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Dimethylpropyleneurea - Water Mixtures: 1. Physical Properties

J. Stroka,[1] I. Herfort,[2] and H. Schneider[2]

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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; $E_T(30)$ 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 dimethylpropylurea. 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

[1]Department of Chemistry, University of Warsaw, 02093 Warsaw, Poland.

[2]Max-Planck-Institut für Biophysikalische Chemie, D-3400 Göttingen, F.R.G.

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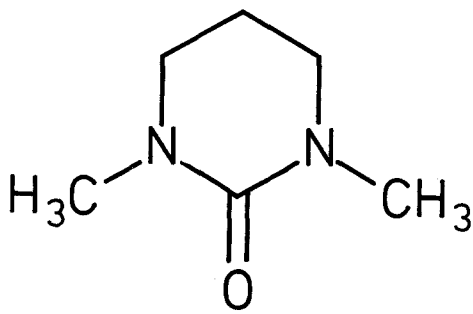
the mixed solvent system DMPU and water. The results are compared with the properties of HMPT + H_2O mixtures and a striking similarity between two binary systems was found.



DMPU

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 $1\text{-}2\times10^{-7}$ $ohm^{-1}\text{-}cm^{-1}$. 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) ClO_4 was prepared from copper(II) perchlorate hexahydrate (Aldrich), N,N,N′,N′-tetramethylethylenediamine (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, $Fe(phen)_2(CN)_2\cdot2H_2O$ was obtained by a reaction of 1,10-phenanthroline 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

with water. The standard deviation of at least three measurements was ±0.02%.

2.3. Refractive Index

The refractive indices were determined at 25.0±0.05°C using a thermostated Abbe refractometer for the sodium D line (λ = 589.3 nm). The accuracy of repeated determinations was less than $\pm 2\times10^{-4}$.

2.4. Viscosity

The kinematic viscosities were measured with a suspended-level Ubbelohde viscosimeter (Schott, Mainz) equipped with photoheads and coupled to an electronic stop-clock (AVS/N, Schott, Mainz). The viscosimeter was thermostated at 25.00±0.02°C and calibrated by measuring the flow time with pure water. Every measurement was repeated at least for three times and was reproduceable to ±0.05%.

2.5. Dielectric Constant

Measurements of static dielectric constants were carried out at *ca.* 2.0 MHz by the heterodyne beat method (Dipolmeter DM 01 of Wissenschaftlich-Technische Werkstatten). The measuring cell (MFL 3/s) (10 cm^3) which covers a range in dielectric constant from about 21 to 90 was thermostated at 25.00±0.02°C. The cell was calibrated at that temperature with four pure liquids:[7] water (ε = 78.46), dimethylsulfoxide (ε = 46.7), methanol (ε = 32.7) and ethanol (ε = 24.6). The linearity of the calibration is characterized by the correlation coefficient 0.999997.

2.6. Spectral Measurements

The visible absorption spectra of the three solvatochromic compounds: $Cu(tmen)(acac)ClO_4$, $Fe(phen)_2(CN)_2$ and diphenyl-betaine were recorded on a Shimadzu UV-240 spectrophotometer equipped with a cell compartment thermostated at 25.00±0.02°C. The optical path was 1 cm and the absorption spectra of every color indicator were determined in the pure solvents at several indicator concentrations to find the optimum concentrations with respect to the technical limits of the instrument and to verify that impurities which interact strongly with an indicator are of no importance. In all cases the concentration dependences of the absorption maxima were insignificant which indicates in addition that there is no decomposition of the copper(II) chelate by solvent attack.[8] The wavelengths of the maximum absorption λ_{max} were ob-

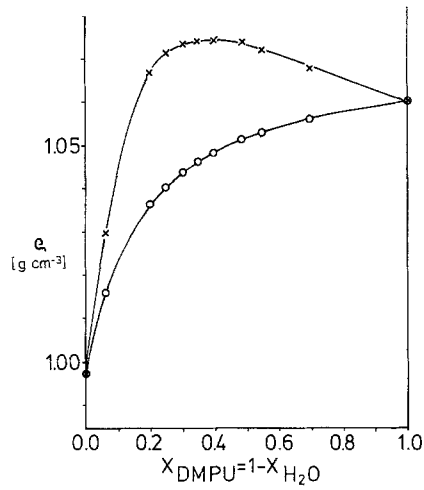


Fig. 1. Experimental densities, ρ, (—×—) and ideal densities, ρ_{id}, (—o—) of DMPU + H_2O mixtures at 25°C.

