er-bridge atoms from 600 to 400 cm⁻¹. Also interference in the area of the free symmetry and asymmetric valence oscillations of the SO₂ (1345 and 1335 cm⁻¹, respectively) can be observed. The average deviation of the experimental partial pressures from the calculated values (eq 6) and parameters of Table VI) is $\pm 0.4\%$.

Solubility of Hydrogen Sulfide and Carbonyl Sulfide

The solution properties of the investigated solvents for H₂S and COS, both less polar than SO₂ (dipole moments (debyes): SO₂, 1.63; H₂S, 0.97; and COS, 0.71), show only gradual differences and differ only slightly in temperature behavior. The experimental data for the partial pressure of the dissolved gas p_i as a function of the mole fraction in the solution x_i fit Henry's law according to eq 1 within the investigated concentration range ($x_{H_2S}^{max} = 0.16$ and $x_{COS}^{max} = 0.10$), with correlation coefficients better than 0.99.

Registry No. H2S, 7783-06-4; SO2, 7446-09-5; COS, 463-58-1; HO-(C2H4O)3,H, 112-27-6; HO(C2H4O)xH, 25322-68-3; CH3(OCH2CH2)3OCH3, 112-49-2; O((CH2CH2O)2CH3)2, 143-24-8; CH3O(CH2CH2O)CHCH3CH3, 71495-18-6; O:P(OC2H5)3, 78-40-0; O:P(OC3H7)3, 513-02-0; O:P(O(CH2)3-CH₃)₃, 126-73-8; O:P(OCH₂CH(CH₃)₂)₃, 126-71-6; O:P(O(CH₂)₈CH₂CH₃)₂OH, 298-07-7; O:P(O(CH₂)₆CH₂CH₃)₃, 78-42-2; O:P(OC₆H₄CH₃)₃, 1330-78-5; H₂CH(CH₃)₂)₂, 84-69-5; (C₆H₄CO₂)(C₁₀H₁₁)₂, 26761-40-0; (C₆H₄CO₂)(C₂H₄-OC4H9)2, 117-83-9; (C6H4CO2)(C2H4OCH3)2, 36339-61-4; tricyclodecanedimethanol, 26896-48-0.

Literature Cited

- Albright, L. F.; Shannon, P. T.; Yu, Sun-Nieu; Chueh, Ping Lin. Chem. Eng. Prog., Symp. Ser. 1963, 59, 66–74.
 Peter, S. German Patent DE-OS 1948253, April 1971.
- Judd, D. K. Hydrocarbon Process. 1978, 57, 122-4.
- (4) Härtel, G. Dissertation, Universität Erlangen-Nürnberg, 8520 Erlangen, FRG. 1980.
- (5) Cooper, D. F.; Smith, J. W. J. Chem. Eng. Data 1974, 19, 133-6.
 (6) Hirai, M.; Odello, R.; Shimamura, H. Chem. Eng. (N.Y.) 1972, 79, 78-9.
- (7)Davis, J. C. *Chem*. *Eng*. (*N*.*Y*.) **1972**, *79*, 66–8. Deschamps, A.; Renault, P. US Patent 3 598 529, 1971.
- (8)
- "Technische Anleitung zur Reinhaltung der Luft". Umwelt 1974, No. (9) 33.6.
- (10) Langner, G. "Vorschriften zur Reinhaltung der Luft"; Bundesanzeiger-Verlag: 5000 Köln 1, FRG, 1983.
- Block, U. VDI-Ber. 1978, No. 253, 71-6. (11)
- Dolezalek, F. Z. Phys. Chem. 1908, 64, 727.
 Prausnitz, J. M. "Molecular Thermodynamics of Fluid-Phase Equilibria"; (13) Prentice-Hall: Englewood Cliffs, NJ, 1969; p 331

- Marquardt, D. W. J. Soco Ind. Appl. Math. 1963, 11, 431–41.
 Gestrich, W.; Reinke, L. Chem.-Ing.-Tech. 1963, 55, 629.
 Petkovic, Dj. J. Inorg. Nucl. Chem. 1963, 30, 603.
 Albertson, N. F.; McReynolds, J. P. J. Am. Chem. Soc. 1943, 65, 657. 1687-91.

Received for review December 12, 1983. Accepted June 27, 1984.

