Commentary on "Study of Assorted Interactions of an Ionic Liquid in Significant Solvent Systems using Compensated Equation of Fuoss Conductance and Vibrational Mode"

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Abstract

Several computational errors in the paper are pointed out pertaining to the calculation of Gibbs energy from the measured overall pairing association constant. The calculation of ionic limiting molar conductances is discussed based on the tetrabutylammonium tetraphenylboride reference electrolyte method.

In a recent paper appearing in this Journal Banik and Roy [1] used electrical conductances and Fourier transform infrared measurements to study molecular interactions in mixtures containing tetrabutylphosphonium methanesulfonate [Bu$_4$PMS] dissolved in dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide. The authors reported the limiting molar conductances (Λ_0) of the dissolved salt, the overall pairing association constant (K_A) of the ionic salt, and the ionic limiting molar conductances ($\lambda_0^{\pm}$) of both the Bu$_4$P$^+$ and MS$^-$ ions in the three solvents studied at 298.15 K. While much of the presentation appears to be correct, there are several incorrect numerical entries in the paper of which journal readers need to be aware.

First, the three sets of numerical entries of K_A, log K_A and ΔG^0 given in Table 3 of the paper by Bannik and Roy [1] are not internally consistent. The first numerical value of K_A =

29.89 dm^3 mol^{-1} and the corresponding log K_A value is not log K_A = 5.48 as the authors give in the next to last column. The natural logarithm is ln 29.89 = 3.398, so this is not the error. Similarly if one substitutes the numerical values of K_A = 29.89 or log K_A = 5.48 into eq 12 of the paper (renumbered below as eq 1), one obtains:

$$\Delta G^0 = -\,RT\,\ln K_A \tag{1}$$

$$\Delta G^0/(\text{kJ mol}^{-1}) = -\,(0.008314)(298.15)\,\ln 29.89 = -\,8.433$$

or

$$\Delta G^0 = -\,2.303\,RT\,\log K_A \tag{2}$$

$$\Delta G^0/(\text{kJ mol}^{-1}) = -\,2.303\,(0.008314)(298.15)\,(5.48 = -\,31.284$$

The latter value differs from the authors' value by a factor of 10. The value that is given in the last column of Table 3 in the paper by Banik and Roy [1] corresponding to K_A = 29.89 dm^3 mol-1 is $\Delta G^0/(\text{kJ mol}^{-1}) = -\,3.12$. Clearly there are inconsistencies in the numerical entries. If the authors had intended for the values of K_A to be a different set of concentration units, then it should have been specified in the published paper. Journal readers should not be expected to guess concentration units. Given the inconsistencies in the K_A, log K_A and ΔG^0 values, readers should exercise caution when using any of these published numerical values.

Second, eq 8 in the manuscript (renumbered below as eq 3) may be in error.

$$K_A = K_R/(1 - \alpha) = K_R/(1 + K_S) \tag{3}$$

The manuscript text immediately below eq 8 states that K_S is the association constant of the contact-pairs, K_R is the associated constant of the solvent-separated pairs, K_A is the overall pairing constant, and α is the fraction of contact pairs. Let's focus on the last two parts of the

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equality, namely $K_R/(1 - \alpha) = K_R/(1 + K_S)$. Let's divide both sides by K_R, and then reciprocate both sides of the equation to get $(1 - \alpha) = (1 + K_S)$. Now subtract 1 from both sides to get, $- \alpha = K_S$. Neither the association constant nor fraction of contact pairs should be negative. The only way to satisfy the mathematical condition of $- \alpha = K_S$ without using a negative value would be for both α and K_S to equal zero.

