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# Solubility of Solid $CCl_4$ in Supercritical $CF_4$

**T. A. Barber,[†] H. D. Cochran,*[,†,‡] and P. R. Bienkowski[†]**

*Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37916-2200, and Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6224*

**A flow apparatus was used to determine the solubility of solid $CCl_4$ in supercritical $CF_4$. An on-line quadrupole mass spectrometer was utilized for analysis of the effluent. The direct coupling of supercritical extraction with mass spectrometry offers a quantitative method for the direct determination of the solute mole fraction in the supercritical fluid. Data were obtained for four isotherms at 234, 239, 244, and 249 K. For pressures ranging from 35 to 310 bar, solubilities were found to range from $3.7 \times 10^{-3}$ to $2.58 \times 10^{-2}$ mole fraction. The data were successfully correlated by two different computational approaches: the compressed gas model using the Peng-Robinson equation of state and the Kirkwood-Buff local composition model.**

## Introduction

Applications of supercritical fluid technology have come to the forefront of technological research. In the past two decades, supercritical fluid extraction (SCFE) has become increasingly important as an alternative process for conventional separations in commercial processes.

Although advances in modeling supercritical solubilities have been made in the past decade, challenges remain in the testing of new theoretical models for correlating and predicting supercritical behavior. Two models were examined in this work. The compressed gas model utilizing the empirical Peng-Robinson equation of state with conventional mixing rules was investigated and compared to results from the Kirkwood-Buff local composition model, which is based on the exact Kirkwood-Buff solution theory.

Most systems for which supercritical solubility data exist consist of large heavy organic solutes in small, simple solvents such as the naphthalene-$CO_2$ system. Indeed, in many systems of industrial interest, the relative size of the solute to that of the solvent may be considerably greater than in the naphthalene-$CO_2$ case. In comparison, the ratio of molecular size of $CCl_4$ to that of $CF_4$ is small, approximately 1.3, while the ratio of intermolecular attractive energy (i.e. Lennard-Jones $\epsilon$ parameter) is uncharacteristically large, about 2.4. This particular solute-solvent system was also advantageous because both components can be approximated reasonably well as spherically symmetric molecules. For purposes of comparison with molecular-based theories, this molecular simplicity minimizes the complicating effects of molecular anisotropy.

## Experimental Section

***Equipment and Operations.*** A flow-type apparatus (see Figure 1) was used to determine solubilities of solid $CCl_4$ in supercritical $CF_4$. A UTI Model 100C quadrupole mass spectrometer was directly coupled to the apparatus to analyze the effluent, providing a method of on-line analysis. Previous work by Smith et al. (*1*, *2*) has applied directly coupled supercritical gas chromatography-mass spectrometry. The mass spectrometer was calibrated with prepared $CCl_4$-$CF_4$ mixtures; the calibration accuracy is estimated to average ±1%, ranging from ±2% at the lowest $CCl_4$ concentration to ±0.5% at the highest concentration. The column was a stainless steel tube (19-cm length, 0.84-cm i.d.) that contained a packed bed of granular, solid $CCl_4$. The $CCl_4$ particles were generally less than 1 mm in diameter (by visual observation), and the bed was packed to about 0.6 volume fraction of solid (determined gravimetrically for some runs). At each end of the bed and every 3.75 cm through the bed, a glass wool pad was placed in an attempt to minimize entrainment and channeling. Pressure was measured by a Heise Bourden tube gauge calibrated to an accuracy of ±0.3 bar. Column temperature was monitored by two chromel/gold (0.07 wt % iron) thermocouples calibrated to an accuracy of ±0.1 K. A detailed description of the equipment, operating procedures, and analysis procedures is given elsewhere (*3*).

***Materials.*** Tetrafluoromethane, $CF_4$, was obtained from Air Products and Chemicals, Inc., in standard cylinders with a stated purity of 99.9%; the $CF_4$ was used without further processing. Tetrachloromethane, $CCl_4$, was obtained from Fisher Scientific as certified ACS grade. The $CCl_4$ was frozen with liquid nitrogen, crushed, and loaded as a solid into the cold equilibrium cell that was then closed and maintained near liquid nitrogen temperature until installation in the apparatus. Handling of $CCl_4$ from the bottle to the closed equilibrium cell was performed in a drybox to prevent contamination by moisture.

