Measurements and correlation of viscosities and conductivities for the mixtures of imidazolium ionic liquids with molecular solutes

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ABSTRACT

Ionic liquids have potentials as green materials in a variety of fields. It is the case that in their application in industry, ionic liquids are often used together with molecular solutes/solvents. In this paper, systematical measurements of viscosities and conductivities for the binary and quasi-binary mixtures of ionic liquids with molecular solutes were performed over the whole concentration range. The variation tendency of viscosities/conductivities with composition of the mixtures was explained through the disruption of molecular solutes to ionic association or aggregation of the ionic liquids. A exponential equation with empirical parameter A suggested initially by Seddon et al. was used to describe the dependence of viscosities on the mole fraction of molecular solutes, and the physical meaning of A was analyzed based on a theoretical equation deduced from rate process theory. At the same time, another exponential equation with parameter C was proposed to correlate the experimental date of the product of conductivity and viscosity, and satisfactory results were obtained over the entire range of concentration. The main factors affecting the parameter C were discussed. It is expected that the new data and correlation equations reported in this work will be useful for the application of ionic liquids in chemical industry.

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1. Introduction

In recent years, room temperature ionic liquids (ILs) have attracted great attention because they are expected to have potentials as green materials in a variety of areas such as catalysis and organic synthesis [1–4], new material preparation [5–7], electrochemistry and energy fields [8–10], extraction and separation processes [11–13] and the other new areas [14–16]. Typically, an ionic liquid is composed of a bulky asymmetric cation and a comparatively small anion. Although typical ionic compounds they are, ILs are difficult to crystallize at room temperature and show a wide range of liquid status. Moreover, ILs possess some other peculiar properties such as undetectable vapor pressure, high thermal and chemical stability, large conductivity, wide electrochemical windows and high flexibility for chemical design. Nowadays, researches on the application of ILs have some successful cases in the chemical industry [17,18], which gives great necessary for the studies of the physical and chemical properties for the systems involving ILs. Recently, some researchers have made great effort to give simple models for the prediction of the physical properties such as density, viscosity and conductivity of new ILs with some empirical parameters obtained from the known series of ILs, and satisfactory results

have been reported for certain types of ILs [19,20]. It is the case that in their application in industry especially in organic synthesis and extraction processes, ILs were often used together with some molecular solvents/solutes. Therefore, how to predict the physical properties for the mixtures containing ILs becomes great importance. However, the related study is very scarce [21,22]. To overcome this deficiency partially, the measurements on molar volume, viscosity and electrical conductance for the mixtures of imidazonium ionic liquids with molecular solutes have been carried out in the authors [23–26] and some other laboratories [27–34]. Although some interesting results have been obtained, there is still lack of an efficient way to predict the composition dependence of physical properties such as viscosity and conductivity for the systems containing ILs over the entire range of concentration.

In this paper, viscosities and conductivities for a series of binary and quasi-binary mixtures composed of imidazolium ILs and molecular solutes have been determined systematically at 298.15 K. The viscosity data were correlated by the one-parameter exponential equation suggested by Seddon et al. Physical meaning of the parameter A was understood based on a theoretical equation derived from rate process theory. Moreover, another one-parameter exponential equation was developed to describe the dependence of the product of viscosity and conductivity on the concentration of the molecular solutes, and good results were obtained over the entire range of concentration. The variation tendency of viscosities and conductivities with the composition

Table 1
Experimental viscosity values for the ionic liquid + molecular solute systems at 298.15 K.

