

Technical paper

Method and Apparatus for Determination of Relative Permittivity of Solvents

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Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

In this work a modification of an existing coaxial cylindrical capacitor cell is described, that is compatible with a system built recently for precise measuring of temperature dependent data in electrolyte solutions. The method and apparatus, presented in detail in this technical paper, turned out to be a reliable and easy procedure for determination of the relative permittivity of diverse solvents. It will be used further in our laboratory for collecting these data which are indispensable for conductivity studies.

Keywords: Relative permittivity, temperature dependence, solvents, coaxial cylindrical capacitor cell

1. Introduction

The static dielectric constant (ϵ_r) or relative permittivity represents the capacitance of a material relative to that of a vacuum. This information is of great value at designing separation, sample preparation and chromatography techniques in analytical chemistry. Further, accurate values of the temperature dependence of ϵ_r are of scientific interest, since they are required for the application of various theories and for reliable process simulation. For example, the temperature dependence of ϵ_r needs to be known to apply the conductivity equations to the experimental conductivity data or for modelling enthalpies of solution and heat capacities.

However, reliable studies of temperature dependent relative permittivity, $\epsilon_r(T)$, of molecular solvents and their mixtures in the literature are scarce. Most of the available experimental data are often obtained for pure solvents over very limited temperature ranges, but there is a lack of data for $\epsilon_r(T)$, especially of very important and often used mixtures of water and organic solvents.

The experimental methods available to determine ϵ_r over a range of temperatures and even pressures have been summarized recently.¹ From this review it is evident, that accurate measurements of ϵ_r are demanding and extremely

time consuming procedures. From a detailed description of application of a three-lobed re-entrant radio frequency resonator for determination the generalized complex permittivity over the pressure range from 0.1 to 5 MPa at temperatures from 278 to 328 K² can be assumed that this type of measurements can be carried out only in specialized laboratories with skilful staff. It seems that even commercially available capacitors demand some upgrade if they are used in broader temperature and/or pressure range.³⁻⁴

In laboratories of the University of Regensburg a coaxial cylinder capacitor cell designed for high-precision measurements (Fig. 1a) has been developed providing the precise ϵ_r data for the temperatures in the range 223.15 < T/K < 343.15.⁵ Temperature-dependent permittivity measurements on the mixed solvent systems were executed with a low-frequency (1–10 kHz) capacitance bridge (General Radio, oscillator type 1316, detector type 1238 and capacitance bridge type 1621) equipped with a conductance-balancing network and a dielectric cell designed for high-precision measurements immersed in the precision thermostat, filled with the silicon oil. The capacitor is described in detail in the literature.⁶

In the present work a small adaptation of this capacitor developed at University Regensburg and donated to University of Ljubljana is described. By applying this mo-

dification it can be used with a system built for determining the precise temperature-dependent electrical conductivity data of solutions.⁷ Some test measurements were carried out and the comparisons with literature data of ϵ_r are presented.

2. Apparatus⁸

The coaxial cylinder capacitor (Fig. 1a), designed by Barthel et al⁵ has been connected to Agilent Technologies 4284A automatic electronic impedance analyzer and immersed in the precise thermostat bath (thermostat Lauda UB40 and Lauda WK1400 as a cold bath), used for precise electrical conductivity measurements in our laboratory.⁷ The thermostat bath is filled with a monoglycol to enable appropriate heat flow when an external circulation is used and works in the temperature range between 273.15 and 313.15 K .

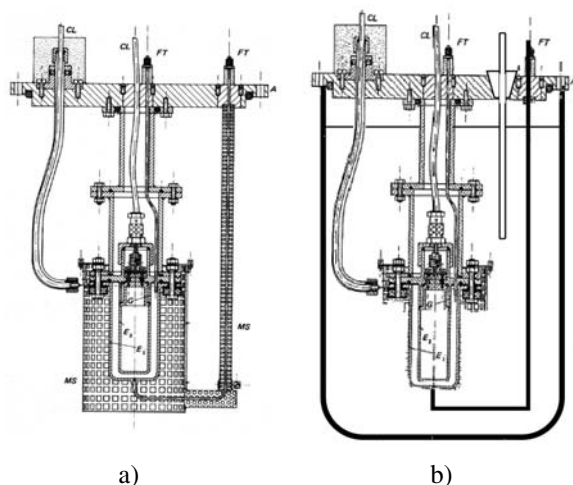


Figure 1. a) Coaxial cylindrical capacitor cell before modification. b) Coaxial cylindrical capacitor, set in the vessel, filled with silicon oil.

