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Measurement and Prediction of Reid Vapor Pressure of Gasoline in the Presence of Additives

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Reid vapor-pressure (RVP) measurements of simulated gasoline with a variety of additives and fuel extenders, including alcohols, ethers, ketones, amides, amines, and esters, at different concentrations and 100 °F using a Setavap Vapor Pressure Tester 22420-3 are presented. Prediction of RVP of simulated gasoline in the presence of the different additives and fuel extenders has been performed using three UNIFAC-based models. Satisfactory predictions are obtained when nonassociating or weak associating additives are involved (average absolute errors in the prediction of RVP of the order of 1−2%), with the most satisfactory being the model of Gmehling et al. (*Ind. Eng. Chem. Res.* **1993**, *32*, 178−193). The results are poorer, however, for mixtures containing strongly associating additives such as methanol, ethanol, 2-propanol and 2-methyl-1-propanol (in many cases the absolute errors in the prediction of RVP were over 5%). UNIFAC models can be used for initial screening of potential additives, but actual effects on gasoline vapor pressure should be determined experimentally.

Introduction

Vapor pressure is one of the most important physical properties of gasoline mixtures since it defines its volatility. It can be determined with a variety of methods that are rather time-consuming. The refinery industry utilizes the Reid methods (ASTM D-323, D-4953 and D-5191) to determine vapor-pressure, which is related to the gasoline performance characteristics and to its storage behavior. In these methods, the liquid chamber of the vapor pressure apparatus is filled with the chilled sample and connected to the vapor chamber that has been heated to 37.8 °C (100 °F) in a bath. The ratio of the two chambers is 4:1 (vapor chamber:liquid chamber). In methods D-323 and D-4953, the assembled apparatus is immersed in a bath at 37.8 °C (100 °F) until a constant pressure is observed. The gauge pressure measurement by this procedure is defined as the Reid vapor pressure (RVP) and is different from the true vapor pressure (TVP), which, in the case of mixtures, refers to the pressure of the liquid at specified concentration and temperature, giving in this manner the bubble-point pressure of the mixture.

The addition of oxygenates, mainly produced from renewable sources, to gasoline, has been of interest owing to their pollution-reducing and octane-enhancing capabilities (Gouli et al., 1997). Vapor−liquid equilibrium data for oxygenate with hydrocarbon mixtures are used for deciding how the addition of an oxygenate affects the total vapor pressure of the gasoline and its vapor-phase composition.

In the first part of this paper vapor-pressure measurements for components of pure gasoline at four different temperatures (37.8, 45.8, 55.8, and 65.8 °C) and RVP measurements of a simulated gasoline with a variety of additives and fuel extenders, at different concentrations at 37.8 °C using a Setavap Vapor Pressure Tester 22420-3 are presented. Furthermore, since the Setavap vapor pressure (SVP) values are not equal to the true vapor pressure (TVP) ones, a correlation that relates the SVP of a gasoline to its TVP has been developed.

In the second part of the paper we examine the applicability of UNIFAC-type models in the prediction of the RVP of simulated gasoline in the presence of additives and fuel extenders.

Table 1. Chemicals Used in This Work Along with Their Purity and Manufacturer

substance	purity	manufacturer
hexane	99.8%	Mallinckrodt
heptane	99.8%	Mallinckrodt
2,2,4-trimethylpentane	99.8%	Mallinckrodt
toluene	99%	Farmitaria Carlo Erba
p-xylene	>99%	Merck
methanol	99.8%	Riedel de Haen
ethanol	99.8%	Merck
2-propanol	analytical	Vioryl
2-methyl-1-propanol	>99.5%	Fluka
MTBE	>98%	Mallinckrodt
N,*N*-dimethylformamide	99.5%	Merck
methyl ethyl ketone	99.5%	Fluka
acetophenone	>98%	Fluka
DIPE	>98.5%	Ferak
n-propylamine	99%	Merck
cyclohexanone	>99%	Fluka
diacetone alcohol	99%	Fluka
phthalic dimethyl ester	99%	Merck
acetone	99%	Mallinckrodt

Experimental Section

Chemicals. All chemicals used in this work are presented in Table 1 along with their purity as reported by the manufacturer. The chemicals used were not treated or checked for purity, because the required properties in this series of experiments, mainly density and RVP, were measured each time, either as components or blends of a mixture.