x_{IL}[a]	η (mpa s)	x_{IL}[a]	η (mpa s)	x_{IL}[a]	η (mpa s)
[C$_4$mim][BF$_4$] + H$_2$O		[C$_4$mim][BF$_4$] + AN		[C$_4$mim][BF$_4$] + DCM	
0.00	0.894	0.00	0.346	0.00	0.434
0.0510	1.845	0.0335	0.481	0.0713	0.883
0.0951	2.728	0.0905	0.778	0.0923	1.078
0.2103	5.083	0.1787	1.529	0.1827	2.254
0.2978	7.383	0.2717	2.854	0.2861	4.456
0.3463	8.868	0.3219	3.886	0.3131	5.214
0.4050	11.041	0.3679	4.871	0.3724	7.224
0.4509	12.908	0.4282	7.057	0.4226	9.371
0.5044	15.654	0.4782	9.278	0.4649	11.429
0.5399	17.871	0.5195	11.546	0.5107	14.157
0.5987	22.383	0.5567	14.013	0.5728	18.650
0.6877	31.171	0.6523	22.416	0.6658	27.054
0.7947	47.513	0.7487	35.711	0.7595	36.725
0.8914	70.099	0.8473	56.112	0.8511	55.483
1.00	110.308	1.00	110.308	1.0000	110.308
[C$_4$mim][BF$_4$] + EtOH		[C$_4$mim][PF$_6$] + butanone		[C$_4$mim][PF$_6$] + acetone	
0.00	1.087	0.00	0.388	0.00	0.316
0.0545	1.453	0.0513	0.606	0.0519	0.516
0.0898	1.811	0.0973	0.861	0.1044	0.810
0.1993	3.432	0.1996	1.861	0.1942	1.648
0.2882	5.276	0.2977	3.701	0.3011	3.690
0.3520	6.848	0.3483	5.150	0.3481	4.986
0.3963	8.200	0.4012	7.271	0.3993	6.964
0.4321	10.800	0.4494	9.819	0.4505	9.680
0.4622	16.700	0.4998	13.549	0.5007	13.406
0.5803	17.500	0.5515	18.183	0.5515	18.463
0.6137	19.756	0.5976	23.549	0.5965	23.998
0.6870	27.000	0.6984	43.329	0.7077	46.683
0.7705	38.560	0.7993	81.624	0.8020	84.774
0.8633	58.400	0.9005	144.875	0.8853	136.974
1.00	110.308	1.00	269.959	1.00	269.959
[C$_6$mim][BF$_4$] + butanone		[C$_6$mim][BF$_4$] + EA		[C$_8$mim][BF$_4$] + butanone	
0.00	0.388	0.00	0.437	0.00	0.388
0.0492	0.600	0.0498	0.738	0.0482	0.625
0.0988	0.914	0.1000	1.188	0.1010	1.026
0.2011	2.059	0.2027	2.674	0.1967	2.287
0.2989	4.063	0.3020	5.221	0.2977	5.037
0.3482	5.578	0.3475	6.846	0.3558	7.539
0.3972	7.507	0.3983	9.328	0.3994	10.257
0.4605	11.080	0.4488	12.307	0.4490	13.820
0.4981	13.673	0.5010	16.471	0.4968	18.400
0.5500	18.570	0.5487	21.492	0.5495	24.781
0.6057	24.459	0.6022	28.479	0.6009	34.241
0.7054	43.382	0.7075	48.111	0.7287	69.932
0.7955	69.399	0.8066	80.426	0.7910	100.303
0.8931	110.337	0.8908	119.875	0.8990	187.796
1.00	195.367	1.00	195.367	1.00	336.322
[C$_8$mim][BF$_4$] + MA		[C$_8$mim][BF$_4$] + EA		[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[b]	
0.00	0.376	0.00	0.437	0.00	1.437
0.0485	0.670	0.0470	0.739	0.0308	1.799
0.1011	1.189	0.0995	1.281	0.0965	2.716
0.1990	2.854	0.1983	3.095	0.1873	4.287
0.2973	6.093	0.2988	6.562	0.2487	5.538
0.3481	8.679	0.3760	10.930	0.2824	6.318
0.3944	11.69	0.4016	12.720	0.3311	7.654
0.4488	16.507	0.4493	17.011	0.4309	11.502
0.5036	23.382	0.5001	23.129	0.4834	13.716
0.5489	30.370	0.5539	31.639	0.5379	16.332
0.5937	37.958	0.6014	41.354	0.5740	18.956
0.7036	71.839	0.7047	69.749	0.6817	29.532
0.8010	117.296	0.7960	115.491	0.7743	42.012
0.8827	183.897	0.8908	181.150	0.8725	63.266
1.00	336.322	1.00	336.322	1.00	110.308
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[c]		[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[d]		[C$_4$mim][BF$_4$] + (AN + DCM)[e]	
0.00	1.932	0.00	2.383	0.00	0.424
0.0339	2.392	0.0480	3.552	0.0451	0.644
0.0977	3.274	0.0848	4.456	0.1015	1.073
0.1944	5.189	0.1421	6.012	0.1201	1.235
0.2792	7.812	0.2488	9.176	0.2169	2.594
0.2625	7.112	0.2867	10.117	0.2950	4.281
0.3033	8.265	0.3337	11.486	0.3632	6.351

Table 1 (*Continued*)

x_{IL}[a]	η (mpa s)	x_{IL}[a]	η (mpa s)	x_{IL}[a]	η (mpa s)
0.4379	13.352	0.3989	14.501	0.3880	7.266
0.4922	16.513	0.4263	15.598	0.4313	8.989
0.5538	20.614	0.4716	18.256	0.5446	14.896
0.5961	24.314	0.5276	21.226	0.6032	20.744
0.6508	28.986	0.6419	33.110	0.6715	27.994
0.7708	46.686	0.7534	48.352	0.8165	51.288
0.8700	67.556	0.8615	70.870	0.8953	68.285
1.00	110.038	1.00	110.308	1.0000	107.320
$[C_4mim][BF_4]+(AN+DCM)$[f]		$[C_4mim][BF_4]+(AN+DCM)$[g]			
0.00	0.405	0.00	0.373		
0.0691	0.759	0.0639	0.680		
0.1000	0.985	0.0855	0.816		
0.2152	2.347	0.1916	1.836		
0.2969	3.979	0.2803	3.301		
0.3452	5.301	0.3397	4.731		
0.3760	6.313	0.3806	5.979		
0.4427	9.082	0.4316	7.926		
0.4945	11.690	0.4891	10.694		
0.5378	14.438	0.5249	12.727		
0.6105	19.712	0.5733	16.078		
0.6981	28.225	0.6531	23.128		
0.7760	39.447	0.7788	38.843		
0.8816	65.160	0.8600	55.221		
1.00	110.308	1.00	110.308		

[a] Mole fraction of ionic liquids.

[b] The molar ratio of EtOH to H_2O is 3:1.

[c] The molar ratio of EtOH to H_2O is 1:1.

[d] The molar ratio of EtOH to H_2O is 1:3.

[e] The molar ratio of AN to DCM is 1:3.

[f] The molar ratio of AN to DCM is 1:1.

[g] The molar ratio of AN to DCM is 3:1.

of the mixtures was explained from the disruption of molecular solutes to the associates and aggregates of the neat ILs.

2. Experiment

1-*n*-Butyl-3-methylimidazolium tetrafluoroborate $[C_4mim][BF_4]$, 1-*n*-butyl-3-methylimidazolium hexafluorophospate $[C_4mim][PF_6]$, 1-*n*-hexyl-3-methylimidazolium tetrafluoroborate $[C_6mim][BF_4]$, and 1-*n*-octyl-3-methylimidazolium tetrafluoroborate $[C_8mim][BF_4]$ ionic liquids were prepared and purified according to the procedures described in literature [35,36]. Karl–Fisher analysis of the samples subjected to this treatment indicated that the water content of the samples is less than 0.20 mass%. Chloride content smaller than 0.018 mol kg^{-1} is determined in the ILs by a chloride-selective electrode, and sodium less than 0.012 mol kg^{-1} was detected with a Z-5000 polarized Zeeman atomic absorption spectrophotometer.

