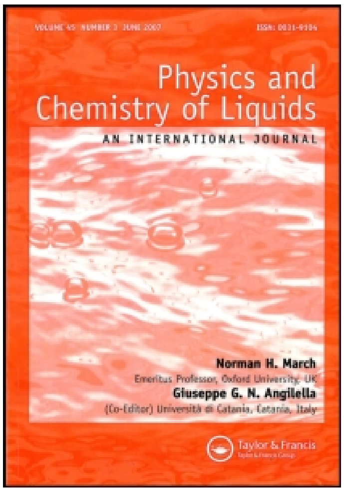

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# An estimation of hydrophilic and hydrophobic interaction of aqueous urea, methylurea, dimethylurea and tetramethylurea from density and apparent molal volume at 30.0°C

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# An estimation of hydrophilic and hydrophobic interaction of aqueous urea, methylurea, dimethylurea and tetramethylurea from density and apparent molal volume at 30.0°C

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Density ($\rho$) for 0.20–1.0 $\mathrm{mol\,kg^{-1}}$ of urea, 1-methylurea, 1,3-dimethylurea and 1,1,3,3-tetramethylurea solutions have been measured at an interval of 0.2 $\mathrm{mol\,kg^{-1}}$. Apparent molal volume ($V_\phi$, $\mathrm{cm^3\,mol^{-1}}$) is calculated from $\rho$ values. Primary data were regressed and extrapolated to zero concentration for the limiting density ($\rho^0$) and limiting apparent molal volume ($V_\phi^0$) values for solute–solvent interactions. $-CH_3$ (methyl) groups of *N*-methylureas weaken hydrophilic interaction and enhance hydrophobic interaction. The value of $\rho^0$ and $V_\phi^0$ reflect the intermolecular forces due to electrostatic charge. The decreasing value of $\rho^0$ and increasing value of $V_\phi^0$ with increasing number of $-CH_3$ groups suggest some weak hydrophilic and strong hydrophobic interactions, so that the structure-breaking effect decreases. It was also found that with increasing concentration, the hydrophilic or hydrophobic interactions become stronger.

**Keywords:** solute–solvent interaction; hydrophilic–hydrophobic interaction; density

## 1. Introduction

Data on physical properties of organic molecules in aqueous solutions has drawn attention to determine the spontaneity of the process [1,2]. Thus, our studies are useful; however, some of the properties of dimethylurea in the context of structural changes are reported [3] along with the influence of alkylureas [4] on CMC (critical micelle concentration: the concentration at which the solution is saturated with micelles) of non-ionic surfactant [5,6]. Data on the role of urea and guanidine hydrochloride in denaturing the proteins are available [7], but no studies involving methylureas could be found [8]. Also, the controversy on the structure making–breaking action of aqueous urea [9] with temperature is a reason for the selection of the current systems. As a result of methyl substitution, hydrophobic interactions hinder the

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hydrogen bonding ability of substituted amino groups, while decreasing the hydrogen bond ability of carbonyl group. However, alkyl substitution of urea explains hydrophobic effects [10–13] and is reported as a structure breaker [14–17] at low temperature [18–22]. Recently, the small angle neutron scattering, NMR relaxation and self-diffusion coefficient studies on aqueous tetramethylurea indicated the presence of hydrophobic interaction [23–24]. In the present study, a series of urea and its methyl derivatives have been taken, and our main interest is to know the effect of methyl groups on hydrophilic or hydrophobic interaction as structure breakers or makers.

## 2. Materials and method

Urea, 1-methylurea, 1,3-dimethylurea (Faluka) and 1,1,3,3-tetramethylurea (Acros Organics) were dried in an oven at 120, 80 and 95°C, respectively, for 24 h and then kept overnight in $P_2O_5$ vacuum dessicator. Tetramethylurea exits in liquid state. The deionised, degassed triple distilled water was used for solutions (w/w). Density of solutions was measured with a double-armed pyknometer at $30.0 \pm 0.01$°C temperature. The temperature was read with a Beckman thermometer, which was calibrated at 30°C at the thermal division of the National Physical Laboratory, New Delhi. Weights of the empty pyknometer and filled with solvent and solution were obtained after drying with tissue paper by using 0.01 mg A&D company, model GR 202 (Japan) digital electronic weighing balance. The weighing balance was calibrated by using calibrated weight (NPL New Delhi). The pyknometer was thermostated for 20 min before weighing.

