

Comments on "Role of Anions (Tetrafluoroborate, Perchlorate) of Tetrabutylammonium Salts in Determining Solvation Effects Prevailing in Industrially Essential Solvents Probed by Conductance and FT-IR Spectra"

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ABSTRACT: Several computational and graphical errors in the paper are pointed out, as well as errors in mathematical equations. The calculation of ionic limiting molar conductances is discussed based on the tetrabutylammonium tetraphenylboride reference electrolyte method.

In a recent paper published in the *Journal of Chemical & Engineering Data (JCED)* Banik and Roy¹ analyzed molecular interactions between tetrabutylammonium perchlorate [Bu₄NClO₄] and tetrabutylammonium tetrafluoroborate [Bu₄NBF₄] ion salts and nitromethane, methylformamide, and formamide using experimental conductance data and FT-IR spectra. The authors reported the limiting molar conductances (Λ_0) of the dissolved ionic salts, the overall pairing association constant (K_A) of the ionic salt, and the ionic limiting molar conductances (λ_0^\pm) of the Bu₄N⁺ cation and ClO₄⁻ and BF₄⁻ anions in the three solvents studied. While many aspects of the study appear to be correct, there are several shortcomings in the published paper of which readers need to be aware.

First, all six of the ΔG° values given in Table 3 of the paper are wrong. If one substitutes the authors' numerical values of K_A into eq 13 of the manuscript (renumbered below as eq 1)

$$\Delta G^\circ = -RT \ln K_A \quad (1)$$

$$\begin{aligned} \Delta G^\circ / (\text{kJ mol}^{-1}) &= -(0.008314)(298.15) \ln 183.09 \\ &= -12.914 \end{aligned}$$

which differs from the authors' value by a factor of 10. The value that is given in Table 1 corresponding to $K_A = 183.09$ is $\Delta G^\circ / (\text{kJ mol}^{-1}) = -1.29$. The miscalculation also makes the graphed values in Figure 4 wrong. The right-hand axis labeling for the graph should range from $\Delta G^\circ / (\text{kJ mol}^{-1}) = -10$ to $\Delta G^\circ / (\text{kJ mol}^{-1}) = -16$.

Second, the data points in Figure 2 have been incorrectly graphed. The authors have graphed limiting molar conductances of the two ionic salts, $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ values, according to the labeling on the left-hand side axis, and have graphed the Walden product of the two ionic salts, $\Lambda_0 \eta \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1} \text{ mPa s})$ values, according to the labeling on the right-hand side axis for each. The text directly above Figure 2 indicates that the values are given in Table 3. Unfortunately, the graphed values do not correspond with the data given in Table 3. The solid triangle according to the figure caption is the limiting molar conductance for Bu₄NBF₄, and the graphed value for nitromethane (solvent designated NM) is somewhere between 150 and 170. The numerical values for Bu₄NBF₄ given

in Table 3 for $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ range between values of 26.18 and 94.60. A value of $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) > 150$ is not in the Table. There are similar problems with other graphed values in Table 3. For example, the labeling on the right-hand axis goes between $\Lambda_0 \eta \cdot 10^4 (\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}) = 35$ and $\Lambda_0 \eta \cdot 10^4 (\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}) = 95$, yet the last value in the sixth column of Table 3 is $\Lambda_0 \eta \cdot 10^4 (\text{S m}^2 \text{ mol}^{-1} \text{ mPa s}) = 118.6$. This value is not represented in the graph.

Third, eq 7 in the manuscript (renumbered below as eq 2) may be in error.

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (2)$$

The manuscript text immediately below eq 7 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 us focus on the last two parts of the equality, namely $K_R / (1 - \alpha) = K_R / (1 + K_S)$. Let us 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.

Fourth, eq 13a in the published paper that pertains to the calculation of A -coefficient is wrong. If one looks at the very last term on the right-hand side of the equation, one sees $(\lambda_+^\circ \lambda_-^\circ / \Lambda_0)^2$. The equation has appeared numerous times in the published literature²⁻⁶

$$A_{\text{theo}} = \frac{0.2577 \Lambda_0}{\eta_0 (\epsilon T)^{0.5} \lambda_+^\circ \lambda_-^\circ} \left[1 - 0.6863 \left(\frac{\lambda_+^\circ - \lambda_-^\circ}{\Lambda_0} \right)^2 \right] \quad (3)$$

and the term in parentheses should contain a negative sign as given by eq 3 above. The negative sign in the equation significantly affects the calculations as one might guess. In the

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JCED paper Banik and Roy¹ state in the first full sentence below eq 13a “Table 3 shows that the A-coefficient is negative and very small, and shows that the existence of the ion–ion interaction is negligible, as compared to the ion–solvent interaction for all of the chosen electrolytes in the studied solvents.” With the negative sign in the equation, there is absolutely no way to calculate a negative value for the A coefficient. This makes all six values in the last column of Table 3 wrong. The error in the *JCED* paper is not a simple typesetting error in that the incorrect equation was used in the authors’ calculations.

