

Solubility of 3,3'-(Oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] Dihexafluorophosphate in Water, Methanol, Ethanol, Acetone, and Acetonitrile and Binary Mixtures (Water + DMF) from (283.00 to 323.00) K

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ABSTRACT: 3,3'-(Oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] dihexafluorophosphate ([$C_4O(\min)_2$][PF_6]₂) was synthesized and confirmed with ¹H NMR and FT-IR. The thermal stability of [$C_4O(\min)_2$][PF_6]₂ was studied with differential scanning calorimetry and thermogravimetric analyses. Using the dynamic method, the solubility of [$C_4O(\min)_2$][PF_6]₂ in five different pure solvents (water, methanol, ethanol, acetone, and acetonitrile) and binary mixtures (water + DMF) was measured at the temperature range from (283.00 to 323.00 K) at atmospheric pressure. The solubility of [$C_4O(\min)_2$][PF_6]₂ in those selected solvents increased with increasing temperature and DMF contents, but the rate of solubility is different. The experimental data were correlated with the modified Apelblat equation. Also, the solubility of [$C_4O(\min)_2$][PF_6]₂ and [$C_6O_2(\min)_2$][PF_6]₂ was been compared in the same solvent.

1. INTRODUCTION

Recently, ionic liquids (ILs) have been paid much attention by industrial and academic as novel liquid materials which are totally composed of ions at room temperature or a similar temperature. Because of their favorable properties such as negligible vapor pressure, noninflammability, reusability, high thermal stability, and favorable and easily tunable physical and chemical properties, ionic liquid technology has been successfully applied to many areas of organic synthesis, biocatalysis reaction, separation process, electrochemistry, and so on.^{1–5} Compared to monocationic ILs, gemini dicationic ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility.^{6,7} As a kind of gemini dicationic ionic liquids, 3,3'-(oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] dihexafluorophosphate([C₄O(mim)₂][PF₆]₂) can be used as a high-temperature solvent.

Furthermore, an understanding of solid–liquid equilibria (SLE) is of paramount importance for the design of separation processes, especially anti-solvent crystallization. There is a pressing need to develop better solvents for separation. The solubilities of ILs in different solvents have been investigated extensively.^{8–14}

As our ongoing study of gemini dicationic ionic liquids,¹⁵ in this work, 3,3'-(oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] dihexafluorophosphate was synthesized and confirmed with ¹H NMR and FT-IR. The thermal stability of $[C_4O(\min)_2][PF_6]_2$



was studied with differential scanning calorimetry and thermogravimetric analyses. The molecular structure of $[C_4O(mim)_2][PF_6]_2$ was illustrated in Figure 1. The solubility of $[C_4O(mim)_2][PF_6]_2$





in water, methanol, ethanol, acetone, acetonitrile, and binary mixtures (water + DMF) was measured over the temperature range from (283.00 to 323.00) K at atmospheric pressure. The modified Apelblat equation was applied to correlate the experimental data. The solubility of $[C_4O(\min)_2][PF_6]_2$ and $[C_6O_2(\min)_2][PF_6]_2$ was been compared in same solvent. To our knowledge, this is the first time the solubilities of $[C_4O(\min)_2][PF_6]_2$ are reported.

2. EXPERIMENTAL SECTION

2.1. Materials. The $[C_4O(mim)_2][PF_6]_2$ was synthesized by our laboratory, and the mass fraction purity was greater than 0.99,

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determined by high-performance liquid chromatography (type Waters 600E, Waters Co.). ¹H NMR spectra was recorded on the AVANCE AV-300 or AVANCE AV-500 (Bruker Co. Ltd., Germany) operating at 400 or 500 MHz, and chemical shifts were given in ppm units relative to tetramethylsilane (TMS). The splitting patterns are designated as follows; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. FT-IR spectra was obtained with Nicolet AUV360 spectrometer (Thermo Fisher Scientific Inc. USA). Approximately 2 mg of sample was mixed with 200 mg of KBr (spectroscopic grade), and FT-IR spectra were recorded in the range of $4000-400 \text{ cm}^{-1}$ at a resolution of 4 cm⁻¹ with 32 scans per sample. Differential scanning calorimetry (DSC) and thermogravimetry analyses (TG) were performed on Netzsch STA 449F3 thermogravimetric analyzer (Netzsch Geratebam GmbH, Germany) over a temperature range of (40 to 500) °C at a heating rate of 10 °C/min in nitrogen atmosphere. All solvents (Shanghai Lingfeng Chemical Co., Ltd.) used for experiments were of analytical reagent grade, and their mass fraction purities were higher than 0.99. The other organic and inorganic compounds (purchased from Shanghai Aladdin Industrial Corporation) with a mass fraction of higher than 0.97 were used without further purification. Water used in this study was double-distilled. More details about the purities of solvent and solute are listed in Table 1.