## Results and Discussion

The solubility of solid $CCl_4$ in supercritical $CF_4$ was measured for pressures ranging from 35 to 310 bar at four temperatures: 234, 239, 244, and 249 K. The solubilities were found to range from $3.7 \times 10^{-3}$ to $2.58 \times 10^{-2}$ mole fraction. The results are tabulated in Table I.

The estimate of the accumulated error for high-pressure data (>136 bar) is less than 5% while that for the low pressure data (<70 bar) approached 50%. The error attributed to the accuracy of temperature and pressure measurements was far greater at lower pressures. Other system errors taken into account were inaccuracies in the following: (1) the preparation of the calibration curve, (2) correction of the ion current of the mass spectrometer for background pressure, and (3) reading the ion current peak height. A formal error analysis has been performed and reported elsewhere (*4*).

Special care was taken to ensure the reliability of the data. The reproducibility of selected data, at 136 bar and 244 and 249 K, was within 1.5% (less than the estimate of the accumulated error), indicating the sampling procedure was consistent and representative sampling had occurred.

Equilibrium flow rate experiments were conducted to determine the superficial velocity below which close approach to equilibrium composition was assured. The solubility data at 244 and 249 K, measured at flow rates below 0.2 cm/min, closely approached equilibrium conditions. Most of the data points on the 239 K isotherm closely approached equilibrium flow conditions; however, at pressures less than 70 bar close approach to equilibrium may not have been achieved because velocities were above 0.2 cm/min. Data points on the 234 K isotherm are judged to be least certain of the approach to equilibrium.

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[†] University of Tennessee.
[‡] Oak Ridge National Laboratory.

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**Table I. Solubility Isotherms of Solid $CCl_4$ in Supercritical $CF_4$**

| $P$, bar | $y \times 10^3$ | $\rho$,[a] g-mol/dm$^3$ | $E$[b] | $P$, bar | $y \times 10^3$ | $\rho$,[a] g-mol/dm$^3$ | $E$[b] |
|---|---|---|---|---|---|---|---|
| | | 249 K | | | | 244 K | |
| 34.49 | 1.63 | 2.30 | 5.74 | 69.70 | 4.95 | 9.44 | 50.61 |
| 68.95 | 5.74 | 8.13 | 40.42 | 103.08 | 10.63 | 11.51 | 160.74 |
| 103.76 | 13.29 | 10.93 | 140.84 | 136.86 | 14.61 | 12.41 | 293.72 |
| 136.51 | 21.01 | 11.98 | 292.93 | 137.55 | 14.48 | 12.43 | 292.17 |
| 137.27 | 22.00 | 12.00 | 308.44 | 138.24 | 14.29 | 12.44 | 289.78 |
| 137.55 | 21.00 | 12.01 | 295.02 | 171.33 | 16.67 | 13.05 | 418.96 |
| 137.89 | 21.00 | 12.02 | 295.78 | 210.98 | 18.31 | 13.60 | 566.65 |
| 171.68 | 22.50 | 12.70 | 394.53 | 240.90 | 19.38 | 13.94 | 684.85 |
| 204.77 | 23.80 | 13.22 | 497.76 | 276.13 | 20.06 | 14.28 | 812.55 |
| 206.49 | 23.60 | 13.24 | 497.72 | | | | |
| 239.24 | 24.90 | 13.64 | 608.40 | | | | |
| 274.06 | 25.50 | 14.01 | 713.77 | | | | |
| 307.85 | 25.80 | 14.32 | 813.84 | | | | |
| | | 239 K | | | | 234 K | |
| 69.67 | 4.55 | 10.31 | 65.82 | 68.95 | 3.67 | 11.31 | 80.18 |
| 136.51 | 9.34 | 12.82 | 272.73 | 86.18 | 5.13 | 12.04 | 140.10 |
| 205.12 | 9.45 | 13.84 | 414.63 | 102.73 | 6.22 | 12.52 | 202.53 |
| 205.94 | 9.52 | 13.85 | 419.37 | 102.73 | 5.07 | 12.52 | 165.08 |
| 273.72 | 9.56 | 14.52 | 559.74 | 103.42 | 5.94 | 12.53 | 194.68 |
| | | | | 135.48 | 6.09 | 13.20 | 261.51 |
| | | | | 136.86 | 6.03 | 13.22 | 261.57 |
| | | | | 136.86 | 6.06 | 13.22 | 262.83 |
| | | | | 171.68 | 5.20 | 13.74 | 282.96 |
| | | | | 205.46 | 6.62 | 14.14 | 431.11 |
| | | | | 206.84 | 5.55 | 14.16 | 363.85 |
| | | | | 243.73 | 5.20 | 14.52 | 387.80 |
| | | | | 273.03 | 6.05 | 14.77 | 523.56 |
| | | | | 274.41 | 6.18 | 14.78 | 537.51 |
| | | | | 275.00 | 6.01 | 14.79 | 523.85 |

