

Conductance Studies of NaCl, KCl, NaBr, NaI, NaBPh₄, Bu₄NI, and NaClO₄ in Water + 2-Butoxyethanol Mixtures at $T = 298.15$ K

Agnieszka Boruń, Anna Florczak, and Adam Bald*

University of Łódź, Department of Physical Chemistry of Solutions, 90-236 Łódź Pomorska 163, Poland

The electrical conductances of solutions of sodium chloride (NaCl), potassium chloride (KCl), sodium bromide (NaBr), sodium iodide (NaI), sodium tetrphenylborate (NaBPh₄), tetrabutylammonium iodide (Bu₄NI), and sodium perchlorate (NaClO₄) in water (1) + 2-butoxyethanol (2) mixtures containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mole fractions of 2-butoxyethanol have been measured at $T = 298.15$ K. The conductance data have been analyzed by the Fuoss–Justice equation. The individual limiting ionic conductivities of Na⁺, K⁺, Bu₄N⁺, BPh₄⁻, I⁻, Cl⁻, Br⁻, and ClO₄⁻ ions have been determined using the Fuoss–Hirsch assumption. The dependencies of the limiting molar conductances, Λ_0 , and Walden products, $\Lambda_0\eta$, versus mixed solvent composition have been discussed.

Introduction

Alkoxyethanols and their aqueous mixtures are extensively studied by many research centers. They are commonly used in industry and modern technologies. These amphiphile molecules are known as surfactants. As it is known, in water-rich mixtures, 2-butoxyethanol molecules (BE) exist in molecular dispersion in water, and the further growth of the 2-butoxyethanol content causes a radical change of the mixture structure and then the formation of micelle-like aggregates.^{1–6}

The thermodynamic and transport properties of aqueous solutions of 2-butoxyethanol have been studied recently by various physicochemical techniques. Therefore, in the literature, we can find the data of densities, relative permittivities, refractive indices, viscosities, surface tension, ultrasonic speeds, excess molar volumes and enthalpies.^{6–12} Because of the nonexistence of the conductometric data in the literature currently available, the present paper presents the electrical conductances of NaCl, KCl, NaBr, NaI, NaBPh₄, Bu₄NI, and NaClO₄ in water-rich (1) 2-butoxyethanol (2) mixtures, which have been measured as a function of the mole fraction at 298.15 K and atmospheric pressure. In earlier papers,^{13,14} we have reported the results of the conductance measurements of these salt solutions in water + 2-methoxyethanol and water + 2-ethoxyethanol systems. The same measurements have been also made in water + 2-butoxyethanol mixtures, but only for NaCl and NaI solutions.¹⁵

Experimental Section

Chemicals. 2-Butoxyethanol (ethylene glycol monobutyl ether) supplied by Fluka (puriss p.a. with a mass fraction purity > 0.995) was dried over freshly activated molecular sieves of type 4A (Sigma) for several days before use, and next it was distilled under vacuum in a dry nitrogen atmosphere. The measured density, viscosity, and refractive index of the pure solvent at $T = 298.15$ K agreed with those values published in the literature (Table 1).

The salts were of puriss grade and were used without further purification (with the exception of Bu₄NI). Sodium chloride (Merck) was dried at $T = 373.15$ K. Potassium chloride, sodium

bromide, and sodium iodide were from Merck and were dried in vacuo at $T = 353.15$ K. Sodium tetrphenylborate (Fluka) and sodium perchlorate (Aldrich) were dried in vacuo at $T = 353.15$ K. Tetrabutylammonium iodide was of Aldrich purum grade and was purified by recrystallization from acetone and dried in vacuo at $T = 333.15$ K.

Double-distilled, deionized, and degassed water with a specific conductance better than $0.5 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ was used for the preparation of the mixed solvents. All of the solutions were prepared by mass using an analytical balance (Sartorius RC 210D) with an uncertainty of $\pm 1 \cdot 10^{-5}$ g. The uncertainty of the composition of the mixtures was 0.0001 in mole fraction.

Measurements. The details of the experimental procedure for conductometric and viscosimetric measurements were described in our previous papers.^{16,17} Conductance measurements were

Table 1. Experimental and Literature Densities, ρ , Viscosities, η , and Refractive Indices, n_D , of 2-Butoxyethanol at $T = 298.15$ K

| ρ | | η | | n_D | |
|--------------------|----------------------|--------|--------------------|--------|-----------------------|
| g·cm ⁻³ | | mPa·s | | | |
| exptl | lit. | exptl | lit. | exptl | lit. |
| 0.896058 | 0.89602 ^a | 2.7956 | 2.786 ^b | 1.4172 | 1.4176 ^{c,d} |
| | 0.89581 ^e | | 3.15 ^c | | 1.4173 ^f |
| | 0.89597 ^g | | | | |
| | 0.8962 ^b | | | | |
| | 0.89625 ^c | | | | |

^a Ref 26. ^b Ref 28. ^c Ref 29. ^d Ref 8. ^e Ref 1. ^f Ref 9. ^g Ref 27.

