

Figure 1. Relation between the logarithms of solubilities (S) of 1,10-phenanthroline and related compounds and their molecular volumes (V^*): 1, bpy; 2, phen; 3, 5-Br(phen); 4, 5-NO₂phen; 5, 4,7-Me₂phen; 6, 3,4,7,8-Me₄phen.

electron releasing or withdrawing effects. Rather they depend on the size of the molecule (3), with solubility decreasing with increasing size. Indeed a plot of logarithm of solubility against molecular volume is linear for all the phenanthrolines and 2,2'-bipyridyl (Figure 1).

The concentration of a saturated aqueous solution of 3,4,7,8-tetramethyl-1,10-phenanthroline at 323.2 K is $3.9 \times 10^{-5} \text{ mol dm}^{-3}$. From this and the solubility at 298.2 K (Table III), an estimate of about -2.6 kJ mol^{-1} can be made for its enthalpy of solution. This value is very similar to those established for 1,10-phenanthroline itself and for 2,2'-bipyridyl. The very different solubilities of these compounds therefore must reflect markedly different entropies of solution.

Acknowledgment

We are grateful to the Royal Society for the award of a grant-in-aid for the purchase of the spectrophotometer used in this investigation.

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Received for review May 3, 1977. Accepted February 28, 1978.

The Apparent Molal Volume and Adiabatic Compressibility of Some Organic Solutes in Water at 25 °C

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The apparent molal volumes and adiabatic compressibilities of aqueous solutions of some ureas, thioureas, acetamide, thioacetamide, dioxane, sugars, and succinic acid have been determined at 25 °C from precise density and sound measurements. The sugars have large negative values for the infinite dilution partial molal adiabatic compressibilities, $\bar{K}_s^\circ \sim -16.2 (\pm 3.3) \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ (of the same order of magnitude as amino acids) suggesting that these molecules are highly hydrated. Positive values of $\bar{K}_s^\circ \sim 7.0 (\pm 2.6) \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ are observed for dioxane, acetamide, thioacetamide, tetramethylurea, and succinic acid suggesting very little hydration for these molecules in water. For urea, 1,3-dimethylurea, and thiourea $\bar{K}_s^\circ \sim -1.9 (\pm 1.5) \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1} \text{ bar}^{-1}$ suggesting these molecules are slightly hydrated. The degree of hydration increases with the number of functional groups which can hydrogen bond with water molecules. The substitution of sulfur for oxygen causes a decrease in hydration.

Introduction

An understanding of solute-water interaction of organic solutes having $>\text{C}=\text{O}$ and $>\text{NH}_2$ functional groups is of paramount

importance in problems concerning helix-random coil transitions (6) and conformational stability of polypeptides (13). Many experiments (1-5, 7, 8, 10-12, 14-18, 23-29, 35, 36, 38, 39, 41-44) on the physicochemical properties of ureas, amides, and sugars indicate that the interactions with water molecules occur through hydrogen bonding with $>\text{NH}$, $>\text{C}=\text{O}$, and $-\text{OH}$ groups. The stability of $>\text{C}=\text{O} \cdots \text{HOH}$, $>\text{NH} \cdots \text{OH}_2$ and $\text{H}_2\text{O} \cdots \text{HOH}$ hydrogen bonds has also been suggested by ab initio molecular orbital calculations for water-water dimers and amide-water systems (21). To better understand the hydration of ureas, thiourea, acetamide, thioacetamide, dioxane, succinic acid, and sugars we have determined the apparent molal volumes and apparent molal adiabatic compressibilities for some of these solutes in water at 25 °C.

Experimental Section

Materials. Urea, 1,3-dimethylurea, 1,1,3,3-tetramethylurea, and D-ribose (Eastman), 1,4-dioxane and acetamide (Fisher reagent grade), dextrose, sucrose, thiourea, and thioacetamide (Baker analyzed), and succinic acid (Aldrich) were used without further purification. All solutions were prepared by weight with Millipore Super Q ion-exchanged water. Tetramethylurea solutions were made by weight dilutions of the stock solution. All weights were vacuum corrected.