[a] Densities of $CF_4$ were calculated by using an equation of state proposed by Rubio et al. (*5*). [b] Enhancement factor, $E = y_2P/p_2^{sat}$, was evaluated by using values of $p_2^{sat}$ from *International Critical Tables* (*6*).

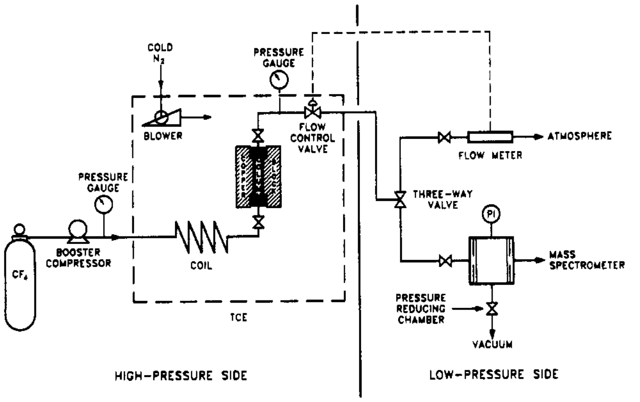

**Figure 1.** Direct-coupled SCFE-MS apparatus.

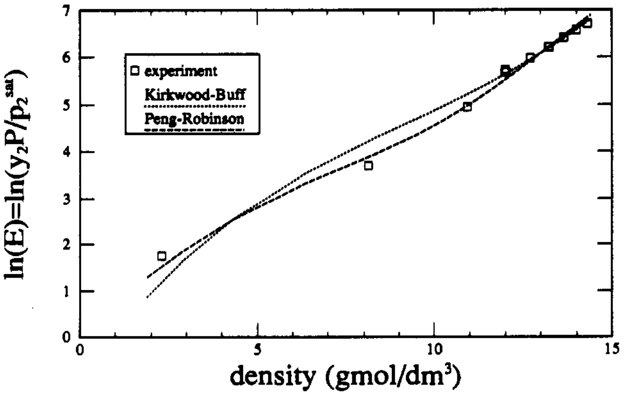

**Figure 2.** Relationship between ln $E$ and $\rho_{CF_4}$ at 249 K.

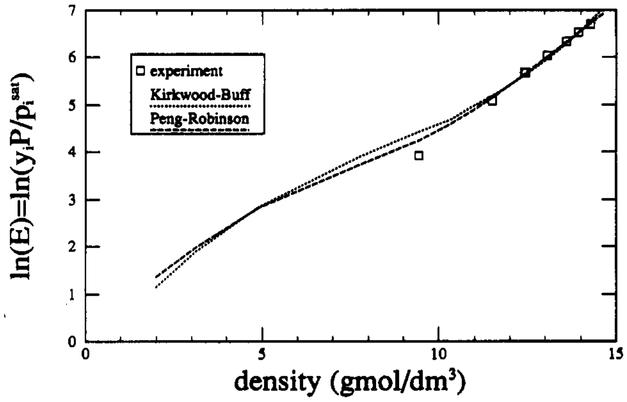

**Figure 3.** Relationship between ln $E$ and $\rho_{CF_4}$ at 244 K.

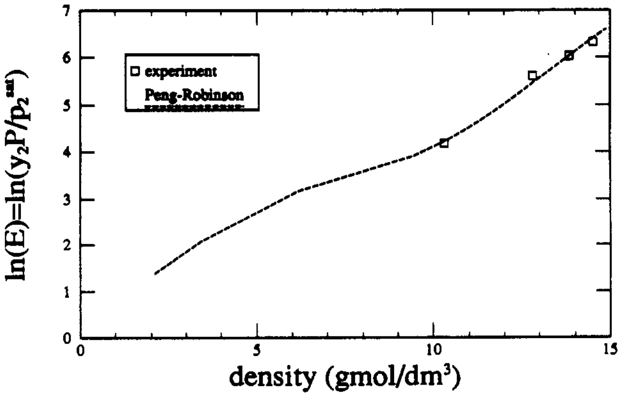

**Figure 4.** Relationship between ln $E$ and $\rho_{CF_4}$ at 239 K.

These experiments at subambient temperatures occassionally developed the usual operating difficulties; however, experiments at 239 K and particularly at 234 K proved to be unexpectedly difficult. Results from experiments that were compromised by operating difficulties have not been reported. It is speculated that difficulties at 234 and 239 K—difficulty in controlling flow rate, occasional plugging, and sometimes erratic composition measurements—may have resulted from the presence of a third, liquid phase.

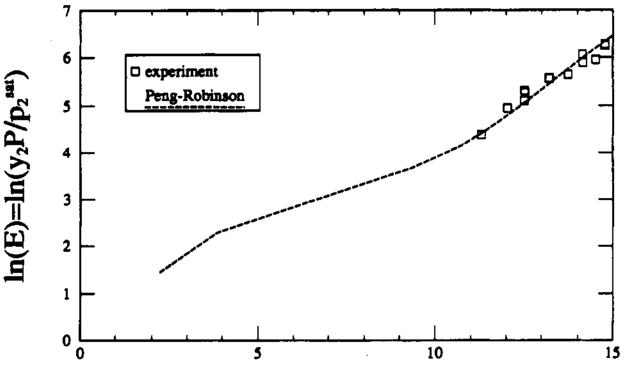

**Figure 5.** Relationship between ln $E$ and $\rho_{CF_4}$ at 234 K.

When the logarithm of the enhancement factor, $E = Py_2/p_2^{sat}$ was plotted against the density, a nearly linear relationship for the 244 and 249 K isotherms and a reasonably linear relationship for the 234 and 239 K isotherms were observed as are commonly observed with