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

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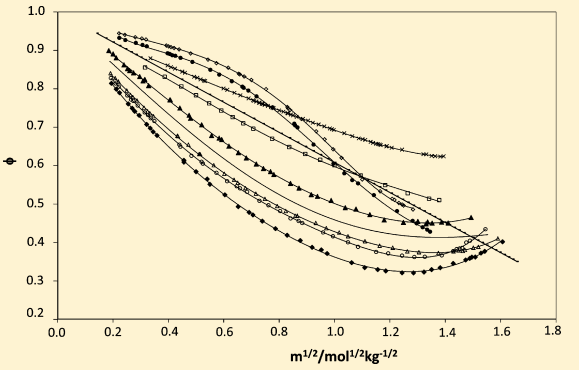
ABSTRACT: Osmotic coefficients of dilute aqueous solutions of ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Me_2NI, and Bu_3EtNI are measured by the isopiestic method at 298.15 K. A branched isopiestic cell was used. The osmotic coefficients of tetraalkylammonium solutions were analyzed with the Debye–Hückel limiting law. The results show that the osmotic coefficient varies in the following way: Pr_3EtNI[11] > *n*-$BuEt_3NI$[11] > Me_4NI[12] > Et_4NI[11] > ter-$BuEt_3NI$ > sec-$BuEt_3NI$ > iso-$BuEt_3NI$ > Bu_2Et_2NI > Bu_3EtNI. The set of Pitzer parameters b = 1.2, α_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, B, 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 nonvolative solutions 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 Bu_4NBr, sec-Bu_4NBr, iso-Bu_4NBr, Bu_2Et_2NBr, and Bu_3EtNBr 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 both temperatures a positive deviation of the osmotic coefficients from the DHLL was found. Also the osmotic coefficients for aqueous solutions of the series $MeEt_3NI$, Et_4NI, $PrEt_3NI$, *n*-$BuEt_3NI$, $PenEt_3NI$, $HexEt_3NI$, and $HepEt_3NI$ at 298.15 K[11] and of Me_4NI, Me_3BuNI, Me_2Bu_2NI, and $MeBu_3NI$ were determined by the isopiestic method at 298.15 K.[12] The partial molal volumes for the isomers of *n*-$BuEt_3NI$ in aqueous solutions at 298.15 K showed a decrease value in the next order: *n*-$BuEt_3NI$ > iso-$BuEt_3NI$ > sec-$BuEt_3NI$ > ter-$BuEt_3NI$.[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 Et_4NI as a basic structure salt. Data of osmotic coefficients for aqueous solutions of ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Et_2NI, and Bu_3EtNI 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.

2. EXPERIMENTAL SECTION

Materials. The TAAI salts were synthesized using a modification of the procedure recommended by Vogel.[16] The

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Table 1. Physical Chemistry Characteristics of Bu_3EtNI to Bu_2Et_2NI[a]

characteristic	Bu_3EtNI	sec-$BuEt_3NI$	ter-$BuEt_3NI$	iso-$BuEt_3NI$	Bu_2Et_2NI
T_m (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.

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-butyliodide and triethylamine (Baker analyzed reagent); for di-*n*-butyldiethylammonium iodide: diethyliodide 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 $\leq 1.2 \cdot 10^{-3}$ *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 $1 \cdot 10^{-5}$ 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 $0.55 \cdot 10^{-6}$ 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: Pr_3EtNI[11] > *n*-$BuEt_3NI$[11] > Me_4NI[12] > Et_4NI[11] > ter-$BuEt_3NI$ > sec-$BuEt_3NI$ > iso-$BuEt_3NI$ > Bu_2Et_2NI > Bu_3EtNI in the range of molality $m < 2.51$ mol·L^{-1}. It shows that the osmotic coefficients of Et_4NI, ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Et_2NI, and Bu_3EtNI solutions lie below the DHLL. When the results are compared with the osmotic coefficients of Bu_4NBr, sec-Bu_4NBr, iso-Bu_4NBr, Bu_2Et_2NBr, and Bu_3EtNBr at 298.15 K.[10] The order of the osmotic coefficient variation is $Bu_2Et_2N^+$ > $BuEt_3N^+$ > sec-Bu_4N^+ > iso-Bu_4N^+ > *n*-Bu_4N^+. 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: Bu_4N^+ > Pr_4N^+ > Et_4N^+ > Me_4N^+. 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 Pr_3EtNI, *n*-$BuEt_3NI$, and Me_4NI solutions are higher than the values from the 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

