Dimethylpropyleneurea - Water Mixtures: 1. Physical Properties

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Densities, refractive indices, viscosities, dielectric constants and the absorptions of several solvatochromic indicators have been determined at 25°C for mixtures of N,N'-dimethyl-N,N'-propyleneurea (DMPU) and water in the complete mole fraction scale. The results are compared with the properties of hexamethylphosphotriamide (HMPT) and its mixtures with water which show a striking similarity to DMPU and its mixtures with water. Since HMPT was found to be carcinogenic in animal tests, DMPU offers a suitable substitute since it may be regarded as safe under laboratory conditions.

KEY WORDS: DMPU; HMPT; density; refractive index; viscosity; static dielectric constant; donor and acceptor numbers; ET(30) parameter.

1. Introduction

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone(1) is a N,N'-dialkylated cyclic urea and its acronym DMPU is related to the earlier name dimethylpropyleneurea. DMPU is an excellent dipolar aprotic solvent whose physical properties at room temperature are similar to those met with some familiar dipolar aprotic solvents like N,N-dimethylformamide (dielectric constant), propylene carbonate and hexamethylphosphotriamide (viscosity) or propylene carbonate (liquid range). However, as cosolvent for highly reactive nucleophiles and bases only DMPU has been shown to be an ideal replacement for hexamethylphosphotriamide (HMPT).2,3 Although HMPT has been found to be carcinogenic in animal tests,4 in several studies it was shown that DMPU may be regarded as safe under normal laboratory conditions.

In this work we report investigations of the physical properties of

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the mixed solvent system DMPU and water. The results are compared with the properties of HMPT + H₂O mixtures and a striking similarity between two binary systems was found.

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\text{DMPU}
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2. Experimental

2.1. Reagents

DMPU (Fluka) was dried for one day over BaO and vacuum distilled (Vigreux column) at 95°C and 5-6 mbar. The specific conductance of the distillate ranged from 1-2×10⁻⁷ ohm⁻¹·cm⁻¹. Solvent mixtures were made up by weight from triply distilled water. The color indicator for solvent basicities (acetyl-acetonato)(N,N,N',N'-tetramethylethylene diamine) copper(II) perchlorate, Cu(tmen)(acac) ClO₄ was prepared from copper(II) perchlorate hexahydrate (Aldrich), N,N,N',N'-tetramethylethylendediamine (tmen; Serva) and acetylacetone (acac; Merck) in aqueous ethanol solution (1:1) and recrystallized from ethanol.⁵

The color indicator for solvent acidities dicyano-bis-(1,10-phenanthroline, iron(II) dihydrate, Fe(phen)₂(CN)₂·2H₂O was obtained by a reaction of 1,10-phenanthrolpine monohydrate (Merck) and ferrous ammonium sulfate hexahydrate (Merck) in aqueous solution after addition of KCN.⁶ 2,6-Diphenyl-4-(2,4,6-triphenylpyridino)phenolate (diphenyl-betaine) was a commercial sample (Aldrich) and used without further purification for the determination of \(E_T(30)\) values.

2.2. Density

The densities were measured using 5 ml Pyrex pycnometers. They were thermostated to 25.0±0.05°C in a water bath and calibrated