Table 2. Densities, ρ , Viscosities, η , and Relative Permittivities, ϵ_r , of Water (1) + 2-Butoxyethanol (2) Mixtures at $T = 298.15$ K

| x_2 | ρ | η | ϵ_r^a |
|--------|--------------------|--------|----------------|
| | g·cm ⁻³ | mPa·s | |
| 0.0100 | 0.995114 | 1.1217 | 74.74 |
| 0.0250 | 0.990681 | 1.5199 | 68.67 |
| 0.0500 | 0.980926 | 2.1954 | 58.85 |
| 0.0750 | 0.972624 | 2.7634 | 50.77 |
| 0.1000 | 0.965618 | 3.1828 | 44.78 |
| 0.1500 | 0.954656 | 3.7113 | 36.81 |
| 0.2000 | 0.946363 | 4.0140 | 30.40 |

^a Ref 7.

* Corresponding author. E-mail: laurent@uni.lodz.pl.

Table 3. Continued

| $x_2 = 0.0100$ | | $x_2 = 0.0250$ | | $x_2 = 0.0500$ | | $x_2 = 0.0750$ | | $x_2 = 0.1000$ | | $x_2 = 0.1500$ | | $x_2 = 0.2000$ | |
|-----------------------------------|--|-----------------------------------|--|-----------------------------------|--|-----------------------------------|--|-----------------------------------|--|-----------------------------------|--|-----------------------------------|--|
| $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ | $c \cdot 10^4$ | Λ |
| $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\text{mol} \cdot \text{dm}^{-3}$ | $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ |
| NaClO ₄ | | | | | | | | | | | | | |
| 5.909 | 95.62 | 9.038 | 74.51 | 16.692 | 56.73 | 11.140 | 46.96 | 19.323 | 39.65 | 7.964 | 31.53 | 7.096 | 26.57 |
| 11.133 | 94.90 | 11.881 | 74.27 | 24.844 | 56.40 | 17.884 | 46.68 | 26.729 | 39.40 | 12.872 | 31.31 | 13.727 | 26.23 |
| 18.855 | 94.15 | 19.487 | 73.72 | 31.402 | 56.18 | 26.418 | 46.41 | 34.640 | 39.22 | 20.506 | 31.00 | 20.686 | 25.91 |
| 26.257 | 93.60 | 27.115 | 73.34 | 46.560 | 55.76 | 35.435 | 46.18 | 47.498 | 38.95 | 27.815 | 30.76 | 28.856 | 25.61 |
| 34.699 | 93.01 | 36.052 | 73.00 | 60.706 | 55.45 | 47.623 | 45.92 | 61.870 | 38.72 | 34.951 | 30.58 | 42.205 | 25.22 |
| 49.655 | 92.13 | 50.173 | 72.47 | 74.335 | 55.18 | 61.973 | 45.67 | 76.149 | 38.51 | 48.782 | 30.27 | 55.386 | 24.92 |
| 63.329 | 91.48 | 65.590 | 72.00 | 88.840 | 54.93 | 77.036 | 45.44 | 89.458 | 38.34 | 61.737 | 30.04 | 69.780 | 24.66 |
| 77.579 | 90.88 | 79.689 | 71.64 | 103.41 | 54.70 | 89.117 | 45.28 | 102.37 | 38.18 | 75.456 | 29.83 | 82.413 | 24.46 |
| 93.097 | 90.27 | 94.124 | 71.31 | 116.70 | 54.50 | 104.00 | 45.10 | 115.99 | 38.05 | 88.733 | 29.66 | 95.554 | 24.27 |
| | | 107.39 | 71.02 | 128.95 | 54.33 | 116.61 | 44.97 | 127.87 | 37.94 | 101.88 | 29.51 | 107.99 | 24.11 |
| | | 121.29 | 70.76 | 142.80 | 54.15 | 132.04 | 44.81 | 140.13 | 37.83 | 113.97 | 29.39 | 120.00 | 23.98 |
| | | 134.74 | 70.53 | | | | | 152.77 | 37.72 | 126.08 | 29.27 | 131.53 | 23.86 |
| | | | | | | | | | | | | 144.04 | 23.74 |