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Table 2. Activity and Osmotic Coefficients of Aqueous Solutions of Bu_3EtNI to Bu_2Et_2NI at 298.15 K

NaCl		Bu_3EtNI			sec-$BuEt_3NI$			ter-$BuEt_3NI$			iso-$BuEt_3NI$			Bu_2Et_2NI	
m		m				ϕ			ϕ			ϕ			ϕ	
mol·kg^{-1}	ϕ	mol·kg^{-1}	ϕ	$\gamma_\pm$	m	mol·kg^{-1}	$\gamma_\pm$	m	mol·kg^{-1}	$\gamma_\pm$	m	mol·kg^{-1}	$\gamma_\pm$	m	mol·kg^{-1}	$\gamma_\pm$
0.0324	0.0378	0.0378	0.8141	0.6891	0.0355	0.8676	0.7342	0.0342	0.8993	0.7642	0.0366	0.8405	0.7118	0.0372	0.8278	0.7064
0.0378	0.0449	0.0449	0.7988	0.6605	0.0419	0.8569	0.7111	0.0403	0.8907	0.7444	0.0433	0.8279	0.6866	0.0441	0.8134	0.6798
0.0418	0.0501	0.0501	0.7894	0.6414	0.0466	0.8491	0.6955	0.0449	0.8804	0.7306	0.0483	0.8186	0.6687	0.0491	0.8055	0.6621
0.0529	0.0653	0.0653	0.7607	0.5922	0.0596	0.8332	0.6571	0.0576	0.8620	0.6966	0.0624	0.7955	0.6257	0.0634	0.7825	0.6174
0.0579	0.0727	0.0727	0.7492	0.5712	0.0659	0.8267	0.6405	0.0639	0.8525	0.6816	0.0695	0.7838	0.6067	0.0706	0.7716	0.5976
0.0612	0.0776	0.0776	0.7413	0.5582	0.0701	0.8202	0.6301	0.0679	0.8472	0.6725	0.0739	0.7785	0.5963	0.0749	0.7681	0.5865
0.0676	0.0868	0.0868	0.7307	0.5355	0.0780	0.8137	0.6116	0.0754	0.8413	0.6564	0.0824	0.7695	0.5764	0.0839	0.7563	0.5647
0.0782	0.1035	0.1035	0.7071	0.4990	0.0914	0.8013	0.5833	0.0880	0.8317	0.6318	0.0975	0.7510	0.5439	0.0992	0.7382	0.5317
0.0837	0.1121	0.1121	0.6976	0.4824	0.0985	0.7939	0.5696	0.0953	0.8204	0.6187	0.1055	0.7412	0.5296	0.1069	0.7314	0.5166
0.0877	0.1191	0.1191	0.6880	0.4695	0.1038	0.7896	0.5599	0.0994	0.8244	0.6116	0.1113	0.7362	0.5191	0.1133	0.7231	0.5048
0.0937	0.1288	0.1288	0.6787	0.4528	0.1115	0.7841	0.5465	0.1082	0.8081	0.5972	0.1200	0.7287	0.5042	0.1221	0.7158	0.4896
0.1378	0.2082	0.2082	0.6140	0.3515	0.1756	0.7278	0.4590	0.1658	0.7710	0.5208	0.1889	0.6767	0.4131	0.1969	0.6492	0.3912
0.1367	0.2083	0.2083	0.6090	0.3515	0.1743	0.7277	0.4605	0.1645	0.7708	0.5222	0.1872	0.6777	0.4149	0.1938	0.6544	0.3939
0.1579	0.2503	0.2503	0.5842	0.3142	0.2078	0.7036	0.4262	0.1950	0.7498	0.4905	0.2234	0.6546	0.3799	0.2338	0.6254	0.3566
0.1784	0.2920	0.2920	0.5649	0.2842	0.2438	0.6765	0.3955	0.2257	0.7308	0.4629	0.2618	0.6301	0.3493	0.2705	0.6098	0.3248
0.1805	0.3027	0.3027	0.5512	0.2774	0.2480	0.6729	0.3922	0.2308	0.7230	0.4586	0.2650	0.6297	0.3470	0.2758	0.6050	0.3213
0.2073	0.3652	0.3652	0.5240	0.2431	0.2939	0.6512	0.3602	0.2710	0.7061	0.4282	0.3183	0.6012	0.3131	0.3292	0.5813	0.2868
0.2275	0.4254	0.4254	0.4933	0.2170	0.3380	0.6208	0.3347	0.3095	0.6780	0.4031	0.3626	0.5787	0.2901	0.3751	0.5594	0.2634
