



Effects of dimethyl or diethyl carbonate as an additive on volatility and flash point of an aviation fuel

Dan Li, Wenjun Fang*, Yan Xing, Yongsheng Guo, Ruisen Lin

Department of Chemistry, Zhejiang University, 38 Zheda Road, Hangzhou 310027, Zhejiang Province, China

ARTICLE INFO

Article history:

Received 7 December 2007
Received in revised form 31 March 2008
Accepted 18 April 2008
Available online 24 April 2008

Keywords:

Aviation fuel
Vapor pressure
Flash point
Dimethyl carbonate
Diethyl carbonate

ABSTRACT

Vapor pressures and flash points for several mixtures of an aviation fuel with dimethyl carbonate (DMC) or diethyl carbonate (DEC) have been measured, respectively, over the entire composition range. Correlation between the experimental vapor pressures and the equilibrium temperatures by the Antoine equation is performed for each mixture. The bubble-point lines of pressure versus composition at different temperatures and those of temperature versus composition at different pressures are then obtained from the Antoine correlations. It is found that DMC and DEC are the oxygenated hydrocarbon additives that can adjust effectively the volatility and flash point of the aviation fuel. The correlation of the flash points with the vapor pressure data for the pseudo-binary mixtures of the fuel and DMC or DEC gives satisfactory results.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Additives into a kerosene-based fuel for military aircraft to improve its properties have been studied broadly. An important consideration is the additive's ability to improve thermal stability, reduce pollutant emissions, enhance heat sink and fast ignition of a fuel. There is a growing interest in adding oxygenated compounds such as ethers, alcohols and esters into a fuel because they can adjust the octane number and improve the performance in military aircraft fuel systems [1–6].

Alkyl carbonates, as very promising fluids, attracted attention in the fuel and chemical industries [7–11]. Dimethyl carbonate (DMC) and diethyl carbonate (DEC), two typical alkyl carbonates possess properties of nontoxicity and biodegradability and both of them have high oxygen contents. DMC or DEC is considered to be the option for meeting the oxygenated specifications on fuel and might serve as an additive for minimizing pollution [12,13]. It was showed [14] that the addition of DMC in diesel fuel improved combustion and made a remarkable decrease in smoke emission without engine modification. The premixed combustion was prolonged and

the duration of the diffusive combustion was shortened with the increase of DMC addition.

Usually, aviation fuels and some organic additives are flammable materials. The fire and explosion hazards of a fuel are primarily related to its volatility and flash point. Vapor pressure is one of the most essential thermodynamic properties that reflect the volatility, stability and safety. The values of the vapor pressure and flash point involve the operability of storage, ignition and the flow system of a fuel [14,15]. To ensure the operation safety, the knowledge of volatility and flash point data for flammable liquids are very important. Measurements on the vapor pressure for a fuel are valuable both to laboratory research and practical application. A fuel blended with DMC or DEC, as potential green propulsion for aircraft, is worthwhile for a trial and a further study. The volatility, however, for the systems of an aviation fuel with DMC or DEC has not been well known.

The aim of this work is to investigate the effects of DMC or DEC as an additive on the volatility and flash point of an aviation fuel. The bubble-point vapor pressures are determined over the whole composition range for the pseudo-binary systems of the aviation fuel with DMC and DEC. The phase lines of pressure and temperature versus composition are given. The flash points for the pseudo-binary mixtures are measured and the correlation of the flash points with the vapor pressure is discussed. It is hoped that

* Corresponding author. Tel.: +86 571 87952371; fax: +86 571 87951895.
E-mail address: fwjun@zju.edu.cn (W. Fang).

Nomenclature

A, B, C	Antoine constants
AAD	average absolute deviation (kPa)
ARD	average relative deviation (%)
$\Delta_{\text{vap}}H_m$	enthalpy of vaporization (kJ mol^{-1})
l_{ij}	variable parameter
l_0, a_0, a_1, a_2	constants in Eq. (11)
LFL	lower flammable limit
M	relative molecular mass
n	number of the experimental datum points
n_D	refractive index
OF	objective function
p	vapor pressure (kPa)
R	gas constant (8.314 J mol^{-1})
T	equilibrium temperature (K)
T_b	normal boiling point temperature (K)
V	molar volume ($\text{m}^3 \text{ mol}^{-1}$)
W	mass fraction
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek letters

γ	activity coefficient
δ	solubility parameter
ρ	density (g cm^{-3})
ϕ	volume fraction

Subscripts

cal	calculated value
exp	experimental value
fp	flash point
i, j	components i and j

Table 2

Characterized properties of the aviation fuel

Property	Value
ρ (g cm^{-3}) (20 °C)	0.7933
T_b (K) (101.3 kPa)	453.90
T_{fp} (K)	317.55
M	154.6
Relative contents (%)	
<i>n</i> -Paraffin	15.5
<i>iso</i> -Paraffin	36.0
Cycloparaffin	47.4
Aromatics	1.2
Boiling range (°C)	
IBP	156.0
10%	175.5
20%	182.5
50%	203.0
70%	216.0
90%	252.0
FBP	274.0

sition, some fundamental properties of the fuel were determined for characterization. The density was measured by Anton Paar DMA55 vibrating tube digital densimeter. The normal boiling point was determined by an inclined ebulliometer [16]. The predominant composition was analyzed by a Hewlett Packard 6890/5973 gas chromatography/mass spectrometry (GC/MS). The experimental conditions were as follows—column: HP-5 MS (30 m \times 0.25 mm \times 0.25 μm) elastic quartz capillary column; carrier gas: helium, 1.0 mL min^{-1} (flow rate); split ratio: 1:50; sample: 0.1 mL; solvent delay: 2 min; temperature program: 60 °C (initial temperature), 2 min (initial hold), 10 °C min^{-1} (rate), 280 °C (final temperature), 2 min (final hold); mass spectrometer scanning range: 35–450 amu.