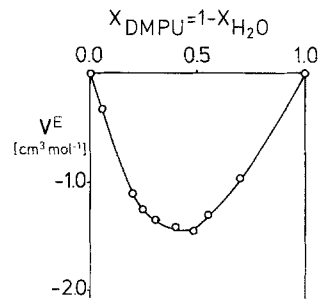


Fig. 2. Excess volumes of DMPU + H_2O mixtures at 25°C.

tained graphically from the bisectors of the symmetrical absorption bands.

3. Results

The measured densities ρ, refractive indices n_D, dynamic viscosities η, and static dielectric constants ε are reported in Table I as a function of the mole fractions of DMPU, x_{DMPU}.

The densities of the mixtures are always larger than the corresponding ideal densities, ρ_{id} [Eq. (1)], which depend only on the mean molar masses

Table I. Density (ρ), Refractive Index (n_D), Dynamical Viscosity (η) and Static Dielectric Constant (ε) of DMPU-Water Mixtures at 25°C

x_{DMPU}	ρ[a]	n_D	η[b]	ε
0.000	0.9971	1.3325	0.893	78.46
0.060	1.0300	1.3832	2.48	
0.200	1.0671	1.4411	7.11	58.1
0.249	1.0715	1.4526		
0.304	1.0735		8.44	
0.348	1.0746		8.47	50.4
0.385				48.8_0
0.400	1.0744	1.4695	8.02	
0.487	1.0740		7.06	
0.548	1.0720	1.4782	6.32	
0.696				41.1
0.699	1.0677	1.4829	4.79	
1.000	1.0600	1.4874	2.95	36.2
1.000	1.0596[c]	1.4881[c]	2.934[c]	36.12[c]

[a] Units: g-cm^{-3}. [b] Units: mPa-s. [c] See Ref. 13.

$$\bar{M} = x_{DMPU} M_{DMPU} + x_{H_2O} M_{H_2O}$$

and the molar volume V of the ideal mixtures

$$V = x_{DMPU} M_{DMPU} \rho_{DMPU}^{-1} + x_{H_2O} M_{H_2O} \rho_{H_2O}^{-1}$$

$$\rho_{id} = \bar{M}/V \tag{1}$$

M_{DMPU} and M_{H_2O} are the molar masses of the components. The variations of ρ and ρ_{id} with mole fraction are shown in Fig. 1. The excess volume V^E is calculated from the densities, according to the relation

$$V^E = (\bar{M}/\rho) - V_{id} \tag{2}$$

The results are shown in Fig. 2. The data can be fitted into the equation of the form

$$V^E = x_{DMPU}(1 - x_{DMPU}) \sum_{i=0}^{n} a_i (2x_{DMPU} - 1)^i \tag{3}$$

The coefficients at 25°C are $a_0 = -5.60$ (−5.2654), $a_1 = 2.50$ (3.0303), $a_2 = 1.05$ (−4.1533) and $a_3 = -0.43$ (3.4911), with the corresponding coefficients for the hexamethylphosphotriamide - H_2O system[9] in brackets.

The molar refraction R

$$R = \frac{n_D^2 - 1}{n_D^2 - 2}(\bar{M}/\rho) = 3.70 + 31.07x_{DMPU} \quad [cm^3\text{-}mol^{-1}] \tag{4}$$

correlation coefficient, $r_{corr} = 0.999997$

and even the molar polarization P

$$P = \frac{\varepsilon - 1}{\varepsilon - 2}(\bar{M}/\rho) = 17.0 + 94.2x_{DMPU} \quad [cm^3\text{-}mol^{-1}] \tag{5}$$

correlation coefficient, $r_{corr} = 0.999992$

are linearly dependent on mole fraction. The polarizability α (in 10^{-30} m^3) is related to the molar refraction by[7]

$$\alpha = (3/4\pi)(R/N) \tag{6}$$

where N is Avogadro's number.