## 3. Theory

The $\rho$ was calculated as:

$$\rho = \left(\frac{W\mathrm{p} + \mathrm{soln}}{W\mathrm{p} + \mathrm{solv}}\right) \times \rho_1 + 0.0012\left(1 - \left(\frac{W\mathrm{p} + \mathrm{soln}}{W\mathrm{p} + \mathrm{solv}}\right)\right), \tag{1}$$

where $\rho$ is density of solution, $\rho_1$ water density ($0.99565\,\mathrm{g\,cm^{-3}}$) [25], 0.0012 $(1-(W\mathrm{p}+\mathrm{soln}/W\mathrm{p}+\mathrm{solv})$ is the buoyancy correction of air, and $W\mathrm{p}+\mathrm{soln}$, $W\mathrm{p}+\mathrm{solv}$ are weights of solution and solvent with pyknometer, respectively.

$V_\phi$ is computed from $\rho$ by using Equation (2):

$$V_\phi = \frac{1}{\rho}\left(M - \left(\frac{1000}{m}\right)\right)\left(\frac{W\mathrm{p} + \mathrm{soln} - Wp + \mathrm{solv}}{W\mathrm{p} + \mathrm{solv} - W\mathrm{ep}}\right), \tag{2}$$

where $M$ is molar mass, $m$ is molality in $\mathrm{mol\,kg^{-1}}$ and $W$ep the weight of the empty pyknometer.

## 4. Results

The $\rho$ data are regressed with linear Equation (3):

$$\rho = \rho^0 + S_d m, \tag{3}$$

Table 1. The density ($\rho$) and apparent molal volumes ($V_\phi$) of U, MU, DMU, TMU in aqueous solution at $30 \pm 0.01$°C temperature.

| System U | m, mol kg$^{-1}$ solvent | $\rho \pm 0.00002$ (g cm$^{-3}$) | $V_\phi \pm 0.002$ (cm$^{-3}$ mol$^{-1}$) | System MU | m, mol kg$^{-1}$ solvent | $\rho \pm 0.00002$ (g cm$^{-3}$) | $V_\phi \pm 0.002$ (cm$^{-3}$ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| | 0.20 | 0.99637 | 42.4256 | | 0.20 | 0.99600 | 53.3759 |
| | 0.40 | 0.997000 | 42.6272 | | 0.40 | 0.99632 | 58.4648 |
| | 0.60 | 0.99755 | 42.8179 | | 0.60 | 0.99658 | 58.5562 |
| | 0.80 | 0.99799 | 43.0525 | | 0.80 | 0.99681 | 58.6463 |
| | 1.0 | 0.99837 | 43.2422 | | 1.0 | 0.99702 | 58.7252 |
| System DMU | | | | System TMU | | | |
| | 0.20 | 0.99582 | 73.4050 | | 0.20 | 0.99549 | 103.2507 |
| | 0.40 | 0.99598 | 73.4072 | | 0.40 | 0.99558 | 102.6341 |
| | 0.60 | 0.99614 | 73.4098 | | 0.60 | 0.99566 | 102.4315 |
| | 0.80 | 0.99629 | 73.4128 | | 0.80 | 0.99574 | 102.3321 |
| | 1.0 | 0.99654 | 73.4162 | | 1.0 | 0.99581 | 102.2761 |

Notes: U – urea, MU – methylurea, DMU – dimethylurea and TMU – tetramethylurea.

where $\rho^0$ depicts the density values at $m \to 0$ referred, to as limiting densities, and $S_d$ is the slope constant.