Table 4. Limiting Molar Conductances, Λ_0 , Association Constants, K_A , Parameters, R , and Walden Products, $\Lambda_0\eta$, for NaCl, KCl, NaBr, NaI, NaBPh₄, Bu₄NI, and NaClO₄ in Water (1) + 2-Butoxyethanol (2) Mixtures at $T = 298.15 \text{ K}^a$

| x_2 | Λ_0 $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | K_A $\text{dm}^3 \cdot \text{mol}^{-1}$ | R \AA | $\Lambda_0\eta \cdot 10^{-2}$ $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$ | Λ_0 $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | K_A $\text{dm}^3 \cdot \text{mol}^{-1}$ | R \AA | $\Lambda_0\eta \cdot 10^{-2}$ $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{mPa} \cdot \text{s}$ |
|--------------------|---|--|---------------------|---|---|--|---------------------|---|
| NaCl | | | | KCl | | | | |
| 0.0000 | 126.59 | | | 1.127 | 149.95 | | | 1.335 |
| 0.0100 | 106.15 ± 0.01 | 2.08 ± 0.04 | 3.8 | 1.191 | 124.78 ± 0.05 | 0.85 ± 0.08 | 3.7 | 1.400 |
| 0.0250 | 88.18 ± 0.03 | 2.26 ± 0.06 | 4.0 | 1.340 | 104.06 ± 0.03 | 0.73 ± 0.04 | 3.9 | 1.582 |
| 0.0500 | 71.10 ± 0.04 | 2.97 ± 0.10 | 4.3 | 1.561 | 83.95 ± 0.02 | 5.50 ± 0.04 | 5.1 | 1.843 |
| 0.0750 | 58.78 ± 0.02 | 3.56 ± 0.07 | 4.5 | 1.624 | 68.79 ± 0.03 | 2.10 ± 0.06 | 4.4 | 1.901 |
| 0.1000 | 49.57 ± 0.04 | 5.51 ± 0.15 | 4.9 | 1.578 | 57.27 ± 0.02 | 5.43 ± 0.08 | 5.2 | 1.823 |
| 0.1500 | 37.42 ± 0.04 | 11.65 ± 0.27 | 5.4 | 1.389 | 42.25 ± 0.01 | 19.05 ± 0.05 | 7.6 | 1.568 |
| 0.2000 | 30.15 ± 0.04 | 22.32 ± 0.31 | 6.0 | 1.210 | 33.18 ± 0.01 | 29.33 ± 0.06 | 8.1 | 1.332 |
| NaBr | | | | NaI | | | | |
| 0.0000 | 128.38 | | | 1.143 | 126.92 | | | 1.130 |
| 0.0100 | 107.32 ± 0.04 | 1.53 ± 0.06 | 3.8 | 1.204 | 104.24 ± 0.02 | 6.09 ± 0.03 | 7.8 | 1.169 |
| 0.0250 | 88.28 ± 0.02 | 1.61 ± 0.04 | 3.9 | 1.342 | 83.51 ± 0.01 | 5.29 ± 0.02 | 7.7 | 1.269 |
| 0.0500 | 71.08 ± 0.03 | 1.63 ± 0.07 | 4.1 | 1.560 | 65.80 ± 0.01 | 4.28 ± 0.03 | 7.8 | 1.445 |
| 0.0750 | 58.76 ± 0.02 | 1.30 ± 0.07 | 4.5 | 1.624 | 54.27 ± 0.01 | 3.77 ± 0.02 | 7.6 | 1.500 |
| 0.1000 | 49.68 ± 0.02 | 2.52 ± 0.09 | 4.9 | 1.581 | 46.03 ± 0.01 | 4.39 ± 0.03 | 8.3 | 1.465 |
| 0.1500 | 38.03 ± 0.04 | 7.76 ± 0.27 | 5.5 | 1.411 | 35.60 ± 0.01 | 5.47 ± 0.04 | 8.0 | 1.321 |
| 0.2000 | 30.89 ± 0.03 | 15.82 ± 0.28 | 5.9 | 1.240 | 29.55 ± 0.02 | 11.67 ± 0.16 | 8.5 | 1.186 |
| NaBPh ₄ | | | | Bu ₄ NI | | | | |
| 0.0000 | 69.98 | | | 0.623 | 96.26 | | | 0.857 |
| 0.0100 | 56.63 ± 0.01 | | 5.6 | 0.635 | 77.77 ± 0.02 | 8.49 ± 0.13 | 4.6 | 0.872 |
| 0.0250 | 43.52 ± 0.05 ^b | | | 0.661 ^b | 60.11 ± 0.01 | 9.16 ± 0.05 | 4.6 | 0.914 |
| 0.0500 | 32.60 ± 0.01 | | 13.2 | 0.716 | 46.67 ± 0.01 | 11.19 ± 0.09 | 13.3 | 1.025 |
| 0.0750 | 27.69 ± 0.01 | | 13.5 | 0.765 | 38.41 ± 0.02 | 17.73 ± 0.20 | 12.8 | 1.061 |
| 0.1000 | 24.16 ± 0.01 | | 11.8 | 0.769 | 33.43 ± 0.01 | 24.05 ± 0.14 | 12.6 | 1.064 |
| 0.1500 | 19.41 ± 0.01 | | 11.9 | 0.720 | 27.10 ± 0.01 | 32.71 ± 0.17 | 11.9 | 1.006 |
| 0.2000 | 16.77 ± 0.02 | | 11.2 | 0.673 | 23.43 ± 0.01 | 46.83 ± 0.20 | 11.9 | 0.940 |
| NaClO ₄ | | | | | | | | |
| 0.0000 | 117.35 | | | 1.045 | | | | |
| 0.0100 | 97.41 ± 0.01 | 1.60 ± 0.02 | 4.1 | 1.093 | | | | |
| 0.0250 | 76.21 ± 0.01 | 0.78 ± 0.02 | 6.0 | 1.158 | | | | |
| 0.0500 | 58.50 ± 0.01 | 1.10 ± 0.03 | 8.8 | 1.284 | | | | |
| 0.0750 | 48.32 ± 0.01 | 0.70 ± 0.02 | 9.1 | 1.335 | | | | |
| 0.1000 | 41.34 ± 0.01 | 1.06 ± 0.03 | 8.6 | 1.316 | | | | |
| 0.1500 | 32.78 ± 0.01 | 3.25 ± 0.10 | 9.0 | 1.217 | | | | |
| 0.2000 | 28.03 ± 0.01 | 8.45 ± 0.06 | 8.7 | 1.125 | | | | |

