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[†]

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Osmotic coefficients of aqueous solutions of Bu_4NBr, *sec*-Bu_4NBr, iso-Bu_4NBr, Bu_2Et_2NBr, and Bu_3EtNBr are measured at T = (283.15 and 288.15) K by the isopiestic method. A branched isopiestic apparatus was used. The osmotic data of the solutions were compared at T = (283.15 and 298.15) K. Osmotic coefficient data are correlated using the Pitzer model. The parameters obtained with the Pitzer model are used to calculate the mean molal activity coefficients. Vapor pressures of the solutions are evaluated from osmotic coefficients, and their depression was used for qualitative deduction of solute−solvent interactions occurring in these solutions.

Introduction

Experimental phase equilibrium data of aqueous electrolyte solutions are required in the prediction of the behavior of electrolyte solutions, the development of the electrolyte models, and the estimation of interactions occurring in these solutions. There is a growing interest in the determination of solvent activity osmotic and activity coefficients of electrolyte solutions over a wide range of concentration as a function of temperature.

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.[1−3] 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.[4−6] Using a twelve-leg manifold attached to round-bottomed cups, the osmotic coefficients of five aqueous solution systems of symmetrical and unsymmetrical quaternary ammonium bromides were measured at T = (283.15 and 288.15) K.

Because of their extensive solubilities in water and by the great volume of the cation, the aqueous solutions of tetraalkylammonium halides (TAAX, X = F, Cl, Br, and I) have been used to study the effect of changing the alkyl chains R ($R_1R_2R_3R_4NX$ with $R_1 \neq R_2$, R_3, and R_4) over the activity coefficients and other related magnitudes in terms of hydrophobic interaction models.[7−10] Moreover, evidence suggests that alkyl chains may have an effect over the surrounding water network.[11−13] When the osmotic data of TAAX was compared to the Debye−Hückel limiting law (DHLL), the deviations of the data were explained in terms of structure−water modification due to the promotion of ion pairing formation.[14,15] From osmotic coefficient measurements, thermodynamic properties of TAAX salts (X = F, Cl, Br, and I) at (298.15 K and 338.15) K have been interpreted in terms of the effect of increasing anion size and increasing temperature on the local structure of water.[16]

The question of hydrophobic interactions between TAA cations in aqueous solutions has also been addressed experimentally both by osmotic coefficient data for aqueous solutions of unsymmetrical series $MeEt_3NI$ to $HepEt_3NI$ at 298.15 K[17] and Me_4NI to $MeBu_3NI$[18] at 298.15 K and theoretically by the analysis of the parameters obtained with the Pitzer model.

In earlier papers, with the goal of looking for evidence of hydrophobic interactions due to the presence of the butyl radical, the osmotic coefficient of the series Bu_2Et_2NBr to Bu_4NBr at (298.15 and 293.15) K was experimentally determined.[19,20]

In the present work osmotic coefficients from equilibrium molalities of aqueous solutions of Bu_4NBr, *sec*-Bu_4NBr, iso-Bu_4NBr, Bu_2Et_2NBr, and Bu_3EtNBr at T = (283.15 and 288.15) K using a branched isopiestic apparatus were obtained. A solution of NaCl served as the isopiestic reference solution. The objective of this work is to evaluate the effect of lower temperatures on the behavior of the osmotic and activity coefficients of aqueous solutions of the TAABr considered here. The activity coefficient data are believed to be precise to within 0.50 %. The results indicate that the Pitzer model works properly at these temperatures. It correlates the osmotic coefficients of the studied solutions with acceptable precision. The results were fitted to the Pitzer model, and the parameters β_0 and β_1 were calculated.

Experimental Section

Materials. In all experiments, distilled deionized water was used. The Bu_4NI and NaCl with a purity of analytically pure grade, higher than 99 %, were employed with no further purification. The TAABr salts were synthesized using a modification of the procedure recommended by Vogel.[21] Stoichiometric amounts of alkyl amine and the selected alkyl bromide in methanol (Merck, Zur Analyze) solution were stirred in a reactor for 48 h. Usually a white sticky solid was obtained. The salts were crystallized from ethanol solution and dried under

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Table 1. Isopiestic Molalities of Aqueous Solutions of TAABr Salts at T = (283.15 to 288.15) K