All the molecular compounds are analytical grade regents purchased from Shanghai Chem. Co. and Beijing Chem. Co. These compounds were further purified according to the methods reported in handbook [37]. All the purified compounds were stored over P_2O_5 in desiccators before use. Water content for the organic compounds analyzed by Karl–Fisher titration was less than 100 ppm.

Mixtures were prepared by mass on the molality concentration scale. Every precaution was taken to minimize contamination by water in the procedure of preparation and measurements [29]. Solution viscosities were measured with a suspended level Ubbelohde viscometer, which was placed in a water thermostat (Schott, Germany) and has a flow time of about 200 s for water at 298.15 K. The temperature of the water thermostat was controlled to within 0.01 K using a CT-1450 temperature controller and a CK-100 ultra cryostat. The viscometer was calibrated using the efflux time of water at 298.15 and 308.15 K. Flow time measurements are performed by a Schott AVS 310 photoelectric time unit with a resolution of 0.01 s. The estimated error of experimental viscosity is ±0.3% mPa s. Details of the experimental procedures are given else-

where [38]. Since the viscosity values are greatly different for the ILs and the molecular solutes, two Ubbelohde viscometers having different diameters were used in the experiments according to the varied viscosity values for the mixtures [23].

Conductivities measurements were performed at 298.15 K with a DDS-12A digital conductivity meter (Xiaoshan Experimental Instrument Factory, China) at a fixed frequency of 1100 Hz. The conductance cell was equipped with a water circulating jacket, and the temperature was controlled within ±0.05 K with a DC-2006 low temperature thermostat (Shanghai Hengping Instrument & Meter Factory, China). The cell constant was 10.62 cm^{-1} as determined in aqueous KCl solutions, and the error in the measurements was about ±0.14%.

3. Results and discussion

The viscosity (η) and conductivity (κ) data at 298.15 K for the binary systems of $[C_4mim][BF_4]$ + dichloromethane (DCM), $[C_4mim][BF_4]$ + water (H_2O), $[C_4mim][BF_4]$ + ethanol (EtOH), $[C_4mim][BF_4]$ + acetonitrile (AN), $[C_4mim][PF_6]$ + butanone, $[C_4mim][PF_6]$ + acetone, $[C_6mim][BF_4]$ + butanone, $[C_6mim][BF_4]$ + ethyl acetate (EA), $[C_8mim][BF_4]$ + butanone, $[C_8mim][BF_4]$ + methyl acetate (MA), and $[C_8mim][BF_4]$ + EA were compiled in Tables 1 and 2 together with those for the quasi-binary systems of $[C_4mim][BF_4]$ + (EtOH + H_2O) and $[C_4mim][BF_4]$ + (AN + DCM) at different molar ratios of the molecular solutes. The viscosities and conductivities for the pure ILs measured in this work agree well with those reported in literature [39,40].

3.1. The effect of molecular solutes on the viscosity and conductivity of the systems

As examples, the variation of viscosities and conductivities against the mole fraction of molecular solutes are illustrated in Figs. 1 and 2 for the binary systems, and in Figs. 3 and 4 for the quasi-binary systems. From Figs. 1 and 3, it is easy to find that the

Table 2
Experimental conductivity values for the mixtures of ionic liquids with molecular solutes at 298.15 K.

