Automation of Dipole Moment Measurements Using Microprocessor Controlled System

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A microprocessor controlled instrument that can be used in physical chemistry research laboratories has been designed and constructed. The intended use is the measurement of the dipole moment and determination of the temperature dependency of the dipole moment for polar substances, especially for macromolecules.

Measurement techniques with conventional dipolmeters require fine adjustments and measurements which seem to be very tedious and time consuming. Provided automation enables very frequent measurements with a step of 1° C and disallows any user-oriented error. The dielectric constant measurement is performed within an accuracy limit of less than ± 0.001. Furthermore, the equipment designed provides the opportunity of processing and evaluating the data obtained with the use of a personal computer.

Introduction

The measurement of dipole moments in solution is a part of many physical chemistry laboratory programs. Determination of the dipole moment plays an important role in the investigation of the molecular structure of a polar substance [1,2] as its measurement is being widely used in the determination of conformation characteristics of macromolecules in solution [3,8].

Conventional measurement techniques require fine adjustments and measurements which seem to be very tedious and time consuming. Therefore measurements can be performed only at a limited number of temperature values [9].

One of the most valuable and powerful advances in the development of measurement and test equipment are the microprocessor controlled test and evaluation systems, often referred to as automatic test equipment (ATE). The task of the microprocessor is the control of the measurement system by providing a proper automation and further processing the measurement data obtained. With the advances in electronics

and computer technology, the demand for microprocessor or computer operated equipment, which can be used in research and development laboratories, is continuously growing[10].

The purpose of this paper is to propose an algorithm for the automation of dipole moment measurements and describe the design of an automatic dipolemeter using a low-cost microprocessor system which also provides the possibility of processing and evaluating the data obtained, by the use of a personal computer.

Method and Instrumentation

Mean square dipole moments per repeat unit of a polymer chain are calculated from an appropriate form of the Guggenheim-Smith equation[11,12],

$$\langle \mu^2 \rangle / X = \frac{27kTM_0}{4\pi.N.(\varepsilon_1+2)^2 d_1} \left[\left(\frac{d\varepsilon}{dW_2} \right)_{W_2 \to 0} - \left(\frac{dn^2}{dW_2} \right)_{W_2 \to 0} \right],$$ (1)

where X is the number of repeat units in the polymer, M_0 is the molar weight of a repeat unit, k is the Boltzmann constant, N is Avogadro's number, T is the absolute temperature, d_1 is the solvent density, ε is the static dielectric constant, n is the refractive index for visible light (546 nm for the increments), W_2 is the weight fraction of the polymer, and the subscript 1 refers to values for pure solvent. Refractive index increment values of polymer solutions are calculated by using the relationships

$$\left(\frac{dn}{dc} \right)_A - \left(\frac{dn}{dc} \right)_B = \frac{n_B - n_A}{\rho_p} \quad \text{and} \quad \left(\frac{dn^2}{dW_2} \right) \cong 2n_1\rho_1 \left(\frac{dn}{dc} \right)$$ (2)

where n_A and n_B denote the refractive indices of the solvents A and B, respectively, and ρ_p is the density of the polymer. Refractive index values of the solvent can be obtained from literature data[13] and used in dipole moment calculations. Detailed procedures are given in Ref[14].

Determination of the dipole moments is based on measurement of the concentration dependence of the dielectric constant $\left(\frac{d\varepsilon}{dW_2} \right)_{W_2 \to 0}$. The dielectric constants of solutions, prepared by dissolving polymer in nonpolar solvent, are measured at different temperatures. The values of $\left(\frac{d\varepsilon}{dW_2} \right)_{W_2 \to 0}$ are obtained by a linear least-square fit using the measured dielectric constant.

Various method's have been described for dielectric constant measurements over a wide frequency range. In this work, the heterodyne beat method has been preferred due to the method's compatibility with microprocessors[15]. Oscillations of two high frequency oscillators are brought to superposition in a mixing section. By means of the variable oscillator, a match in the two frequencies to zero beat is provided. The capacitance values providing this condition, lead to the data for determining the dielectric constant.

