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13. ABSTRACT *(Maximum 200 words)*

The main purpose of the research program (September 1989 - September 1992) has been to offer chemists or engineers (interested in building a high density capacitor, capable of storing electrical energy, to be delivered continuously or by short pulses) the knowledge of the dielectric spectrum of relevant polar-apolar liquid mixtures, in a frequency range as broad as possible. This would enable the construction of capacitors using liquids of known dielectric properties at frequencies as high as feasible. To this end we have extended the microwave frequency range to 130 GHz (1 GHz = 10^9Hz). We have also explored the dielectric far-infrared to infrared range form 0.9 to 150 THz (1 THz = 10^{12}Hz) or 30 cm^{-1} to 5000 cm^{-1} in wave numbers. This has required the procurement (through another grant of the School) of a FTIR spectrometer covering the above range, which has been adapted to our purpose. Extension of the determination of the real part of the permittivity of the solution $e^1 = n^2$ to visible frequencies, namely to the doublet emission line of Na at λ = 589.3 nm, by conventional high precision visible refractometry, has also been accomplished with the purchase and setting up of a Bellingham and Stanley high precision refractometer capable of determining n_D to within $\pm$ 1 x 10^{-5} units. At about the end of the grant tenure we have interpreted the imaginary part of the complex permittivity e'' vs frequency, in the far infrared range (for organic carbonate solutions in apolar solvents) by the Powles-Rocard resonant-relaxation function [2], which modifies the Debye relaxation function[3] by retention of inertial effects. We have explored four systems of liquid mixtures.

a) Acetonitrile -CCl_4 and Benzonitrile -CCl_4; b) N-Methylacetamide -CCl_4 and dimethylacetamide -CCl_4 c) Acyclic dimethylcarbonate and cyclic ethylene carbonate $CHCl_3$ mixtures vs the same liquids -CCl_4 mixtures (to probe the effect of H-bonding on the complex permittivity $e^* = e' - Je''$). d) Acyclic dimethylcarbonate-cyclohexane and dimethylcarbonate-benzene mixtures, and cyclic ethylene carbonate-benzene mixtures.

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"Dielectrics for the Supercapacitors"

FINAL REPORT

by

S. Petrucci

December 1992

U.S. ARMY RESEARCH OFFICE

Grant #DAAL03-89-K-0148
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Table of Contents

Body of Report

A) Statement of the problem studied

The main purpose of the research program (September 1989 - September 1992) has been to offer chemists or engineers (interested in building a high density capacitor, capable of storing electrical energy, to be delivered continuously or by short pulses) the knowledge of the dielectric spectrum of relevant polar-apolar liquid mixtures, in a frequency range as broad as possible. This would enable the construction of capacitors using liquids of known dielectric properties at frequencies as high as feasible.

To this end we have extended the microwave frequency range to 130 GHz [1] (1 GHz = 10^9Hz). We have also explored the dielectric far-infrared to infrared range from 0.9 to 150 THz (1 THz = 10^{12}Hz) or 30 cm^{-1} to 5000 cm^{-1} in wave numbers. This has required the procurement (through another grant of the School) of a FTIR spectrometer covering the above range, which has been adapted to our purpose, as explained below.

Extension of the determination of the real part of the permittivity of the solution $\epsilon' = n^2$ to visible frequencies, namely to the doublet emission line of Na at λ = 589.3 nm, by conventional high precision visible refractometry, has also been accomplished with the purchase and setting up of a Bellingham and Stanley high precision refractometer capable of determining n_D to within $\pm$ 1 x 10^{-5} units.[1]

At about the end of the grant tenure we have interpreted the imaginary part of the complex permittivity ϵ'' vs frequency, in the far infrared range (for organic carbonate solutions in apolar solvents) by the Powles-Rocard resonant-relaxation function [2], which modifies the Debye relaxation function[3] by retention of inertial effects.

Because we consider this last development a breakthrough in to a new and exciting field, as a result of the above study, we naturally look with gratitude at the Army Research Office Grant for having given us the opportunity to engage in this endeavor. As predicted in the original proposal, we have explored four systems of liquid mixtures.

a) Acetonitrile -CCl_4 and Benzonitrile -CCl_4

b) N-Methylacetamide -CCl_4 and dimethylacetamide -CCl_4

c) Acyclic dimethylcarbonate and cyclic ethylene carbonate $CHCl_3$ mixtures vs the same liquids -CCl_4 mixtures (to probe the effect of H-bonding on the complex permittivity $\epsilon^* = \epsilon' - J\epsilon''$).

d) Acyclic dimethylcarbonate-cyclohexane and dimethylcarbonate-benzene mixtures, and cyclic ethylene carbonate-benzene mixtures.

