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A Study of Density for Pullulan/Ionic Liquid Solutions

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Empirical relationships were obtained at temperatures 10–80 °C between density ρ and mass concentration C (wt%) of pullulan, which was used as a standard polymer in aqueous solutions containing two representative ionic liquids, 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidaolium acetate. Water content effect on ρ was also examined. Pullulan was successfully dissolved into these ionic liquids without degradation, confirmed by the recovered samples. This indicates that pullulan is a suitable standard for ionic liquid soluble polymers. The empirical relationships provide easy conversion of C to concentration c (g/cm^3), which is essential for systematic studies of properties of pullulan in ionic liquids.

1. Introduction

Ionic liquids (IL) are low melting point organic salts that exist in the liquid state at around room temperature.[1)] Because of their unique characteristics such as extremely low vapor pressure, thermal stability, and high ionic conductivity, ILs have been widely used in many fields involving organic and inorganic synthesis,[2),3)] catalysis,[2)] physical chemistry,[4),5)] and advanced materials.[6)–8)] Imidazolium-based ILs has been reported to dissolve cellulose and other polysaccharides, which are insoluble in conventional solvents. To date, reports have focused on 1-butyl-3-methylimidazolium chloride (BmimCl),[9)] 1-allyl-3-methylimidazolium chloride (AmimCl),[10)] and 1-ethyl-3-methylimidaolium acetate (EmimAc) as new environmentally friendly solvents for cellulose.[11)] Ionic liquid solutions of cellulose are expected to lead new materials.[12,13)] In addition, rheological studies of polymers using ILs as solvents have been reported.[14–17)]

Basic understanding of synthetic polymer properties in dilute solution, in close relationship with molecular characterization, has contributed to the progress of polymer science and industry. Standard samples with narrow molecular weight distributions (MWD) have played an important role in this progress. Physical property investigations of so-called insoluble natural polymers in dilute IL solutions are expected to contribute to advances in the science and technology of these polymers.

The linear polysaccharide pullulan consists of maltotriose units called α-1,4 and α-1,6-glucan. Because this polysaccharide is a water soluble polymer with well-understood properties in aqueous solutions,[18–20)] pullulan samples fractionated by molecular weight have been used as standard polymers for water soluble polymers. In addition, as reported in this study, its solubility into ILs makes it a potential candidate as a standard sample for IL soluble polymers.

Accurate evaluations of physical properties in solution rely on empirical relationships between the density and concentrations in wt% and g/cm^3. Note that, because ILs are glass forming liquids, their density may depend more strongly on temperature compared with conventional solvents. Moreover, polysaccharides exhibit higher densities than synthetic polymers. Therefore, the density of pullulan should not be assumed to be 1 g/cm^3, as seen in many recent studies on polymer solutions. In this study, pullulan was dissolved into BmimCl and EmimAc without sample degradation. The densities of sample solutions were determined for concentrations of up to *ca.* 16 wt%. The influence of water content on the density was also examined to account for the effects of residual water and moisture adsorption in the ILs.

2. Experimental section

2.1 Materials

EmimAc (purity: 97%, water content: ≤0.5%) was purchased from Sigma-Aldrich and used as received. BmimCl was synthesized and purified according to previously reported methods with slight modifications.[1),21)] Toluene was used as solvent in this synthesis. Pullulan (about 100 kg/mol) was used as received from Hayashibara Co., Ltd. Before solution preparation, all pullulan samples and ILs were dried *in vacuo* at 60 °C for 12 h.