Dielectric constants of solutions are measured by observing the change in the capacitance of a cell in which the solution is introduced[16]. Measurement cells are usually constructed as two concentric cylinders which form a capacitor.

The capacitance of an empty cell consisting of two concentric cylinders can be expressed as:

$$C_0 = \frac{2.\pi.\varepsilon_0.h}{\ln \frac{b}{a}}$$ (3)

where

h: the height of the cylinders

b: the radius of the outer cylinder

a: the radius of the inner cylinder

ε_0: the permittivity of vacuum ($8.85\text{x}10^{-12}$ F/m.

   When a solution is introduced into the cell the capacitance changes by the factor ε_r and results in a capacitance value of $C = \varepsilon_r C_0$ where ε_r is the relative permittivity, often called dielectric constant, and is equal to the ratio $\varepsilon_r = \varepsilon/\varepsilon_0$ where ε is the permittivity of the dielectric.

   The cell used in this study was designed to measure capacitance of polar substances with dielectric constant values in the range of 2-3. The cell consists of two concentric cylinders made of brass. The dimensions of the cell were chosen to provide a volume of 20 cc which yields a maximum capacitance value of 20 pF for the above mentioned range of the dielectric constant. It is obvious that a new cell should be designed if a different dielectric constant range is being considered. The heating process has been carried out by the use of a water bath.

Hardware

The block diagram of the measurement equipment is illustrated in Figure 1. The hardware section consists of capacitance and temperature measurement circuits as well as a microprocessor system which provides the automation of the instrument.

   The block diagram of the capacitance measurement section is shown in Figure 2a. The capacitance measurement section of the system consists of six main blocks including two high frequency oscillators, a mixer, a low-pass filter, a wideband amplifier and a Schmitt trigger.

   The variable high frequency oscillator is the most critical part of the system, since the accuracy of the measurements depends almost only on this circuit. This oscillator yields an output frequency of f_v ranging from 1.1MHz to 1.6MHz depending on the cell capacitance and hence on the dielectric constant to be determined. The relative variation in oscillation frequency caused by the change in dieletric constant can be calculated as

$$\frac{\Delta f}{f} = \frac{1.6MHz - 1.1MHz}{1.1MHz} = 0.3125 \tag{4}$$

   The second high frequency oscillator generates a signal with a constant frequency of $f_c = 1MHz$ which is to be mixed with the output signal of the first oscillator. The mixing procedure provides a relatively wider frequency variation range at lower frequencies ranging from 100kHz to 600 kHz so that the relative variation in frequency is increased from 0.3125 to 0.83, which is more suitable for the microprocessor to process.

   Obviously the mixer is used to mix the output signals of the two high frequency oscillators for the heterodyne beat operation. The modulation of two sinusoidal signals concludes with a frequency translation in the spectrum. This frequency translation is performed by applying signals with two different frequencies to the two inputs of the mixer, which yields sum $(f_v + f_c)$ and difference $(f_v - f_c)$ frequency components at the output. The low-pass filter has been used to pick out the difference frequency component $(f_v - f_c)$ which is expected to change in the frequency range of 100-600 kHz. A second order OTA-C configuration has been used for the realization of the low-pass filter to obtain a wideband structure[17]. The Schmitt trigger translates the output signal to a proper form suitable for processing by the microprocessor system.