0.2482	0.4783	0.4783	0.4783	0.1981	0.3717	0.6155	0.3178	0.3407	0.6715	0.3851	0.4063	0.5631	0.2708	0.4189	0.5462	0.2415
0.2548	0.4980	0.4980	0.4715	0.1919	0.3901	0.6020	0.3094	0.3517	0.6677	0.3792	0.4229	0.5553	0.2643	0.4343	0.5407	0.2351
0.2705	0.5470	0.5470	0.4555	0.1778	0.4310	0.5782	0.2924	0.3830	0.6506	0.3635	0.4602	0.5415	0.2508	0.4687	0.5317	0.2213
0.2930	0.6197	0.6197	0.4362	0.1601	0.4744	0.5697	0.2766	0.4265	0.6337	0.3439	0.5128	0.5270	0.2343	0.5317	0.5083	0.2037
0.3129	0.6878	0.6878	0.4189	0.1461	0.5204	0.5536	0.2619	0.4648	0.6198	0.3286	0.5607	0.5138	0.2214	0.5800	0.4967	0.1904
0.3381	0.7684	0.7684	0.4050	0.1322	0.5785	0.5380	0.2458	0.5151	0.6042	0.3106	0.6289	0.4949	0.2056	0.6463	0.4815	0.1748
0.3558	0.8453	0.8453	0.3875	0.1209	0.6240	0.5249	0.2347	0.5530	0.5922	0.2985	0.6797	0.4819	0.1956	0.7082	0.4625	0.1660
0.3756	0.9080	0.9080	0.3808	0.1127	0.6650	0.5199	0.2257	0.5917	0.5843	0.2871	0.7370	0.4691	0.1857	0.7580	0.4561	0.1556
0.3822	0.9478	0.9478	0.3712	0.1080	0.6928	0.5079	0.2200	0.6100	0.5768	0.2821	0.7490	0.4697	0.1837	0.7808	0.4506	0.1521
0.4257	1.1280	1.1280	0.3475	0.0900	0.8000	0.4900	0.2011	0.7078	0.5538	0.2583	0.8695	0.4508	0.1669	0.9199	0.4261	0.1348
0.4472	1.2309	1.2309	0.3346	0.0816	0.8470	0.4863	0.1940	0.7607	0.5414	0.2473	0.9418	0.4373	0.1587	0.9899	0.4161	0.1266
0.4780	1.3369	1.3369	0.3295	0.0739	0.9185	0.4796	0.1842	0.8399	0.5244	0.2327	1.0339	0.4260	0.1496	1.0998	0.4005	0.1171
0.4967	1.4046	1.4046	0.3260	0.0695	0.9780	0.4682	0.1770	0.8805	0.5200	0.2259	1.1000	0.4162	0.1440	1.1780	0.3887	0.1131
0.5388	1.5480	1.5480	0.3211	0.0611	1.0907	0.4557	0.1651	0.9759	0.5093	0.2118	1.2319	0.4035	0.1343	1.3240	0.3754	0.1042
0.5738	1.6521	1.6521	0.3207	0.0557	1.1900	0.4452	0.1562	1.0800	0.4905	0.1986	1.3523	0.3918	0.1271	1.4262	0.3715	0.0988
0.6123	1.7514	1.7514	0.3231	0.0510	1.3062	0.4332	0.1471	1.1620	0.4870	0.1896	1.4651	0.3863	0.1213	1.5479	0.3656	0.0944
0.6497	1.8245	1.8245	0.3295	0.0478	1.4072	0.4272	0.1402	1.2720	0.4726	0.1791	1.5950	0.3769	0.1156	1.6604	0.3620	0.0909
0.6891	1.9097	1.9097	0.3342	0.0443	1.5450	0.4131	0.1320	1.3915	0.4587	0.1693	1.7030	0.3748	0.1115	1.7596	0.3628	0.0885
0.7599	2.0418	2.0418	0.3455	0.0393	1.7151	0.4113	0.1234	1.5598	0.4523	0.1579	1.8913	0.3730	0.1055	1.9259	0.3663	0.0852
0.8275	2.1727	2.1727	0.3545	0.0349	1.8910	0.4073	0.1159	1.6930	0.4549	0.1504	2.0438	0.3768	0.1013	2.0420	0.3772	0.0821
0.8532	2.2158	2.2158	0.3587	0.0335	1.9278	0.4123	0.1144	1.7710	0.4488	0.1466	2.0958	0.3793	0.0994	2.0778	0.3825	0.0809
0.8689	2.2390	2.2390	0.3618	0.0328	1.9877	0.4075	0.1122	1.7860	0.4535	0.1459	2.1417	0.3782	0.0984	2.1080	0.3842	0.0807

