OSMOTIC COEFFICIENTS, DENSITY, AND RELATIVE VISCOSITY DATA FOR AQUEOUS SOLUTIONS OF THIOUREA AT 25°*

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The properties of aqueous solutions of urea have been studied in considerable detail. In several investigations of the binary thermodynamic properties, it was possible to interpret[1-3] the experimental data by assuming the presence of urea dimers in equilibrium with the monomeric unit. An extension of this interpretation has also been used to interpret the behaviour of urea in the ternary system water–urea–sucrose.[3] This note reports osmotic coefficients (cf.[4] for some approximate activity data), densities, and relative viscosities for aqueous thiourea solutions at 25° for comparison with those of urea and discusses them in terms of an association mechanism.

Experimental

The thiourea, a Grade A material from Calbiochem, U.S.A., was once recrystallized from doubly distilled water. One isopiestic experiment was performed with a portion of the sample which had been twice recrystallized, but no difference between the two recrystallizations could be detected. The sodium chloride sample which was used as the reference sample for the isopiestic measurements has been described previously.[5]

All solutions were prepared by weight using doubly distilled water as solvent. The density of solid thiourea and sodium chloride were taken to be $1 \cdot 405$ and $2 \cdot 165$ g cm^{-3}, respectively, while the corresponding molecular weights[6] used for calculating the solution molalities, m, were taken to be $76 \cdot 120$ and $58 \cdot 443$, respectively.

The osmotic coefficients,§ ϕ, were measured by the isopiestic method. The technique as used in this laboratory has been described elsewhere.[5] On all previous occasions cast silver dishes were used to contain the solutions; however, preliminary experiments with silver dishes containing thiourea solutions indicated that there was a marked reaction between the silver and the thiourea. This problem was overcome by using dishes spun from Pallau.‖

§ The *practical* osmotic coefficient, ϕ, is defined for a non-electrolyte by the relation

$$\phi = -\frac{1000}{mM_0}\ln a_0$$

where m is the molality of the solution and a_0 the corresponding activity of the solvent. M_0 is the molecular weight of the solvent.

‖ This alloy contains 80% gold and 20% palladium.

[1] Schellman, J. A., *C. r. Trav. Lab. Carlsberg*, 1955, **29**, 223.

[2] Stokes, R. H., *J. phys. Chem.*, 1965, **69**, 4012.

[3] Ellerton, H. D., and Dunlop, P. J., *J. phys. Chem.*, 1966, **70**, 1831.

[4] Redlich, O., Gable, C. M., Beason, L. T., and Millar, R. W., *J. Am. chem. Soc.*, 1950, **72**, 4161.

[5] Ellerton, H. D., Reinfelds, G., Mulcahy, D. E., and Dunlop, P. J., *J. phys. Chem.*, 1964, **68**, 398.

[6] Using atomic weights compiled in *Inf. Bull. int. Un. pure appl. Chem.*, No. 14b (1961).

The solution densities were measured in triplicate or quadruplicate in matched, Pyrex, 30 cm³ pycnometers using $0 \cdot 997048$ g cm^{-3} for the density of pure water.

The relative viscosities were obtained with an Ubbelohde viscometer with a flow time of approximately 290 sec. A small kinetic energy correction was applied to each result.

Results

Table 1 summarizes the osmotic coefficient data for all the isopiestic experiments performed with thiourea. The concentration of each reference solution of sodium

TABLE 1

OSMOTIC COEFFICIENTS[a] FOR AQUEOUS THIOUREA SOLUTIONS AT 25°

m_{NaCl}	m_{thio}	ϕ	m_{NaCl}	m_{thio}	ϕ
$0 \cdot 1336$	$0 \cdot 2566$	$0 \cdot 967_0$	$0 \cdot 5108$	$1 \cdot 0723$	$0 \cdot 877_4$
$0 \cdot 1353$	$0 \cdot 2597$	$0 \cdot 967_3$	$0 \cdot 5868$	$1 \cdot 2618$	$0 \cdot 858_2$
$0 \cdot 1833$	$0 \cdot 3561$	$0 \cdot 952_6$	$0 \cdot 5912$	$1 \cdot 2730$	$0 \cdot 857_1$
$0 \cdot 1862$	$0 \cdot 3618$	$0 \cdot 952_3$	$0 \cdot 6557$	$1 \cdot 4386$	$0 \cdot 842_7$
$0 \cdot 2565$	$0 \cdot 5066$	$0 \cdot 934_2$	$0 \cdot 6688$	$0 \cdot 4735$	$0 \cdot 839_5$
$0 \cdot 2644$	$0 \cdot 5226$	$0 \cdot 933_3$	$0 \cdot 6981$	$1 \cdot 5513$	$0 \cdot 833_1$
$0 \cdot 3696$	$0 \cdot 7481$	$0 \cdot 909_6$	$0 \cdot 7238$	$1 \cdot 6216$	$0 \cdot 827_0$
$0 \cdot 3730$	$0 \cdot 7556$	$0 \cdot 908_8$			

[a] The osmotic coefficients for sodium chloride are tabulated in Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions." 2nd Edn, p. 476. (Butterworths: London 1959.)