The pseudo-binary mixtures with different compositions of the aviation fuel and DMC or DEC were prepared by directly weighing the individual components with a Mettler balance having a precision of ± 0.0001 g.

2.2. Vapor pressure measurements

Because the aviation fuel has a relatively large boiling range with a high value of average boiling point and the fuel under storage or transportation has approximate bubble-point values of vapor pressures, the comparative ebulliometry was used to obtain the bubble-point pressures of the multicomponent system. An inclined ebulliometer with a pump-like stirrer designed on the basis of the comparative ebulliometry was used to measure the vapor pressure data. The principle, structure and operation of the apparatus were described in detail previously [16]. The bubble-point temperatures of a sample and a reference material, ethanol, in two separate

the experimental and calculated results provide important information for the choice of additives and the operation safety of the fuel.

2. Experimental

2.1. Materials and characterization

Both of dimethyl carbonate and diethyl carbonate (mass fraction >99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China. Absolute ethanol (mass fraction >99.8%) was obtained from Shanghai Chemical Corporation, China. The reagents were used without further purification.

The aviation fuel investigated was a refined kerosene-based one produced from crude oil. Because of its complicated compo-

Table 1

Physical properties of pure liquids in comparison with literature data

Liquid	T_b (K)		ρ (g cm^{-3}) (25 °C)		n_D (25 °C)		T_{fp} (°C)		M (g mol^{-1})
	Exp	Literature	Exp	Literature	Exp	Literature	Exp	Literature	
DEC	399.48	399.95 ^a , 399.32 ^b	0.96704	0.96927 ^a	1.3830	1.3827 ^a	30.0	31 ^c	118.13
DMC	363.52	363.46 ^b	1.06387	1.06330 ^a	1.3662	1.3666 ^a	21.5	21.7 ^d	90.08
Ethanol	351.58	351.443 ^e	0.78506	0.78510 ^e	1.3595	1.35941 ^e			46.07

^a Ref. [7].

^b Ref. [10].

^c Ref. [18].

^d Ref. [19].

^e Ref. [20].

Table 3
Correlation results of vapor pressure by Antoine equation for fuel + DMC mixtures

W_{DMC}	Temperature range (K)	Datum points	Antoine equation coefficients			AAD (kPa)	ARD (%)
			A	$B \times 10^{-3}$	C		
0.0000	382–451	17	11.136	2.0109	145.32	1.18	2.03
0.0199	356–435	15	8.736	1.0790	173.65	0.40	0.83
0.0407	342–418	15	9.831	1.5260	125.43	0.37	0.66
0.0609	337–410	15	9.673	1.4590	121.95	0.22	0.46
0.0805	330–400	15	9.742	1.3692	132.88	0.43	0.73
0.1003	322–394	16	11.303	2.1053	79.330	0.38	0.65
0.2003	327–379	16	11.250	1.8001	107.93	0.21	0.37
0.3011	317–372	17	12.486	2.2457	86.324	0.15	0.29
0.3972	312–369	17	13.383	2.6356	68.146	0.10	0.19
0.4973	312–367	15	14.449	3.1706	44.497	0.08	0.18
0.6069	316–366	15	14.286	3.0218	53.274	0.05	0.09
0.7948	313–364	15	14.242	2.9179	60.942	0.07	0.13
1.0000	314–362	17	14.570	3.0381	56.744	0.08	0.11

Table 4
Correlation results of vapor pressure by Antoine equation for fuel + DEC mixtures

W_{DEC}	Temperature range (K)	Datum points	Antoine equation coefficients			AAD (kPa)	ARD (%)
			A	$B \times 10^{-3}$	C		
0.0000	382–451	17	11.136	2.0109	145.32	1.18	2.03
0.0200	381–448	15	9.998	1.5362	163.94	1.14	2.21
0.0404	378–443	14	10.737	1.8737	137.71	1.02	2.14
0.0601	376–438	14	10.676	1.7962	141.97	0.46	0.83
0.0800	372–434	18	10.285	1.5776	156.52	0.46	0.96
0.0999	366–432	16	10.667	1.7291	145.73	0.49	0.88
0.1997	363–421	17	11.753	2.1746	116.71	0.19	0.43
0.3001	357–413	15	12.092	2.2694	109.49	0.38	0.74
0.3999	348–408	14	12.931	2.6052	94.988	0.19	0.37
0.5000	350–405	18	13.959	3.1391	69.390	0.11	0.24
0.5949	347–403	17	14.131	3.2153	65.462	0.12	0.31
0.8001	345–400	15	14.009	3.0382	76.589	0.09	0.17
1.0000	340–398	17	14.345	3.1759	71.040	0.01	0.04

ebulliometers were measured simultaneously under the same pressure. Two standard platinum resistance thermometers inside the two ebulliometers were employed to be connected with a Keithley 195A digital multimeter to record the equilibrium temperatures. The equilibrium pressure was calculated as the bubble-point vapor pressure from the boiling point temperature of ethanol and its well-known pressure–temperature behavior [17]. This comparative ebulliometry avoided the necessity of measuring the equilibrium pressure directly with a mercury manometer. For each sample, the bubble-point vapor pressures at various temperatures were measured over the equilibrium pressure range from about 12 to 101.3 kPa.

2.3. Flash point measurements

A SYD-261 closed-cup flash point analyzer (Changji Instrument Co. Ltd., Shanghai, China) was used to measure the flash points of the pseudo-binary mixtures with different compositions of the aviation fuel and DMC or DEC. This flash-point analyzer is operated according to the Chinese standard test method, GB/Y 261, in reference to the standard test method, ASTM D93. The analyzer incorporates control devices to adjust the heating rate of a sample. The operation conditions are with the start temperature of 20 °C, the test interval of 0.5 °C and the heat rate of 1–2 °C min⁻¹. The flash point is tested with the igniter at specified temperature intervals.

