Solvent Mixtures for Studying Electron Transfer Reactions

Master’s Thesis

Submitted for partial fulfillment of the requirements for the degree of

Master of Science

by

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Graz, February 2012

To my family

Statutory Declaration

I declare that I have authored this thesis independently, that I have not used other than the declared sources / resources, and that I have explicitly marked all material which has been quoted either literally or by content from the used sources.

Graz, 29th February 2012

Wankmüller A.

Wankmüller Alexander

Acknowledgements

As there are always people in the background, who helped in various ways during the creation of this work, I want to dedicate this page to them in order to thank them.

I want to thank especially Prof. Dr. Stephan Landgraf, who acted as my supervisor for this thesis. He let me work and think myself, but was always there if a helping hand was needed. He provided enlightening discussions, which broadened my mind, and encouragement. Also the whole institute and I benefitted greatly from his knowledge about electronics and mechanics. I admire his ability to solve problems by logic instead of trying without reflecting, which is quite common unfortunately. I am really glad for having had the opportunity to work with him.

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Last but not least I want to thank everybody who proofread this work for me and my family for their continuous support in every field possible for them.

Thank you!

Abstract

As electron transfer reactions form the basis for many chemical reactions, the knowledge of the mechanism and the dependencies of these reactions are of great interest. In this work solvent mixtures are developed, which should allow clarification of the influence of solvent properties on electron transfer reactions. This is achieved by ternary mixtures that allow only one solvent property to change, while keeping the rest constant. Three different mixtures were sought after, named after the property which changes: A temperature mixture, a viscosity mixture and a dielectric constant mixture.

Different mathematical models are used for calculating the mole fractions of the mixtures. Differential Evolution is used for the fitting of the equations. Only the Dielectric Constant Mixture could be successfully determined. For the rest of the mixtures methods for improvement are included. For every mixture application ideas are discussed. These mixtures are the basis, which allow a systematic research of electron transfer reactions.

Zusammenfassung

Elektrontransferreaktionen bilden die Basis für sehr viele chemische Reaktionen. Deshalb ist das Wissen über den Mechanismus und die Abhängigkeiten dieser Reaktionen von hohem Wert. In dieser Arbeit werden Lösungsmittelgemische hergestellt, um den Einfluss der unterschiedlichen Lösungsmitteleigenschaften auf Elektronentransferreaktionen zu untersuchen. Das wird durch ternäre Gemische erreicht, welche eine Eigenschaft variieren lässt, während der Rest konstant gehalten wird. Drei verschiedene Gemische wurden gesucht, benannt nach der Eigenschaft welche sich ändert: eine Temperaturmischung, eine Viskositätsmischung und eine Dielektrizitätskonstantenmischung

Verschiedene mathematische Modelle werden angewandt in dem Versuch, den Molenbruch der Gemische zu bestimmen. Zum Fitten der Daten an die Gleichung wird Differential Evolution herangezogen. Nur die Dielektrizitätskonstantenmischung konnte erfolgreich gefunden werden. Für die restlichen Mischungen werden Fehler analysiert und Verbesserungsvorschläge angegeben. Für jedes der Gemische sind Anwendungsideen angeführt. Diese Gemische sind die Basis für eine systematische Untersuchung von Elektrontransferreaktionen.

Table of Content

1 Introduction

The motivation for this thesis is the discovery of solvent mixtures, where, by varying the mole fraction, it is possible to change one solvent property while keeping the others constant. The properties in questions for this work are: the dielectric constant, the dynamic viscosity, the refractive index, and the temperature. In the course of this thesis three different mixtures were sought after, named after the property which changes: A temperature mixture, a viscosity mixture, and a dielectric constant mixture. Also different application ideas for electron transfer reactions using these mixtures will be given.

This work is important because with these mixtures systematic analysis of electron transfer reactions are possible. Different dependencies can be eliminated, which simplifies the analysis of results.

A basis for this was already given from a personal communication between Dr. Stephan Landgraf and Sabine Richter, MSc. There have also been a few experiments, giving a general idea of which solvent mixtures can be used.

The temperature mixture uses acetonitrile (AN), butyronitrile (BN), and propylene carbonate (PC). The dielectric constant mixture uses propyl acetate (PA), butyronitrile (BN), and diethyl phthalate (DEP). The viscosity mixture uses dimethyl sulfoxide (DMSO) and glycerol.

In “2 Theory” the different solvent properties are discussed and an explanation for the theoretical calculation of these properties for the mixtures is given.

First during “3 Experiment and Apparatus” the used chemicals are listed. Subsequently the applied apparatus and the configuration of these are described in detail. Sketches are included to further understanding. Afterwards the measurements, of the different mixtures are described and lastly measurements are compared between Graz and Regensburg.

In “4 Results and Discussion” the values for the found mixtures are listed and reasons for the failure of finding the composition for the other mixtures are pointed out. And last but not least application ideas and improvements for the mixtures are discussed in detail during “5 Outlook”.

> *The mind is like a parachute.*
> *It works best when it's open.*
> FRANK ZAPPA

2 Theory

2.1 Viscosity

The viscosity describes the resistance of a fluid against deformation and is the inverse of the fluidity. A low viscosity means a low resistance and an ease of flow. It can be distinguished between the dynamic (η) and the kinematic (ν) viscosity, which are connected by the following formula:

Equation 1 Viscosity

$$\nu = \frac{\eta}{\rho}$$

ρ = density

If the viscosity is mentioned in this thesis, it always refers to the dynamic viscosity (η). The viscosity is highly temperature dependant, which is shown in the following figure. The values have been normalized.

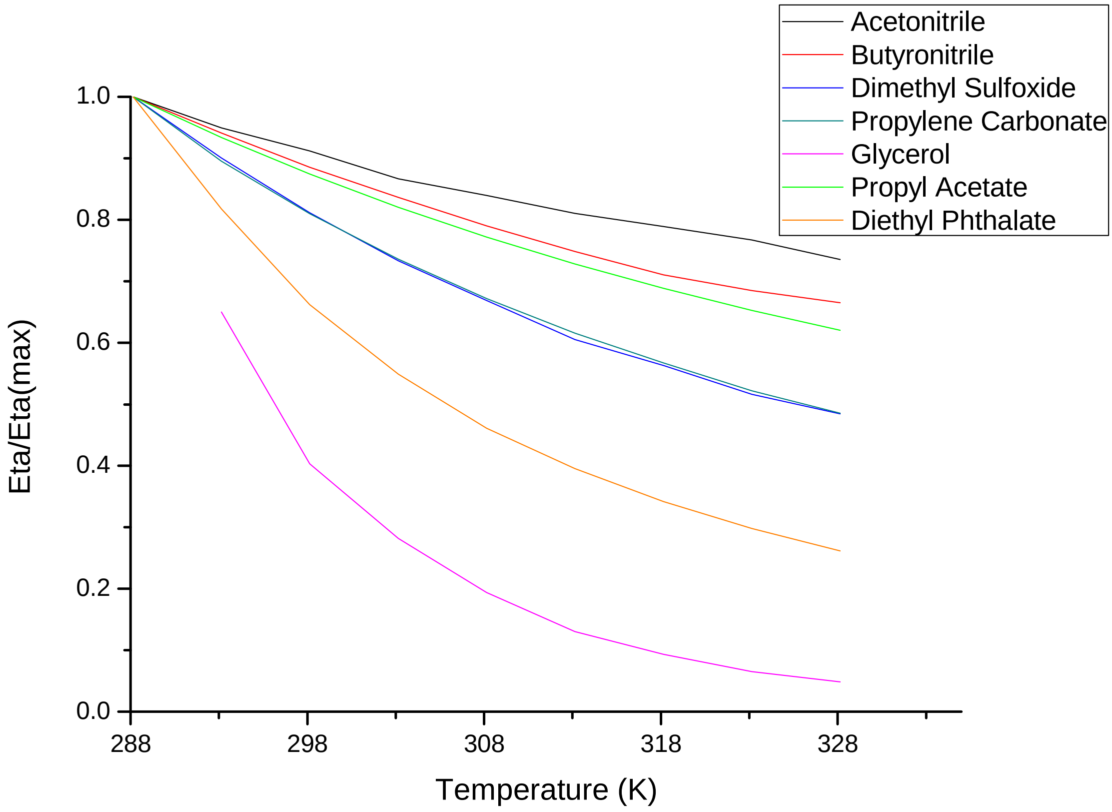

Figure 1 Temperature Dependence Viscosity

The highest viscosity[1] was taken as η_{max}. This was done independently for each solvent in order to increase the readability of the plot. As there was no value available for glycerol at 288,15K, this value has been extrapolated for the normalisation, but has not been depicted. The figure shows that the viscosity can drop to under 10% of its starting value by increasing the temperature by 35K in the most extreme case[2]. Even in the case of acetonitrile, which has the lowest η drop, the viscosity drops to about 80%. A correlation with the temperature is given by the Arrhenius-Andrad relation:

Equation 2 Arrhenius-Andrad Relation

$$\eta = \eta_0 e^{\frac{E_A}{RT}}$$

η_0 = a material constant
E_A = activation energy for the transposition
R = gas constant
T = temperature in Kelvin

This means that a plot, where the natural logarithm of the viscosity is plotted against the inverse of the temperature, results theoretically in a straight line:

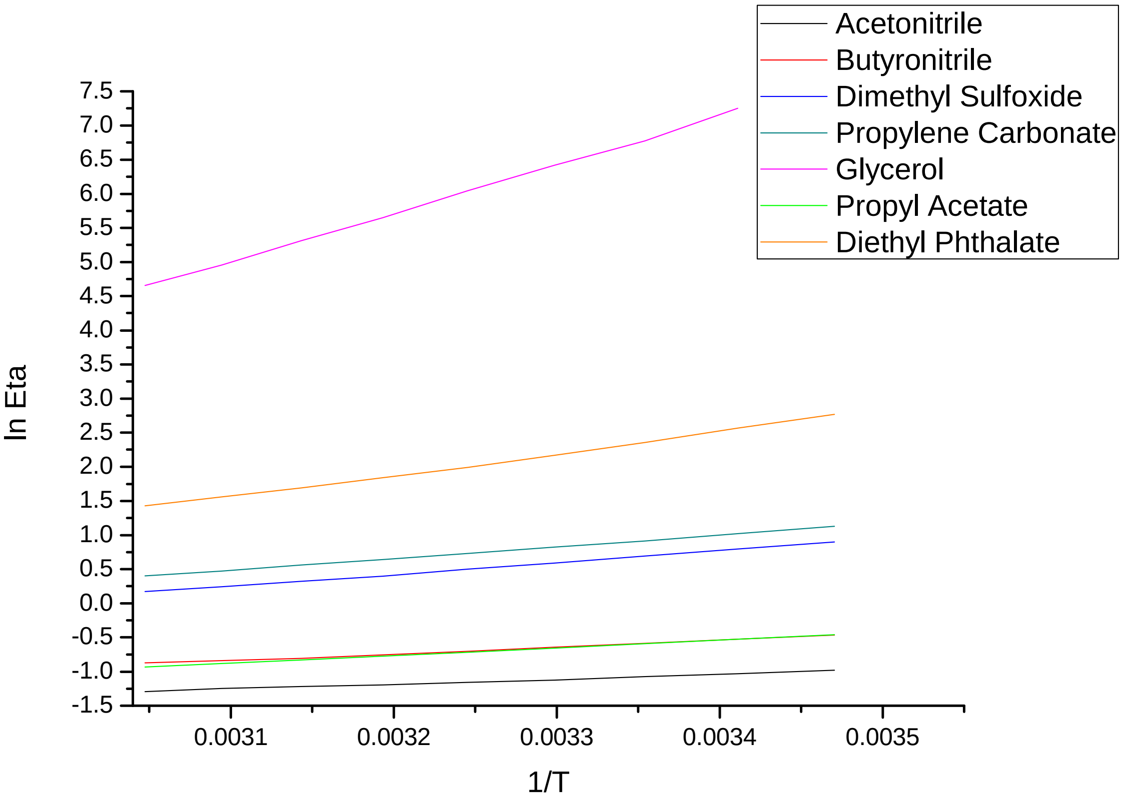

Figure 2 Arrhenius-Andrad Relation

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[1] viscosity at lowest temperature
[2] glycerol