Table I. Relative Sound Velocities, Relative Densities, Apparent Molal Compressibilities, and Apparent Molal Volumes of Some Ureas, Thiourea, Acetamide, Thioacetamide, Dioxane, Sugars, and Succinic Acid

m	Δu^a	$10^3 \Delta d^b$	$10^4 \phi_K^c$	ϕ_V^d	m	Δu^a	$10^3 \Delta d^b$	$10^4 \phi_K^c$	ϕ_V^d
Urea									
0.052 35	1.36	0.831	-2.95	44.23	0.611 50	15.46	9.433	-2.43	44.30
0.088 15	2.38	1.396	-3.54	44.24	0.794 20	19.86	12.140	-2.24	44.32
0.148 60	3.87	2.347	-2.95	44.25	0.890 80	22.14	13.550	-2.13	44.33
0.522 50	13.33	8.097	-2.58	44.29	1.100 60	27.00	16.568	-1.92	44.36
1,3-Dimethylurea									
0.067 611	3.68	0.559	-0.64	80.01	0.735 010	36.36	5.982	1.78	79.71
0.177 253	9.38	1.462	0.20	79.96	0.910 463	44.06	7.376	2.17	79.63
0.369 828	19.14	3.037	0.69	79.87	1.154 928	54.56	9.294	2.63	79.54
0.414 837	21.32	3.403	0.87	79.85					
1,1,3,3-Tetramethylurea									
0.010 330	0.74	0.006	8.82	115.92	0.264 632	18.06	0.278	9.75	115.42
0.042 334	3.04	0.030	8.31	115.79	0.539 495	35.07	0.754	10.85	115.01
0.060 806	4.33	0.041	8.72	115.82	0.703 619	44.45	1.094	11.48	114.81
0.083 046	5.88	0.063	8.87	115.73	1.030 254	61.70	1.863	12.61	114.47
0.099 891	7.11	0.078	8.57	115.71					
Thiourea									
0.052 514	1.51	1.117	-2.28	54.89	0.493 352	13.68	10.232	-1.59	54.92
0.088 533	2.52	1.889	-2.19	54.78	0.726 041	19.84	14.855	-1.31	54.94
0.180 506	5.14	3.821	-2.15	54.84	0.854 946	23.18	17.315	-1.11	55.02
0.326 427	9.14	6.852	-1.84	54.85					
Thioacetamide									
0.031 389	0.94	0.278	7.70	66.42	0.161 310	4.47	1.416	9.04	66.43
0.049 260	1.41	0.436	8.49	66.42	0.492 930	12.90	4.239	9.81	66.42
0.082 814	2.35	0.731	8.68	66.42	0.663 890	17.09	5.645	10.00	66.42
Acetamide									
0.023 821	0.66	0.086	6.56	55.61	0.245 548	6.89	0.882	6.30	55.58
0.049 322	1.48	0.178	5.29	55.60	0.486 740	13.38	1.738	6.54	55.56
0.069 874	2.07	0.252	5.46	55.60	0.735 190	19.72	2.608	6.82	55.53
0.095 438	2.79	0.344	5.70	55.60	0.992 053	26.11	3.494	7.01	55.51
0.121 310	3.44	0.437	6.21	55.60	1.275 837	32.77	4.456	7.26	55.48
1,4-Dioxane ^e									
0.097 779	3.83	0.718	9.30	80.93	1.362 646	43.25	9.213	12.77	80.82
0.210 587	8.09	1.536	9.66	80.91	1.485 665	46.20	9.958	13.07	80.82
0.327 532	12.34	2.372	10.02	80.89	2.254 797	61.80	14.293	14.83	80.84
0.553 223	20.06	3.950	10.67	80.87	3.298 884	76.43	19.333	16.92	80.91
0.790 259	27.56	5.556	11.31	80.85					
Dextrose									
0.053 681	3.32	3.638	-17.47	112.11	0.675 660	40.98	42.598	-15.00	112.47
0.105 818	6.52	7.134	-17.21	112.07	0.808 458	48.86	50.217	-14.55	112.54
0.140 974	8.69	9.469	-17.17	112.06	0.962 752	57.77	58.732	-13.91	112.69
0.184 168	11.29	12.293	-16.77	112.17	1.209 553	72.04	71.930	-13.20	112.74
0.466 105	28.47	30.130	-15.86	112.28					
D-Ribose									
0.026 418	1.34	1.450	-12.48	95.22	0.192 810	9.62	10.414	-11.75	95.25
0.043 235	2.19	2.367	-12.38	95.28	0.332 749	16.65	17.723	-11.57	95.30
0.070 653	3.56	3.859	-12.27	95.26	0.440 710	21.80	23.204	-11.01	95.39
0.096 394	4.81	5.257	-11.92	95.21					
Sucrose									
0.011 191	1.00	1.465	-17.87	211.32	0.108 072	9.66	13.848	-17.10	211.48
0.023 278	2.15	3.038	-19.53	211.39	0.209 906	18.81	26.309	-16.36	211.65
0.041 604	3.70	5.408	-17.39	211.41	0.316 509	28.34	38.780	-15.48	211.82
0.058 851	5.41	7.623	-19.05	211.40	0.437 506	39.17	52.256	-14.55	212.05
0.083 649	7.64	10.776	-18.49	211.44	0.644 328	57.33	73.810	-12.91	212.36
Succinic Acid									
0.047 230	1.29	1.672	4.56	82.69	0.236 700	6.29	8.206	5.29	82.88
0.065 640	1.77	2.321	4.80	82.68	0.296 790	7.81	10.232	5.48	82.91
0.081 960	2.21	2.888	4.89	82.75	0.400 830	10.40	13.674	5.79	82.98
0.181 010	4.87	6.312	5.03	82.84					