NaCl	Bu_4NBr			*sec*-Bu_4NBr			iso-Bu_4NBr			Bu_2Et_2NBr			$BuEt_3NBr$		
m/mol·kg^{-1}	m/mol·kg^{-1}	ϕ	$\gamma_\pm$	m/mol·kg^{-1}	ϕ	$\gamma_\pm$	m/mol·kg^{-1}	ϕ	$\gamma_\pm$	m/mol·kg^{-1}	ϕ	$\gamma_\pm$	m/mol·kg^{-1}	ϕ	$\gamma_\pm$
							283.15 K								
0.1035	0.1035	0.9257	0.7683	0.1033	0.9270	0.7691	0.1035	0.9253	0.7692	0.1034	0.9261	0.7700	0.1033	0.9271	0.7702
0.1372	0.1380	0.9204	0.7478	0.1377	0.9222	0.7488	0.1376	0.9231	0.7493	0.1376	0.9232	0.7503	0.1376	0.9231	0.7506
0.2181	0.2197	0.9146	0.7146	0.2195	0.9154	0.7159	0.2192	0.9167	0.7168	0.2189	0.9178	0.7186	0.2187	0.9188	0.7196
0.2971	0.2995	0.9111	0.6932	0.2991	0.9123	0.6948	0.2986	0.9138	0.6961	0.2978	0.9163	0.6989	0.2974	0.9175	0.7005
0.3316	0.3343	0.9104	0.6858	0.3339	0.9114	0.6877	0.3332	0.9133	0.6892	0.3324	0.9156	0.6923	0.3319	0.9169	0.6942
0.4704	0.4739	0.9101	0.6641	0.4732	0.9114	0.6661	0.4724	0.9129	0.6687	0.4702	0.9172	0.6736	0.4688	0.9200	0.6768
0.5591	0.5629	0.9111	0.6545	0.5619	0.9128	0.6574	0.5608	0.9146	0.6600	0.5576	0.9198	0.6660	0.5550	0.9241	0.6701
0.6892	0.6903	0.9136	0.6445	0.6887	0.9157	0.6480	0.6871	0.9179	0.6513	0.6825	0.9240	0.6588	0.6790	0.9288	0.6642
0.7907	0.7953	0.9160	0.6386	0.7927	0.9190	0.6426	0.7904	0.9217	0.6465	0.7842	0.9289	0.6553	0.7801	0.9340	0.6618
0.8634	0.8682	0.9180	0.6355	0.8651	0.9213	0.6399	0.8617	0.9249	0.6442	0.8544	0.9328	0.6538	0.8485	0.9393	0.6611
0.9705	0.9751	0.9217	0.6320	0.9705	0.9261	0.6369	0.9658	0.9307	0.6419	0.9569	0.9393	0.6528	0.9497	0.9464	0.6612
							288.15 K								
0.1021	0.1045	0.9107	0.7367	0.1042	0.9130	0.7425	0.1041	0.9142	0.7470	0.1041	0.9139	0.7509	0.1039	0.9158	0.7464
0.1531	0.1582	0.8964	0.6979	0.1572	0.9021	0.7055	0.1569	0.9038	0.7115	0.1562	0.9080	0.7177	0.1569	0.9040	0.7112
0.2706	0.2837	0.8776	0.6396	0.2811	0.8859	0.6512	0.2795	0.8908	0.6599	0.2772	0.8982	0.6708	0.2793	0.8916	0.6613
0.3651	0.3864	0.8681	0.6075	0.3824	0.8772	0.6225	0.3804	0.8818	0.6328	0.3749	0.8947	0.6477	0.3789	0.8853	0.6362
0.4636	0.4954	0.8596	0.5817	0.4912	0.8670	0.5999	0.4856	0.8770	0.6120	0.4763	0.8941	0.6309	0.4818	0.8840	0.6178
0.5828	0.628	0.8539	0.5571	0.6212	0.8632	0.5797	0.6127	0.8752	0.5933	0.6002	0.8934	0.6167	0.6069	0.8837	0.6019
0.6706	0.7262	0.8512	0.5429	0.7168	0.8624	0.5681	0.7082	0.8728	0.5825	0.6897	0.8963	0.6093	0.6983	0.8853	0.5933
0.7752	0.8429	0.8501	0.5287	0.8295	0.8638	0.5569	0.8192	0.8747	0.5722	0.7971	0.8989	0.6029	0.8052	0.8899	0.5857
0.8529	0.9276	0.8517	0.5198	0.9119	0.8663	0.5500	0.9012	0.8766	0.5660	0.8741	0.9038	0.5995	0.8847	0.8929	0.5813
0.9927	0.8566	0.5063	1.0605	0.8713	0.5399	1.0495	0.8804	0.5568	1.0119	0.9132	0.5956	1.0280	0.8989	0.8989	0.5756

vacuum for 48 h. To avoid water salt contamination, salts were deposited in a desiccator, and the purity was analyzed before use.