^a In all cases, $\Delta R = 0.5 \cdot 10^{-8} \text{ cm}$. ^b For NaBPh₄ ($x_2 = 0.025$) the value of $\Lambda_0\eta$ was interpolated from the dependence $\Lambda_0\eta = f(x_2)$, and then the value of $\Lambda_0 = \Lambda_0\eta/\eta$ was calculated.

performed in the solutions containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mole fractions of 2-butoxyethanol (2), usually for (9 to 14) molar concentrations of salts, with the use of a precise component analyzer type 6430B (Wayne-Kerr, UK). All conductance values were the results of an extrapolation to infinite frequency. All data were corrected with the specific conductance of the solvent. The temperature was kept constant within 0.003 K (Ultra thermostat UB 20F with through-flow cooler DLK 25, Lauda, Germany). The uncertainty of the measured values of conductivity was 0.03 %.

Viscosities were measured with a AVS 350 viscosimeter (Schott Geräte, Germany). The viscosimeter filled with the liquid was placed vertically in a glass-sided water thermostat. An electronic stopwatch with a precision of 0.01 s was used for flow time measurements. The temperature was kept constant using a precision thermostat Julabo F32 (Julabo Laborotechnik GmbH, Germany). The uncertainty in the viscosity measurements was better than 0.05 %.

Densities were measured with an Anton Paar DMA 5000 oscillating U-tube densimeter equipped with a thermostat with

a temperature stability within ± 0.001 K. The densimeter was calibrated with extra pure water, previously degassed ultrasonically. The uncertainty in the density measurements was $5 \cdot 10^{-6} \text{ g} \cdot \text{cm}^{-3}$.

The refractive indices (Na-D line, at $\lambda = 589$ nm) were measured using an automatic precision refractometer DR 5000 Krüss. The uncertainty in the refractive index measurements was $2 \cdot 10^{-5}$.

Results and Discussion

The densities, dynamic viscosities, and relative permittivities of water (1) + 2-butoxyethanol (2) mixtures are listed in Table 2. Viscosity and density data were interpolated for the full composition on the basis of our experimental data. The relative permittivities were interpolated on the basis of literature data.⁷

The experimental molar conductances, Λ , as a functions of the electrolyte concentration, c , for the investigated salts in the mixed solvent are presented in Table 3.

The conductance data were analyzed using the Fuoss–Justice equation^{18,19} in the form

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c) \ln(\alpha c) + J(\alpha c) + J_{3/2}(\alpha c)^{3/2}] \quad (1)$$

together with

$$K_A = (1 - \alpha)/(\alpha^2 c y_{\pm}^2) \quad (2)$$

and

$$\ln y_{\pm} = -(A\alpha^{1/2} c^{1/2})/(1 + BR\alpha^{1/2} c^{1/2}) \quad (3)$$

In these equations, Λ_0 is the limiting molar conductance; α is the dissociation degree of an electrolyte; K_A is the ionic association constant; R is the distance parameter of the ions; y_{\pm} is the activity coefficient of ions on the molar scale; A and B are the Debye–Hückel equation coefficients. The analytical form of the parameters S , E , J , and $J_{3/2}$ was presented previously.^{20–22} The values of Λ_0 , K_A , and R were obtained using the well-known procedure given by Fuoss.¹⁹

The values of density, dynamic viscosity, and relative permittivity necessary for the calculation are collected in Table 2. The values of Λ_0 , K_A , R , and the Walden products, $\Lambda_0\eta$, for the investigated salts in water (1) + 2-butoxyethanol (2) mixtures are collected in Table 4. The limiting molar conductances for salts in water are the same as in ref 14. The limiting ionic conductances are taken from ref 23.

