

Apparent molar heat capacities and volumes of unsaturated heterocyclic solutes in aqueous solution at 25°C¹

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Measurements at 25°C with flow calorimeters and densimeters have led to heat capacities and densities of aqueous solutions of 15 unsaturated heterocyclic compounds containing nitrogen. From the results of these measurements we have obtained apparent molar heat capacities and volumes of the solutes. Extrapolations to infinite dilution have led to corresponding standard state apparent and partial molar heat capacities and volumes, which have been analyzed in terms of atomic and group additivity relationships.

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On a déterminé les capacités calorifiques et les densités de 15 composés hétérocycliques non saturés contenant de l'azote en solution aqueuse en effectuant des mesures à 25°C à l'aide d'un calorimètre et d'un densimètre dynamiques. A partir des résultats de ces mesures, on a obtenu les capacités calorifiques molaires apparentes et les volumes molaires apparents des solutés. Par extrapolation à dilution infinie, on obtient les capacités calorifiques et les volumes molaires partiels et apparents dans l'état standard qui sont analysés en fonction des relations d'additivité atomique et de groupe.

[Traduit par le journal]

Introduction

Thermodynamic properties of aqueous solutions of nonelectrolytes have been of interest for a long time. Most early research in this area focussed on free energies (solubilities, activity coefficients, etc.), followed by increasing interest in the temperature dependences of free energies and thence the corresponding enthalpies. More recently, there has been substantial interest in such properties as volumes and heat capacities, which are first and second derivatives of free energies with respect to pressure and temperature, respectively. Reasons for these latter interests are generally of two kinds. (i) There is frequently interest in measuring thermal and volumetric properties of aqueous solutions so that the derived thermodynamic functions (\bar{C}_p^0 and \bar{V}^0 in this paper) can be used for thermodynamic calculations of properties of solutions at different temperatures and pressures. (ii) Thermodynamic properties, including partial molar heat capacities and volumes, are proving to be useful probes for investigating relationships between structures of solute molecules, solute-solvent interactions, and the "structures" of aqueous solutions.

Various atomic and group additivity schemes for both partial molar heat capacities and volumes

have been proposed and used in connection with both (i) and (ii) above.

In this paper we report the results of our calorimetric and volumetric measurements at 25°C on aqueous solutions of 15 unsaturated nitrogen heterocyclic compounds. Results are given in forms that are appropriate to interests (i) and (ii) above and are also discussed briefly in relation to additivity schemes.

Experimental

All of our heat capacity measurements have been made with Picker flow calorimeters of the type that has been described in several publications (1-3) from the Université de Sherbrooke. Operation of the calorimeters has been checked as recently recommended (4). Densities of solutions were measured with flow densimeters that have been described previously (5). The results of all measurements refer to 25.0°C.

Compounds from Aldrich were purified by distillation (pyridazine and quinoline), by vacuum sublimation (2,2'-bipyridyl, 4,4'-bipyridyl, *sym*-triazine, quinazoline, imidazole, pyrimidine, and 4-phenylpyrimidine), or by repeated recrystallizations from appropriate solvents (quinoxaline, pyrazole, and benzimidazole). Aldrich gold label compounds (pyrazine, benzotriazole, and 1,10-phenanthroline) were used as received. Purities of all compounds were tested by melting point and by gas chromatography. In addition, water content of each sample was determined by Karl Fischer titration.

Most solutions were prepared from known masses of organic solute and freshly deionized and deaerated water. A few other solutions were prepared by dilution of these original solutions. Finally, the pH of each solution was measured to ensure that acid-base reactions between solute and water were negligible.

¹Research reported here was done during 1978 when Octavian Enea was on leave in Sherbrooke and Lethbridge from the Université de Poitiers.

Results

Results of measurements with the Picker flow calorimeter are heat capacities per unit volume of solution, which we express in terms of $\text{J K}^{-1} \text{cm}^{-3}$. Combinations of these heat capacities with the densities permits calculation of specific heat capacities expressed in terms of $\text{J K}^{-1} (\text{g of solution})^{-1}$. These latter heat capacities are then used in obtaining the desired apparent molar heat capacities that we represent by ϕ_c and express in terms of $\text{J K}^{-1} \text{mol}^{-1}$. Similarly, densities lead to apparent molar volumes that we represent by ϕ_v and express in terms of $\text{cm}^3 \text{mol}^{-1}$. For these calculations of apparent molar properties we have used equations of the type

$$[1] \quad \phi_Y = [Y(\text{solution}) - n_1 Y_1^0]/n_2$$

in which the symbols have the following meaning: Y is the extensive property (heat capacity or volume here) of a specified quantity of solution, n_1 is the amount (moles) of solvent in this specified quantity of solution, Y_1^0 is the property (heat capacity or volume) of 1 mol of pure solvent, and n_2 is the amount (moles) of solute in the specified quantity of solution.