2.2 Sample preparation

According to a preliminary study,[22)] homogeneous pullulan/BmimCl solutions cannot be prepared below 80 °C. On the other hand, intrinsic viscosity measurements of aqueous solution of pullulan recovered

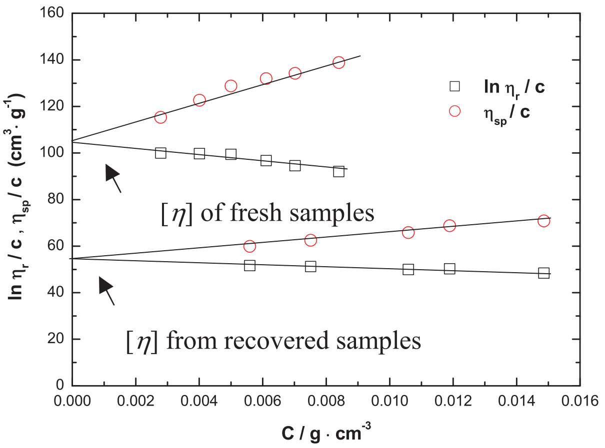

Fig. 1 Intrinsic viscosities [η] of pullulan in aqueous solution from recovered samples prepared at 80°C and from fresh samples.

from the BmimCl solution indicated that the sample underwent degradation and oxidation when the temperature exceeded 80 °C (Figure 1). Therefore, pullulan solution in BmimCl was prepared by the following method. An aqueous solution of pullulan was first prepared and mixed with a prescribed amount of BmimCl. Next, the sample solution was dried at 60 °C for 72 h *in vacuo* to remove the water. Water contents of sample solutions were measured by Karl–Fischer titration to ensure that they were below 2 wt%. Pullulan solutions in EmimAc were prepared by direct dissolution at 60 °C *in vacuo* for 72 h. The solutions were clear and their water contents did not exceed 1 wt%. The intrinsic viscosities [η] of pullulan amounted to 106.9 and 105.1 cm^3/g in aqueous solutions of samples recovered from BmimCl and EmimAc, respectively. These values are in reasonable agreement with data obtained for the fresh sample (105.3 cm^3/g), confirming no sample degradation during dissolution.

2.3 Density measurements

Densities ρ (g/cm^3) of pullulan/BmimCl and pullulan/EmimAc solutions were measured for different concentrations under atmospheric pressure in a DMA 4500 Anton Parr density meter between 10.00 and 80.00 °C. Temperatures were controlled within ± 0.05 °C for each measurement. The uncertainty of the measurements was estimated to lower than $\pm 1 \times 10^{-4}$ g/cm^{-3}. All the measured data are tabulated in Appendix I.

3. Results and discussion

3.1 Density of pullulan in IL solutions

Figures 2a and 2b show the influence of concentration C (wt%) on the densities of pullulan/BmimCl and pullulan/EmimAc solutions, respectively. All solutions exhibited a linear increase in their densities with increasing concentration. Figures 3a and 3b show the effect of temperature T on the densities of pullulan/BmimCl and pullulan/EmimAc solutions, respectively. These plots indicated that densities increased linearly with decreasing temperature for all solutions. An empirical relationship between density and concentration was derived from these results as

$$\rho = \alpha C + \rho_0 \quad (g/cm^3) \quad (1)$$

where ρ_0 is the density of pure ILs and α is the prefactor. For all pullulan/IL solutions, α values are shown in Table 1. The uncertainties of α were estimated to be $\pm 2 \times 10^{-5}$ and $\pm 8 \times 10^{-5}$ for pullulan/BmimCl and pullulan/EMimAc solutions, respectively. Therefore, equation (1) provides the density of any pullulan/IL solution in this concentration range. Furthermore, the concentration c in g/cm^3 was obtained using

$$c = \rho C / 100 \ (g/cm^3) \quad (2)$$

Temperature effects on density were complex near the glass transition temperature. However, between 10.00 and 80.00 °C, the following linear relationship was obtained between density and temperature:

$$\rho = bT + K \quad (g/cm^3) \ (3)$$

where K is the density at 0 °C and b is the prefactor. Values of b for several concentrations are listed in Table 2. The uncertainties of b were estimated to be $\pm 5 \times 10^{-6}$ for both pullulan/BmimCl and pullulan/EMimAc solutions, respectively.