As seen from Table 4, the association constant values increase with an increasing amount of 2-butoxyethanol (2) in the mixture, because the relative permittivity of the medium decreases. NaBPh₄ is not associated in the mixed solvent media, and for the remaining salts the association constants are practically negligible. The values of Λ_0 decrease intensively during the addition of 2-butoxyethanol (2) to water, as in the case of 2-methoxy- (ME) and 2-ethoxyethanol (EE).^{13,14} In the case of water (1) + 2-butoxyethanol (2) mixtures the values of Λ_0 at $x_2 = 0.2$ are the smallest. It can be easily explained taking into account the changes of viscosity in the order: H₂O + ME < H₂O + EE < H₂O + BE. From simple hydrodynamic models it follows that the ionic mobility decreases as the viscosity increases. The values of Walden product, $\Lambda_0\eta$, increase clearly along with an increase in the mole fraction of 2-butoxyethanol (2) in the very dilute region, and after reaching a maximum (at about $x_2 = 0.075 - 0.10$), the values of $\Lambda_0\eta$ decrease monotonically. It should be noted that the above-mentioned order (H₂O + ME < H₂O + EE < H₂O + BE) also applies to

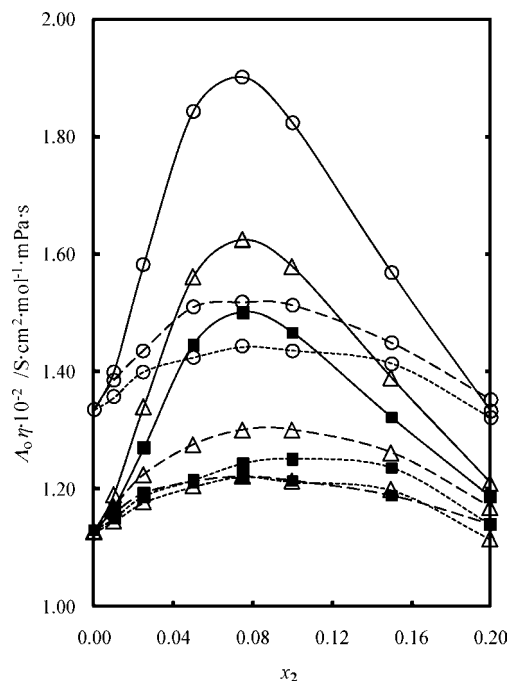


Figure 1. Walden product, $\Lambda_0\eta$, for some salts as a function of the mole fraction, x_2 , in water (1) + 2-methoxyethanol (2), water (1) + 2-ethoxyethanol (2), and water (1) + 2-butoxyethanol (1) mixtures at 298.15 K: Δ , NaCl; \circ , KCl; \blacksquare , NaI; \cdots , H₂O + ME (ref 13); $---$, H₂O + EE (ref 14); $-$, H₂O + BE (this work).

the changes of the Walden product values, which means that the maximum peaks are the highest in water (1) + 2-butoxyethanol (2) mixtures. A comparison of the Walden product for some salts in water + 2-methoxyethanol, water + 2-ethoxyethanol, and water + 2-butoxyethanol is presented in Figure 1.

The values of Λ_0 for NaCl and NaI obtained in this paper are in very good agreement with those values published previously¹⁵ (see Figure 2), and very slight differences between values of $\Lambda_0\eta$ may result from the viscosity data. In this paper, the viscosity measurements were conducted using better equipment.

The single-ion conductances were obtained on the basis of the Fuoss–Hirsch assumption²⁴

$$\lambda_0(\text{Bu}_4\text{N}^+) = \lambda_0(\text{BPh}_4^-) = [\Lambda_0(\text{Bu}_4\text{NI}) + \Lambda_0(\text{NaBPh}_4) - \Lambda_0(\text{NaI})]/2 \quad (4)$$

The dependencies $\lambda_0^+ = f(x_2)$ and $\lambda_0^- = f(x_2)$ are presented in Figures 3 and 4, respectively. The factors having an influence on these dependencies are the macroscopic viscosity and the effective size of ions. The values of limiting ionic conductances decrease with an increase of the macroscopic viscosities and of the effective ion size. Therefore, it is no wonder that in the case of the large ions (Bu_4N^+ and BPh_4^-) the values of λ_0 are the smallest.

The changes of the values of $\lambda_0^{\pm}\eta$ as a function of the mixed solvent composition are independent from the changes of the macroscopic viscosity. Thus, the difference between the values of $\lambda_0^{\pm}\eta$ for different ions may provide information about the differences in the ion–solvent interactions. The dependencies $\lambda_0^+\eta = f(x_2)$ and $\lambda_0^-\eta = f(x_2)$ are presented in Figures 5 and 6, respectively.