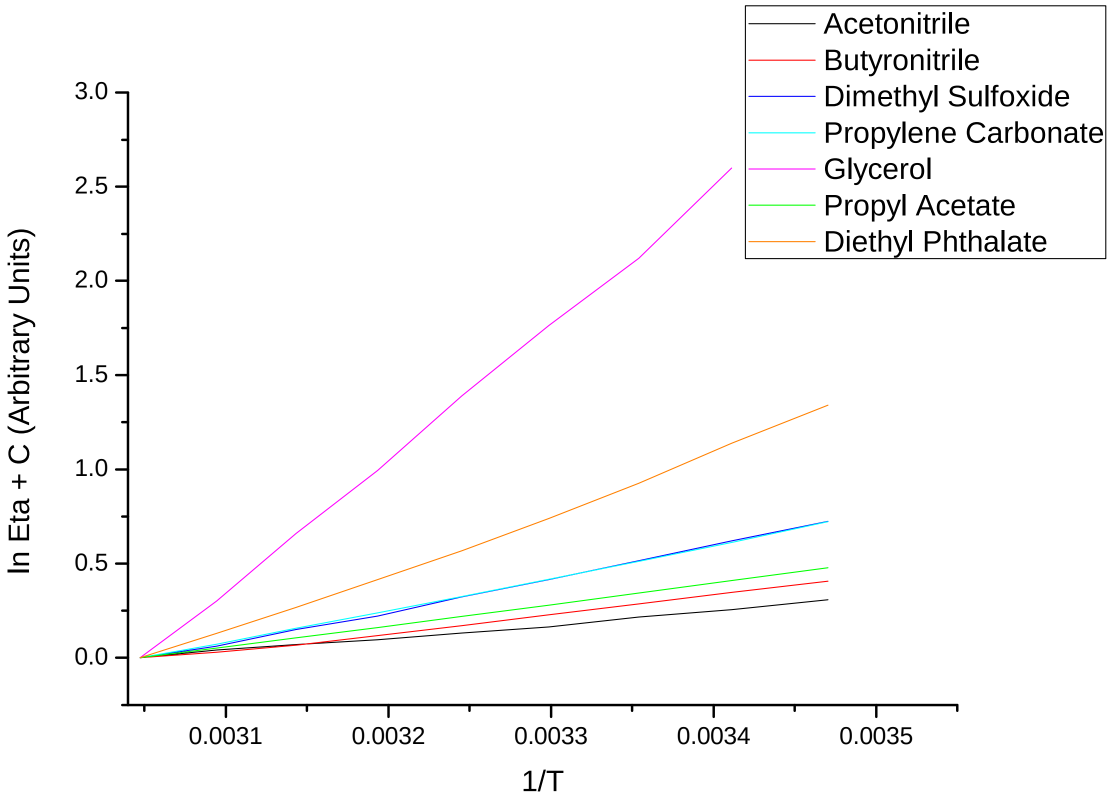


Figure 3 Arrhenius-Andrad Relation Normalized

As expected “Figure 3 Arrhenius-Andrad Relation Normalized” shows straight lines for every solvent when plotting ln(η) vs. the inverse of the temperature.
The viscosity also has a direct relation to the diffusion coefficient:

Equation 3 Diffusion Coefficient

$$D = \frac{k_B T}{6\pi\eta R_0}$$

D = diffusion coefficient
k_B = Boltzmann constant
T = temperature in Kelvin
η = dynamic viscosity
R_0 = hydrodynamic radius of the diffusing particles.

The diffusion coefficient is of major importance, because for most chemical reactions the particles have to meet in order to react with each other. The slower the diffusion of particles is the lower the reaction rate[3].
The temperature dependency of the viscosity makes the measurement of low activation energies difficult. These are calculated using the Arrhenius equation:

Equation 4 Arrhenius Equation

$$\ln k = \ln A - \frac{E_A}{RT}$$

---

[3] assuming diffusion control

k = rate constant
E_A = activation energy
A = pre-exponential factor
R = universal gas constant
T = temperature in Kelvin

In order to get the activation energy the rate constant is measured at different temperatures and the following plot is generated:

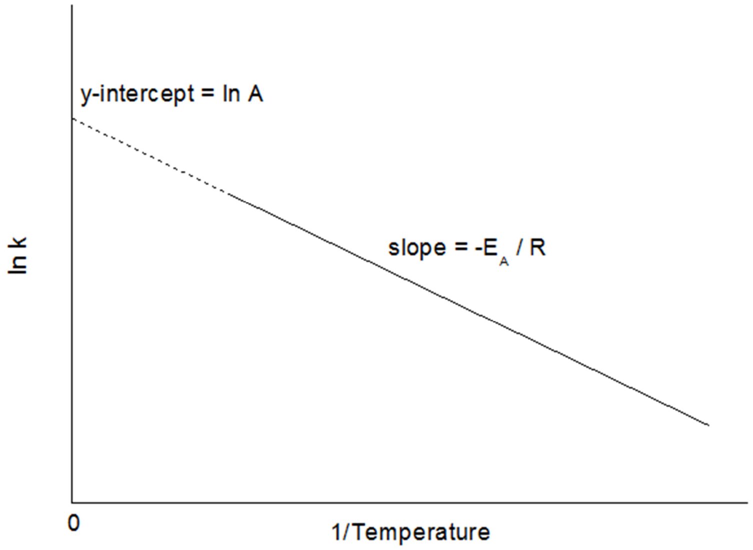


Figure 4 Arrhenius Plot

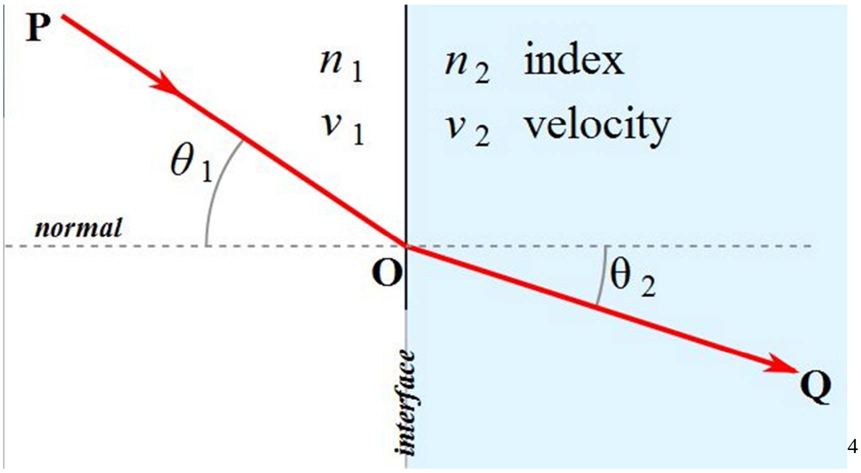
From the slope of the line the activation energy can then be calculated by multiplying with –R. The pre-exponential factor is an empirical factor which includes how often particles collide in the correct orientation for a reaction to occur. Of course the rate of collision between particles is dependent on the diffusion and consequently also on the viscosity, which in turn is highly temperature dependent. That means that A also has a temperature dependency. By plotting in the above mentioned way a temperature independence of A is assumed, which is not the case. Consequently the influence of the temperature on A is completely ignored. The lower the value for the activation energy becomes, the greater the influence of the error produced by this. The measurement can only be correctly done when each measuring point at different temperatures has the same reaction conditions. This can be achieved by a constant viscosity.

2.2 Refractive Index

The refractive index (n_D) describes the change of direction of the propagation of light, when it moves from one medium to another one. It also stands for the ratio of the speed of light in the medium compared to vacuum.
It can be defined by the following formula:

Equation 5 Refractive Index

$$n_D = \frac{\sin\theta_1}{\sin\theta_2}$$



[4]

Figure 5 Refractive Index Definition

The refractive index plays an important role in the Marcus Theory, as it has an influence on the outer reorganisation energy via the Pekar factor.

Equation 6 Marcus Activation Energy

$$\Delta G^* = \frac{\lambda}{4} * \left(1 + \frac{\Delta G_0}{\lambda}\right)^2$$

Equation 7 Reorganization Energy

$$\lambda = \lambda_i + \lambda_o$$

Equation 8 Outer Reorganization Energy

$$\lambda_O = \frac{z^2 e_0^2 N_A}{4\pi\varepsilon_0}\left(\frac{1}{2r_A} + \frac{1}{2r_D} - \frac{1}{d_{AD}}\right)\gamma$$

Equation 9 Pekar Factor

$$\gamma = \left(\frac{1}{n_D^2} - \frac{1}{\varepsilon_r}\right)$$

z = number of charges
e_0 = elementary charge
N_A = Avogadro constant
ε_0 = static dielectric constant of vacuum
ε_r = dielectric constant of solvent
r_A = radius of the electron acceptor
r_D = radius of the electron donor
d_{AD} = reaction distance between the electron acceptor and donor
ΔG^* = activation energy
$-\Delta G_0$ = driving force

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[4] http://en.wikipedia.org/wiki/Refractive_index

In “Equation 9 Pekar Factor” it is assumed that ε_∞, measured at infinite high frequency, is about the same as the square of the refractive index. The original definition includes ε_∞, but n_D^2 is the more commonly used form. This means the refractive index has an impact on the reaction rate, because the latter is dependent on the activation energy[5], which in turn depends on the outer reorganisation energy according to Marcus.

The refractive index is mostly dependent on the composition of the mixture, while the temperature has almost no influence on it. The following plot shows the temperature dependence of the refractive index of the pure solvents. The values have been normalized.

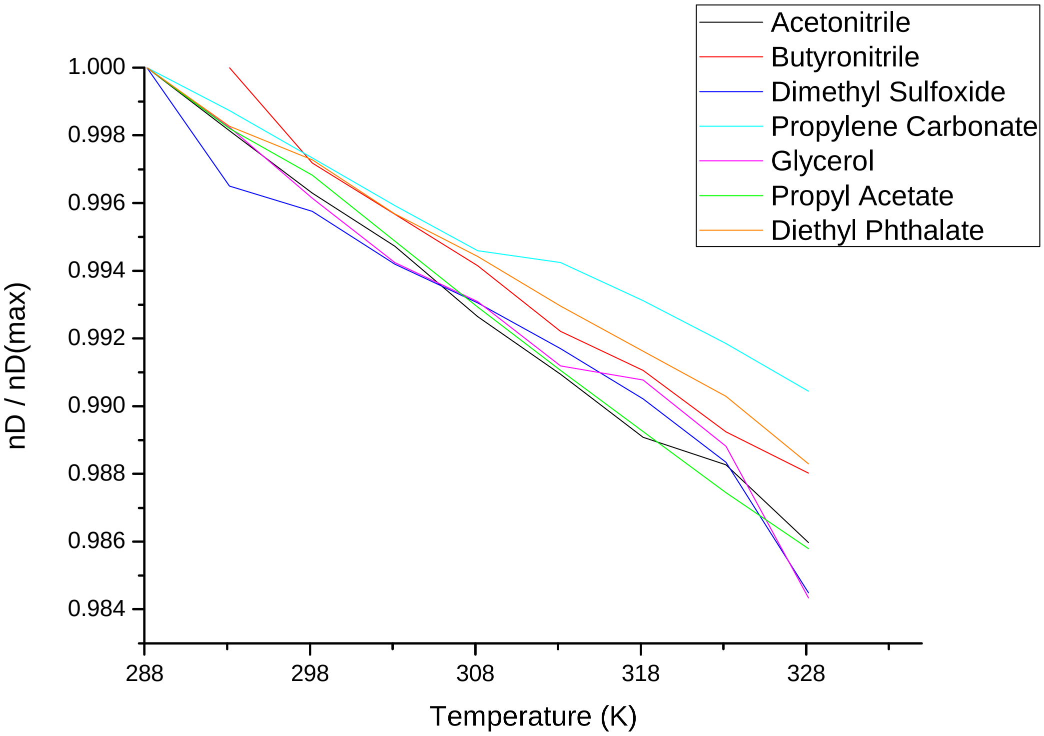

Figure 6 Temperature Dependence Refractive Index

As can be seen in the plot the refractive index only drops about 1.5% when the temperature is increased by 40K. This is due to the change in density, caused by volume expansion at higher temperatures. The variations from the lines in the plot are experimental reading errors.