x_{IL}[a]	$10^3\kappa$ (S cm^{-1})	x_{IL}[a]	$10^3\kappa$ (S cm^{-1})	x_{IL}[a]	$10^3\kappa$ (S cm^{-1})
[C$_4$mim][BF$_4$] + H$_2$O		[C$_4$mim][BF$_4$] + AN		[C$_4$mim][BF$_4$] + DCM	
0.0473	27.91	0.0335	18.90	0.0713	5.42
0.0589	32.10	0.0905	21.80	0.0923	7.01
0.0753	35.32	0.1787	23.29	0.1827	10.51
0.0993	37.81	0.2717	20.25	0.2861	11.22
0.1705	37.55	0.3219	16.60	0.3131	11.24
0.2496	32.20	0.3679	16.11	0.3724	10.67
0.3108	28.10	0.4282	13.06	0.4226	10.11
0.3730	24.08	0.4782	10.20	0.4649	9.43
0.4433	21.41	0.5195	10.22	0.5107	8.76
0.4735	19.90	0.5567	9.37	0.5728	7.71
0.5917	15.08	0.6523	7.07	0.6658	6.64
0.7361	10.30	0.7487	4.88	0.7595	5.78
0.8525	7.07	0.8473	3.27	0.8511	4.35
1.00	2.48	1.0000	2.48	1.00	2.48
[C$_4$mim][BF$_4$] + EtOH		[C$_4$mim][PF$_6$] + butanone		[C$_4$mim][PF$_6$] + acetone	
0.0545	6.47	0.0516	14.13	0.0519	25.69
0.0898	9.09	0.1043	18.52	0.1067	31.21
0.1993	14.84	0.2084	19.28	0.2130	28.77
0.2882	15.13	0.2977	17.28	0.3011	21.41
0.3520	15.95	0.3483	15.43	0.3481	19.85
0.3963	13.77	0.4012	13.52	0.3993	16.97
0.4321	13.13	0.4494	11.90	0.4505	14.47
0.4622	12.60	0.4998	10.26	0.5007	12.30
0.5803	10.61	0.5515	8.81	0.5515	9.96
0.6137	9.58	0.5976	7.69	0.5965	8.38
0.6870	9.46	0.6984	5.39	0.7077	5.46
0.7705	6.06	0.7993	3.59	0.8020	3.75
0.8633	4.62	0.9005	2.42	0.8853	2.61
1.00	2.48	1.00	1.55	1.00	1.55
[C$_6$mim][BF$_4$] + butanone		[C$_6$mim][BF$_4$] + EA		[C$_8$mim][BF$_4$] + butanone	
0.0492	7.32	0.0498	0.78	0.0482	4.95
0.0988	9.07	0.1000	2.10	0.1010	6.24
0.2011	10.09	0.2027	4.11	0.1967	6.33
0.2989	9.13	0.3020	4.76	0.2977	4.98
0.3482	8.46	0.3475	4.82	0.3558	4.34
0.3972	7.82	0.3983	4.59	0.3994	3.90
0.4605	6.43	0.4488	4.43	0.4490	3.47
0.4981	5.87	0.5010	4.00	0.4968	3.00
0.5500	5.23	0.5487	3.59	0.5495	2.52
0.6057	4.43	0.6022	3.24	0.6009	2.13
0.7054	3.14	0.7075	2.54	0.7287	1.56
0.7955	2.38	0.8066	1.87	0.7910	1.11
0.8931	1.73	0.8908	1.48	0.8990	0.74
1.00	1.11	1.00	1.11	1.00	0.49
[C$_8$mim][BF$_4$] + EA		[C$_8$mim][BF$_4$] + MA		[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[b]	
0.0470	0.68	0.0485	2.27	0.0308	7.74
0.0995	1.72	0.1011	4.41	0.0965	15.17
0.1983	2.87	0.199	5.61	0.1873	18.22
0.2988	3.06	0.2973	5.08	0.2487	18.09
0.3760	2.87	0.3481	4.56	0.2824	16.67
0.4016	2.73	0.3944	4.09	0.3311	15.37
0.4493	2.52	0.4488	3.65	0.4309	13.86
0.5001	2.24	0.5036	2.95	0.4834	12.97
0.5539	2.00	0.5489	2.55	0.5379	11.22
0.6014	1.75	0.5937	2.28	0.5740	10.18
0.7047	1.36	0.7036	1.42	0.6817	7.71
0.7960	0.99	0.8010	1.10	0.7743	5.91
0.8908	0.80	0.8827	0.86	0.8725	4.29
1.00	0.49	1.00	0.49	1.0000	2.48
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[c]		[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[d]		[C$_4$mim][BF$_4$] + (AN + DCM)[e]	
0.0339	12.28	0.0482	19.60	0.0451	10.27
0.0977	21.66	0.0848	25.25	0.1015	15.90
0.1944	23.62	0.1421	27.21	0.1201	16.84
0.2792	21.24	0.2488	24.82	0.2169	17.68
0.2625	21.99	0.2867	23.08	0.2950	15.78
0.3033	20.33	0.3337	20.79	0.3632	14.70
0.4379	14.59	0.3989	18.51	0.3880	13.19
0.4922	12.35	0.4263	16.52	0.4313	12.90
0.5538	10.56	0.4716	14.49	0.5446	10.98
0.5961	9.55	0.5276	12.34	0.6032	9.24
0.7708	6.10	0.6419	8.62	0.6715	7.85

Table 2 (*Continued*)

x_{IL}[a]	$10^3 \kappa$ (S cm^{-1})	x_{IL}[a]	$10^3 \kappa$ (S cm^{-1})	x_{IL}[a]	$10^3 \kappa$ (S cm^{-1})
0.6508	7.62	0.7534	6.53	0.8165	5.31
0.8700	4.90	0.8615	4.90	0.8953	4.46
1.0000	2.48	1.0000	2.48	1.0000	2.48
[C$_4$mim][BF$_4$] + (AN + DCM)[f]		[C$_4$mim][BF$_4$] + (AN + DCM)[g]			
0.0691	12.75	0.0639	16.76		
0.1000	18.31	0.0855	17.96		
0.2152	19.79	0.1916	20.46		
0.2969	20.38	0.2803	19.17		
0.3452	18.00	0.3397	17.65		
0.3760	16.97	0.3806	14.27		
0.4427	14.51	0.4316	13.80		
0.4945	12.38	0.4891	11.02		
0.5378	11.50	0.5249	10.96		
0.6105	9.69	0.5733	9.96		
0.6981	7.39	0.6531	7.87		
0.7760	6.32	0.7788	6.54		
0.8816	4.32	0.8600	5.75		
1.0000	2.48	1.0000	2.48		

[a] Mole fraction of ionic liquids.
[b] The ratio of EtOH to H$_2$O is 3:1.
[c] The ratio of EtOH to H$_2$O is 1:1.
[d] The ratio of EtOH to H$_2$O is 1:3.
[e] The ratio of AN to DCM is 1:3.
[f] The ratio of AN to DCM is 1:1.
[g] The ratio of AN to DCM is 3:1.

viscosities for both binary and quasi-binary systems follow similar tendencies with mole fraction of the molecular solutes. They decrease sharply with the increase of the mole fraction of molecular solutes in IL-rich region and then tend to decrease gently in molecular solute-rich region. From Figs. 2 and 4, it can be seen that the conductivities for the studied binary and quasi-binary systems also show similar tendencies with mole fraction of the molecular solutes. They increase with mole fraction of the molecular solutes in a large composition range and then decrease, showing maximums at $x_s = 0.8$. It is interesting to note that the maximum values increase with the increase of the dielectric constant of the molecular solutes for a given IL.