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Apparatus and Procedure. All measurements of vapor pressure were performed in a Setavap Vapor Pressure Tester 22420-3 provided by Stanhope Seta Company. This instrument is used to determine the vapor pressure of low-viscosity petroleum products. It is a "dry" test method with the additional benefit of testing samples containing oxygenates. Tests can be carried out at temperatures in the range of 30 °C to 120 °C and at a vapor-to-liquid ratio chosen by the user, provided that the resulting pressures do not exceed 400 kPa.

The accuracy of the temperature readings is about ±0.01 K. The pressure is sensed by a solid-state, low volumetric displacement transducer with a digital indicator. Vacuum is achieved by an optional vacuum pump recommended by Stanhope-Seta for this type of application. It is a two-stage pump with an oil mist filter on its efflux port that effectively traps exhaust vapors. It is capable of achieving and maintaining a pressure of better than 0.01 kPa.

The vapor-to-liquid ratio is determined by the volume of the sample used. The chamber has the precise volume of 15 mL, so if a 3-mL sample is injected, the remaining vapor volume is 12 mL, giving a ratio of 4:1. Typically vapor-pressure measurements are carried out at 37.8 °C with a vapor-to-liquid ratio equal to 4:1. The resulting vapor pressure (SVP) is the total vapor pressure of the sample, which includes dissolved air. The following formula is used to convert SVP values to RVP ones (ASTM, D-5191):

$$\mathrm{RVP} = 0.965\cdot\mathrm{SVP} - 3.78 \tag{1}$$

where RVP and SVP are given in kPa.

All the samples were prepared in strict conformance with the requirements of ASTM D-5191. The injections of the samples into the chamber were done with a gastight syringe provided by Setavap. Before the injection of the samples, the samples and the syringe were prechilled to avoid losses due to vaporization.

The repeatability of the Setavap tester vapor-pressure measurements is 1.2 kPa and their reproducibility 2.8 kPa, as they are given by Stanhope-Seta. In all measurements performed in this study the corresponding values were always within the range recommended by the manufacturer.

Experimental Results

The selection of gasoline components, additives, and fuel extenders used in this study was made on the basis of their distillation range and research octane number (RON) criteria (Papachristos et al., 1991).

The first series of measurements deals with pure compounds. Our objective here was to develop a correlation relating SVP to TVP, applicable to the components of gasoline. For this purpose the vapor pressures (SVP) of common components of gasoline (straight-chain, branched, and cyclic alkanes as well as aromatic hydrocarbons) and of alcohols and ethers were measured at four temperatures (37.8 °C, 45.8 °C, 55.8 °C, and 65.8 °C) and the results are presented in Table 2. In the same table the values of the true vapor pressure of these compounds (TVP) taken from the DIPPR data compilation (Daubert and Danner, 1989) are also presented. The values of the SVP differ from those of the TVP. The explanation for this is the difference in the methodology that is followed for the determination of the vapor pressure, mainly the fact that the samples used for the measurement of SVP values were not degassed.

Table 2. Measurements of Gasoline Components and Correlation Results

compound	t/°C	TVP/ kPa	SVP/ kPa	CSVP/ kPa	ΔSVP %[a]
hexane	37.8	34.40	40.4	40.2	0.50
	45.8	46.53	52.9	52.5	0.76
	55.8	66.19	72.8	72.3	0.69
	65.8	91.84	99.5	98.2	1.31
heptane	37.8	11.28	17.5	16.9	3.43
	45.8	15.99	22.4	21.7	3.13
	55.8	24.02	30.4	29.8	1.97
	65.8	35.04	41.4	40.9	1.21
2,2,4-trimethylpentane	37.8	11.79	18.3	17.4	4.92
	45.8	16.51	23.4	22.2	5.13
	55.8	24.47	31.7	30.2	4.73
	65.8	35.27	42.2	41.1	2.61
MTBE	37.8	55.02	61.3	61.0	0.49
	45.8	73.58	79.4	79.8	−0.50
	55.8	103.37	110.0	109.8	0.18
	65.8	141.86	151.1	148.7	1.59
methanol	37.8	31.83	35.6	37.7	−5.90
	45.8	46.07	50.1	52.0	−3.79
	55.8	71.04	75.1	77.2	−2.80
	65.8	106.40	109.9	112.9	−2.73
ethanol	37.8	16.05	19.8	21.7	−9.60
	45.8	24.13	28.1	29.9	−6.41
	55.8	38.88	42.6	44.8	−5.16
	65.8	60.61	63.7	66.7	−4.71
2-propanol	37.8	12.68	18.4	18.3	0.54
	45.8	19.41	26.1	25.1	3.83
	55.8	31.89	40.2	37.7	6.22
	65.8	50.56	61.2	56.6	7.52
methylcyclohexane	37.8	11.07	15.8	16.7	−5.70
	45.8	15.57	20.4	21.2	−3.92
	55.8	23.16	28.0	28.9	−3.21
	65.8	33.50	38.3	39.3	−2.61
toluene	37.8	7.12	12.5	12.7	−1.60
	45.8	10.23	16.4	15.9	3.05
	55.8	15.63	21.8	21.3	2.29
	65.8	23.19	29.6	28.9	2.36