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.[22]

Apparatus and Procedure. The isopiestic apparatus employed in the present work is essentially similar to the one used described previously.[19] Temperatures were measured with a Pt-100 resistant temperature probe, which was placed at the bottom of the equilibrium chamber and connected to a temperature control with a precision of ± 0.02. The uncertainty calibration was ± 0.01. The uncertainty of the whole temperature measurement system estimated to be ± 0.05 K. The apparatus was held in a constant temperature bath at least for 130 h for equilibration at each temperature.

The NaCl(aq) isopiestic reference standard stock solutions were prepared by mass from oven-dried analytical reagent grade NaCl (analytical) and purified water. Molar masses used for molality calculations or gravimetric analysis of solutions are 58.443 g·mol^{-1} for NaCl.

Results and Discussion

Isopiestic equilibrium molalities of the investigated solutions with reference standard solutions of NaCl as a function of molality and temperature enabled us to calculate the osmotic coefficients of the investigated solutions in Table 1, ϕ, from

$$\phi^* = \frac{v_r m_r \phi_r}{v^* m^*} \tag{1}$$

Here, v 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 strike (*) indicates the TAABr solution. Osmotic coefficients of the isopiestic reference solution in the isopiestic equilibrium at m_r were obtained from the extended Bradley−Pitzer correlation.[23] Figures 1 and 2 show the osmotic coefficients of the aqueous solutions of TAABr at T = (283.15 and 288.15) K, respectively. The following manner can be deduced from Figure 1 for the osmotic data relation at T = 283.15 K:

$$\phi_{Bu_3EtNBr} > \phi_{Bu_2Et_2NBr} > \phi_{iso\text{-}Bu_4NBr} > \phi_{sec\text{-}Bu_4NBr} > \phi_{Bu_4NBr}$$

and the relation at T = 288.15 K:

$$\phi_{Bu_2Et_2NBr} > \phi_{Bu_3EtNBr} > \phi_{iso\text{-}Bu_4NBr} > \phi_{sec\text{-}Bu_4NBr} > \phi_{Bu_4NBr}$$

It would be expected that lower temperatures would affect the ability of larger TAA cations to promote local water structure.[12] The change in the order of the osmotic coefficient

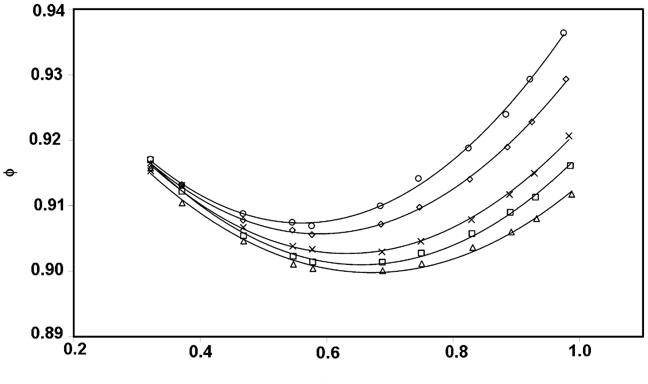

Figure 1. Concentration dependence of the osmotic coefficients for aqueous solutions of TAABr salts at T = 283.15 K. ○, $BuEt_3NBr$; ◇, Bu_2Et_2NBr; x, iso-Bu_4NBr; Δ, Bu_4NBr; □, *sec*-Bu_4NBr.

