Advanced Materials Research *Online: 2011-11-22*
ISSN: 1662-8985, Vols. 393-395, pp 1322-1327
doi:10.4028/www.scientific.net/AMR.393-395.1322

pH of N,N-dimethylformamide in [Bmim][BF_4] and [Bmim][PF_6] ionic liquids

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Keywords: pH, N,N-dimethylformamide, [Bmim][BF_4], [Bmim][PF_6], ionic liquids

Abstract. The pH value of binary mixtures containing N,N-dimethylformamide (DMF) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF_6]) ionic liquids over the range of N,N-dimethylformamide mole fraction from (0.1 to 0.9) and temperature range from (293.15 to 338.15) K were measured. The range of pH values of N,N-dimethylformamide and [Bmim][BF_4] and [Bmim][PF_6] were from (3.42 to 6.50) and (6.98 to 9.74), respectively. Comparison showed that the pH of N,N-dimethylformamide in the two ionic liquids was in sequence: [Bmim][BF_4] < [Bmim][PF_6] at the same conditions. The temperature dependency of the pH value was correlated using an empirical equation. The correlations gave satisfactory results.

Introdution

Room-temperature ionic liquids (ILs) are organic salts that are liquid at room temperature and composed of organic cations and organic or inorganic anions. Due to their unique properties such as negligible vapor pressure, high conductivity, excellent thermal, and stabilities, wide electrochemical windows, ionic liquids are regarded as green solvents in both industry and academic[1-3]. Ionic liquids are initially utilized in electroplating and electrolysis, however, their applications have been expanded greatly, e.g. used as a catalyst for some reaction, as solvents in a separation process[4-5]. Recently many studies focus on obtaining specific ILs for a range of applications[6-7]. The areas of application include gas solubility and separations, cellulose processing, catalysis, extraction, and high-temperature pyrochemical processing, etc. The best aim of any research is applied to industry, and its industrial applications has gained tremendous interest in days. But industrial applications of ILs base on theoretical foundation which contains physical and chemical properties, e.g. viscosity, thermal stability, conductivity, and surface tension[8-9]. Experimental data for various physical properties are useful for the development of theoretical models to explain and predict them. In spite of the importance and utility of ILs, accurate values for many of these properties are still scarce.

1-alkyl-3-methylimidazolium hexafluorophosphate, also known as [$C_n$mim][PF_6], is a viscous, colourless, hydrophobic and non-water soluble ionic liquid. Together with 1-alkyl-3-methylimidazolium tetrafluoroborate, [$C_n$mim][BF_4], it is one of the most widely studied ionic liquids and is commercially available from most of the major international suppliers of chemicals. Wang measured volumetrics and viscosities for mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]) ionic liquid with acetonitrile, dichloromethane, 2-butanone, and N,N-dimethylformamide (DMF) at 298.15K[10]. Arce measured densities, refractive indices, speeds of sound, and dynamic viscosities of 1-methyl-3-octylimidazolium tetrafluoroborate ([Omim][BF_4]) in binary mixtures with methanol, ethanol, 1-propanol, and 2-propanol at 298.15K and atmospheric pressure[11]. Geng reported the densities, viscosities, and electrical conductivities of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]) in monoethanolamine (MEA) and N,N-dimethylethanolamine (DMEA)[12]. Li measured the densities and viscosities of pure ionic liquid 1-hexyl-3-methylimidazoliumbromide ([C_6mim][Br]) and the binary system (water + [C_6mim][Br]) at 0.1 MPa and in the (293.15 to 333.15) K range[13]. Gao investigated the volumetric properties of mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF_4] and benzaldehyde at the temperature range from (298.15 to 313.15) K. And they also studied densities and volumetric properties of binary mixtures of amino acid ionic liquid [Bmim][Glu] or [Bmim][Gly] with benzylalcohol[14-15]. The pH of ionic liquids is one of the very important physical properties. Bogel-Łukasik has shown the pH of 1-alkyl-3-methylimidazolium chloride ([Bmim][Cl]) in alcohols and found that the range of pH values is from (3.0 to 8.5)[16]. However, for binary mixtures of imidazolium-based ILs with N,N-dimethyllformamide, the studies on pH are rather rare.