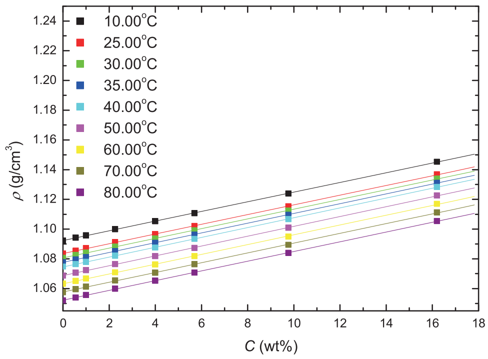

Fig. 2a Effect of concentration on the densities of pullulan/BmimCl solutions at different temperatures.

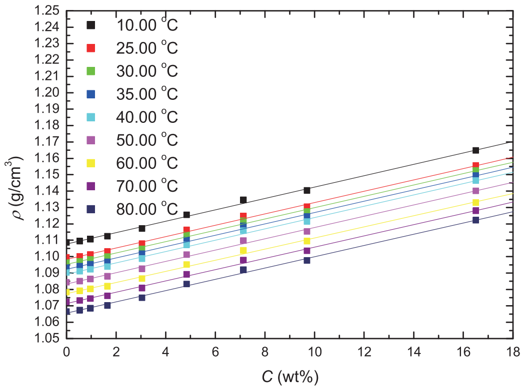

Fig. 2b Effect of concentration on the density of pullulan/EmimAc solution at different temperatures.

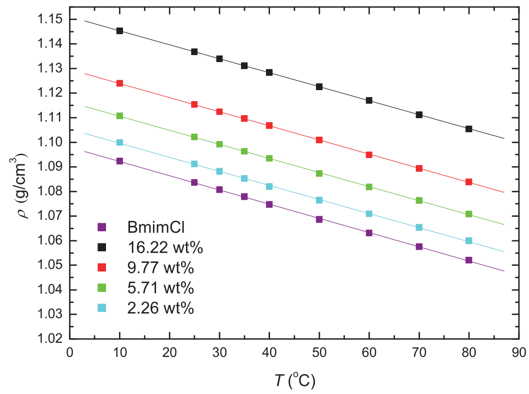

Fig. 3a Effect of temperature on the density of pullulan/BmimCl solutions at different concentrations.

Table 1. Prefactor values α obtained using eq. (1) for pullulan/IL solutions from 10 to 80 °C.

	α	
T	Pullulan/BmimCl	Pullulan/EmimAc
10.00 °C	3.25×10^{-3}	3.47×10^{-3}
25.00 °C	3.27×10^{-3}	3.46×10^{-3}
30.00 °C	3.27×10^{-3}	3.46×10^{-3}
35.00 °C	3.28×10^{-3}	3.46×10^{-3}
40.00 °C	3.31×10^{-3}	3.46×10^{-3}
50.00 °C	3.31×10^{-3}	3.45×10^{-3}
60.00 °C	3.30×10^{-3}	3.39×10^{-3}
70.00 °C	3.29×10^{-3}	3.44×10^{-3}
80.00 °C	3.27×10^{-3}	3.44×10^{-3}

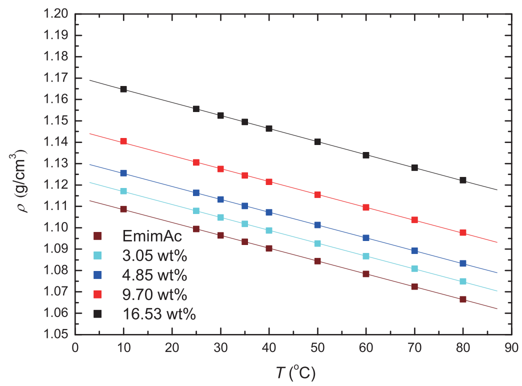

Fig. 3b Effect of temperature on the density of pullulan/EmimAc solutions at different concentrations.

