J. Chem. Thermodynamics 68 (2014) 117–121

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Apparent molal volumes of symmetrical and asymmetrical isomers of tetrabutylammonium bromide in water at several temperatures

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ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 26 August 2013
Accepted 31 August 2013
Available online 8 September 2013

Keywords:
Apparent molal volumes
Asymmetrical cations
Partial molar volumes
Aqueous solutions
Quaternary ammonium cations

ABSTRACT

Apparent molal volumes of a series of differently substituted quaternary ammonium bromides, namely tetra-*iso*-butyl-, tetra-*sec*-butyl-, tetra-*n*-butyl-, di-*n*-butyl-di-*sec*-butyl- and di-*n*-butyl-di-*iso*-butylammonium bromide have been determined as a function of molal concentration at (298.15, 303.15 and 308.15) K. Partial molar volumes at infinite dilution and ionic molar volumes of these quaternary ammonium cations were determined. Structural volume contributions to the ionic molar volume were also calculated. The symmetric and asymmetric quaternary ammonium cations are "structure making" ions. The contribution of the branched butyl chains predominates over the linear butyl chains in the asymmetric cations.

1. Introduction

Quaternary ammonium cations are widely used in several areas of chemistry [1]. Since their hydrophobicity is easily tuned by changing the length and/or the three-dimensional structure of the non-polar moieties these cations are often used as model systems for the investigation of ion–ion, ion–solvent and solvent–solvent interactions in electrolyte solutions [1–3].

Studies of the volumetric properties of symmetrical quaternary *n*-alkylammonium cations in aqueous solution are abundant in the literature and various reviews have summarized and commented the results [1–3]. However, corresponding investigations of symmetrical and asymmetrical quaternary ammonium cations having branched alkyl chains are still scarce [4–6]. These cations are of special interest because they provide a way of establishing the influence of the geometry of the non polar groups on the structural properties of water.

This contribution intends to widen the available data base on the effect of the geometry of the non-polar alkyl side chain on the solvent by a systematic study of the volumetric behavior of aqueous solutions of five isomers of tetrabutylammonium bromide as a function of concentration (0.01 to 0.1 mol · kg^{-1}) at three temperatures (298.15, 303.15 and 308.15 K). Three symmetrical cations, namely tetra-*n*-butylammonium (Bu_4N^+), tetra-*iso*-butylammonium (*iso*Bu_4N^+) and tetra *sec*-butylammonium (*sec*Bu_4N^+) were selected in addition to the asymmetric ions di-*n*-butyl-di-*iso*-butylammonium (Bu_2*iso*Bu_2N^+) and di-*n*-butyl-di-*sec*-butylammonium (Bu_2*sec*Bu_2N^+), figure 1. Apparent molal volumes were determined by density measurements to an uncertainty of ±5 · 10^{-6} g · cm^{-3}. Limiting partial molar ionic volumes of the cations were calculated from the limiting partial molar volumes at infinite dilution of the solutes. The concentration dependence of these apparent molal volumes was also examined.

2. Experimental

2.1. Materials

The salt Bu_4NBr was obtained from Sigma and used without further purification, whereas *iso*Bu_4NBr, *sec*Bu_4NBr, Bu_2*iso*Bu_2NBr and Bu_2*sec*Bu_2NBr were synthesized and purified according to established methods in literature [7,8]. The purity of all salts was better than 0.99 in mass. The water used was doubly distilled from an alkaline $KMnO_4$ solution and degassed before use. The conductivity of the water employed always was less than 2 μS · cm^{-1}. The detailed specifications of chemical samples are given in table 1.

2.2. Apparatus and procedures

Solution densities, ρ, were measured using an Anton Paar density meter, model DSA 5000 M, with a reproducibility of ±1 · 10^{-6} g · cm^{-3}. This instrument is equipped with a Peltier type thermostating unit, which permitted a temperature control of

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http://dx.doi.org/10.1016/j.jct.2013.08.031