Although this temperature independency seems favourable at first, it complicates things when taking the other solvent properties into account. In order to counter a high change of the other properties, caused by the temperature, the mole fractions are adjusted. As the refractive index scales almost linearly with the composition without significant temperature influence, the changes in the mole fraction for adjustment cause the refractive index to deviate. As this is counterproductive only the dielectric constant and the dynamic viscosity were included in the calculations. The refractive index is not ignored, because the pure solvents chosen for the mixtures have similar refractive indices, it can be kept in a reasonable range without great effort.

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[5] see Equation 4 Arrhenius Equation

2.3 Dielectric Constant

The dielectric constant (ε or ε_r) describes the permeability of a material to electromagnetic fields in relation to the permeability of vacuum to electromagnetic fields. That means, when the medium is exposed to an electric field, it adjusts itself according to the electric field vector. This polarisation can have different reasons. For example the whole molecule is a dipole and turns to adjust to the field vector. Or a dipole is induced in the molecule according to the field vector. Of course the first needs more time to happen as a rotation of the molecule must occur, while for the latter only the charge distribution in the molecule has to adjust.

If the medium is now exposed to an alternating field instead of an unidirectional field, the medium adjusts itself anew for every alternation. If the alternation is too fast for the rotation to happen[6] this part of the dielectric constant contribution is damped and finally vanishes. This of course means that the dielectric constant is frequency dependent.

In order to describe this ε is seen as complex-valued:

Equation 10 Complex Dielectric Constant

$$\varepsilon = \varepsilon' + i\varepsilon''$$

ε = dielectric constant
ε' = real part of dielectric constant
ε'' = imaginary part of dielectric constant

The imaginary part describes the omitted parts of the dielectric constant, while the real part is the still observable part at the used frequency.

As there can be many understanding with different notations for the dielectric constant, the notations used in this thesis will be explained in detail.

Dielectric constant is the old, but still commonly used terminus. The official term would be permittivity. This has been changed, because ε is no constant. As most people still refer to the dielectric constant, this expression is also used in this thesis. ε or ε_r in this thesis always refer to the relative dielectric constant of the solvent measured at infinite low frequency.[7] ε_0 refers to the dielectric constant of vacuum also measured at infinite low frequency, always refered to as static dielectric constant in this thesis. ε_∞ refers to the dielectric constant of the solvent measured at infinite high frequency.

The dielectric constant is also included in the Pekar factor like the refractive index, and plays the same role in that context.

Additionally the dielectric constant is included in the Coulombic work term, which is included in the equation for the free energy of the electron transfer.

Equation 11 Coulombic Work Term

$$\omega = \frac{(z_{D^+} z_{A^-} - z_D z_A) e_0^2}{4\pi\varepsilon_0\varepsilon_r d_{DA}}$$

Equation 12 Weller Equation

$$\Delta G_{ET} = nF\left(E_{ox}(D^+/D) - E_{red}(A/A^-)\right) - \omega - E(S \to S_0)$$

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[6] Meaning while the molecule is turning the electric field already changes again before the molecule has adjusted itself to the old field vector.

[7] This means without dielectric loss

ω = Coulombic work term
z_i = number of charges of i
e_0 = elementary charge
d_{DA} = distance between the electron acceptor and donor
ε_0 = static dielectric constant
ΔG_{ET} = free energy of the electron transfer
n = number of electrons transferred
F = Faraday constant
$E_{ox/red}$ = potential of the oxidation/reduction of the species in brackets
$E(S \rightarrow S_0)$ = energy needed for the excitation

Coulomb terms always describe a force, or effects of this force, caused by charges. In this case the Coulomb work term describes the energy that results from this force. It is included in the Weller equation, because after the electron transfer, two differently charged species are created, which are then attracted to each other and result in a release of energy. Of course the contrary can also happen. In either case the free energy is influenced by it and the term has to be included. The only exception would be a self-exchange reaction, where the charge of the particles is the same before and after the electron transfer. For example:

$Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$

In this case $z_{D^+} z_{A^-} - z_D z_A$ would amount to zero.
Of course the redox potentials of the species are also dependent on the dielectric constant. As a consequence the dielectric constant has three points of influence on the reaction rate. The outer reorganisation energy, the redox potentials and the driving force[8].
The capacity of a capacitor is dependent on the dielectric constant. The simplest form of a capacitor are two parallel plates in a defined distance to each other. Depending on the dielectric constant of the medium filling the space between the two plates the capacity changes according to the following formula:

Equation 13 Capacity

$$C = \varepsilon_0 \varepsilon_r * \frac{A}{D}$$

C = capacity
ε_0 = static dielectric constant
ε_r = relative dielectric constant
A = area of the plate
D = distance between the plates

Depending on the shape of the capacitor the A/D term changes. This correlation was used for the dielectric constant measurements described later on.
For binary mixtures the behaviour of the dielectric constant at constant temperature is roughly the same. The two points which stand for the pure solvents are connected by a curve. The strength and direction of the curvature can vary depending on the solvents[9]. It can also happen that the bulge is not in the middle but shifted in the direction of one of the pure solvents[10]. If

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[8] free energy of the electron transfer
[9] Figure 7 DMSO-Propanol and Figure 8 Acetonitrile-Propanol
[10] Figure 9 Acetonitrile-Methanol

that is the case it can happen that the dielectric constant of the mixture exceeds the dielectric constant of the pure solvents. If the temperature is changed the curve is translated up- or downwards.[11]

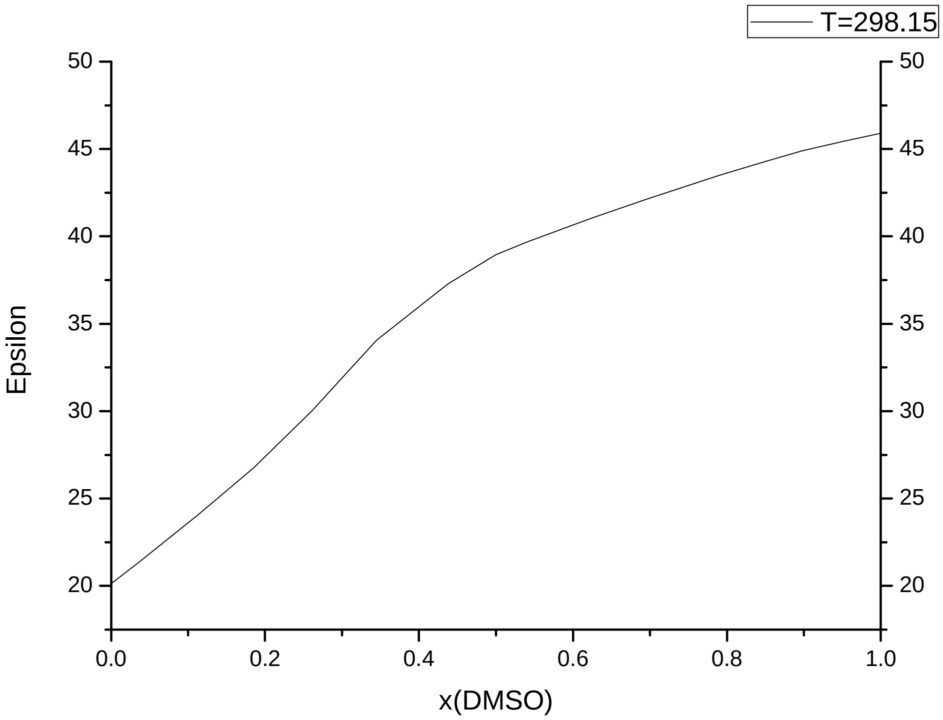

Figure 7 DMSO-Propanol

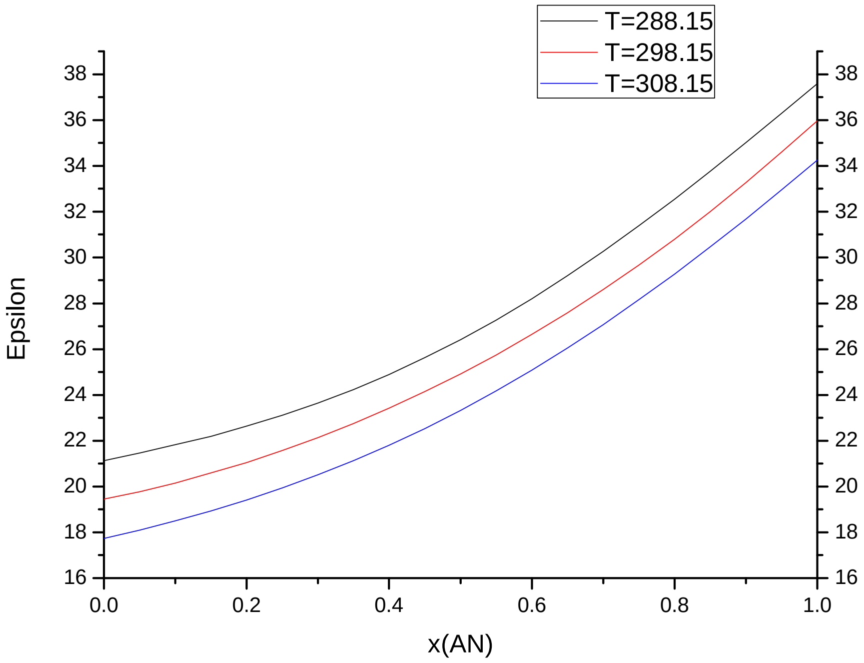

Figure 8 Acetonitrile-Propanol

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[11] As shown in Figure 8 Acetonitrile-Propanol

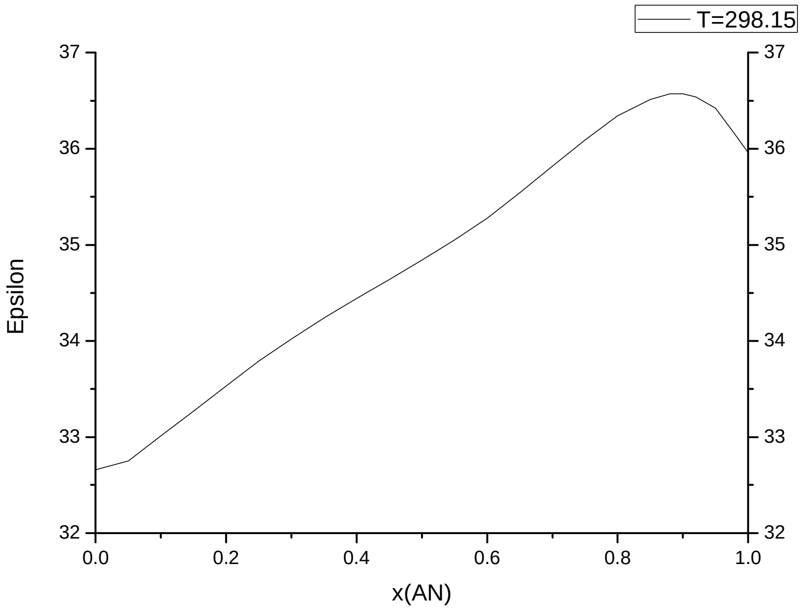

Figure 9 Acetonitrile-Methanol

The values of these plots have been taken from (1).
For ternary mixtures it was not possible to ascertain this kind of rule. It seems that if the dielectric constant is plotted against two mole fractions at constant temperature, the resulting graph is somewhat like an undulating surface. This is only a rough guess, because more data points are necessary for a more accurate description.
Also the dielectric constant is a function of temperature. The following figure shows this. The values have been normalized.