Table 2. Prefactor values b obtained using eq. (3) for pullulan/IL solutions at different concentrations.

	b
C	Pullulan/BmimCl
0.00 wt%	-5.78×10^{-4}
2.26 wt%	-5.72×10^{-4}
5.71 wt%	-5.72×10^{-4}
9.77 wt%	-5.74×10^{-4}
16.22 wt%	-5.69×10^{-4}
C	Pullulan/EmimAc
0.00 wt%	-6.02×10^{-4}
3.05 wt%	-6.03×10^{-4}
4.85 wt%	-6.02×10^{-4}
9.70 wt%	-6.05×10^{-4}
16.53 wt%	-6.11×10^{-4}

3.2 Influence of water content of the density of pullulan/IL solutions

The influence of water content on ρ was also discussed because ILs easily absorb moisture. The effect of water content C_w (wt%) on the densities of pullulan/BmimCl and pullulan/EmimAc solutions is shown in Figures 4 and 5, respectively. For pullulan/BmimCl solutions, the water content displayed little influence on the density below 6.6 wt%. Because all pullulan/BmimCl solutions contained less than 2 wt% water in this study, it can be assumed that water content does not affect their densities.

For pullulan/EmimAc solutions, the densities increased with increasing water content. In this study, however, C_w values remained below 1 wt% for pullulan/EmimAc solutions. Therefore, the influence of water content was also negligible.

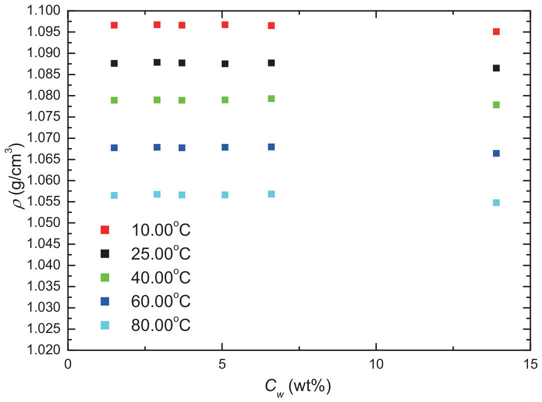

Fig. 4. Effect of water content on the density of pullulan/BmimCl solutions at different temperatures.

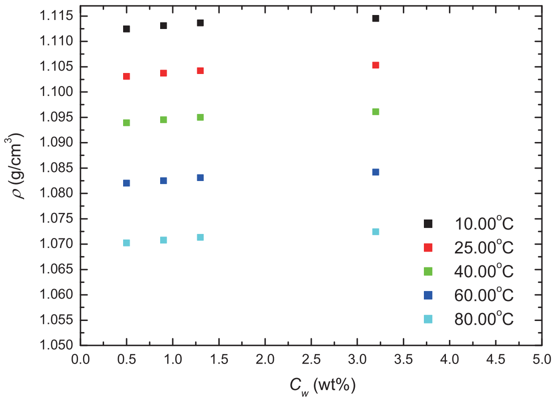

Fig. 5 Effect of water content on the density of pullulan/EmimAc solutions at different temperatures.

4. Conclusion

In this study, pullulan was successfully dissolved into BmimCl and EmimAc without degradation. The densities of these pullulan/IL solutions were measured and empirical relationships were obtained to describe concentration and temperature effects on these densities. Using these results, the concentration *C* in wt% could be converted into *c* in g/cm^3. This will play an important role in future understanding of the pullulan/IL solutions used as standards for IL soluble polymers.

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Appendix: Tables for row data.

Table A1. Densities ρ of pullulan/BmimCl solutions between 10 and 80 °C.