The $V_\phi$ values are fitted by Equation (4):

$$V_\phi = V_\phi^0 + S_v m, \tag{4}$$

where $V_\phi^0$ is limiting partial molal volume and $S_v$ denotes slope constant.

## 5. Discussion

Table 1 and Figures 1 and 2 show values of density and apparent molal volume, and Table 2 shows the values of limiting constant of density, $S_d$ slope constant, apparent molal volume and $S_v$ slope constant.

The value of $\rho$ was found in order of urea > methylurea > dimethylurea > tetramethylurea. The increment in density with concentration inferring strengthening of hydrogen bonds also reveals that the increasing number of –$CH_3$ group in methyl derivatives of urea (methylurea, dimethylurea and tetramethylurea) weakens the intermolecular forces between water and methyl derivatives of urea and seems to cause weaker forces than urea. The electron density on –$NH_2$ and >C=O groups keep shifting from one to another; this could probably be rationalised to the fact that urea shows more structure breaking action [26] on water than methyl derivatives of urea.

The order of $S_d$ values is listed as urea > methylurea > dimethylurea > tetramethylurea. Thus, the composition of –$CH_3$ group weakens the intermolecular forces and structure breaking action of urea, and enhances structure making effect. Due to hydrophobic interactions the centre of hydrogen bonding diminishes the caging effect [27]. The higher $S_\mathrm{d}$ values of urea infer slightly stronger structural changes with composition than those of methylurea, dimethylurea and tetramethylurea. Thus, stronger

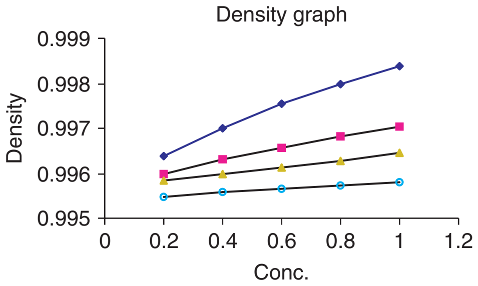

Figure 1. The *Y* axis represents the density and *X* axis represents the concentration of systems. The symbols ■, ■, ▲ and ο indicate U, MU, DMU and TMU, respectively.

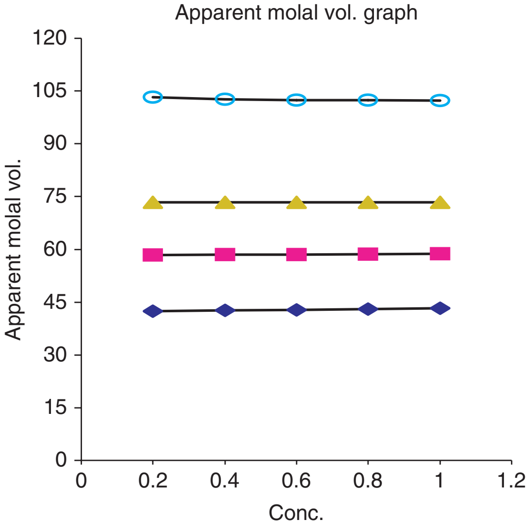

Figure 2. The *Y* axis represents the limiting apparent molal volume density and *X* axis represents the concentration of system. The symbols ■, ■, ▲ and ο indicate U, MU, DMU and TMU, respectively.

Table 2. The regression constants of density $\rho^0$ and apparent molal volume $V_\phi^0$ of U, MU, DMU, TMU in aqueous solution at 30.0 ± 0.01°C temperature.

| System | $\rho^0$ (g cm$^{-3}$) | Sd ($10^3$ g$^2$ cm$^3$ mol$^{-1}$) | $V_\Phi^o$ (cm$^3$ mol$^{-1}$) | S$_v$ (cm$^3$ $10^3$ g mol$^{-2}$) |
|---|---|---|---|---|
| U | 0.9960 | 0.0025 | 42.216 | 1.0292 |
| MU | 0.9958 | 0.0013 | 58.290 | 0.44 |
| DMU | 0.9957 | 0.0008 | 73.402 | 0.0141 |
| TMU | 0.9954 | 0.0004 | 103.26 | −1.1301 |

Notes: U – urea, MU – methylurea, DMU – dimethylurea and TMU – tetramethylurea.

urea–urea interactions exist due to the $>$CO and –$NH_2$ groups over substitution of H, so that –$CH_3$ inhibits the forces due to election releasing and weakens the function of the $>$CO and –$NH_2$.