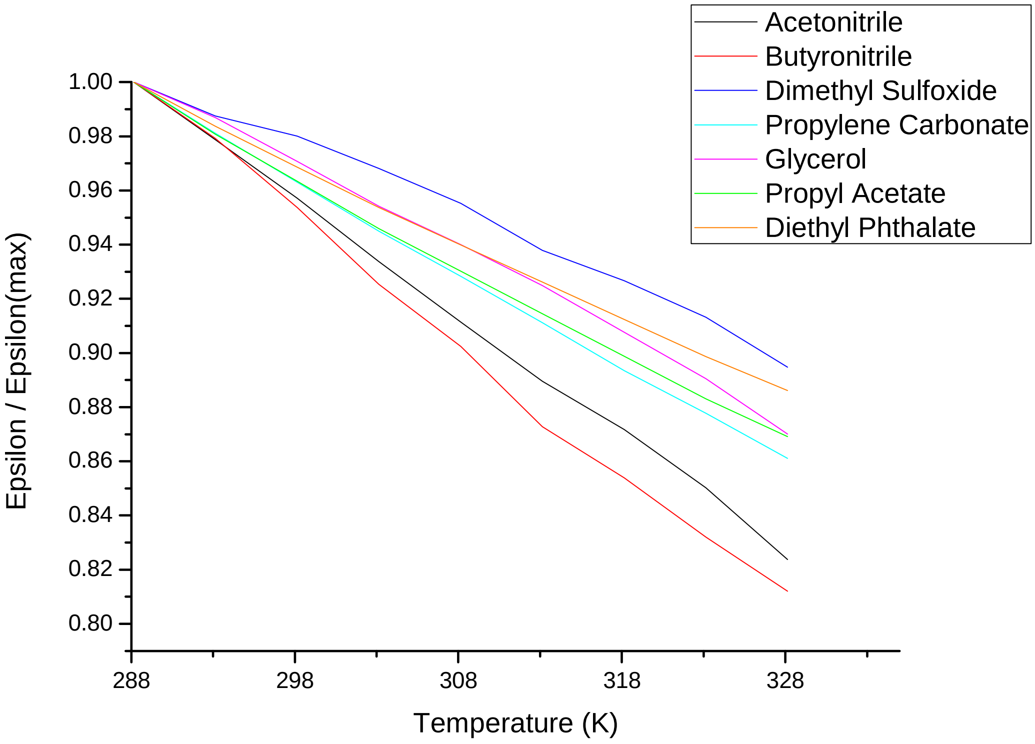

Figure 10 Temperature Dependence Dielectric Constant

Compared to the viscosity, the influence of the temperature on the dielectric constant is much lower. Where at “Figure 1 Temperature Dependence Viscosity” acetonitrile had the smallest drop to ~80%, here the biggest drop is to about 82% for butyronitrile.

The temperature dependence of the dielectric constant goes with 1/T. This can be deduced from the Clausius-Mossotti relation:

Equation 14 Clausius-Mossotti Relation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_A \rho \alpha}{3 M \varepsilon_0}$$

With α as:

Equation 15 Molecular Polarizability

$$\alpha = \frac{\mu^2}{3kT}$$

N_A = Avogadro constant
ρ = density
α = molecular polarizability
M = molar mass of the substance
ε_0 = static dielectric constant
μ = dipole moment
k = Boltzmann constant
T = temperature in Kelvin

The following figure shows the plotting of the dielectric constant against 1/T:

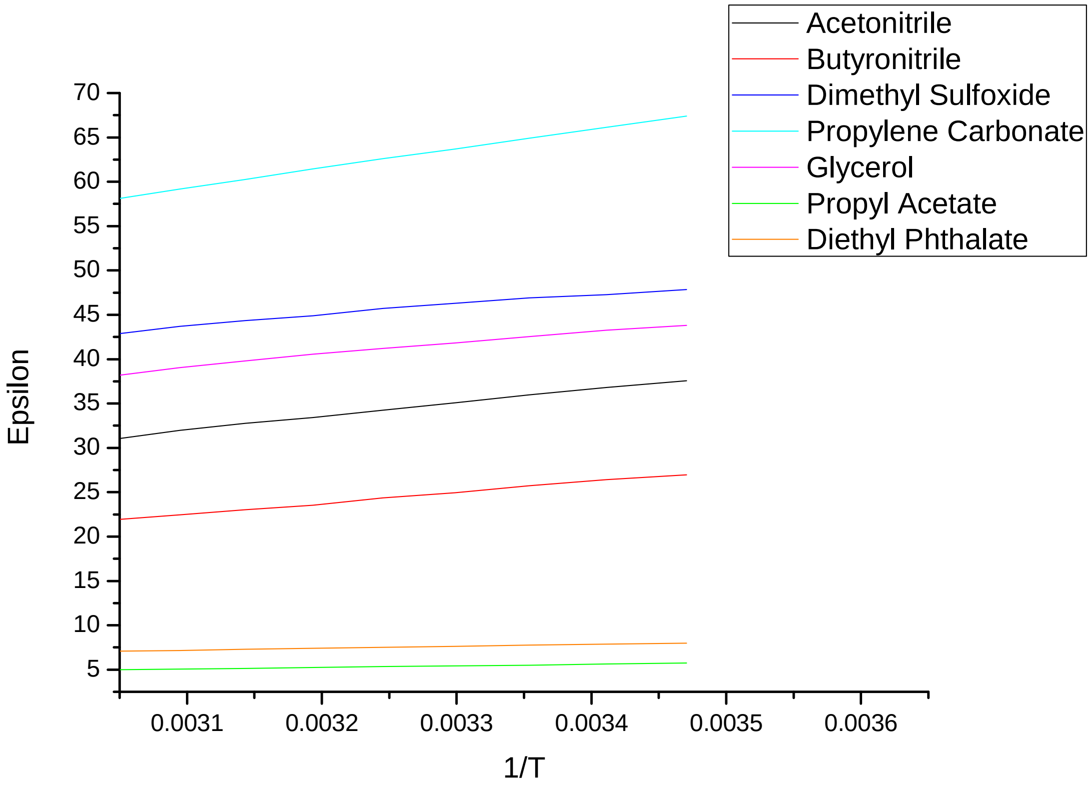

Figure 11 Simplified Clausius-Mossotti Relation

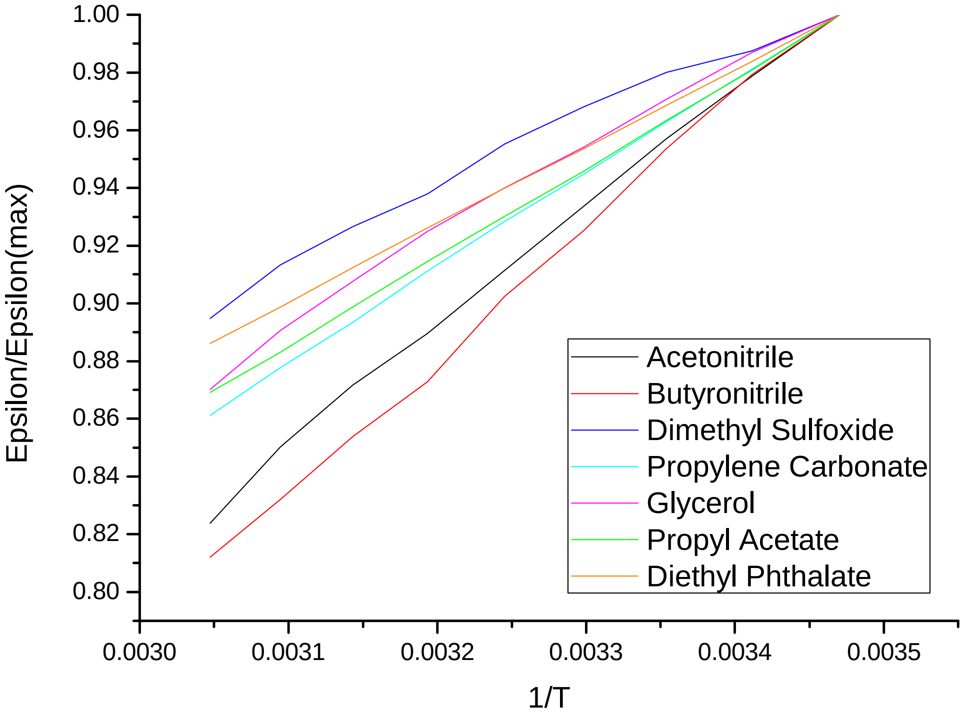

Figure 12 Simplified Clausius-Mossotti Relation normalized

The plot generates nearly straight lines.

2.4 Calculation

Different models were used to calculate the solvent properties based on data of the pure solvents and on data of the ternary mixture. Most models need the value of the pure solvent as a basis for calculation. If they were available the values were taken from (1). Values in the temperature range of 15°C to 55°C which were not present were measured.
The following table shows the values for each solvent at the corresponding temperature:

Table 1 Base Values Pure Solvents

	ε			η [cP]			n_D		
	AN	BN	PC	AN	BN	PC	AN	BN	PC
288.15	37.58	27.01	67.34	0.3751	0.6278	3.0011	1.3475	1.3878	1.4231
293.15	36.76	26.30	66.14	0.3565	0.5915	2.6834	1.3450	1.3850	1.4207
298.15	35.94	25.61	64.95	0.3404	0.5569	2.4108	1.3425	1.3824	1.4188
303.15	35.12	24.94	63.77	0.3264	0.5247	2.1775	1.3401	1.3798	1.4172
308.15	34.30	24.28	62.60	0.3143	0.4953	1.9774	1.3377	1.3774	1.4157
313.15	33.49	23.65	61.45	0.3040	0.4693	1.8046	1.3354	1.3751	1.4143
318.15	32.67	23.03	60.30	0.2953	0.4473	1.6532	1.3332	1.3730	1.4128
323.15	31.86	22.43	59.17	0.2879	0.4299	1.5172	1.3310	1.3710	1.4112
328.15	31.04	21.85	58.05	0.2816	0.4176	1.3908	1.3289	1.3691	1.4093

The model with the best results was taken from (2). This model used the following formulas:

Equation 16 Calculation Dielectric Constant

$$\ln \varepsilon_{m,T} = x_1 \ln \varepsilon_{1,T} + x_2 \ln \varepsilon_{2,T} + x_3 \ln \varepsilon_{3,T} + x_1 x_2 \sum_{j=0}^{2} \left[\frac{A_j (x_1 - x_2)^j}{T}\right] + \\ + x_1 x_3 \sum_{j=0}^{2} \left[\frac{B_j (x_1 - x_3)^j}{T}\right] + x_2 x_3 \sum_{j=0}^{2} \left[\frac{C_j (x_2 - x_3)^j}{T}\right] + x_1 x_2 x_3 \sum_{j=0}^{2} \left[\frac{D_j (x_1 - x_2 - x_3)^j}{T}\right]$$

Equation 17 Calculation Viscosity

$$\ln \eta_{m,T} = x_1 \ln \eta_{1,T} + x_2 \ln \eta_{2,T} + x_3 \ln \eta_{3,T} + x_1 x_2 \sum_{j=0}^{3} \left[\frac{A_j (x_1 - x_2)^j}{T}\right] + \\ + x_1 x_3 \sum_{j=0}^{3} \left[\frac{B_j (x_1 - x_3)^j}{T}\right] + x_2 x_3 \sum_{j=0}^{3} \left[\frac{C_j (x_2 - x_3)^j}{T}\right] + x_1 x_2 x_3 \sum_{j=0}^{3} \left[\frac{D_j (x_1 - x_2 - x_3)^j}{T}\right]$$

x_i = mole fraction of species i
$A_j/B_j/C_j/D_j$ = empirical parameters
T = temperature in Kelvin
$\varepsilon_{m,T}$ = dielectric constant of the mixture at temperature T
$\varepsilon_{i,T}$ = dielectric constant of species i at temperature T
$\eta_{m,T}$ = viscosity of the mixture at temperature T
$\eta_{i,T}$ = viscosity of the species i at temperature T

The formulas “Equation 16 Calculation Dielectric Constant” and “Equation 17 Calculation Viscosity” have 12 and 15 different empirical parameters, respectively. The first optimisation with these formulas used 20 data points for calibration. Calibration means that the values of the parameters are chosen in a way that, the calculated values match the measured values used for calibration. Afterwards these parameter values are used to calculate the values of still unknown mixtures. If the measured values of the mixture, identified by calculation, differed too much from the predicted value, the calibration process was repeated, with the new value included.

