, 303K). The phases separation between upper organic phase and lower aqueous phase was observed. The water solubility in organic phase has been determined by *Cou-Lou Karl Aquamax* device by Karl Fischer volumetric titration analysis method. The detailed procedure was

presented in our previous paper [16]. The results correspond to the average of the tests carried out in triplicate.

Results and discussions

The experimental results of water solubility in B1 and B2 oxygenated gasoline at different temperatures are illustrated in figures 1 and 2 along with polynomial fit curves.

The water amount in gasoline is almost inevitable somewhere along its transportation path and storage. In storage tank, the leaky fittings, the fill caps and faulty gaskets are few sources of moisture entries [20]. The atmospheric moisture is another source of water.

The main factors that control the phases separation are temperature and water content. From figures 1 and 2 it can be seen that as temperature increases the amount of water needed for phases separation increases, at constant volume of ETBE in both gasoline. The water solubility in ETBE - gasoline blends is due to ETBE molecular configuration. Higher temperatures produce an increase of internal molecular dynamics. The probability of ether group to build hydrogen bonds with water is increased and then higher water solubility is observed. From above figures it is shown that as ETBE content (expressed as vol%) increase the amount of water needed for phase separation increases, at constant temperature. This is due to the higher amount of ETBE that provided an increasing availability to form hydrogen bond with water molecules.

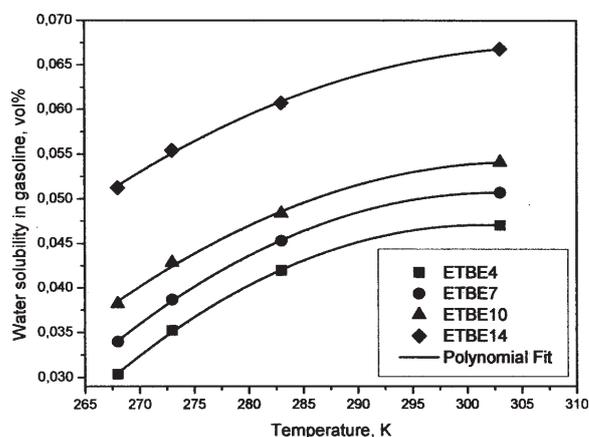


Fig. 1. Phases separation lines in B1 gasoline oxygenated with ETBE.

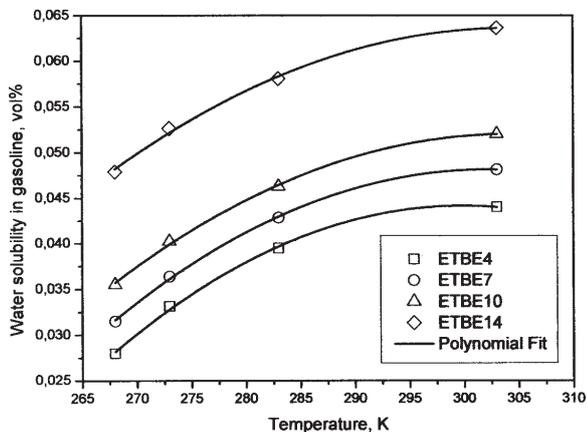


Fig. 2. Phase separation lines in B2 gasoline oxygenated with ETBE.

Table 2
FITTED PARAMETERS AND STATISTICAL INDICES VALUES OF WATER SOLUBILITY IN ETBE - GASOLINE B1 BLENDS

Coeff.	A		B		C		Statistics	
	Value	Error	Value	Error	Value	Error	Adj- R^2	RSS
ETBE 4	-1.30780	0.06851	0.00899	4.80E-04	-1.49E-05	8.38E-07	0.99921	4.26E-08
ETBE 7	-1.22276	0.06396	0.00842	4.48E-04	-1.39E-05	7.83E-07	0.99931	3.72E-08
ETBE 10	-1.01150	0.18407	0.00699	0.00129	-1.15E-05	2.25E-06	0.99349	3.08E-07
ETBE 15	-0.84395	0.14458	0.00591	0.00101	-9.58E-06	1.77E-06	0.99581	1.90E-07

On the other hand, the solubility of water in gasoline-ETBE blends can be also affected by hydrocarbon composition of the base gasoline. Due to the existence of π -bonds in molecule, aromatics and olefins would easily be miscible with water compared with saturated hydrocarbons. It is obvious that gasoline B1 by its content of unsaturated hydrocarbons keeps more water than gasoline B2 (table 1).

Based on above experimental data it can be concluded that lowering the phase separation temperature can be accomplished by:

- increasing the aromatic and/or olefinic hydrocarbon content in gasoline. But this is not in accordance with the most recent trends of increasing the non-aromatic hydrocarbons content in automotive fuels;
- minimization of moisture access into storage tanks and distribution pipelines. Special attention must be taken every time the tank is opened for service or filling to avoid the contamination with water.