The wavelengths, λ_{max} (nm), of the visible absorption bands of the three color indicators are listed in Tables IIa, IIb and IIc. The wave number $\tilde{\nu}$ (cm^{-1}), $\tilde{\nu} = 10^7\ \lambda_{max}^{-1}$, of the d-d transitions of Cu(tmen)(acac)ClO_4 is transformed into Gutmann's donor number DN according to equation[10]

$$DN = 195.5 - 0.0102\tilde{\nu} \tag{7}$$

The charge transfer band $t_{2g} \rightarrow \pi^*$ of the ferrous complex $Fe(phen)_2(CN)_2$ shows two maxima and the wave number of the long wavelength absorption is correlated with the acceptor number through[10]

$$AN = -133.8 + 0.00933\tilde{\nu} \tag{8}$$

The Dimroth-Reichardt $E_T(30)$ value of the diphenyl-betaine is the transition energy (in kcal-mol^{-1}) of the longest wavelength absorption band. $E_T(30)$ values are calculated from the absorption band position, λ_{max} by the relationship[11,12]

$$E_T(30) = 28590/\lambda_{max} \quad [kcal\text{-}mol^{-1}] \tag{9}$$

Table IIa. λ_{max} of the d-d Transitions of $Cu(tmen)(acac)ClO_4$ at 25°C

x_{DMPU}	0.0	0.059	0.200	0.397	0.487	0.548	
λ_{max}(nm)	$595._2$	$605._0$	$612._5$	$620._0$	$618._0$	$616._1$	
x_{DMPU}	0.631	0.671	0.700	0.766	0.848	0.925	1.0
λ_{max}(nm)	$616._3$	$618._1$	$619._1$	$626._0$	$631._1$	$640._0$	$667._9$

Table IIb. λ_{max} of the $t_{2g} \rightarrow \pi^*$ Band of $Fe(phen)_2(CN)_2$ at 25°C

x_{DMPU}	0.0	0.060	0.203	0.398	0.696	1.0
λ_{max}(nm)	511.8[a]	540	562	583	604	626

[a] The related AN of 58.5 differs from the literature value of 55.5 because of the low correlation factor of Eq. (8), See Ref. 10.

Table IIc. λ_{max} of Dimroth-Reichardt's Diphenyl-Betaine at 25°C

x_{DMPU}	0.0	0.097	0.254	0.486	0.682	0.897	1.0
λ_{max}(nm)	454	517	560	608	637	667	678

1. Discussion

Among the group of N-alkylated acyclic and cyclic ureas DMPU was shown to be the most versatile medium for a variety of chemical and physicochemical applications.[13] It has a wide liquid range from around -20°C to 230°C (at 754 mm Hg) comparable with that of propylene carbonate, a high static dielectric constant (ε = 36.12)[14] and a large dipole moment (μ = 4.23 D)[14] which are similar to the corresponding physical properties of N,N-dimethylformamide. Therefore DMPU is a good dissociating medium for electrolyte solutions[15] with reasonable solubilities for many electrolytes.[1]

When in animal tests HMPT was found to be carcinogenic,[4] a suitable substitute for this compound with its excellent properties and numerous applications as dipolar aprotic solvent[16,17] was looked for. Seebach,[2] and later also Liljefors,[3] showed that DMPU can satisfactorily replace HMPT as co-solvent for highly reactive nucleophiles and bases.

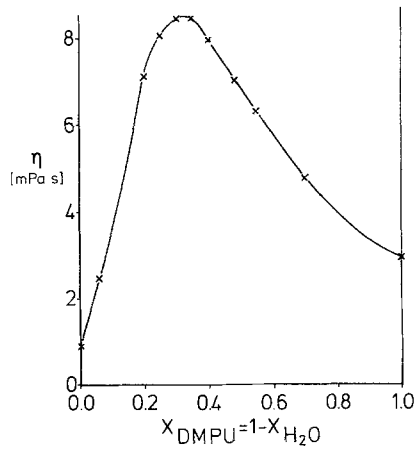


Fig. 3. Dynamic viscosities of DMPU + H_2O mixtures at 25°C.

bases. After a series of tests DMPU was regarded as being safe.[4]

Since the physical properties of DMPU are rather similar to those of the dipolar aprotic donor solvents with high Lewis basicities like N,N-dimethylformamide, dimethylsulfoxide, N-methyl-2-pyrrolidinone or HMPT, we were interested to know whether the remarkable similarity of HMPT and DMPU mentioned before is also found in the properties of their aqueous mixtures. Water was chosen as the second component because in mixtures it discriminates strongly between different solvent molecules due to its hydrogen-bond structure.