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Table 2. continued

NaCl		Bu_3EtNI		sec-$BuEt_3NI$		ter-$BuEt_3NI$		iso-$BuEt_3NI$		Bu_2Et_2NI	
m / mol·kg^{-1}	ϕ	m / mol·kg^{-1}	ϕ	$\gamma_\pm$	m	ϕ / mol·kg^{-1}	$\gamma_\pm$	m	ϕ / mol·kg^{-1}	$\gamma_\pm$	m	ϕ / mol·kg^{-1}	$\gamma_\pm$
0.8837	2.2758	2.2758	0.3622	0.0317	2.0195	0.4081	0.1110	1.8300	0.4504	0.1440	2.1635	0.3810	0.0981	2.1360	0.3859	0.0802
0.9321	2.3389	2.3389	0.3724	0.0299	2.0900	0.4168	0.1086	1.9238	0.4528	0.1401	2.2539	0.3865	0.0955	2.1790	0.3997	0.0789
0.9590	2.3800	2.3800	0.3770	0.0288	2.1720	0.4130	0.1059	1.9900	0.4508	0.1377	2.3085	0.3886	0.0941	2.2180	0.4045	0.0782
1.1023	2.5825	2.5825	0.4018	0.0236	2.4128	0.4301	0.0987	2.2310	0.4651	0.1303	2.5283	0.4104	0.0917	2.3885	0.4345	0.0748

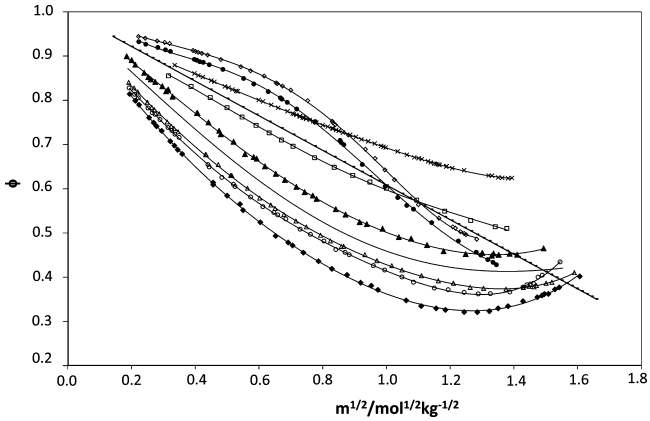

Figure 1. Concentration dependence of the osmotic coefficients for aqueous solutions of TAAI salts at T = 298.15 K. Experimental data: -, DHLL; ◇, $PrEt_3NI$;[9] ○, Bu_2Et_2NI; ●, n-$BuEt_3NI$;[9] ▲, ter-$BuEt_3NI$; ■, sec-$BuEt_3NI$; △, iso-$BuEt_3NI$; ♦, Bu_3EtNI; ×, Me_4NI;[12] □, Et_4NI.[9]

in the solutions of Pr_3EtNI, n-$BuEt_3NI$, and Me_4NI solutions are stronger than those values that occur in the ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Et_2NI, and Bu_3EtNI solutions. The stronger ion association may occur in the Bu_3EtNI 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 Me_4NI aqueous solutions show that ion−solvent interactions dominate over ion−ion interactions; in the case of Pr_3EtNI and n-$BuEt_3NI$ 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