Third, the authors completely misused the tetrabutylammonium tetraphenylborate [Bu$_4$NBPh$_4$] reference electrolyte method when calculating the individual ionic molar conductances of the Bu$_4$P$^+$ and MS$^-$ ions in dimethyl sulfoxide, N,N-dimethylformamide and N,N-dimethylacetamide. The tetrabutylammonium tetraphenylborate reference electrolyte method traces back to a paper by Fuoss and Hirsch [2] where the ionic limiting molar conductance of Bu$_4$N$^+$ cation was set equal to the ionic limiting molar conductance of BPh$_4^-$ anion. The rationale for equating the ionic limiting molar conductances of these specific two ions was that both ions were large and were of approximately equal size. Neither ion was expected to undergo much (if any) specific interactions with surrounding solvent molecules. This is not necessarily the case for the ions studied by Banik and Roy. As an information note several researchers [3-5] have modified the Bu$_4$NBPh$_4$ reference electrolyte method:

$$\frac{\lambda_\pm^0(Bu_4N^+)}{\lambda_\pm^0(BPh_4^-)} = \frac{crystallographic\ radius\ of\ BPh_4^-}{cyrstallographic\ radius\ of\ Bu_4N^+} \tag{3}$$

to allow for slight differences in Bu$_4$N$^+$ and BPh$_4^-$ ionic sizes.

I think that Banik and Roy mistook the above approximation that others have used for calculating the ionic limiting molar conductances of Bu$_4$N$^+$ and BPh$_4^-$ ions to apply to all ions. The reason that I think this is the ratio of crystallographic radii is $r_c(Bu_4N^+)/r_c(MS^-) = 4.42/2.83 = 1.562$ which equals the ionic limiting molar conductances of $\lambda_\pm^0(MS^-)/\lambda_\pm^0(Bu_4P^+) = 1.562$,

$\lambda_{\pm}^0(MS^-)/ \lambda_{\pm}^0(Bu_4P^+) = 1.561$, and $\lambda_{\pm}^0(MS^-)/ \lambda_{\pm}^0(Bu_4P^+) = 1.562$ in dimethyl sulfoxide, N,N-dimethylacetamide and N,N-dimethylformamide, respectively. The numerical values of r_c and of $\lambda_{\pm}^0$ used in the preceding calculations came from Table 4 in the paper by Banik and Roy [1]. The problem with calculating ionic limiting molar conductances of individual ions in this fashion is that one does not have a unique value for the individual ion in a given solvent as required by Kohlrausch's law of independent migration of ions [6].

The correct application of the tetrabutylammonium tetraphenylborate reference electrolyte method would be to set $\lambda_{\pm}^0(Bu_4N^+) = \lambda_{\pm}^0(BPh_4^+)$ in all three solvents, and then find sufficient limiting molar conductance data for other salts to permit the calculation of either $\lambda_{\pm}^0(Bu_4P^+)$ or $\lambda_{\pm}^0(MS^+)$. The remaining ion value then would be calculated from the experimental Λ_0 data of the dissolved Bu_4PMS given in the second column of Table 3 in the Banik and Roy paper. This is easy to do in the case of N,N-dimethylformamide as Borun and Bald [7] have already calculated the ionic limiting molar conductances of both the Bu_4N^+ cation $(\lambda_{\pm}^0\ x\ 10^4/(S\ m^2\ mol^{-1}) = 24.91)$ and BF_4^- anion $(\lambda_{\pm}^0\ x\ 10^4/(S\ m^2\ mol^{-1}) = 54.77)$ based on the tetrabutylammonium tetraphenylborate reference electrolyte method (e.g., $\lambda_{\pm}^0(Bu_4N^+) = \lambda_{\pm}^0(BPh_4^+)$) using measured Λ_0 data for Bu_4NBPh_4, $NaBPh_4$ and $NaBF_4$ dissolved in N,N-dimethylformamide at 298.15 K. The ionic limiting molar conductance of the Bu_4P^+ can be derived by subtracting the BF_4^- value of $\lambda_{\pm}^0\ x\ 10^4/(S\ m^2\ mol^{-1}) = 54.77$ from the value of $\Lambda_0\ x\ 10^4/(S\ m^2\ mol^{-1}) = 60.84$ determined by Roy and coworkers [8] for Bu_4PBF_4 in N,N-dimethylformamide at 298.15 K. Performing the indicated subtraction, a value of $\lambda_{\pm}^0\ x\ 10^4/(S\ m^2\ mol^{-1}) = 6.07$ is computed for the ionic limiting molar conductance of Bu_4P^+ in N,N-dimethylformamide. The ionic limiting molar conductance of the methanesulfonate anion is obtained in similar fashion, by subtracting the just calculated value for the Bu_4P^+ cation from the

$\Lambda_0(Bu_4PMS)$ value in Table 3, namely $\lambda_{\pm}^0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 57.07 - 6.07 = 51.00$ for MS^- in N,N-dimethylformamide. The values given by Banik and Roy [1] were $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 22.28$ and $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 34.79$ for the tetrabutylphosphonium and methanesulfonate ions, respectively.