^a Units in $m s^{-1}$. ^b Units in $g cm^{-3}$. ^c Units in $cm^3 mol^{-1} bar^{-1}$. ^d Units in $cm^3 mol^{-1}$. ^e The density and ϕ_V results are taken from Desnoyers et al. (23).

Procedure. The densities were measured at 25 °C to $\pm 3 \times 10^{-6} g cm^{-3}$ with a vibrating flow densimeter (Sodev, Inc.). A detailed description of the densimeter is given elsewhere (40). The values of $\Delta d = d - d_0$, where d and d_0 are the densities of the solution and water, are listed in Table I. The system was calibrated with N_2 gas and ion-exchanged water using the

densities of Kell (22). Standard seawater solutions (32) were used to determine the accuracy (± 3 ppm) of the system.

The sound velocities were measured at 2 MHz to a precision of $\pm 0.02 m s^{-1}$ using a "sing around" sound velocimeter (Nusonic, Inc.). The procedure has been described elsewhere (31). The system was calibrated with pure water using the sound

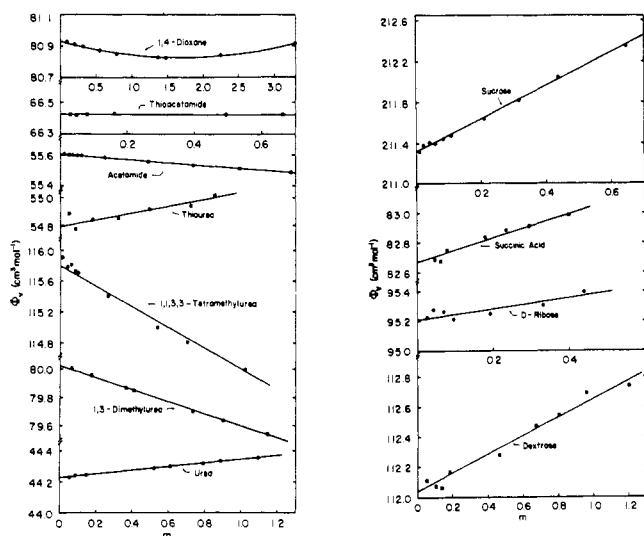


Figure 1. Plot of ϕ_v vs. m for some ureas, thiourea, acetamide, thioacetamide, 1,4-dioxane, succinic acid and sugars in water at 25 °C. The ϕ_v values for 1,4-dioxane were taken from Desnoyers et al. (23).

velocities of Del Grosso and Mader (9). The accuracy (± 0.1 m s⁻¹) has been determined by measuring the speed of sound in seawater solutions (37).