To obtain apparent molar heat capacities and apparent molar volumes at infinite dilution, where apparent molar properties become identical with the corresponding partial molar properties, we have fitted our experimental results² for dilute solutions to the equations

$$[2] \quad \phi_c = \phi_c^0 + B_c m$$

and

$$[3] \quad \phi_v = \phi_v^0 + B_v m$$

in which $\phi_c^0 = \bar{C}_p^0$ and $\phi_v^0 = \bar{V}^0$ are the desired properties at infinite dilution and B_c and B_v are adjustable parameters. Our derived ϕ_c^0 , B_c , ϕ_v^0 , and B_v values are listed in Table 1. We estimate that total uncertainties (chemicals, calorimetry, densities, extrapolations) in our ϕ_c^0 and ϕ_v^0 values are about $\pm 5 \text{ J K}^{-1} \text{mol}^{-1}$ and $\pm 0.5 \text{ cm}^3 \text{mol}^{-1}$ for most solutes; uncertainties for the less soluble compounds are a little larger. In Table 1 we also list values for the same quantities obtained previously (6) for aqueous pyridine.

²A complete set of the experimental results is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ont., Canada K1A 0S2.

Discussion

Earlier investigators have proposed various additivity schemes for ϕ_c^0 (6–18) and ϕ_v^0 (6, 15–24). These additivity schemes, all useful in various ways, were developed in relation to the ϕ_c^0 and ϕ_v^0 values that were then available; hence these earlier schemes are not generally applicable to unsaturated heterocyclics of the sort under consideration here for the first time.










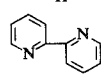
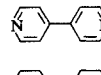
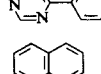



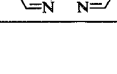
The ϕ_c^0 values listed in Table 1 for isomers show that atomic group additivity schemes that do not take into account the arrangements of these atoms or groups cannot account very accurately for the experimental results. For example, the ϕ_c^0 values for aqueous pyrazine, pyrimidine, and pyridazine should be the same on the basis of any simple atomic or group additivity scheme. But the experimental ϕ_c^0 values cover a range of $16 \text{ J K}^{-1} \text{mol}^{-1}$. Experimental ϕ_c^0 values for the isomeric imidazole and pyrazole differ by $28 \text{ J K}^{-1} \text{mol}^{-1}$ while those for the isomeric 2,2'-bipyridyl, 4,4'-bipyridyl, and 4-phenylpyrimidine cover a range of $52 \text{ J K}^{-1} \text{mol}^{-1}$. Finally, the ϕ_c^0 values for the isomeric quinazoline and quinoxaline differ by $27 \text{ J K}^{-1} \text{mol}^{-1}$. All of these ranges and differences are larger than likely uncertainties ($\pm 5 \text{ J K}^{-1} \text{mol}^{-1}$) in the ϕ_c^0 values.

We also consider the ϕ_c^0 values for isomers in another way, as follows. For the isomeric pyrazine, pyrimidine, and pyridazine we calculate the average $\phi_c^0 = 210.1 \text{ J K}^{-1} \text{mol}^{-1}$ and find that differences between experimental values and this average amount to 7.3, 1.2, and $8.6 \text{ J K}^{-1} \text{mol}^{-1}$. Similar calculations for other isomers lead to similar average values and thence to differences between experimental values and averages for sets of isomers. The average of all these 10 differences is $13.1 \text{ J K}^{-1} \text{mol}^{-1}$, which is more than twice the uncertainty assigned to most of our ϕ_c^0 values.

Similar considerations of ϕ_v^0 values lead to the following. The largest range of values for any set of isomers is $1.31 \text{ cm}^3 \text{mol}^{-1}$ for the imidazole–pyrazole pair. The average of the various differences calculated from ϕ_v^0 values as described in the preceding paragraph amounts to $0.39 \text{ cm}^3 \text{mol}^{-1}$, which is less than the uncertainty ($\pm 0.5 \text{ cm}^3 \text{mol}^{-1}$) assigned to most individual ϕ_v^0 values.