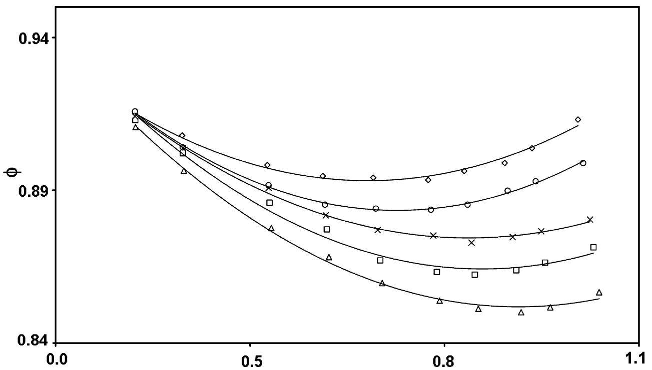

Figure 2. Concentration dependence of the osmotic coefficients for aqueous solutions of TAABr salts at T = 288.15 K. ○, $BuEt_3NBr$; ◇, Bu_2Et_2NBr; x, iso-Bu_4NBr; Δ, Bu_4NBr; □, *sec*-Bu_4NBr.

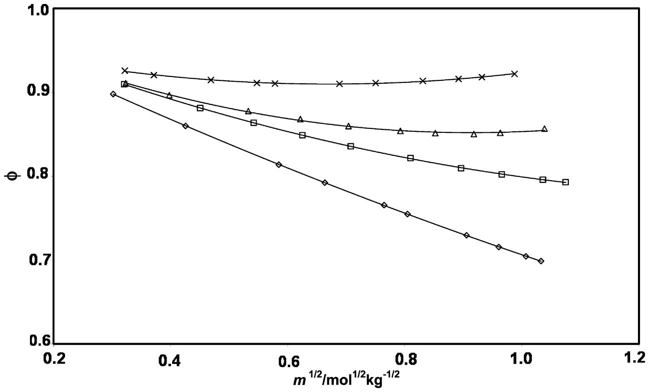

Figure 3. Concentration dependence of the osmotic coefficients for aqueous solutions of Bu_4NBr at the following temperatures: ◇, 298.15 K, ref 19; □, 293.15 K, ref 20; Δ, 288.15 K; x, 283.15 K.

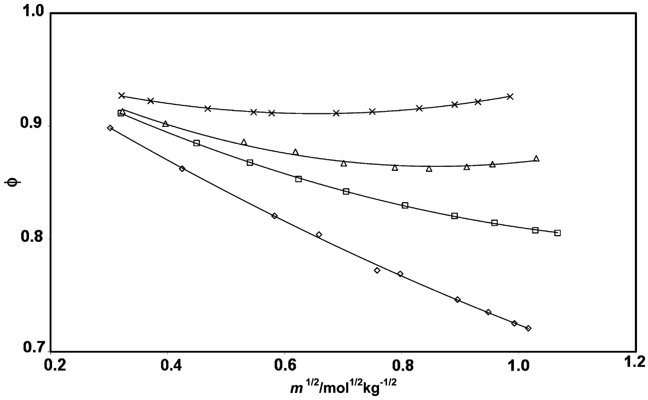

Figure 4. Concentration dependence of the osmotic coefficients for aqueous solutions of *sec*-Bu_4NBr at the following temperatures: ◇, 298.15 K, ref 19; □, 293.15 K, ref 20; Δ, 288.15 K; x, 283.15 K.

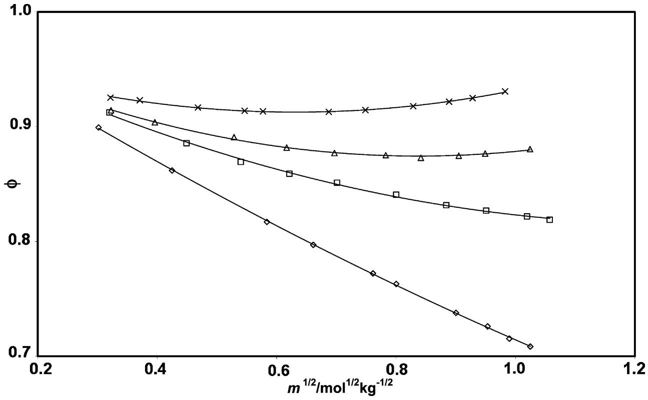

Figure 5. Concentration dependence of the osmotic coefficients for aqueous solutions of iso-Bu_4NBr at the following temperatures: ◇, 298.15 K, ref 19; □, 293.15 K, ref 20; Δ, 288.15 K; x, 283.15 K.

data to $BuEt_3NBr$ and Bu_2Et_2NBr may reflect the effect of an unsymmetric cation molecule on the solvent−solute interactions.