[a] ΔSVP % = (SVP − CSVP)/SVP × 100, where CSVP (correlated Setavap vapor pressure) is computed by eq 2 using TVP data (DIPPR compilation).

A simple linear correlation of SVP to TVP was developed for all pure compounds involved in this study. This relation is given in the following equation:

$$\mathrm{SVP} = 1.0091\cdot\mathrm{TVP} + 5.53 \tag{2}$$

where the SVP and TVP values are given in kPa. The standard error of eq 2 is 1.63 kPa and the value of R^2 is 0.998, whereas the standard deviations of the x-coefficient is 0.0087 and that of the intercept 0.4408.

In Table 2 correlated SVP (CSVP) values using eq 2 along with the percent errors in the prediction of SVP are presented. The correlation is good given that very different compounds were used for the development of the correlation. Also in Figure 1 the experimental (points) and correlated (line) SVP values are plotted versus TVP for all the compounds and temperatures involved. In this figure the compounds are marked with symbols according to the homologous series they belong to. The paraffins correspond to hexane, heptane, and 2,2,4-trimethylpentane and the alcohols to methanol, ethanol, and 2-propanol. Finally, methyl *tert*-butyl ether (MTBE), methylcyclohexane, and toluene are marked separately. Different correlations for each homologous series could be developed, but eq 2 provides a generally applicable correlation for converting the SVP of a component to its true vapor pressure and vice versa.

The influence of additives (or fuel extenders) on the RVP of a simulated gasoline base fuel (BF) was the main emphasis of the experimental work. BF is a five-component mixture approximating the performance of a real

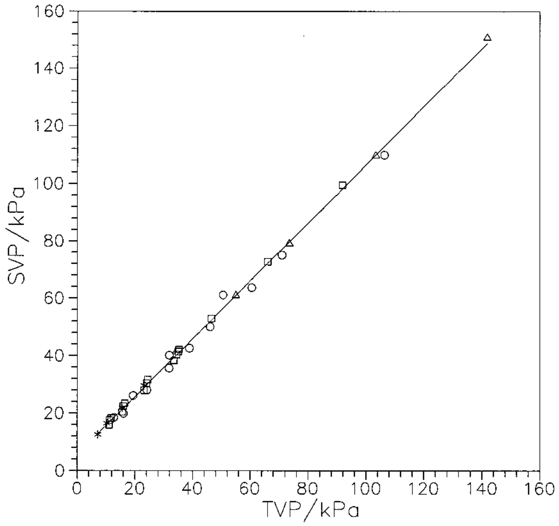

Figure 1. Experimental and predicted, through eq 2, SVP values versus true vapor-pressure ones for various gasoline components. (□) alkanes; (○) alcohols; (△) MTBE; (*) toluene; (—) eq 2.

Table 3. Antiknock Performance of the Compounds Referred to in Table 4 When Blended in a Gasoline, in a Concentration Range between 2 and 3 wt %, in Comparison to MTBE

		relative effectiveness MTBE = 1	
compound	BRON[a]	molar	weight
N,*N*-dimethylformamide	97	0.10	0.10
methyl ethyl ketone	115	0.82	1.00
acetophenone	108	0.91	0.70
diisopropyl ether	105	0.58	0.50
n-propylamine	130	0.74	1.10
cyclohexanone	112	0.50	0.60
diacetone alcohol	112	0.50	0.70
acetone	105	0.33	0.50
dimethyl terephthalate	95	0.50	0.60

[a] BRON is the blended research octane number defined as BRON = $[M - F(1 - V)]/V$, where M is the RON of the fuel blend, F is the RON of the base fuel, and V is the concentration of the component in the blend (vol/vol).

