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Rheological behaviour of binary mixtures containing hexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) between 288.15 K and 343.15 K

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ABSTRACT

Variation of the viscosity as a function of temperature and composition in Cyanex 272–Cyphos IL 101 binary mixtures has been investigated between 288.15 K and 343.15 K in the whole range of mole fraction. Valuable information regarding intermolecular interactions between Cyanex 272 and Cyphos IL 101 has been deduced from viscosity data by calculating excess viscosities, activation enthalpies and entropies and ion contributions to the activation energy and the activation entropy for the viscous flow. Peculiarly Cyphos IL 101 and Cyanex 272 exist as contact ion-pairs and ion-pairs separated by hydrochloride molecule depending on the mole fraction of Cyphos IL 101 in the binary mixture.

1. Introduction

Room Temperature Ionic Liquids (RTIL) are an alternative to replace the use of organic solvents because they are able to dissolve both polar and non-polar compounds and they are considered as green solvents. They were extensively studied for various applications [1–10]. For instance, numerous papers concern the use of RTIL in liquid–liquid extraction of metal ions [4,10]. Among these RTIL, trihexyl(tetradecyl)phosphonium chloride (Cyphos IL 101) was used for the recovery of Zn(II), Fe(II), Bi(III), Pd(II) or Pt(II) from various aqueous media [11–17].

In spite of the interest of RTIL for solvent extraction systems, very few reports can be found in literature about the mixtures of RTIL and extractants. Biswas et al. [18] reported properties of bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) diluted in different kinds of solvents, but no RTIL have been included in this work.

In this paper, viscosity (η) of Cyanex 272 and Cyphos IL 101 mixtures has been studied and a semi-empirical model describing the variation of the viscosity of these mixtures as a function of temperature (288.15–343.15 K) and mole fraction (0–1) has been derived.

Valuable information regarding intermolecular interactions between Cyanex 272 and Cyphos IL 101 has been deduced from viscosity data by calculating excess viscosities (η^E), activation energies, activation entropies and ion contributions to the activation energy and the activation entropy for the viscous flow (E_a^{ion} and $\Delta S^{\ddagger ion}$).

2. Experimental

Cyphos IL 101 (trihexyl-(tetradecyl)phosphonium chloride) and Cyanex 272 (bis-2,4,4-trimethylpentylphosphinic acid) were kindly provided by Cytec Industries Inc. Cyanex 272 was purified by using the procedure described elsewhere [19] and the purity was estimated by ^{31}P NMR and ^{1}H NMR (98% Cyphos IL 101, 96% Cyanex 272 whereas the initial purity of Cyanex 272 was equal to 80%). It was identified that the impurities in Cyanex 272 are mainly trialkyl phosphine oxide (R_3PO) [20,21].

All the experiments were performed under nitrogen atmosphere to avoid water contamination. Binary mixtures were prepared in an inert atmosphere glovebox (nitrogen) by weighing both compounds with a Mettler–Toledo AG285 Balance with an uncertainty of $\pm 10^{-4}$ g. Binary mixtures were stocked in the glovebox and all physicochemical

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measurements (density, viscosity) were performed under nitrogen atmosphere to avoid water contamination (*vide infra*).

Density measurements were carried out with a pycnometer (5 mL) under nitrogen atmosphere at 295.15 K.

Dynamic viscosity measurements (η) between 288.15 K and 343.15 K ($\pm$0.1 K) were carried out with a Gemini 150 rotational viscometer (Bohlin Instruments) with a cone-plate geometry (40 mm diameter, 4°) under nitrogen atmosphere at shear rates ($\dot{\gamma}$) ranging from 0.1 to 100 s^{-1}. In this range of shear rate, Cyanex 272, Cyphos IL 101 and their mixtures behave as a Newtonian fluid. Viscosities of the mixtures were first determined as a function of temperature during a heating cycle from 288.15 K to 343.15 K. After cooling the solution down to 298.15 K, the measurements were duplicated by measuring the viscosity of the mixtures as a function of shear rates. No chemical decomposition and no phase separation were observed as well as no significant variation of the viscosity occurred between the heating cycle and the cooling cycle. Each measurement was repeated five times at each temperature for all mixtures for the sake of consistency and reproducibility. The average precision of the viscosity measurements was estimated to 0.2%.

Water content was measured under inert atmosphere by the Karl Fischer titration method with a Mettler–Toledo coulometric Titrator (V20) before and after viscosity measurements. No water contamination occurred as no variation of viscosity was observed and the residual water content in the mixtures was found lower than 115 ppm as reported in Table 1.