As could be expected, the addition of small amounts of 2-butoxyethanol (2) to water (1) leads to an increase of the values of the ionic Walden product for inorganic ions, but they remain almost constant for Bu_4N^+ and BPh_4^- . The big organic

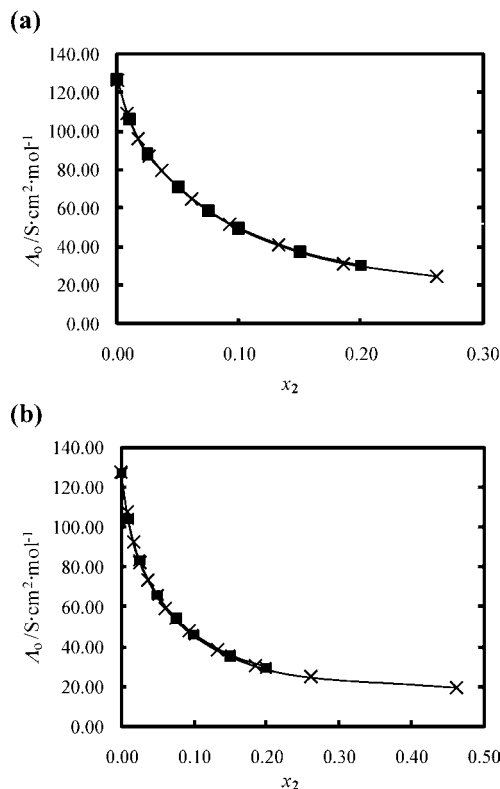


Figure 2. Comparison of the limiting molar conductances, Λ_0 , of (a) NaCl and (b) NaI in water (1) + 2-butoxyethanol (2) mixtures at 298.15 K: \times , ref 15; \blacksquare , this work.

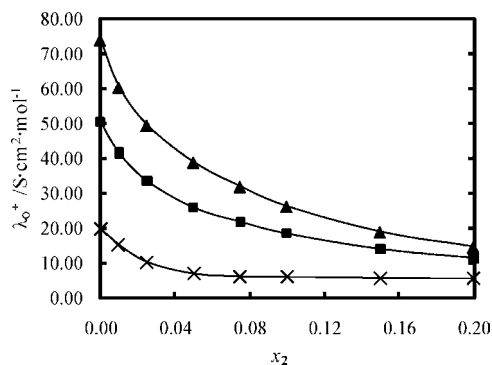


Figure 3. Limiting ionic conductances of the individual cations, λ_0^+ , as a function of the mole fraction, x_2 , in water (1) + 2-butoxyethanol (2) mixtures at 298.15 K: \blacktriangle , K^+ ; \blacksquare , Na^+ ; \times , Bu_4N^+ .

ions having small surface charge densities are practically unsolvated in the solution. The differences between the changes of ionic Walden products (Figures 5 and 6) may result from the differences in the electronegativity of these ions. In the course of the dependence $\lambda_0^\pm \eta = f(x_2)$ for inorganic ions, we can see a maximum, as in the case of aqueous mixtures of 2-methoxy- and 2-ethoxyethanol.^{13,14} The similar behavior of electrolyte solutions in water–alcohol mixtures was explained by Kay on the basis of the assumption of the preferential solvation of ions by the water dipoles (“sorting effect”).²⁵ Furthermore, it should be noted that the intensity of the growth of the ionic Walden product values while adding alkoxyethanols to water can be put, for the mixtures examined by us, in the following order: $H_2O + ME < H_2O + EE < H_2O + BE$.

Conclusions

The electrical conductances of solutions of sodium chloride, potassium chloride, sodium bromide, sodium iodide, sodium

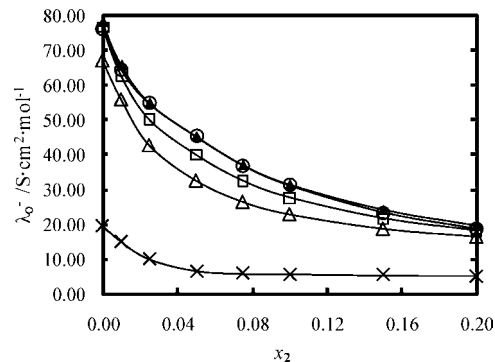


Figure 4. Limiting ionic conductances of the individual anions, λ_0^- , as a function of the mole fraction, x_2 , in water (1) + 2-butoxyethanol (2) mixtures at 298.15 K: \circ , Cl^- ; \blacktriangle , Br^- ; \square , I^- ; \times , BPh_4^- ; \triangle , ClO_4^- .