2.2. Synthesis of Gemini Dicationic lonic Liquids. The synthesis processes of $[C_4O(mim)_2][PF_6]_2$ were as follows:

Table 1. Provenance and Purity of the Materials Used

compound	provenance	mass fraction purity
$[C_4O(mim)_2][PF_6]_2$	our laboratory	≥ 0.99
methanol	Shanghai Lingfeng Chemicals	≥ 0.9970
ethanol	Shanghai Lingfeng Chemicals	≥ 0.9980
acetone	Shanghai Lingfeng Chemicals	≥ 0.9970
acetonitrile	Shanghai Lingfeng Chemicals	≥ 0.9970
N,N-dimethylformamide	Shanghai Lingfeng Chemicals	≥ 0.9970
water	our laboratory	double-distilled

Synthesis of 1-bromo-2-(2-bromoethoxy)ethane ($C_4H_8OBr_2$) (yield 0.786 in mass fraction): The diethylene glycol ($C_4H_{10}O_3$, 26.5 g, 0.25 mol) was stirred at 20 °C, and then phosphorus tribromide (54.2 g, 0.20 mol, distilled) was added dropwise over 1 h. The mixture was stirred at 80 °C for another 4 h and then was poured into NaHCO₃ saturated aqueous solution (50 mL). The lower organic layer was washed with water (3 × 40 mL), and it was dried with MgSO₄. Finally, the target compound $C_4H_8OBr_2$ was obtained as a white liquid.

Synthesis of 3,3'-(oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] dibromide ($[C_4O(mim)_2]Br_2$) (yield 0.923 in mass fraction): A solution of 1-methylimidazole (8.77 g, 0.107 mol) and 1-bromo-2-(2-bromoethoxy) ethane ($C_4H_8OBr_2$, 11.87 g, 0.054 mol) in 1,1,1-trichloroethane (50 mL) was heated at 80 °C for 24 h, and then solvent was removed under reduced pressure on a rotary evaporator. The resulting product as a white viscous liquid was washed with ether and then dried in vacuo for 12 h.

Synthesis of 3,3'-(oxidi-2,1-ethanediyl)bis[1-methyl-imidazolium] dihexafluorophosphate ($[C_4O(mim)_2][PF_6]_2$, yield 0.964 in mass fraction): To a solution of $[C_4O(mim)_2][Br]_2$ (3.98 g, 0.01 mol) in distilled water (50 mL), another solution of potassium hexafluorophosphate (3.68 g, 0.02 mol) in distilled water (50 mL) was added dropwise over 30 min. The mixture was stirred for 4 h at room temperature. Then the product was washed with water to remove $[C_4O(mim)_2]Br_2$ and potassium hexafluorophosphate thoroughly and recrystallized twice with water. Finally, white solid of $[C_4O(mim)_2][PF_6]_2$ was obtained, and the product was dried in vacuo at 25 °C for 12 h.

Purity of $[C_4O(\min)_2][PF_6]_2$: The packed column (C18 250 × 4.6 mm, 5 μ m) was filled with octadecyl silane bonded silica gel (5 μ m). The mobile phase was acetonitrile, the detection wavelength was 220 nm, and the velocity was 1.0 mL/min.

