

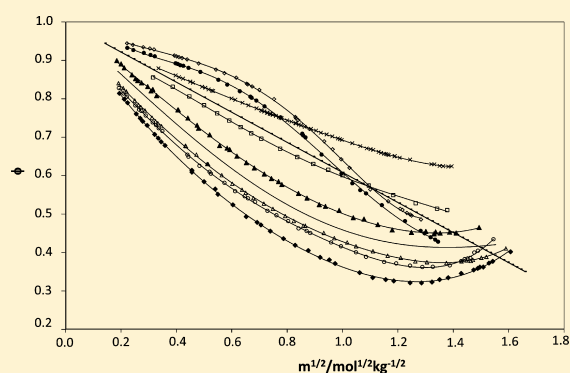
Osmotic and Activity Coefficients of Dilute Aqueous Solutions of Unsymmetrical Tetraalkylammonium Iodides at 298.15 K

Eliseo Amado-Gonzalez^{*,†} and Luis H. Blanco^{‡,§}

[†]IBEAR, Universidad de Pamplona, Pamplona, Colombia

[‡]LIB, Universidad Nacional de Colombia, Bogotá, Colombia

ABSTRACT: Osmotic coefficients of dilute aqueous solutions of *ter*-BuEt₃NI, *sec*-BuEt₃NI, *iso*-BuEt₃NI, Bu₂Me₂NI, and Bu₃EtNI are measured by the isopiestic method at 298.15 K. A branched isopiestic cell was used. The osmotic coefficients of tetraalkylammonium solutions were analyzed with the Debye–Hückel limiting law. The results show that the osmotic coefficient varies in the following way: Pr₃EtNI¹¹ > *n*-BuEt₃NI¹¹ > Me₄NI¹² > Et₄NI¹¹ > *ter*-BuEt₃NI > *sec*-BuEt₃NI > *iso*-BuEt₃NI > Bu₂Et₂NI > Bu₃EtNI. The set of Pitzer parameters $b = 1.2$, $\alpha_1 = 2.0$ was used. The results were fitted to the Pitzer model, and the parameters β_0 , β_1 , and C_γ were calculated. The results was interpreted in terms of solute–solvent interactions.



1. INTRODUCTION

Tetraalkylammonium salts (TAAX, where X: Cl, F, Br, or I) give the possibility to develop new materials that may have different industrial uses. The physicochemical properties of TAAX salts can be finely adjusted via slight structural modifications of the cation because of the possibility of changing the length of the alkyl chains as was proposed by Lowe and Rendall.¹ This feature makes them excellent models for the study of the interactions occurring in electrolyte solutions.

Experimental phase equilibrium data of aqueous electrolyte solutions are required in the prediction of the behavior of electrolyte solutions, the development of electrolyte models, and the estimation of interactions occurring in these solutions. The solvent activity of nonvolatile solutes has been measured by several methods that include freezing point depression, boiling point elevation, dynamic and static vapor pressure measurements, osmotic pressure measurements, and the isopiestic method which has become one of the most frequent techniques for osmotic coefficient determination, because of its simplicity.^{2–4} Unfortunately, the expense of traditional isopiestic equipment severely handicaps many laboratories for its use. However, different kinds of an inexpensive legged glass apparatus have been developed to measure solvent activities with good precision.^{5–7} Using a twelve-leg manifold attached to round-bottomed cups, the osmotic coefficients of five aqueous solution systems of symmetrical and unsymmetrical tetraalkylammonium iodides (TAAI) were measured at $T = 298.15$ K.

In our laboratory a systematic investigation has been done to evaluate the effect of the chain length on the osmotic and activity coefficients of aqueous solutions of a different series of tetraalkylammonium halides (TAAX, X = Cl, Br, and I). In earlier papers, the osmotic coefficients of aqueous solutions of

the series Bu₄NBr, *sec*-Bu₄NBr, *iso*-Bu₄NBr, Bu₂Et₂NBr, and Bu₃EtNBr at (283.15, 288.15, 298.15, and 293.15) K^{8–10} were analyzed by comparing them with the Debye–Hückel limiting law (DHLL). At those temperatures a positive deviation of the osmotic coefficients from the DHLL was found. Also the osmotic coefficients for aqueous solutions of the series MeEt₃NI, Et₄NI, PrEt₃NI, *n*-BuEt₃NI, PenEt₃NI, HexEt₃NI, and HepEt₃NI at 298.15 K¹¹ and of Me₄NI, Me₃BuNI, Me₂Bu₂NI, and MeBu₃NI were determined by the isopiestic method at 298.15 K.¹² The partial molal volumes for the isomers of *n*-BuEt₃NI in aqueous solutions at 298.15 K showed a decrease value in the next order: *n*-BuEt₃NI > *iso*-BuEt₃NI > *sec*-BuEt₃NI > *ter*-BuEt₃NI.¹³