The following table shows the results of the latest calculation in contrast to the measurements of the mixtures:

Table 2 Calculation Results

T [K]	x AN	x BN	x PC	ε meas.	ε calc.	Δε	η meas.	η calc.	Δη
288.15	0.47	0.53	0.00	30.42	30.42	0.00	0.5022	0.5062	0.0040
288.15	0.69	0.26	0.05	38.84	38.21	0.63	0.4998	0.5026	0.0028
288.15	0.83	0.14	0.03	41.71	41.71	0.00	0.4482	0.4512	0.0030
293.15	0.33	0.60	0.07	35.59	35.59	0.00	0.5789	0.5828	0.0039
293.15	0.33	0.66	0.01	41.08	41.08	0.00	0.4696	0.4729	0.0033
293.15	0.45	0.53	0.02	31.72	32.17	0.45	0.5015	0.4911	0.0104
293.15	0.78	0.18	0.04	39.39	39.90	0.51	0.4489	0.4492	0.0003
298.15	0.38	0.57	0.05	33.18	34.38	1.20	0.5267	0.5048	0.0219
298.15	0.45	0.51	0.04	33.45	33.02	0.43	0.4851	0.4884	0.0033
298.15	0.59	0.31	0.10	42.24	44.83	2.59	0.5123	0.5126	0.0003
298.15	0.68	0.26	0.06	38.84	38.84	0.00	0.4561	0.4591	0.0030
303.15	0.37	0.53	0.10	37.70	37.40	0.30	0.5645	0.5323	0.0322
303.15	0.45	0.48	0.07	35.8	35.75	0.05	0.4806	0.4892	0.0086
303.15	0.64	0.29	0.07	37.62	38.93	1.31	0.4517	0.4497	0.0020
303.15	0.64	0.31	0.05	36.47	33.98	2.49	0.4597	0.4444	0.0153
303.15	0.72	0.21	0.07	42.86	42.86	0.00	0.4679	0.4642	0.0037
308.15	0.32	0.55	0.13	37.91	39.25	1.34	0.5489	0.5348	0.0141
308.15	0.44	0.47	0.09	36.7	37.33	0.63	0.4795	0.4796	0.0001
308.15	0.52	0.34	0.14	43.32	46.18	2.86	0.5023	0.5062	0.0039
308.15	0.57	0.34	0.09	38.16	40.33	2.17	0.4568	0.4534	0.0034
313.15	0.32	0.55	0.13	37.75	38.14	0.39	0.5042	0.5072	0.0030
313.15	0.43	0.47	0.10	37.39	37.39	0.00	0.4629	0.4645	0.0016
313.15	0.51	0.38	0.11	40.48	41.14	0.66	0.4719	0.4558	0.0161
313.15	0.55	0.34	0.11	45.70	41.92	3.78	0.4610	0.4517	0.0093
318.15	0.42	0.46	0.12	38.77	38.76	0.01	0.4520	0.4560	0.0040
318.15	0.47	0.40	0.13	40.16	41.66	1.50	0.4786	0.4545	0.0241
318.15	0.50	0.38	0.12	44.31	41.08	3.23	0.4721	0.4446	0.0275
318.15	0.57	0.30	0.13	43.08	43.08	0.00	0.4459	0.4161	0.0298
323.15	0.19	0.71	0.10	33.20	33.20	0.00	0.4705	0.4736	0.0031
323.15	0.28	0.58	0.14	37.59	37.59	0.00	0.4766	0.4803	0.0037
323.15	0.39	0.39	0.22	49.18	49.18	0.00	0.5241	0.5245	0.0004
323.15	0.42	0.43	0.15	41.81	41.64	0.17	0.4563	0.4527	0.0036
323.15	0.44	0.42	0.14	41.32	40.90	0.42	0.4451	0.4453	0.0003
323.15	0.64	0.29	0.07	37.03	34.93	2.10	0.3768	0.3807	0.0039
328.15	0.32	0.58	0.10	34.67	31.24	3.43	0.4364	0.4377	0.0013
328.15	0.38	0.42	0.20	46.23	46.23	0.00	0.4813	0.4797	0.0016
328.15	0.41	0.53	0.06	33.31	29.82	3.49	0.3861	0.3935	0.0074
328.15	0.43	0.42	0.15	40.52	40.64	0.12	0.4312	0.4363	0.0051
328.15	0.57	0.31	0.12	43.10	39.79	3.31	0.4094	0.4133	0.0039

The first problem with this model is that not all measured data points could be fitted well enough to the formula. A data point has been accepted as a good fit when the difference between the calculated and the measured value was lower than 0.4 for the dielectric constant and 0.004cP for the viscosity. These values have been chosen as an acceptable deviation.

The next problem is that the difference between the calculated and the measured value, for a new sample, although in the range of single percentage[12], was still too big because it alternated between too high and too low. This means that when after the calibration of the formula the calculated value for a new mixture is given at ε_1=39.9 and for another mixture at ε_2 = 40.3 the measured results will be either $\varepsilon_1 * 1.03 = 41.1$ and $\varepsilon_2 * 0.97 = 39.1$ or $\varepsilon_1 * 0.97 = 38.7$ and $\varepsilon_2 * 1.03 = 41.5$, which equates to a span of 2 and 2.8 respectively. The aspired measured value is in the range of ±1.25% of the calculated value. At a dielectric constant of about 40 this equates to a measured value between 39.5 and 40.5, ergo a span of 1.

Many, but not all, of the values used for calibration achieve this, but almost every new mixture calculated with the formula, when compared to the measurement results, deviate further than the desired range. So the fine tuning was done manually as described later on. Thus the model was not able to predict the values of the mixtures to a satisfactory degree.

The mathematical model used for the fit is Differential Evolution (3). In this model a number of vectors called agents, are generated. The number should be about 10 times the number of parameters used. This is the first generation of agents. Now in each optimization process step a new generation of agents is created until the stop criterion is fulfilled. The parameters for each vector are generated at random in the parameter space. If the solution can be narrowed down in any way, this can be used in this generation, by setting the constraints of the random number generator. This first step is called initialisation. The next step is mutation. Here for each target vector a mutant vector is generated. The mutant vector is generated by choosing 3 agents at random that are different from the target vector. These 3 agents are then subjected to the following formula:

Equation 18 Mutation

$$M_{i,G+1} = A_{r1,G} + F * \left(A_{r2,G} - A_{r3,G}\right)$$

M	= generated mutant vector.
A	= agent
r_1, r_2, r_3	= random indices that must be different from i.
G	= the current generation;
G+1	= the next generation.
F	= constant factor between 0 and 2

F controls the amplification of difference between two agents.

The next step is called crossover, where a trial vector is generated from the mutation vector.

The trial vector is formed by taking parameters either from the target or from the mutation vector. At first a random index is determined. The parameter with this index will then be taken from the mutation vector, to make sure that the whole vector cannot stay the same. For the rest of the parameters a random number between 0 and 1 is generated. If the number is smaller or identical to parameter CR, then the value from the mutation vector is taken. Otherwise the value from the target vector is taken. CR is a value between 0 and 1. The higher CR is chosen the higher is the chance that values from the mutation vector will be taken.

After generating the trial vector the last step is selection. The function value of the newly generated trial vector is compared with the function value of the target vector. If the trial vector is an improvement, then he replaces the target vector in the new generation. Otherwise the old target vector is taken over to the new generation.

This whole process is done for each agent and the whole cycle is repeated until the stop criterion is fulfilled. In this case the abort criterion was chosen to be the function value of the

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[12] ~3% most of the time

best agent to be under a certain value. The best agent is the one with the lowest function value (=error). From this agent the parameters were taken for the calculation of the composition of new mixtures. 140 agents were used. F was set at 0.8 and CR at 0.9. The VBA Code that was used for the calculation of the dielectric constant in Excel 2003 can be found in “6.1 VBA Code”. The code for the viscosity is in general the same with an adjusted function value formula.

> *People who say it cannot be done should not interrupt those who are doing it.*
>
> CHINESE PROVERB

3 Experiment and Apparatus

3.1 Chemicals

The following chemicals were used in this work:

❖ Acetonitrile	Rotisolv HPLC 99.9%	CAS: 75-05-8
❖ Butyronitrile	MERCK	CAS: 109-74-0
❖ Dimethyl Sulfoxide	ROTIDRY 99.5%	CAS: 67-68-5
❖ Propylene Carbonate	Sigma-Aldrich 99%	CAS: 108-32-7
❖ Glycerol	Roth 99.5% p.a.	CAS: 56-81-5
❖ Propyl Acetate	Sigma-Aldrich 99%	CAS:109-60-4
❖ Diethyl Phthalate	MERCK-Schuchardt > 99%	CAS: 84-66-2

Dimethyl sulfoxide was recrystallized. Acetonitrile, butyronitrile, and propyl acetate were dried and distilled. Glycerol, diethyl phthalate, and propylene carbonate were used without further purification steps.

3.2 Temperature Control

A circuit connected to a water bath from Haake type C and each apparatus was established for temperature control. The prism of the refractometer is inlaid in a metal block which can be temperature controlled. The measuring cell for the dielectric constant measurement can also be temperature controlled. The viscosimeter was put in a glass container, which has a double wall to allow temperature control. To control the temperature of the pycnometer a clamp has been built to allow the pycnometer to be inserted directly into the water bath. An extra circuit connected to another water bath, from Werk Lauda Messgeräte the Ultra-Thermostat type NB, was established to keep the temperature of the electronics in the frequency counter for the dielectric measurement constant at 25°C. Each tube is equipped with a latch at the end. Each connection between the apparatuses is made by plugging two latches together. Water flow is only enabled, if two latches are connected. This allows changing the water connection setup during the experiment if needed.
The following graphic shows a sketch of the whole configuration:

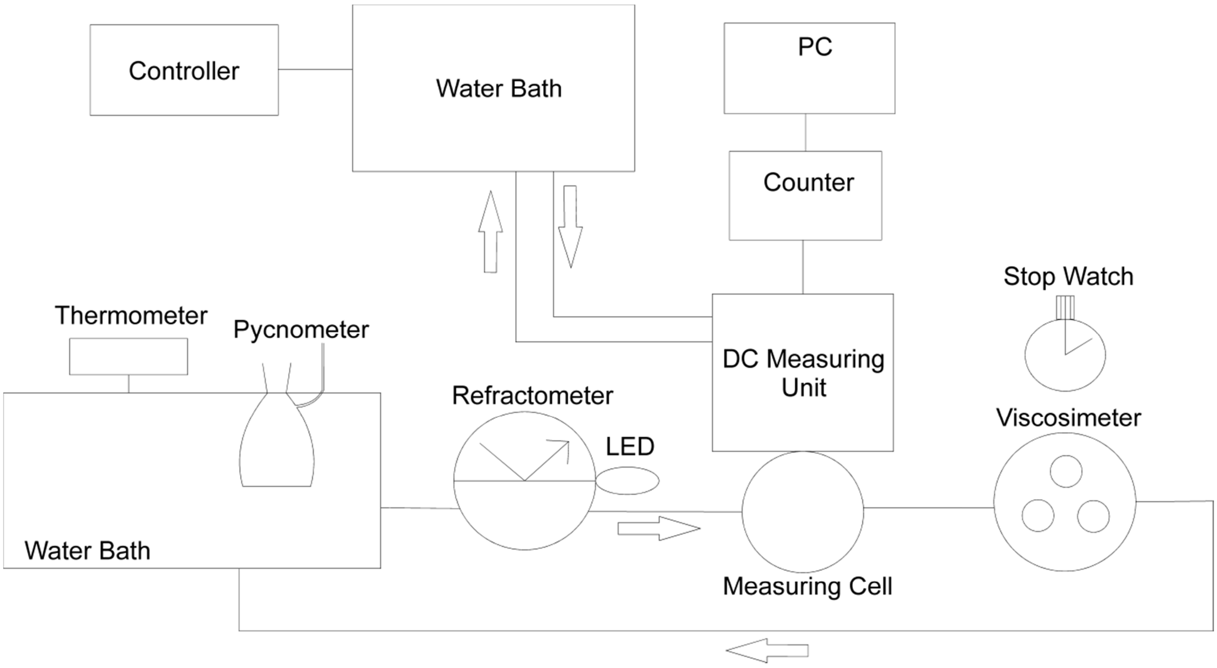

Figure 13 Configuration

3.3 Density

For the density measurements a pycnometer with 10 ml volume was used. It is installed with a thermometer that can measure up to 34°C. Measurements which required a temperature of 35°C or higher were done by substituting the thermometer with a self-made plug. The volume of the pycnometer with the plug was determined by measuring the density of a solvent with the thermometer equipped and afterwards measuring the same solvent with the plug instead. From the known density and the measured mass the volume could be calculated, which has then be used for the measurements at 35°C and above.
Normally the process was: filling the pycnometer, inserting the plug/thermometer and expelling fluid with that, so that the pycnometer was filled completely without any bubbles. Then it was put into the water bath to get the desired temperature. During this process additional fluid was expelled through the capillary by the expansion of the mixture because of the heating. Afterwards the capillary was capped, the pycnometer cleaned and weighed.