The relative sound velocities (Δu) of the aqueous solutions at 25 °C are listed in Table I and were determined from the frequency measurements using

$$\Delta u = u - u_0 = \frac{(f - f^0)u_0}{f^0(1 - f\tau)} \quad (1)$$

where u and u_0 are the speed of sound in the solution and in water, f and f^0 are the pulse repetition frequencies in solution and water, and τ is the electronic delay time. The value of τ was determined by the calibration with (Millipore Super Q) ion-exchanged water at various temperatures.

The thermostated bath systems regulating the densimeter and sound velocimeter were set to ± 0.002 °C using a platinum resistance thermometer (calibrated by the National Bureau of Standards) and a G-2 Mueller bridge.

Results and Discussion

The apparent molal volumes, ϕ_v , and the adiabatic apparent molal compressibilities, $\phi_{K(S)}$, were calculated respectively from the density, d , and adiabatic compressibility, β_s , of the solution using the equations

$$\phi_v = \frac{M}{d} + \frac{(d_0 - d)10^3}{mdd_0} \quad (2)$$

and

$$\phi_{K(S)} = \frac{1000(\beta_s d^0 - \beta_s^0 d)}{mdd_0} + \frac{\beta_s M}{d} \quad (3)$$

where d_0 is the density of water, m is the molality, M is the molecular weight of the solute and $\beta_s^0 = 44.7735 \times 10^{-6}$ bar⁻¹ is the adiabatic compressibility for water. The adiabatic compressibilities (β_s) of the aqueous solutions at 25 °C were determined from the sound speeds (u) using

$$\beta_s = 1/u^2 d \quad (4)$$

The densities and sound velocities were determined from the relative densities and sound speeds given in Table I using $d_0 = 0.997045$ g cm⁻³ (22) and $u_0 = 1496.69$ m s⁻¹ (9). The values ϕ_v and $\phi_{K(S)}$ are listed in Table I, and are plotted respectively vs. m in Figures 1 and 2. The curves represent the least-squares lines.

The values of ϕ_v and $\phi_{K(S)}$ were least-squares fitted to the equations

$$\phi_v = \phi_v^0 + S_v m \quad (5)$$

and

$$\phi_{K(S)} = \phi_{K(S)}^0 + S_{K(S)} m \quad (6)$$

where $\phi_v^0 = \bar{V}^0$ and $\phi_{K(S)}^0 = \bar{K}^0$ are, respectively, the infinite dilution partial molal volumes and adiabatic partial molal compressibilities, and S_v and $S_{K(S)}$ are the experimental slopes. For 1,4-dioxane eq 5 has one additional term in m (i.e., $B_v m^2$). The values of ϕ_v^0 , $\phi_{K(S)}^0$, S_v , and $S_{K(S)}$ for the compounds studied at 25 °C are listed in Table II along with the standard deviations (σ) of the fit. The densities and ϕ_v 's of 1,4-dioxane were calculated from the work of Desnoyers et al. (23). We