Thermodynamics of Nucleoside–Solvent Interactions. Uridine and Cytidine in Pure Water and in 3 m Ethanol between 17 and 37 $^\circ$ C

John H. Stern* and Lisa P. Swanson

Department of Chemistry, California State University-Long Beach, Long Beach, California 90840

Enthalpies of solution of the nucleosides uridine and cytidine in water and in 3 m ethanol were measured between 17 and 37 °C. From these were calculated positive enthalpies of transfer from water to 3 m ethanol. Heat capacities of solution obtained from the temperature variation of the enthalpies of solution and combined with estimated heat capacities of the solids yielded partial molal heat capacities of the nucleosides. In pure water these are 96 and 93 cal/(mol deg) for uridine and cytidine, respectively. The small difference between the values indicates that the partial molal heat capacities in pure water are almost independent of the interchange of the base groups uracll and cytosine. In 3 m ethanol the values are 98 and 84 cal/(mol deg) and show that ethanol tends to reduce the leveling effect observed in water.

Introduction

The structural stabilities of DNA and RNA depend in part on the interaction of their repeating nucleoside components with the solvent, and thermodynamic studies may provide useful information on these poorly understood systems. This is the second contribution on the thermodynamics of nucleosidesolvent interactions in agueous solutions and follows a study of enthalpies and heat capacities of solution of inosine and adenosine in pure water, ΔH° , and in 1 *m* ethanol, ΔH , from 25 to 35 °C (1). The present work is concerned with the enthalpies of solution of the major pyrimidine nucleosides uridine and cytidine in water and in 3 m ethanol between 17 and 37 °C. The results allow calculation of enthalpies of transfer from



water to the mixed aqueous solvent, $\Delta \bar{H},$ from $\Delta \bar{H}$ = ΔH - ΔH° .

Enthalpies of transfer to aqueous ethanol reflect the complicated disturbing effects of ethanol on the solvent properties of water (2). It may be noted that the presence of alcohol also has a profound effect on the double-helical structure of DNA, since one form is favored in water, transforming to another form in aqueous alcohol (3).

The temperature variation of the enthalpies of solution yields the heat capacity of solution in pure water, ΔC_{p}° , in 3 m ethanol, ΔC_p , and the heat capacity of transfer $\Delta \bar{C}_p = \Delta C_p$ - ΔC_{ρ}° , where $\Delta \bar{C}_{\rho}$ in part reflects the difference in the ordering or structuring of solvent molecules around the solutes upon transfer.

Experimental Section

The calorimeter and calorimetric procedure have been described elsewhere (4). Uridine and cytidine were obtained from

Table I. Enthalpies of Solution

	t,		ΔH° and ΔH ,	t,		ΔH° and ΔH ,	
	°C	runs	cal/mol	°C	runs	cal/mol	
Uridine–H ₂ O				Cytidine–H ₂ O			
	17	7	4980 ± 39	18	7	4991 ± 46	
	25	5	5197 ± 24	25	6	5296 ± 26	
	30	10	5414 ± 23	30	6	5320 ± 50	
	37	13	5625 ± 42	37	6	5525 ± 36	
Uridine–3 <i>m</i> Ethanol				Cytidine–3 <i>m</i> Ethanol			
	17	7	6600 ± 19	18	5	6538 ± 22	
	25	7	6795 ± 13	25	9	6733 ± 27	
	30	12	7037 ± 47	30	8	6828 ± 34	
	37	13	7384 ± 70	37	6	6908 ± 34	

Table II. Enthalpies of Transfer at 25 °C and Heat Capacities of Solution and Transfer at 17-35 °C

solute	∆Ħ,ª kcal/mol	$\Delta C_p \circ b$	$\Delta C_p{}^b$	$\Delta ilde{C}_p,^c ext{ cal}/ \ (ext{mol deg})$
uridine	1.60	35	37	2
cytidine	1.46	28	22	-6

^a Overall experimental error is ± 0.05 kcal/mol, based on the rounded-off value of the square root of the sums of the squares of the standard deviations of the means of ΔH° and ΔH . ^bOverall experimental error is $\pm 8 \text{ cal/(mol deg)}$, based on the average difference between worst and chosen slopes of Figures 1 and 2. ^c Values are almost negligible, based on overall experimental errors.^t



Figure 1. Enthalples of solution of uridine: (a) in H₂O; (b) in 3 m ethanol.

Sigma. Ethanol was AR grade and the water was distilled and deionized. The overall range was 0.4-0.9 mmol of nucleoside dissolved in 180 g of solvent. The average of four or more measurements is reported as the enthalpy of solution at infinite dilution, with uncertainties equal to the standard deviation of the means.