There is published conductivity data for tetrabutylammonium tetraphenylborate in dimethyl sulfoxide [3]. One would calculate a numerical value of $\lambda_o^{\pm} \ x \ 10^4 = 10.15$ for the tetrabutylammonium cation from the authors' data. (Tsierkezos and Philippopoulos [3] calculated a slightly different numerical value of $\lambda_o^{\pm} \ x \ 10^4 = 10.50$ as they assumed that the molar conductivity of the tetrabutylammonium was slightly larger than the molar conductivity of the tetraphenylborate anion, e.g., $\lambda_o^{\pm}$ cation $= 1.07 \ x \ \lambda_o^{\pm}$ anion – this particular approach takes into account the slight differences in the crystallographic radii of the two reference ions). There is published of $\Lambda_0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 35.65$ and $\Lambda_0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 37.45$ determined by Arrington and Griswold [9] for Bu_4NBr and Pr_4NBr in dimethyl sulfoxide to permit the calculation of $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 25.50$ and $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 11.95$ for the Br^- and Pr_4N^+ ions, respectively. McDonagh and Reardon [10] reported a value of $\Lambda_0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 40.07$ for the ionic limiting molar conductance of Pr_4NBF_4, which one combined with the above value of $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 11.95$ for the Pr_4N^+ cation, yields a value of $\lambda_o^{\pm} \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 28.12$ for the BF_4^-. The ionic limiting molar conductance of the Bu_4P^+ can be derived by subtracting the BF_4^- value of $\lambda_{\pm}^0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 28.12$ from the value of $\Lambda_0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 35.74$ determined by Roy and coworkers [8] for Bu_4PBF_4 in dimethyl sulfoxide at 298.15 K. Performing the indicated subtraction, a value of $\lambda_{\pm}^0 \ x \ 10^4/(S \ m^2 \ mol^{-1}) = 7.63$ is computed for the ionic limiting molar conductance of Bu_4P^+ in dimethyl sulfoxide. The ionic limiting molar conductance of the methanesulfonate anion is obtained in similar fashion, by

subtracting the just calculated value for the Bu_4P^+ cation from the $\Lambda_0(Bu_4PMS)$ value in Table 3, namely $\lambda_\pm^0$ x 10^4/(S m^2 mol^{-1}) = 33.97 − 7.63 = 26.34 for MS^- in dimethyl sulfoxide. The values given by Banik and Roy [1] were $\lambda_o^\pm$ x 10^4/(S m^2 mol^{-1}) = 13.26 and $\lambda_o^\pm$ x 10^4/(S m^2 mol^{-1}) = 20.71 for the tetrabutylphosphonium and methanesulfonate ions, respectively. There are other methods that have been suggested in the published literature for calculating ionic limiting molar conductances of individual ions based on reference electrolytes. The method used in the present commentary is the tetrabutyammonium tetraphenylborate method with $\lambda_\pm^0(Bu_4N^+) = \lambda_\pm^0(BPh_4^+)$.

Computations are not performed for Bu_4PMS dissolved in N,N-dimethylacetamide as I was not able to found Λ_0 data for an appropriate set of ionic salts. Experimental data for tetrabutylammonium tetraphenylborate [4] , tetrabutylammonium bromide [4] and alkali metal halides [4] are available, but not for the tetrabutylphosphonium halide salts.

My comments should not be taken as a criticism of the authors' work. Rather, I think that it is important to point out some of the shortcomings in the published *Ionics* paper to avoid anyone from using the internally inconsistent K_A, log K_A and ΔG^0 values given in Table 3, and to point out what I think is a more appropriate method for calculating ionic limiting molar conductances based on the tetrabutylammonium tetraphenylborate reference electrolyte approach.

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