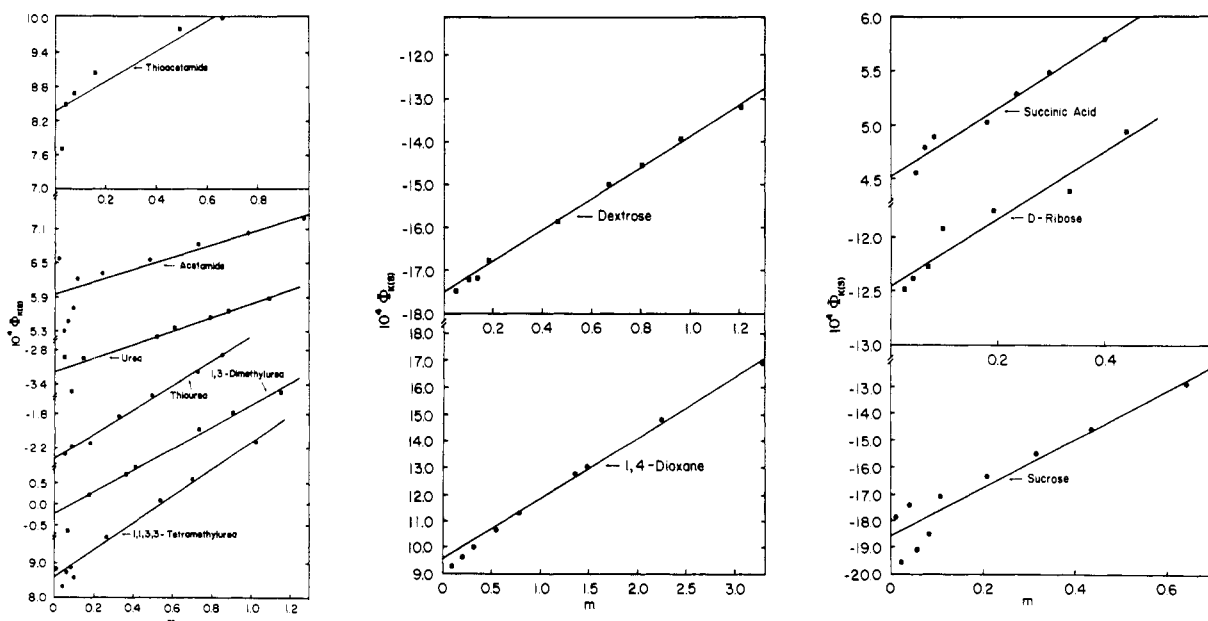


Figure 2. Plot of $\phi_{K(S)}$ vs. m for some ureas, thiourea, acetamide, thioacetamide, 1,4-dioxane, succinic acid, and sugars in water at 25 °C.

Table II. Limiting Values of Apparent Molal Volumes, ϕ_V° , Adiabatic Compressibilities, $\phi_{K(S)}^\circ$, S_V , and $S_{K(S)}$ for Some Ureas, Thioureas, Acetamides, Thioacetamides, Sugars, and Succinic Acid in H_2O at 25 °C

Compound	ϕ_V° ^a	S_V	b_V	σ^b	$10^4\phi_{K(S)}^\circ$ ^c	$10^4S_{K(S)}$	$10^4\sigma^d$
Urea	44.23	0.117		0.001	-3.20	1.19	0.08
1,3-Dimethylurea	80.03	-0.428		0.004	-0.24	2.57	0.13
1,1,1,3-Tetramethylurea	115.80	-1.331		0.060	8.58	3.98	0.15
Thiourea	54.79	0.242		0.020	-2.34	1.44	0.03
Thioacetamide	66.42	-0.004		0.002	8.35	2.63	0.24
Acetamide	55.60	-0.097		0.002	5.94	1.07	0.18
1,4-Dioxane ^e	80.94	-0.172	0.061	0.003	9.58	2.26	0.15
Dextrose	112.04	0.609		0.040	-17.50	3.63	0.08
D-Ribose	95.21	0.367		0.030	-12.46	3.15	0.12
Sucrose	211.32	1.627		0.020	-18.56	8.96	0.50
Succinic acid	82.67	0.808		0.020	4.52	3.17	0.05

^a Units in $cm^3 mol^{-1}$. ^b Standard error in ϕ_V , $cm^3 mol^{-1}$. ^c Units in $cm^3 mol^{-1} bar^{-1}$. ^d Standard error in $\phi_{K(S)}$, $cm^3 mol^{-1} bar^{-1}$. ^e The ϕ_V° , S_V , and b_V values are taken from Desnoyers et al. (23).

Table III. A Comparison of the Infinite Dilution Partial Molal Volumes for Some Ureas, Acetamides, Sugars, and Succinic Acid Obtained in This Study with Literature Values

Compound	ϕ_V° , $cm^3 mol^{-1}$	
	This work	Literature
Urea	44.23	44.24, ^a 44.40 ^b
1,3-Dimethylurea	80.03	80.04 ^a
1,1,1,3-Tetramethylurea	115.80	115.30 ^a
Thiourea	54.79	
Thioacetamide	66.42	
Acetamide	55.60	55.82 ^c
Dextrose (α -D-glucose)	112.04	112.2 ^d 111.9, ^{e,f} 111.5 ^g
D-Ribose	95.21	95.3 ^h
Sucrose	211.32	211.49, ⁱ 211.12, ^b 210.2, ^d 209.9, ^e 211.0 ^{a,f}
Succinic acid	82.67	82.94, ^{j,k} 82.9 ^l