2.3. Apparatus and Procedure. The solubilities of $[C_4O(\min)_2][PF_6]_2$ in water, methanol, ethanol, acetone, acetonitrile, and binary mixtures (water + DMF) were measured by the dynamic method at atmospheric pressure (101.3 K Pa).^{16,17} Before the solubility measurement, high-purity nitrogen (0.9999 %



Figure 2. ¹HNMR of $[C_4O(mim)_2][PF_6]_2$.

by mass, $10 \text{ mL} \cdot \text{min}^{-1}$) was fed into the solvent for 2 h to remove the dissolved water and oxygen. A total of 8 mL of solvent and excess amount of $([C_4O(mim)_2][PF_6]_2)$ was added into a 10 mL glass tube with stopper. The glass test tubes were maintained within a double layer jacketed glass (120 mL, Heng Tai Experiment Institute Industry, China) which was full of water. The temperature of the inner water was controlled by circulating water from a low-temperature thermostatic bath (type DC-1006, Shanghai Heng Ping Instruments Co., Ltd., China) and a mercury-in-glass thermometer (type WNG-01, Changzhou Rui Ming Instrument and Meter Plant, China) which was inserted into the inner chambers of the vessel for the measurement of the temperature. The uncertainty of temperature was \pm 0.02 K. The mixtures were constantly stirred for 12 h by a magnetic stirrer (type DF-101S, Gongyi Yu Hua Instruments Co., Ltd., China) to ensure the solution reached equilibrium. After the period of 12 h, the magnetic stirrer was taken off to allow the solution settle at least 8 h to ensure the suspended solid phase settled down. Then portions of $[C_4O(mim)_2]$ [PF₆]₂ saturated solutions were transferred to a 5 mL beaker which had been weighted beforehand, and the total weight was measured immediately. Finally, the beaker was put into a dryer at 298 K and weighed regular until getting the constant weight. The masses of the samples and solvents were weighed by an analytical balance (type BS 124S, Beijing Sartorius Instruments System Co., Ltd., China) which had an accuracy of \pm 0.0001 g, with a range of measurement up to 120 g.

In this study, each experiment was conducted at least three times to check reproducibility, and the mean value was used to calculate the mole fraction solubility.

3. RESULTS AND DISCUSSION

3.1. Characterization of $[C_4O(mim)_2][PF_6]_2$. The ¹HNMR of $[C_4O(mim)_2][PF_6]_2$ is shown in Figure 2. As shown in Figure 1, $[C_4O(mim)_2][PF_6]_2$ was a symmetrical structure. Therefore, the H integrals (number of proton) at different chemical shifts were doubled. ¹HNMR (DMSO-d6, 500 MHz) of $[C_4O(mim)_2][PF_6]_2$: 3.75 ppm (t, 4H), 3.85 ppm (s, 6H), 4.33 ppm (t, 4H), 7.65 ppm (s, 4H), 8.98 ppm (s, 2H).

The FT-IR of $[C_4O(\min)_2][PF_6]_2$ is shown in Figure 3. The signal at 2920 cm⁻¹ ascribed to C–H stretching vibration of imidazolium ring. The signal at 1580 cm⁻¹ was the frame vibration



of the imidazolium ring. The signal at (1460 to 1350) cm⁻¹ assigned to C–H deformation vibration of methyl in the imidazolium ring. The signal at 1160 cm⁻¹ was the C–H deformation vibration of imidazolium ring. The signal at 1080 cm⁻¹ was the C–O–C frame vibration. The signal at 837 cm⁻¹ assigned to the PF_6^- vibration.

3.2. Thermal Stability of $[C_4O(\min)_2][PF_6]_2$. The DSC and TGA results of $[C_4O(\min)_2][PF_6]_2$ are shown in Figure 4. From the DSC curve, an endothermic peak was found at 98 °C which meant $[C_4O(\min)_2][PF_6]_2$ absorbed heat to melt at 98 °C. Another exothermic peak appeared at 427 °C which meant the product started to disintegrate. The TGA curve showed that the sample was stable when the temperature was below 350 °C. The TGA curve continuously declined with the rising of temperature. When the temperature was above 450 °C, the weight loss became not so obvious and tended to be stable. It was concluded that the melting point of $[C_4O(\min)_2][PF_6]_2$ was near 98 °C and $[C_4O(\min)_2][PF_6]_2$ had good heat resistance when the temperature was below 350 °C.

