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# Ionic Conductivity in Binary Solvent Mixtures. 6. Behavior of Selected 1:1 Electrolytes in 80 mass % Propylene Carbonate + *p*-Xylene at 25 °C

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The electrolytic conductance behavior of certain univalent electrolytes, viz., tetrabutylammonium tetraphenylborate, tetrabutylammonium halides, tetrabutylammonium perchlorate, tetraethylammonium perchlorate, tetraethylammonium iodide, tetraethylammonium 2,5-dichlorobenzenesulfonate, tetraethylammonium *p*-toluenesulfonate, tetramethylammonium iodide, sodium tetraphenylborate, sodium iodide, and potassium iodide in 80 mass % propylene carbonate + *p*-xylene, was studied. The conductance data were analyzed by the Fuoss conductance−concentration equation. The ionic conductivities have been calculated using the $\Lambda_0$ value of tetrabutylammonium tetraphenylborate as a reference value that is independent of solvent. The association constants and cosphere diameters for the above electrolytes are reported. The variations of ionic conductivities are explained in terms of viscosity, the Stokes radii in some specific cases, and specific ion−solvent interactions.

## 1. Introduction

Despite the accumulation of a considerable amount of information concerning the general behavior of electrolytes in binary solvent mixtures containing propylene carbonate with some selected dipolar aprotic solvents such as dimethyl sulfoxide, acetonitrile, ethylene carbonate, and so forth,[1] little information is available on the electrochemical aspects of electrolytes in the binary solvent mixtures involving aromatic hydrocarbon solvents, probably due to the inertness of these solvents and also due to the nonavailability of sufficient physicochemical and thermodynamic data of these systems. However, the recently reported data on the physicochemical properties of propylene carbonate + toluene[2] and propylene carbonate + *p*-xylene[3] have generated interest in exploring the possibility of using these solvent mixtures for electrochemical investigations.

Propylene carbonate, a popular dipolar aprotic solvent,[4−7] with a high relative permittivity (64.4), high dipole moment (4.94 D), and a reasonably high viscosity (2.51 mPa·s) is widely used in high-energy reactions and is a convenient solvent for a variety of organic and inorganic salts. *p*-Xylene is a dipolar aprotic aromatic hydrocarbon solvent with a very low relative permittivity (2.26), a negligible dipole moment,[8] and a very low viscosity (0.618 mPa·s).

Taking advantage of the change in the physical properties of 80 mass % propylene carbonate + *p*-xylene, which has a reasonable relative permittivity of 46.1, as compared to that of *p*-xylene, and a low viscosity of 1.822 mPa·s, as compared to that of propylene carbonate, an attempt has been made in the present study to explore the possibility of using this system for carrying out some electrochemical investigations.

In continuation of the conductance studies reported earlier[9−12] carried out in the author's laboratory in some selected binary solvent mixtures containing propylene carbonate, in this paper we report the behavior of certain univalent electrolytes, viz., tetrabutylammonium tetraphenylborate (TBATPB), tetrabutylammonium halides (TBAX, X = Cl, Br, I), tetrabutylammonium perchlorate (TBAP), tetraethylammonium perchlorate (TEAP), tetraethylammonium iodide (TEAI), tetrethylammonium 2,5-dichlorobenzenesulfonate (TEADCBS), tetraethylammonium *p*-toluenesulfonate (TEAPTS), tetramethylammonium iodide (TMAI), sodium tetraphenylborate (NaTPB), sodium iodide, and potassium iodide, determined by a conductance study. The data were analyzed according to the Fuoss[16] equation. The ionic conductivities have been calculated using the $\Lambda_0$ of TBATPB as a reference value that is independent of solvent. The association constants and cosphere diameters of the above electrolytes are reported.

## 2. Experimental Section

***2.1. Chemicals.*** Propylene carbonate was purified and stored as described earlier.[9] *p*-Xylene (99% pure; Sisco) was held over molecular sieves overnight and distilled thrice without molecular sieves in it. The middle fraction boiling in the range 138−139 °C, comprising about 80%, was collected, stored in an amber bottle, and sealed for subsequent use in the present investigation. Calculated masses of propylene carbonate and *p*-xylene were mixed to give (80 ± 0.05) mass % composition just prior to use. All known solutions were prepared using a digital single-pan balance (Mettler Toledo AB204). The conductivity of the freshly prepared 80 mass % propylene carbonate ranged from (1.0 to 1.2) $\mu$S·cm$^{-1}$ (at 25 ± 0.05) °C.