N,N-dimethyllformamide is an excellent organic comound and can completely miscible with both organic solvents and many inorganic liquids. It is known as a universal solvent and widely used in the petroleum, fiber synthesis, acrylic spinning, polyester synthesis leather, and dyestuff industries. The knowledge of pH value of the mixtures of DMF and ionic liquids may help to reveal new potential applications for the utilization of both DMF and ionic liquids. So a better understanding of the pH value of DMF and [Bmim][BF_4] and [Bmim][PF_6] ionic liquids is necessary and useful. In this work, the pH values of the mixtures of DMF and [Bmim][BF_4] and [Bmim][PF_6] ionic liquids at temperature from (293.15 to 338.15) K and atmospheric pressure were measured and summarized into a formula proposed and verified by experimental solubility data, respectively.

Experimental Methods

Materials. [Bmim][BF_4] and [Bmim][PF_6] were obtained from Chengjie Chemical Co. LTD., Shanghai, China, the purities of which were up to 99%. DMF was bought from Fuyu Chemical Co. LTD, Tianjing, China, the content of which was up to 99%. Three kinds of pH standard buffer solutions delivered from Shanghai Rex Co-perfect Instrment Co., LTD, China with pH values equal to 4.00 ± 0.01, 6.86 ± 0.01 and 9.18 ± 0.01 were used for calibration of the pH apparatus. The water contamination of ILs was determined using the Karl-Fischer technique. The water content of ILs was < 0.02 mol percent.

pH measurements of ILs and Solvents. The investigations were carried out in the cell over a wide range of mole fraction of DMF from (0.1 to 0.9) and temperature from (293.15 to 338.15) K. The temperature was controlled using a precision thermometer to determine the temperature with an uncertainty of ± 0.01 K. The mixtures of the pure components, solute and solvent, were weighed using a balance with an uncertainty of ± 0.0001 g. pH was assessed directly by inserting the probe in the mixtures. The pH measurement was carried out with a Mettler-Toledo pH/conductivity meter using a combination pH electrode LE409. The accuracy of pH measurements was ± 0.01 pH unit. Before each pH value reading, the pH buffer solution was used to check the measurements of the electrode.

Results and discussion

In Fig.1, the pH values of the binary mixtures of DMF and [Bmim][BF_4] ionic liquid were shown. As seen from this figure, the pH values decreased with the increase of temperature, and the decrease of the mole fraction of DMF. As shown in Fig.2, the pH values of the mixture of DMF and [Bmim][PF_6] ionic liquid were measured. It was clearly seen that the pH values of the studied systems decreased as the decrease of the mole fraction of DMF and the increase of temperature.

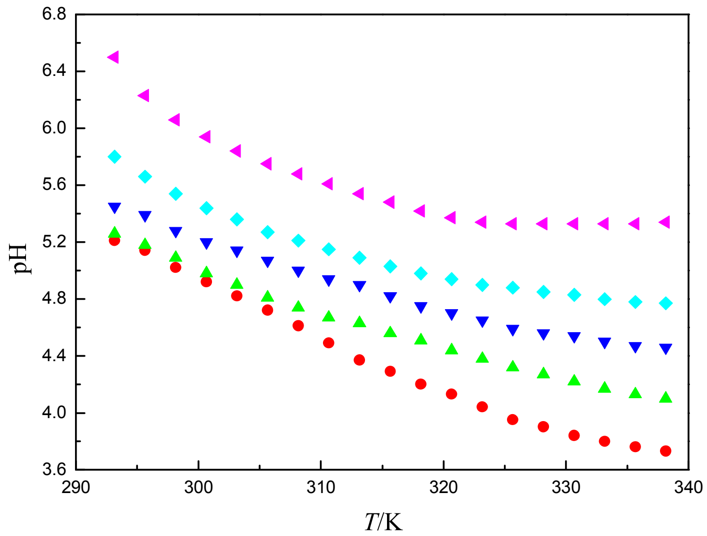

Fig.1 The pH values for binary systems DMF (1) + [Bmim][BF_4] ionic liquid (2) as a function of temperature:●, x_1 = 0.1; ▲, x_1 = 0.3; ▼, x_1 = 0.5; ♦, x_1 = 0.7, ◀, x_1 = 0.9.