From Figures 3, 4, 5, 6, and 7, it can be seen that the relative order of the osmotic coefficient of the TAABr solutions at $T =$ (283.15 and 298.15) K values suggest that the asymmetry of the cation has an important effect over the increasing osmotic coefficient. At $T = 283.15$ K, the osmotic coefficients of TAABr are greater than those at $T = 298.15$ K.

If the behavior of osmotic coefficients versus molality is interpreted in terms of solute−solvent interactions and ion association phenomena,[16] the data may suggest that solute−solvent interactions in the solutions of TAABr at lower temperatures are stronger than those that occur at higher temperatures.

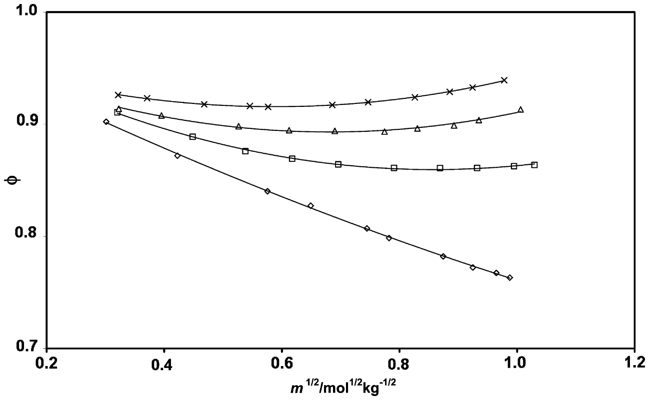

Figure 6. Concentration dependence of the osmotic coefficients for aqueous solutions of Bu_2Et_2NBr at the following temperatures: ◇, 298.15 K, ref 19; □, 293.15 K, ref 20; Δ, 288.15 K; x, 283.15 K.

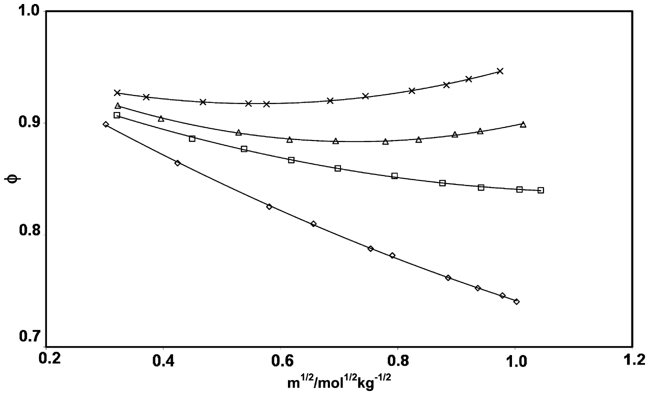

Figure 7. Concentration dependence of the osmotic coefficients for aqueous solutions of $BuEt_3NBr$ at the following temperatures: ◇, 298.15 K, ref 19; □, 293.15 K, ref 20; Δ, 288.15 K; x, 283.15 K.

Table 2. Values Obtained for Pitzer Ion Parameters for TAABr Salts at $T =$ (283.15 and 288.15) K

parameter	Bu_4NBr	*sec*-Bu_4NBr	iso-Bu_4NBr	Bu_2Et_2NBr	$BuEt_3NBr$
			283.15 K		
β_0, kg·mol^{-1}	0.0782	0.0822	0.0872	0.0429	0.1090
β_1, kg·mol^{-1}	0.1375	0.1373	0.1319	0.0102	0.1038
σ, ϕ	0.008	0.007	0.006	0.002	0.006
			288.15 K		
β_0, kg·mol^{-1}	0.0259	0.05095	0.0836	0.0429	0.0462
β_1, kg·mol^{-1}	−0.0008	−0.0698	−0.0853	0.0102	0.0104
σ, ϕ	0.01	0.009	0.005	0.007	0.005

Correlation Data. The Pitzer ion interaction model has been successfully used for aqueous electrolyte solutions.[24] It has the following form:

$$\phi - 1 = |z_+z_-|f^{\phi} + m\left(\frac{2v_+v_-}{v}\right)B^{\phi} + m^2\left(\frac{2(v_+v_-)^{3/2}}{v}\right)C^{\phi} \tag{2}$$

where

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

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

$$\ln \gamma_{\pm} = |z_+z_-|f^{\gamma} + m\left(\frac{2v_+v_-}{v}\right)B^{\gamma} + m^2\left(\frac{2v_+v_-}{v}\right)C^{\gamma} \tag{5}$$

where β_0 (kg·mol^{-1}), β_1 (kg·mol^{-1}), and C^{ϕ} (kg·mol^{-1})^2 are Pitzer ion-interaction parameters. The optimum values of $\alpha =$