According to the equation suggested by Every et al., solution conductivity can be expressed by [41]

$$\kappa = \sum n_i q_i u_i \qquad (1)$$

where n_i is the number of charge carriers of type i, q_i is the charge and u_i is the mobility of each species which is related to the viscosities of the mixtures. It can be seen that the increase in the conductivity of a given system must due to the increase in ion mobility and/or the number of charge carriers. NMR and molecular dynamics studies [42–45] indicate that there is significant ionic association or aggregation in neat ILs, which lead to the high viscosity, limited conductivity and other peculiar properties in these novel materials. Introduction of molecular solutes into ILs will decrease coulomb interactions in ILs and liberate free ions from their associates and aggregates, leading to the decreased viscosities and increased conductivities as a consequence. It is known that solution fluidity ($1/\eta$) is one of the main factors to affect the mobility of charge carries, so the decrease in viscosity will also lead to the increase of conductivity. When the mole fraction of molecular solutes reached at 0.8, further addition of the molecular solutes will have dilution effect on the free ions in unit volume. According to the ionic association theory [46,47], the association constant of
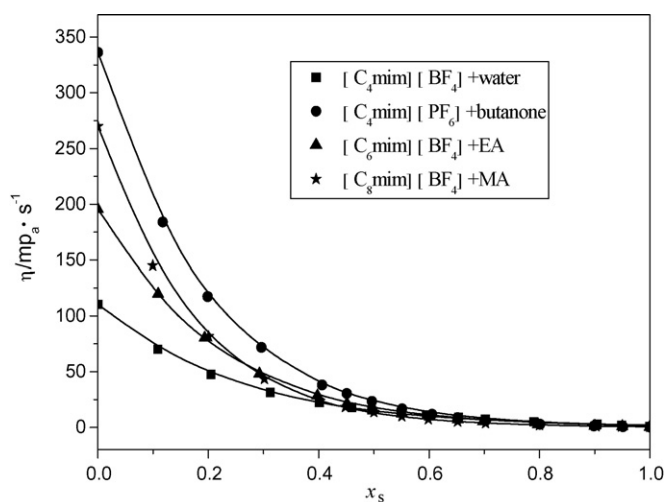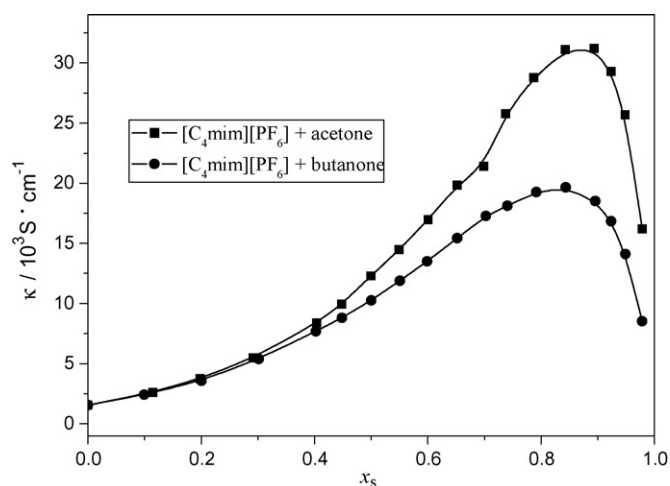

Fig. 1. Viscosities for the ionic liquids + molecular solutes binaries vs. mole fraction of the solutes at 298.15 K; the solid line represent the theoretical fit of the data according to Eq. (2).

Fig. 2. Conductivities for the [C$_4$mim][PF$_6$] + molecular solutes mixtures vs. mole fraction of the solutes at 298.15 K.
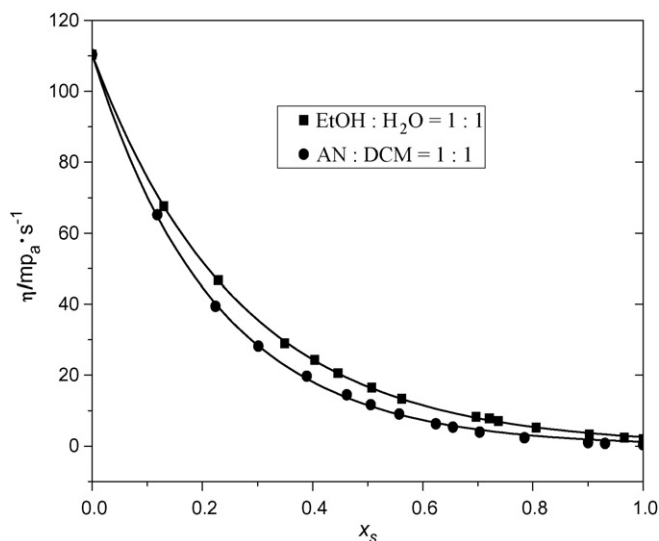
Fig. 3. Viscosities for the quasi-binary systems of [C$_4$mim][BF$_4$] + molecular solutes as a function of mole fraction of the solutes at 298.15 K; the solid lines represent the theoretical fit of the data according to Eq. (2).

an electrolyte decreases with increasing dielectric constant of the solvents. This is the possible reason why the observed conductivity maximums increase with the increase of dielectric constants of the molecular solutes.

3.2. The correlation between viscosities and mole fraction of the molecular solutes

For a long time, development of the methods for predicting the transport properties of electrolyte or non-electrolyte solutions is intriguing because of their great importance in the industrial applications [48]. Seddon et al. [21] proposed a simple empirical equation

$$\eta = \eta_{IL} \exp(Ax_s) \tag{2}$$

to fit the concentration dependence of viscosity for the mixtures of IL with molecular solutes with correlation coefficients >0.98. Here, η and η_{IL} refer to the viscosities of the mixtures and the pure ILs, respectively. x_s is the mole fraction of the molecular solutes in the mixtures, and A is a characteristic constant. Based on the observation that A is a constant determined only by the properties of the
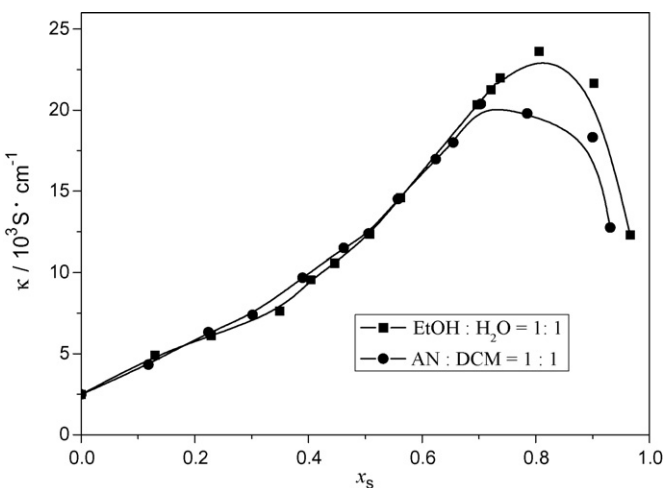