In this work the effect of *ter*-butyl, *sec*-butyl, *iso*-butyl, dibutyl, and tributyl radicals on the behavior of the osmotic and activity coefficients is analyzed by using Et₄NI as a basic structure salt. Data of osmotic coefficients for aqueous solutions of *ter*-BuEt₃NI, *sec*-BuEt₃NI, *iso*-BuEt₃NI, Bu₂Et₂NI, and Bu₃EtNI were determined by the isopiestic method at 298.15 K, and the results were fitted to the Pitzer model.^{14,15} The osmotic coefficients have been obtained from the isopiestic equilibrium molalities of the investigated solutions. The activity coefficient data are believed to be precise to within 0.50 %. The results indicate that the Pitzer model works properly in the present case. It correlates the osmotic coefficients of the studied solutions with acceptable precision.

Received: August 25, 2011

Accepted: February 15, 2012

Published: March 1, 2012

Table 1. Physical Chemistry Characteristics of Bu₃EtNI to Bu₂Et₂NI^a

characteristic	Bu ₃ EtNI	sec-BuEt ₃ NI	ter-BuEt ₃ NI	iso-BuEt ₃ NI	Bu ₂ Et ₂ NI
<i>T_m</i> (K)	403	448.5	446.5	425	407
anion (%)	99.3 ± 0.25	99.2 ± 0.2	99.8 ± 0.2	99.3 ± 0.25	99.3 ± 0.25
cation (%)	99.5 ± 1.0	99.3 ± 0.5	99.6 ± 0.2	99.5 ± 1.0	99.5 ± 1.0

^a*T_m*: melting temperature.

2. EXPERIMENTAL SECTION

Materials. The TAAI salts were synthesized using a modification of the procedure recommended by Vogel.¹⁶ The synthesis procedure is the same as has been explained in previous paper.¹⁷

In all cases anion analysis was done by potentiometric titration with silver nitrate (Fischer Scientific Co.), and cation analysis was done by potentiometric titration with NaTPB.¹⁸ The results are summarized in Table 1.

Synthesis. For the synthesis of the salts some standard procedures were used. In each case a reaction time of 48 h in methanol solution (Merck) was required. A white sticky powder was obtained. A wash process of the salt was done at least twice in ethanol solution. A full precipitation of the salt was done with diethyl ether; then, the salt was dried using vacuum process for 48 h. The iodides were synthesized from the alcohol and iodide, respectively. The synthesis of diethylamine involved catalytic hydrogenation of acetonitrile (99.9 %) to give a mixture of diethylamine and ethylamine. The two amines were separated by counter-current distribution, and the yield of diethylamine was increased by reacting the ethylamine with ammonia and acetaldehyde.¹⁹

Reagents are as follows: for sec-butyltriethylammonium iodide: sec-butyl iodide and triethyl amine (Baker analyzed reagent); for ter-butyltriethylammonium iodide: ter-butyl iodide and triethylamine (Baker analyzed reagent); for iso-butyltriethylammonium iodide: iso-butyl iodide and triethylamine (Baker analyzed reagent); for di-*n*-butyldiethylammonium iodide: diethyl iodide and di-*n*-butyl amine (J.T. Baker); and for tri-*n*-butylethylammonium iodide: tri-*n*-butylamine (J.T. Baker) and ethyl iodide (Merck).