TBATPB,[9] TBAP,[10] TEAP,[13] and TEADCBS[14] were prepared as described earlier. TBABr (Fluka) and NaTPB (Merck) were rerystallized from alcohol and dried in a vacuum at 70 °C. TBAI (Sisco) and TEAI (Sisco) were recrystallized from water followed by alcohol and dried in a vacuum at 80 °C. TMAI (Sisco) was recrystallized from alcohol and dried in a vacuum at 90 °C. Potassium iodide

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**Table 1. Relative Permittivity, $\epsilon$, Density, $\rho$, and Viscosity, $\eta$, for 80 mass % Propylene Carbonate (1) + $p$-Xylene (2) at 25 °C**

| $100w_1$ | $\rho$/g·cm$^{-3}$ | $\eta^a$/mPa·s | $\epsilon$ |
|---|---|---|---|
| 100 | $1.995^c$ | 2.505 | $64.4^c$ |
| 80 | $1.1107^b$ | 1.822 | $46.10^b$ |
| 0 | $0.8566^b$ | 0.618 | $2.26^b$ |

[a] Present work. [b] Reference 3. [c] Reference 7.

(BDH) and sodium iodide (S. D. Fine) were recrystallized from aqueous ethanol and dried in a vacuum at 90 °C before use.

TEAPTS was prepared by neutralizing the aqueous solution of $p$-toluenesulfonic acid (S. D. Fine) with tetraethylammonium hydroxide (Fluka) solution by monitoring the pH with a pH meter, carefully evaporating the contents to near dryness, and then cooling to get the salt. The product thus obtained was recrystallized twice with water, followed by alcohol, and then dried in a vacuum at 65 °C for 6 h before use.

TBACl was prepared by neutralizing tetrabutylammonium hydroxide (25% in methanol; Sisco) with dilute hydrochloric acid by monitoring the pH with a pH meter. The resulting solution was carefully evaporated to a syrupy stage and then immediately cooled in an ice bath to get the white crystalline mass. The product was washed with water and then recrystallized with alcohol.

***2.2. Conductance Measurements.*** The details of the procedure and the apparatus used for the conductance measurements are as described earlier.[13] The uncertainty in the conductance measurements was ±0.1 $\mu$S.

***2.3. Viscosity Measurements.*** The viscosity measurements were made as per the ASTM D 445-83 method using a U-tube capillary viscometer (size 1 with a calibration factor of 0.0024). The viscosities of the above purified solvents propylene carbonate, $p$-xylene, and 80 mass % propylene carbonate + $p$-xylene were measured at (25 ± 0.05) °C. The values obtained are given in Table 1 and are found to be well within the range reported in the literature.[3,4] The uncertainty in the viscosity measurements was ±0.001 mPa·s, and that of temperature measurements was ±0.05 °C.

## 3. Results and Discussion

The physical properties (density and relative permittivity) of the 80 mass % propylene carbonate + $p$-xylene,[3] including the viscosity data obtained in the present work, are summarized in Table 1. The molar conductivity $\Lambda$ as a function of concentration $c$ for all the electrolytes studied in the present system at 25 °C is reported in Table 2.

The conductivity data for all the univalent electrolytes were analyzed by the Fuoss conductance−concentration equation,[16] basically a physical model, which is in effect a mathematical device that permits separate treatment of long- and short-range effects visualized for ions in electrolytic solutions. The method of calculation and the symbols used are as suggested by Fuoss. The computer program SCAN ON RHO, as described in the previous paper,[13] was used to get the best-fit conductivity parameters (Table 3), such as limiting molar conductivity, $\Lambda_0$, association constant, $K_A$, and cosphere diameter, $R$, corresponding to the minimum in the $\sigma$/%−$R$ curve, where $\sigma$/% is the standard deviation.