   The temperature measurement circuit, shown in Figure 2b, provides temperature-frequency conversion for microprocessor system and consists of three blocks including a temperature voltage converter, an amplifier and a voltage-controlled oscillator. The linearity of this section has been provided for a temperature range
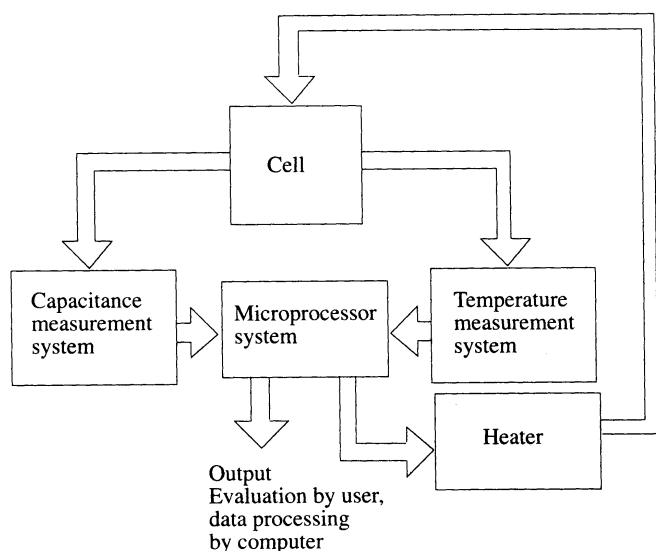
of 15°C-115°C^{15}.

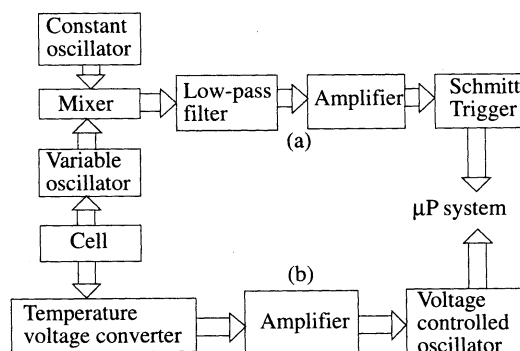**Figure 1.** Block diagram of measurement equipment

Figure 2. Block diagrams of capacitance and temperature measurement sections, a) capacitance measurement, b) temperature measurement

The flow graph of the derived algorithm is illustrated in Figure 3. Here, the lower and the upper boundaries of the temperature range are denoted with T_1 and T_2, respectively. First, the instrument requires the limits of the temperature range $(T_1 \leq T \leq T_2)$ and the difference ΔT between two measurement temperatures to be given through the keyboard. The system then switches the heater on, performs temperature measurements continuously, displays a four digit number proportional to the capacitance of the measurement cell and stores these values at every desired temperature value.

If the upper boundary T_2 is reached, the system switches off the heater. The stored measurement values are ready for evaluation by the user for further data processing by computer.

Experimental results and discussion

The determination of the dielectric constant is carried out as follows:

1. First, measurements are performed for the empty cell at temperatures desired. Then the measurement is repeated for the cases where

2. the cell is filled with a standard solvent, also called calibration liquid, of which the dielectric constant is known,

3. the cell is filled with the solution of which the dielectric constant is unknown and the dipole moment is to be determined.

The instrument gives the results of a capacitance measurement as a four digit number (S). The dielectric constant to be determined can be extracted from measurement data using the following equation:

$$\varepsilon_X = \frac{S_X - S_A}{S_S - S_A}(\varepsilon_S - 1) + 1, \tag{5}$$

where ε_S is the dielectric constant of the calibration solvent, S_A, S_S and S_X denote values obtained for the empty cell and for the cases where the cell is filled with the calibration solvent and with the polymer solution, respectively.
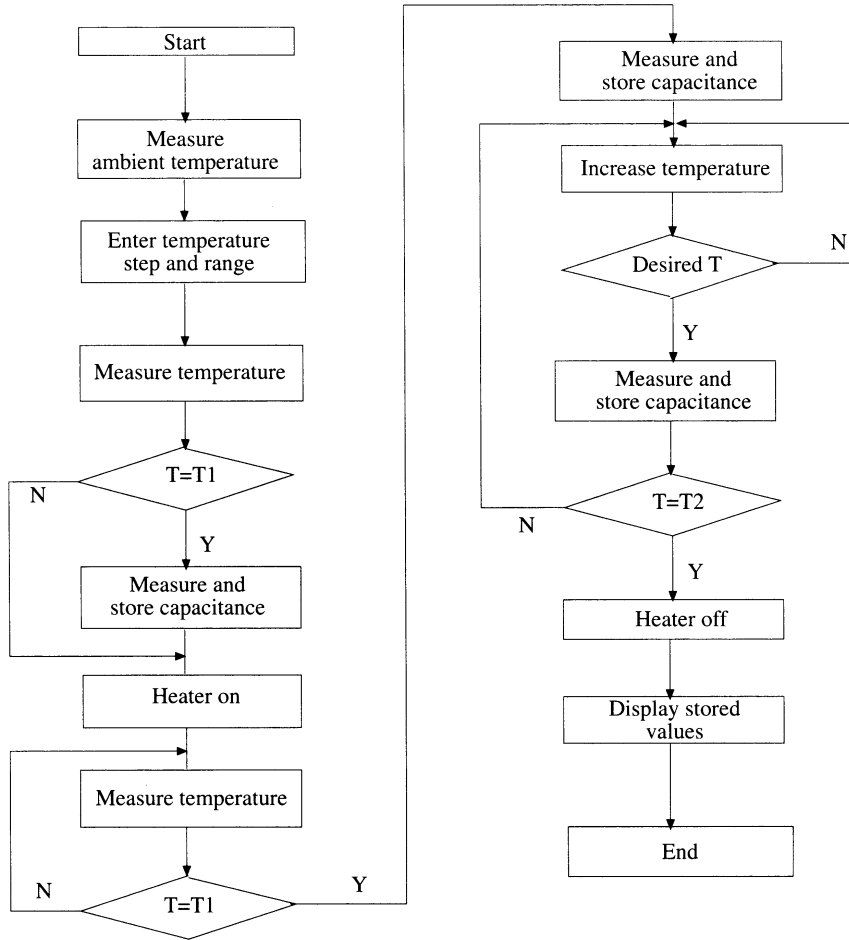
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Figure 3. Flow graph of the algorithm

To determine the dipole moment of the corresponding polar substance the dielectric constant measurements should be carried out at least for three different concentrations at each measurement temperature. The accuracy of the dielectric constant measurements is within ± 0.001. For $\varepsilon_X = 2$ the difference frequency at the output of the low-pass filter is $f_v - f_c = 600$ KHz. This value decreases to $f_v - f_c = 100$ kHz when the dielectric constant is increased to $\varepsilon_X = 3$. A change of $\Delta\varepsilon_X = 1$ in the dielectric constant yields a change of $\Delta f = 500$ kHz in the output frequency. Depending on the frequency stability of the variable oscillator designed, this frequency can be determined with an accuracy of 0.1 kHz which results in N=5000 different frequency values for the corresponding range. Hence, the accuracy of the dielectric constant measurements can be expressed as

$$A = \frac{\Delta\varepsilon_X}{N} = \frac{1}{5000} = 2x10^{-4}, \tag{6}$$

which is less than ± 0.001. The dipole moment is calculated easily by substituting the measurement data obtained in Eq. 1^{14}.

In this work, benzene has been chosen as the standard solvent, which was purified according to standard procedures[18]. The dielectric constant of benzene is given as $\varepsilon_r = 2.274$ for $25^\circ\mathrm{C}^{19}$. The temperature dependency of the dielectric constant of benzene is given by the expression below:

$$\varepsilon' = \varepsilon - a \cdot (t' - t), \tag{7}$$

where t and t' are any two temperature which correspond to ε and ε', respectively. a is a constant related

with a value of 0.002 for benzene [19].

As stated in Section-2, the cell used was designed to measure the capacitance of polar substance with dielectric constant values ranging from 2 to 3. In this study, Poly(ethyl methacrylate) (PEMA) and Poly(methyl methacrylate) (PMMA) were chosen as test materials.

Table 1 shows the dielectric constant of PEMA in benzene solution.

Table 1. Measured values of PEMA in benzene solution at temperatures between $25 - 55°$ C.