Precise capacity measurements have to be carried out in the low permittivity medium at constant stray capacitance. For this reason the capacitor has been set in the fixed stainless steel vessel, filled with a silicon oil (Scan, P3, PK 001 106-T) as it is shown in Fig. 1b. The valve in the lid serves for the pressure levelling due to the temperature, and therefore also pressure, variation in the vessel. At the same time the temperature is controlled by inserting a Pt100 in the silicon oil. This modification enables the application of already built system for conductivity measurements for capacity measurements as well (Fig. 2).

It should also be mentioned that the temperature of the cooler and thermostat should be set appropriately to

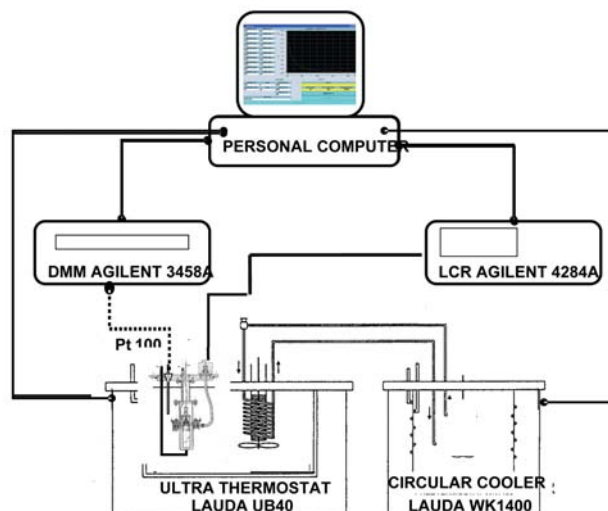


Figure 2. Thermostat assembly with a cold bath (Lauda WK1400), a precise thermostat (Lauda UB40) with an immersed capacitor, attached to an Agilent Technologies 4284A automatic electronic impedance analyzer of highest measuring accuracy. The temperature in the vessel with the capacitor is controlled by Pt 100 (MPMI 1004/300 Merz) attached to an Agilent 3458A Multimeter.

obtain the desired temperature with sufficient accuracy. In general, the temperature of cooler should be about 3 K lower than the set temperature of precise thermostat. So far these values have been obtained by carrying out of some additional measurements of temperatures following the temperature oscillations in the measurement thermostat and vessel with the silicon oil and capacitor. Consequently, the actual temperature is controlled separately by the help of the calibrated Pt 100 resistant thermometer (MPMI 1004/300 Merz), placed into the silicon oil trough the valve in the capacitor's lid (Fig. 1b) and connected with a HP 3458A Multimeter.

The control of the measuring instruments and process is executed by the computer, which gathers measured data (Fig. 3).

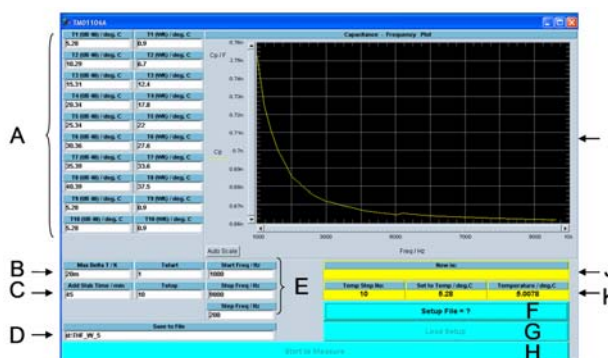


Figure 3. An example of the display with graphical user interface showing the measurement process. For explanation see the text.