3.3. Solubility Data of $[C_4O(\min)_2][PF_6]_2$. The experimental mole fraction solubilities of $[C_4O(\min)_2][PF_6]_2$ in five different pure solvents (water, methanol, ethanol, acetonitrile, and acetone) and (DMF + water) binary solvent mixtures from

Table 2. Mole Fraction Solubilities (x) of $([C_4O(mim)_2][PF_6]_2)$ in Water, Methanol, Ethanol, Acetonitrile, and Acetone at the Temperature Range from (283.00 to 323.00) K under Atmospheric Pressure^{*a*}

T/K	$10^2 x_i^0$	$10^2 \varepsilon$	T/K	$10^2 x_i$	$10^2 \varepsilon$
		Wa	ater		
283.00	0.0118	0.0204	308.00	0.0446	0.5325
288.00	0.0157	0.4633	313.00	0.0560	0.0400
293.00	0.0210	0.9191	318.00	0.0697	0.2323
298.00	0.0271	0.1091	323.00	0.0865	0.1425
303.00	0.0345	1.0431			
		Metl	nanol		
283.00	0.0171	0.7074	308.00	0.0553	0.1009
288.00	0.0234	1.4048	313.00	0.0640	0.5770
293.00	0.0298	0.5006	318.00	0.0735	0.2863
298.00	0.0376	0.3821	323.00	0.0817	0.0589
303.00	0.0464	0.2951			
		Eth	anol		
283.00	0.0032	1.1285	308.00	0.0082	0.5978
288.00	0.0038	1.6229	313.00	0.0097	0.1318
293.00	0.0047	0.2407	318.00	0.0115	0.2208
298.00	0.0056	1.1496	323.00	0.0136	0.1576
303.00	0.0069	1.2981			
		Aceto	nitrile		
283.00	7.2560	0.0232	308.00	8.6634	0.0501
288.00	7.4915	0.0033	313.00	9.0081	0.0171
293.00	7.7467	0.0371	318.00	9.3852	0.0026
298.00	8.0245	0.0667	323.00	9.7864	0.0116
303.00	8.3377	0.0593			
Acetone					
283.00	5.9931	0.0186	308.00	6.5176	0.0231
288.00	6.0967	0.0364	313.00	6.6248	0.0041
293.00	6.2124	0.1405	318.00	6.7311	0.0149
298.00	6.3066	0.0339	323.00	6.8364	0.0086
303.00	6.4114	0.0379			

^{*a*}The standard uncertainty for the temperatures u(T) is 0.02 K, and the relative standard uncertainty in solubility $u_r(x_i)$ is 0.02. ^{*b*}Notation: the experimental solubility value (x_i) , the relative deviations (ε) .



Figure 4. DSC and TGA of $[C_4O(mim)_2][PF_6]_2$. (a) DSC; (b) TGA.



Figure 5. Correlation of experimental mole fraction solubilities (x_i) of $[C_4O(\min)_2][PF_6]_2$ in pure solvents. ∇ , methanol; \bigcirc , water; \bigstar , ethanol; \bigcirc , acetonitrile; \bigstar , acetone. Solid line, calculated from the modified Apelblat equation.

(283.00 to 323.00) K at atmospheric pressure are listed in Tables 2 and 3. To understand the solubility data better, they were also depicted as a function of temperature in Figures 5 and 6. In the (DMF + water) binary solvent mixtures, the mass fraction of water (*w*) in the solvents was 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90. The mole fraction solubilities of $[C_4O(\min)_2][PF_6]_2$ were found to increase with the increase of temperature in both different pure solvents and (DMF + water) binary solvent mixtures, but the rate of solubility increasing was different.

From Table 2 and Figure 5, we found that the solubility of $[C_4O(\min)_2][PF_6]_2$ in water, ethanol, methanol, acetonitrile, and acetone increased with the increase of temperature. The highest solubility of $[C_4O(\min)_2][PF_6]_2$ in pure solvents was obtained in acetonitrile. The solubility of $[C_4O(\min)_2][PF_6]_2$ in different pure solvents at constant temperature was in the following order: acetonitrile > acetone > methanol > water > ethanol. The solubilities of $[C_4O(\min)_2][PF_6]_2$ not only depended on the nature of the Gemini ionic liquid, but also the influence of solvent polarity. $[C_4O(\min)_2][PF_6]_2$ was a kind of hydrophobic ionic liquids, so it showed poor solubility in

water. In the above systems, acetonitrile and acetone were strong polar solvents compared to ethanol and methanol. Also we found that the calculated solubilities in different pure solvents showed good agreement with the experimental data, which indicated that these data could be used to correlate solvent selection and model research in crystallization of $[C_4O(\min)_2][PF_6]_2$.