Predictive tool of phase solubility estimation

The water solubility in ETBE-blended gasolines shown in figure 1 and 2 indicate the similar shapes and follows

the second order polynomial functions. The volume percents of water content in organic phase are mathematically expressed by:

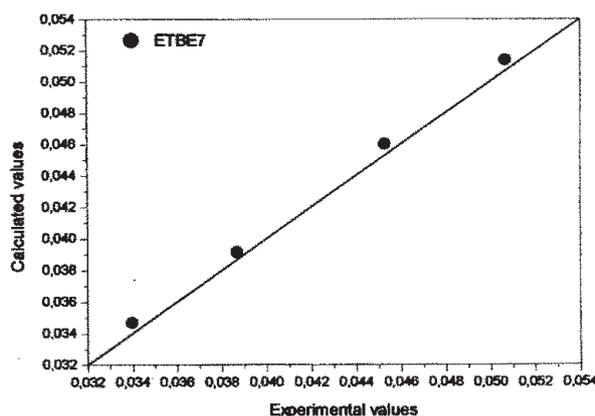
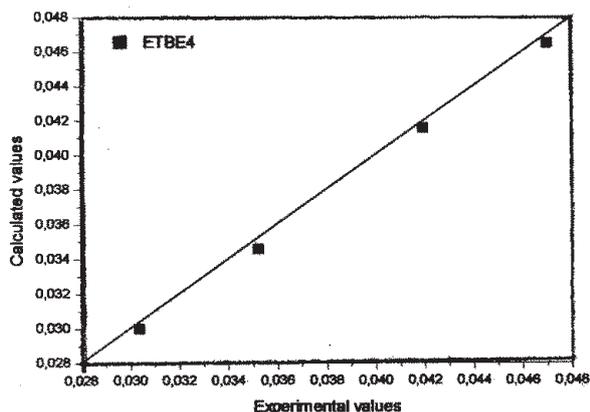
$$w(\text{vol}\%) = A + B \cdot T + C \cdot T^2 \quad (1)$$

The precision of the regression method was evaluated by the adjusted R^2 and the residual sum of square (RSS) values.

The model parameters and statistical indices values of water solubility in ETBE-gasoline B1 blends are reported in table 2. The model parameters from eq. (1) are denoted as A , B and C .

The values of statistical indices reported in table 2 shows that the proposed predictive tool gives excellent results, namely: all adjusted R^2 values are above 0.99, all RSS values as well as the errors of A , B , C parameters are very small. Furthermore, these results are supported by the parity plots between experimental and calculated water solubility values in ethanol-gasoline B1 blends shown in figure 3.

The viability of proposed predictive tool (i.e eq (1)) was supplementary tested by calculation of absolute relative deviation (ARD %) between experimental and predicted



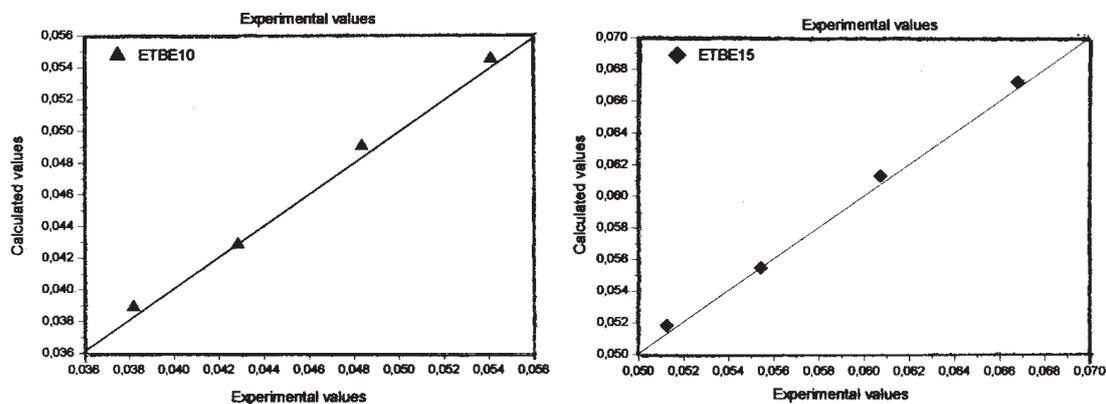


Fig. 3. Comparison of predicted and reported values of water solubility in ETBE-B1 blends

