

**Table I. Solubility of Benzoic Acid in Aqueous Polyethylene Glycol Solutions**

concn, wt %	temp, °C					
	30	35	40	45	50	55
Mol Wt = 4000						
0.5	4.402	5.210	6.021	7.105	8.403	9.509
1.0	4.800	5.410	6.404	7.712	8.907	10.201
2.0	5.407	6.031	7.152	8.431	9.812	11.101
3.0	5.901	6.701	7.600	8.903	10.706	11.903
4.0	6.100	7.100	7.951	9.407	11.503	12.91
5.0	6.411	7.451	8.602	10.307	12.102	13.503
6.0	6.603	7.607	8.901	10.211	12.207	13.81
Mol Wt = 6000						
0.5	4.200	4.903	5.800	6.807	7.910	8.901
1.0	4.510	5.200	6.010	7.200	8.230	9.607
2.0	5.107	5.803	6.610	7.800	8.906	10.21
3.0	5.400	6.210	7.110	8.220	9.603	11.11
4.0	5.810	6.750	7.600	8.810	10.22	11.50
5.0	6.002	7.210	8.010	9.207	10.91	12.20
6.0	6.200	7.250	8.303	9.520	11.10	12.52
Mol Wt = 20 000						
0.5	4.110	4.750	5.610	6.590	7.420	8.750
1.0	4.400	5.120	5.980	6.920	8.100	9.410
2.0	4.910	5.421	6.412	7.302	8.410	9.911
3.0	5.200	6.011	6.803	7.411	9.023	10.5
4.0	5.601	6.307	7.210	7.904	9.409	10.81
5.0	5.903	6.400	7.617	8.521	9.913	11.203
6.0	6.090	6.612	8.021	8.620	10.101	11.513

were PEG (mol wt = 4000, Lab.-Chem. Industries, Bombay, India) and PEG (mol wt = 6000 and 20 000, BDH Chemicals, Poole, UK). The benzoic acid (AR) used was obtained from IDPL, Hyderabad, India. Aqueous polymer solutions were prepared in batches of 6 L by dissolving a known amount of polymer in an appropriate amount of distilled water and were allowed to stand for 36 h before use in the actual experiments.

Solubilities of benzoic acid in each of these solutions at different temperatures were determined by "equilibrated solution" technique as described elsewhere (1). Measurements were made with polymer solutions containing 0.5, 1.0, 2.0, 3.0, 4.0,

5.0, and 6.0% polymers by weight in the temperature range 30-55 °C. The thermostated bath used was capable of providing a temperature control with an accuracy of  $\pm 0.1$  °C. Special care was taken to exclude carbon dioxide from all of the systems during experimentation. All measurements were made in quadruplicate and the reproducibility was within  $\pm 1-2\%$  of the mean value.

## Results and Discussion

The measured solubilities of benzoic acid in the aqueous solutions of the three polymers investigated are listed in Table I. The solubility in aqueous polymer solutions is more than that in water and increases to a constant value with increasing polymer concentration and decreases with increasing polymer molecular weight.

The observed enhancement in the solubility in the polymer solutions over that in water and its approach toward a constant value at higher polymer concentrations at any particular temperature are due to the reasons mentioned elsewhere (2). The decrease in the solubility with increasing polymer molecular weight is once again due to decrease in the solvolysis of the solute molecules with increasing polymer molecular weight. Thermodynamically speaking, increasing polymer molecular weight results in a decrease in entropy of mixing and in turn increases the free energy of mixing and hence a decrease in the solubility values.

## Literature Cited

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# Several Properties of 1,1,3,3-Tetramethylurea-Water Systems

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**Dielectric constants, viscosities, densities and partial molar volumes for aqueous tetramethylurea mixtures have been determined at 25 °C. Where possible, the data are compared with previously reported values. Molar polarization for the tetramethylurea-water mixtures are shown to be linear functions of the mole percent through the complete range of the solvent mixtures.**

The data presented here were accumulated during the course of an extensive investigation of conductances in the tetramethylurea-water systems. Despite the usefulness of the material as a good solvent for many organic substances, physicochemical studies on tetramethylurea solutions are very few. Tetramethylurea is one of the few urea derivatives which are liquid at room temperatures and acts only as a hydrogen-bond acceptor without an ability as a proton donor. The so-

lute-solvent interactions in tetramethylurea solutions will be discussed.

## Experimental Section

The dielectric constants were measured at 1 MHz by a dekameter (Dk 300, Karl Kolb) with a digital readout.