The value of $V_\phi$ is found in order of tetramethylurea $>$ dimethylurea $>$ methylurea $>$ urea. The $V_\phi$ values increases from urea to tetramethylurea with increments of $-CH_3$ group, which proves the 'principle of additivity' and depicts that in tetramethylurea the weakening of intermolecular force is higher than other ureas, that seems to enhance the force. It concludes that urea does not expand too much, i.e. the atomic motions remain in the influence of the $>$C=O and –$NH_2$ groups of urea. It also proves that the hydrophilic interactions are stronger with urea, while hydrophobic interactions are stronger with –$CH_3$ groups.

The order of $V_\phi^0$ values are listed as tetramethylurea $>$ dimethylurea $>$ methylurea $>$ urea. The increase in the $V_\phi^0$ due to –$CH_3$ depicts a weakening of the intermolecular forces between methylurea derivative and water, and it also concludes that due to –$NH_2$ and $>$C=O polar groups, urea develops stronger interaction with the dipoles of water than methylurea, dimethylurea and tetramethylurea, and denotes that an increase in $V_\phi^0$ with –$CH_3$ results from the decrease in electrostriction of water by causing a larger cohesive force on water.

The positive $V_\phi^0$ values supports a stronger solute–solvent interaction, indicating that urea and its methyl derivatives behave as structure breakers and makers. An increase in $V_\phi^0$ with –$CH_3$ results from a decrease in electrostriction. Fundamentally, the $V_\phi^0$ comprise four contributions, as $V_\phi^0 = (V_{vw} + V_v) + (V_s + V_h)$.

The $V_{vw}$ is the intrinsic/van der Waals volume, $V_v$ is the void volume, $V_s$ is the contribution from solute–solvent interactions and $V_h$ is the hydrophobic hydration. The $(V_{vw} + V_v)$ for aqueous urea remains almost unchanged, so that the change in $(V_s + V_h)$ explains the observed trends in $V_\phi^0$. The value of $(V_s + V_h)$ is given by $(V_{vw} + V_v)_w = (V_{uw} + V_{ww})$ and $(V_s + V_h)_{w+s} = (V_{uw} + V_{uu} + V_{ww})$, where $V_{uw}$, $V_{uu}$ (subscript u indicates ureas) and $V_{ww}$ are the contributions from urea–water, urea–urea or (solute–solute) and water–water interaction respectively, so that the relation becomes $V_\phi^0 = (V_{uw} + V_{uu} + V_{ww})$. Thus a positive value of $V_\phi^0$ is due to the interactions between solute–solvent, solute–solute and solvent–solvent. The contribution from changes in $V_{ww}$ can be taken as relatively small.

Likewise, the $S_v$ values follow the order as, urea $>$ methylurea $>$ dimethylurea $>$ tetra methylurea. The positive value of $S_v$ explains stronger and negative values explain weaker solute–solute interactions; [27] thus the higher positive $S_v$ value of urea indicates, it is a structure breaker, whereas negative $S_v$ values of tetramethylurea indicate that it is a structure maker. The smaller $S_v$ values for methylurea and dimethylurea prove that it behaves as a mild structure breaker.

## 6. Conclusion

The density from urea to tetramethylurea decreases and $V_\phi^0$ increases, which proves that the system attains an order as hydrophilic interactions shift to hydrophobic ones on substitution of the H atom by –$CH_3$ groups.

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