unleaded gasoline. It consists of 20 vol % hexane, 5 vol % heptane, 55 vol % 2,2,4-trimethylpentane, 15 vol % toluene and 5 vol % *p*-xylene. The gasoline additives (or fuel extenders) are divided into two groups. The first group consists of compounds that are commonly used as additives (or fuel extenders) in gasoline, i.e., MTBE, methanol, and ethanol, or have been more extensively tested as possible fuel additive candidates, e.g., 2-propanol or 2-methyl-1-propanol (Popuri and Bata, 1993). In the second group belong additives (or fuel extenders) that are still at an early stage of investigation as potential fuel additives such as *N*,*N*-dimethylformamide, methyl ethyl ketone, acetophenone, diisopropyl ether (DIPE), *n*-propylamine, cyclohexanone, diacetone alcohol, acetone, and dimethyl terephthalate. These compounds exhibit a satisfactory anti-knock performance when blended in a gasoline, in comparison to MTBE, as shown in Table 3. It must be emphasized that some of these additives may present some problems of material compatibility or fuel stability (diisopropyl ether), which must be resolved in the future before they are chosen as gasoline additives.

In Table 4 SVP and RVP values of mixtures of BF with the additives of the first group in amounts of 2 vol %, 5 vol %, 10 vol %, and 15 vol % at 37.8 °C are presented, expressed in mass/volume equivalent units. The base fuel has been produced four times, as many as the different concentrations used, and this explains the slightly different SVP and, consequently, RVP values of BF reported for each different concentration. The chemicals used each time had slightly different purity. The BF's prepared, although they had the same component concentration, gave slightly different values for RVP or density, owing to the alteration in purity. Table 3 gives the difference between the RVP of the BF and that of the mixture of BF with the additive. These values show directly the effect of the different additives on the RVP of the gasoline. The conclusion drawn from the results is that the addition of 2-methyl-1-propanol and MTBE, and to a lesser extent 2-propanol, has a very small effect on the Reid vapor pressure of the gasoline blend, while the addition of methanol and ethanol significantly increases its Reid vapor pressure. All experimental values measured here are the average values of at least three repetitions.

In Table 5 the measurements pertaining to the second group of additives are presented. In this table the concentrations are also defined as the mass of the additive per 100 mL of BF. We produced nine samples of BF, one for each of the nine additives. The results show that most of the new additives examined in this study, except for *n*-propylamine, acetone and to a lesser extent methyl ethyl ketone, have only marginal effect on the Reid vapor pressure of the gasoline mixture, which indicates, from this point of view, their good performance as fuel additives. An exception is acetophenone, which actually depresses RVP, and if one considers its blended research octane number (BRON), value of 108 and relative effectivess of 0.91 (on a molar basis) compared to MTBE, it could be considered as a potential candidate for further scrutiny as a gasoline additive.

Models Considered

The performance of the UNIFAC group-contribution model to the prediction of RVP of gasoline mixtures has been investigated. In UNIFAC (Fredensund et al., 1975), the logarithm of the activity coefficient is given as the sum of two contributions: a combinatorial one that accounts for the differences in the size and the shape of the molecules in the mixture and a residual one that accounts mainly for the energetic interactions between the groups of the molecules. For a molecule i in any solution:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{comb}} + \ln \gamma_i^{\mathrm{res}} \tag{3}$$

Recently, many different UNIFAC-type models have been developed, and we examined the performance of three of the most reliable models of the UNIFAC class. The models considered are the following:

1. UNIFAC-I (Hansen et al., 1991)

This model uses the same combinatorial expression as the one used in the UNIFAC model (Fredenslund et al. 1975) and temperature-independent group-interaction parameters obtained by fitting to a large database of vapor−liquid equilibrium data (Hansen et al., 1991).

2. UNIFAC-II (Larsen et al., 1987)

In this model two modifications with respect to the UNIFAC model of Fredenslund et al. (1975) have been made. First, the combinatorial part has been modified on the basis of the work of Kikic et al. (1980), and also the group-interaction parameters have been made temperature-dependent by fitting to both vapor−liquid equilibria and excess enthalpy experimental data (Larsen et al., 1987).