supercritical solubility data. Figures 2-5 illustrate the consistency of the data. Inasmuch as the experimental data and the data correlations (see below) are least accurate at low density, the logarithmic presentation, which emphasizes the low-density region, presents the results in an unfavorable fashion.

## Data Correlation

Two models were used for the correlation of the experimental results: the compressed gas model utilizing the Peng-Robinson equation of state and the Kirkwood-Buff local composition model.

For correlation with the compressed gas model (*7*), the following expression was used:

$$y_i = \frac{p_i^{sat}}{P}\frac{1}{\phi_i^f}\exp\left[\frac{v_i^s[P - p_i^{sat}]}{RT}\right] \tag{1}$$

where $p_2^{sat}$ is the vapor pressure, $v_2^s$ is the solid-phase molar volume, and $\phi_2^f$ is the fluid-phase fugacity coefficient of the solute. The fugacity coefficient, $\phi_2^f$, was calculated

$$\ln \phi_i^f = \frac{b_i}{b}(Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\left[\frac{2\sum y_i a_{ij}}{a} - \frac{b_i}{b}\right]\ln\left[\frac{Z + 2.414B}{Z - 0.414B}\right] \tag{2}$$

by expressing the Peng-Robinson equation in terms of compressibility factor, $Z$, and using conventional mixing rules

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} y_i y_j a_{ij} \tag{3}$$

$$b = \sum_{i=1}^{n} y_i b_i \tag{4}$$

where

$$A = aP/(RT)^2 \tag{5}$$

$$B = bP/RT \tag{6}$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \tag{7}$$

and $k_{ij}$ is a binary interaction parameter, which is obtained by regression from data.