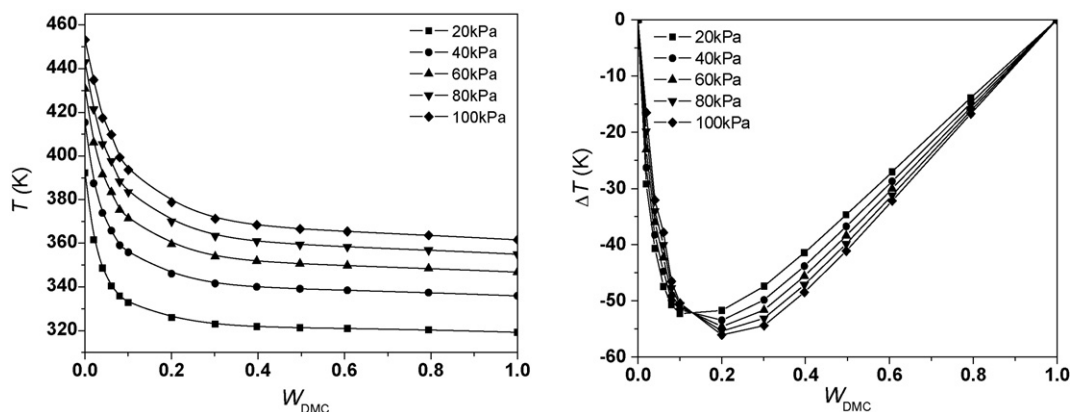


Fig. 1. Bubble-point temperature against composition at several pressures (left) and departures of equilibrium temperature from the linear addition values (right) for (1 – W_{DMC}) fuel + W_{DMC} .

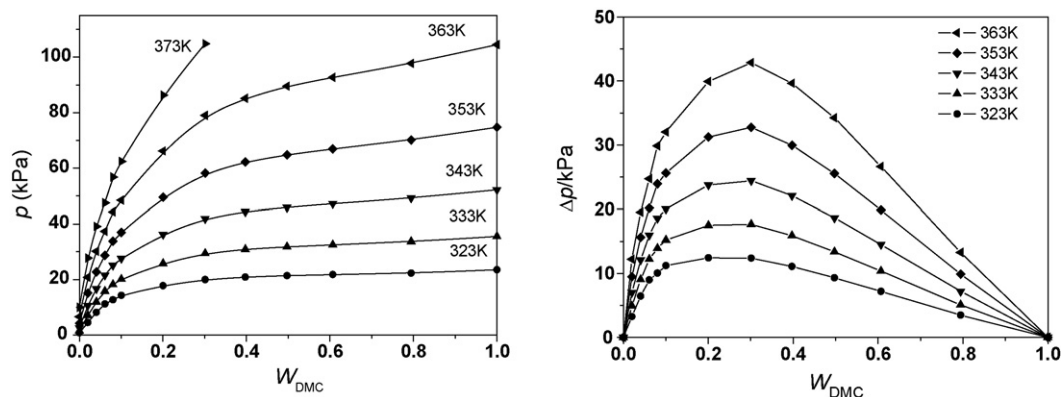


Fig. 2. Bubble-point vapor pressure against composition at several temperatures (left) and departures of equilibrium pressure from the linear addition values (right) for (1 - W) fuel + WDMC.

The flash point of each sample was measured under atmospheric pressure.

3. Results and discussion

3.1. Physical properties of pure liquids and the aviation fuel

The physical properties of DMC, DEC and ethanol are listed in Table 1. T_b is the normal boiling point measured by the ebulliometer, ρ is the density, n_D is the sodium-D line refractive index, p is the vapor pressure and T is the temperature. The experimental data exhibit satisfactory agreement with the literature values [18–20].

Some fundamental physical properties used to characterize the aviation fuel under study are listed in Table 2, where, T_{fp} is the flash point and M is the average relative molecular mass. The value of M , and the relative contents of *n*-paraffin, *iso*-paraffin, cycloparaffin and aromatics in the aviation fuel are estimated from the GC/MS analysis results. The fuel is a complex mixture of hydrocarbons mainly with carbon number ranging from C_7 to C_{25} . The true-boiling point (TBP) distillation data shows that the initial and final boiling point (IBP and FBP) temperatures of the fuel are 156 and 274 °C, respectively.

3.2. Vapor pressures and phase lines for pseudo-binary mixtures

Bubble-point vapor pressures at various temperatures for the pseudo-binary mixtures with different compositions of the aviation

fuel and DMC or DEC were measured. The temperature ranges of the measurements and the correlation results are summarized in Tables 3 and 4. The experimental data in detail can be found in Tables A.1 and A.2 in Appendix A.

The vapor pressure data are fitted to the Antoine equation

$$\ln p = A - \frac{B}{(T - C)} \quad (1)$$

where p is the vapor pressure in kPa, T is the equilibrium temperature in K, and A , B , C are constants. The average absolute deviation

$$AAD = \sum_{k=1}^n \frac{|p_{cal} - p_{exp}|_k}{n} \quad (2)$$

and average relative deviation

$$ARD = \sum_{k=1}^n \frac{|(p_{cal} - p_{exp})|_k}{p_{exp} \times 100\% / n} \quad (3)$$

are given for each sample, where n is the number of the experimental datum points.

From the vapor pressure–temperature correlation results, the bubble-point lines of T – W at several pressures and those of p – W at several temperatures can be obtained, respectively, where W is the mass fraction. Figs. 1–4 show these phase lines for the pseudo-binary systems of (fuel + DMC) and (fuel + DEC), along with the departures of the equilibrium temperature (ΔT) or pressure (Δp) from the corresponding linear addition values of two components.