The laboratory worker needs only to

- i. select a temperature range (between 273.15 and 323.15 K) (A)
- ii. define the allowed temperature deviation (B) and
- iii. define the time of the temperature stabilization of the sample (C)
- iv. specify the file where the data are stored (D) and
- v. select the desired frequency range and step (E).

All these data can also be written in the “setup file” (F) and confirmed by “load setup” (G). At this point the measurement can be started (H). The cold bath and the measurement thermostat are set at the first temperature value of the program. After reaching the desired temperature with defined precision (B), the program will proceed with thermostating the sample (stabilization time) which is followed by measuring the capacitance in the desired range of the frequencies (usually between 500 and 10000 Hz in steps of 200 or 500 Hz). The measured capacitance values are shown on the display (I) in relation to the frequency. Finally, the temperature in the measurement thermostat is controlled and displayed (K). Then the system is switched to another temperature of the program and the procedure is repeated.

Thus the graphical user interface keeps the experimenter updated on the measurement process status (J) and displays the measured results. The remote control of the entire measurement process is possible either through local area network or through the internet. The results (temperature and the frequency dependent resistance) are saved in a file (D) and available for further analysis.

Basic specifications of the improved measurement system are:

- i. temperature range 273.15 – 313.15 K, repeatability ± 0.005 K, uncertainty ± 0.008 K
- ii. uncertainty in capacitance measurement: $< 0.5\%$.
- iii. measuring frequency range: 20 Hz – 10 kHz.

The entire device and procedure has been patented recently.⁸

However, the temperature range is still limited by the characteristics of the cooler and the thermostat in our system.

3. Testing the Measuring Equipment

3. 1. Theory of Measurement

The relative permittivity, (ϵ_r), indicates the energy value of a material in an electric field. It is represented as a complex quantity and defined as a ratio of the material's dielectric constant (ϵ) to that of a vacuum ($\epsilon_0 = 8.854 \cdot 10^{-12}$ F m⁻¹).

At frequencies (ν) below several hundred MHz, ϵ_r can be deduced from the ratio of two electric impedances: the impedance of the capacitor filled with the fluid under study by the impedance of the same capacitor when it is evacuated. In general, this impedance ratio is a complex

number ϵ^*

$$\epsilon^* = \epsilon' - i\epsilon'' \quad (1)$$

where ϵ' and ϵ'' may be frequency dependent. At any measurement frequency, the real part of the impedance ratio, ϵ' , is the static dielectric constant (relative permittivity). The imaginary part of the impedance ratio (dielectric loss),

$$\epsilon'' = \frac{\sigma}{\omega\epsilon_0} \quad (2)$$

accounts for electrical dissipation within the dielectric fluid, where σ is the conductivity and ω is the angular frequency, $\omega = 2\pi\nu$. ϵ' and $i\epsilon''$ can be calculated from the capacitance C and the electrode dimensions,

$$\epsilon' = \frac{\ell}{S} \cdot \frac{C}{\epsilon_0} \quad \text{and} \quad \epsilon'' = \frac{\ell}{S \cdot R} \cdot \frac{1}{\omega \cdot \epsilon_0} \quad (3)$$

where S is the surface area of the electrodes, ℓ gap between them, and R the equivalent parallel resistance (measured data).

The dielectric constant of a vacuum, ϵ_0 , is calculated from the capacitance of the vacuum, approximately equal to air or argon capacitance (measured data), C_0 ,

$$\epsilon_0 = \frac{\ell}{S} C_0 \quad (4)$$

Therefore, Eq. 1 can be rewritten as

$$\epsilon^* = \frac{C}{C_0} - i \frac{1}{\omega \cdot R \cdot C_0} \quad (5)$$

The measured data (C , C_0) contain the stray capacitance, which is altered by the dielectric constant. It can be eliminated by multiplying the Eq. 5 by the empirical correction coefficient, α ,

$$\epsilon^* = \alpha \left(\frac{C}{C_0} - i \frac{1}{\omega \cdot R \cdot C_0} \right) \quad (6)$$