From Table 3 and Figure 6, we found that the solubility of $[C_4O(\min)_2][PF_6]_2$ in (DMF + water) binary solvent system increased with the increasing amount of DMF in the mixed solvent at a constant temperature. The solubility of $[C_4O(\min)_2][PF_6]_2$ in the mixed solvent was lower and slowly increased at temperatures between (283.00 to 303.00) K, but it quickly increased at high temperatures between (303.00 to 323.00) K. Also we found that the calculated solubility of $([C_4O(\min)_2][PF_6]_2)$ was in good agreement with the experimental data, which suggested that the experimental solubility data and the correlation equations in this work could be used as fundamental data and models in the purification process of $[C_4O(\min)_2][PF_6]_2$.

3.4. Correlation of $[C_4O(mim)_2][PF_6]_2$ **Solubility.** The experimental mole fraction solubility data of $[C_4O(mim)_2][PF_6]_2$

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Table 3. Mole Fraction Solubilities (x) of $([C_4O(\min)_2][PF_6]_2)$ in (w) Water + (1 - w) DMF at the Temperature Range from (283.00 to 323.00) K under Atmospheric Pressure, w Is the Mass Fraction^a

T/K	$10^2 x_i^b$	$10^2 \epsilon$	T/K	$10^2 x_i$	$10^2 \epsilon$
		w =	0.1		
283.00	6.7225	0.0055	308.00	7.7673	0.0057
288.00	6.9219	0.0063	313.00	7.9908	0.0055
293.00	7.1263	0.0095	318.00	8.2179	0.0043
298.00	7.3364	0.0045	323.00	8 4 4 8 7	0.0074
303.00	7.5497	0.0006	020100	011107	010071
303.00	7.5177	1w =	0.2		
283.00	4.7975	0.0006	308.00	6.2389	0.0041
288.00	5.0625	0.0027	313.00	6.5632	0.0021
293.00	5,3395	0.0091	318.00	6,9009	0.0072
298.00	5 6261	0.0147	323.00	7 2 5 0 3	0.0081
303.00	5,9265	0.0033	020100	,12000	010001
0.0000	0.7200	w =	0.3		
283.00	3.0934	0.0164	308.00	4.6718	0.0237
288.00	3,2836	0.0111	313.00	5.2253	0.0212
200.00	3 5285	0.0111	318.00	5 8973	0.0070
293.00	3.8359	0.0105	323.00	67085	0.0070
303.00	4 2128	0.0127	525.00	0.7005	0.0122
505.00	7.2120	0.0172 w =	04		
283.00	1 6578	0.0621	308.00	3 7061	0.0204
289.00	1.05/0	0.1262	313.00	4 3128	0.0204
200.00	2 3080	0.0517	318.00	5.0087	0.0203
293.00	2.3009	0.00017	373.00	5 7084	0.0100
298.00	2.7102	0.0094	323.00	5./904	0.0120
303.00	5.1/42	0.0150	0.5		
283.00	07173	w –	308.00	2 5065	0.0007
283.00	0.0087	0.0077	212.00	2.3003	0.0007
203.00	1 1 5 0 9	0.01/9	218.00	3.2740 4 2012	0.0372
293.00	1.1390	0.0280	318.00	5.6726	0.0027
298.00	1.4910	0.0033	323.00	3.0720	0.0129
303.00	1.92/4	0.0156	0.6		
282.00	0 2765	w -	208.00	1 2002	0.0448
283.00	0.2703	0.0155	212.00	1.2995	0.0440
203.00	0.3009	0.0003	218.00	2 6091	0.0300
293.00	0.4941	0.0207	318.00	2.0081	0.0093
298.00	0.0754	0.0373	323.00	5./439	0.0143
303.00	0.9301	0.0100	07		
283.00	0 1010	0 1220	308.00	0 5202	0.0420
283.00	0.1019	0.1220	313.00	0.5292	0.0429
200.00	0.1393	0.2750	318.00	1 0800	0.0102
293.00	0.1915	0.0743	373.00	1.5585	0.0343
303.00	0.2004	0.0745	525.00	1.5505	0.0217
303.00	0.3739	0.0302	0.8		
283.00	0.0474	0.0295	308.00	0.2465	0.0832
283.00	0.0474	0.0275	313.00	0.2403	0.0032
200.00	0.0027	0.2338	318.00	0.5541	0.0702
298.00	0.1187	0.1236	323.00	0.8530	0.0600
303.00	0.1696	0.1230	525.00	0.0000	0.0000
505.00	0.1070	40 -	0.9		
283.00	0.0261	0 2988	308.00	0.0940	0 1611
288.00	0.0201	0.2900	313.00	0 1 2 2 2	0.0768
200.00	0.0319	0.1511	318.00	0.1904	0.0700
293.00	0.0370	0.0311	372.00	0.1704	0.0230
290.00	0.0313	0.1003	525.00	0.2002	0.0000
303.00	0.0088	0.1090			