The increase in experimental density over the calculated ideal density on mixing of DMPU with water (Fig. 1) and the distinct maximum in viscosity (Fig. 3) are complementary effects of the non-ideal behavior of the binary solvent system. The excess volumes of DMPU + H_2O (Fig. 2) and of HMPT + H_2O[9] are negative with nearly the same minimum values but at different mole fractions. Also the viscosity of mixtures of HMPT and water[9] passes a maximum and its value is almost identical with that of DMPU + H_2O mixtures. Only the mole fractions belonging to the maxima are different: $x_{DMPU} = 0.3_3$ and $x_{HMPT} = 0.1_8$. In order to stress the similarities of the two systems more clearly, the excess viscosities of the mixtures were calculated by the relation suggested by Ford and Moore[18] for solutions of two components A and B

$$\eta^E = \eta - (x_A\eta_a + x_B\eta_B) \qquad (10)$$

and are plotted *vs.* the volume fractions of the components DMPU and

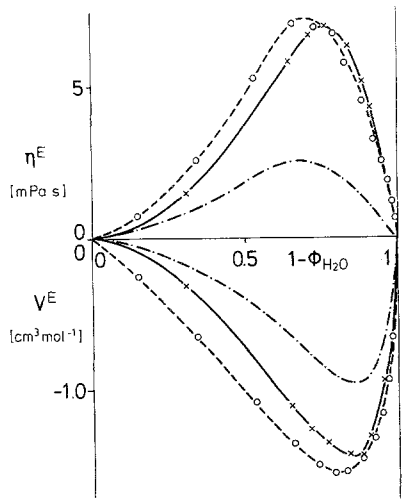


Fig. 4. Excess viscosities and excess volumes of the mixtures DMPU + H_2O (—×—), HMPT + H_2O (- - O - -) and DMSO + H_2O (—•—•—) at 25°C.

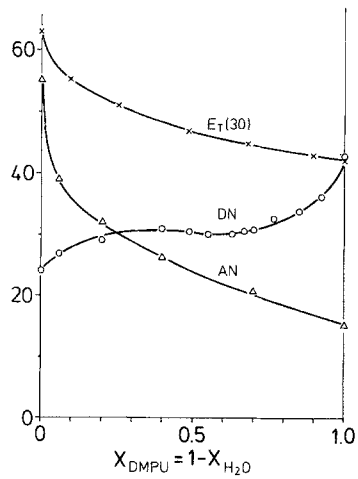


Fig. 5. $E_T(30)$ (kcal-mol^{-1}), donor numbers, DN and acceptor numbers, AN in DMPU + H_2O mixtures at 25°C. (The $E_T(30)$ value in water is taken from Ref. 12.)

HMPT (Fig. 4). Figure 4 also shows the excess volumes as functions of volume fractions. The close similarity of the properties of the two mixed solvent systems is evident. The corresponding quantities of DMSO + H_2O mixtures[19] are indicated for contrast and show that the excess functions are clearly smaller in magnitude. The volume fractions of the extrema of the three systems are very similar.

The Dimroth-Reichardt $E_T(30)$ polarity value[12,20] and the acceptor number AN are solvatochromic parameters indicating the electron pair acceptance abilities of solvents. Adding DMPU to water, $E_T(30)$ as well as AN decrease sharply (Fig. 5) and at higher mole fractions of DMPU more slowly towards the values in pure DMPU. The variation of $E_T(30)$ with mole fraction parallels with that found for DMSO + H_2O mixtures[22] but at lower values and also the decrease of AN with increasing properties of organic component follows the sequence DMSO < DMPU ~ HMPT.[7,23] The results show that the reduction in electron pair acceptance abilities of the solvent mixtures is stronger than according to a purely additive contribution of the components especially at low concentrations of DMPU. This behavior is reflected in an increase of the donor number, DN,[24] as a measure of the electron pair donation ability of the solutions. After a steep increase up to $x_{DMPU} \sim 0.25$, the donor number passes a plateau value until it increases further at $x_{DMPU} > 0.7$. The donor number of DMPU is still larger than that of HMPT and much larger than that of DMSO. Unfortunately no donor numbers of the HMPT + H_2O solutions are available.

5. Conclusion

DMPU was recommended as the only dipolar aprotic solvent whose stability as cosolvent for highly reactive nucleophiles and bases is comparable to that of HMPT.[4] The results presented in this paper show that not only the physical properties of the pure solvents DMPU and HMPT are rather similar inspite of their quite different structures but also that solution properties of their mixtures with water are remarkably parallel in their dependence on volume fraction.

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