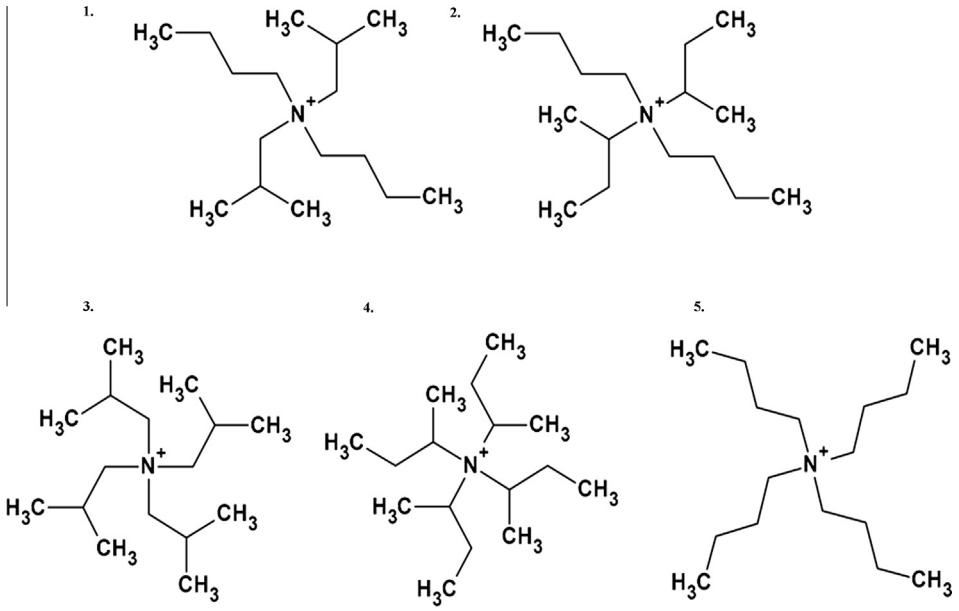

FIGURE 1. Structures of the investigated asymmetric (**1** $Bu_2isoBu_2N^+$; **2** $Bu_2secBu_2N^+$) and symmetric (**3** $isoBu_4N^+$; **4** $secBu_4N^+$; **5** Bu_4N^+) quaternary ammonium cations.

TABLE 1
Specification of chemical samples.

Compounds	Source	Purification Method	Mass fraction purity	Analysis method
Bu_4NBr	Sigma		0.99	Potentiometric titration
$isoBu_4NBr$	Synthesis	Recrystallization	0.99	Potentiometric titration
$secBu_4NBr$	Synthesis	Recrystallization	0.99	Potentiometric titration
Bu_2isoBu_2NBr	Synthesis	Recrystallization	0.99	Potentiometric titration
Bu_2secBu_2NBr	Synthesis	Recrystallization	0.99	Potentiometric titration
Water		Doubly distilled		

±0.001 K. The density meter was calibrated using dry air and pure water and the calibration was periodically checked. The experimental uncertainty, determined using aqueous solutions of KCl, was better than $\pm 5 \cdot 10^{-6}\,g \cdot cm^{-3}$ at all temperatures. The solutions were prepared by mass using an Ohaus Analytical Plus balance that has an uncertainty of $1 \cdot 10^{-5}$ g in the range of interest.

3. Results and discussion

The densities, ρ, of the studied aqueous quaternary ammonium bromide solutions are given in tables S1 to S3 in Supporting Information. The apparent molal volumes, V_ϕ, of the solutes were calculated from ρ and the density of water, ρ_o, according to

$$V_\phi = \frac{M_2}{\rho} - \frac{1000(\rho - \rho_o)}{m\rho\rho_o}, \tag{1}$$

where m is the molal concentration of the solute and M_2 its molar mass. Water densities at the three studied temperatures were taken from reference [9]. Tables S1 to S3 also list the apparent molal volumes of the solutes with their uncertainties at the studied temperatures. The uncertainties were calculated according to the law of propagation of uncertainties [10].

The dependency of the apparent molal volumes on solute molality was fitted by means of a weighted linear regression of the Redlich–Meyer equation [11]

$$V_\phi = V_\phi^\circ + S_V m^{1/2} + B_V m, \tag{2}$$

where V_ϕ° is the apparent molal volume at infinite dilution (which is equal to the partial molal volume of the solute at infinite dilution,V_2°), S_V is the Debye–Hückel limiting slope for 1:1 electrolytes at the given temperature (1.8743, 1.9616 and 2.0547 $cm^3 \cdot kg^{1/2} \cdot mol^{-3/2}$ at 298.15, 303.15 and 308.15 K, respectively) [12] and B_V is an empirical constant. The values of V_ϕ° and B_V at the studied temperatures, and their uncertainties, are summarized in table 2. Values of V_ϕ° for Bu_4NBr in aqueous solutions reported by other authors [6,13–16] are also included in table 2. Generally, a good agreement between this study and the literature is observed.The partial molar volume at infinite dilution, V_2°, can be expressed in terms of the ionic molar volume of the quaternary ammonium cation, $V^\circ(QA^+)$, and bromide anion, $V^\circ(Br^-)$, as:

$$V_2^\circ = V^\circ(QA^+) + V^\circ(Br^-). \tag{3}$$

To our knowledge, there are no systematic studies in the literature that report the ionic molar volumes of the bromide ion as a function of temperature. However, the method reported by Hefter and Marcus [17] and Hedwig and Hakin [18] can be used to calculate $V^\circ(Br^-)$ for the temperature range employed in this study. This method assumes that the partial molar volume at infinite dilution of a suitably chosen electrolyte can be separated into well-defined cation and anion contributions. Hence, the ionic molar volume of the bromide ion, $V^\circ(Br^-)$, can be calculated from the following set of equations:

$$V^\circ(Br^-) = V_2^\circ(NaBr) + V_2^\circ(HCl) - V_2^\circ(H^+) - V_2^\circ(NaCl), \tag{4}$$

$$V_2^\circ(H^+) = -5.1 - 0.008(T/^\circ C) - 1.7 \cdot 10^{-4}(T/^\circ C), \tag{5}$$

$$V_2^\circ(HCl) = 16.22 + 0.108(T/K - 273.15) - 1.99 \cdot 10^{-3}(T/K - 273.15)^2 + 9.7 \cdot 10^{-6}(T/K - 273.15)^3, \tag{6}$$