^{*a*}The standard uncertainty for the temperatures u(T) is 0.02 K, and the relative standard uncertainty in solubility $u_t(x_i)$ is 0.02. ^{*b*}Notation: the experimental solubility value (x_i) , the relative deviations (ε) .

Table 4. Apelblat Parameters (A, B, and C) and rmsd for the
$[C_4O(mim)_2][PF_6]_2$ in Water, Methanol, Ethanol,
Acetonitrile, and Acetone ^a

solvent	A^b	В	С	10^4 (rmsd)
water	76.29	-7665.93	-10.32	0.02
methanol	492.54	-25547.84	-72.79	0.02
ethanol	-33.82	-1749.66	5.25	0.01
acetonitrile	-9.04	27.51	1.08	0.35
acetone	-65.01	2231.94	9.65	0.33

"Notation: root-mean-square deviations (rmsd). ^bApelblat coefficients were determined by multivariate least-squares method.

Table 5. Apelblat Parameters (*A*, *B*, and *C*) and rmsd for the $[C_4O(\min)_2][PF_6]_2 + DMF + Water System at Various Contents of Water ($ *w*) in the Mixed Solvent^{*a*}

w	A^{b}	В	С	10^4 (rmsd)
0.10	-18.69	280.07	2.66	0.05
0.20	-26.71	271.63	4.02	0.05
0.30	-316.84	12615.34	47.61	0.08
0.40	-48.53	-408.11	8.14	0.12
0.50	-337.87	11009.86	52.08	0.06
0.60	-526.47	18419.47	80.68	0.04
0.70	-459.29	15120.71	70.67	0.03
0.80	-804.96	30330.16	122.25	0.02
0.90	-906.48	35870.72	136.66	0.01

"Notation: root-mean-square deviations (rmsd). ^bApelblat coefficients were determined by multivariate least-squares method.

were correlated with a simple Apelblat equation. The modified Apelblat equation was shown as follows: $^{18-20}\,$

$$\ln x = A + \frac{B}{T} + C \ln(T) \tag{1}$$

where *x* is the mole fraction of the solubility of $[C_4O(\min)_2][PF_6]_2$ calculated by the Apelblat equation; *T* is the absolute temperature; *A*, *B*, and *C* are the model parameters determined by the experimental solubility data which are listed along with the root-mean-square deviations in Tables 4 and 5 respectively.

The root-mean-square deviations (rmsd) between x_{ci} and x_i for $([C_4O(\min)_2][PF_6]_2)$ were calculated using eq 2.

rmsd =
$$\left[\sum_{i=1}^{N} \frac{(x_{ci} - x_i)^2}{N}\right]^{1/2}$$
 (2)

where *N* was the number of experimental points, x_{ci} was the solubility calculated by eq 1, and x_i was the experimental solubility value.

The relative deviation (ε) between the experimental and the calculated values is listed in Tables 2 and 3, which is defined as follows

$$\varepsilon = \frac{|x_{ci} - x_i|}{x_i} \cdot 100\%$$
(3)

where x_i and x_{ci} are the experimental and calculated values, respectively.

From Table 2, Table 4, and Figure 5, the values of ε did not exceed 0.02, and the calculated solubilities were in good agreement with the experimental data, which indicated that the equation used in this work could be used to correlate the solubilities data of $[C_4O(mim)_2][PF_6]_2$ in different pure solvents.



Figure 6. Correlation of experimental mole fraction solubilities (x_i) of $[C_4O(\min)_2][PF_6]_2$ in (w) water +(1-w) DMF, where w is the mass fraction: $\bigcirc, w = 0.1; \blacktriangle, w = 0.2; \Box, w = 0.3; \triangle, w = 0.4; \bigstar, w = 0.5; \bigstar, w = 0.6; \bigtriangledown, w = 0.7; \blacktriangledown, w = 0.8; \oplus, w = 0.9;$ solid line, calculated from the modified Apelblat equation.