TBATPB was used as a reference electrolyte for the determination of limiting ionic conductivities, as it is considered to be a solvent independent system. On the basis of the assumption of Fuoss et al.,[17] the limiting ionic conductivity, $\lambda_0$, of TBA$^+$ was calculated as per the following relation:

$$\lambda_0(\mathrm{TBA}^+) = 0.519\Lambda_0(\mathrm{TBATPB})$$

Subsequently, the limiting molar conductivities of all the ions were calculated (Table 4) using the $\lambda_0$ values of TBA$^+$ and TPB$^-$, by taking the $\Lambda_0$ of each system from the calculated data, based on the consideration that the limiting molar conductivity is an algebraic sum of ionic conductivities of all ions present in the molecule.

The $\lambda_0$ values were in turn utilized for the evaluation of Stokes hydrodynamic radii, $R_S$, according to the classic expression[18]

$$R_S = F^2/6\pi N_A(\lambda_0\eta)$$

where $R_S$ is expressed in Å, $F$ is expressed in C·mol$^{-1}$ , $\lambda_0$ is expressed in S·cm$^2$·mol$^{-1}$, $\eta$ is expressed in mPa·s, and $N_A$ is expressed in mol$^{-1}$. The $R_S$ values calculated for the present system compared with those reported for propylene carbonate are reported in Table 5.

The trend in the $\lambda_0$ values is as follows

$$\mathrm{TBA}^+ < \mathrm{TMA}^+ < \mathrm{TEA}^+;\ \mathrm{Na}^+ < \mathrm{K}^+ \text{ and}$$
$$\mathrm{TPB}^- < \mathrm{PTS}^- < \mathrm{ClO_4}^- < \mathrm{Cl}^- < \mathrm{DCBS}^- < \mathrm{I}^- < \mathrm{Br}^-$$

Contrary to the expectation that the $\lambda_0$ values should be lower in 80 mass % propylene carbonate + $p$-xylene, due to the decrease in the relative permittivity of propylene carbonate (64.4) with the addition of the very low relative permittivity solvent $p$-xylene (2.26), in general, $\lambda_0$ values of all the ions in the present system are higher, which can be attributed to the lowered viscosity of the medium playing a dominating role on the mobilities of ions. Ritzoulis et al.[19] made similar observations in propylene carbonate + toluene mixtures in the case of TBATPB. The very high $\lambda_0$ values of TEA$^+$ and DCBS$^-$ ions obtained in 80 mass % propylene carbonate + $p$-xylene as compared to propylene carbonate can be explained on the basis of the observed smaller Stokes radii in this medium (Table 5), since the smaller the sizes, the greater will be the mobilities of the ions. Evans and Gardam observed a similar kind of anomaly in $\lambda_0$ values of tetraalkylammonium salts[20,21] in the case of alcohols.

As proposed by Fuoss in the model,[16] which is based on coupled equilibria, the ions in an electrolytic solution are represented by the equilibria

$$\mathrm{A}^+ + \mathrm{B}^- \rightleftharpoons (\mathrm{A}^+\cdots\mathrm{B}^-) \rightleftharpoons \mathrm{A}^+\mathrm{B}^- \rightleftharpoons (\mathrm{AB})$$

where the symbol (A$^+\cdots$B$^-$) represents a solvent-separated pair, A$^+$B$^-$ a contact pair, and AB a neutral molecule. The first equilibrium is diffusion controlled and denoted by $K_R$, which describes the formation and separation of solvent-separated pairs of diffusion in and out of spheres of diameter $R$ around cations and can be calculated by continuum theory; the second equilibrium denoted by $K_S$ is the constant describing the short-range process by which contact pairs form and dissociate. The association constant ($K_A$) is the combination of $K_R$ and $K_S$, and is expressed as $K_A = K_R(1 + K_S)$.

