A Rheological Study of Binary Mixtures of Ionic Liquid $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ and Ethanol

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Abstract:
In this paper, by means of Advanced Rheometric Expanded System (ARES), oscillatory and steady shear behavior of binary mixtures of a quaternary ammonium based ionic liquid $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ with ethanol (EtOH) were determined at 25°C and 25-50°C, respectively. The effects of shear rate, temperature and concentration on viscosity were elucidated sufficiently. It was found that the solutions show pseudo-plastic behavior at low shear rate and Newtonian property at higher shear rate. The addition of EtOH caused a substantial decrease in viscosity of the ionic liquid and the viscosity of binary mixtures could be described by an exponential equation. Arrhenius Equation and Power Law equation were applied to describe the respective effects of temperature and shear rate on viscosity. Activation energy derived from Arrhenius equation decreased with increasing the EtOH fraction in the mixture.

Zusammenfassung:
In diesem Artikel wird mit Hilfe des Advanced Rheometric Expanded Systems (ARES) das Verhalten bei Oszillation und in stationärer Scherung von binären Mischungen aus einer quaternären auf Ammonium basierenden ionischen Flüssigkeit $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ und Ethanol (EtOH) bei 25°C bzw. 25 - 50°C untersucht. Der Einfluss der Schergeschwindigkeit, der Temperatur und der Konzentration auf die Viskosität wurden herausgestellt. Es wurde gefunden, dass die Lösungen ein pseudo-plastisches Verhalten bei niedrigen Schergeschwindigkeiten und ein Newtonsches Verhalten bei höheren Schergeschwindigkeiten aufweisen. Die Zugabe von Ethanol verursachte eine deutliche Abnahme der Viskosität der ionischen Flüssigkeit. Die Viskosität der binären Mischung konnte mit Hilfe einer Exponentialgleichung beschrieben werden. Die Arrhenius-Gleichung und die Potenzgesetzgleichung wurden angewandt, um den Einfluss der Temperatur und der Schergeschwindigkeit auf die Viskosität zu beschreiben. Die aus der Arrhenius-Gleichung erhaltene Aktivierungsenergie nahm mit zunehmendem Ethanolanteil in der Mischung ab.

Résumé:
Dans cet article, le comportement dynamique et stationnaire du cisaillement des mélanges binaires d'un liquide ionique à base d'ammonium quaternaire $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ avec l'éthanol (EtOH) ont été déterminés respectivement à 25°C et à 25 - 50°C, au moyen d'un système avancé d'expansion rhéomètrique (ARES). Les effets du taux de cisaillement, de la température et de la concentration sur la viscosité ont été élucidés. On a constaté que les solutions montrent un comportement pseudoplastique à bas taux de cisaillement mais ont une propriété Newtonienne à un taux de cisaillement plus élevé. L'addition de EtOH a causé une diminution substantielle de la viscosité du liquide ionique. La viscosité des mélanges binaires pourrait enfin être décrite par une fonction exponentielle. L'équation d'Arrhenius et l'équation de loi de puissance ont été appliquées pour décrire les effets respectifs de la température et du taux de cisaillement sur la viscosité. L'énergie d'activation dérivée de l'équation d'Arrhenius diminue en augmentant la fraction de EtOH dans le mélange.

Key words: room temperature ionic liquid, rheological property, viscosity, activation energy, Arrhenius equation

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V	x	w	η [Pa·s]	$(\ln \eta)^E$ [Pa·s]
0.0	0.0	0.0	0.00162	0.0
0.2	0.05884	0.35906	0.00558	0.5599
0.3	0.09819	0.49383	0.01914	1.3398
0.4	0.14402	0.60122	0.0312	1.3014
0.5	0.19451	0.68393	0.08045	1.6677
0.6	0.26281	0.76160	0.31572	2.2493
0.7	0.35958	0.83420	1.06171	2.3489
0.8	0.50005	0.89963	4.33628	2.1401
0.9	0.70774	0.95595	20.6843	1.3135
1.0	1.0	1.0	162.424	0.0

Table 2: Apparent viscosity (at 10 s^{-1}) and excess logarithm viscosity for the binary mixtures of $[Me_3NC_2H_4OH]^+$ $[Zn_2Cl_5]^-$ + ()EtOH at 298.15K. x stands for mole fraction of RTIL.

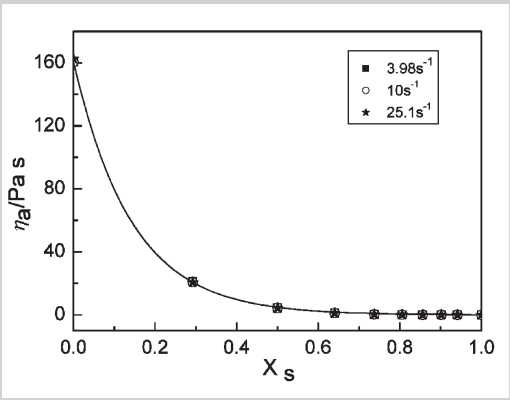

Figure 7 (above): Apparent viscosity plot as a function of the mole fraction of EtOH at shear rates of 3.98, 10 and 25.1 s^{-1}. The solid line represents the fit by Eq. 5.

