# Piezo-Optic Coefficient of Some Aqueous Electrolytes

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The piezo-optic coefficient or pressure derivative of refractive index at constant temperature was measured interferometrically at 25° for water and aqueous solutions of NaCl, LiCl, NaI, $MgCl_2$, $MgSO_4$, $Ca(NO_3)_2$, and $MnSO_4$.

The isothermal pressure derivative of the refractive index, $(\partial n/\partial P)_T$, is frequently called the piezo-optic coefficient. Few measurements have been reported in the literature since the classical work of Röntgen and Zehnder (3). Thus, in a recent paper on Brillouin scattering by aqueous electrolytes (2), Maret and Yeager had to estimate the required values of the piezo-optic coefficient with a semiempirical relation. Experimental values are presented here for some of the solutions they studied.

## Experimental

Measurements were made at three wavelengths, the red HeNe laser line, and the mercury green and blue lines. The mercury lamp was a sealed tube containing argon at 40 torr and a drop of mercury. It was excited by a 50-W RF transmitter to obtain narrow emission lines.

Refractive index was determined with a Bausch & Lomb Precision (Abbe) refractometer. The piezo-optic coefficient was determined with an Optical Engineering Model 18A Jamin interferometer as depicted in Figure 1. The cell was similar to that of Coumou et al. (1). It was made from aluminum and had two channels, $\frac{3}{8}$ in. diameter and 10.00 cm long, to hold the liquid sample. The inlet tubes to one channel were attached to a vacuum system with a mercury manometer. The other channel was at atmospheric pressure. The windows were 1-in. Pyrex discs, $\frac{3}{8}$ in. thick, and flat to $\lambda/20$. They were held in place by clamps (not shown in Figure 1) and sealed to the cell by gaskets of thermoplastic Parafilm "M", the seal being made by heating to 80–90°.

The cell was immersed in a covered water bath. Water was circulated through channels in the aluminum walls of the bath from a thermostated circulator.

One side of the cell was slowly evacuated so that dissolved air could be removed gradually from the sample solution without creating concentration gradients by evaporation. Such gradients caused a distortion of the interferometric fringe pattern and were clearly visible. A run consisted of setting the air pressure on the vacuum side a bit above the vapor pressure of water, moving the crosshairs of the micrometer telescope onto a fringe, introducing air slowly until atmospheric pressure was reached, and counting the number of fringes passing ($\Delta m$) to 1/100 of the fringe separation with aid of the micrometer slide. The pressure was reduced to its initial value again to check for drift in the fringe system. Two or three runs were made at each wavelength.

Compressional heating was not a problem, since the adiabatic piezo-optic coefficient of water and aqueous electrolytes differs only a few percent from the isothermal value. From the relation

$$(\partial n/\partial P)_T - (\partial n/\partial P)_S = -(\partial n/\partial T)_P(TV\alpha/C_p)$$

where $(\partial n/\partial P)_S$ is the adiabatic value, $(\partial n/\partial T)_P$ is the temperature derivative of the refractive index at constant pressure, $V$ is the volume, and $C_p$ the heat capacity, one finds a 1.2%

difference for water at 25°. The values used here are $(\partial n/\partial T)_P = -1.00 \times 10^{-4}$ $K^{-1}$, $V = 1.00 \times 10^{-3}$ $m^3$ $kg^{-1}$, $\alpha = 2.57 \times 10^{-4}$ $K^{-1}$, $C_p = 239$ J $kg^{-1}$, and $(\partial n/\partial P)_T = 14.86 \times 10^{-11}$ $m^2$ $N^{-1}$.

The piezo-optic coefficient was calculated from the formula $(\partial n/\partial P)_T = \Delta m\lambda/\Delta Pd$, where $\lambda$ is the wavelength of the source in vacuum, and $d$ is the path length in the cell. The pressure change, $\Delta P$, was read in meters of mercury and converted to N $m^{-2}$ by multiplying by the density of mercury (13 534 kg $m^{-3}$ at 25°) and the gravitational constant at Atlanta (9.79524 m $s^{-2}$). The precision in $\Delta m$ was ±0.02, resulting in a precision of about ±0.1 × $10^{-11}$ $m^2$ $N^{-1}$ in $\partial n/\partial P$.