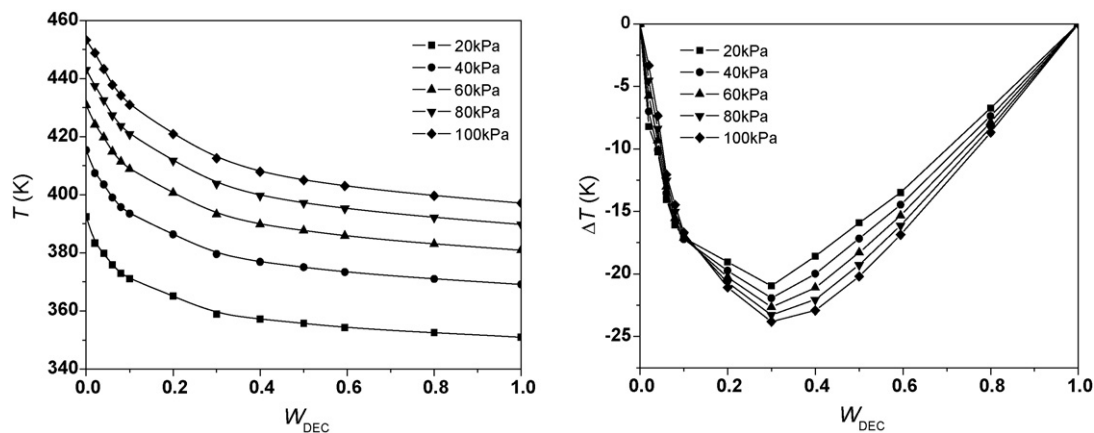


Fig. 3. Bubble-point temperature against composition at several pressures (left) and departures of equilibrium temperature from the linear addition values (right) for (1 - W) fuel + WDEC.

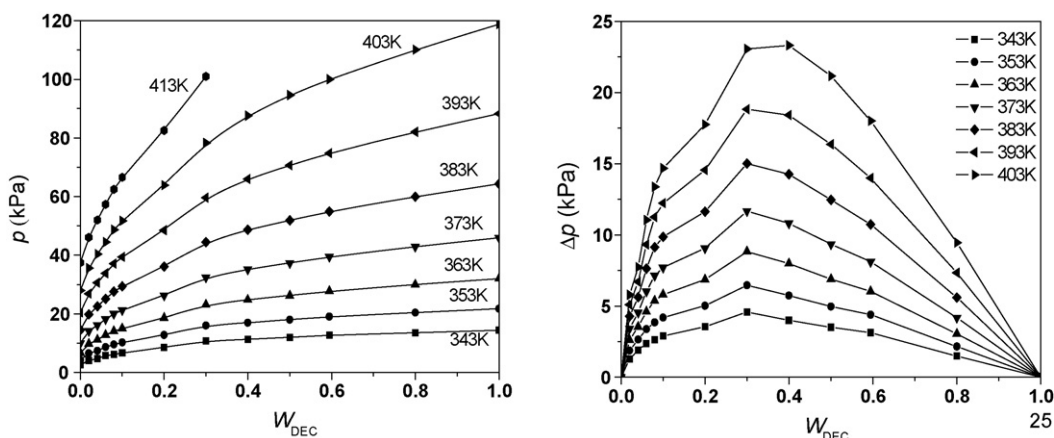


Fig. 4. Bubble-point vapor pressure against composition at several temperatures (left) and departures of equilibrium pressure from the linear addition values (right) for $(1 - W)$ fuel + WDEC.

It can be found that both of the pseudo-binary systems have obviously positive deviations from the Raoult's law. The maximum deviations of vapor pressures appear around 0.2–0.4 mass fraction of DMC or DEC. For the system of (fuel + DMC), the maximum pressure departure at 363 K is about 42.8 kPa and the maximum temperature departure at 100 kPa is about -56.0 K. While for the system of (fuel + DEC), the maximum pressure departure at 403 K is about 23.3 kPa and the maximum temperature departure at 100 kPa is about -23.8 K. It is shown that the additions of alkyl carbonates have critical effects on the vapor pressure and the phase equilibrium behavior of the fuels, and that the effect of DMC as an additive on the volatility of the aviation fuel is stronger than that of DEC. The positive pressure departures or negative temperature departures indicate that the blended fuels increase the fire and explosion hazards to a certain extent. Therefore, the vapor pressure change should be noted for the development and usage of fuels with additives.

3.3. Estimation of enthalpies of vaporization for pseudo-binary mixtures

From the bubble-point vapor pressures, the average initial enthalpy of vaporization, $\Delta_{\text{vap}}H_m$, for each mixture in the exper-

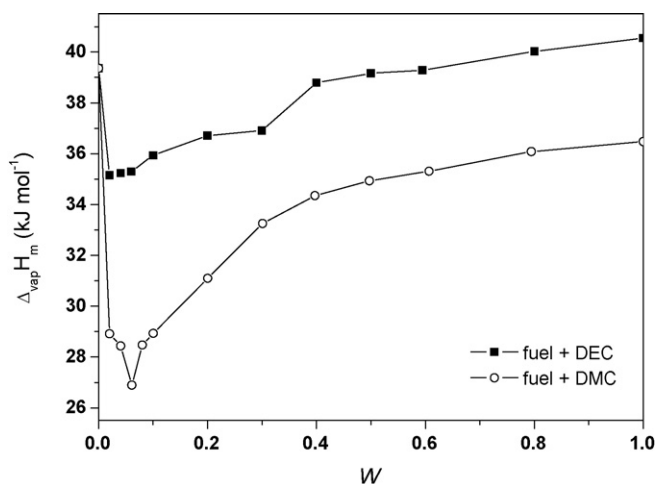


Fig. 5. Enthalpies of vaporization vs. composition for $(1 - W)$ fuel + WDMC and $(1 - W)$ fuel + WDEC.