Apparatus and Procedure. The isopiestic apparatus employed in the present work is essentially similar to one used previously and described in a previous paper.¹⁰ Known masses of anhydrous NaCl and of the salts were added to each isopiestic sample cup, along with sufficient purified water to produce initial solutions approximately at the desired equilibrium molalities. The sample cups were then placed in the isopiestic apparatus, air was removed, and the apparatus with its samples were equilibrated in a constant temperature water bath for periods of 4 to 9 days at (298.15 ± 0.05) K. A water bath was put in an air thermostat. After reaching isopiestic equilibrium, the sample cups were removed for weighing. All of the weighings were done around room temperature at (293 ± 2) K. All apparent sample masses were converted to masses using buoyancy corrections. The molalities of each solution were calculated from the total mass of that capped cup plus solution, from the mass(es) of anhydrous solute(s) added to that cup. Duplicate samples of the same aqueous salt were used in an experiment; their measured equilibrium molalities agreed to ≤ 1.2 · 10⁻³ *m* where *m* denotes the molality of the solution.

The NaCl_(aq) isopiestic reference standard stock solutions were prepared by mass from oven-dried analytical reagent grade NaCl (analytical) and purified water. Solutions were prepared

by weight using doubly distilled water at room temperature (293 ± 2) K. A Metler AT 261 balance was used to weigh the sample cups and solution samples. It has a precision of 1 · 10⁻⁵ g. Buoyancy corrections were applied. NaCl (analytical reagent grade) isopiestic reference standard stock solutions were prepared by weight. NaCl was oven-dried at 383 K. Molar mass of NaCl used for molality calculations was 58.443 g · mol⁻¹. All solutions were prepared by weight in deionized water which had a specific conductivity less than 0.55 · 10⁻⁶ S · cm⁻¹.

3. RESULTS AND DISCUSSION

The isopiestic equilibrium molalities of the investigated solutions compared to reference standard solutions of NaCl as reported in Table 2 enabled the calculation of the osmotic coefficient of the investigated solutions from:

$$\phi^* = \frac{\nu_r m_r \phi_r}{\nu^* m^*} \quad (1)$$

in which ν and m are respectively the total number of ions produced by one mole of the salt and the molality of the salt; r stands for isopiestic standard solution and $*$ indicates the transition metal chloride solution. Equation 1 assumes complete dissociation of both the reference and the studied compounds. Osmotic coefficients of the isopiestic reference solution in the isopiestic equilibrium at m_r were obtained as a function of molality from the extended Bradley–Pitzer correlation proposed by Archer.²⁰

Table 2 also contains the equilibrium isopiestic molalities of the NaCl(aq) reference solutions and the activity coefficients of the investigated solutions. The osmotic coefficient may be reproduced with an average error of 0.5 % for TAAI aqueous solutions in the range (0.1 to 4.22) mol · kg⁻¹ at 298.15 K.

Figure 1 shows that the osmotic coefficients of the solutions of the TAAI solutions against the $m^{1/2}$ of the salts varies as: Pr₃EtNI¹¹ > *n*-BuEt₃NI¹¹ > Me₄NI¹² > Et₄NI¹¹ > ter-BuEt₃NI > sec-BuEt₃NI > iso-BuEt₃NI > Bu₂Et₂NI > Bu₃EtNI in the range of molality $m < 2.51$ mol · kg⁻¹. It shows that the osmotic coefficients of Et₄NI, ter-BuEt₃NI, sec-BuEt₃NI, iso-BuEt₃NI, Bu₂Et₂NI, and Bu₃EtNI solutions lie below the DHLL. When the results are compared with the osmotic coefficients of Bu₄NBr, sec-Bu₄NBr, iso-Bu₄NBr, Bu₂Et₂NBr, and Bu₃EtNBr at 298.15 K.¹⁰ The order of the osmotic coefficient variation is Bu₂Et₂N⁺ > BuEt₃N⁺ > sec-Bu₄N⁺ > iso-Bu₄N⁺ > *n*-Bu₄N⁺. The results suggest that large, nonpolar TAA⁺ cations have the greater effect over the osmotic coefficient. Earlier results over osmotic analysis at 298.15 K propose that bromides and iodides at low concentrations show the same behavior, suggesting that ion pairing occurs.²¹ Also, the osmotic coefficients for the chlorides increased with the size of the cation: Bu₄N⁺ > Pr₄N⁺ > Et₄N⁺ > Me₄N⁺. Even it is expected that large, nonpolar TAA⁺ will enforce the water structure around them, there is a clear effect of the halide. In the case of the TAAI, the osmotic coefficients did not increase with the size of the cation.