Tetramethylurea (Sigma Chemical Co.) was used after being refluxed with calcium hydride under nitrogen atmosphere and distilled at 10 mmHg. Densities of aqueous solutions were measured with an Ostwald-type pycnometer at 25 °C, and partial molar volumes were calculated. Viscosity coefficients for the solutions were measured with an Ostwald-type viscometer at 25 °C.

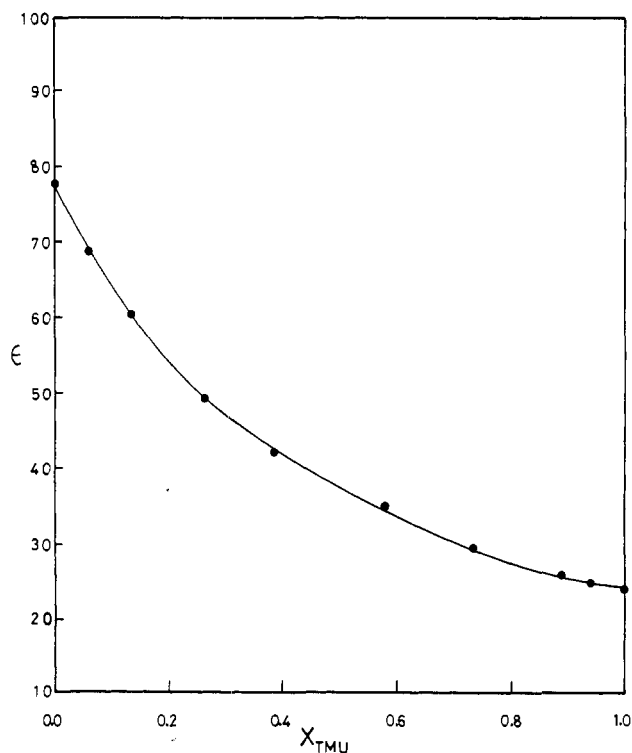
Temperature regulation at  $25 \pm 0.001$  °C for the above measurements was obtained in a thermostatically controlled water bath with the absolute temperature determined by a

Table I. Experimental Dielectric Constants, Viscosities, and Densities of 1,1,3,3-Tetramethylurea-Water Mixtures at 25 °C

$X_{\text{TMU}}$	$\epsilon$	$\eta, \text{g cm}^{-1} \text{s}^{-1}$	$\rho, \text{g cm}^{-3}$
0.0000	78.40	0.8904	0.9971
0.0601	68.41	2.2037	1.0049
0.1302	60.75	3.7356	1.0089
0.1803	56.50	4.9619	1.0102
0.2250	52.98	5.2001	1.0091
0.2581	49.30	4.6474	1.0065
0.3740	43.11	3.8375	0.9978
0.4580	37.13	3.2683	0.9919
0.5732	34.92	2.6643	0.9828
0.6311	32.21	2.3970	0.9798
0.7390	28.25	1.9727	0.9730
0.8962	26.00	1.5502	0.9660
0.9423	24.97	1.4801	0.9639
1.0000	23.60	1.3950	0.9619

Table II. Calculated Values of Partial Molar Volumes and Molar Polarizations Using the Experimental Data Obtained

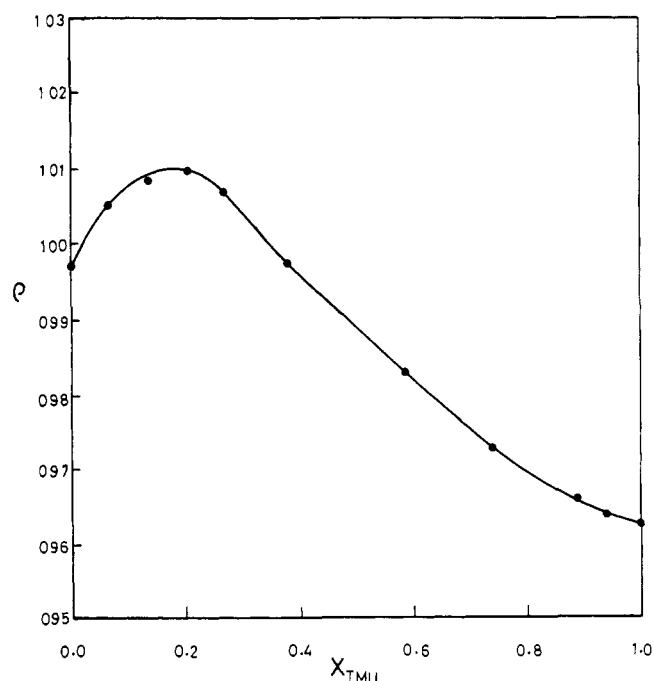
$X_{\text{TMU}}$	$\bar{V} - V_0$	$P_{12}$
0.000	-4.301	17.39
0.0601	-10.501	22.75
0.1302	-8.402	29.00
0.2581	-4.821	40.42
0.3740	-3.601	50.77
0.4580	-2.611	58.27
0.5732	-1.303	68.54
0.6311	-0.921	73.71
0.7390	-0.451	83.35
0.8962	-0.014	97.36
0.9423	-0.006	101.47
1.000	0.000	106.65