Solutions were made up from reagent grade salts and distilled water and analyzed by standard analytical procedures to ±0.1 m units. Concentrations were chosen to cover the range up close to saturation.

## Results

The experimental values of the refractive index and its pressure coefficient are given at each of the three wavelengths in Table I. The dispersion of the piezo-optic coefficient is not much greater than the experimental uncertainty, as evidenced by the occasional violation of the expected increase with decreasing wavelength. Smoothing was done with the approximation, $n - 1 \sim$ density, which gave

$$\left(\frac{\partial n}{\partial P}\right)_{T,\lambda_2} = \left(\frac{\partial n}{\partial P}\right)_{T,\lambda_1} \left\{ 1 + \frac{n(\lambda_2) - n(\lambda_1)}{n(\lambda_1) - 1} \right\}$$

All values of $\partial n/\partial P$ were corrected to 546.1 nm with this relation. Then, the values for a given solution were averaged to give a smoothed value at 546.1 nm. The average deviation among each set of three adjusted values was no more than 3% and was 1–2% for most sets.

The measurements of Röntgen and Zehnder (3) on water extend only up to 22° for 589.2 nm and were made at other wavelengths (687.6 and 486.3 nm) only at 18°. Their results, extrapolated to 25° and the present wavelengths assuming the same dispersion (Table II), are 1–2% lower than the present results.

Comparison of the present results with the estimated values of Maret and Yeager (2) indicates that their equation holds to within 2–3% at concentrations of 1 or 2 m, except for NaI and $Ca(NO_3)_2$. In particular, the discrepancy they found between the experimental and theoretical intensity ra-
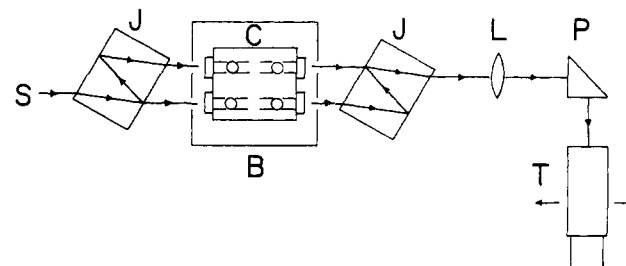
**Figure 1.** Experimental arrangement for measuring pressure derivative of refractive index of liquid. S, extended source; J, Jamin interferometer; C, cell; B, cell bath; L, lens; P, prism; T, telescope mounted on micrometer slide

Table I. Refractive Index and Piezo-Optic Coefficient at 25°

| Molality, m | λ, nm | n | $10^{11} \, \partial n/\partial P$, m² N⁻¹ Exptl | Smoothed |
|---|---|---|---|---|
| | | NaCl | | |
| 2.0 | 632.8 | 1.3493 | 12.45 | |
| 2.0 | 546.1 | 1.3523 | 12.57 | 12.63 |
| 2.0 | 435.8 | 1.3588 | 12.90 | |
| 4.0 | 632.8 | 1.3641 | 10.74 | |
| 4.0 | 546.1 | 1.3674 | 11.15 | 10.93 |
| 4.0 | 435.8 | 1.2748 | 11.02 | |
| 6.0 | 632.8 | 1.3771 | 10.13 | |
| 6.0 | 546.1 | 1.3806 | 9.96 | 10.05 |
| 6.0 | 435.8 | 1.3881 | 10.16 | |
| | | LiCl | | |
| 6.3 | 632.8 | 1.3694 | 10.67 | |
| 6.3 | 546.1 | 1.3728 | 11.20 | 11.12 |
| 6.3 | 435.8 | 1.3801 | 11.61 | |
| 9.6 | 632.8 | 1.3962 | 9.00 | |
| 9.6 | 546.1 | 1.4000 | 9.54 | 9.37 |
| 9.6 | 435.8 | 1.4084 | 9.49 | |
| 14.2 | 632.8 | 1.4146 | 8.34 | |
| 14.2 | 546.1 | 1.4187 | 8.73 | 8.61 |
| 14.2 | 435.8 | 1.4279 | 8.85 | |
| | | NaI | | |
| 4.1 | 632.8 | 1.4009 | 13.15 | |
| 4.1 | 546.1 | 1.4058 | 13.23 | 13.22 |
| 4.1 | 435.8 | 1.4171 | 13.49 | |
| 7.6 | 632.8 | 1.4500 | 11.53 | |
| 7.6 | 546.1 | 1.4564 | 11.69 | 11.81 |
| 7.6 | 435.8 | 1.4717 | 12.45 | |
| 10.9 | 632.8 | 1.4866 | 10.22 | |
| 10.9 | 546.1 | 1.4942 | 10.56 | 10.55 |
| 10.9 | 435.8 | 1.5125 | 11.11 | |
| | | MgCl₂ | | |
| 2.2 | 632.8 | 1.3728 | 11.29 | |
| 2.2 | 546.1 | 1.3762 | 11.51 | 11.47 |
| 2.2 | 435.8 | 1.3833 | 11.50 | |
| 4.2 | 632.8 | 1.4052 | 9.25 | |
| 4.2 | 546.1 | 1.4090 | 9.90 | 9.66 |