These systems and the associated results will be reported below in the same order.

B) Summary of the most important results

a) Benzonitrile, Acetonitrile and their Mixtures with CCL_4 at 25°C

Infrared refractive indices at $\bar{\nu} \sim 300$ cm^{-1} (f = 9000 GHz) and $\bar{\nu} \sim 400$ cm^{-1} (f = 12000 GHz) and complex permittivities $\epsilon^* = \epsilon' - J\epsilon''$ at $\bar{\nu} \sim 300$ cm^{-1} and $\bar{\nu} \sim 400$ cm^{-1} for acetonitrile and acetonitrile-carbon tetrachloride as well as benzonitrile and benzonitrile-carbon tetrachloride mixtures at $\bar{\nu} \sim 125$ cm^{-1} (3750 GHz) at 25°C are reported. Microwave complex permittivities ϵ^*, in the frequency range ~0.4 - 90 GHz for the same systems at 25°C, are also reported. Visible refractive indices at λ = 589.3 nm (the sodium D line) for benzonitrile and benzonitrile-carbon tetrachloride mixtures and for acetonitrile and acetonitrile-carbon tetrachloride mixtures and static dielectric permittivities for the same systems at 25°C are reported. The observed dielectric relaxation processes at microwave frequencies up to 13.8 GHz for pure benzonitrile and up to 80 GHz for acetonitrile can be described by a single Debye relaxation function, using a parameter ϵ_∞. This value is larger than the figure for n_{IR}^2 at $\bar{\nu}$ = 125 cm^{-1} for pure benzonitrile. For pure benzonitrile, an almost complete profile of $\epsilon' \sim n^2$ vs wavenumber $\bar{\nu}$ has been determined up to the visible. For the mixtures, a single Debye relaxation function can describe the microwave dielectric data by using a parameter ϵ_∞. The latter becomes practically equal to n_{IR}^2, within experimental error, for mixtures of composition $X_{C_6H_5CN} \leq 0.10$ and $X_{CH_3CN} \leq 0.05$, respectively. Potential applications of ϵ_∞(or n_{IR}^2) data in evaluating the longitudinal relaxation times τ_L and the short-range structural relaxation time τ_G in femptosecond-picosecond molecular dynamics studies of solvation and the need for a better understanding of the dielectric properties of mixed liquids in the development of supercapacitors are both noted.

b) N-Methylacetamide, N, N-Dimethylacetamide, and Their Mixtures in CCl_4 at 32°C

Static dielectric permittivities, ϵ_0, and visible refractive indices, n_D (at the sodium doublet λ = 589.3 nm) are reported for N-methylacetamide (NMA), N, N-dimethylacetamide (DMA), their mixtures with CCl_4 over a broad concentration range, and NMA-DMA mixtures over a broad range of concentrations at 32°C. UHF and microwave complex permittivities from 0.3 to 90 GHz and far-infrared refractive indices at $\bar{\nu}$ = 130 and $\bar{\nu}$ = 380 cm^{-1} for NMA and their mixtures with CCl_4 and at $\bar{\nu}$ = 130 cm^{-1} for DMA-CCl_4 mixtures up to 1 M DMA at 32°C are also reported. Dramatic differences between NMA and DMA in both the static permittivities and relaxation times (for both pure liquids and their mixtures in CCl_4) are attributed to chain formation through H bonding for the monosubstituted amides. DMA acts as a kind of "chain-terminator" when added to NMA. The difference in behavior between the two liquids disappears in the cases of infrared permittivities and visible n_D^2 values.

c) Microwave and Infrared Dielectric Relaxation of Alkylcarbonates, Chloroform and Their Mixtures at 25°C