imental temperature range is obtained from the linear regression of $\ln p$ against $1/T$ on the basis of the Clapeyron–Clausius equation. The changes of $\Delta_{\text{vap}}H_m$ against the composition are shown in Fig. 5. A low content of DMC or DEC can distinctly lower the enthalpy of vaporization of the fuel. It means that the blended fuel with low composition of DMC or DEC increases the volatility and consumes lower energy than the usual one to obtain the same evaporation amount. This might be attributed to high oxygen contents (53% for DMC and 41% for DEC) and strong polarities of alkyl carbonates. The strong dipole–dipole interactions between DMC or DEC molecules because of C=O and C–O groups can be damaged when a

Table 5
Temperature-dependent parameters for the flash point prediction for the pseudo-binary mixtures of (fuel + DMC) and (fuel + DEC)

Parameter	Fuel + DMC	Fuel + DEC
l_0	0.03159	0.01182
a_0	-0.36625	6053.598
a_1	0.94401	0.84455
a_2	0.00581	0.0074

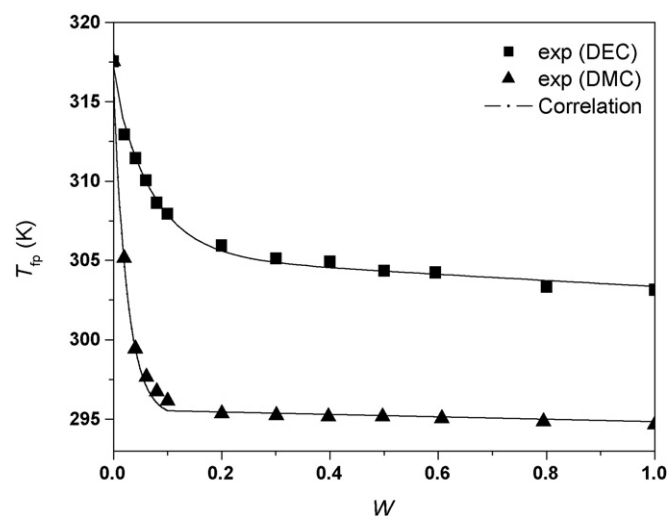


Fig. 6. Comparison of flash point correlation curves with experimental data for $(1 - W)$ fuel + WDMC and $(1 - W)$ fuel + WDEC.

large amount of nonpolar hydrocarbon fuels are mixed. The molecular interactions in the blended fuels are always weaker than those in the constituted components. As a result, the components in the blended fuels need lower energies to be vaporized into the vapor phase. Although the average enthalpies of vaporization for the mixtures in practical should be higher than the calculated initial values from bubble-point vapor pressure measurements because of the multiple components in the fuel with a given boiling point range, it can be concluded that DMC or DEC as an additive has strong effects on the vaporization behavior of the fuel. The results might be very useful to the development of environmentally friendly alternative fuels and their oxygenated additives.

3.4. Calculation of flash points from vapor pressure data

The flash point of any flammable liquid is defined as the temperature at which the vapor pressure of the liquid is sufficient to produce a concentration of vapor in the air, corresponding to the lower flammable limit (LFL) in air. At the LFL of a gas mixture, there is a rule expressed as [21,22]:

$$\sum \left(\frac{y_i}{\text{LFL}_i} \right) = 1 \quad (4)$$

where y_i is the mole fraction of a flammable substance i in the vapor phase, and LFL_i is the LFL of the pure component i . From the definition of the flash point, the value of LFL_i is expressed relating to the vapor pressure at the flash point, $p_{i,\text{fp}}$, as

$$\text{LFL}_i = \frac{p_{i,\text{fp}}}{p} \quad (5)$$

where p is the ambient pressure. The flash point is generally measured under atmospheric pressure, which can be considered low enough for a gas to be ideal and for y_i to be that for vapor–liquid equilibrium (VLE), so

$$\sum \left(\frac{x_i \gamma_i p_i}{p_{i,\text{fp}}} \right) = 1 \quad (6)$$

where x_i is the liquid mole fraction of component i , and γ_i is the liquid-phase activity coefficient. The vapor pressure of each pure component i , p_i varies with temperature according to the Antoine equation (Eq. (1)). The vapor pressure of pure liquid i at its flash point, $p_{i,\text{fp}}$, can be estimated by substituting $T_{i,\text{fp}}$, the flash point of component i , into the Antoine equation.

For a binary mixture of flammable liquids, Eq. (6) becomes

$$\sum \left(\frac{x_i \gamma_i p_i}{p_{i,\text{fp}}} \right) = \frac{x_1 \gamma_1 p_1}{p_{1,\text{fp}}} + \frac{x_2 \gamma_2 p_2}{p_{2,\text{fp}}} = 1 \quad (7)$$

As an example, the liquid-phase activity coefficients, γ_i ($i = 1, 2$), can be estimated from the regular solution model [23],

$$\ln \gamma_i = \frac{V_i(1 - \phi_i)^2[(\delta_i - \delta_j)^2 + 2l_{ij}\delta_i\delta_j]}{RT} \quad (8)$$

$$\delta_i^2 = \frac{\Delta_{\text{vap}}H_{m,i} - RT}{V_i} \quad (9)$$

$$\phi_i = \frac{x_i V_i}{\sum (x_i V_i)} \quad (10)$$

where V_i is the molar volume of component i , l_{ij} is the variable parameter. $\Delta_{\text{vap}}H_m$ is the average initial enthalpy of vaporization, and the values of $\Delta_{\text{vap}}H_m$ for DMC, DEC and the aviation fuel are 36.48, 40.55 and 39.36 kJ mol⁻¹ respectively. The temperature-

dependence of l_{ij} is expressed as

$$l_{ij} = l_0 + a_0 \exp \left(\frac{a_1 - T/T_0}{a_2} \right) \quad (11)$$

where T_0 is an arbitrarily chosen reference temperature, in this case 317.55 K, the flash point of the 'pure' fuel. l_0 , a_0 , a_1 and a_2 are constants. On the basis of Eqs. (1) and (7)–(11), along with the corresponding properties of the 'pure' components, the parameters in Eq. (11) can be correlated from the experimental flash points with nonlinear optimization method by minimizing the objective function

$$\text{OF} = \sum_{k=1}^n \frac{[(T_{\text{fp,cal}} - T_{\text{fp,exp}})^2]_k}{n} \quad (12)$$