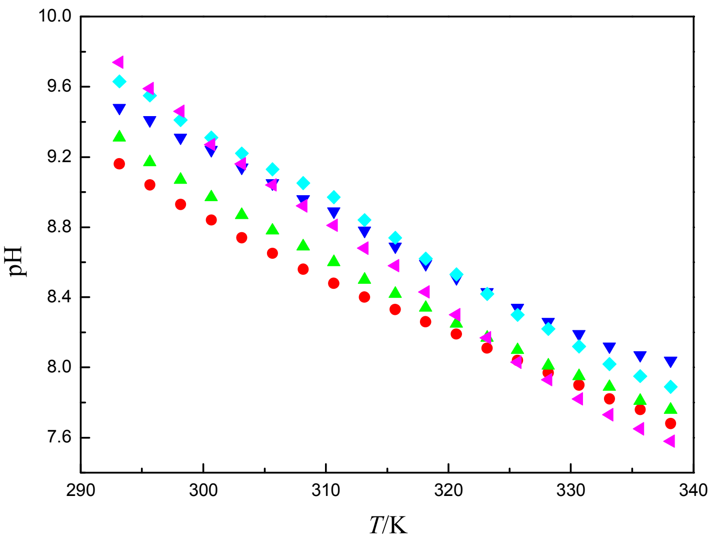

Fig.2 The pH values for binary systems DMF (1) + [Bmim][PF_6] ionic liquid (2) as a function of temperature:●, x_1 = 0.1; ▲, x_1 = 0.3; ▼, x_1 = 0.5; ♦, x_1 = 0.7, ◀, x_1 = 0.9.

Comparison showed that the pH of DMF in the two ionic liquids was in sequence: [Bmim][BF_4] < [Bmim][PF_6]. Although both [BF_4]$^-$ and [PF_6]$^-$ were inorganic anions, the polar of [BF_4]$^-$ was higher than that of [PF_6]$^-$[17]. So the pH value of the binary mixture of DMF and [Bmim][BF_4] is lower than that of the mixture DMF and [Bmim][PF_6] at the same condition.

The change of the pH values with temperature for the binary mixtures of DMF and [Bmim][BF_4] and [Bmim][PF_6] ionic liquids from Fig.1 to Fig.2 looks nonlinear. For the purpose of comparison and application, the measured pH values of the mixtures were expressed as a function of temperature as follows (Eq.1):

$$x_i^{calcd} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 + d(T/\mathrm{K})^3 + e(T/\mathrm{K})^4 \quad (1)$$

Where T is for the absolute temperature and a, b, c, d and e refer to the fit coefficients. The pH values of the solution (x_i^{calcd}) are given in Table 1 to Table 2 . The values of the relative deviation (RD) are also given in Table 1 to Table 2. The RD is defined as the Eq.2.

$$RD = \frac{\left|\ x_i - x_i^{calcd}\ \right|}{x_i} \tag{2}$$

Where x_i^{calcd} represents the pH values calculated from eq.1 and x_i represents the experimental values of the pH values. The values of parameters a, b, c, d and e the root-mean-square deviations ($rmsd$) are listed in Table 3 and 4. The rmsd is defined as the Eq.3.

$$rmsd = \left\{ \frac{\sum_{i=1}^{N} \left[\left(x_i^{calcd} - x_i \right)^2 \right]}{N} \right\}^{1/2} \tag{3}$$

Where x_i is the pH values of the mixture in different temperature and concentration. N is the number of experimental points; and the superscripts calcd refer to the values calculated from Eq.1.