The values of the osmotic coefficients of Pr₃EtNI, *n*-BuEt₃NI, and Me₄NI solutions are higher than the values from the

Table 2. continued

NaCl		Bu ₃ EtNI		sec-BuEt ₃ NI		ter-BuEt ₃ NI		iso-BuEt ₃ NI		Bu ₂ Et ₂ NI	
<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ	<i>m</i>	ϕ
mol·kg ⁻¹		mol·kg ⁻¹		mol·kg ⁻¹		mol·kg ⁻¹		mol·kg ⁻¹		mol·kg ⁻¹	
0.8837	0.9327	2.2758	0.3622	2.0195	0.4081	1.8300	0.4504	2.1635	0.3810	2.1360	0.3859
0.9321	0.9345	2.3389	0.3724	2.0900	0.4168	1.9238	0.4528	2.2539	0.3865	2.1790	0.3997
0.9590	0.9355	2.3800	0.3770	2.1720	0.4130	1.9900	0.4508	2.3085	0.3886	2.2180	0.4045
1.1023	0.9414	2.5825	0.4018	2.4128	0.4301	2.2310	0.4651	2.5283	0.4104	2.3885	0.4345
			γ_{\pm}		γ_{\pm}		γ_{\pm}		γ_{\pm}		γ_{\pm}
			0.0317		0.1110		0.1440		0.0981		0.0802
			0.0299		0.1086		0.1401		0.0955		0.0789
			0.0288		0.1059		0.1377		0.0941		0.0782
			0.0236		0.0987		0.1303		0.0917		0.0748

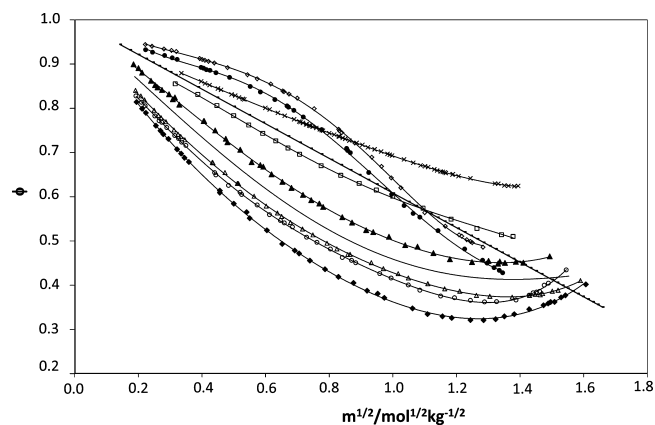


Figure 1. Concentration dependence of the osmotic coefficients for aqueous solutions of TAAI salts at $T = 298.15$ K. Experimental data: -, DHLL; \diamond , PrEt₃NI;⁹ \circ , Bu₂Et₂NI; \bullet , *n*-BuEt₃NI;⁹ \blacktriangle , ter-BuEt₃NI; \blacksquare , sec-BuEt₃NI; \triangle , iso-BuEt₃NI; \blacklozenge , Bu₃EtNI; \times , Me₄NI;¹² \square , Et₄NI.⁹

DHLL. The behavior of the osmotic coefficients may be interpreted in terms of solute–solvent interactions and ion association phenomena.¹³ Probably, solute–solvent interactions in the solutions of Pr₃EtNI, *n*-BuEt₃NI, and Me₄NI solutions are stronger than those values that occur in the ter-BuEt₃NI, sec-BuEt₃NI, iso-BuEt₃NI, Bu₂Et₂NI, and Bu₃EtNI solutions. The stronger ion association may occur in the Bu₃EtNI solutions. The data in the range of dilute solutions where ion–solvent interactions should predominate are indicative of competition between the ion–ion interactions and ion–solvent interactions. Also it could be suggested that there is a concentration where ion–ion and ion–solvent interaction equilibrium exists. The osmotic coefficients of the Me₄NI aqueous solutions show that ion–solvent interactions dominate over ion–ion interactions; in the case of Pr₃EtNI and *n*-BuEt₃NI the behavior of the osmotic coefficient change from ion–solvent interaction to ion–ion interaction predominates.