^a Reference 38. ^b Reference 41. ^c Reference 15. ^d Reference 42. ^e Reference 27. ^f Reference 36. ^g Reference 35. ^h Reference 12. ⁱ Reference 14. ^j References 4, 5. ^k Reference 19. ^l Reference 20.

note the $\phi_{K(S)}^\circ$ change sign being negative for urea, dimethylurea, thiourea, dextrose, ribose, and sucrose, and positive for tetramethylurea, acetamide, thioacetamide, dioxane, and succinic acid. The largest negative values of $\phi_{K(S)}^\circ$ (-12.46 to -18.56 $cm^3 mol^{-1} bar^{-1}$) are observed for the sugars and largest positive values (4.52 to 9.58 $cm^3 mol^{-1} bar^{-1}$) are observed for the amides, tetramethylurea, dioxane, and succinic acid. The infinite dilution apparent molal volumes of the compounds reported in the literature (4, 5, 12, 14, 15, 19, 20, 27, 35, 36, 38, 41, 42) are compared with our results in Table III. Our results are in good agreement with the literature values. Since compressibility data are lacking in the literature, a comparison of the $\phi_{K(S)}^\circ$ values cannot be made at this time.

The ϕ_V and $\phi_{K(S)}$ of ureas, amides, dextrose, ribose, sucrose, and succinic acid are linear functions of the molal concentration (Figures 1 and 2). All the solutes investigated have positive $S_{K(S)}$ slopes. The largest values of $S_{K(S)}$ are observed for molecules (dextrose, ribose, sucrose, and succinic acid) with functional groups which hydrogen bond with water. The S_V slopes are negative for dimethylurea, tetramethylurea, thioacetamide, acetamide, and dioxane, and are positive for the sugars, succinic acid, urea, and thiourea. The largest S_V values are observed for the sugars and succinic acid. Thioacetamide shows a very small negative S_V slope (Table II).

The infinite dilution values for the partial molal volume, \bar{V}° , and compressibility, \bar{K}° , of these solutes can be examined by using a simple hydration model

$$\bar{V}^\circ(\text{solute}) = \bar{V}^\circ(\text{int}) + \bar{V}^\circ(\text{elect}) \quad (7)$$

$$\bar{K}^\circ(\text{solute}) = \bar{K}^\circ(\text{int}) + \bar{K}^\circ(\text{elect}) \quad (8)$$

where $\bar{V}^\circ(\text{int})$ and $\bar{K}^\circ(\text{int}) = -\partial\bar{V}^\circ(\text{int})/\partial P$ are the intrinsic partial molal volume and compressibility (which contains terms related to the size of the solute and to packing effects); $\bar{V}^\circ(\text{elect})$ and $\bar{K}^\circ(\text{elect}) = -\partial\bar{V}^\circ(\text{elect})/\partial P$ are the electrostriction partial molal

volume (the decrease in volume due to hydration). Since a reasonable estimate of $\bar{V}^\circ(\text{int})$ cannot be made at present, it is not possible to determine $\bar{V}^\circ(\text{elect})$ for the solutes studied. Since the effect of pressure on $\bar{V}^\circ(\text{int})$ for crystalline solutes is small (30), one might expect $\bar{K}^\circ(\text{int})$ for organic solutes to be near zero. For charged solutes $\bar{K}^\circ(\text{elect}) \approx \bar{K}^\circ(\text{solute})$ is negative and it is possible to calculate hydration numbers from (34, 37)

$$n_H = -\bar{K}^\circ(\text{elect})/\bar{V}_B^\circ\beta_B^\circ \quad (9)$$

where \bar{V}_B° is the molar volume and β_B° is the compressibility of water. For most charged organic solutes (for example, amino acids) (32) \bar{K}° is negative while for uncharged solutes \bar{K}° is small and positive. These results indicate that $\bar{K}^\circ(\text{int})$ is small and positive ($\sim 5 \times 10^{-4} cm^3 mol^{-1} bar^{-1}$) for uncharged organic solutes. If we assume that $\bar{K}^\circ(\text{int})$ is the same for the various ureas, our results indicate that hydration decreases with increasing methyl substitution. The substitution of sulfur for oxygen also causes a decrease in hydration. The large negative values of \bar{K}° for the sugars indicate that they are highly hydrated (the same order of magnitude as amino acids) (34). The number of water molecules hydrated to the sugars increases with an increasing number of -OH groups as one would suspect. The positive values of \bar{K}° for dioxane, thioacetamide, acetamide, tetramethylurea, and succinic acid suggest that they are only slightly hydrated. Since one would expect the effect of pressure on the size of the molecules to be small, this increase in \bar{V}° is probably due to a decrease in packing volumes at higher pressures. As more \bar{K}° data becomes available for other organic solutes we should be able to make an estimate of how $\bar{K}^\circ(\text{int})$ depends upon the structure of the organic molecules.