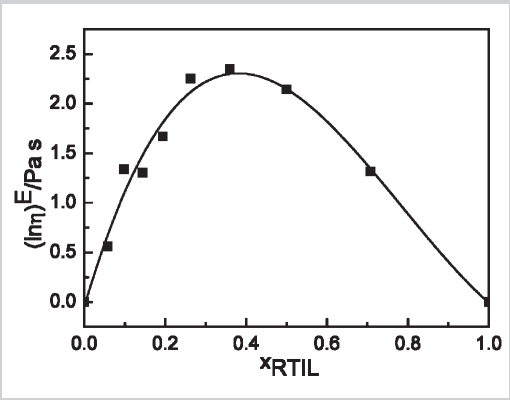

Figure 8: The excess logarithm viscosities for mixtures of x $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ + (1 - x) EtOH at 298.15 K.

where y refers to E_η, *v* refers to volume fraction of ionic liquid. B_j (*j* = 0, 1, 2) are fitting parameters, corresponding to 24.23, -36.07, 92.24, respectively.

3.2.3 Effect of EtOH concentration on viscosity

Figure 7 shows a plot of the viscosity of binary mixture against mole fraction of EtOH. An exponential equation proposed by Seddon and coworkers [4] is used to fit the data with a correlation coefficient > 0.999.

$$\eta = \eta(IL)e^{-x_s/a} \quad (5)$$

where x_s is the mole fraction of EtOH, *a* is a constant characteristic for the mixture, and $\eta(IL)$ is the viscosity of pure ionic liquid. The *a* obtained in this work for $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ is 0.14, smaller than the reported values of 0.23 for $[C_4mim][BF_4]$, 0.19 for $[C_4mim][PF_6]$ [4], and 0.216 for $[Bmim][BF_4]$ [6].

Considering the logarithmic scale in Fig. 7, it is clear that the viscosity decreases rapidly when EtOH is added to the ionic liquid. We interpret this result by the fact that the strong coulomb interaction and hydrogen bonding between the ions are weakened upon the addition of ethanol, leading to a higher mobility of the ions. The viscosity of EtOH is appropriately 1 cP, very close to that of water at room temperature; while the viscosity of the pure RTIL is 160 Pa·s, approximately 1.6 x 10^5 times higher than that of EtOH. The added EtOH tunes the viscosity of RTIL but the viscosity of binary mixture does not follow the linear logarithmic addition of the viscosities of EtOH and RTIL.

Excess property of a solution is defined as the difference between the actual mixture property and that would be obtained for an ideal solution under the same condition. Here, excess logarithm viscosity is applied to represent the deviation from an ideal rheological behavior of the mixtures. Values of $(\ln \eta)^E$ are generated according to Eq. 6, where η_{mix} is the viscosity of binary mixture, x_i, η_i denote the mole fraction and viscosity of component *i*, respectively. The viscosities of solutions were chosen at a shear rate of 10 s^{-1} (data shown in Table 2).

$$(\ln\eta)^E = \ln\eta_{mix} - \sum_{i=1}^{2} x_i \ln\eta_i \quad (6)$$

Figure 8 shows the variation of $(\ln \eta)^E$ as a function of mole fraction of the ionic liquid. It is clear that all values are positive in the studied range of composition for the binary mixtures. The maximum value is at about *x* = 0.38. This indicates probably a phase transformation in the vicinity of *x* = 0.38, i.e. the change from the EtOH enriched phase to the RTIL enriched phase. Wang et al. [6] previously also suggested that an unusual structure possibly occurs in the vicinity of *x* = 0.3 for the binary mixtures of $[bmim][BF_4]$ with organic solvents.

4 CONCLUSIONS

The dynamic and steady rheological properties of binary mixtures of $[Me_3NC_2H_4OH]^+[Zn_2Cl_5]^-$ and EtOH were examined at 25°C and 25 - 50°C, respectively. The effects of concentration, temperature and shear rate on viscosity were thoroughly discussed. The solutions show pseudoplastic behavior at low shear rate and Newtonian

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property at higher shear rate. Viscosity of the RTIL was greatly decreased by the addition of EtOH and activation energy of the RTIL/EtOH also decreased with increasing the EtOH fraction. Additionally, excess logarithm viscosities were positive for all the binary mixtures and the maximum point was observed at x_{RTIL} = 0.38.

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