The plots of $\ln \gamma_{\pm}$ versus m for both mixed solvents are shown in Figure 2. The decrease in $\ln \gamma_{\pm}$ with the increase in m and decrease of $\ln \gamma_{\pm}$ for a given m value with the increasing concentration of TAAI in the studied systems are obvious. These profiles were observed in the similar systems, such as in the series Me₄NI to MeBu₃NI.¹² For comparison, it was shown

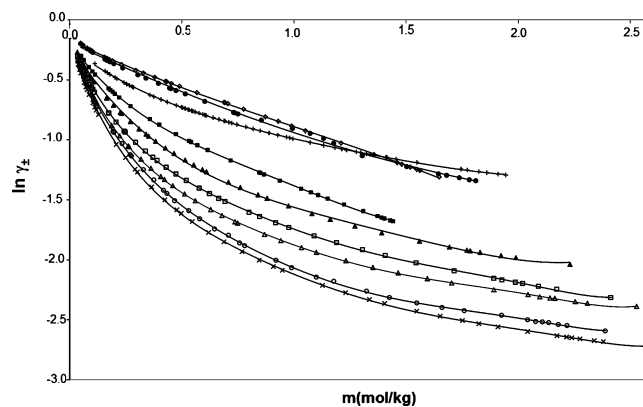


Figure 2. Concentration dependence of the activity coefficients for aqueous solutions of TAAI salts at $T = 298.15$ K. Data: \diamond , PrEt₃NI;⁹ \circ , Bu₂Et₂NI; \bullet , *n*-BuEt₃NI;⁹ \blacktriangle , ter-BuEt₃NI; \blacksquare , sec-BuEt₃NI; \triangle , iso-BuEt₃NI; \blacklozenge , Bu₃EtNI; \times , Me₄NI;¹² \square , Et₄NI.⁹

that Figure 2 shows the activity coefficient data for Pr₃EtNI,¹¹ *n*-BuEt₃NI,¹¹ Me₄NI,¹² Et₄NI,¹¹ ter-BuEt₃NI, sec-BuEt₃NI, iso-BuEt₃NI, Bu₂Et₂NI, and Bu₃EtNI. The activity coefficients decrease in the following order: Pr₃EtN⁺ > *n*-BuEt₃N⁺ > Me₄N⁺ > Et₄N⁺ > ter-BuEt₃N⁺ > sec-BuEt₃N⁺ > iso-BuEt₃N⁺ > Bu₂Et₂N⁺ > Bu₃EtN⁺ in the range of molality $m < 2.58$ mol·kg⁻¹. The behavior of the activity coefficient may be an indication of extensive ion–ion association, presumably through hydrogen bonding. Also it can be seen that solutions of Bu₂Et₂NI and Bu₃EtNI may have the strongest ion-pair formation.

The volumetric behavior of the asymmetric iodides show a decreasing value: *n*-BuEt₃N⁺ > iso-BuEt₃N⁺ > sec-BuEt₃N⁺ > ter-BuEt₃N⁺, which was interpreted as structure enforced ion pairing.²²

Correlation Data. Several models are available in the literature for the correlation of osmotic coefficients as a function of molalities. The Pitzer and Mayorga (1973) model has been successfully used for aqueous electrolyte solutions. For details refer to refs 14 and 15, In this model the osmotic coefficient is given by:

$$\phi - 1 = |z_+ z_-| f^\phi + m[(2\nu_+ \nu_-) / \nu] B^\phi + m^2 [2(\nu_+ \nu_-)^{3/2} / \nu] C^\gamma \quad (2)$$

where

$$f^\phi = -A_\phi I^{1/2} / (I + bI^{1/2}) \quad (3)$$

$$B^\phi = \beta_0 + \beta_1 \exp(-\alpha I^{1/2}) \quad (4)$$

In eqs 2 and 4, β_0 , β_1 , and C_γ are Pitzer's ion parameters. α and b are adjustable parameters. z_+ and z_- are positive and negative ionic charges. A_ϕ is the Debye–Hückel constant for the osmotic coefficient and can be computed using the pure solvent properties via the equation:

$$A_\phi = \frac{1}{3} \sqrt{2\pi N_0 d_1} \left(\frac{e^2}{4\pi \epsilon_0 D k T} \right)^{1.5} \quad (5)$$