Table 1 pH values x_i^{calcd} and relative deviation RD of the binary mixture of DMF (1) + [Bmim][BF_4] (2) at different temperature

T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	T[K]
					x_1=0.1						
293.15	5.21	0	305.65	4.71	0.00	318.15	4.20	0	330.65	3.85	0
295.65	5.13	0	308.15	4.60	0.00	320.65	4.11	0	333.15	3.80	0
298.15	5.03	0	310.65	4.49	0.00	323.15	4.03	0	335.65	3.76	0
300.65	4.93	0	313.15	4.39	0.00	325.65	3.96	0	338.15	3.73	0
303.15	4.82	0	315.65	4.29	0.00	328.15	3.90	0			
					x_1=0.3						
293.15	5.26	0	305.65	4.83	0	318.15	4.48	0.01	330.65	4.23	0
295.65	5.16	0	308.15	4.76	0	320.65	4.27	0.04	333.15	4.19	0
298.15	5.08	0	310.65	4.68	0	323.15	4.37	0	335.65	4.14	0
300.65	5.00	0	313.15	4.61	0	325.65	4.32	0	338.15	4.08	0
303.15	4.91	0	315.65	4.55	0	328.15	4.28	0			
					x_1=0.5						
293.15	5.45	0	305.65	5.08	0	318.15	4.75	0	330.65	4.53	0
295.65	5.36	0.01	308.15	5.00	0	320.65	4.70	0	333.15	4.50	0
298.15	5.29	0	310.65	4.94	0	323.15	4.65	0	335.65	4.48	0
300.65	5.22	0	313.15	4.87	0.01	325.65	4.61	0	338.15	4.45	0
303.15	5.15	0	315.65	4.81	0	328.15	4.57	0			
					x_1=0.7						
293.15	5.80	0	305.65	5.29	0	318.15	4.98	0	330.65	4.83	0
295.65	5.63	0.01	308.15	5.21	0	320.65	4.94	0	333.15	4.81	0
298.15	5.54	0	310.65	5.14	0	323.15	4.90	0	335.65	4.79	0
300.65	5.46	0	313.15	5.08	0	325.65	4.88	0	338.15	4.76	0
303.15	5.37	0	315.65	5.02	0	328.15	4.85	0			
					x_1=0.9						
293.15	6.51	0	305.65	5.76	0	318.15	5.41	0	330.65	5.33	0
295.65	6.19	0.01	308.15	5.67	0	320.65	5.38	0	333.15	5.33	0
298.15	6.08	0	310.65	5.59	0	323.15	5.35	0	335.65	5.33	0
300.65	5.97	0.01	313.15	5.52	0	325.65	5.34	0	338.15	5.33	0
303.15	5.86	0	315.65	5.46	0	328.15	5.33	0			

Table 2 pH values x_i^{calcd} and relative deviation RD of the binary mixture of DMF (1) + $[Bmim][PF_6]$ (2) at different temperature