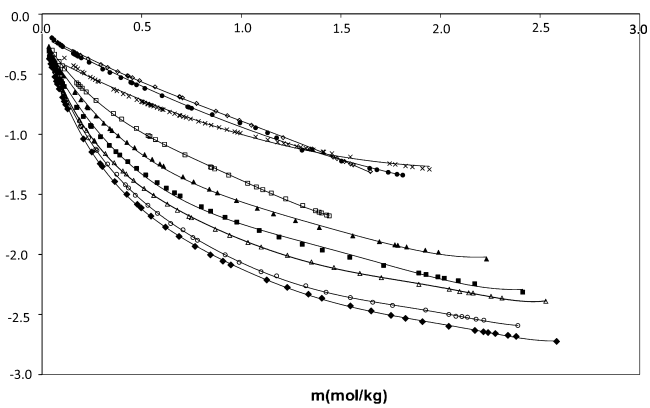

Figure 2. Concentration dependence of the activity coefficients for aqueous solutions of TAAI salts at T = 298.15 K. Data: ◇, $PrEt_3NI$;[9] ○, Bu_2Et_2NI; ●, n-$BuEt_3NI$;[9] ▲, ter-$BuEt_3NI$; ■, sec-$BuEt_3NI$; △, iso-$BuEt_3NI$; ♦, Bu_3EtNI; ×, Me_4NI;[12] □, Et_4NI.[9]

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 Me_4NI to $MeBu_3NI$.[12] For comparison, it was shown that Figure 2 shows the activity coefficient data for Pr_3EtNI,[11] n-$BuEt_3NI$,[11] Me_4NI,[12] Et_4NI,[11] ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Et_2NI, and Bu_3EtNI. The activity coefficients

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decrease in the following order: Pr_3EtN^+ > *n*-$BuEt_3N^+$ > Me_4N^+ > Et_4N^+ > ter-$BuEt_3N^+$ > sec-$BuEt_3N^+$ > iso-$BuEt_3N^+$ > $Bu_2Et_2N^+$ > Bu_3EtN^+ 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 Bu_2Et_2NI and Bu_3EtNI may have the strongest ion-pair formation.

The volumetric behavior of the asymmetric iodides show a decreasing value: *n*-$BuEt_3N^+$ > iso-$BuEt_3N^+$ > sec-$BuEt_3N^+$ > ter-$BuEt_3N^+$, 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:

$$A_{\phi} = \frac{1}{3}\sqrt{2\pi N_o d_1}\left(\frac{e^2}{4\pi\varepsilon_o DkT}\right)^{1.5} \quad (5)$$

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 σ (ϕ) = 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:

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

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-$BuEt_3NI$ and 0.022 to Bu_3EtNI. 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.

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.

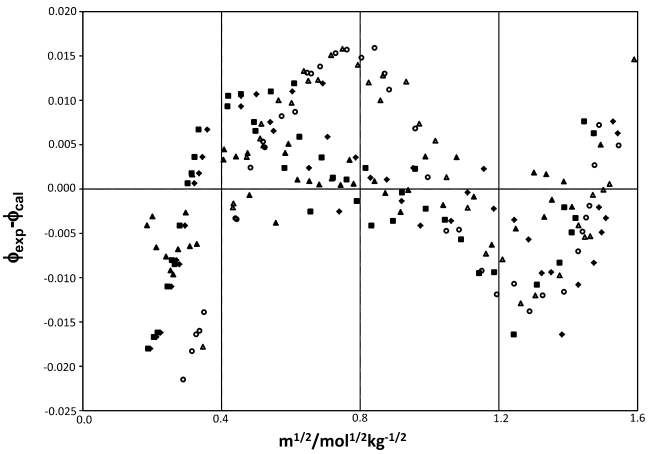

Figure 3. Differences (residuals) between experimental osmotic coefficients ϕ and least-squares fit values ϕ (cal) of TAAI as a function of m at T = 298.15 K, for fits in the molality region (0−1.00) mol kg^{-1}. Data: ○, Bu_2Et_2NI; ▲, ter-$BuEt_3NI$; ■, sec-$BuEt_3NI$; △, iso-$BuEt_3NI$; ♦, Bu_3EtNI.