At measurements below room temperature this was not possible, because the filling process was done at room temperature. This means that, when the fluid is cooled in the water bath, the volume decreases. So it is impossible to get a filled pycnometer this way. In order to circumvent this, the pycnometer was filled without inserting the thermometer and put into the water bath. During the cooling process inert gas was directed at the inlet to impede condensation of water. After an appropriate time, when it was assumed that the desired temperature has already been reached, the thermometer was inserted while the pycnometer was still in the water bath and temperature controlled, thus expelling spare fluid and assuring a completely filled pycnometer. If correct, the capillary was capped and the pycnometer weighed after cleaning, otherwise the process had to be repeated.
The following sketch shows the apparatus:

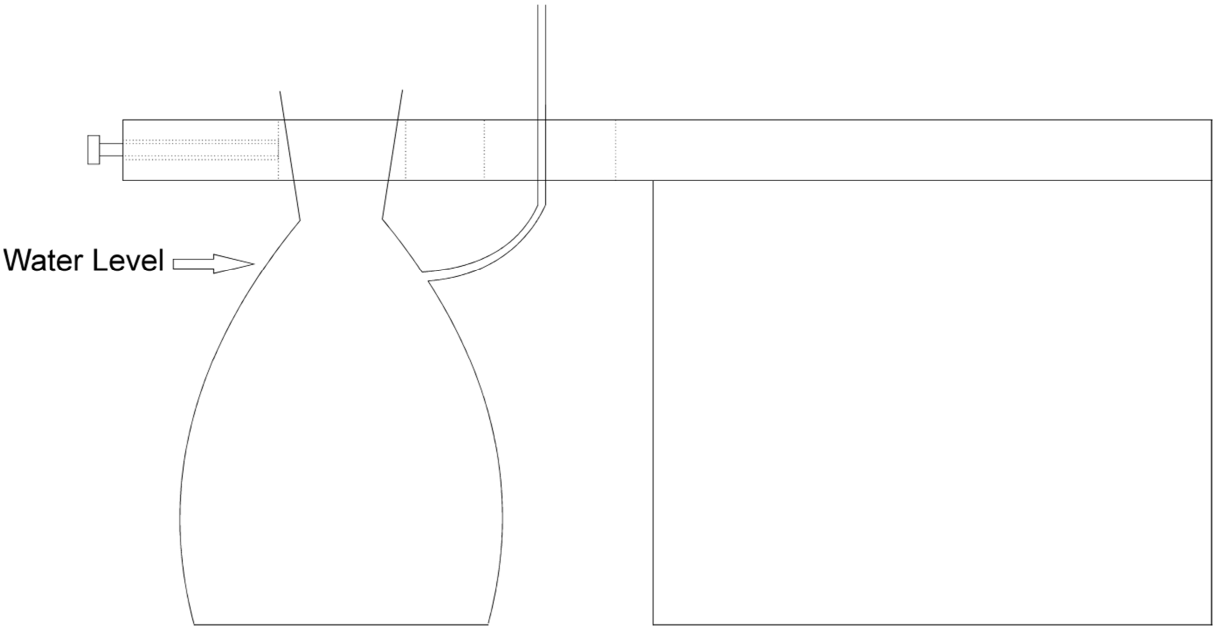

Figure 14 Pycnometer

The upper block could be placed atop the water bath instead of the normal cover to allow the pycnometer to be submerged in the water. The arrow indicates the water level of the water bath, which had to be completely filled. The block at the lower right was used as a mount to place the clamp so that during fastening the screw the clamp and the pycnometer must not be held in the hand. With this setup everything can be placed on the table and the screw fastened without the danger of something tilting. To prevent slipping, fabric films were added at the top of the block and the bottom of the clamp[13].

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[13] shifted 90° to each other

3.4 Viscosity

For the viscosity measurements an Ubbelohde Viscosimeter was used.

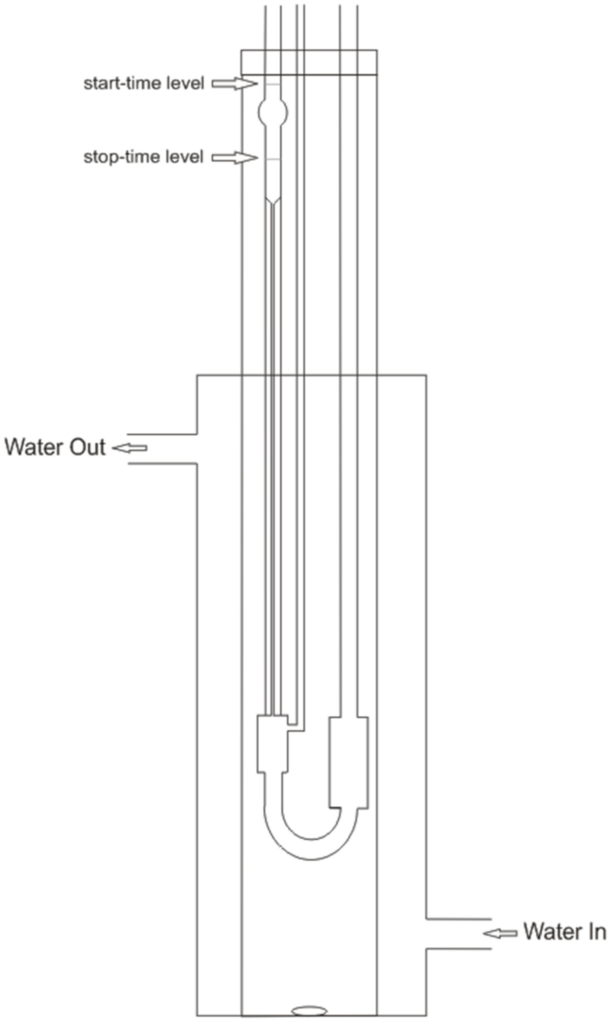

Figure 15 Ubbelohde Viscosimeter

The lower glass block with the Water In and Water Out marks is the connection to the water bath and is not connected to the interior, which was also filled with water and stirred, so that the upper parts are also tempered. The grey lines at the top of the leftmost column are the marks for stopping the time.

The viscosimeter was filled with ~20ml of the mixture. The minimum volume needed for the measurement is 15ml. After waiting for about 20 minutes[14] the measurements were started, by measuring the time the fluid needs to fall from the upper marker to the lower one. The resulting time was multiplied by an instrument constant[15] to get the kinematic viscosity; multiplying the latter one with the measured density results in the dynamic viscosity. The instrument constant was taken from (4) and checked by measuring solvents with known viscosity at different temperatures. Higher temperatures can still use the same constant, because the difference from the expanding of the capillary at higher temperatures influences the resulting viscosity only on a small scale that is still within the measurement error.

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[14] For the temperature to adjust itself

[15] $K = 0.003164 mm^2/s^2$

3.5 Refractive Index

For the refractive index measurements an Abbe Refractometer was used. A yellow LED with a wavelength of 585nm has been installed at the inlet[16] to guarantee that the measurements are done at the same wavelength.[17] The original apparatus measured with ambient light, which is never constant and as such the results were not trustworthy. 585nm was chosen, because this is closest the most common wavelength[18] for refractive index measurements of solvents. With our design it is possible to exchange the LED, if measurements at different wavelengths are desired.

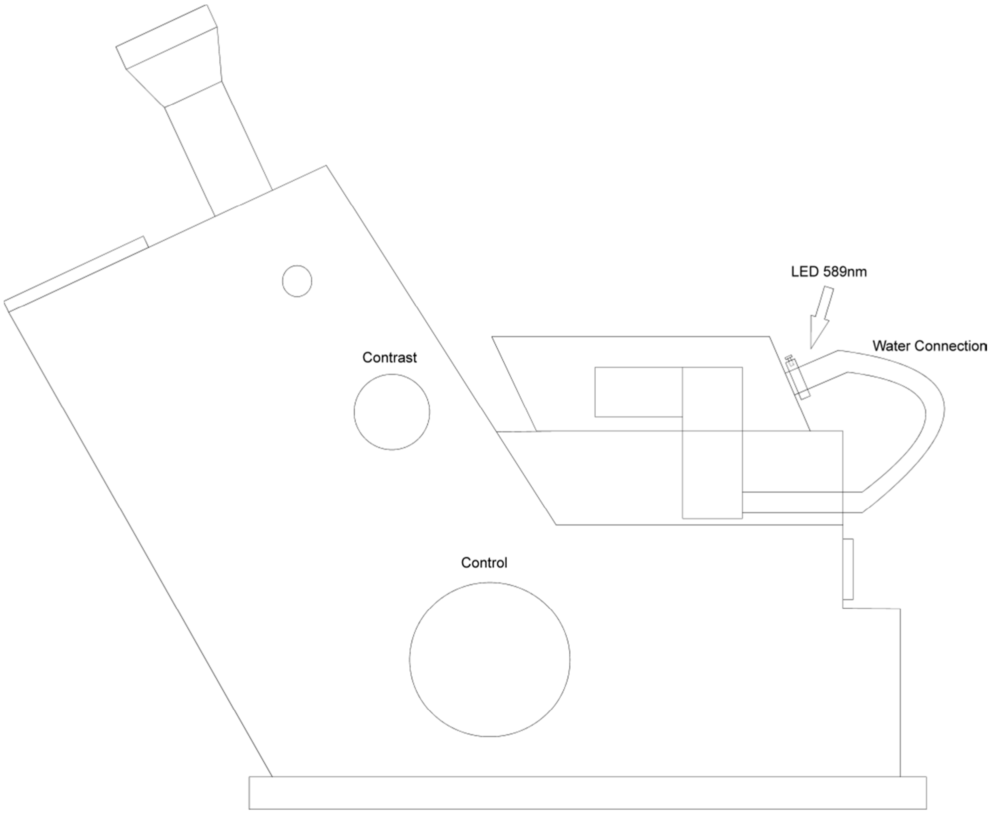

Figure 16 Refractometer

The in- and outlet for the water tubes are located on the other side of the apparatus and cannot be seen in this perspective. The water connection is there to connect the water supply from the lower part of the metal block, where the inlet is located, to the upper one, where the outlet is located. A drop of the mixture was put onto the prism. After waiting for about 1 minute, for the temperature to adjust itself, the measurement was taken.

3.6 Dielectric Constant

For the dielectric constant measurements a self-made device was used. It consists of a frequency counter with an electronic oscillator circuit. The actual frequency is influenced by both the capacitance of the device itself and the capacitance of the sample cell, which in turn

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[16] hidden behind the Water Connection tube in the sketch
[17] Because the refractive index is a function of the wavelength
[18] 589nm

is dependent on the dielectric constant of the medium filling it. The capacitance of the empty cell is about 6pF, while, with a solvent, the capacitance increases to over 100pF.

Different problems occurred with this apparatus. The first was noticed, because the measurement results varied. This can be seen in “Figure 18 Acetone - High Noise / Unstable Measurements” below. For a stable measurement the frequency drops shown should be the same instead of increasing. To have a better understanding of what happens during measurements the apparatus was modified to allow recording of the frequency values in an ASCII list on a computer. This was achieved by connecting the apparatus to a counter, namely the universal counter 5316A from HP, per BNC cable. This counter is then connected to a computer via a GPIB cable.

As a result a time vs. frequency plot could be generated.

It was discerned that the apparatus needs a warm-up time of about 2 hours to reduce the drift as can be seen in the following diagram:

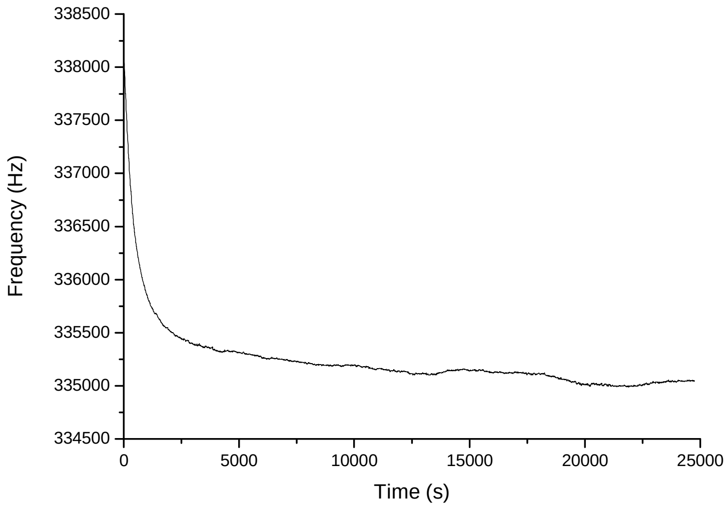


Figure 17 Idle Running

Also the measurements were not stable and had partially a high noise.