| Molality, m | λ, nm | n | $10^{11} \, \partial n/\partial P$, m² N⁻¹ Exptl | Smoothed |
|---|---|---|---|---|
| | | MgCl₂ | | |
| 4.2 | 435.8 | 1.4173 | 9.84 | |
| 5.8 | 632.8 | 1.4290 | 8.39 | |
| 5.8 | 546.1 | 1.4331 | 8.84 | 8.84 |
| 5.8 | 435.8 | 1.4422 | 9.39 | |
| | | MgSO₄ | | |
| 1.0 | 632.8 | 1.3528 | 12.25 | |
| 1.0 | 546.1 | 1.3557 | 12.13 | 12.25 |
| 1.0 | 435.8 | 1.3616 | 12.46 | |
| 2.0 | 632.8 | 1.3710 | 9.68 | |
| 2.0 | 546.1 | 1.3740 | 9.74 | 9.75 |
| 2.0 | 435.8 | 1.3803 | 9.91 | |
| 3.0 | 632.8 | 1.3859 | 8.13 | |
| 3.0 | 546.1 | 1.3890 | 8.19 | 8.15 |
| 3.0 | 435.8 | 1.3955 | 8.20 | |
| | | Ca(NO₃)₂ | | |
| 2.2 | 632.8 | 1.3749 | 11.81 | |
| 2.2 | 546.1 | 1.3784 | 12.23 | 12.09 |
| 2.2 | 435.8 | 1.3860 | 12.36 | |
| 5.0 | 632.8 | 1.4096 | 10.08 | |
| 5.0 | 546.1 | 1.4137 | 10.06 | 10.14 |
| 5.0 | 435.8 | 1.4228 | 10.39 | |
| 8.0 | 632.8 | 1.4341 | 8.69 | |
| 8.0 | 546.1 | 1.4387 | 8.55 | 8.64 |
| 8.0 | 435.8 | 1.4489 | 8.79 | |
| | | MnSO₄ | | |
| 1.0 | 632.8 | 1.3544 | 12.29 | |
| 1.0 | 546.1 | 1.3572 | 12.66 | 12.60 |
| 1.0 | 435.8 | 1.3634 | 12.96 | |
| 2.0 | 632.8 | 1.3754 | 11.12 | |
| 2.0 | 546.1 | 1.3785 | 10.28 | 10.76 |
| 2.0 | 435.8 | 1.3851 | 10.99 | |
| 4.0 | 632.8 | 1.4078 | 7.44 | |
| 4.0 | 546.1 | 1.4112 | 8.04 | 7.78 |
| 4.0 | 435.8 | 1.4181 | . . . | |

Table II. Refraction Index and Piezo-Optic Coefficient of Water at 25°

| λ, nm | n | $10^{11} \, \partial n/\partial P$, m² N⁻¹ This work | Röntgen and Zehnder |
|---|---|---|---|
| 632.8 | 1.3312 | 14.83 | 14.65 |
| 546.1 | 1.3339 | 14.88 | 14.76 |
| 435.8 | 1.3397 | 15.02 | 14.94 |

tios in the Brillouin spectra of MgSO₄ and MnSO₄ solutions is not removed by using the values of $\partial n/\partial P$ reported here.

**Literature Cited**

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(2) Maret, A. R., Yeager, E., J. Chem. Phys., 59, 206 (1973).
(3) Röntgen, W. C., Zehnder, L., Ann. Phys., 44, 24 (1891).