Temperature, K		268	273	283	303
Blends					
ETBE 4	Exp.	0.03036	0.03523	0.04195	0.04703
	Calc.	0.02999	0.03459	0.04154	0.04649
	ARD	1.21176	1.82585	0.98158	1.14844
ETBE 7	Exp.	0.03397	0.03867	0.04528	0.05069
	Calc.	0.03469	0.03916	0.04601	0.05138
	ARD	2.10499	1.25910	1.62093	1.36462
ETBE 10	Exp.	0.03820	0.04285	0.04836	0.05410
	Calc.	0.03890	0.04285	0.04905	0.05457
	ARD	1.82335	0.00929	1.42738	0.86577
ETBE 15	Exp.	0.05124	0.05542	0.06072	0.06680
	Calc.	0.05183	0.05547	0.06130	0.06722
	ARD	1.15468	0.08452	0.95545	0.62659

Table 3
ABSOLUTE RELATIVE DEVIATION (ARD %) BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF WATER SOLUBILITY IN ETBE-GASOLINE B1 BLENDS

data. Table 3 presents the summary of accuracies with the proposed predictive tools in terms of absolute deviation percent for water solubility in ETBE-gasoline B1 blends.

Table 3 shows that the proposed correlation was found in excellent agreement with the experimental data for entire range of conditions, wherein the highest absolute relative deviation between calculated and experimental water solubilities is 2.10499% for B1 gasoline oxygenated with 7 vol% ETBE, whereas the lowest value is 0.02999% for B1 gasoline oxygenated with 4 vol% ETBE.

In table 4 are reported the parameters of the predictive tool and the statistical indices values of water solubility in ETBE-gasoline B2 blends.

As in the above case, results presented in table 4 are excellent: all adjusted R^2 values are above 0.99, all RSS values are very small, as well the errors of A, B, C parameters. Figure 4 support the results from table 4 and represent the parity plots between experimental and calculated water solubility values in ETBE-gasoline B2 blends.

Supplementary, the viability of proposed predictive tool was tested by the absolute relative deviation (ARD %) between experimental and predicted data. Table 5 present the summary of accuracies with the proposed predictive tools in terms of absolute deviation percent for water solubility in ETBE-gasoline B2 blends.

Results presented in table 5 show that the proposed predictive tool has a very good agreement with the experimental data with highest absolute deviation percent of 2.92050% for B2 gasoline oxygenated with 7 vol% ETBE,

whereas the lowest value is 0.02799% for B2 gasoline oxygenated with 4 vol% ETBE.

The predictive tool proposed in this work has a limitation, respectively it is applicable only for two types of base gasoline prepared according to experimental procedure previously described.

Sample calculations shown below clearly demonstrates the simplicity and the benefits of the proposed tool.

Example 1

A gasoline station must prepare a blend of gasoline type B2 and 10 vol% ETBE. The storage tank has at 280K and was completely emptied before filling (ideal case). What is the estimated water solubility (vol%) which cause the phases separation?

According to eq. (1) and parameters of the predictive tool from table 4, the estimated water solubility was found at 0.04499 vol%.

Example 2

The storage tank is half filled with B1 gasoline oxygenated with ETBE 10 vol% blend at 290K. It is taken into account a storage tank with 10 m³ capacity that must be filled with B2 gasoline oxygenated with ETBE 15vol% blend at the same temperature. It is assumed that the water bottom layer is completely moved up during the filling operation and thus the cumulative water content it is expected. What is the estimated water solubility (vol%) which cause the new phase separation?

Table 4
FITTED PARAMETERS AND STATISTICAL INDICES VALUES OF WATER SOLUBILITY IN ETBE-GASOLINE B2 BLENDS

Coeff.	A		B		C		Statistics	
	Value	Error	Value	Error	Value	Error	Adj- R^2	RSS
ETBE 4	-1.3695	0.14477	0.00943	1.01E-03	-1.57E-05	1.77E-06	0.99617	1.90E-07
ETBE 7	-1.24957	0.10143	0.00859	7.10E-04	-1.42E-05	1.24E-06	0.99824	9.34E-08
ETBE 10	-1.11061	0.13914	0.00765	9.74E-04	-1.26E-05	1.70E-06	0.99659	1.76E-07
ETBE 15	-1.01652	0.20911	0.00710	0.00146	-1.17E-05	2.56E-06	0.99139	3.97E-07