The obtained values of the parameters for the two pseudo-binary systems are given in Table 5. With these parameters and Eqs. (1) and (7)–(11), the flash points of the pseudo-binary mixtures can then be calculated and are shown in Fig. 6, which display agreement with the experimental data. These results suggest that the addition of DMC or DEC into a kerosene-based aviation fuel could be used to reduce flash point and improve combustion, but may increase the potential hazard of the fuel storage and transportation because the flame spread is dependent upon the fuel temperature and the fuel flash point [24]. The ambient temperature should be controlled to reduce the risk of fire according to the variation of flash points for the safe storage of the blended fuels.

4. Conclusions

- Bubble-point vapor pressures for several mixtures of a refined kerosene-based aviation fuel with dimethyl carbonate or diethyl carbonate were measured with satisfactory results by the comparative ebulliometry. The flash points for the same pseudo-binary systems were presented.
- The bubble-point lines of equilibrium pressure or temperature versus composition were obtained from the pressure–temperature correlation with the Antoine equation. These phase lines indicated that the two pseudo-binary systems had large positive deviations on the value of pressure from the Raoult's law and negative deviations on the value of temperature.
- A low content of DMC or DEC can distinctively increase the volatility and lower the flash points and the enthalpies of vaporization of the aviation fuel. The correlation of the flash points with the vapor pressures for the pseudo-binary mixtures of the fuel and DMC or DEC can be made with satisfactory results from the activity coefficient model.

Acknowledgements

The authors are grateful for the financial supports from the National Natural Science Foundation of China (No. 20573096) and the Natural Science Foundation of Zhejiang Province, China (No. Y404329).

Appendix A

The experimental bubble-point vapor pressures at various temperatures for the pseudo-binary mixtures with different compositions of the aviation fuel and DMC or DEC are listed in Tables A.1 and A.2, where W is the mass fraction, T is the bubble-point temperature, and p is the bubble-point vapor pressure.

Table A.1
Bubble-point vapor pressure data for fuel + DMC mixtures

$W_{DMC} = 1.0000$		$W_{DMC} = 0.7948$		$W_{DMC} = 0.6069$		$W_{DMC} = 0.4973$		$W_{DMC} = 0.3972$	
T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)
314.96	16.49	313.59	14.74	316.08	16.21	312.17	13.59	312.47	13.47
320.81	21.42	321.41	20.94	323.48	22.30	318.84	17.98	314.21	14.43
325.29	25.99	326.30	25.77	328.95	27.82	325.19	23.42	320.42	18.80
329.63	31.09	331.52	31.78	333.40	33.08	330.52	28.73	329.18	26.74
333.11	35.76	335.28	36.80	341.64	45.00	334.76	34.03	333.75	31.77
336.93	41.51	343.12	49.42	344.99	50.73	338.58	39.20	337.90	37.02
340.12	46.94	346.77	56.41	347.74	55.89	342.08	44.54	341.70	42.38
342.99	52.29	349.08	61.25	350.36	61.15	345.16	49.71	344.87	47.33
345.58	57.41	351.47	66.52	352.91	66.70	348.17	55.09	348.01	52.81
347.86	62.35	353.98	72.54	355.40	72.42	353.30	65.54	351.01	58.39
350.55	68.64	355.85	77.28	357.61	77.94	355.45	70.35	353.41	63.02
352.63	73.74	357.95	82.87	359.64	83.38	359.91	81.22	355.52	67.77
354.28	78.06	360.15	89.43	361.52	88.47	362.04	87.13	360.20	78.27
356.05	82.90	362.15	95.05	363.32	93.61	364.15	92.65	361.75	82.17
357.88	88.25	364.06	101.15	365.57	100.62	366.97	101.05	364.19	88.04
359.58	93.25							366.43	94.19
361.73	100.82							368.91	101.38
$W_{DMC} = 0.3011$		$W_{DMC} = 0.2003$		$W_{DMC} = 0.1003$		$W_{DMC} = 0.0805$		$W_{DMC} = 0.0609$	
317.25	15.88	327.19	20.98	322.68	14.35	330.83	16.97	337.45	18.41
324.80	21.57	333.58	26.24	333.79	20.46	333.64	18.51	345.32	22.94
330.40	26.59	338.59	31.33	339.70	24.97	340.75	23.33	351.64	27.54
335.31	31.97	343.39	37.03	345.30	29.62	350.46	31.92	357.38	32.60
339.93	37.73	347.79	42.43	351.03	34.60	362.77	44.04	363.51	37.77
344.03	43.42	351.52	47.15	355.32	39.50	366.18	48.67	369.68	43.69
347.41	48.69	355.49	53.28	364.28	49.88	370.91	53.34	378.38	53.55
349.84	53.33	358.71	58.12	367.49	55.05	373.99	58.09	382.97	59.34
353.94	59.25	361.31	63.28	371.38	60.11	377.64	62.96	385.95	63.51
356.56	65.26	364.55	69.34	374.27	64.48	381.27	68.04	390.01	68.97
358.71	69.47	367.55	74.63	376.97	69.19	384.41	73.29	393.26	73.58
361.66	75.87	369.32	78.85	380.08	73.93	389.77	83.17	399.18	82.66
363.78	81.03	371.73	83.80	383.88	79.72	393.36	88.13	403.08	88.52
366.19	86.68	374.03	88.83	387.43	86.13	395.62	94.26	406.38	93.37
368.14	91.55	376.33	93.67	390.38	93.53	399.93	101.10	410.04	100.52
370.17	96.98	379.38	101.31	393.71	101.28				
371.69	101.33								
$W_{DMC} = 0.0407$		$W_{DMC} = 0.0199$		$W_{DMC} = 0.0000$		$W_{DMC} = 0.0000$		$W_{DMC} = 0.0000$	
342.88	16.66			356.83	17.06			382.88	14.55
351.06	21.41			361.72	20.47			390.11	19.20
357.98	26.59			368.64	24.65			397.97	24.74
364.01	31.20			376.72	30.03			403.05	28.08
370.47	36.73			382.28	35.18			409.32	32.48
375.41	41.78			387.33	40.24			418.12	41.69
380.14	46.39			398.39	50.66			425.73	53.24
385.15	51.81			402.38	55.99			429.10	57.16
389.42	56.72			411.70	67.34			432.09	60.05
392.53	61.98			419.07	75.72			434.23	63.74
397.81	67.28			421.95	80.30			436.55	67.60
405.44	80.01			425.69	85.75			439.90	73.51
408.71	86.35			429.85	92.31			442.83	78.69
412.63	91.94			434.80	100.78			445.77	84.50
417.70	100.58							447.39	89.56
								450.04	95.75
								451.33	100.68