Table 4. Measurements of RVP of BF-Containing Oxygenated Compounds at Preselected Volumetric Ratios and Estimation of Their Effect on the RVP of the Base Fuel at 37.8 °C. Predicted Values of RVP Using UNIFAC-type Models Are Also Presented

system	SVP/kPa	RVP/kPa	ΔRVP[a]/kPa	predicted RVP/kPa UNIFAC-I	predicted RVP/kPa UNIFAC-II	predicted RVP/kPa UNIFAC-III
		BF1				
	21.5	17.0		17.0	16.7	17.1
1.514 g of MTBE/100 mL of BF1	23.0	18.4	1.4	18.3	17.9	18.2
1.616 g of methanol/100 mL of BF1	44.4	39.1	22.1	36.0	42.3	40.3
1.612 g of ethanol/100 mL of BF1	30.1	25.3	8.3	23.9	24.6	25.1
1.592 g of 2- propanol/100 mL of BF1	28.8	24.0	7.0	20.7	20.9	20.9
1.635 g of 2-methyl-1-propanol/100 mL of BF1	23.2	18.6	1.6	17.5	17.2	17.7
		BF2				
	21.8	17.3		17.0	16.7	17.1
3.905 g of MTBE/100 mL of BF2	24.9	20.2	2.9	20.1	19.6	19.8
4.168 g of methanol/100 mL of BF2	47.4	42.0	24.9	44.7	46.4	44.0
4.158 g of ethanol/100 mL of BF2	31.3	26.4	9.1	27.1	28.0	27.5
4.105 g of 2- propanol/100 mL of BF2	30.4	25.6	8.3	22.8	23.1	22.5
4.216 g of 2-methyl-1-propanol/100 mL of BF2	25.4	20.7	3.4	17.7	17.5	17.9
		BF3				
	21.6	17.1		17.0	16.7	17.1
8.244 g of MTBE/100 mL of BF3	27.4	22.7	5.6	23.0	22.3	22.3
8.8 g of methanol/100 mL of BF3	48.2	42.7	25.6	47.1	47.2	44.9
8.777 g of ethanol/100 mL of BF3	32.2	27.3	10.2	28.3	29.0	28.5
8.666 g of 2- propanol/100 mL of BF3	30.8	25.9	8.8	23.9	24.2	23.3
8.9 g of 2-methyl-1-propanol/100 mL of BF3	22.1	17.5	0.4	17.7	17.5	17.9
		BF4				
	21.9	17.4		17.0	16.7	17.1
13.09 g of MTBE/100 mL of BF4	29.8	25.0	7.6	25.7	24.9	24.7
13.976 g of methanol/100 mL of BF4	48.4	42.9	25.5	46.8	47.1	45.1
13.941 g of ethanol/100 mL of BF4	32.4	27.5	10.1	28.5	29.1	28.8
13.764 g of 2- propanol/100 mL of BF4	30.8	25.9	8.5	24.2	24.4	23.6
14.135 g of 2-methyl-1-propanol/100 mL of BF4	22.6	18.0	0.6	17.6	17.5	17.8

[a] ΔRVP = RVP(BF + additive) − RVP(BF).

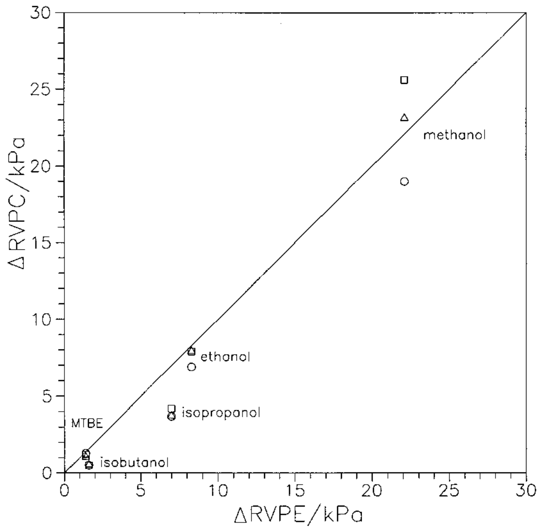

Figure 2. Experimental and predicted differences between the Reid vapor pressure of the BF and the one of the BF with 2% (v/v) of an oxygenated additive. ΔRVPE is the experimental ΔRVP (defined in Table 3) and ΔRVPC is the calculated one. (○) UNIFAC-I; (□) UNIFAC-II; (△) UNIFAC-III.

