

HEATS OF SOLUTION IN WATER OF SALTS OF THE TYPE R_4NBr AND $R_2R'_2NBr$

L. H. Blanco^{1*}, Yina P. Salamanca¹ and E. F. Vargas²

¹Departamento de Química Universidad Nacional de Colombia, Bogota, D.C., Colombia

²Departamento de Química, Universidad de Los Andes, Bogota, D.C., Colombia

The tetra-alkyl-ammonium halides are electrolytes that have special characteristics due to the presence of hydrocarbon chains. They have been used as model compounds to study hydrophobic interactions due to their fairly large solubility in water and because of the possibility of change in the length and geometry of the alkyl chains. In this work the solution enthalpies of tetra-*n*-butyl-ammonium bromide, tetra-*sec*-butyl ammonium bromide, tetra-*iso*-butyl-ammonium bromide and di-*n*-butyl-di-*sec*-butyl ammonium bromide were determined at 298.15 K at concentrations between 0.001 and 0.01 mol kg⁻¹. The experimental method used was isoperibol calorimetry. The results were extrapolated fitting the experimental data by least squares to obtain the solution enthalpies at infinite dilution. The hydrocarbon chains studied were so chosen because the tetra-*n*-butyl-ammonium ion is considered to be a structure maker for water. The results show that the geometry of the ion and of the hydrocarbon chains play an important role in the behavior properties of the solutions.

Keywords: dilute solutions, enthalpy of solution, geometric isomers, tetra-butyl-ammonium salts

Introduction

The tetra-alkyl-ammonium salts have played an important role when the interactions between hydrocarbon chains and water are studied. In a way they serve as model compounds of more complicated molecules such as peptides and proteins. They provide a way of getting significant concentrations of hydrocarbons in aqueous solutions since they are quite soluble. Also, the length and geometry of one or several chains can be easily changed, allowing for the isolation of the effect of their contribution.

In this laboratory salts of the symmetric R_4NX and asymmetric $R_2R'_2NX$ and RR'_3NX have been studied by different experimental techniques [1–3].

Several times the contributions to the thermodynamic properties have been assigned as functions of the number of carbon atoms in the cations. Also, the length of the chains has been associated with the structural effects of the salts in water. Even though there is a not complete agreement on this point the tetra-methyl-ammonium cation is considered to be a ‘structure breaker’, the tetra-ethyl-ammonium cation to have very little structural effect, the tetra-propyl-ammonium cation is slightly ‘structure maker’ and the tetra-butyl-ammonium cation is clearly a ‘structure maker’ [4–8]. In this work the heat of solution of tetra-*n*-butylammonium bromide (*n*-Bu₄NBr), tetra-*sec*-butylammonium bromide (*sec*-Bu₄NBr), tetra-*iso*-butylammonium bromide (*iso*-Bu₄NBr) and di-*n*-butyl-di-*sec*-butylammonium (*n*-Bu₂*sec*-Bu₂NBr) bromide were determined in water at 298.15 K, us-

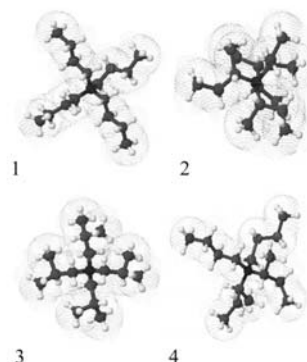


Fig. 1 Molecular structures of 1– *n*-Bu₄NBr, 2 – *sec*-Bu₄NBr, 3 – *iso*-Bu₄NBr and 4– *n*-Bu₂*sec*-Bu₂NBr

ing the isoperibol calorimetry technique [9]. The molecular structures are shown in Fig. 1. The enthalpy behavior of some tetra-alkyl-ammonium salts has been reported in literature [1, 10, 11] most of the data in this paper is new.

Experimental

Materials and methods

The tetra-*n*-butyl-ammonium bromide was purchased from the SIGMA Co. and used after recrystallization from methanol-acetone mixtures and kept in a desiccator. The other salts were synthesized and purified in this laboratory using methods already reported [12–14]. The purity was determined by bromide titration and found to be near 100±1% in all cases.

* Author for correspondence: lhblancoc@unal.edu.co

Also, NMR of ^1H and ^{13}C was used to be sure that no impurities were present in significant quantities and that the structures of the ions were the needed.

The calibration compounds KCl and THAM (tris(hydroxymethyl)aminomethane) were Merck proanalysis products. They were powdered and then dried at 423 K for 24 h [15] their purity was around 99.8%.