Fifth, the authors’ discussion of how the ionic limiting molar conductances for Bu_4N^+ cation, and for BF_4^- and ClO_4^- anions is extremely vague and noninformative. On the fifth page of the published paper the authors state “The ionic conductances λ_o^\pm for the $[\text{Bu}_4\text{N}]^+$ cation and BF_4^- , ClO_4^- anion in different solvent arrangements were computed as described in the literature values (cited reference 19). The ionic limiting molar conductances λ_o^\pm in investigated solvents were determined by interpolation of the conductance from the literature (cited reference 20) using cubic spline fitting.” The cited reference 19 pertains to electrical conductances and viscosities of tetrabutylammonium thiocyanate in acetonitrile where Chakraborty and Das⁷ estimated the ionic contributions to Λ_0 using the reference electrolyte tetrabutylammonium tetraphenylboride. Cited reference 20 pertains to conductances of tetrabutylammonium tetraphenylboride in propylene carbonate, and in binary mixtures containing carbon tetrachloride and nitrobenzene. Essentially, since the cation and anion were both large and had approximately the same volume, Fuoss and Hirsch⁸ set the ionic limiting molar conductance of the cation equal to that of the anion. Since the solvents studied by Banik and Roy¹ are completely different, as well as the electrolytes, it is not apparent how the authors’ statement pertaining to references 19⁷ and 20⁸ is pertinent to their calculations of λ_o^\pm .

If one looks at the ratio $\lambda_o^\pm(\text{cation})/\lambda_o^\pm(\text{anion})$ for Bu_4NBF_4 the values equal 0.562 for nitromethane, 0.563 for *N*-methylformamide, and 0.563 for formamide. The ratio of the crystallographic radii of the anion/divided by radii of the cation equals 0.563. Similarly, one can look at the ratio $\lambda_o^\pm(\text{cation})/\lambda_o^\pm(\text{anion})$ for Bu_4NClO_4 , the values equal 0.486 for nitromethane, 0.486 for *N*-methylformamide, and 0.486 for formamide. Again, the ratio of the crystallographic radii anion/divided by radii cation equals 0.486. It appears that the authors have built this requirement into the calculation.

Banik and Roy¹ imply in the abstract of their paper that the tetrabutylammonium tetraphenylboride reference electrolyte was used to estimate the ionic limiting molar conductances of Bu_4N^+ , BF_4^- and ClO_4^- ions. The tetrabutylammonium tetraphenylboride reference electrolyte method assumes that the ionic limiting molar conductance of tetrabutylammonium is equal to (or in some applications nearly equal to) the ionic limiting molar conductance of tetraphenylboride. The tetrabutylammonium and tetraphenylboride ions are large (small charge density), are of comparable size and are expected to undergo very little specific interactions with the solvents. This is not the case for the ions studied by Banik and Roy. I think that the authors may have mistook the approximation that others^{9–11} have used for calculating ionic limiting molar conductances of tetrabutylammonium tetraphenylboride, $\lambda_o^\pm(\text{cation})/\lambda_o^\pm(\text{anion}) = \text{crystallographic radii of the anion}/\text{divided by radii of the cation}$ to apply to all ions. That would be

an incorrect interpretation of the tetrabutylammonium tetraphenylboride reference electrolyte method.

A more appropriate calculation of the λ_o^\pm numerical values would be based on the tetrabutylammonium tetraphenylboride reference electrolyte method. The numerical values of λ_o^\pm for the tetrabutylammonium cation would be set equal to the numerical values of λ_o^\pm for the tetraphenylboride anion in each of the three solvents studied. This is easy to do in the case of nitromethane as Dewan and Roy¹² published a value of $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 66.74$ for tetrabutylammonium tetraphenylboride in nitromethane. This would give a numerical value of $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 33.37$ for both the tetrabutylammonium and tetraphenylboride ions. One would then be able to calculate $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ for the perchlorate ion as $111.42 - 33.37 = 78.08$ from the value of $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ listed in Table 3, and a value of $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 94.60 - 33.37 = 61.23$ for the tetrafluoroborate anion. The values given by Banik and Roy¹ were $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 74.99$ and $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 60.53$ for the perchlorate and tetrafluoroborate ions, respectively. The method illustrated above is based on the reference electrolyte method proposed by Fuoss and Hirsch.⁸ One could alternatively use another version^{9,10} that takes into account the slight differences in ion size.

There is published conductivity data for tetrabutylammonium tetraphenylboride in *N*-methylformamide.⁹ One would calculate a numerical value of $\lambda_o^\pm \cdot 10^4 = 13.55$ for the tetrabutylammonium cation from the authors’ data. (Tsierkezos and Philippopoulos⁹ calculated a slightly different numerical value of $\lambda_o^\pm \cdot 10^4 = 14.09$ as they assumed that the molar conductivity of the tetrabutylammonium was slightly larger than the molar conductivity of the tetraphenylborate anion; that is, $\lambda_o^\pm(\text{cation}) = 1.07 \cdot \lambda_o^\pm(\text{anion})$. This particular approach takes into account the slight differences in the crystallographic radii of the two reference ions). One would then be able to calculate $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ for the perchlorate ion as $50.55 - 13.55 = 37.00$ from the value of $\Lambda_0 \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1})$ listed in Table 3, and a value of $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 41.04 - 13.55 = 27.49$ for the tetrafluoroborate anion. The authors’ values were $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 34.02$ and $\lambda_o^\pm \cdot 10^4 / (\text{S m}^2 \text{ mol}^{-1}) = 26.26$ for the perchlorate and tetrafluoroborate ions, respectively. It is noted that the method used here for the computation of the ionic limiting molar conductances of ClO_4^- and BF_4^- is essentially the same as that used by Tsierkezos and Philippopoulos for the PF_6^- . Conductivity data for tetrabutylammonium tetraphenylboride in formamide was not found in a quick search of the published literature.

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 *JCED* paper to avoid incorrect equations (such as eq 13a) being propagated in the literature, and to point out what I think is a more appropriate method for calculating ionic limiting molar conductances based on the tetrabutylammonium tetraphenylboride reference electrolyte approach.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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