If C and C_0 are determined by extrapolation to $\nu \rightarrow \infty$, the imaginary part in Eq. (6) is neglected. In this case ϵ^* becomes the value of the static dielectric constant (relative permittivity), denoted by ϵ_r and thus determined as

$$\epsilon_r = \alpha \frac{C}{C_0} \quad (7)$$

The value of α for our (modified) system was empirically determined as

$$\alpha = \frac{0.98082 \cdot C / C_0}{C / C_0 - 0.01918} \quad (8)$$

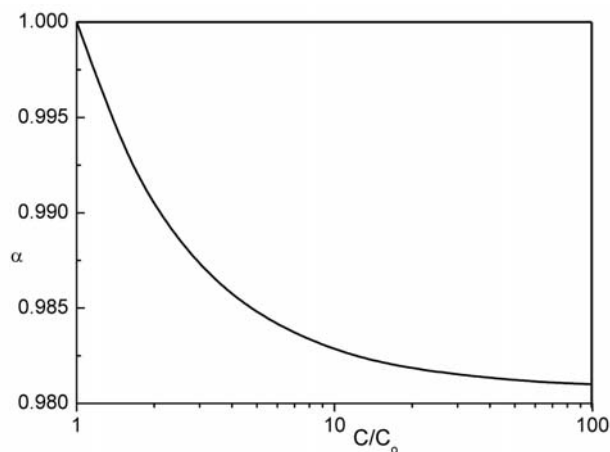


Figure 4. Correction coefficient α as a function of C/C_0 ratio.

The dependence of C/C_0 ratio on correction coefficient α (characteristic of the system) is shown in Fig. 4.

3. 2. Calibration

According to Eqs. 6 and 7 the frequency dependent measurement of capacitance of the capacitor filled with the solvent under investigation and the capacitance of vacuum is necessary. By extrapolation to $\nu \rightarrow \infty$ $C(T)$ and $C_0(T)$ are obtained. Two examples of this extrapolation are shown in Fig. 5.

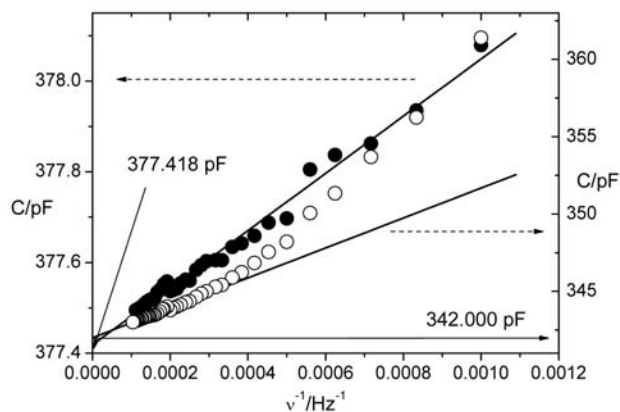


Figure 5. Frequency dependence of measured capacity of the capacitors, filled with methanol (O) and acetonitrile (●) at 298.15 K.

$C_0(T)$ of the capacitor has been obtained by measurements of the capacity of the capacitor, filled with pure argon (99.999%, Messer, Slovenia), C_{Ar} at every temperature T

$$C_0(T) = \frac{C_{Ar}(T,p)}{\varepsilon_{Ar}(T,p)} \quad (9)$$

where the permittivity of argon $\varepsilon_{Ar}(T,p)$ is given by⁹

$$\varepsilon_{Ar}(T,p) = 1 + \frac{p \cdot \text{atm}^{-1}}{1 + 3.411 \cdot 10^{-3} \text{K}^{-1}(T - 293.15 \text{K})} \cdot (\varepsilon^0 - 1) \quad (10)$$

In our case, p is the atmospheric pressure (in atm), measured by a barometer in the laboratory; and $\varepsilon^0 = \varepsilon(293.15 \text{ K}, 1 \text{ atm}) = 1.0005172 \pm 4$.⁹ Obtained temperature dependence of C_0 for the applied capacitor is shown in Fig. 6.