T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	RD	T[K]	x_i^{calcd}	RD
					x_1=0.1						
293.15	9.16	0	305.65	8.66	0	318.15	8.25	0	330.65	7.91	0
295.65	9.02	0	308.15	8.57	0	320.65	8.18	0	333.15	7.84	0
298.15	8.93	0	310.65	8.48	0	323.15	8.10	0	335.65	7.76	0
300.65	8.84	0	313.15	8.40	0	325.65	8.04	0	338.15	7.67	0
303.15	8.75	0	315.65	8.32	0	328.15	7.98	0			
					x_1=0.3						
293.15	9.31	0	305.65	8.79	0	318.15	8.33	0	330.65	7.95	0
295.65	9.16	0	308.15	8.69	0	320.65	8.25	0	333.15	7.89	0
298.15	9.07	0	310.65	8.60	0	323.15	8.17	0	335.65	7.82	0
300.65	8.97	0	313.15	8.50	0	325.65	8.09	0	338.15	7.75	0
303.15	8.88	0	315.65	8.41	0	328.15	8.02	0			
					x_1=0.5						
293.15	9.48	0	305.65	9.06	0	318.15	8.59	0	330.65	8.19	0
295.65	9.39	0	308.15	8.97	0	320.65	8.50	0	333.15	8.13	0
298.15	9.32	0	310.65	8.87	0	323.15	8.42	0	335.65	8.08	0
300.65	9.24	0	313.15	8.78	0	325.65	8.34	0	338.15	8.03	0
303.15	9.15	0	315.65	8.69	0	328.15	8.26	0			
					x_1=0.7						
293.15	9.63	0	305.65	9.15	0	318.15	8.62	0	330.65	8.12	0
295.65	9.50	0.01	308.15	9.05	0	320.65	8.52	0	333.15	8.04	0
298.15	9.42	0	310.65	8.94	0	323.15	8.41	0	335.65	7.95	0
300.65	9.34	0	313.15	8.84	0	325.65	8.31	0	338.15	7.88	0
303.15	9.25	0	315.65	8.73	0	328.15	8.22	0			
					x_1=0.9						
293.15	9.74	0	305.65	9.07	0	318.15	8.41	0	330.65	7.84	0
295.65	9.55	0	308.15	8.93	0	320.65	8.29	0	333.15	7.74	0
298.15	9.44	0	310.65	8.02	0.09	323.15	8.17	0	335.65	7.65	0
300.65	9.32	0.01	313.15	8.67	0	325.65	8.05	0	338.15	7.56	0
303.15	9.19	0	315.65	8.54	0	328.15	7.94	0			

Table 3 Parameters of Eq.1 and rmsd of Eq.3 for pH values of DMF (1) + $[Bmim][BF_4]$ (2) binary mixture at different mole fractions of DMF (x_1)

x_1	$a(\times10^{-3})$	$b(\times10^{-1})$	$c(\times10)$	$d(\times10^{4})$	$e(\times10^{7})$	$rmsd(\times10^{3})$
0.1	-2.590	3.224	-1.493	3.057	-2.337	8.73
0.3	-3.185	4.075	-1.946	4.120	-3.264	39.9
0.5	-1.893	2.379	-1.113	2.303	-1.781	12.7
0.7	-4.036	5.185	-2.486	5.280	-4.196	10.7
0.9	-4.549	5.834	-2.790	5.910	-4.678	15.9

Table 4 Parameters of Eq.1 and rmsd of Eq.3 for pH values of DMF (1)+$[Bmim][BF_6]$ (2) binary mixture at different mole fractions of DMF (x_1)

x_1	$a(\times10^{-3})$	$b(\times10^{-1})$	$c(\times10)$	$d(\times10^{4})$	$e(\times10^{7})$	$rmsd(\times10^{3})$
0.1	-3.623	4.656	-2.232	4.746	-3.779	9.26
0.3	-2.516	3.189	-1.505	3.145	-2.461	6.55
0.5	-0.996	1.186	-0.5174	0.988	-0.697	9.00
0.7	-0.856	1.012	-0.4363	0.823	-0.573	17.7
0.9	-1.901	2.338	-1.065	2.142	-1.608	17.4

From table 1 to table 2, we believe that the experimental values of the pH values represented well the pH values calculated from Eq.1. This empirical equation can be applied over a wide range of temperature as it correlated well the new experimental results.

Conclusions

In conclusion, the pH values of binary mixtures of DMF and ILs, [Bmim][BF_4] and [Bmim][PF_6], decreased with the increase of temperature and decrease of the mole fraction of DMF. At the same condition, the pH values of the binary mixtures of DMF and [Bmim][BF4] were lower than that of the mixtures of DMF and [Bmim][PF6], the ranges of which were from (3.42 to 6.50) and (6.98 to 9.74), respectively. An empirical equation that calculated the pH value of binary mixtures of DMF and ILs at different temperature was gained. The result of this work can be applied to numerous industrial applications, since pH data is essential information for its rational design.

Acknowledgment

This research is supported by Ministry of Environmental Protection of China (the Project No. 201109004).

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