Figure 1. Dielectric constants of TMU-H<sub>2</sub>O mixtures at 25 °C.

calibrated Beckman thermometer. All solvent mixtures were made up by weight and vacuum corrected.

## Results

The data for tetramethylurea mixtures are given in Table I at various mole fractions of tetramethylurea. The accuracy of all the dielectric and viscosity data is estimated to be 0.1%, and that of densities to be 0.01%. The dielectric data are plotted

Figure 2. Density of TMU-H<sub>2</sub>O mixtures at 25 °C.

in Figure 1 as a function of mole fraction. Only one measurement at 25 °C was available in the literature. Our value of  $23.60 \pm 0.06$  (1 MHz) compares very well with the Barker and Caruso (1) value of  $23.45 \pm 0.06$  (1 Mz) at 25 °C.

The density data at 25 °C are shown in Figure 2. The partial molar volume obtained from density data is given in Figure 3. The partial molar volume of the solute rapidly decreased to  $\sim 4$  mol %.

Viscosity data at 25 °C are shown in Figure 4.

The molar polarization calculated from

$$P_{12} = \frac{(\epsilon - 1)(X_1 M_1 + X_2 M_2)}{(\epsilon + 2)\rho}$$

is linear in the mole fraction of tetramethylurea through the whole range of solvent compositions as shown in Figure 5.

## Discussion

The densities go through a maximum near mole fraction of 0.2 indicating a TMU(H<sub>2</sub>O)<sub>*n*</sub> complex where *n* is between 3 and 6. The formation of hydrogen bonds leads to an increase in density and vice versa. Since both the formation and rupturing of hydrogen bonds are occurring in this system, these results are not expected. Tetramethylurea acts only as a hydrogen-bond acceptor, since all hydrogens of the amide nitrogen are substituted by CH<sub>3</sub> groups. Thus, it is assumed that tetramethylurea tetrahydrates are formed in aqueous solutions by hydrogen bonding (2). The deviations in properties of the TMU-water mixtures from a linear interpolation between the properties of the pure components result not only from the formation of TMU-water complexes but also from the disruption of the water structure.

The partial molar volumes,  $\bar{V} - V_0$ , were obtained by the intercept method. The volumes of the mixtures at various mole fractions were calculated from the experimental densities. These volumes were then plotted against the mole fraction of TMU-water mixtures, and then the intercept of the tangent to the curve at various mole fractions is equal to  $\bar{V}$  at those mole fractions.  $\bar{V} - V_0$  values were then calculated, where  $V_0$  is the partial molar volume for pure TMU (120.80).

Table II presents calculated values of partial molar volume of the solute, TMU, in the various aqueous mixtures. The sharp

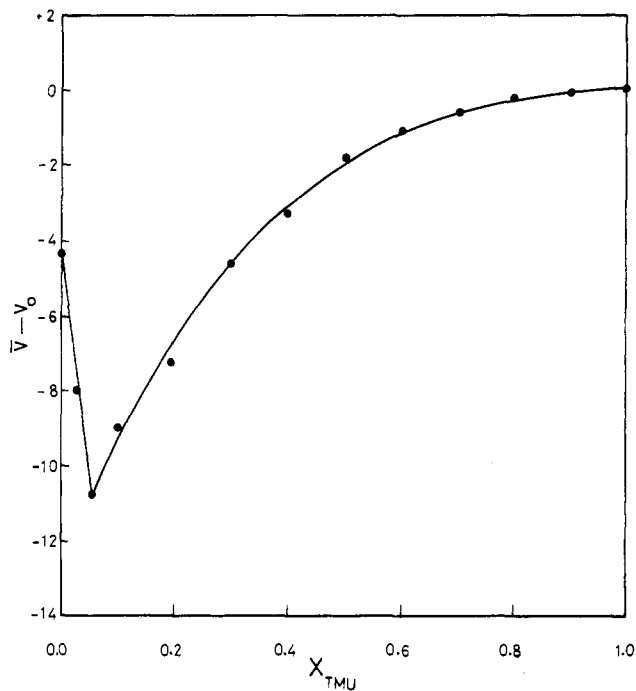


Figure 3. Partial molar volume for TMU-H<sub>2</sub>O mixtures at 25 °C.