In eq 5 d_1 and D are the density and the dielectric constant of the pure solvent. N_0 , ϵ_0 , and k are Avogadro's number, the permittivity of the vacuum, and the Boltzmann constant, respectively. The value of A_ϕ is 0.3915 kg^{1/2}·mol^{-1/2}. In the above equations, I is the ionic strength based on molality. For aqueous electrolyte solutions, $b = 1.2$ kg^{1/2}·mol^{-1/2} is used, and the quantity α_1 is usually assigned a value of 2.0 kg^{1/2}·mol^{-1/2}. Using this set of Pitzer parameters, the osmotic coefficient may be reproduced with an average absolute error of 0.5 % (standard deviation of $\sigma(\phi) = 0.04$) for TAAI aqueous solutions in the range (0.03 to 2.5) mol·kg⁻¹ at 298.15 K. The standard deviation between experimental and calculated osmotic coefficients is given by:

$$\sigma(\phi) = \sqrt{\frac{\sum_i (\phi_{\text{exp}} - \phi_{\text{cal}})_i^2}{n}} \quad (6)$$

in which n is the number of data, and ϕ_{exp} and ϕ_{cal} stand for experimental and calculated values. Standard deviations of the fit are between 0.011 to sec-BuEt₃NI and 0.022 to Bu₃EtNI. Figure 3 shows the residuals between experimental osmotic coefficients and least-squares fit values for TAAI salts as a function of $m^{1/2}$ at 298.15 K.

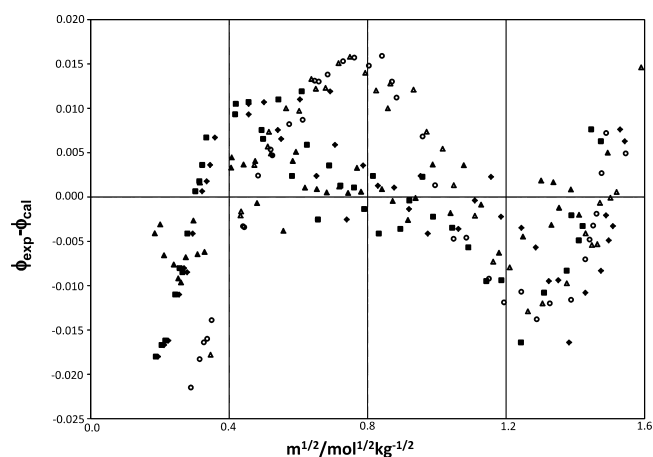


Figure 3. Differences (residuals) between experimental osmotic coefficients ϕ and least-squares fit values ϕ (cal) of TAAI as a function of m at $T = 298.15$ K, for fits in the molality region (0–1.00) mol kg⁻¹. Data: ○, Bu₂Et₂NI; ▲, ter-BuEt₃NI; ■, sec-BuEt₃NI; △, iso-BuEt₃NI; ◆, Bu₃EtNI.

Pitzer model parameters were calculated using the osmotic coefficient data of Table 2 and are shown in Table 3. Both forms of the Pitzer model (with and without the C_γ) were considered. However, on the basis of standard deviations, calculated with eq 6, it was noted that for all of the investigated systems that the best agreement is obtained with the Pitzer model including the β_1 and C_γ terms.

Table 3 shows the Pitzer's ion parameters where β_1 varies as ter-BuEt₃NI > sec-BuEt₃NI > iso-BuEt₃NI > Bu₂Et₂NI > Bu₃EtNI which is in the same order as the osmotic coefficient variation. In Figure 4 a linear relation with $r^2 = 0.911$ is found between β_0 and β_1 for TAAI where TAAI: Me₄NI;¹² MeEt₃NI;¹¹ PrEt₃NI;⁹ *n*-BuEt₃NI;¹¹ ter-BuEt₃NI; PenEt₃NI;¹¹ Et₄NI;¹¹ HexEt₃NI;¹¹ HepEt₃NI;¹¹ sec-BuEt₃NI; iso-BuEt₃NI; Bu₂Et₂NI; Bu₃EtNI. This results confirm that there may be a physical relationship of β_1 with ion–solvent interactions, where positive values of β_1 may be related with predominant ion–solvent interactions and negative values of β_1 with ion–ion interactions in the aqueous solutions.

4. CONCLUSIONS

Osmotic coefficients of dilute aqueous solutions of ter-BuEt₃NI, sec-BuEt₃NI, iso-BuEt₃NI, Bu₂Me₂NI, and Bu₃EtNI are measured by the isopiestic method at 298.15 K. The osmotic coefficients of TAAI solutions were analyzed by comparing with the DHLL. The osmotic coefficient data vary in the following way: Pr₃EtNI¹¹ > *n*-BuEt₃NI¹¹ > Me₄NI¹² > Et₄NI¹¹ > ter-BuEt₃NI > sec-BuEt₃NI > iso-BuEt₃NI > Bu₂Et₂NI > Bu₃EtNI. The order of the osmotic coefficients have been interpreted qualitatively in terms of ion–ion interactions and ion–solvent interactions.