Results and Discussion

Table I and Figures 1 and 2 show the means of the enthalpies of solution for both nucleosides in pure water and in 3 m ethanol. Table II reports enthalpies of transfer at 25 °C, $\Delta \bar{H}$, together with heat capacities of solution ΔC_{ρ} °, ΔC_{ρ} , and transfer, $\Delta \bar{C}_{\rho}$, based on the slopes of the linear enthalpies of solution from Figures 1 and 2.

It is of interest to compare the separate enthalpies of transfer of the appropriate free base and ribose with the total $\Delta \overline{H}$ of the nucleoside. Preliminary measurements show that the enthalpies of transfer of cytosine and ribose (5) are 0.7 and 1.0 kcal/mol, respectively, with their sum 0.2 kcal/mol higher than that of cytidine. The positive difference may be due to changes in size, conformation, and solvation of the two constituents relative to the single nucleoside. The large positive values of ΔH may reflect in part the energy difference of solute cavity formation in pure water and in the more structured aqueous ethanol (6).



Figure 2. Enthalpies of solution of cytidine: (a) in H₂O, (b) in 3 m ethanol

The heat capacities of transfer $\Delta \tilde{C}_{\rho}$ of each nucleoside are almost negligible, within the limits of the overall experimental error. If the ordering of the solvents around the nucleosides contributes to their partial molal heat capacities \bar{C}_{ρ}° in water or \bar{C}_p in 3 *m* ethanol ($\Delta \bar{C}_p = \bar{C}_p - \bar{C}_p^{\circ}$), this result indicates that the difference is very small, whatever the detailed nature of ordering in the two solvent media may be. Heat capacities of the solid nucleosides, C(s), are needed in order to calculate the partial molal heat capacities, where $\bar{C}_{p}^{\circ} = \Delta C_{p} + C(s)$, and $\bar{C}_{o} = \Delta C_{o} + C(s)$. In the absence of reported values, C(s) was estimated by Benson's method of group additivities (7). Since these group contributions at 25 °C are for the ideal gas, the following estimates include corrections for loss of translational and rotational degrees of freedom of the gas offset by the gain of vibrational degrees of freedom of the solids. When a group value was not available, a tabulated one for a similar group was substituted. The method was tested on solid uracil, one of the very few related substances for which the experimental C(s)is available (8), with estimated and experimental values of 29 and 28 cal/(mol deg), respectively. Kopp's law, which was used previously with inosine and adenosine (1), gives 34 cal/(mol deg). The estimated values of C(s) are 61 and 65 cal/(mol deg) for uridine and cytidine, yielding 96 and 93 cal/(mol deg) for their partial molal heat capacities in pure water, respectively. This difference between values of \bar{C}_{p}° is negligible, and thus partial molal heat capacities in pure water seem to be almost independent of the bonding and functional group differences of the two nucleosides. In 3 m ethanol the partial molal heat capacities for uridine and cytidine are 98 and 87 cal/(mol deg). The somewhat larger difference shows that ethanol appears to reduce the leveling effect on the heat capacities in pure water. with similar behavior observed earlier with inosine and adenosine (1).

Acknowledgment

We express our appreciation to Professor H. E. O'Neal for helpful discussions.

Registry No. Uridine, 58-96-8; cytidine, 65-46-3; ethanol, 64-17-5.

Literature Cited

- Stern, J. H.; Oliver, D. J. Chem. Eng. Data 1980, 25, 221.
 Franks, F.; Ives, D. J. G. Q. Rev., Chem. Soc. 1966, 20, 1.
 Drew, H. R.; Dickerson, R. E. J. Mol. Biol. 1981, 151, 535.
 Stern, J. H.; Goeders, B. L.; Withers, G. L.; Wujs, S. L. J. Chem. Eng. Data 1979, 14, 566.
- Stern, J. H.; Hubler, P. M. J. Phys. Chem. 1984, 88, 1680.
- (6) Stern, J. H.; Lowe, E. J. Chem. Eng. Data 1978, 4, 341.
 (7) Benson, S. W. "International Kinetics"; Wiley: New York, 1968.
 (8) Kilday, M. V. J. Res. Natl. Bur. Stand. (U.S.) 1978, 83, 547.

Received for review December 19, 1983. Accepted July 23, 1984. We are grateful for financial assistance by the Long Beach California State University Research Committee and the California Heart Association.