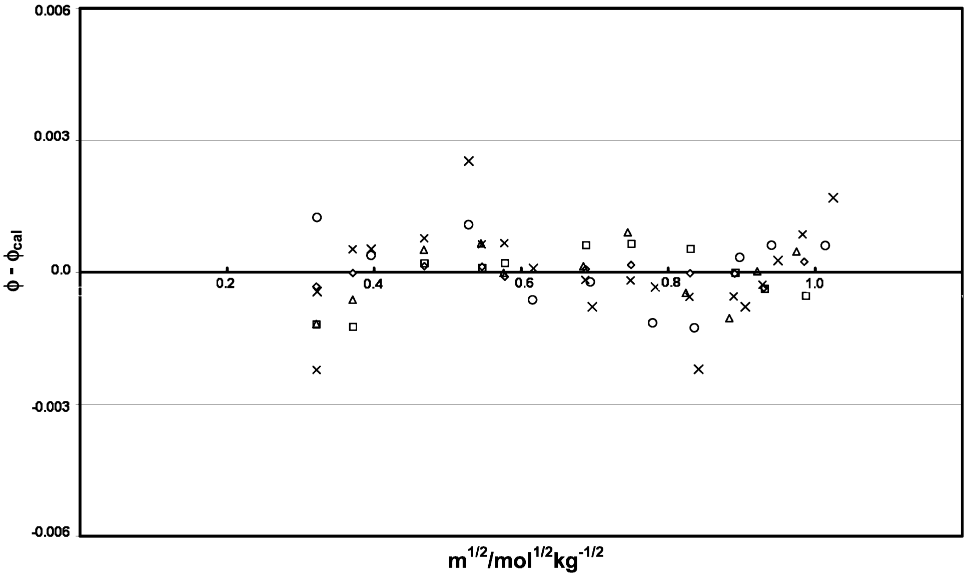

Figure 8. Differences (residuals) between experimental osmotic coefficients ϕ and least-squares fit values ϕ (cal) of TAABr as a function of m at T = (283.15 and 288.15) K, for fits with the molality region (0 to 1.00) mol·kg^{-1}. Experimental data: ○, $BuEt_3NBr$; ◇, Bu_2Et_2NBr; x, iso-Bu_4NBr; Δ, Bu_4NBr; □, *sec*-Bu_4NBr.

Table 3. Vapor Pressure, Molar Volume, and Virial Coefficient of Water with Temperature

T / K	P / kPa	$V°$ / $m^3 \cdot mol^{-1}$	B_2 / $m^3 \cdot mol^{-1}$
283.15	1227.57	18.022	−1.475
288.15	1705.03	18.032	−1.357
293.15	2338.34	18.054	−1.252
298.15	3168.62	18.069	−1.157

2 (kg·mol^{-1})$^{1/2}$ and b = 1.2 (kg·mol^{-1})$^{1/2}$ in the Pitzer model are respectively selected for all studied solutions. The osmotic coefficients of the reference solution are reproduced with a standard deviation of 0.005. The Debye−Hückel constants for the osmotic coefficient, A_ϕ (kg·mol^{-1})$^{1/2}$, at T = 283.15 K and T = 288.15 K are 0.3821 and 0.3847, respectively.[2] In Table 2, experimental osmotic coefficients and molal activity coefficients calculated from eq 5 at T = (283.15 and 288.15) K are reported. Table 2 contains the standard deviations of the Pitzer parameters, defined as

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

in which n is the number of data and exp and cal stand for experimental and calculated values.

The results collected in Table 2 show that the average standard deviations for TAABr solutions are 0.0058 at T = 283.15 K and 0.0072 at T = 288.15 K. Thus, the capability of the Pitzer model for the correlation of the osmotic coefficients of the TAABr solutions with two parameters is within the experimental error. Figure 8 shows the differences (residuals) between experimental osmotic coefficients ϕ and least-squares fit values ϕ (cal) of TAABr as a function of m at T = (283.15 and 288.15) K, for fits with the molality region (0 to 1.00) mol·kg^{-1} with a maximum variation of ± 0.0022. The maximum uncertainty in the osmotic coefficient (ϕ) is estimated to be ± 0.04 %.