Table II. Peng-Robinson Modeling Correlations

| isotherm, K | $k_{ij}$ | AAD% | isotherm, K | $k_{ij}$ | AAD% |
|---|---|---|---|---|---|
| 249 | 0.131 | 10.8 | 239 | 0.178 | 5.3 |
| 244 | 0.142 | 6.2 | 234 | 0.199 | 11.4 |

Table III. Kirkwood-Buff Modeling Correlations

| case | isotherm(s) regressed, K | $V_{12}$ | $b_0$ | $b_1$ | AAD% |
|---|---|---|---|---|---|
| a | 244 | 286 | 5.33 | -1185 | 12.2 |
| b | 249 | 327 | 5.39 | -1239 | 13.8 |
| c | 249 + 244 | 312 | 5.39 | -1226 | 19.7 |

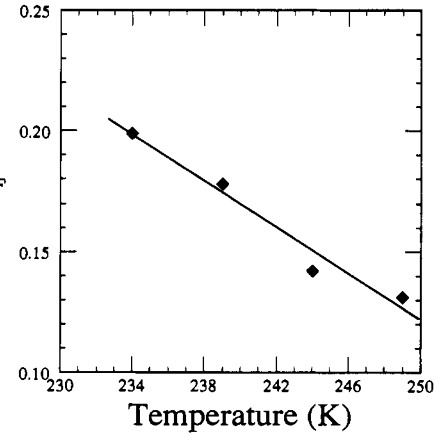

**Figure 6.** Temperature dependence of $k_{ij}$.

The Kirkwood-Buff local composition model (*8*) is based on the Kirkwood-Buff theory of solutions (*9*). For the common case of a single, pure, incompressible solid at equilibrium with a supercritical solvent and with the simplifying assumption that the solution is dilute, then the mole fraction, $y$, can be expressed as

$$\ln y_2 = \ln(p_2^{sat}/P) + \ln(Z_1) - \alpha_{12}\ln(f_1 V_1/RT) + (v_2^s + V_{12}\exp[b_0 + b_1/T] - V_{12})(P - p_2^{sat})/RT \tag{8}$$

where $f_1$ is the pure solvent fugacity and $V_{12}$, $b_0$, and $b_1$ are parameters to be fitted by regression of the data.

The correlations of the data are presented in Figures 2-5 and Tables II and III. As is often observed in correlating supercritical solubility data with the compressed gas model, the $k_{ij}$ was temperature-dependent. We note that the magnitudes of the fitted values of $k_{ij}$ are relatively large for a mixture of nearly spherical molecules. The magnitude is not unusual, however, when compared with other supercritical solubility results (*8*) nor when compared with other results for systems containing a fluorocarbon and another type of substance (e.g., ref 10). When plotted against temperature (Figure 6), a near-linear temperature dependence in $k_{ij}$ is observed.

In summary, the 244 and 249 K isotherms are presented with confidence that they are valid equilibrium data. Although the 239 and 234 K experiments may not have reached equilibrium, the consistency of the data could not be ignored. On the basis of the column superficial velocities at which they were taken, it is speculated that the 239 K data presented are within 95% of the equilibrium value and the 234 K data are within 85% of the equilibrium value.

The data were successfully correlated with both the compressed gas model using the Peng-Robinson equation of state and the Kirkwood-Buff local composition model. The models effectively accounted for the large difference in intermolecular attraction and the small difference in size of the system. Both models performed well, and there appears to be no correlative advantage by either model. For this system, the absolute average deviations for both models were comparable to or less than that for binary supercritical solubility data reported in the literature (*8*).

## Glossary

| | |
|---|---|
| $a$ | energy parameter in Peng–Robinson equation of state (P–R EOS), (bar cm$^3$)/g-mol$^2$ |
| $A$ | dimensionless constant, $A = aP/R^2T^2$ |
| $b$ | covolume term in P–R EOS, cm$^3$/g-mol |
| $B$ | dimensionless constant, $B = bP/RT$ |
| $b_0$ | Kirkwood–Buff (K–B) fitted parameter |
| $b_1$ | K–B fitted parameter, K |
| $E$ | enhancement factor, $y_2P/p_2^{sat}$ |
| $f$ | fugacity, bar |
| $k_{ij}$ | binary interaction parameter between unlike molecules $i$ and $j$ |
| $P$ | pressure, bar |
| $p^{sat}$ | saturation pressure, bar |
| $T$ | temperature, K |
| $V$ | molar volume, cm$^3$/g-mol |
| $V_{12}$ | K–B fitted parameter, cm$^3$/g-mol |
| $v^s$ | solid-state molar volume, cm$^3$/g-mol |
| $y$ | solubility (mole fraction) |
| $Z$ | compressibility factor, $Z = PV/RT$ |
| $\alpha$ | K–B scaling factor, $\alpha_{12} = (T_{c,1}/T_{c,2})^{1/2}(V_{c,1} + V_{c,2})/2$ |
| $\phi^v$ | vapor-phase fugacity coefficient |
| $\rho$ | molar density, (g-mol/dm$^3$) |