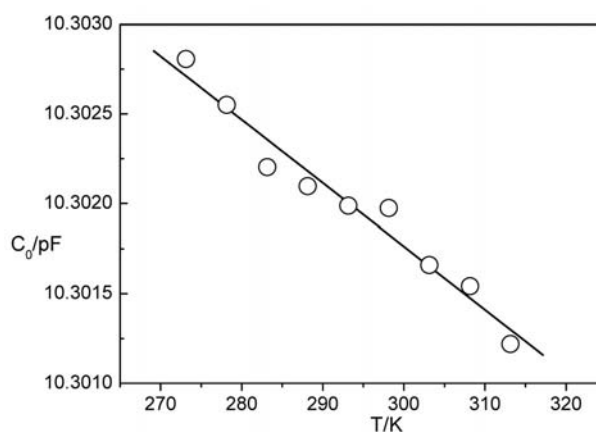


Figure 6. Temperature dependence of the vacuum capacity of the applied cylindrical capacitor; line: linear fit, $C_0/\text{pF} = 10.3123 - 3.53 \cdot 10^{-5} T/\text{K}$.

The calibration with argon is necessary to be carried out before every set of measurements and then the obtained C_0 is to be applied in ε_r evaluations.

3. 3. Results: Determined Data and Comparison with the Literature Data

So far, many test measurements were carried out and the comparison with the (reliable) literature data was made. In these measurements triply distilled water and the solvents of the highest quality were used.

The relative permittivity of the sample at each temperature was calculated from the ratio of the capacitance of the capacitor filled with the sample at this temperature to that of the cell filled with dry argon at the same temperature, by multiplying it by the correction coefficient (Eq. 8),

$$\varepsilon_r(T) = \alpha \frac{C(T)}{C_0(T)} \quad (11)$$

The obtained data of methanol and acetonitrile, obtained in two series of measurements are given in Table 1 together with the literature data. In all evaluations the same value of the correction coefficient in the Eq. (8) was applied.

Table 1. Relative permittivity, ϵ_r , of methanol and acetonitrile as obtained in two sets of measurements and comparison with the literature data.

T/K	ϵ_r					
	methanol			acetonitrile		
	run I	run II	lit. ¹⁰	run I	run II	lit. ¹¹
273.15		37.70	37.92		39.89	40.11
278.15	36.78	36.74	36.78	39.04	39.20	39.24
283.15	35.76	35.65	35.68	38.53	38.34	38.39
288.15	34.70	34.60	34.63	37.74	37.53	37.56
293.15	33.69	33.57	33.61	36.91	36.73	36.76
298.15	32.69	32.58	32.63	36.12	35.95	35.96
303.15	31.75	31.62	31.69	35.35	35.19	35.19
308.15	30.83	30.69	30.78	34.60	34.47	34.43
313.15	29.94	29.80	29.90	33.86	33.74	33.96

These results confirm the assumption that the stray capacity is constant (and not “time dependent”) when setting the capacitor in the “closed” vessel filled with silicon oil.

In Table 2 obtained data for ethanol, acetone, dimethyl sulfoxide (DMSO) and water are listed together with the literature data.

Table 2. Comparison of the measured relative permittivity, ϵ_r , with the literature data for ethanol, acetone, DMSO and water.

T/K	ϵ_r								
	ethanol		acetone		DMSO		water		
	lit ¹²	lit ¹²	lit ¹³	lit ¹³	lit ¹⁴	lit ¹⁴	lit ¹⁵	lit ¹⁶	
278.15	27.62	27.62	22.68	22.74			85.24	85.897	85.89
283.15	26.88	26.76	22.31	22.21			83.98	83.945	83.93
288.15	26.05	25.94	21.76	21.69	47.26	47.15	82.12	82.039	82.24
293.15	25.26	25.13	21.22	21.18	46.64	46.52	80.24	80.176	80.31
298.15	24.46	24.36	20.69	20.69	46.00	45.89	78.37	78.358	78.32
303.15	23.71	23.6	20.19	20.20	45.36	45.24	76.57	76.581	76.39
308.15	22.97	22.86	19.70	19.72	44.71	44.59	74.77	74.846	74.91
313.15	22.24	22.15	19.22	19.25	47.26	47.15	72.99	73.151	