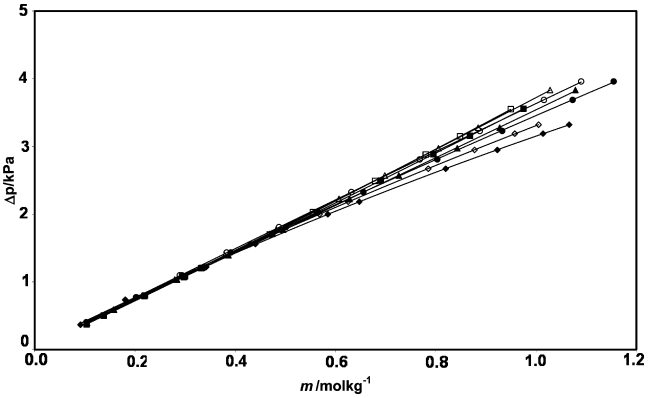

Figure 9. Vapor pressure vs molality of solutions of Bu_4NBr: ◆, T = 298.15 K; ●, 293.15 K; ▲, 288.15 K; ■, 283.15 K. Solutions of Bu_2Et_2NBr: ◇, T = 298.15 K; ○, 293.15 K; Δ, 288.15 K; □, 283.15 K.

The vapor pressures of solution behavior, p, were compared at isopiestic equilibrium molalities and were calculated to evaluate the solute−solvent interactions. In this case two systems were selected, the symmetrical Bu_4NBr solutions and the unsymmetrical Bu_2Et_2NBr at T = (283.15 and 298.15) K. The vapor pressures of the solutions can be obtained using the following equations:

$$\phi = -\frac{\ln a_1}{\upsilon m M_1} \tag{7}$$

$$\ln a_1 = \ln\left(\frac{p}{p^0}\right) + \frac{(\beta - V^0)(p - p^0)}{RT} \tag{8}$$

In these equations M_1, β, V_0, and p_0 are the molar mass (kg·mol^{-1}), the second virial coefficient (m^3·mol $^{-1}$), molar volume (m^3·mol^{-1}), and vapor pressure (Pa) of the pure solvent, and R and T are the gas constant (8.314 J·K^{-1}·mol^{-1}) and absolute temperature, respectively. The values of the pure solvent parameters used here are given in Table 3. Figure 9 shows the vapor pressure variation (Δp) versus molality of Bu_4NBr and Bu_2Et_2NBr solutions at T = (283.15 and 298.15) K. Δp was calculated from the vapor pressures of the solutions (p) and the pure solvent pressure by the equation

$$\Delta p = p^0 - p \tag{9}$$

From Figure 9 it may be clear that the order of vapor pressure may be directly correlated to the solute−solvent interactions.

The vapor pressure of both Bu_4NBr and Bu_2Et_2NBr solutions is smaller at $T = 298.15$ K compared with the data at $T = 283.15$ K. However, it is also clear that at a concentration of $m < 0.6$, it is not a clear effect of temperature on the vapor pressure data. The following manner can be deduced from this figure:

$$\Delta p_{283.15\ \mathrm{K}} > \Delta p_{288.15\ \mathrm{K}} > \Delta p_{293.15\ \mathrm{K}} > \Delta p_{298.15\ \mathrm{K}}$$

Conclusions

Experimental osmotic coefficients of Bu_4NBr, *sec*-Bu_4NBr, iso-Bu_4NBr, Bu_2Et_2NBr, and Bu_3EtNBr have been measured at $T = (283.15$ and $288.15)$ K by an isopiestic method. A branched isopiestic apparatus was used. The order of the osmotic data and the vapor pressure of the TAABr have been interpreted in terms of solute−solvent interactions. Experimental osmotic data was correlated using the Pitzer model with good precision. The osmotic coefficient order at $T = (283.15$ and $288)$ K show that solute−solvent interactions may be stronger in solutions with unsymmetrical cations like $Bu_2Et_2N^+$ and $BuEt_3N^+$ and at lower temperatures. From the vapor pressure data, it can be seen that, in solutions at $m < 0.6$, there is no evidence of a difference in solute−solvent interactions.

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