Table A.2
Bubble-point vapor pressure data for fuel + DEC mixtures

$W_{DEC} = 1.0000$		$W_{DEC} = 0.8001$		$W_{DEC} = 0.5949$		$W_{DEC} = 0.5000$		$W_{DEC} = 0.3999$	
T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)
340.59	12.96	345.61	15.13	347.62	15.47	350.92	16.61	348.79	14.50
347.69	17.54	353.86	21.12	349.83	16.74	358.32	22.05	351.15	15.81
352.84	21.63	359.64	26.40	354.83	20.39	362.71	25.76	359.13	21.31
355.72	24.29	364.02	31.19	359.82	25.17	367.68	31.44	372.32	34.27
360.29	28.94	368.07	36.30	372.04	38.14	372.30	36.48	380.05	44.43
364.48	33.85	371.86	41.21	375.41	42.69	375.95	41.16	383.64	49.95
367.84	38.19	376.65	48.61	378.19	46.88	378.97	45.54	389.74	59.78
371.47	43.51	382.01	58.02	381.15	51.58	381.78	49.81	392.70	65.20

Table A.2
(Continued)

$W_{DEC} = 1.0000$		$W_{DEC} = 0.8001$		$W_{DEC} = 0.5949$		$W_{DEC} = 0.5000$		$W_{DEC} = 0.3999$	
T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)	T (K)	p (kPa)
375.06	49.33	385.10	64.01	384.02	56.53	384.56	54.40	395.54	70.75
377.74	54.04	387.56	69.23	386.54	61.24	387.11	58.95	397.47	75.32
380.35	58.97	390.33	75.48	389.66	67.60	390.40	65.25	399.46	79.86
382.92	64.16	392.47	80.99	392.44	73.55	392.89	70.39	401.96	85.36
385.84	70.52	394.77	86.52	394.64	78.51	394.89	74.72	404.91	92.04
388.03	75.61	396.87	92.11	397.72	85.98	396.30	77.96	408.13	100.46
390.85	82.58	399.67	100.21	399.66	91.12	398.54	83.29		
393.74	90.28			401.49	95.94	400.80	88.98		
397.38	100.79			403.14	100.66	402.57	93.66		
						405.15	100.53		
$W_{DEC} = 0.3001$		$W_{DEC} = 0.1997$		$W_{DEC} = 0.0999$		$W_{DEC} = 0.0800$		$W_{DEC} = 0.0601$	
357.43	19.06	363.46	18.86	366.85	17.24	372.89	20.33	376.11	20.62
364.70	24.34	368.79	23.09	373.59	21.48	379.04	24.62	383.85	25.68
369.65	29.31	375.41	28.14	378.58	25.84	379.28	24.79	391.20	31.88
374.64	33.82	377.05	30.26	385.47	31.16	384.53	28.42	396.77	37.45
378.51	38.69	382.63	35.47	389.17	34.90	384.65	28.98	401.19	42.09
382.55	44.58	386.31	39.59	399.58	46.73	389.41	33.69	404.92	46.75
385.68	48.67	390.43	44.87	403.38	52.17	396.62	40.42	412.68	55.97
389.20	53.12	390.55	45.18	407.77	57.27	401.60	45.54	415.79	60.97
392.56	58.17	395.34	52.13	411.26	62.68	404.79	50.63	419.43	67.08
396.14	64.53	399.37	57.93	413.71	67.48	409.83	58.08	421.37	71.02
399.14	70.27	402.32	62.75	418.02	75.27	412.21	62.90	426.60	79.94
401.64	75.39	405.23	67.88	420.26	80.04	416.32	67.71	430.74	86.52
404.18	80.77	408.48	73.46	423.58	85.35	419.80	72.86	433.35	90.76
409.38	92.74	412.00	80.66	423.70	85.46	422.90	78.12	438.44	100.63
412.51	100.73	415.83	88.76	426.30	90.41	425.24	82.56		
		417.93	92.77	431.95	100.64	428.39	87.96		
		421.14	100.66			433.91	99.93		
						434.11	100.18		
$W_{DEC} = 0.0404$						$W_{DEC} = 0.0200$			
378.92			20.30			381.86			19.58
385.22			23.87			385.99			22.31
392.53			29.69			389.09			24.53
405.13			40.21			396.96			30.86
410.11			45.48			399.80			33.40
414.17			50.48			403.87			37.29
421.17			62.27			414.35			48.71
424.84			69.01			418.08			53.27
428.93			74.94			421.69			57.96
432.75			80.00			423.86			60.91
435.82			85.84			427.91			66.65
440.10			94.40			430.90			71.13
440.43			94.62			436.61			80.21
443.18			100.90			444.76			94.40
						448.35			101.12