In summary, highly hydrated molecules have large negative molal compressibilities (\bar{K}°) and slightly hydrated molecules have small positive molal compressibilities. In all instances, the values of \bar{K}° decrease with the number of functional groups in a

molecule which can hydrogen bond with water molecules.

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Received for review October 27, 1977. Accepted February 17, 1978. The authors wish to acknowledge the support of the Office of Naval Research (N00014-75-C-0173) and the Oceanographic Section of the National Science Foundation (OCE73-00351-A01) for this study.

Enthalpies of Combustion and Formation of 3-Methylisoxazole and 5-Methylisoxazole

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The enthalpies of combustion of 3-methylisoxazole and 5-methylisoxazole were measured by precision oxygen-bomb calorimetry. The following values, based on the mass of sample burned, are reported for the standard enthalpy of combustion, $\Delta H_c^\circ(298.15\text{ K})/\text{kcal mol}^{-1}$, of these compounds in the liquid state: 3-methylisoxazole, -546.00 ± 0.14 ; and 5-methylisoxazole, -545.65 ± 0.17 . Enthalpies of vaporization, determined calorimetrically, are 3-methylisoxazole, $9.51 \pm 0.05\text{ kcal mol}^{-1}$, and 5-methylisoxazole, $9.48 \pm 0.04\text{ kcal mol}^{-1}$. These data were used to calculate standard enthalpies of formation for the gaseous compounds, $\Delta H_f^\circ(\text{g})$, which are: 3-methylisoxazole, $8.52 \pm 0.16\text{ kcal mol}^{-1}$, and 5-methylisoxazole, $8.14 \pm 0.18\text{ kcal mol}^{-1}$. Throughout this paper $\text{cal}_{\text{th}} = 4.184\text{ J}$ and $\text{atm} = 101.325\text{ kPa}$.

Introduction

The enthalpies of combustion of liquid 3-methylisoxazole and 5-methylisoxazole were measured as part of a continuing study of the thermodynamic properties of nitrogen compounds. This paper presents basic experimental data for the enthalpy-of-combustion measurements of two methylisoxazoles. Values of the enthalpy of combustion were used to derive values of the enthalpy of formation in the liquid state. Enthalpies of vaporization of the two compounds were determined by direct calorimetric measurements. Values of the enthalpy of formation in the gaseous state were derived.

Experimental Section

Apparatus and Procedures. The apparatus and experimental procedures have been described (2). The temperature rise was measured by quartz thermometry. The internal volume of the bomb was 0.342 dm^3 . For every experiment approximately 1 g of water was added to the bomb, and the bomb was flushed and charged to 30 atm with pure oxygen. Fragile flexible ampules of borosilicate glass confined the liquid samples. The samples were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied. Ignition was accomplished by discharging a large capacitor through a 10-cm length of no. 44 Brown and Sharpe gauge platinum wire in contact with a small piece ($\approx 4\text{ mg}$) of Whatman No. 1 filter paper. The electrical ignition energy was calculated by noting the charge on the capacitor before and after discharge. The value of $\Delta E_c^\circ/M$ for the filter paper was taken as $-(4118 \pm 10)\text{ cal g}^{-1}$ (8). The extent of combustion was based on the mass of sample. All calculations, including conversion of time and temperature measurements to initial and final temperature, correction for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer (11). The computer program followed the procedure of Hubbard et al. (3).

Materials. 3-Methylisoxazole was obtained from Aldrich Chemical Co., Inc., and had a claimed purity of 98%. 5-Methylisoxazole was obtained from Roche Chemical Division, Hoffmann-La Roche, Inc. Both compounds were further purified by drying over calcium hydride and distilling under reduced