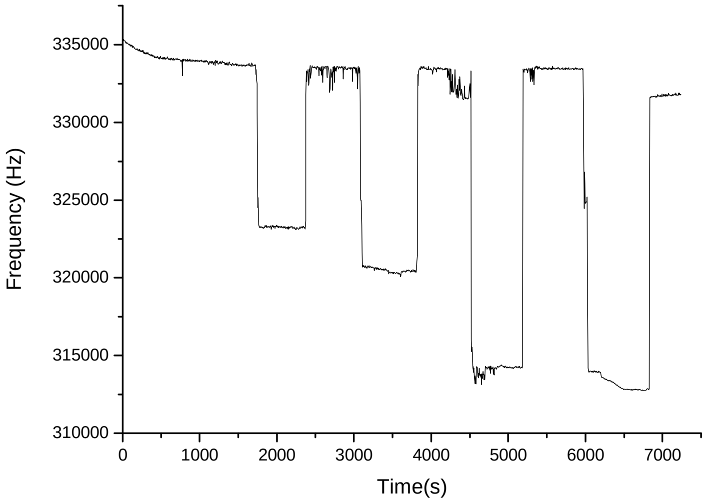


Figure 18 Acetone - High Noise / Unstable Measurements

The next modification was to replace the power supply. The idea came up after comparing measurements with the normal power supply with measurements with an accumulator.

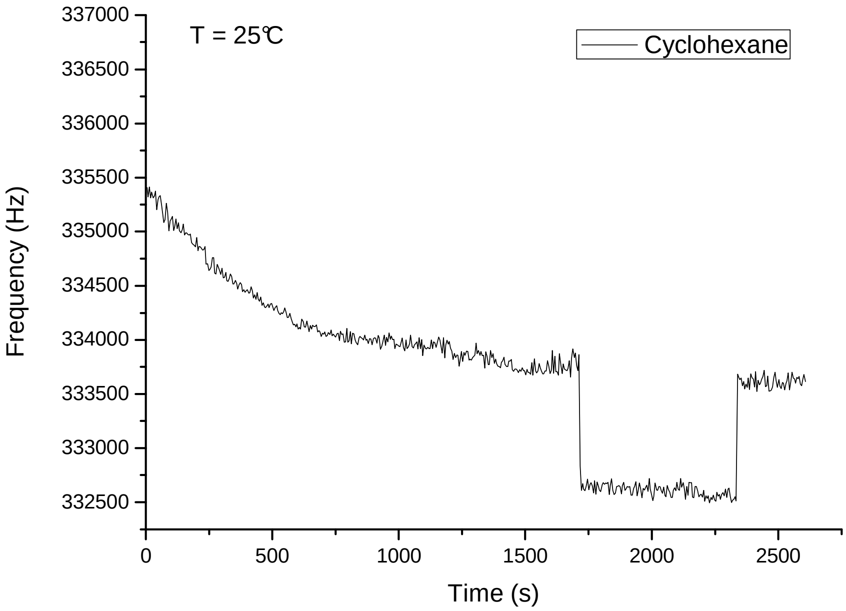


Figure 19 Old Power Supply Measurement

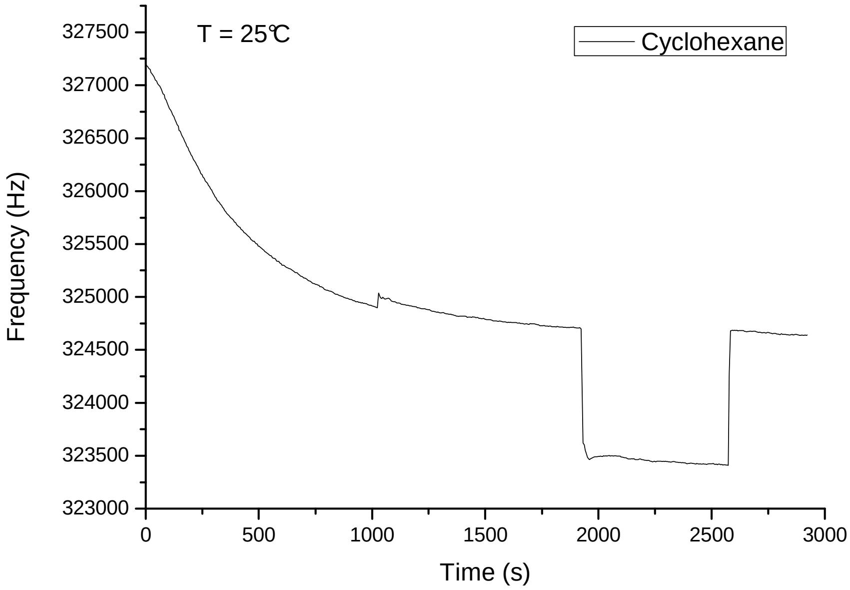


Figure 20 Accumulator Measurement

The voltage for the display (+5V) and for the oscillator (-32V) now come from a single transformer coil to avoid interference between the two. The oscillator oscillates according to the overall capacity as shown in “Figure 41 Circuit Diagram”. Also an output amplifier and a voltage stabilizer were included in the design. The electronic of the apparatus is tempered separately at 25°C so that influences occurring due to temperature changes are eliminated. Circuit diagrams for this apparatus can be found at “6.2 Circuit Diagrams”.

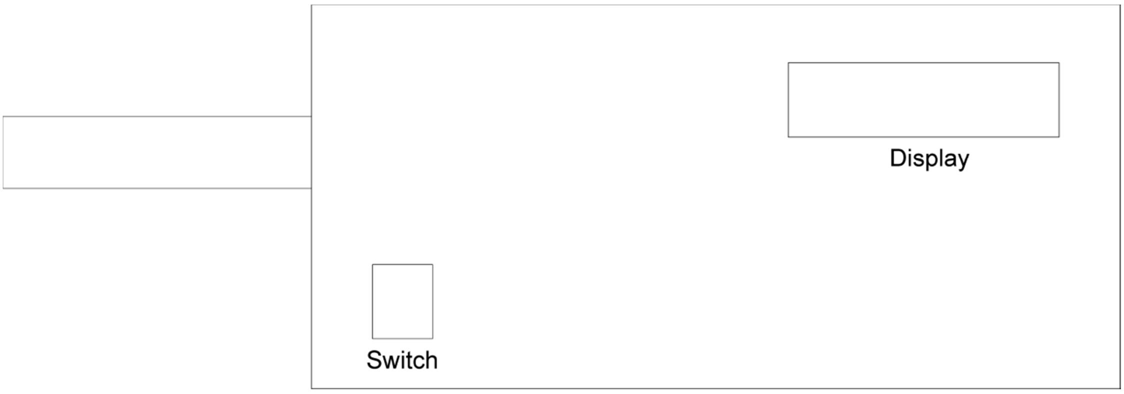


Figure 21 Dielectric Constant Measuring Unit Front

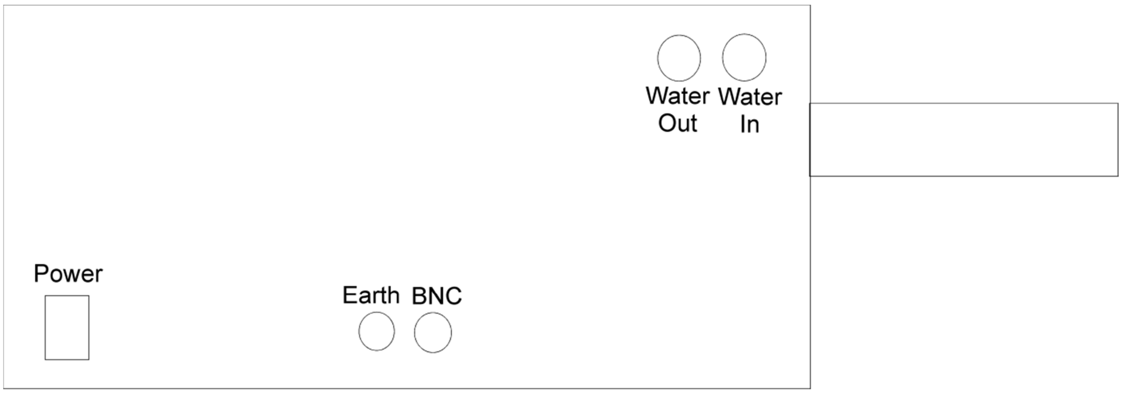


Figure 22 Dielectric Constant Measuring Unit Back

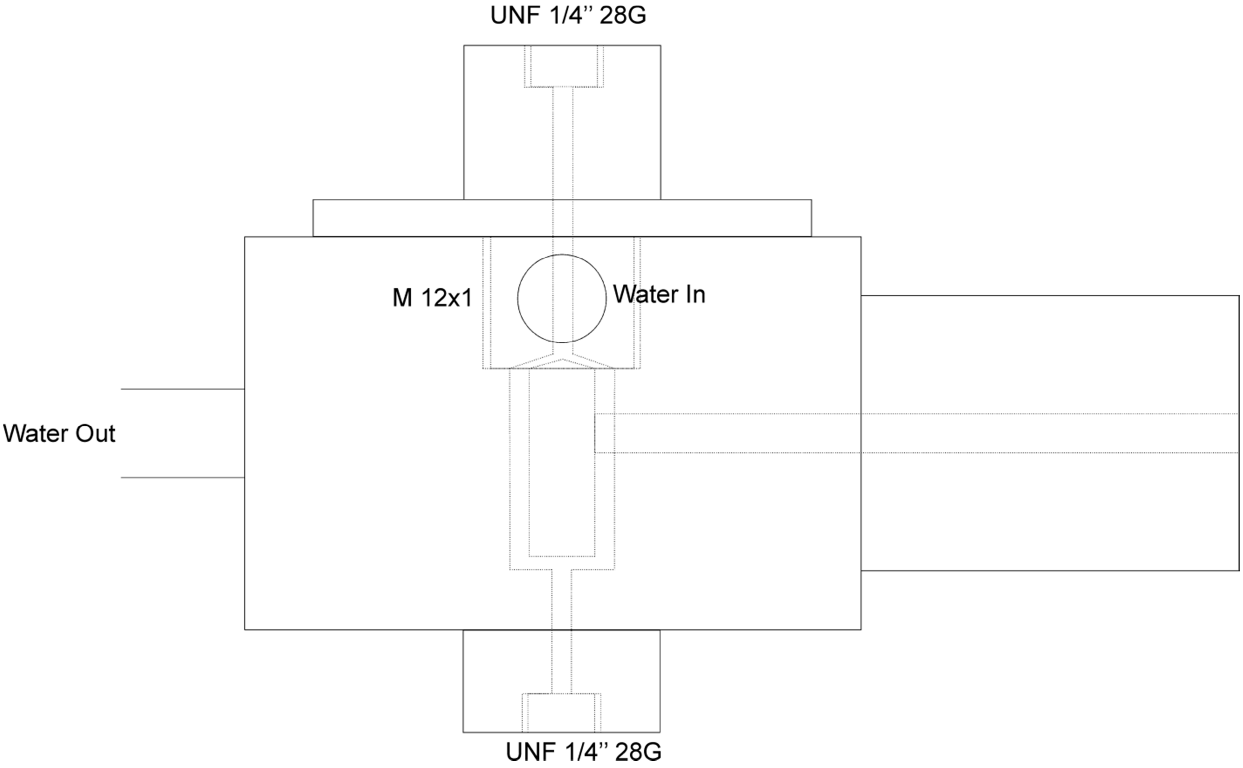
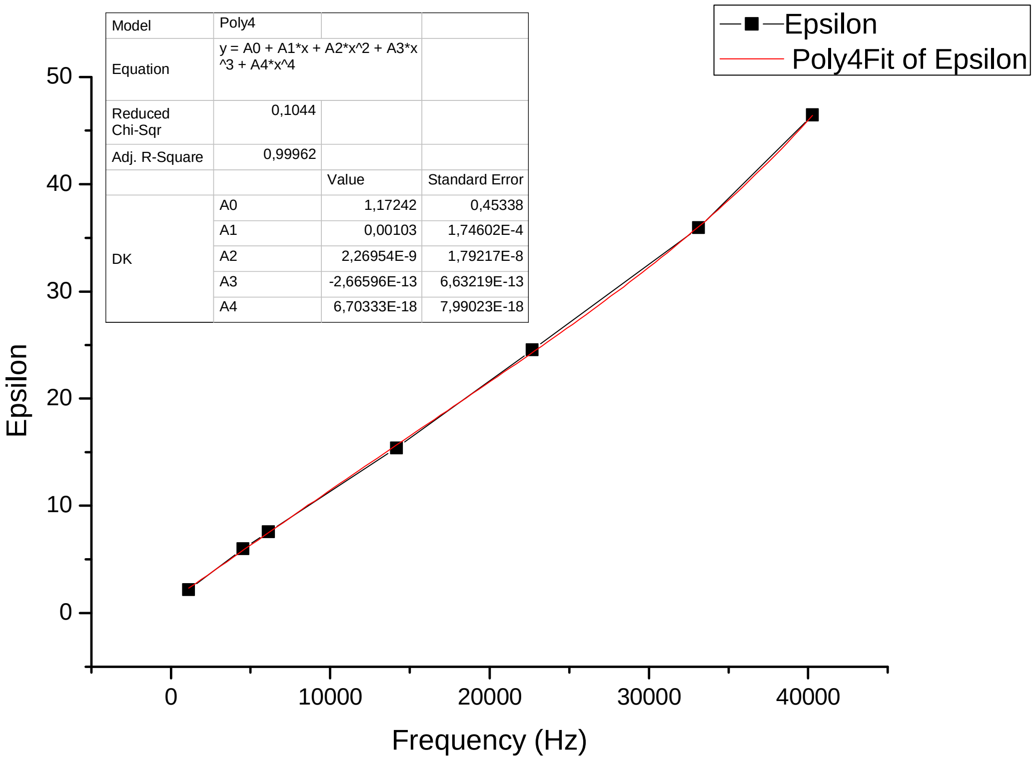