Lastly, water was doubly distilled according to literature recommendations [16] and had a conductivity of $2\ \mu\text{S cm}^{-1}$.

The calorimetric work was performed using an isoperibolic apparatus that has been previously described in [9]. It consists basically of a Dewar flask, an electrical stirrer, a sample cell, an electric heater and systems for control and measurement of temperature. The measurable signal was read each second using a Hewlett Packard Agilent 34401-A multimeter with 61/2 digit resolution. The data were recorded using an interphase with a regular PC. The data acquisition software was Agilent Intuilink for Multimeters, version 1.0. The calorimetric determinations are reproducible to $\pm 0.3\%$.

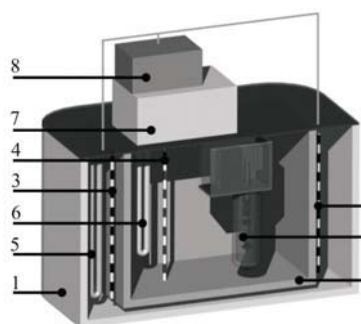


Fig. 2 The complete experimental setup. 1 – External tank (cooling system); 2 – internal tank; 3 – external tank temperature sensor; 4 – internal tank temperature sensor; 5 – external tank heater; 6 – internal tank heater; 7 – internal tank temperature control; 8 – external tank temperature control; 9 – solution isoperibol calorimeter (Fig. 2 for details)

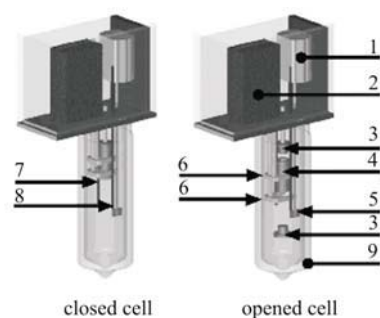


Fig. 3 The solution isoperibol calorimeter. 1 – Sample cell; 2 – teflon caps; 3 – servomotor; 4 – Dewar vessel; 5 – thermistor probe; 6 – electrical heater; 7 – stirrer; 8 – electric motor; 9 – cap openers

All solutions were prepared by mass using an Ohaus Analytical Plus balance that has an uncertainty of $\pm 1 \cdot 10^{-5}$ g in the range of interest. The schematic diagrams of the isoperibol solution calorimeter and of the sample cell are shown in Figs 2 and 3.

Results and discussion

The results of the calibration runs of KCl in H_2O at 298.15 K and the molar enthalpies of protonation THAM–0.1 M HCl are given in the Table 1. They are compared with literature values. As it is seen they agree within experimental uncertainty. Table 2, shows the results for the ΔH_s at different concentrations and at 298.15 K for the salts studied. Figure 4 is the plot for the solution enthalpy of the symmetrical salts as a function of concentration. Figure 5 corresponds to the results for the $n\text{-Bu}_2\text{sec-Bu}_2\text{NBr}$. The extrapolated values of enthalpy at zero concentration are given in Table 3.

In literature were found three comparable values -8.45 [20], -8.58 ± 0.06 [19] and -8.58 ± 0.04 for $n\text{-Bu}_4\text{NBr}$ [11]. Previous work is summarized in Table 4.

The effect of the anion has been studied by several workers and some of them separate the effect of anion and cation. As a sample of such data, a few results are shown in Table 5.

Table 1 Standard molar enthalpies for KCl in H_2O and THAM–0.1 M HCl at 298.15 K

Substance	$\Delta H_s/\text{kJ mol}^{-1}$ [reference]	$\Delta H_s/\text{kJ mol}^{-1}$ this work
KCl in water	17.584 ± 0.050 [17]	17.57 ± 0.05
THAM–0.1 M HCl	-29.75 ± 0.02 [18]	-29.74 ± 0.06