Microwave data yielding the complex permittivity $\epsilon^* = \epsilon' - J\epsilon''$, infrared and visible refractive indices, and infrared attenuation coefficients for liquid dimethyl-carbonate [$(CH_3O)_2CO$; abbrev:DMC], chloroform, and their mixtures have been recorded at 25°C. For pure DMC the real part of the complex permittivity ϵ' versus frequency shows two relaxation domains: the microwave frequency range interpreted as the rotational relaxation of the methoxy groups, $-OCH_3$, around the carbonyl moiety, C=O, and a newly discovered relaxation domain at infrared frequencies. The profile of n^2_{IR} (the squared refractive index) versus frequency for pure $CHCl_3$ reveals a new dielectric phenomenon hinted at by literature data obtained at far-IR frequencies. Mixtures of DMC and $CHCl_3$ have a microwave dielectric spectrum that differs markedly from that which would be expected for mole fraction $X_{DMC}=0.50$, if the two components did not interact strongly with each other. The dielectric relaxation frequencies of pure DMC and pure $CHCl_3$ are $f_r=22$ GHz and 27 GHz respectively. When mixed at a composition $X_{DMC}=0.50$, a dielectric relaxation spectrum is produced that can be interpreted by a Cole-Cole distribution with an average relaxation frequency f_r = 17 GHz and a distribution relaxation parameter $\alpha=0.08$ ($0<\alpha<1$ with $\alpha=0$ for a singe Debye relaxation process). This dielectric relaxation is ascribed to the formation of H-bonded complexes arising form interactions of the proton of $CHCl_3$ and the carbonyl moiety of DMC. A similar $X_{DMC}=0.50$ mixture of DMC and CCl_4 does not produce the same dielectric relaxation thus supporting the attribution of the phenomenon to the formation of a hydrogen bonded $CHCl_3$-DMC complex.

d) Femptosecond and Picosecond Molecular Dynamics of Acyclic and Cyclic Carbonate Solutions

Microwave and infrared loss coefficients ϵ'' of the complex permittivity $\epsilon^* = \epsilon' - J\epsilon''$, in the respective frequency ranges 0.46 to 130 GHz and 0.9 to 6 THz (30 to 180 cm^{-1}), have been measured for acyclic dimethylcarbonate (DMC) dissolved in cyclohexane and (for one solution) in benzene, and for cyclic ethylene carbonate (EtC) dissolved in benzene at 25°C. For the DMC solutions in cyclohexane, the spectral profiles are described by the sum of two Debye relaxation processes and by a Powles-Rocard relaxation process retaining the angular velocity or inertial relaxation time τ_{J3}. A fourth resonant process centered at 4.1 THz (~135 cm^{-1}) is described by a Gaussian-Lorentzian product function. For the EtC solutions in benzene, the spectral profiles are described by the sum of two Debye and one Powles-Rocard relaxation process. The solvent benzene, however, contributes to the loss with a process centered around 60 to 70 cm^{-1} as already reported in the literature. A fourth resonant process for EtC in benzene, centered at ~215 cm^{-1}, can be described by a separate Gaussian-Lorentzian product function. The two Debye

processes for both solute carbonates are attributed to molecular rotation around two axes of symmetry of the molecules. The Powles-Rocard process is interpreted as arising from molecular librations. The resonant process for DMC at ~135 cm^{-1} has been assigned to molecular torsion. The resonant process for EtC is ascribed to out-of-plane vibration of the ring or ring puckering also in accord with literature interpretations. An alternate description of the fourth process for DMC in cyclohexane in terms of a second Powles-Rocard process is also offered. Static permittivity data, and sodium doublet refractive index values for the above mixtures at 25°C required to elaborate the data have also been measured.

C) List of all Publications and Technical Reports

Publications

"Infrared and Microwave Dielectric Relaxation of Benzonitrile, Acetonitrile and their Mixtures with Carbontetrachloride at 25°C"
by P. Firman, A. Marchetti, M. Xu, Edward M. Eyring, S. Petrucci
J. Phys. Chem. *1991*, 95, 7055

"Static, Microwave, Infrared and Visible Permittivity Related to Chemical Structure: N-Methylacetamide, N-N-Dimethylacetamide and Their Mixtures in CCl_4 at 32°C"
by P. Firman, Edward M. Eyring, M. Xu, A. Marchetti, S. Petrucci
J. Phys. Chem. *1992*, 96, 41

Technical Reports

1) "Infrared and Microwave Dielectric Relaxation of Benzonitrile, Acetonitrile and Their Mixtures with CCl_4 at 25°C"

2) "Static Microwave, Infrared and Visible Permittivity Related to Chemical Structure: N-Methylacetamide, N-Dimethylacetamide and Their Mixtures in CCl_4 at 32°C"

3) "Microwave and Infrared Dielectric Relaxation of Alkylcarbonate, Chloroform and Their Mixtures at 25°C"

D) List of All Participating Scientific Personnel

1) Prof. Edward M. Eyring, Professor Department of Chemistry, University of Utah, (no financial retribution received by this grant).

2) Meizhen Xu, Research Associate

3) Andrea Marchetti, Post-doctoral fellow

4) Paul Firman, Research Associate

5) Rinku Chandra, High School student, Summer "YES" program participant

6) Sergio Petrucci, Professor

Reports of Inventions

None to date

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