Water mixtures are often of interest for our investigations, because these mixtures may be prepared within a wide range of ϵ_r values. There is a lack of reliable $\epsilon_r(T)$ data in the literature. In Fig. 7 the measured temperature dependent values of ϵ_r for tetrahydrofuran (THF) and water mixtures are shown together with the literature data at 298.15 K.¹⁷ Because the mixture compositions in the literature are not the same, for a better comparison a polynomial fit to the literature data of mixtures was applied, $\epsilon_r(\text{lit}) = 78.556 - 0.629 \cdot w - 4.79 \cdot 10^{-3} \cdot w^2 + 4.002 \cdot 10^{-5} \cdot w^3$, where w is wt. % of THF in the mixture. In the inset of Fig. 6, the difference between our data and the values from this fit in form of relative deviations are shown. Evidently, the deviations are about 1% or even lower. Interestingly, the measured relative permittivity of pure THF at 298.15 K ($\epsilon_r = 7.38$) is in excellent agreement with literature data at the same temperature ($\epsilon_r(\text{lit})=7.39$).

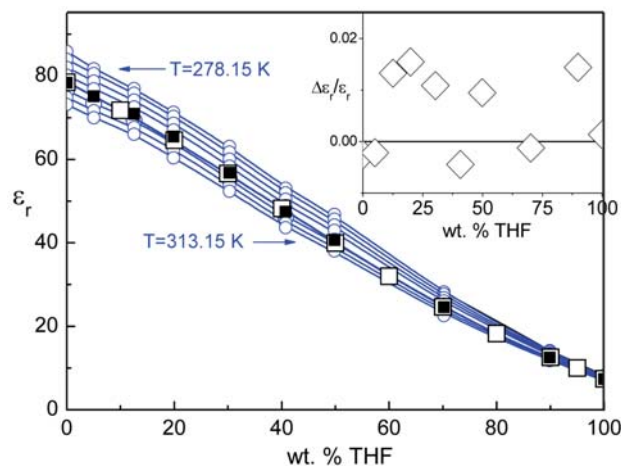


Figure 7. Temperature dependence of relative permittivity, ϵ_r , for mixtures of tetrahydrofuran (THF) and water; (■) our values at 298.15 K, (□) literature values at 298.15 K,¹⁷ (○) our values in the temperature range from 278.15 K to 313.15 K in steps of 5 K. Inset: The relative differences between our measured values and values obtained by polynomial fit of literature data¹⁷ at 298.15 K (see please explanation in the text).

Nevertheless, the observed deviations are distinctly higher than assessed uncertainty in capacitance measurement (< 0.5 %) and can be ascribed to different sources of error (composition of mixtures, fitting procedure...).

It can be concluded, that data of ϵ_r determined in this work and the literature data are in reasonable agreement and thus the described method and apparatus can be treated as reliable procedure for determination of relative permittivity of diverse solvents. It is quite an acquisition for our laboratory and will be advantageously applied for gathering the relative permittivity data needed especially for our conductivity studies in different solvents.

4. Acknowledgement

M. B.-R. would like to express Prof. Dr. Gorazd Vesnaver a deep debt and a profound appreciation of his

friendship, kindness, help, good advice, jovial and pleasant atmosphere in personal relations.

There were some years when she could not write this, but finally she has to admit that he set her the borders, which she has to overcome; he built the mountains, which she has to climb on; he never forgot to warn her that she made a mistake; he always made the entropy positive in an isolated system and therefore the processes made progress ...

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Povzetek

Opisali smo modifikacijo obstoječe kondenzatorske celice – cilindričnega kondenzatorja za določanje temperaturne odvisnosti dielektrične konstante topil. Le ta v kombinaciji z že vpeljanim sistemom za merjenje električne prevodnosti raztopin s pomočjo podpornega programa omogoča avtomatski, računalniško voden postopek merjenja. S tem smo rešili problem napornih in zamudnih načinov določanja dielektrične konstante topil. Opisan postopek pomeni pomembno pridobitev našega laboratorija.