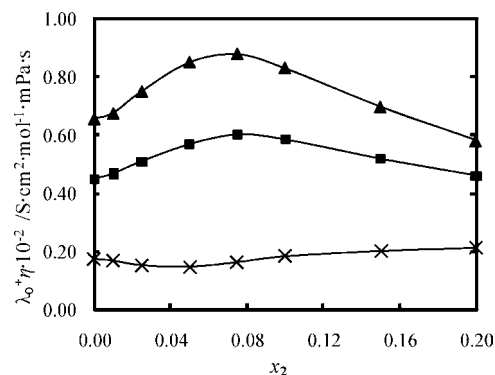


Figure 5. Walden product for cations, $\lambda_0^+ \eta$, as a function of the mole fraction, x_2 , in water (1) + 2-butoxyethanol (2) mixtures at 298.15 K: \blacktriangle , K^+ ; \blacksquare , Na^+ ; \times , Bu_4N^+ .

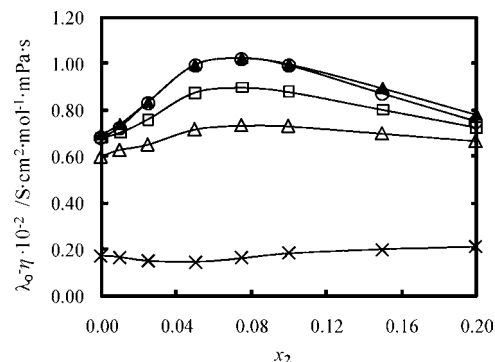


Figure 6. Walden product for anions, $\lambda_0^- \eta$, as a function of the mole fraction, x_2 , in water (1) + 2-butoxyethanol (2) mixtures at 298.15 K: \circ , Cl^- ; \blacktriangle , Br^- ; \square , I^- ; \times , BPh_4^- ; \triangle , ClO_4^- .

tetraphenylborate, tetrabutylammonium iodide, and sodium perchlorate have been measured in aqueous 2-butoxyethanol (2) mixtures containing (0.01, 0.025, 0.05, 0.075, 0.10, 0.15, and 0.20) mole fractions of 2-butoxyethanol (2) at $T = 298.15$ K. The limiting molar conductances, Λ_0 , and Walden products, $\Lambda_0 \eta$, have been determined. The limiting molar conductances and the limiting ionic conductances decrease along with an increase of 2-butoxyethanol (2) content. The values of the Walden product increase with the increase in the mole fraction of 2-butoxyethanol (2) in the very dilute region and after reaching a maximum decrease monotonically. In the range of composition containing a large amount of water (1), slight additions of 2-butoxyethanol (2) do not cause significant changes in the hydration shells of ions.