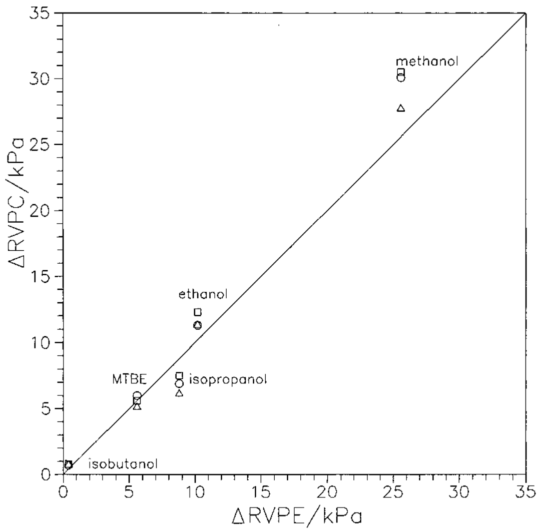

Figure 3. Experimental and predicted differences between the Reid vapor pressure of the BF and the one of the BF with 10% (v/v) of an oxygenated additive. (○) UNIFAC-I; (□) UNIFAC-II; (△) UNIFAC-III.

3. UNIFAC-III (Gmehling et al., 1993)

In this model two modifications with respect to the UNIFAC model of Fredenslund et al. (1975) have been made. The first modification is in the combinatorial part and the second one in the residual part where temperature-dependent group-interaction parameters are determined by fitting to a large database consisting of experimental vapor–liquid equilibrium, liquid–liquid equilibrium, and excess enthalpy and infinite dilution activity coefficient data (Gmehling et al., 1993). The advantages in this method are (1) a better description of the temperature dependence of the activity coefficients and (2) the better prediction of infinite dilution activity coefficients especially in asymmetric polar mixtures (Voutsas and Tassios, 1996).

For the prediction of RVP with the UNIFAC model, the conventional "liquid activity coefficient–vapor-phase fugacity" approach has been used. The fugacity coefficients of the vapor phase have been calculated by the virial EoS truncated to the second term, with second virial coefficients from the Tsonopoulos correlation (Tsonopoulos, 1974, 1975).

Table 5. Measurements of RVP of BF in the Presence of Additives at 37.8 °C and Estimation of Their Effect on the Vapor Pressure of the Base Fuel. Predicted Values of RVP Using the UNIFAC-type Models Are Also Presented

simulated gasoline + mixture additive	g of additive/ 100 mL of BF	SVP/kPa	RVP/kPa	ΔRVP[a]/kPa	predicted RVP/kPa UNIFAC-I	predicted RVP/kPa UNIFAC-II	predicted RVP/kPa UNIFAC-III
BF5 + *N*,*N*-dimethylformamide	0.00	21.6	17.1		17.0		17.1
	0.73	22.0	17.5	0.4	17.2	*b*	17.2
	1.68	22.2	17.6	0.5	17.4	*b*	17.2
	2.65	22.2	17.6	0.5	17.6	*b*	17.2
	4.64	21.6	17.1	0.0	17.7	*b*	17.2
BF6 + methyl ethyl ketone	0.00	21.9	17.4		17.0	16.7	17.1
	0.98	22.8	18.2	0.8	17.7	17.6	18.2
	1.92	23.6	19.0	1.6	18.3	18.4	19.0
	2.91	24.7	20.1	2.7	18.9	19.1	19.8
	4.89	25.6	20.9	3.5	19.9	20.3	21.1
BF7 + acetophenone	0.00	22.0	17.5		17.0	16.7	17.1
	0.72	21.7	17.2	−0.3	16.9	16.6	17.1
	1.78	21.3	16.8	−0.7	16.8	16.5	17.0
	2.72	21.6	17.1	−0.4	16.7	16.4	16.9
	4.47	20.9	16.4	−1.1	16.6	16.2	16.7
BF8 + diisopropyl ether	0.00	21.8	17.3		17.0	16.7	17.1
	1.05	22.2	17.6	0.3	17.3	17.0	17.4
	2.03	22.3	17.7	0.4	17.5	17.3	17.6
	2.96	22.5	17.9	0.6	17.7	17.5	17.8
	4.83	23.1	18.5	1.2	18.1	18.0	18.3
BF9 + *n*-propylamine	0.00	21.9	17.4		17.0	16.7	17.1
	1.02	23.6	19.0	1.6	19.3	19.6	19.5
	1.94	26.3	21.6	4.2	21.3	21.9	21.5
	2.98	28.3	23.5	6.1	23.3	24.3	23.5
	4.98	30.6	25.7	8.3	26.7	28.2	27.0
BF10 + cyclohexanone	0.00	21.6	17.1		17.0	16.7	17.1
	0.73	21.9	17.4	0.3	16.9	16.6	17.0
	1.73	22.1	17.5	0.4	16.7	16.5	16.9
	2.60	22.1	17.5	0.4	16.6	16.3	16.8
	4.69	22.2	17.6	0.5	16.3	16.1	16.5
BF11 + diacetone alcohol	0.00	21.6	17.1		17.0	16.7	17.1
	0.60	22.0	17.5	0.4	17.0	16.8	17.3
	1.55	21.8	17.3	0.2	17.1	16.9	17.4
	2.60	22.2	17.6	0.5	17.1	16.9	17.4
	4.09	21.7	17.2	0.1	17.2	16.9	17.4
BF12 + acetone	0.00	21.3	16.8		17.0	16.7	17.1
	0.98	24.8	20.2	3.4	19.7	20.3	21.0
	1.97	29.1	24.3	7.5	22.2	23.4	24.3
	2.98	31.2	26.3	9.5	24.4	26.2	27.2
BF13 + dimethyl terephthalate	0.00	21.6	17.1		17.0	16.7	17.1
	0.37	21.6	17.1	0.0	17.0	16.7	17.1
	1.28	21.3	16.8	−0.3	16.9	16.6	17.1
	2.35	21.3	16.8	−0.3	16.8	16.6	17.0
	4.11	21.0	16.5	−0.6	16.7	16.5	16.9