Fig. 4. Conductivities for the quasi-binary systems of [C$_4$mim][BF$_4$] + molecular solutes as a function of mole fraction of the solutes at 298.15 K.

Table 3
The A values and the standard deviation of the fit for the viscosities of IL + molecular solute systems at 298.15 K.

System	A	S.D.
[C$_4$mim][BF$_4$] + DCM	−4.382 ± 0.054	1.147
[C$_4$mim][BF$_4$] + EtOH	−4.383 ± 0.088	1.923
[C$_4$mim][BF$_4$] + H$_2$O	−4.004 ± 0.029	0.736
[C$_4$mim][BF$_4$] + AN	−4.619 ± 0.062	1.197
[C$_4$mim][PF$_6$] + acetone	−5.946 ± 0.021	0.674
[C$_4$mim][PF$_6$] + butanone	−6.072 ± 0.030	0.900
[C$_6$mim][BF$_4$] + butanone	−5.220 ± 0.037	1.045
[C$_6$mim][BF$_4$] + EA	−4.779 ± 0.056	1.855
[C$_8$mim][BF$_4$] + butanone	−5.784 ± 0.013	0.554
[C$_8$mim][BF$_4$] + MA	−5.298 ± 0.036	1.716
[C$_8$mim][BF$_4$] + EA	−5.382 ± 0.044	2.059
[C$_4$mim][BF$_4$] + (AN + DCM)[a]	−4.680 ± 0.046	0.875
[C$_4$mim][BF$_4$] + (AN + DCM)[b]	−4.514 ± 0.031	0.635
[C$_4$mim][BF$_4$] + (AN + DCM)[c]	−4.345 ± 0.053	1.087
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[d]	−4.135 ± 0.031	0.768
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[e]	−3.766 ± 0.013	0.360
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[f]	−3.379 ± 0.024	0.759

[a] The molar ratio of AN to DCM is 1:3.
[b] The molar ratio of AN to DCM is 1:1.
[c] The molar ratio of AN to DCM is 1:3.
[d] The molar ratio of EtOH to H$_2$O is 3:1.
[e] The molar ratio of EtOH to H$_2$O is 1:1.
[f] The molar ratio of EtOH to H$_2$O is 1:3.

ILs, they suggested that this equation could be used to predict the viscosities of a reaction mixture as a function of concentration of the dissolved reactants and/or products.

In the present work, the viscosity data for binary and quasi-binary systems were fitted according to Eq. (2) with correlation coefficients >0.99. The A values for these systems obtained from a least-square analysis are listed in Table 3 together with the standard deviation of the fit. It can be seen that the A values are not a constant for the systems consisting of a given IL and different molecular solutes. They do vary with nature of the ILs and the molecular solutes. A similar observation has been reported by Zhang et al. [49]. However, careful examination of the data in Table 3 reveals that for a given IL (say [C$_4$mim][PF$_6$]), the A values are, indeed, approximately equal to each other when the viscosity values or the structure of the molecular solutes (say acetone and butanone) are similar. This result explained the observation from Seddon et al. [21]. Therefore, by using Eq. (2), it is possible to predict the viscosities of a reaction system in which the difference in structure or viscosity among the reactants and products was not significant. Transesterification reactions are excellent examples. For quasi-binary systems, it can be seen that the A values are also affected by the molar ratio of the two kinds of molecular solutes.

3.3. Physical meaning of the parameter A in viscosity equation

Based on the equation of Goldsack and Franchetto [50] derived from rate process theory, Chirife and Buera [51] deduced a successful equation which was adequate for describing the viscosity of concentrated sugar and oligosaccharide aqueous solutions as

$$\eta = a \exp(Ex_s). \tag{3}$$

In this equation, x_s stands for the mole fraction of sugar or oligosaccharide in the mixtures. Chirife et al. observed that the parameter a is close to unity at 293 K for all of the studied systems. This parameter should have the physical meaning as the viscosity of water since the viscosity of water is 1.005 cp at 293 K. They also suggested that the parameter E in Eq. (3) is defined as

$$E = \frac{\delta G_s^* - \delta G_w^*}{RT} \tag{4}$$

where δG_s^* is the Gibbs energy of activation for viscous flow per mole of sugar or oligosaccharide, and δG_w^* is the Gibbs energy of activation for viscous flow per mole of water, R is gas constant, and T is Kelvin temperature.