### *Subscripts*

| | |
|---|---|
| $i,j$ | components $i$ and $j$ |
| 1 | $CF_4$ |
| 2 | $CCl_4$ |
| c | critical |

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# Extension of the Falkenhagen–Leist–Kelbg Equation to the Electrical Conductance of Concentrated Aqueous Electrolytes

**S. S. Islam, R. L. Gupta, and K. Ismail***

*Department of Chemistry, North-Eastern Hill University, Bijni Campus, Laitumkhrah, Shillong 793 003, India*

**The Falkenhagen-Leist-Kelbg (FLK) conductance equation, which is otherwise applicable only to dilute electrolyte solutions, has been modified by substituting into this equation the viscosity and dielectric constant of the solution in place of those of the solvent. This modified FLK equation with the ion-size parameter as the only adjustable parameter has been found to describe the reported equivalent conductance data of aqueous LiCl, NaCl, NaBr, NaI, and KF solutions satisfactorily up to 4 mol·dm$^{-3}$.**

## Introduction

Several arbitrary relations based on the Debye-Hückel model of an ionic atmosphere are available to deal with the concentration dependence of electrical conductance. The commonly used expressions for describing the electrical conductance behavior of electrolytic solutions at higher concentrations are obtained by modifying the Falkenhagen-Leist-Kelbg (FLK) equation (*1*) of the form

$$\Lambda_{FLK} = \left[\Lambda_0 - \frac{B_1c^{1/2}}{1 + Ba_0c^{1/2}}\right]\left[1 - \frac{B_2c^{1/2}F}{1 + Ba_0c^{1/2}}\right] \quad (1)$$

where for 1:1 electrolytes $B = 50.29 \times 10^8/(\epsilon_0T)^{1/2}$, $B_1 = 82.5/[\eta_0(\epsilon_0T)^{1/2}]$, $B_2 = 8.204 \times 10^5/(\epsilon_0T)^{3/2}$, and $F = [\exp(0.2929Ba_0^{1/2}) - 1]/(0.2929Ba_0c^{1/2})$. $\eta_0$ and $\epsilon_0$ are the viscosity and dielectric constant of water, respectively. $c$ is the molar concentration, and $T$ is the absolute temperature.

Wishaw and Stokes (*2*) empirically modified the FLK eq 1 by introducing into it a relative viscosity term. This modified equation may be written as

$$\Lambda_{WS} = \Lambda_{FLK}(\eta_0/\eta) \quad (2)$$

where $\eta$ is the viscosity of the solution. Equation 2 has been found to fit with moderate success the conductance data of electrolytic solutions up to fairly high concentrations. However, eq 2 fails to reproduce the conductance data when the viscosity ratio, $\eta/\eta_0$, becomes very high (*3-5*). Goldsack et al. (*6*) modified eq 1 by taking into consideration the effect of hydration on $a_0$, the ion-size parameter. Recently, Monica et al. (*3-5*) made another modification to eq 1 by taking into account the dependence of the electrophoretic term $B_1$ on the solution viscosity. From the expression for $B_1$ it is obvious that $B_1$ is inversely dependent on the viscosity of the solvent, $\eta_0$. They, however, incorporated this modification in eq 2 rather than in the FLK eq 1 and obtained an expression essentially of the same form as eq 2 with the $B_1$ term replaced by $B_{1\eta} = B_1\eta_0/\eta$. This new equation of Monica et al. was found (*3-5*) to describe the concentration dependence of $\Lambda$ for several 1:1 electrolytes up to high concentrations.

One of the important factors ignored in the theoretical conductance equations is the variation in the dielectric constant of water caused by the addition of electrolyte. Although this point was highlighted by Goldsack et al. (*6*), no serious effort was

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