[a] ΔRVP is defined as in Table 3. [b] No group interaction parameters exist for the pairs containing DMF.

The same equation has been used for the estimation of the pure saturated liquid fugacity coefficients. The saturated vapor pressures of the pure components have been calculated from the correlation of the DIPPR data compilation. The liquid molar volumes that are necessary for the calculation of the Poynting corrections have been calculated by the Rackett equation (Rackett, 1970). The activity coefficients of the mixture components have been predicted by the different UNIFAC-type models mentioned above. Finally, the TVP values predicted by this methodology are converted to RVP ones using eqs 1 and 2.

Prediction Results

Table 3 presents RVP predictions obtained by the three UNIFAC models while Figures 2 to 4 show experimental and predicted changes in the Reid vapor pressure of the base fuel with the addition of an additive of the first class for three different concentrations of each additive. The UNIFAC-type models give satisfactory predictions for the cases of MTBE with average absolute errors in the prediction of RVP of the order of 1−2%. Higher errors are obtained for the strongly hydrogen-bonding compounds: methanol, ethanol, 2-propanol and 2-methyl-1-propanol. For the cases of methanol and ethanol the models tend to overpredict the effect of their presence on the RVP of gasoline yielding in many cases absolute errors in the prediction of RVP over 5%, while for the cases of 2-propanol and 2-methyl-1-propanol the models tend to underpredict the effect of their presence on the RVP of gasoline yielding errors over 10% for the case of 2-propanol and over 5% for the case of 2-methyl-1-propanol. The most satisfactory results are obtained by the UNIFAC-III model. When strongly associating additives are involved, more sophisticated models such as SAFT EoS (Huang and Radosz, 1990), CPA EoS (Kontogoergis et al., 1996), and UNIFAC-association (Fu et al., 1996), which take into account special interactions due to the presence of hydrogen bonds, are needed.

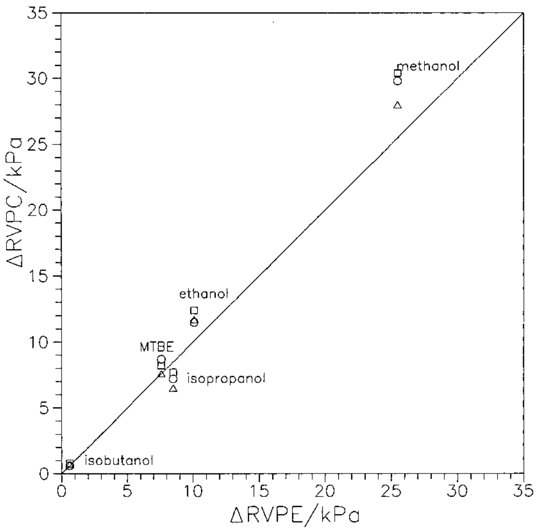

Figure 4. Experimental and predicted differences between the Reid vapor pressure of the BF and the one of the BF with 15% (v/v) of an oxygenated additive. (○) UNIFAC-I; (□) UNIFAC-II; (△) UNIFAC-III.