Our consideration in the three preceding paragraphs show that a simple additivity scheme for ϕ_v^0 values might fit the experimental results with an average accuracy comparable to the experimental accuracy, while a similar additivity scheme for ϕ_c^0 values cannot fit with an average accuracy better than about two or three times the uncertainty in the

TABLE 1. Parameters for eqs. [2] and [3]

Solute	ϕ_c^0 J K ⁻¹ mol ⁻¹	B_C J K ⁻¹ mol ⁻² kg	ϕ_v^0 cm ³ mol ⁻¹	B_V cm ³ mol ⁻² kg
Pyridine 	305.7	-41.2	77.5	-1.4
Pyrazine 	217.4	-23	70.8 ₂	-0.0 ₇
Pyrimidine 	211.3	-17.1	70.3 ₃	0.11
Pyridazine 	201.5	-9.2	70.4 ₂	-0.16
<i>sym</i> -Triazine 	13.9	-113	54.7 ₉	0
Imidazole 	182.1	-12	59.9 ₅	0.1 ₂
Pyrazole 	210.2	-11.6	62.2 ₆	0.10
Benzimidazole 	302.8	-23	98.53	0
Benzotriazole 	314.8	192	94.49	-0.0 ₃
2,2'-Bipyridyl 	498.3	-424	134.29	-5
4,4'-Bipyridyl 	445.9	-621	133.21	6
4-Phenylpyrimidine 	461.9	-1023	134.09	~-28
Quinoline 	419.6	-156	115.53	1.4
Quinazoline 	365.1	-26	108.48	-3.1
Quinoxaline 	391.7	-65	109.16	-2.7
1,10-Phenanthroline 	537.9	-1495	142.42	~-12

individual values. Because the considerations described so far have not been concerned with relationships between ϕ_c^0 and ϕ_v^0 values for different sets of isomers or those compounds that are not isomeric with others listed in Table 1, we now turn to testing two specific additivity schemes.

We first consider atomic additivity schemes for ϕ_c^0 and ϕ_v^0 values according to which

$$[4] \quad \phi_v^0 = n_C(C)_Y + n_H(H)_Y + n_N(N)_Y$$

Here n_C , n_H , and n_N represent the numbers of indicated atoms in the molecule of interest while $(C)_Y$, $(H)_Y$, and $(N)_Y$ represent the contributions of the

indicated atoms to the molar ϕ_v^0 values. We have chosen to apply eq. [4] in the form

$$[5] \quad \phi_v^0/n_N = (N)_Y + (n_C/n_N)(C)_Y + (n_H/n_N)(H)_Y$$

which permits convenient multiple linear regression for the desired $(C)_Y$, $(H)_Y$, and $(N)_Y$ values.

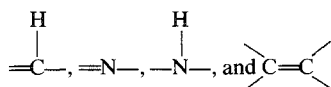
Application of eq. [5] to ϕ_v^0 values leads to $(C)_Y$, $(H)_Y$, and $(N)_Y$ equal to 4.86, 9.45, and 5.34 cm³ mol⁻¹, respectively. We have used these values in eq. [4] to calculate ϕ_v^0 values for all solutes listed in Table 1 and then have found that the average magnitude of the difference between calculated and experimental values is 2.07 cm³ mol⁻¹, which is

about four times the uncertainty assigned to most individual ϕ_V^0 values.

Similar application of eq. [5] to ϕ_C^0 values leads to $(C)_C$, $(H)_C$, and $(N)_C$ equal to 13.11, 48.71, and $-21.13 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. We have used these values in eq. [4] to calculate ϕ_C^0 values for all solutes listed in Table 1 and then have found that the average magnitude of the difference between calculated and experimental values is $27.41 \text{ J K}^{-1} \text{ mol}^{-1}$, which is about five times the uncertainty assigned to most individual ϕ_C^0 values.

We thus see that this simple atomic additivity scheme works about as well (or badly) for ϕ_C^0 values as for ϕ_V^0 values for our unsaturated heterocyclic solutes, fitting both sets of results with an average accuracy corresponding to about five times the uncertainty assigned to most experimental values.

We also consider simple group additivity schemes as follows, based upon



groups that we henceforth represent by (CH), (N), (NH), and (CC), with subscripts Y , C , and V as used previously. Instead of applying multiple linear regression to all of the ϕ_V^0 values in Table 1 to obtain "best" values of the four parameters $(\text{CH})_Y$, $(\text{N})_Y$, $(\text{NH})_Y$, and $(\text{CC})_Y$ simultaneously, we have applied the following stepwise procedure. Application of

$$[6] \quad \phi_V^0/n_N = (\text{N})_Y + (n_{\text{CH}}/n_N)(\text{CH})_Y$$

to ϕ_V^0 values for the first five compounds listed in Table 1 permits simple least squares evaluation of desired $(\text{CH})_Y$ and $(\text{N})_Y$ group values. Next, average $(\text{NH})_Y$ values are obtained by application of

$$[7] \quad (\text{NH})_Y = \phi_V^0 - 3(\text{CH})_Y - (\text{N})_Y$$

to results listed in Table 1 for aqueous imidazole and pyrazole. Finally, average $(\text{CC})_Y$ values are obtained from ϕ_V^0 values for the last nine compounds listed in Table 1.