The values of $K_R$ along with $K_S$ obtained in the present work are reported in Table 3. The association constants ($K_A$) of all the systems studied are found to be appreciable (>15) in 80 mass % propylene carbonate + $p$-xylene. Arranging the $K_A$ values of the quaternary ammonium iodide salts studied in a descending order of the cation

**Table 2. Molar Conductivity, $\Lambda$, at Concentration $c$ of Various Salts in 80 mass % Propylene Carbonate + $p$-Xylene at 25 °C**

| $10^4c$ | $\Lambda$ | $10^4c$ | $\Lambda$ | $10^4c$ | $\Lambda$ | $10^4c$ | $\Lambda$ | $10^4c$ | $\Lambda$ |
|---|---|---|---|---|---|---|---|---|---|
| $\mathrm{mol \cdot dm^{-3}}$ | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | $\mathrm{mol \cdot dm^{-3}}$ | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | $\mathrm{mol \cdot dm^{-3}}$ | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | $\mathrm{mol \cdot dm^{-3}}$ | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | $\mathrm{mol \cdot dm^{-3}}$ | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ |
| TBATPB | | TBAP | | TBACl | | TBABr | | TBAI | |
| 18.38 | 23.26 | 14.52 | 32.62 | 4.55 | 32.80 | 19.45 | 32.54 | 4.25 | 33.80 |
| 27.06 | 22.75 | 19.17 | 32.42 | 9.03 | 32.38 | 28.62 | 32.04 | 8.42 | 33.21 |
| 35.41 | 22.61 | 45.31 | 31.02 | 19.93 | 31.58 | 37.45 | 31.16 | 20.43 | 32.65 |
| 51.21 | 22.17 | 61.21 | 30.79 | 40.51 | 30.50 | 54.17 | 30.55 | 28.09 | 32.32 |
| 65.93 | 21.77 | 76.03 | 30.09 | 59.61 | 29.78 | 69.74 | 30.18 | 39.04 | 31.55 |
| 79.66 | 21.45 | 89.88 | 29.75 | 77.39 | 29.51 | 84.27 | 28.90 | 52.73 | 31.25 |
| 92.52 | 21.31 | 102.84 | 29.31 | 93.99 | 28.99 | 97.86 | 28.25 | 65.50 | 30.70 |
| 126.53 | 20.72 | 126.46 | 28.75 | 116.89 | 28.41 | 112.57 | 27.53 | 77.43 | 30.20 |
| 146.65 | 20.35 | 147.41 | 28.25 | 137.71 | 27.99 | 144.46 | 26.68 | 88.61 | 29.95 |
| 163.50 | 20.19 | 166.13 | 28.19 | 162.68 | 27.62 | 181.50 | 26.09 | 99.09 | 29.42 |
| 179.25 | 19.98 | 182.86 | 27.57 | 190.14 | 26.70 | 204.65 | 25.63 | 118.24 | 28.57 |
| 193.48 | 19.70 | 198.16 | 27.37 | 214.16 | 26.26 | | | 135.29 | 28.26 |
| | | 211.96 | 27.11 | | | | | 154.14 | 27.90 |
| TEAP | | TEAI | | TEADCBS | | TEAPTS | | | |
| 5.16 | 40.31 | 4.80 | 40.80 | 1.99 | 41.29 | 1.51 | 39.18 | | |
| 10.16 | 39.78 | 9.52 | 39.50 | 5.91 | 39.71 | 2.24 | 38.82 | | |
| 19.32 | 38.65 | 18.67 | 38.44 | 9.78 | 39.25 | 3.67 | 38.24 | | |
| 29.32 | 37.94 | 22.47 | 37.97 | 19.18 | 37.22 | 5.41 | 38.07 | | |
| 38.37 | 37.61 | 35.95 | 37.45 | 36.94 | 35.30 | 7.08 | 37.29 | | |
| 47.09 | 37.28 | 52.00 | 36.62 | 61.24 | 33.21 | 10.24 | 36.29 | | |
| 63.61 | 36.47 | 66.94 | 36.13 | 76.07 | 32.26 | 15.94 | 35.45 | | |
| 79.02 | 35.28 | 80.88 | 35.08 | 96.52 | 31.12 | 27.32 | 33.45 | | |
| 93.41 | 34.85 | 100.14 | 34.60 | 128.70 | 29.27 | 35.86 | 32.63 | | |
| 106.89 | 34.48 | 123.14 | 33.87 | 142.49 | 29.12 | 42.50 | 31.93 | | |
| 119.54 | 34.17 | 143.54 | 33.13 | 229.13 | 25.20 | | | | |
| 131.43 | 33.90 | 161.77 | 32.30 | | | | | | |
| 148.00 | 33.41 | 178.15 | 31.91 | | | | | | |
| 168.00 | 33.01 | 192.55 | 31.33 | | | | | | |
| 185.95 | 32.51 | | | | | | | | |
| 202.15 | 31.80 | | | | | | | | |
| TMAI | | KI | | NaI | | NaTPB | | | |
| 6.59 | 35.31 | 8.91 | 34.03 | 9.65 | 31.49 | 8.91 | 21.62 | | |
| 9.53 | 34.70 | 13.23 | 33.86 | 18.94 | 29.89 | 20.03 | 21.11 | | |
| 10.92 | 34.58 | 21.63 | 33.33 | 36.47 | 28.67 | 38.18 | 20.84 | | |
| 18.35 | 34.15 | 29.71 | 32.82 | 52.76 | 28.36 | 54.78 | 20.60 | | |
| 23.54 | 33.42 | 45.01 | 31.88 | 67.92 | 27.77 | 70.24 | 20.25 | | |
| 31.92 | 32.70 | 59.24 | 31.31 | 82.07 | 26.88 | 84.67 | 20.00 | | |
| 37.04 | 32.33 | 72.52 | 30.81 | 95.30 | 26.50 | 98.16 | 19.91 | | |
| 44.45 | 31.89 | 84.93 | 30.21 | 119.37 | 25.52 | 122.71 | 19.68 | | |
| 49.39 | 31.54 | 99.36 | 29.84 | 140.69 | 24.92 | 144.46 | 19.34 | | |
| 55.56 | 31.20 | 120.23 | 29.32 | 159.70 | 24.50 | 163.85 | 19.01 | | |
| 63.50 | 30.80 | 138.78 | 28.86 | 176.76 | 24.18 | 189.32 | 18.88 | | |
| 74.00 | 30.23 | 155.38 | 28.35 | 195.77 | 23.73 | | | | |
| | | 170.32 | 27.98 | | | | | | |
| | | 187.02 | 27.67 | | | | | | |