Experimental osmotic coefficient data for the investigated systems are satisfactorily correlated with the Pitzer model. A relation between the two parameters of β_0 and β_1 for TAAI was found ($r^2 = 0.911$).

Results show β_1 varies from -1.305 for ter-BuEt₃NI to -3.172 for Bu₃EtNI, in the same order as the osmotic coefficient variations: ter-BuEt₃NI > sec-BuEt₃NI > iso-BuEt₃NI > Bu₂Et₂NI > Bu₃EtNI. Our results confirm that there may be a physical relationship of β_1 with ion–solvent interactions.

Table 3. Values Obtained for Pitzer Ion-Parameters for TAAI Salts at 298.15 K

parameter	ter-BuEt ₃ Ni	sec-BuEt ₃ Ni	iso-BuEt ₃ Ni	Bu ₂ Et ₂ Ni	Bu ₃ EtNi
β_0 (kg·mol ⁻¹)	-0.1925	-0.1166	-0.076	-0.058	-0.019
β_1 (kg·mol ⁻¹)	-1.305	-1.956	-2.43	-2.668	-3.172
$C\gamma$ (kg ² ·mol ⁻²)	0.0494	0.020	0.008	0.006	-0.011
σ (ϕ) ^c	0.018	0.011	0.016	0.019	0.022

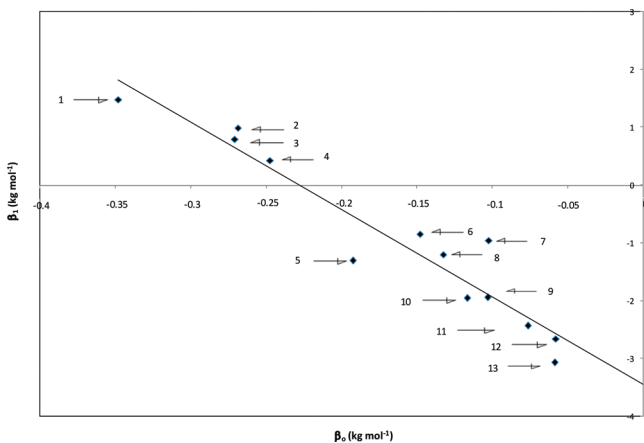


Figure 4. Linear relation of β_0 to β_1 for TAAI salts with a $r^2 = 0.911$ at 298.15 K. Experimental data: (1) Me₄Ni;¹² (2) MeEt₃Ni;¹¹ (3) PrEt₃Ni;⁹ (4) *n*-BuEt₃Ni;¹¹ (5) ter-BuEt₃Ni; (6) PenEt₃Ni;¹¹ (7) Et₄Ni;¹¹ (8) HexEt₃Ni;¹¹ (9) HepEt₃Ni;¹¹ (10) sec-BuEt₃Ni; (11) iso-BuEt₃Ni; (12) Bu₂Et₂Ni; (13) Bu₃EtNi.

AUTHOR INFORMATION

Corresponding Author

* E-mail: eamado@unipamplona.edu.co. Fax: (057)+(7)+5685303.

Funding

The authors thank Pamplona University and National University of Colombia for their financial support.

Notes

The authors declare no competing financial interest.

[§]E-mail: lhblancoc@unal.edu.co. Phone: (057)+(1)+3150188.

ACKNOWLEDGMENTS

The authors are grateful to Dr. D. Archer, N.I.S.T., for permitting us to use his computer programs.