T[°C]	S_A	S_S	S_X	ε_X	ε'_X
25	9000	4452	4398	2.291	2.291
26	9000	4449	4386	2.289	
27	9000	4446	4382	2.287	
28	8995	4444	4378	2.286	
29	8997	4440	4375	2.284	
30	8989	4435	4374	2.380	
31	8989	4432	4371	2.278	
32	8980	4428	4367	2.276	
33	8982	4426	4365	2.274	
34	8978	4421	4361	2.272	
35	8978	4416	4358	2.270	2.271
36	8977	4412	4355	2.267	
37	8979	4407	4350	2.265	
38	8981	4404	4346	2.263	
39	8980	4400	4344	2.261	
40	8978	4398	4341	2.259	
41	8978	4396	4336	2.258	
42	8976	4392	4331	2.256	
43	8975	4387	4329	2.253	
44	8966	4383	4326	2.251	
45	8961	4380	4323	2.249	2.250
46	8965	4376	4319	2.247	
47	8966	4372	4315	2.245	
48	8967	4367	4310	2.243	
49	8962	4364	4305	2.241	
50	8965	4362	4301	2.240	
51	8968	4357	4298	2.237	
52	8971	4354	4294	2.235	
53	8974	4351	4290	2.234	
54	8975	4348	4286	2.232	
55	8976	4346	4282	2.230	2.230

S_A: The value displayed for the empty cell
S_S: The value displayed for the standard solution
S_X: The value displayed for the unknown solution
ε_X: The dielectric constant measured
ε'_X: Previously measured dielectric constant [14]

Atactic poly(ethyl methacrylate) used in this work was prepared by free radical polymerization of pure monomer. Details of the experimental procedure were given in Ref. [14]. Table 2 presents measured dielectric increments and calculated mean-square dipole moments per repeat unit for atactic PMMA in benzene for the temperature range of $25°$ C-$55°$ C. Results of earlier works obtained by using a conventional dipolemeter have also been given in the tables in order to compare the accuracy of the instrument designed with known measurement data [14,6]. It can be observed from Table 1 and 2 that the measurement data obtained from the instrument designed is in good agreement with the data obtained from the conventional measurement technique.

Table 2. Dielectric constant and dipole moment values of PMMA in benzene solutions

$T[^\circ C]$	ε_{X1}	ε_{X2}	ε_{X3}	ε'_{X1}	ε'_{X2}	ε'_{X3}	$\frac{\langle\mu^2\rangle}{X}[D^2]$	$\frac{\langle\mu^2\rangle'}{X}[D^2]$
25	2.2815	2.2866	2.2920	2.2816	2.2868	2.2921	1.73	1.69
35	2.2619	2.2654	2.2720	2.2613	2.2675	2.2709	1.71	1.68
45	2.2410	2.2442	2.2510	2.2410	2.2477	2.2516	1.78	1.95
55	2.2208	2.2263	2.2307	2.2206	2.2266	2.2303	1.93	1.88

ε_{X1}, ε_{X2}, ε_{X2}: The dielectric constant values measured for PMMA- benzene solutions in this work

ε'_{X1}, ε'_{X2}, ε'_{X2}: Previously measured dielectric constant values measured for PMMA-benzen solutions[14]

$\frac{\langle\mu^2\rangle}{X}$ and $\frac{\langle\mu^2\rangle'}{X}$: mean square dipole moments per repeat unit of the PMMA chain. The superscript ' refers to previously calculated values.

It is obvious from Table 1 that the realized automation enables the user to perform dielectric constant measurements with very frequent temperature steps ($\Delta T = 1^\circ C$). In conventional measurement technique this step was chosen as $10^\circ C$ in order to reduce the number of tedious and time consuming adjustments and measurements. The increased number of measurement data provides the user the possibility of evaluating the results correctly by comparing them with each other and eliminating erroneous values using a further data processing program, which cannot be obtained with conventional techniques where only a limited number of data is available.

Conclusion

In this paper, an algorithm for the automation of dipole moment measurements was suggested, the design and construction of a low-cost microprocessor controlled dipolemeter was described. The provided automation allows very frequent measurements with a step of $1^\circ C$ and disallows any user-oriented error. The dielectric constant measurement is performed within an accuracy limit of less than ± 0.001. Furthermore, the instrument designed provides the opportunity to process and evaluate the information obtained, by the use of a personal computer.

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