Table 3 shows the Pitzer's ion parameters where β_1 varies as ter-$BuEt_3NI$ > sec-$BuEt_3NI$ > iso-$BuEt_3NI$ > Bu_2Et_2NI > Bu_3EtNI 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: Me_4NI;[12] $MeEt_3NI$;[11] $PrEt_3NI$;[9] *n*-$BuEt_3NI$;[11] ter-$BuEt_3NI$; $PenEt_3NI$;[11] Et_4NI;[11] $HexEt_3NI$;[11] $HepEt_3NI$;[11] sec-$BuEt_3NI$; iso-$BuEt_3NI$; Bu_2Et_2NI; Bu_3EtNI. 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-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, Bu_2Me_2NI, and Bu_3EtNI 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: Pr_3EtNI[11]> *n*-$BuEt_3NI$[11]> Me_4NI[12]> Et_4NI[11] > ter-$BuEt_3NI$ > sec-$BuEt_3NI$ > iso-$BuEt_3NI$ > Bu_2Et_2NI > Bu_3EtNI. 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 $\beta_1$varies from −1.305 for ter-$BuEt_3NI$ to −3.172 for Bu_3EtNI, in the same order as the osmotic coefficient variations: ter-$BuEt_3NI$ > sec-$BuEt_3NI$ > iso-$BuEt_3NI$ > Bu_2Et_2NI > Bu_3EtNI. Our results confirm that there may be a physical relationship of β_1 with ion−solvent interactions.

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

parameter	ter-$BuEt_3NI$	sec-$BuEt_3NI$	iso-$BuEt_3NI$	Bu_2Et_2NI	Bu_3EtNI
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
Cγ (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

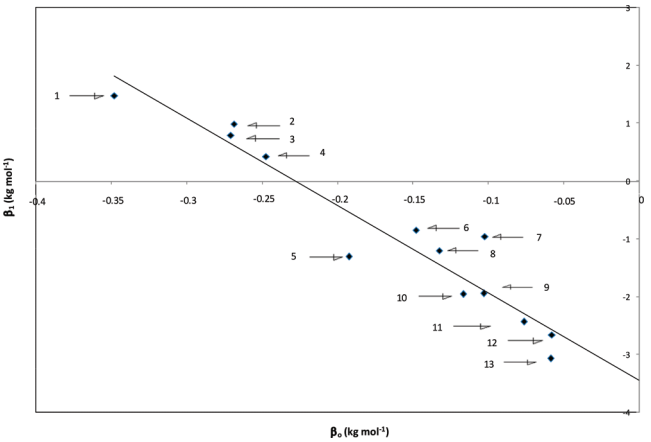

Figure 4. Linear relation of β_0 to β_1 for TAAI salts with a r^2 = 0.911 at 298.15 K. Experimental data: (1) Me_4NI;[12] (2) $MeEt_3NI$;[11] (3) $PrEt_3NI$;[9] (4) *n*-$BuEt_3NI$;[11] (5) ter-$BuEt_3NI$; (6) $PenEt_3NI$;[11] (7) Et_4NI;[11] (8) $HexEt_3NI$;[11] (9) $HepEt_3NI$;[11] (10) sec-$BuEt_3NI$; (11) iso-$BuEt_3NI$; (12) Bu_2Et_2NI; (13) Bu_3EtNI.

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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 Chemisty 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 activites 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 and 288.15) 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 $MeEt_3NI$ to $HepEt_3NI$ 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 Me_4NI to $MeBu_3NI$ 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. I I. 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 ^{14}C-Diäthylamin und ^{14}C-Lysergsäure-diäthylamid. 34. Mitteilung über Mutterkornalkaloide. *Helv. Chim. Acta* **1954**, *37*, 820−820.

(20) Archer, D. Thermodynamic properties of the KCl + H_2O 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 solutionts 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.