From Table 3, Table 5, and Figure 6, we found that the calculated solubilities showed good agreement with the experimental data; these results indicated the good fitting of experimental solubility data with the Apelblat equation.

3.5. Comparison between the Solubility of $[C_4O(\min)_2]$ -[PF₆]₂ and $[C_6O_2(\min)_2]$ [PF₆]₂. The solubility of $[C_4O(\min)_2]$ -[PF₆]₂ in water, methanol, and ethanol is listed in Table 2, and those of $[C_6O_2(\min)_2]$ [PF₆]₂ in water, methanol, and ethanol were shown in our previous work.²¹ To understand the solubility data better, they were also depicted as a function of temperature in Figure 7. As shown in Figure 7, the solubility of



Figure 7. Solubility of $[C_4O(\min)_2][PF_6]_2$ and $[C_6O_2(\min)_2][PF_6]_2$ in water, methanol, and ethanol. \blacksquare , $[C_4O(\min)_2][PF_6]_2$ in water; \bigstar , $[C_6O_2(\min)_2][PF_6]_2$ in water; \bigstar , $[C_4O(\min)_2][PF_6]_2$ in methanol;, \bigtriangledown , $[C_6O_2(\min)_2][PF_6]_2$ in methanol; \blacklozenge , $[C_4O(\min)_2][PF_6]_2$ in ethanol; \diamondsuit , $[C_6O_2(\min)_2][PF_6]_2$ in ethanol.

 $[C_6O_2(\min)_2][PF_6]_2$ was higher than that of $[C_4O(\min)_2]$ - $[PF_6]_2$ in water and methanol. The solubility of $[C_6O_2(\min)_2]$ - $[PF_6]_2$ and $[C_4O(\min)_2][PF_6]_2$ in ethanol was lower and almost the same. The reason was that $[C_6O_2(\min)_2][PF_6]_2$ had more C-O-C in its chemical structure which was incline to increasing the solubility. Therefore, $[C_6O_2(\min)_2][PF_6]_2$ had better solubility than $[C_4O(\min)_2][PF_6]_2$ in the same solvent.

4. CONCLUSION

In this paper, $([C_4O(mim)_2][PF_6]_2)$, as a kind of gemini dicationic ionic liquids, was synthesized and confirmed with ¹HNMR and FT-IR. The thermal stability of $[C_4O(mim)_2][PF_6]_2$ was studied with differential scanning calorimetry and thermogravimetric analyses. The solubility of $([C_4O(mim)_2][PF_6]_2)$ in five different pure solvents (water, methanol, ethanol, acetone and acetonitrile) and binary mixtures (water+DMF) was measured at the temperature range from (283.00 to 323.00 K) at atmospheric pressure. Also, the solubility of $[C_4O(mim)_2][PF_6]_2$ and $[C_6O_2(mim)_2][PF_6]_2$ was compared in same solvents. Form the experiments, we drew the following conclusions:

(1) As a kind of gemini dicationic ionic liquids, the melting point of $[C_4O(\min)_2][PF_6]_2$ was near 98 °C and it had a higher heat resistance than ordinary ILs, which could be used as good high-temperature green solvent in organic reactions.

(2) The structure of material and the polarity of solvent affected the solubility in different solvents. Acetonitrile presented a relatively good ability of dissolving $[C_4O(\text{mim})_2][PF_6]_2$ than water, ethanol, and methanol. Also the solubility of $[C_4O(\text{mim})_2][PF_6]_2$ increased with the rising of temperature.

(3) The solubility of $[C_4O(\min)_2][PF_6]_2$ in binary mixtures (water + DMF) decreased with increasing water content at constant temperature, which indicated water could be used as effective antisolvent in the crystallization process.

(4) The calculated solubilities of $[C_4O(\min)_2][PF_6]_2$ in different solvents show good agreement with the experimental values. The experimental solubility and parameters in this study may be used for $[C_4O(\min)_2][PF_6]_2$ purification in the industry. (5) $[C_6O_2(\min)_2][PF_6]_2$ had better solubility than $[C_4O_2(\min)_2][PF_6]_2$

 $(mim)_2$ [[PF₆]₂ in the same solvent owing to the more polar C-O-C structure.

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Notes

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