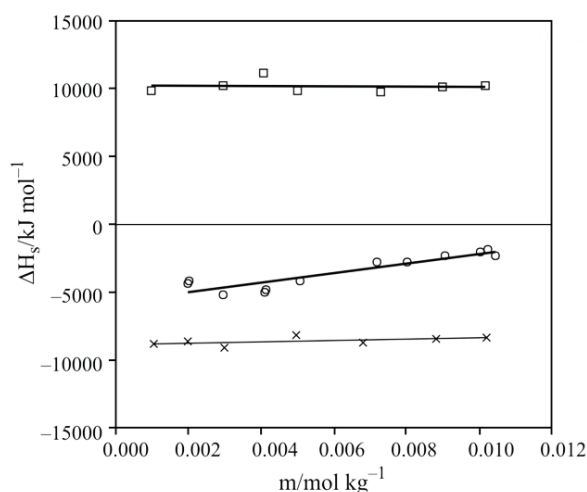


Fig. 4 Solution enthalpies of \times – $n\text{-Bu}_4\text{NBr}$, \square – $\text{sec-Bu}_4\text{NBr}$, \circ – $\text{iso-Bu}_4\text{NBr}$ in water, ΔH_s (kJ mol^{-1}), as a function of molality and at 298.15 K

Table 2 Solution enthalpies of tetraalkylammonium bromides in water, ΔH_s^0 , as a function of molality and at 298.15 K

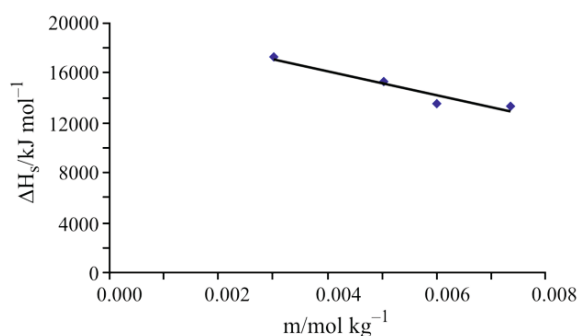
<i>n</i> -Bu ₄ NBr		<i>iso</i> -Bu ₄ NBr		<i>sec</i> -Bu ₄ NBr		<i>n</i> -Bu ₂ <i>sec</i> -Bu ₂ NBr	
<i>m</i> /kg mol ⁻¹	ΔH_s^0 /kJ mol ⁻¹	<i>m</i> /kg mol ⁻¹	ΔH_s^0 /kJ mol ⁻¹	<i>m</i> /kg mol ⁻¹	ΔH_s^0 /kJ mol ⁻¹	<i>m</i> /kg mol ⁻¹	ΔH_s^0 /kJ mol ⁻¹
0.0011	-8.76	0.0020	-4.31	0.0010	9.84	0.0030	17.25
0.0020	-8.57	0.0021	-4.15	0.0030	10.15	0.0050	15.30
0.0030	-9.07	0.0030	-5.14	0.0041	11.10	0.0060	13.56
0.0050	-8.15	0.0041	-4.97	0.0050	9.82	0.0074	13.30
0.0068	-8.72	0.0041	-4.82	0.0073	9.69		
0.0088	-8.42	0.0051	-4.16	0.0090	10.11		
0.0101	-8.32	0.0072	-2.75	0.0101	10.20		
		0.0080	-2.82				
		0.0091	-2.32				
		0.0100	-2.01				
		0.0102	-1.82				
		0.0104	-2.30				

Table 3 Solution enthalpies at zero concentration, ΔH_s^0 , of tetraalkylammonium bromides in water at 298.15 K

Salt	ΔH_s^0 /kJ mol ⁻¹
<i>n</i> -Bu ₄ NBr	-8.75±0.11
<i>iso</i> -Bu ₄ NBr	-6.35±0.20
<i>sec</i> -Bu ₄ NBr	10.15±0.23
<i>n</i> -Bu ₂ <i>sec</i> -Bu ₂ NBr	20.08±0.38

Table 4 Solution enthalpies at zero concentration, ΔH_s^0 , for some tetra-alkyl-ammonium bromides literature values at 298.15 K

Salt	ΔH_s^0 /kJ mol ⁻¹
Me ₄ NBr	24.71 [19]
Et ₄ NBr	5.77 [20]; 5.88 [21]; 6.12±0.08 [10]
Pr ₄ NBr	-4.40 [21]; -4.3 [1]
<i>n</i> -Bu ₄ NBr	-8.45 [20]; -8.58±0.06 [19]; -8.58±0.04 [11]

**Fig. 5** Solution enthalpies of *n*-Bu₂*sec*-Bu₂NBr in water, ΔH_s (kJ mol⁻¹), as a function of molality at 298.15 K

As it can be seen the kind of halide has a strong influence in the enthalpy of solution extrapolated at zero concentration.