3. Results and discussion

3.1. Viscosity

3.1.1. Influence of strain rate on the viscosity

All the mixtures behave as perfectly Newtonian liquids at 298.15 K for strain rate ranging between 0.1 s^{-1} and 100 s^{-1} since shear stress (τ) vs. strain rate ($\dot{\gamma}$) follows the linear equation:

$$\tau = \eta\dot{\gamma} \tag{1}$$

The values of the viscosity η and the correlation coefficient (R^2) related to Eq. (1) are reported in Table 2.

The viscosities at 298.15 K of Cyanex 272 and Cyphos IL 101 are 109.7 mPa.s and 2160 mPa.s, respectively. The viscosity of Cyanex 272 from this work is in agreement with the value found by Biswas et al. [18]. The small difference of viscosity between this work and the value reported by Biswas et al. can be attributed to the difference of purity (purity = 96% in our work and 98% in the paper of Biswas et al.).

A comparison of the viscosity of Cyphos IL 101 vs. temperature between the present work and literature is displayed in Fig. 1 [22,23]. A discrepancy is observed depending on the origin of the data. Indeed, for instance at 298.15 K, η = 2729.1 mPa.s or 1824 mPa.s in literature [6,23] while η = 2160 mPa.s in this study. The difference may arise from the purity of Cyphos IL 101 which differs from one study to another one. Unfortunately, there is no information about the purity of Cyphos IL 101 in literature. Conversely, in this work, the purity of Cyphos IL 101 was estimated to 98% by ^{31}P NMR and ^{1}H NMR and water content is less than 115 ppm.

Table 1
Water content in Cyphos IL101–Cyanex 272 mixtures.

x_2	Water content (ppm)
0.00	58
0.20	59
0.31	68
0.40	72
0.50	78
0.61	78
0.70	82
0.80	83
0.90	81
1.00	113

Table 2
Values of η derived from Eq. (1) by measuring shear stress vs. strain rate between 0.1 s^{-1} and 100 s^{-1}. R^2: correlation coefficient.

x_2	η (mPa.s)	R^2
0.00	109.7	0.9996
0.20	704.9	1.0000
0.31	969.6	1.0000
0.40	1095.3	1.0000
0.50	1235.9	1.0000
0.61	1159.6	1.0000
0.70	1639.5	1.0000
0.80	1856.7	1.0000
0.90	2043.1	1.0000
1.00	2160.8	1.0000

3.1.2. Modelling temperature and composition dependence for the viscosity

Various semi-empirical models to describe the variation of the viscosity in mixtures of solvents or electrolytic solutions have been reported in literature [24–27]. In the present work, the variation of the viscosity vs. temperature and composition of the binary mixtures has been modelled by using a semi-empirical relationship developed for solvent and electrolyte mixtures [27]:

$$\eta = \exp\left[x_1\ln(\eta_1^\circ) + x_2\ln(\eta_2^\circ) + x_1x_2a(1+2x_1b)\,(1+2x_2c)\,(T_r/T)^p\right] \tag{2}$$

wherein η_i° is the pure component viscosity of each solvent at the system temperature, a–c are adjustable mixing parameters, T_r is the reference temperature (here, 298.15 K), and T is the system temperature in K. Subscripts 1 and 2 denote the mole fraction of Cyanex 272 and Cyphos IL 101, respectively.

The signs and magnitudes of parameters a–c depend on the nature of interaction between different solvent molecules and p is an empirical parameter equal to 5 for solvent mixtures [28]. This expression can use as few as one mixing parameter for simple solvent mixtures (set a at unity, then set either b or c equal to zero) and as many as three parameters for other complex solvent mixtures (a–c values nonzero and unity not imposed). In the present work the model

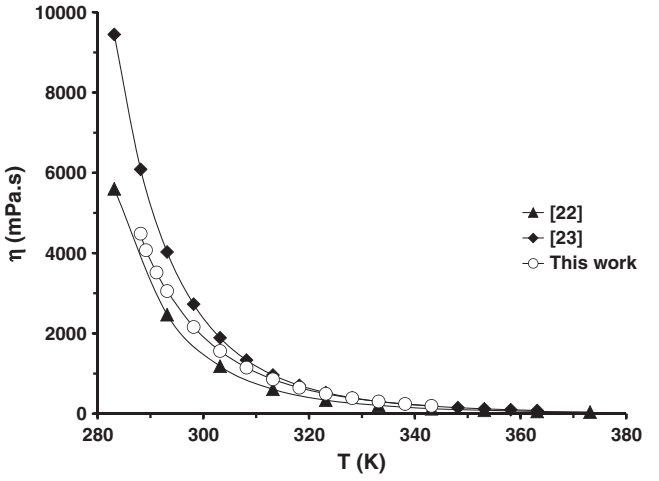

Fig. 1. Comparison of the Viscosity of Cyphos IL 101 vs. temperature from the present work and literature data [22,23].