**Table 3. Derived Conductivity Parameters for Various Electrolytes in 80 mass % Propylene Carbonate + $p$-Xylene at 25 °C**

| | $\Lambda_0 \pm \Delta\Lambda_0$ | | | | | $\sigma^a$ |
|---|---|---|---|---|---|---|
| electrolyte | $\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | $K_A$ | $K_R$ | $K_S$ | $R$/Å | % |
| TBATPB | 24.24 ± 0.05 | 20.04 | 3.02 | 5.63 | 5.20 | 0.26 |
| TBAP | 33.98 ± 0.11 | 22.64 | 3.76 | 5.02 | 6.40 | 0.34 |
| TBACl | 33.48 ± 0.11 | 28.99 | 6.91 | 3.19 | 8.20 | 0.51 |
| TBABr | 35.36 ± 0.25 | 44.29 | 6.25 | 6.09 | 7.60 | 0.73 |
| TBAI | 34.57 ± 0.13 | 28.85 | 5.28 | 4.46 | 7.40 | 0.59 |
| TEAP | 41.29 ± 0.11 | 31.44 | 5.85 | 4.38 | 7.20 | 0.43 |
| TEAI | 41.43 ± 0.17 | 35.82 | 6.33 | 4.66 | 7.60 | 0.68 |
| TEADCBS | 41.81 ± 0.23 | 66.64 | 4.42 | 14.08 | 6.40 | 0.89 |
| TEAPTS | 40.02 ± 0.09 | 179.28 | 66.70 | 1.69 | 25.00 | 0.37 |
| TMAI | 36.55 ± 0.11 | 45.71 | 6.46 | 6.08 | 7.80 | 0.29 |
| KI | 35.52 ± 0.10 | 33.19 | 6.46 | 4.14 | 7.80 | 0.28 |
| NaI | 32.70 ± 0.25 | 43.71 | 5.85 | 6.48 | 7.20 | 0.76 |
| NaTPB | 22.08 ± 0.08 | 16.83 | 4.60 | 2.66 | 7.40 | 0.37 |

[a] $\sigma/\% = 100\sigma/\Lambda_0$.