Table 5 Enthalpy of solution at zero concentration, ΔH_s^0 , at 298.15 K for different halides of some tetra-alkyl-ammonium cations

Salt	ΔH_s^0 /kJ mol ⁻¹
Me ₄ NI	41.80 [23]; 41.4±1.3 [1]
Et ₄ NI	28.20 [22]; 28.6 [23]
Me ₄ NBr	24.71 [21]
Et ₄ NBr	5.77 [23]; 5.88 [21]; 6.12±0.08 [11]
<i>n</i> -Bu ₄ NBr	-8.45 [20]; -8.58±0.06 [19]; -8.58±0.04 [11]
Me ₄ NCl	4.43 [20]
Et ₄ NCl	-12.97 [20]; -12.64 [23]
Bu ₄ NCl	-29.87 [20]

The interpretation of the experimental data has classified [4, 5] the anions as structure breakers (positive contributions to the enthalpy of solution at zero concentration). Their influence decreases in the order I⁻>Br⁻>Cl⁻. In the same way, the cations can be classified as makers or breakers according to the sign of their contributions to the values. From the net effect of the salts it can be shown that a positive value means a structure breaker salt while a negative one implies a structure maker salt.

It is somehow surprising the change in sign when going from *n*-Bu₄NBr and *iso*-Bu₄NBr to *sec*-Bu₄NBr. This means that the geometry of the alkyl chains is of great importance in the interactions with water. The behavior of the asymmetric *n*-Bu₂*sec*-Bu₂NBr should arise because of two factors: the opposite tendency of the two chains *n*-butyl and *sec*-butyl and the asymmetry of the cation R₂R'₂N⁺.

From this work it can be seen that the linear dependence of enthalpies of solution with number of atoms in the cation [1] do not hold for the isomer chains studied.

Acknowledgements

The authors wish to thank the Universidad Nacional de Colombia, the Universidad de Los Andes and Colciencias for financial support.

References

- 1 L. H. Blanco, A. Gómez and G. Bermúdez, *Acta. Sud. Quím.*, 1 (1981) 107.
- 2 E. Amado and L. H. Blanco, *Phys. Chem. Liq.*, 38 (2000) 451.
- 3 L. H. Blanco and E. F. Vargas, *J. Sol. Chem.*, 35 (2006) 21.
- 4 H. S. Franks and M. W. Evans, *J. Chem. Phys.*, 13 (1945) 507.
- 5 H. S. Franks and W. Y. Wen, *Discuss. Faraday Soc.*, 24 (1957) 133.
- 6 W. Y. Wen, *Water and Aqueous solutions*, R. A. Horne, Ed., Wiley-Interscience, New York 1972, p. 613.
- 7 R. L. Kay and D. F. Evans, *J. Phys. Chem.*, 70 (1966) 2325.
- 8 R. M. Diamond, *J. Phys. Chem.*, 67 (1963) 2513.
- 9 E. F. Vargas, J. C. Moreno, J. Forero and D. F. Parra, *J. Therm. Anal. Cal.*, 91 (2008) 659.
- 10 S. J. Lindenbaum, *J. Phys. Chem.*, 70 (1965) 814.
- 11 V. P. Korolev, N. L. Smirnova and A. V. Kustov, *Thermochim. Acta*, 427 (2005) 43.
- 12 H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, *J. Am. Chem. Soc.*, 55 (1933) 4571.
- 13 A. I. Vogel, *Text-book of Practical Organic Chemistry Including Qualitative Organic Analysis*, Logman Green and Co., London 1963.
- 14 A. K. R. Unni, L. Elias and H. I. Schiff, *J. Phys. Chem.*, 67 (1963) 1216.
- 15 B. Yff, P. G. Royall, M. B. Brown and G. P. Martin, *Int. J. Pharm.*, 269 (2004) 361.
- 16 A. Weinsbergen, Ed., *Physical Methods of Chemistry*, Vol. 1, Part 4, 4th Ed., Wiley Interscience, New York 1972.
- 17 I. Wadso and R. N. Goldberg, *Pure Appl. Chem.*, 73 (2001) 1625.
- 18 S. R. Gunn, *J. Phys. Chem.*, 69 (1965) 2902.
- 19 C. de Visser and G. Somsen, *J. Phys. Chem.*, 78 (1974) 1719.
- 20 C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, 74 (1970) 3900.
- 21 C. Shin, I. Worsley and C. M. Criss, *J. Solution. Chem.*, 5 (1976) 867.
- 22 O. N. Bhatnagar and C. M. Criss, *J. Phys. Chem.*, 73 (1969) 174.
- 23 E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, 88 (1966) 2598.

DOI: 10.1007/s10973-008-9014-2