Therefore, Eq. (3) has the same form as Eq. (2), and the parameter A in Eq. (2) should have the same physical meanings as parameter E in Eq. (3). In our studies, the A values are always negative, indicating that the viscosities for the mixtures decrease exponentially with increasing mole fraction of the molecular solutes, and the higher the absolute A values are, the stronger the concentration dependence of the viscosities. It can be suggested from Eq. (4) that the constant A in Eq. (2) should contain the temperature dependent part, which allows one to extrapolate these correlations to different temperature regions and to predict the viscosities of mixtures at different temperatures. It is can also be concluded that the increase of temperature will lead to the decrease of the absolute A values. This has been confirmed by the examination of the [C$_4$mim][BF$_4$] + DMF systems in the temperature range of 298.15–318.15 K [52]. The parameter A also contains the remaining energy part of the E term, which on theoretical grounds is somewhat related to the Gibbs energy of activation for viscous flow per mole of ILs and molecular solutes as suggested by Eq. (4). However, the reported values of the activation energy of viscous flow for the ILs such as [C$_4$mim][BF$_4$] (25.83 kJ mol^{-1}) and [C$_4$mim][PF$_6$] (23.94 kJ mol^{-1}) [27] and the molecular solutes such as acetone (2.40 kJ mol^{-1}) [53] gave it a large difference from the fitting A values, suggesting that ionic nature of the ILs makes them greatly different from sugar and oligosaccharides. Therefore, the physical meanings of A should be modified according to Eq. (5)

$$A = \frac{E + G_{IL}}{RT} = \frac{\delta G_S^* - \delta G_{IL}^* + G_{IL}}{RT}. \tag{5}$$

Due to the existence of ionic association and aggregation in ILs, the δG_{IL}^* values for the studied ILs should be significantly larger than the δG_S^* values for the traditional molecular solutes, which makes the E values in Eq. (5) negative. The modified item G_{IL} in this equation reflects the interaction between the IL and the molecular solutes. In another word, G_{IL} item was determined by the degree in the effect of the molecular solutes on the ionic association and aggregation of the ILs. Therefore, G_{IL} is an indicator for the strength of the interaction between IL and molecular solutes or for the ability of molecular solutes to disrupt the ionic association or aggregation. For the mixtures of a given IL with different molecular solutes whose viscosities or structure are similar, their approximate equal A values are perhaps due to the similar values of δG_S^* and G_{IL}.

According to the above discussion, it is clear that the A values are affected not only by the activation energies for viscous flow of the ILs and the molecular solutes, but also by the interaction between the ILs and the molecular solutes. Those factors affecting the strength of the interactions such as the structure, dielectric constant and molecular weight of the molecular solutes will have effect on the A values. The stronger interactions will make it more difficult for a particle to overcome the attraction with its neighbors, leading to the increase of G_{IL} or the decrease of the absolute A values. This suggestion has been supported by the system of [C$_4$mim][BF$_4$] + water, which has the lowest absolute A value (see Table 3) due to the high dielectric constant of water and the strong ability of water to form hydrogen bonds with anion of the ILs [54].

3.4. The correlation of the product of viscosity and conductivity with mass fraction of the molecular solutes

As mentioned above, conductivities for the mixtures of ILs with molecular solutes were affected by the number and mobility of free charge carriers, and those factors affecting the dissociation of ILs and the viscosity of the mixtures will affect the conductivity simultaneously. Therefore, compared with viscosities of the mixtures, conductivity is much more sensitive to the concentration of the molecular solutes. Li et al. [55] have tried to correlate the molar conductivity data for some IL + organic compound systems, but they can only give satisfactory result in the IL mole fraction range of 0–0.8. Here, we found that data of the product of viscosity and conductivity for the binary and quasi-binary systems studied in this work can be fit using the exponential equation

$$\kappa\eta = B\exp(C\omega_s) \tag{6}$$

over the entire concentration range, where κ refers to the conductivity of the mixtures, ω_s represents the mass fraction of the molecular solutes in the mixtures, B and C are empirical parameters and their values derived from a least-square analysis are collected in Table 4 together with the standard deviation of the fit. For the sake of comparison, the experimental values for the product of the viscosity and conductivity for the pure ILs ($\eta_{IL}\lambda_{IL}$) were also given in this table. It can be seen that the B values are very close to the measured values of $\eta_{IL}\lambda_{IL}$ within the experimental errors. Therefore, Eq.

Table 4
Values of B and C derived from a least-square analysis using Eq. (7), the standard deviation of the fit for the product of conductivity and viscosities, and the experimental values of $\eta_{IL}\kappa_{IL}$ for the pure ILs at 298.15 K.

Systems	B	C	$\eta_{IL}\kappa_{IL}$	10^3 S.D.
[C$_4$mim][BF$_4$] + DCM	283.9 ± 8.8	−3.337 ± 0.145	273.6	9.5
[C$_4$mim][BF$_4$] + AN	264.8 ± 8.2	−5.350 ± 0.254	273.6	9.0
[C$_4$mim][BF$_4$] + EtOH	288.5 ± 5.7	−3.694 ± 0.152	273.6	8.5
[C$_4$mim][BF$_4$] + (AN + DCM)[a]	282.9 ± 13.3	−3.042 ± 0.209	273.6	14.4
[C$_4$mim][BF$_4$] + (AN + DCM)[b]	287.2 ± 8.4	−3.151 ± 0.152	273.6	9.9
[C$_4$mim][BF$_4$] + (AN + DCM)[c]	276.0 ± 4.1	−4.021 ± 0.094	273.6	4.7
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[d]	274.4 ± 6.7	−2.180 ± 0.134	273.6	10.9
[C$_4$mim][BF$_4$] + (EtOH + H$_2$O)[e]	281.1 ± 4.3	−3.108 ± 0.108	273.6	7.2
[C$_4$mim][PF$_6$] + acetone	409.1 ± 5.5	−5.397 ± 0.138	418.4	8.5
[C$_4$mim][PF$_6$] + butanone	407.7 ± 4.7	−5.311 ± 0.110	418.4	7.5
[C$_6$mim][BF$_4$] + butanone	219.2 ± 1.2	−4.433 ± 0.041	216.9	1.6
[C$_6$mim][BF$_4$] + EA	217.0 ± 1.6	−4.705 ± 0.059	216.9	2.1
[C$_8$mim][BF$_4$] + butanone	162.2 ± 2.6	−5.220 ± 0.151	164.8	3.6
[C$_8$mim][BF$_4$] + MA	170.5 ± 3.1	−4.457 ± 0.151	164.8	4.5
[C$_8$mim][BF$_4$] + EA	167.8 ± 1.5	−4.939 ± 0.079	164.8	2.1