**Table 4. Limiting Ionic Conductivities of Cations and Anions in 80 mass % Propylene Carbonate + $p$-Xylene and Propylene Carbonate at 25 °C**

| | $\lambda_0/\mathrm{S \cdot cm^2 \cdot mol^{-1}}$ | |
|---|---|---|
| ion[a] | 80 mass % propylene carbonate + $p$-xylene[b] | propylene carbonate[c] |
| $TBA^+$ | 12.58 | 9.30, 9.39, 8.98, 8.6 |
| $TEA^+$ | 19.89 | 13.28, 13.0, 13.18 |
| $TMA^+$ | 14.56 | 14.6 |
| $Na^+$ | 10.42 | 8.8, 9.45 |
| $K^+$ | 13.53 | 11.97, 10.5, 11.12 |
| $TPB^-$ | 11.66 | 8.57 |
| $Cl^-$ | 21.90 | 20.20, 18.5 |
| $Br^-$ | 22.78 | 19.26, 20.20, 18.91 |
| $I^-$ | 21.99 | 18.78, 18.35 |
| $ClO_4{}^-$ | 21.40 | 18.78, 19.6, 18.46 |
| $DCBS^-$ | 21.92 | 11.7[d] |
| $PTS^-$ | 20.13 | |

[a] $DCBS^-$, 2,5-dichlorobenzenesulfonate ion; $PTS^-$, $p$-toluenesulfonate ion. [b] Present work. [c] Reference 1. [d] Reference 15.

sizes, viz., TBAI < TEAI < TMAI, it can be inferred that the bulkier tetraalkylammonium salts will have greater electrostatic interaction with the present solvent system.

Further, the observed behavior of various TBA salts in the present case (TBATPB < TBAP < TBAI < TBACl <

**Table 5. Stokes Radii, $R_S$, of Various Ions in 80 mass % Propylene Carbonate + *p*-Xylene and Propylene Carbonate at 25 °C**

| | $R_S$/Å | |
|---|---|---|
| ion | 80 mass % propylene carbonate[b] + *p*-xylene[a] | propylene carbonate[b] |
| $TBA^+$ | 3.58 | 3.47 |
| $TEA^+$ | 2.26 | 2.34 |
| $TMA^+$ | 3.09 | 2.18 |
| $Na^+$ | 4.32 | 3.10 |
| $K^+$ | 3.33 | 2.75 |
| $TPB^-$ | 3.86 | 3.65 |
| $Cl^-$ | 2.05 | 2.03 |
| $Br^-$ | 1.98 | 1.73 |
| $I^-$ | 2.05 | 1.70 |
| $ClO_4^-$ | 2.10 | 1.77 |
| $DCBS^-$ | 2.05 | 2.80[c] |
| $PTS^-$ | 2.23 | |

[a] Present work. [b] Reference 1. [c] Calculated in the present work.

TBABr) supports this viewpoint. However, the same is not found in the corresponding potassium and sodium salts (KI < NaI). Also, the ion association constants of the tetrabutylammonium halides (TBAI < TBACl < TBABr) do not follow the same pattern, with the bromide salt appearing to be more associated in the medium. The exceptional behavior of bromide ion compared with the other halides has been reported in propylene carbonate[6] and other systems too.[22−24] Among all tetraethylammonium salts studied, the dissociation of perchlorate salt seems to be more prominent in this medium (TEAP < TEAI < TEADCBS < TEAPTS). A similar trend for perchlorate in the case of certain potassium salts in 20 mass % propylene carbonate + ethylene carbonate has been reported earlier.[9]

The cosphere diameter values, $R$ (which indicate the distance of closest approach of ions), of all the electrolytes studied in the present system are placed in Table 3. Since, in this mathematical model, the best-fit conductance parameters (lowest standard deviation between the observed and the calculated values of the limiting molar conductivities of the electrolyte) are reproduced equally well over a wide range of arbitrarily chosen $R$ values, a comprehensive correlation of the cosphere diameter of the electrolytes studied in the present system could not be made. However, an examination of the data placed in Table 3 reveals that $R < 10$ in all the cases except in the case of tetraethyl *p*-toluenesulfonate. This exceptional increase in the value of $R$ and the abnormally high $K_R$ value observed may be attributed to the specific long-range electrostatic interactions of *p*-toluenesulfonate ion in this medium.

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