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# Some Observations About the Subdivision of the Viscosity *B*-Coefficient in Water

## Short Communication

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The subdivision of the viscosity $B$-coefficient in water assuming $B_{Ph_4P^+} = B_{Ph_4B^-}$ has been analysed at different temperatures. The results show the inapplicability of this assumption at temperatures below 30 °C.

*(Keywords: B-coefficient; Water; Subdivision)*

*Beobachtungen zur Unterteilung des Viskositäts-B-Koeffizienten in Wasser*

*(Kurze Mitteilung)*

Die Unterteilung des Viskositäts-$B$-Koeffizienten in Wasser unter der Annahme $B_{Ph_4P^+} = B_{Ph_4B^-}$ wurde für verschiedene Temperaturen untersucht. Die Resultate zeigen, daß bei Temperaturen unter 30 °C diese Annahme unzulässig ist.

In a recent paper[1] a new criterion for separating the viscosity $B$-coefficient of the *Jones-Dole* equation[2] into ionic contributions in water, based on the equality $B_{Ph_4P^+} = B_{Ph_4B^-}$, was proposed. The splitting of the $B$-coefficient at 25 °C by means of this method for different electrolytes in water—compared with the most accepted method suggested by *Kaminsky*[3], which assumes the equality $B_{K^+} = B_{Cl^-}$—gives perceptible differences exceeding largely the experimental error. Nevertheless, a rapid inspection of the results at higher temperatures reveals a better agreement between the two methods.

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In the present communication, the viscosity $B$-coefficients of aqueous solutions of sodium tetraphenylborate at 15 and 35 °C are reported. With these values, together with other values taken from the literature[1,4], an analysis of the $B_{Ph_4\mathrm{P}^+} = B_{Ph_4\mathrm{B}^-}$ assumption has been carried out at different temperatures.

The experimental techniques and procedures for the measurements of the viscosities and densities of the electrolyte solutions have been described in detail before[5].

The sodium tetraphenylborate was Fluka of reagent grade, it was recrystallized from acetone and dried at 80 °C under reduced pressure. All solutions were prepared using distilled and previously deionized water.

The densities and relative viscosities of tetraphenylborate aqueous solutions were measured within a concentration range of 0.004 to 0.04 $M$ at 15 and 35 °C. The results are shown in Table 1. The $B$-coefficients obtained by plotting $(\eta_r{}^{-1})/c^{1/2}$ vs. $c^{1/2}$, are 1.28 and 1.05 dm$^3$ mol$^{-1}$ at 15 and 35 °C, respectively. With these $B$-values and others taken from the literature at different temperatures[1] the splitting of the $B$-coefficient for $\mathrm{NaB}Ph_4$ has been carried out following *Kaminsky*'s procedure. In Table 2 are reported the ionic $B$-coefficients for $\mathrm{B}Ph_4^-$ ion at 15, 25, 30, 35, 40, and 50 °C, considering $B_{\mathrm{Na}^+} = 0.086$ dm$^3$ mol$^{-1}$ at all temperatures[3]. Also in Table 2 are given the ionic $B$-values for the $\mathrm{P}Ph_4^+$ ion obtained by the same way from the $B$-coefficients of $\mathrm{P}Ph_4\mathrm{Br}$ at different temperatures[1,4], together with the $B$-values of the $\mathrm{Br}^-$ ion used in order carry out the subdivision.

Table 1. *Densities and relative viscosities of sodium tetraphenylborate aqueous solutions at 15 and 35 °C*

| $c/M$ | 15 °C | | $c/M$ | 30 °C | |
|---|---|---|---|---|---|
| | $d$/g ml$^{-1}$ | $\eta_r$ | | $d$/g ml$^{-1}$ | $\eta_r$ |
| 0.004020 | 0.9994 | 1.0041 | 0.004000 | 0.9942 | 1.0043 |
| 0.009676 | 0.9996 | 1.0119 | 0.009627 | 0.9944 | 1.0101 |
| 0.01642 | 0.9999 | 1.0210 | 0.01634 | 0.9947 | 1.0187 |
| 0.02883 | 1.0003 | 1.0386 | 0.02869 | 0.9950 | 1.0322 |
| 0.04224 | 1.0020 | 1.0568 | 0.04203 | 0.9958 | 1.0466 |

As can be seen from Table 2, the $B$-coefficients for $Ph_4\mathrm{P}^+$ and $Ph_4\mathrm{B}^-$ ions are practically the same within the experimental error,

± 0.01 dm³ mol⁻¹, from 30 °C to higher temperatures. At temperatures below 30 °C the differences between both coefficients become more significant and are greater with decreasing temperature. This fact evidences the different solvation effects for $Ph_4B^-$ and $Ph_4P^+$ ions in water at temperatures below 30 °C, which leads to erroneous ionic *B*-coefficients, if one assumes the criterion $B_{Ph_4P^+} = B_{Ph_4B^-}$ as a method of subdivision of *B*.

From a variety of studies it has been concluded that $Ph_4P^+$ and $Ph_4B^-$ ions interact with water molecules in a different fashion[6–8]. Although the interactions between $Ph_4P^+$ ion and water molecules are weak because the charge in the central atom is partially shielded due to the presence of phenyl groups in the ion[7]. In the other hand, it has been recognized that $Ph_4B^-$ ion form a weak hydrogen bonding since the water molecules can interact with the $\pi$-electron orbitals of phenyl groups[7]. In this way, the validity of the equality $B_{Ph_4P^+} = B_{Ph_4B^-}$ at 30 °C and higher temperatures, suggests that an increase in the temperature produces a decrease in the strength of these weak interactions between tetraphenyl ions and water molecules vanishing gradually. Therefore, at these temperatures the unique solvation effects for $Ph_4P^+$ and $Ph_4B^-$ ions are probably due to its structure breaking ability, which one can assume identical for the two ions, provided that they have the same volume[9].

Table 2. *Ionic B-values (dm³ mol⁻¹) for* $Ph_4B^-$, $Ph_4P^+$ *and* $Br^-$ *ions in water at different temperatures*

| Ion | Temperature/°C | | | | | |
|---|---|---|---|---|---|---|
| | 15 | 25 | 30 | 35 | 40 | 50 |
| $Ph_4B^-$[a] | 1.33 | 1.08 | 1.05 | 0.96 | 0.94 | 0.86 |
| $Ph_4P^+$[b] | 1.22 | 1.12 | 1.04 | 0.97 | 0.95 | 0.87 |
| $Br^-$ | −0.05[c] | −0.042[d] | −0.028[e] | −0.022[e] | −0.017[e] | −0.002[e] |

[a] Data from Ref.[1], except at 15 and 35 °C which are from this work.

[b] Ref.[1,4].

[c] Ref.[4].

[d] Ref.[3].

[e] Values obtained from *B*-data for NaBr or Ref.[1], considering $B_{Na^+} = 0.086$ dm³ mol⁻¹ at all temperatures; at 35 °C, the *B*-value has been obtained by extrapolation from its temperature dependence.

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