Literature Cited

- (1) Douhéret, G.; Pal, A.; Davis, M. I. Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 99–108.
- (2) D'Arrigo, G.; Paparelli, A. Sound propagation in water-ethanol mixtures at low temperatures. I. Ultrasonic velocity. *J. Chem. Phys.* **1988**, *88*, 405–415.
- (3) Mallamace, F.; Micali, N.; D'Arrigo, G. Dynamical effects of supramolecular aggregates in water-butoxyethanol mixtures studied by viscosity measurements. *Phys. Rev. A* **1991**, *44*, 6652–6658.
- (4) D'Arrigo, G.; Mallamace, F.; Micali, N.; Paparelli, A.; Vasi, C. Molecular aggregations in water-2-butoxyethanol mixtures by ultrasonic and Brillouin light-scattering measurements. *Phys. Rev. A* **1991**, *44*, 2578–2587.
- (5) Kato, S.; Jobe, D.; Rao, N. P.; Ho, C. H.; Verrall, R. E. Ultrasonic relaxation studies of 2-butoxyethanol-water and 2-butoxyethanol-water-cetyltrimethylammonium bromide solutions as a function of composition. *J. Phys. Chem.* **1986**, *90*, 4167–4174.
- (6) Elizalde, F.; Gracia, J.; Costas, M. Effect of Aggregates in Bulk and Surface Properties. Surface Tension, Foam Stability and Heat Capacities for 2-Butoxyethanol + Water. *J. Phys. Chem.* **1988**, *92*, 3565–3568.
- (7) Douhéret, G.; Pal, A. Dielectric Constants and Densities of Aqueous Mixtures of 2-Alkoxyethanols at 25°C. *J. Chem. Eng. Data* **1988**, *33*, 40–43.
- (8) Shindo, Y.; Kusano, K. Densities and Refractive Indices of Aqueous Mixtures of Alkoxy Alcohols. *J. Chem. Eng. Data* **1979**, *24*, 106–110.
- (9) Chu, K.-Y.; Thompson, A. R. Densities and Refractive Indices of Glycol Ether-Water Solutions. *J. Chem. Eng. Data* **1960**, *5*, 147–149.
- (10) Davis, M. I.; Molina, M. C.; Douhéret, G. Excess molar volumes and enthalpies of the 2-butoxyethanol + water system at 25°C. *Thermochim. Acta* **1988**, *131*, 153–170.
- (11) Douhéret, G.; Pal, A.; Davies, M. I. Excess Thermodynamic Properties of some 2-Alkoxyethanol-Water Systems. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2723–2736.
- (12) Chiou, D.-R.; Chen, S.-Y.; Chen, L.-J. Density, Viscosity, and Refractive Index for Water + 2-Butoxyethanol and + 2-(2-Butoxyethoxy)ethanol at Various Temperatures. *J. Chem. Eng. Data* **2010**, *55*, 1012–1016.
- (13) Boruń, A.; Florczak, A.; Bald, A. Conductance studies of NaCl, KCl, NaBr, NaBPh₄, Bu₄NI and NaClO₄ in water + 2-methoxyethanol mixtures at 298.15 K. *J. Mol. Liq.* **2009**, *149*, 74–80.
- (14) Boruń, A.; Florczak, A.; Bald, A. Conductance Studies of NaCl, KCl, NaBr, NaBPh₄, and Bu₄NI in Water + 2-Ethoxyethanol Mixtures at 298.15 K. *J. Chem. Eng. Data* **2010**, *55*, 1252–1257.
- (15) Piekarski, H.; Tkaczyk, M.; Bald, A.; Szejgis, A. Conductivity Study of NaCl and NaI Solutions in Water-2-Butoxyethanol Mixtures at 298.15 K. The Effect of Ion Pairing on the Standard Dissolution Enthalpies of NaCl and NaI. *J. Mol. Liq.* **1997**, *73–74*, 209–221.
- (16) Wypych-Stasiewicz, A.; Szejgis, A.; Chmielewska, A.; Bald, A. Conductance Studies of NaBPh₄, NBu₄I, NaI, NaCl, NaBr, NaClO₄ and the Limiting Ionic Conductance in Water + Propan-1-ol Mixtures at 298.15 K. *J. Mol. Liq.* **2007**, *130*, 34–37.
- (17) Gregorowicz, J.; Bald, A.; Szejgis, A.; Chmielewska, A. Gibbs Energy of Transfer and Conductivity Properties of NaI Solutions in Mixtures of Water with Butan-1-ol at 298.15 K, and Some Physicochemical Properties of Mixed Solvent. *J. Mol. Liq.* **2000**, *84*, 149–160.
- (18) Fuoss, R. M. Paired Ions: Dipolar Pairs as Subset of Diffusion Pairs. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 16–20.
- (19) Fuoss, R. M. Conductance-Concentration Function for the Paired Ion Model. *J. Phys. Chem.* **1978**, *82*, 2427–2440.
- (20) Justice, J.-C. An Interpretation for the Distance Parameter of the Fuoss-Onsager Conductance Equation in the Case of Ionic Association. *Electrochim. Acta* **1971**, *16*, 701–712.
- (21) Renard, E.; Justice, J.-C. A Comparison of the Conductimetric Behavior of Cesium Chloride in Water-Tetrahydrofuran, Water-Dioxane, and Water-1,2-Dimethoxyethane Mixtures. *J. Solution Chem.* **1974**, *3*, 633–647.
- (22) Fuoss, R. M.; Accascina, L. *Electrolytic Conductance*; Interscience: New York, 1959.
- (23) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Physical Chemistry of Electrolyte Solutions: modern aspects*; Springer: New York, 1998; Vol. 5.
- (24) Fuoss, R. M.; Hirsch, E. Single Ion Conductances in Non-aqueous Solvents. *J. Am. Chem. Soc.* **1960**, *82*, 1013–1117.
- (25) Kay, R. L.; Broadwater, T. L. Solvent Structure in Aqueous Mixtures. III. Ionic Conductances in Ethanol-Water Mixtures at 10 and 25°C. *J. Solution Chem.* **1976**, *5*, 57–76.
- (26) Rao, N. P.; Verrall, R. E. Ultrasonic velocity, excess adiabatic compressibility, apparent molar volume, and apparent molar compressibility properties of binary liquid mixtures containing 2-butoxyethanol. *Can. J. Chem.* **1987**, *65*, 810–816.
- (27) Tamura, K.; Osaki, A.; Murakami, S.; Ohji, H.; Ogawa, H.; Laurent, B.; Grolier, J.-P. E. Thermodynamic properties of binary mixtures {an alkoxyethanol + n-octane}. Excess molar enthalpies and excess molar heat capacities at 298.15 K. *Fluid Phase Equilib.* **1999**, *156*, 137–147.
- (28) MacNeil, J. H.; Palepu, R. Viscosities and densities of binary liquid mixtures of 2-butoxyethanol with aniline and N-alkylaniline. *Thermochim. Acta* **1989**, *149*, 275–286.
- (29) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley: New York, 1986.

Received for review March 18, 2010. Accepted April 19, 2010. The research was sponsored by the Polish State Committee for Scientific Research (Grant No. 505/669).

JE100259J