References

- [1] E.W. de Menezes, R. da Silva, R. Cataluña, R.J.C. Ortega, Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests, *Fuel* 85 (2006) 815–822.
- [2] S. Boyde, Green lubricants: environmental benefits and impacts of lubrication, *Green Chem.* 4 (2002) 293–307.
- [3] R. da Silva, R. Cataluña, E.W. de Menezes, D. Samios, C.M.S. Piatnicki, Effect of additives on the antiknock properties and Reid vapor pressure of gasoline, *Fuel* 84 (2005) 951–959.
- [4] M.B. Gramajo de Doz, C.M. Bonatti, H.N. Solimo, Water tolerance and ethanol concentration in ethanol–gasoline fuels at three temperatures, *Energy Fuels* 18 (2004) 334–337.
- [5] Z.D. Nan, Z.C. Tan, L.X. Sun, Investigation on thermodynamic properties of ethanol+gasoline blended fuel, *Energy Fuels* 18 (2004) 84–89.
- [6] Z.H. Huang, H.B. Lu, D.M. Jiang, K. Zeng, B. Liu, J.Q. Zhang, X.B. Wang, Performance and emissions of a compression ignition engine fueled with diesel/oxygenate blends for various fuel delivery advance angles, *Energy Fuels* 19 (2005) 403–410.
- [7] F. Comelli, R. Francesconi, S. Ottani, Isothermal vapor–liquid equilibria of dimethyl carbonate + diethyl carbonate in the range (313.15–353.15) K, *J. Chem. Eng. Data* 41 (1996) 534–536.
- [8] H.P. Luo, J.H. Zhou, W.D. Xiao, K.H. Zhu, Isobaric vapor–liquid equilibria of binary mixtures containing dimethyl carbonate under atmospheric pressure, *J. Chem. Eng. Data* 46 (2001) 842–845.
- [9] A. Rodríguez, J. Canosa, J. Tojo, Physical properties of the binary mixtures (diethyl carbonate+hexane, heptane, octane and cyclohexane) from $T = 293.15$ K to $T = 313.15$ K, *J. Chem. Thermodyn.* 35 (2003) 1321–1333.
- [10] A.B. Pereiro, A. Rodríguez, J. Canosa, J. Tojo, VLE of the binary systems (dimethyl carbonate with 2-propanol or 2-butanol) and (diethyl carbonate with methylcyclohexane) at 101.3 kPa, *J. Chem. Thermodyn.* 37 (2005) 249–257.
- [11] A. Rodríguez, J. Canosa, A. Domínguez, J. Tojo, Viscosities of dimethyl carbonate or diethyl carbonate with alkanes at four temperatures: new UNIFAC-VISCO parameters, *J. Chem. Eng. Data* 48 (2003) 146–151.
- [12] B.C. Dunn, C. Guenneau, S.A. Hilton, J. Pahnke, E.M. Eyring, Production of diethyl carbonate from ethanol and carbon monoxide over a heterogeneous catalyst, *Energy Fuels* 16 (2002) 177–181.
- [13] M.A. Pacheco, C.L. Marshal, Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive, *Energy Fuels* 11 (1997) 2–29.
- [14] Z.H. Huang, D.M. Jiang, K. Zeng, B. Liu, Z.L. Yang, Combustion characteristics and heat release analysis of a compression ignition engine fueled with diesel–dimethyl carbonate blends, *Proceedings of the Institution of Mechanical Engineers, J. Automob. Eng.* 217 (2003) 595–606.
- [15] Y.D. Lei, F. Wania, D. Mathers, S.A. Mabury, Determination of vapor pressures, octanol–air, and water–air partition coefficients for polyfluorinated sulfon-

- amide, sulfonamidoethanols, and telomer alcohols, *J. Chem. Eng. Data* 49 (2004) 1013–1022.
- [16] H.Y. Sun, W.J. Fang, Y.S. Guo, R.S. Lin, Investigation of bubble-point vapor pressures for mixtures of an endothermic hydrocarbon fuel with ethanol, *Fuel* 84 (2005) 825–831.
- [17] H.P. Diogo, R. Santos, P.M. Nunes, M.E. Minas da Piedade, Ebulliometric apparatus for the measurement of enthalpies of vaporization, *Thermochim. Acta* 249 (1995) 113–120.
- [18] H.J. Liaw, C.L. Tang, J.S. Lai, A model for predicting the flash point of ternary flammable solutions of liquid, *Combust. Flame* 138 (2004) 308–319.
- [19] H.J. Liaw, Y.Y. Chiu, A general model for predicting the flash point of miscible mixtures, *J. Hazard. Mater.* A137 (2006) 38–46.
- [20] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, New York, 2000.
- [21] D. White, C.L. Beyler, C. Fulper, J. Leonard, Flame spread on aviation fuels, *Fire Safety J.* 215 (1997) 1–31.
- [22] J.A. Riddick, W.B. Bunger, T.K. Sakano, *Organic Solvents Techniques of Chemistry*, vol. II, 4th ed., Wiley, New York, 1986.
- [23] K.C. Möller, T. Hodal, W.K. Appel, M. Winter, J.O. Besenhard, Fluorinated organic solvents in electrolytes for lithium ion cells, *J. Power Sources* 97/98 (2001) 595–597.
- [24] P. Tundo, M. Selva, The Chemistry of dimethyl carbonate, *Acc. Chem. Res.* 35 (2002) 706–716.