The procedure described in the paragraph above has led to $(\text{CH})_C$, $(\text{N})_C$, $(\text{NH})_C$, and $(\text{CC})_C$ values equal to 71.99, -47.69 , 27.87, and $10.80 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. We have used these group contribution values to calculate ϕ_C^0 values for all solutes listed in Table 1 and have then found that the average magnitude of the difference between calculated and experimental values is $31.56 \text{ J K}^{-1} \text{ mol}^{-1}$, which is about six times the uncertainty assigned to most individual ϕ_C^0 values.

Application of a similar procedure for ϕ_V^0 values leads to $(\text{CH})_V$, $(\text{N})_V$, $(\text{NH})_V$, and $(\text{CC})_V$ values

equal to 14.52, 5.45, 11.60, and $8.99 \text{ cm}^3 \text{ mol}^{-1}$. The average magnitude of differences between resulting calculated and experimental ϕ_V^0 values is $1.87 \text{ cm}^3 \text{ mol}^{-1}$, which is a little less than four times the uncertainty assigned to most individual ϕ_V^0 values.

This group additivity scheme fits the ϕ_V^0 and ϕ_C^0 results with an average accuracy of about four and six times the uncertainties of individual experiment results.

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1. P. PICKER, P.-A. LEDUC, P. R. PHILIP, and J. E. DESNOYERS. *J. Chem. Thermodyn.* **3**, 631 (1971).
2. J.-L. FORTIER, P.-A. LEDUC, and J. E. DESNOYERS. *J. Solution Chem.* **3**, 323 (1974).
3. G. PERRON, J.-L. FORTIER, and J. E. DESNOYERS. *J. Chem. Thermodyn.* **7**, 1177 (1975).
4. J. E. DESNOYERS, C. DE VISSER, G. PERRON, and P. PICKER. *J. Solution Chem.* **5**, 605 (1976).
5. P. PICKER, E. TREMBLAY, and C. JOLICOEUR. *J. Solution Chem.* **3**, 377 (1974).
6. O. ENEA, P. P. SINGH, and L. G. HEPLER. *J. Solution Chem.* **6**, 719 (1977).
7. S. CABANI, G. CONTI, A. MARTINELLI, and E. MATTEOLI. *J. Chem. Soc. Faraday Trans. I*, **69**, 2112 (1973).
8. S. CABANI, G. CONTI, and E. MATTEOLI. *J. Solution Chem.* **5**, 125 (1976).
9. S. J. GILL and I. WADSÖ. *Proc. Natl. Acad. Sci. USA*, **73**, 2955 (1976).
10. N. NICHOLS and I. WADSÖ. *J. Chem. Thermodyn.* **7**, 329 (1975).
11. S. J. GILL, N. F. NICHOLS, and I. WADSÖ. *J. Chem. Thermodyn.* **8**, 445 (1976).
12. N. NICHOLS, R. SKÖLD, C. SPINK, J. SUURKUUSK, and I. WADSÖ. *J. Chem. Thermodyn.* **8**, 1081 (1976).
13. J. P. GUTHRIE. *Can. J. Chem.* **55**, 3700 (1977).
14. S. CABANI, G. CONTI, and E. MATTEOLI. *J. Chem. Soc. Faraday Trans. I*, **74**, 2408 (1978).
15. O. KIYOHARA, G. PERRON, and J. E. DESNOYERS. *Can. J. Chem.* **53**, 2591 (1975).
16. C. JOLICOEUR and G. LACROIX. *Can. J. Chem.* **54**, 624 (1976).
17. J. C. AHLUWALIA, C. OSTIGUY, G. PERRON, and J. E. DESNOYERS. *Can. J. Chem.* **55**, 3364 (1977).
18. G. PERRON and J. E. DESNOYERS. *Fluid Phase Equil.* **2**, 239 (1979).
19. S. CABANI, G. CONTI, and L. LEPORI. *J. Phys. Chem.* **78**, 1030 (1974).
20. J. T. EDWARD and P. G. FARRELL. *Can. J. Chem.* **53**, 2965 (1975).
21. S. TERASAWA, H. ITSUKI, and S. ARAKAWA. *J. Phys. Chem.* **79**, 2345 (1975).
22. F. SHAHIDI, P. G. FARRELL, and J. T. EDWARD. *J. Solution Chem.* **5**, 807 (1976).
23. F. J. MILLERO, A. LO SURDO, and C. SHIN. *J. Phys. Chem.* **82**, 784 (1978).
24. F. SHAHIDI and P. G. FARRELL. *J. Chem. Soc. Faraday Trans. I*, **74**, 858 (1978); **74**, 1268 (1978).