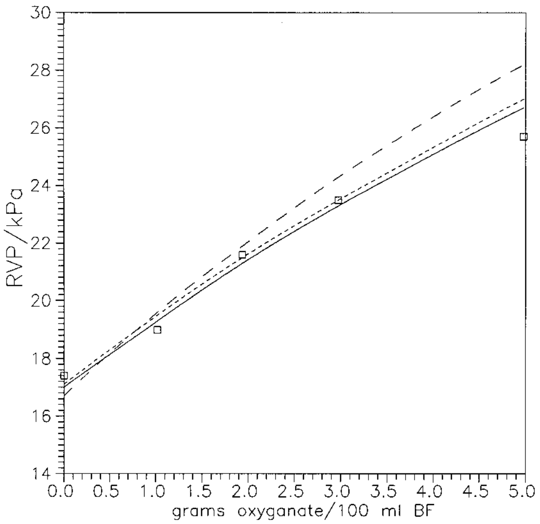

Figure 5. Experimental and predicted Reid vapor pressures of the mixture of BF/*n*-propylamine for different concentrations of *n*-propylamine. (□) Experimental points; (—) UNIFAC-I; (– –) UNIFAC–II; (- - -) UNIFAC-III.

Table 4 presents RVP predictions results obtained by the three UNIFAC models, while Figures 5 and 6 present typical experimental and predicted Reid vapor-pressure values for gasoline mixtures containing the less polar additives of the second class. For the mixtures of this class the UNIFAC-type models give satisfactory predictions with average absolute percent errors in the prediction of RVP of the order of 2%. Again the UNIFAC-III model gives better results than the others.

Finally, it must be noted that our findings are in good agreement with the ones of Zudkevitch et al. (1995).

Conclusions

Experimental Reid vapor-pressure measurements gasoline mixtures are presented using a Setavap Vapor Pressure Tester system. To convert Setavap vapor-pressure values or Reid vapor-pressure ones to true vapor pressures a correlation is also provided.

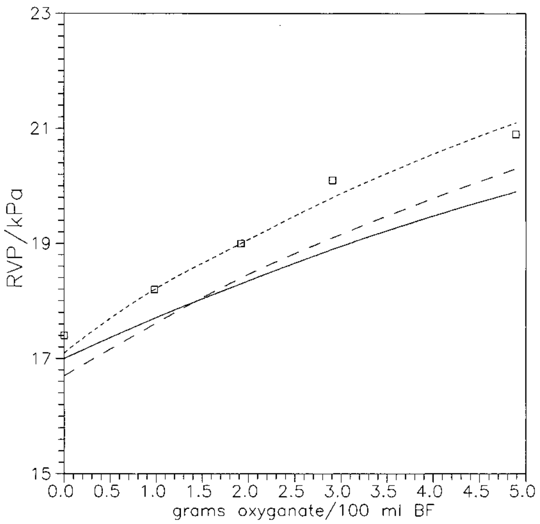

Figure 6. Experimental and predicted Reid vapor pressures of the mixture of BF/methyl ethyl ketone for different concentrations of methyl ethyl ketone. (□) Experimental points; (—) UNIFAC-I; (– –) UNIFAC-II; (- - -) UNIFAC-III.

Experimental measurements for a variety of additives and fuel extenders are presented and indicate that most of them have a small effect on the vapor pressure of the gasoline when they are added to a relatively small concentration.

Three different versions of the UNIFAC model have been applied to the prediction of Reid vapor pressures of simulated gasoline mixtures in the presence of additives measured here. All UNIFAC-type models give satisfactory predictions (average absolute errors in the prediction of RVP of the order of 1–2%) with the model of Gmehling et al. (1993) giving the best ones. Poorer results are obtained, however, for mixtures containing strongly hydrogen-bonded additives such as methanol, ethanol, 2-propanol, and 2-methyl-1-propanol (in many cases the absolute errors in the prediction of RVP where over 5%) since conventional models do not take these interactions explicitly into account.

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