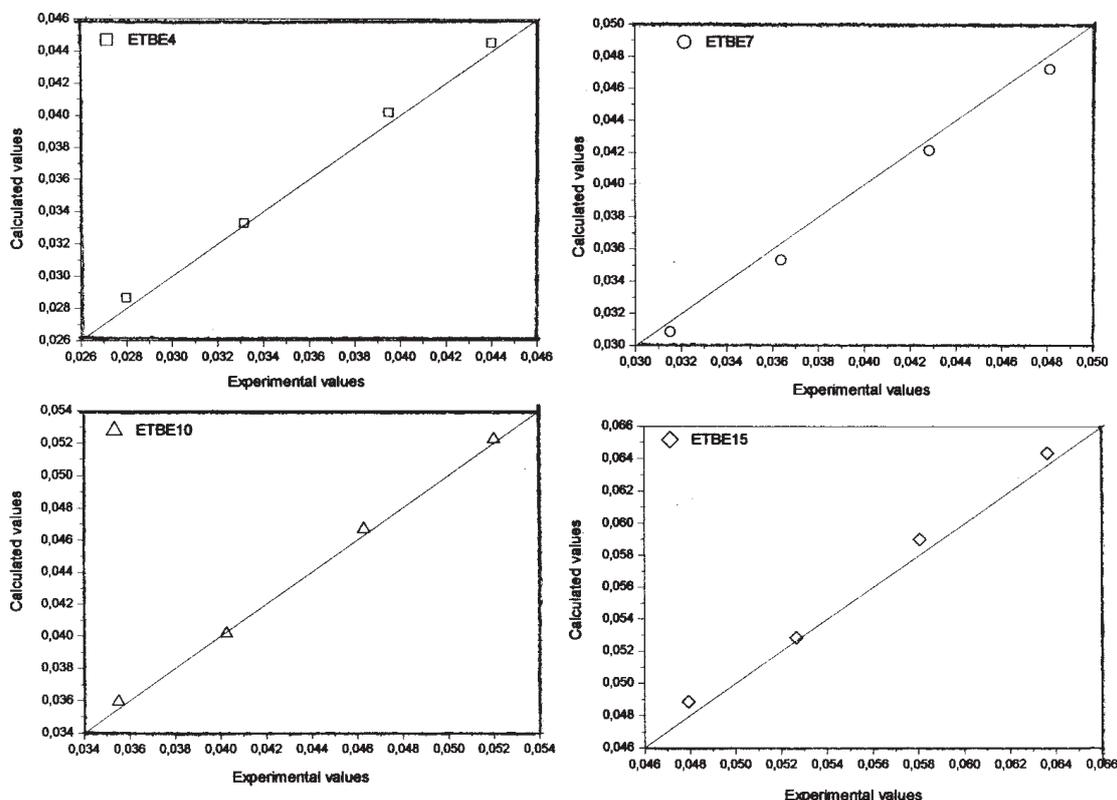


Fig. 4. Comparison of predicted and reported values of water solubility in ETBE-B2 blends

Table 5
ABSOLUTE RELATIVE DEVIATION (ARD %) BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF WATER SOLUBILITY IN ETBE-GASOLINE B2 BLENDS

Temperature, K		268	273	283	303
Blends					
ETBE4	Exp.	0.02799	0.03315	0.03951	0.04403
	Calc.	0.02866	0.03329	0.04018	0.04454
	ARD	2.39206	0.41227	1.70314	1.16588
ETBE 7	Exp.	0.03151	0.03638	0.04286	0.04814
	Calc.	0.03085	0.03532	0.04213	0.04721
	ARD	2.10594	2.92050	1.71263	1.93645
ETBE 10	Exp.	0.03552	0.04026	0.04629	0.05201
	Calc.	0.03593	0.04015	0.04669	0.05224
	ARD	1.15192	0.28332	0.86895	0.43431
ETBE 15	Exp.	0.04792	0.05265	0.05805	0.06364
	Calc.	0.04886	0.05282	0.05900	0.06435
	ARD	1.96669	0.33054	1.63363	1.11773

The phase separation point for B1-ETBE10 blend was estimated based on eq. (1) and parameters of the predictive tool from table 2 at 0.05202 vol%. (meaning 0.0026 m³ water). Accordingly to eq. (1) and specific parameters from table 4, the phase separation point for B2-ETBE15 blend was found at 0.06193 vol% (meaning 0.0031 m³ water). The new mix has 12.49 vol% ETBE and 0.056946 vol% water at phase separation point.

Conclusions

In this work, a simple tool is developed for the prediction of water solubility of ETBE-gasoline mixtures as a function of temperature. For this purpose, an experimental study was performed for two different base gasoline (labeled as B1 and B2) in temperature range of 268 - 303K and for ETBE volumetric content of 4-15%. The graphical correlations between phase separation and temperature indicate shapes which follow the second order polynomial functions. The fitted parameter values of predictive tool were estimated based on the least-squares method. The precision of the fit was evaluated by three ways: by values of statistical indices (i.e. adjusted R² and the residual sum of square), by parity plots between experimental and

calculated water solubility values and by values of the absolute relative deviation (ARD %). All of these show that the water solubility estimations are in excellent agreement with the experimental data.

Finally, two examples clearly demonstrate the usefulness of the proposed method for practical purposes.

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