REFERENCES

- (1) Lowe, B.; Rendall, H. Aqueous solutions of unsymmetrical quaternary ammonium iodides. *Trans. Faraday Soc.* **1971**, 2318–2327.
- (2) Pytkowicz, R. M., Ed. *Activity Coefficients in Electrolyte Solutions*; CRC Press: Boca Raton, FL, 1979.
- (3) Clegg, S. L.; Whitfield, M. In *Activity Coefficients in Electrolyte Solutions*, 2nd ed.; Pitzer, K. S., Ed.; CRC Press: Boca Raton, FL, 1991.
- (4) Barthel, J.; Krienke, H.; Kunz, W. In *Physical Chemistry of Electrolyte Solutions*, Topics in Physical Chemistry; Baumgartel, H., Franck, E. U., Grünbein, W., Eds.; Springer: New York, 1998; Vol. 5.
- (5) Thiessen, D. B.; Wilson, A. J. An isopiestic method for measurement of electrolyte activity coefficients. *AIChE J.* **1987**, 33, 11–13.
- (6) Ochs, L.; Badr, M.; Cabezas, H. An improved isopiestic method to determinate activities in multicomponent mixtures. *AIChE J.* **1990**, 36, 1908–1912.
- (7) Dong-Qiang, L.; Le-He, M.; Zi-Qiang, Z.; Zhao-Xiong, H. An improved isopiestic method for measurement of water activities in aqueous polymer and salt solutions. *Fluid Phase Equilib.* **1996**, 118, 241–248.

(8) Amado, E.; Blanco, L. H. Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Solutions of Symmetrical and Unsymmetrical Quaternary Ammonium Bromides at $T = (283.15 \text{ and } 288.15) \text{ K}$. *J. Chem. Eng. Data* **2009**, 54, 2696–2700.

(9) Amado, E.; Blanco, L. H. Osmotic and activity coefficients of dilute aqueous solutions of symmetrical and unsymmetrical quaternary ammonium bromides at 293.15 K. *Fluid Phase Equilib.* **2006**, 243, 166–170.

(10) Amado, E.; Blanco, L. H. Isopiestic determination of the osmotic and activity coefficients of dilute aqueous solutions of symmetrical and unsymmetrical quaternary ammonium bromides with a new isopiestic cell at 298.15 K. *Fluid Phase Equilib.* **2005**, 233, 230–233.

(11) Blanco, L. H.; Amado, E.; Avellaneda, J. Isopiestic determination of the osmotic and activity coefficients of dilute aqueous solutions of the series MeEt₃Ni to HepEt₃Ni at 298.15 K. *Fluid Phase Equilib.* **2006**, 249, 147–152.

(12) Blanco, L. H.; Amado, E.; Calvo, J. Osmotic and activity coefficients of dilute aqueous solutions of the series Me₄Ni to MeBu₃Ni at 298.15 K. *Fluid Phase Equilib.* **2008**, 268, 90–94.

(13) Amado, E.; Blanco, L. H. Partial molal volumes of asymmetric iodides of butyl-triethyl-ammonium in aqueous solutions at 298.15 K. *Phys. Chem. Liq.* **2000**, 38, 451–458.

(14) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equation. *J. Phys. Chem.* **1973**, 77, 268–277.

(15) Pitzer, K. S.; Mayorga, G. J. Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with one or both Ions Univalent. *J. Phys. Chem.* **1973**, 77, 2300–2308.

(16) Vogel, A. *Vogel's Textbook of Practical Organic Chemistry*; John Wiley and Sons: New York, 1989.

(17) Blanco, L. H.; Amado, E. Conductance of asymmetric iodides of butyl-triethylammonium in toluene-acetonitrile mixtures at 25 °C. *Phys. Chem. Liq.* **1995**, 30, 213–226.

(18) Dick, J. *Analytical Chemistry*, International Student ed.; McGraw-Hill: Tokyo, 1973.

(19) Stoll, A.; Rutschmann, J.; Hofmann, A. Über die Synthese von ¹⁴C-Diäthylamin und ¹⁴C-Lysergsäure-diäthylamid. 34. Mitteilung über Mutterkornalkaloide. *Helv. Chim. Acta* **1954**, 37, 820–820.

(20) Archer, D. Thermodynamic properties of the KCl + H₂O system. *J. Phys. Chem. Ref. Data* **1999**, 28, 1–17.

(21) Lindenbaum, S.; Boyd, G. E. Osmotic and activity coefficients for the symmetrical tetralkyl ammonium halides in aqueous solutions at 25 °C. *J. Phys. Chem.* **1964**, 68, 911–917.

(22) Amado, E.; Blanco, L. H. Partial molal volumes of asymmetric iodides of butyl-triethyl-ammonium in a aqueous solutions at 298.15 K. *Phys. Chem. Liq.* **2000**, 38, 451–458.