	ρ g/cm^3								
C (wt%)	10.00 °C	25.00 °C	30.00 °C	35.00 °C	40.00 °C	50.00 °C	60.00 °C	70.00 °C	80.00 °C
0.00	1.0923	1.0836	1.0807	1.0778	1.0747	1.0687	1.0631	1.0575	1.0520
0.55	1.0942	1.0855	1.0826	1.0796	1.0764	1.0707	1.0651	1.0595	1.0540
1.01	1.0958	1.0871	1.0841	1.0811	1.0779	1.0723	1.0668	1.0612	1.0557
2.26	1.0999	1.0912	1.0882	1.0852	1.0820	1.0764	1.0709	1.0654	1.0599
4.02	1.1052	1.0965	1.0936	1.0907	1.0876	1.0818	1.0762	1.0707	1.0652
5.71	1.1107	1.1021	1.0992	1.0963	1.0934	1.0873	1.0818	1.0763	1.0708
9.77	1.1239	1.1153	1.1124	1.1096	1.1067	1.1009	1.0949	1.0894	1.0839
16.22	1.1453	1.1368	1.1339	1.1311	1.1283	1.1226	1.1170	1.1112	1.1054

Table A2. Densities ρ of pullulan/EmimAc solutions between 10 and 80 °C.

	ρ g/cm^3								
C (wt%)	10.00 °C	25.00 °C	30.00 °C	35.00 °C	40.00 °C	50.00 °C	60.00 °C	70.00 °C	80.00 °C
0.00	1.1087	1.0994	1.0964	1.0934	1.0903	1.0843	1.0783	1.0724	1.0665
0.54	1.1095	1.1001	1.0971	1.0941	1.0911	1.0851	1.0791	1.0732	1.0673
0.97	1.1107	1.1013	1.0983	1.0953	1.0923	1.0863	1.0803	1.0744	1.0685
1.65	1.1124	1.1031	1.1000	1.0969	1.0939	1.0880	1.0820	1.0761	1.0702
3.05	1.1171	1.1079	1.1048	1.1018	1.0987	1.0926	1.0866	1.0808	1.0749
4.85	1.1255	1.1163	1.1132	1.1102	1.1072	1.1012	1.0952	1.0892	1.0833
7.13	1.1346	1.1248	1.1218	1.1188	1.1158	1.1098	1.1038	1.0979	1.0920
9.70	1.1404	1.1305	1.1274	1.1244	1.1214	1.1154	1.1095	1.1036	1.0977
16.50	1.1648	1.1556	1.1525	1.1495	1.1464	1.1402	1.1330	1.1281	1.1222

Table A3. Densities of a pullulan/BmimCl solution (1.35 wt%) at different C_w values between 10and 80 °C.

	ρ g/cm^3					
T	C_w : 1.5 wt%	C_w : 2.9 wt%	C_w : 3.7 wt%	C_w : 5.1 wt%	C_w : 6.6 wt%	C_w : 13.9 wt%
10.00 °C	1.0966	1.0967	1.0966	1.0967	1.0965	1.0951
25.00 °C	1.0876	1.0878	1.0877	1.0875	1.0877	1.0865
40.00 °C	1.0789	1.0790	1.0789	1.0790	1.0793	1.0778
60.00 °C	1.0677	1.0678	1.0677	1.0678	1.0679	1.0664
80.00 °C	1.0565	1.0567	1.0566	1.0566	1.0568	1.0548

Table A4. Densities of pullulan/EmimAc solution (1.65 wt%) at different C_w values between 10and 80 °C.

	ρ g/cm^3			
T	C_w :0.5 wt%	C_w : 0.9 wt%	C_w : 1.3 wt%	C_w : 3.2 wt%
10.00°C	1.1124	1.1131	1.1136	1.1145
25.00°C	1.1031	1.1037	1.1042	1.1053
40.00°C	1.0939	1.0945	1.0950	1.0961
60.00°C	1.0820	1.0825	1.0831	1.0842
80.00°C	1.0702	1.0708	1.0713	1.0724