TABLE 2

DENSITIES AND RELATIVE VISCOSITIES OF AQUEOUS SOLUTIONS OF THIOUREA AT 25°

C, mole/1000 cm³; ρ, g cm^{-3}

C	ρ	η_r	C	ρ	η_r
$0 \cdot 09889_5$	$0 \cdot 99914_5$	$1 \cdot 001_6$	$0 \cdot 9450_0$	$1 \cdot 01703_1$	$1 \cdot 022_1$
$0 \cdot 2941_3$	$1 \cdot 00330_2$	$1 \cdot 005_2$	$1 \cdot 2094_3$	$1 \cdot 02257_7$	$1 \cdot 029_7$
$0 \cdot 4851_9$	$1 \cdot 00735_4$	$1 \cdot 009_1$	$1 \cdot 4658_0$	$1 \cdot 02791_2$	$1 \cdot 039_3$
$0 \cdot 6720_1$	$1 \cdot 01129_9$	$1 \cdot 013_3$			

chloride is also included in the table. The experimental osmotic coefficient data may be represented by the equation

$$\phi = 1 - 0 \cdot 135_9 m + 0 \cdot 0184_1 m^2 \qquad m \ll 1 \cdot 6 \qquad (1)$$

with an average deviation of $\pm 0 \cdot 09 \%$. Using equation (1) the activity coefficients, γ, for the molality concentration scale for aqueous solutions of thiourea were computed[5] to be

$$\ln \gamma = -0 \cdot 271_8 m + 0 \cdot 0276_2 m^2 \qquad m \ll 1 \cdot 6 \qquad (2)$$

The densities, ρ, and relative viscosities, η_r, of seven solutions of thiourea are reported in Table 2. The densities may be represented by the relation

$$\rho = 0 \cdot 997048 + 0 \cdot 021311 C - 0 \cdot 000171 C^2 \qquad C \ll 1 \cdot 5 \qquad (3)$$

with an average deviation of $\pm 0 \cdot 0005\%$, while the relative viscosities are reproduced by the equation

$$\eta_r = 1 + 0 \cdot 015_1 C + 0 \cdot 0079_9 C^2 \qquad C < 1 \cdot 5 \qquad (4)$$

with an average deviation of $\pm 0 \cdot 02\%$. The density data are in reasonable agreement with those of Indelli[7] who obtained a limiting apparent molar volume for thiourea of $54 \cdot 79$ cm^3 mole^{-1} compared with the value of $54 \cdot 97$ cm^3 mole^{-1} obtained from equation (3).

Discussion

Previous workers[2,3] have shown that the water activity of urea solutions up to approximately 4 molal can be reproduced by assuming an equilibrium constant, K_N, of dimerization of approximately $1 \cdot 8$. This equilibrium constant, together with further association constants, has also been used to represent the water activities of relatively dilute solutions of the ternary system water–urea–sucrose. Using equations (22) and (24) of ref.[3] we find that an equilibrium constant for dimerization of $8 \cdot 3$ will reproduce the osmotic coefficients (i.e. water activity) of thiourea solutions up to $0 \cdot 5$ molal with an average deviation of approximately $\pm 0 \cdot 15\%$. The deviation* at $1 \cdot 6$ molal is $+3 \cdot 5\%$.

Now, if one compares the relative viscosities of aqueous urea and thiourea solutions at the same molar concentrations, one finds that at one molar the thiourea solution is $1 \cdot 8\%$ less viscous than the corresponding urea solution. However, if the above equilibrium constants of dimerization are correct for urea and thiourea, one would expect the reverse situation, since both the partial molar volume and the molar volume of thiourea are greater than the corresponding values for urea. One speculative way of explaining the experimental differences in the viscosities of these solutions is to assume that the equilibrium constant of dimerization is correct as reported above for thiourea, and then to assume that urea is *both* dimerized and hydrated in aqueous solutions.† Thus, if one arbitrarily assumes a hydration number of unity for urea, then an equilibrium constant of $3 \cdot 2_0$ will represent the osmotic coefficients of urea up to $1 \cdot 2$ molal with an average deviation of less than $\pm 0 \cdot 1\%$. The deviation at 2 molal is $+0 \cdot 4\%$.

Acknowledgment

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* This may indicate that higher polymers than dimers are important in solutions more concentrated than $0 \cdot 5$ molal. However, if one considers the percentage of the saturation concentrations as a reduced concentration scale, the equilibrium constant of dimerization for thiourea covers a larger range than the corresponding constant for urea.

† At 25° urea is more than ten times more soluble in water than thiourea. This fact would suggest that hydration of urea is not an unreasonable assumption.

[7] Indelli, A., *Annali Chim.*, 1963, **53**, 605.