[a] The molar ratio of AN to DCM is 1:3.
[b] The molar ratio of AN to DCM is 1:1.
[c] The molar ratio of AN to DCM is 3:1.
[d] The molar ratio of EtOH to H$_2$O is 1:1.
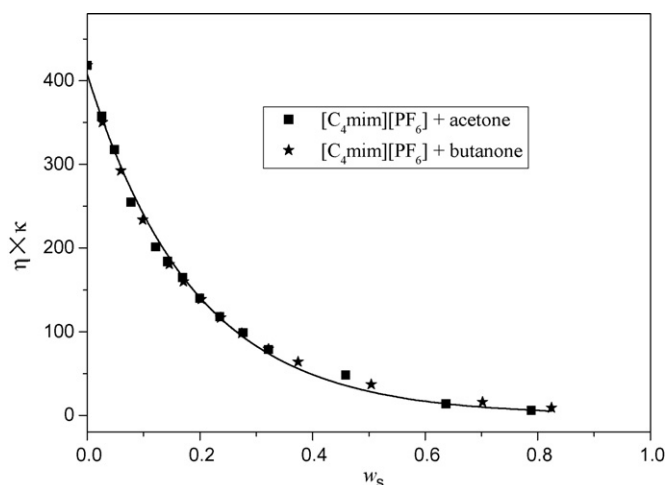[e] The molar ratio of EtOH to H$_2$O is 3:1.

Fig. 5. The product of viscosity and conductivity for the binary systems of $[C_4mim][PF_6]$ + molecular solutes at 298.15 K as a function of the solutes; the solid lines represent the theoretical fit of the data according to Eq. (7).

(6) may be expressed in the form:

$$\kappa\eta = \kappa_{IL}\eta_{IL}\exp(C\omega_s). \tag{7}$$

For all of the studied binary and quasi-binary systems, the correlation coefficients based on Eq. (7) are greater than 0.99. The selected fitting results are illustrated in Figs. 5 and 6. When Eq. (7) was compared with Eq. (2), we find that the two equations have the same form. Similarly, the C values are always negative, suggesting that the values of $\kappa\eta$ decrease with the increase of the molecular solutes concentration. From the point of view of physical chemistry, C term should contain the activation energy of both ionic migration and viscous flow of the components as well as the energy from the interaction between the IL and the molecular solute. Therefore, the related properties such as molecular structure, dielectric constant and molar mass of the solutes will also have effect on the C values.

However, it is noted that the calculated results of $\kappa\eta$ by Eq. (7) have large positive deviations from the experimental data of $[C_4mim][BF_4]$ + H_2O and $[C_4mim][BF_4]$ + ($EtOH$ + H_2O) with the molar ratio of EtOH to H_2O at 1:3. The possible reason is that ions have different transference mechanism in water [56,57].
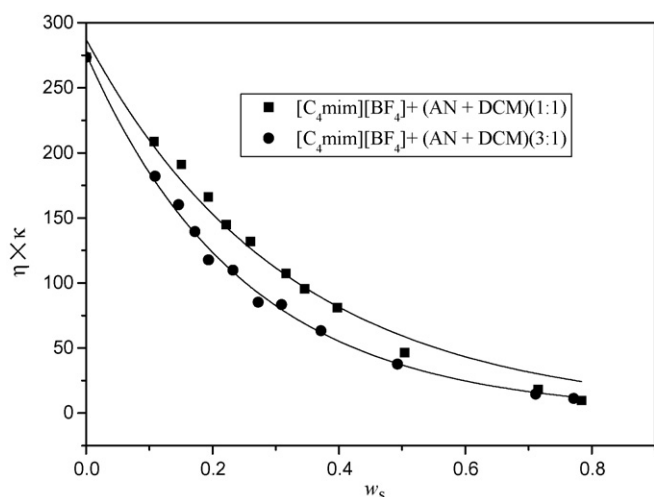

Fig. 6. The product of viscosity and conductivity for the quasi-binary systems of $[C_4mim][BF_4]$ + molecular solutes at 298.15 K as a function of mass fraction of the solutes; the solid lines represent the theoretical fit of the data according to Eq. (7).

4. Conclusions

In this paper, new viscosity and conductivity data have been reported for the binary and quasi-binary systems of ILs + molecular solutes. Based on the results of NMR and molecular dynamics studies reported in literature, the effect of molecular solutes on the viscosities and conductivities is suggested to come from their disruption to the associates and aggregates of the neat ILs. The dependence of viscosities of the mixtures on the mole fraction of molecular solutes has been described by an exponential equation with one empirical parameter A proposed by Sedden et al. with satisfactory results. The physical meaning of parameter A was analyzed with a theoretical equation deduced from rate process theory. It was found that A values were affected not only by the nature of the ILs and the molecular solutes, but also by their interactions. Those factors affecting ionic association and aggregation of the ILs as well as the strength of the interaction between IL and molecular solutes such as anionic type and alkyl chain length of the ILs, molecular structure, dielectric constant and molar mass of the solutes will have effect on the A values. For a given IL, this viscosity equation can be used to predict the viscosities of a reaction system in which the reactants and products have similar molecular structure or similar viscosity values. Moreover, another exponential equation with one empirical parameter C was developed to correlate the data of the product of viscosity and conductivity as a function of mass fraction of the molecular solutes, and good results were obtained in the entire concentration range. It is expected that the new viscosity and conductivity data and the correlation equations descried in the present work will be useful for the application of ILs in chemical industry.

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