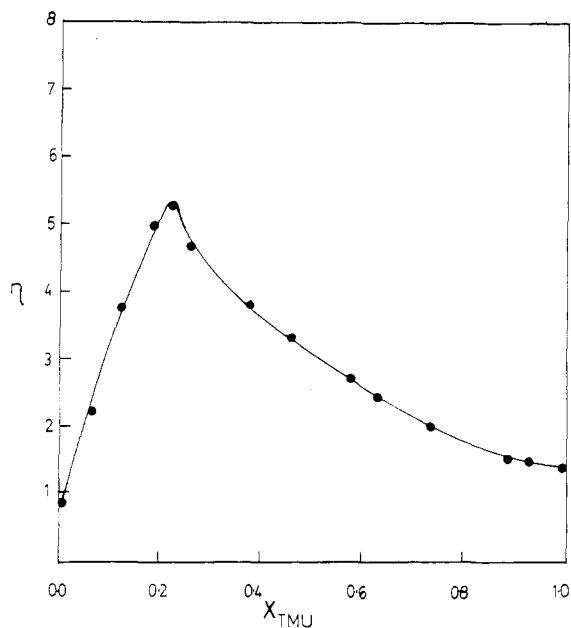


Figure 4. Viscosity of TMU-H<sub>2</sub>O mixtures at 25 °C.

minimum of the partial molar volume vs. mole fraction curve corresponds to sound velocity vs. concentration curves at different temperatures (3). The explanation for such an effect must be looked for in terms of solute-water interactions. The depth of the minimum and the concentration at which it occurs are critically dependent on the temperature and the steric configuration of the alkyl group, and many physical processes in TMU-water mixtures exhibit extreme values at the TMU concentration corresponding to the minimum in the partial molar volume which can therefore be regarded as corresponding to a well-defined structural configuration in the liquid phase.

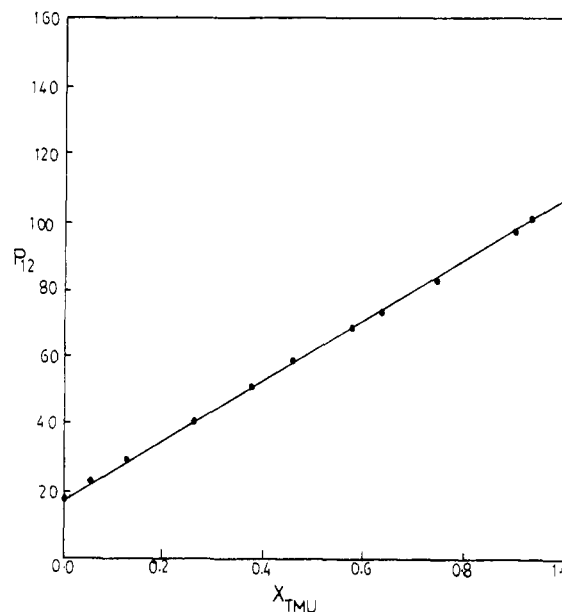


Figure 5. Molar polarization of TMU-H<sub>2</sub>O mixtures.

The viscosities of the TMU-water mixtures are presented in Table I. They are plotted against  $X_{\text{TMU}}$  (Figure 4). The viscosities pass through a maxima near a mole fraction of 0.20. It may appear that small additions of the TMU to water lead to an increase in long-range order of whatever structural entities do exist in water. The maximum corresponds to an increased structural effect which reaches a maximum.

The plot of dielectric constants vs. mole fraction is a smooth curve (Figure 1). There exists only one value in the literature to compare our data. The value of Barker and Caruso compares excellently with our data (1).

Table II presents the calculated values of molar polarization. The linearity of molar polarization vs. mole fraction of TMU (Figure 5) does not imply that the TMU mixtures studied here can be considered ideal noninteracting mixtures.

These examples, viscosities, densities, partial molar volume, and dielectric constants, will suffice to illustrate the anomalous behaviour of dilute aqueous solutions of TMU which cannot be accounted for in terms of changes in molar polarization.

#### Glossary

TMU	tetramethylurea
$M$	molecular weight
$P_{12}$	molar polarization
$\rho$	density, g cm <sup>-3</sup>
$\eta$	viscosity, g cm <sup>-1</sup> s <sup>-1</sup>
$\epsilon$	dielectric constant
$\bar{V} - V_0$	partial molar volume
$X_{\text{TMU}}$	mole fraction of TMU in water

#### Literature Cited

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