Figure 23 Dielectric Constant Measuring Sample Cell

The calibration of this apparatus was done by measuring solvents with known dielectric constant to establish a relation between the frequency gap[19] and the dielectric constant. A frequency gap was used to better counteract drifts, which were occurring in varying strengths during the measurements. For calibration pure solvents with known dielectric constant (5) were measured at 25°C. At least 3 jumps were measured for each solvent[20]. The measured frequency gaps were plotted against the dielectric constant resulting in the following graph:



Model	Poly4		
Equation	y = A0 + A1*x + A2*x^2 + A3*x^3 + A4*x^4		
Reduced Chi-Sqr	0,1044		
Adj. R-Square	0,99962		
		Value	Standard Error
DK	A0	1,17242	0,45338
	A1	0,00103	1,74602E-4
	A2	2,26954E-9	1,79217E-8
	A3	-2,66596E-13	6,63219E-13
	A4	6,70333E-18	7,99023E-18

Figure 24 Dielectric Constant Calibration

The used fit is an empirical one and the formula depicted in the top left box of the figure is the one used for calculations. A polynomial of the 4th degree was chosen for the fit, because it was the simplest fit that describes the measured curve to a satisfactory degree. DMF was measured at 15°C, 25°C, 35°C, 45°C, 55°C and the known values of the dielectric constant compared to the ones measured by using the calibration formula above to control the calibration. The following table shows the measured values with the above mentioned calibration in contrast to the literature values (6):

Table 3 Dielectric Constant Calibration Control

T [°C]	ε meas.	ε lit.
15	39.7	39.29
25	38.0	37.59
35	35.6	35.78
45	34.1	34.16
55	32.3	32.64

---

[19] frequency with air – frequency with solvent

[20] resulting in 6 data points

The difference is still acceptable and the calibration seems correct over the desired temperature region.

3.7 Temperature Mixture

For starters the mole fraction of the sample for every 5°C in the range of 15°C to 55°C were calculated by using the following formulas:

Equation 19 Dielectric Constant Mixture

$$\varepsilon_{m,T} = \varepsilon_{1,T}x_{1,T} + \varepsilon_{2,T}x_{2,T} + \varepsilon_{3,T}x_{3,T}$$

Equation 20 Viscosity Mixture

$$\ln \eta_{m,T} = x_{1,T}\ln \eta_{1,T} + x_{2,T}\ln \eta_{2,T} + x_{3,T}\ln \eta_{3,T}$$

Equation 21 Refractive Index Mixture

$$n_{D,m,T} = n_{D1,T}x_{1,T} + n_{D2,T}x_{2,T} + n_{D3,T}x_{3,T}$$

$x_{i,T}$ = mole fraction of species i at temperature T
$\varepsilon_{i,T}$ = dielectric constant of species i at temperature T
$\eta_{i,T}$ = dynamic viscosity of species i at temperature T
$n_{Di,T}$ = refractive index of species i at temperature T
$\varepsilon_{m,T}$ = dielectric constant of the mixture at temperature T
$\eta_{m,T}$ = dynamic viscosity of the mixture at temperature T
$n_{Dm,T}$ = refractive index of the mixture at temperature T

After observing that these formulas were not correctly reflecting the behaviour of the solvent properties, with exception of the refractive index, different solutions to correctly calculate the values were sought after, until arriving at the formula mentioned at 2.4 Calculation. After each measurement the new measured values were included in the calibration of the formula. The resulting parameters where then used to search for the desired mole fraction by setting a range of reference values of the dielectric constant and the dynamic viscosity[21] and then calculating the values for all combinations of these 3 properties for every mole fraction. The output was the mole fraction with the lowest error, which was calculated by the following formula:

Equation 22 Error Criteria

$$error = w_1\sqrt{\left(\eta - \eta_{ref}\right)^2} + w_2\sqrt{\left(n_D - n_{D,ref}\right)^2} + w_3\sqrt{\left(\varepsilon - \varepsilon_{ref}\right)^2}$$

w_i = weighting parameters
ε = calculated dielectric constant
η = calculated dynamic viscosity
n_D = calculated refractive index
ε_{ref} = reference dielectric constant
η_{ref} = reference dynamic viscosity
$n_{D,ref}$ = reference refractive index

---

[21] the refractive index was excluded as explained at 2.2 Refractive Index

w_1, w_2 and w_3 stand for weighting parameters and were modified after each calculation cycle to check if different values yield better results. After the calculations did not show any improvements in the measured results, new mole fractions were defined manually, by comparing with old measurement results. The idea behind that was that, if a set mole fraction is taken and only slight changes are made, the dependence of the viscosity and the dielectric constant on the mole fraction behaves almost linear in a small scale. This can be shown in the following example:

Table 4 Temperature Mixture Manual Modifications

T [K]	x AN	x BN	x PC	ε	η [cP]
303.15	0.61	0.32	0.07	40.15	0.4643
303.15	0.62	0.31	0.07	40.77	0.4563
303.15	0.63	0.30	0.07	41.78	0.4508
303.15	0.64	0.29	0.07	37.62	0.4517

As can be seen only two mole fraction volumes were changed while one was kept constant. At first the dielectric constant and the viscosity change linear[22] but the last row is a break point. These break points are the reason some kind of undulating surface plot for the ternary mixtures was suspected. So if a good starting point is available the dielectric constant and the viscosity can be modified in a small scale with trial and error.

When checking which results were already available, a dielectric constant of about 40 and a viscosity of about 0.46cP were set as target values. In the following table the underlined row is the value for this temperature which was used as starting point for the manual adjustments. The following lines were the measurements until the desired values (bold) were obtained.

---

[22] the higher the mole fraction of acetonitrile the lower the dielectric constant and the viscosity

Table 5 Temperature Mixture Results

T [K]	x AN	x BN	x PC	ε	η [cP]
288.15	0.83	0.14	0.03	41.71	0.4482
288.15	0.81	0.16	0.03	40.72	0.4530
288.15	**0.80**	**0.17**	**0.03**	**40.03**	**0.4603**
293.15	0.78	0.18	0.04	39.39	0.4489
293.15	0.77	0.18	0.05	43.30	0.4568
293.15	0.71	0.25	0.04	38.95	0.4664
293.15	0.72	0.24	0.04	38.51	0.4577
293.15	**0.73**	**0.23**	**0.04**	**39.98**	**0.4572**
298.15	0.68	0.26	0.06	38.84	0.4561
298.15	**0.69**	**0.25**	**0.06**	**40.30**	**0.4545**
303.15	0.64	0.29	0.07	37.62	0.4517
303.15	0.66	0.26	0.08	44.27	0.4592
303.15	0.62	0.32	0.06	40.23	0.4484
303.15	0.60	0.34	0.06	39.52	0.4509
303.15	0.63	0.30	0.07	41.78	0.4508
303.15	0.62	0.31	0.07	40.77	0.4563
303.15	**0.61**	**0.32**	**0.07**	**40.15**	**0.4643**
308.15	0.57	0.34	0.09	38.16	0.4568
308.15	**0.61**	**0.30**	**0.09**	**39.91**	**0.4563**
313.15	0.51	0.38	0.11	40.48	0.4719
313.15	0.53	0.37	0.10	42.02	0.4497
313.15	**0.48**	**0.42**	**0.10**	**40.05**	**0.4639**
318.15	0.42	0.46	0.12	38.77	0.4520
318.15	0.43	0.45	0.12	41.30	0.4787
318.15	**0.43**	**0.46**	**0.11**	**40.10**	**0.4573**
323.15	0.28	0.58	0.14	37.59	0.4766
323.15	0.30	0.56	0.14	39.60	0.4758
323.15	0.38	0.48	0.14	42.26	0.4619
323.15	0.39	0.47	0.14	42.47	0.4560
323.15	0.35	0.52	0.13	42.19	0.4559
323.15	**0.31**	**0.57**	**0.12**	**39.73**	**0.4571**
328.15	0.43	0.42	0.15	40.52	0.4312
328.15	0.21	0.66	0.13	38.40	0.4602
328.15	**0.20**	**0.67**	**0.13**	**39.37**	**0.4637**

3.8 Dielectric Constant Mixture

Based on the experiments by Sabine Richert, MSc a mixture of propyl acetate and butyronitrile was used. Both solvents have a similar viscosity, which guarantees that at the same temperature the viscosity of the mixture only varies slightly. The dielectric constant on the other hand differs greatly, which allows to variation of this property of the mixture according to the molar fraction. Experiments proved this theory.

The next step for improvement was to get the same viscosity for all temperatures[23]. In order for this to work a solvent that has a rather low dielectric constant, so that the range is not shifted too high, and at the same time a high viscosity, so that it can be used to increase the viscosity at higher temperatures of the mixture, was needed. Diethyl phthalate fulfils these

---

[23] 15°C, 25°C, 35°C, 45°C and 55°C

requirements. By trial and error the mole fraction necessary to reach a similar viscosity over the whole temperature range was ascertained.

3.9 Viscosity Mixture

Also based on previous experiments glycerol and DMSO were chosen as solvents for this mixture. With a difference of about 10^3 between the viscosity of pure DMSO and pure glycerol a large variety of viscosities can be achieved by adjusting the molar fraction. It was not possible to measure this mixture in Graz, because glycerol as well as DMSO react with the water in the air and change their properties quite radically. At this point no option to measure the viscosity under inert gas was available and the measurement time is too long for measurements under air, so that changes can be noticed during measurement. The dielectric constant measurement was not possible, because of a rather small inlet and the high viscosity of mixtures with more than 40 mole percent glycerol. The time to fill the measuring cell is so high that the mixture has enough time to react with water in the air.

3.10 Regensburg

The results from our experiments were compared with the results obtained by using the laboratory from Professor Buchner at the University of Regensburg. They could measure the same properties, but had a different measuring system for each, which made a comparison very interesting.

The viscosity was measured by a falling ball viscosimeter, namely the AMVn from Anton Paar. This type of viscosimeter is also known as a “Höppler viscosimeter”. The dielectric constant was measured with a Vector Network Analyzer E8364B (Agilent) with ECal Modul and the density was measured by an oscillating U-tube, the DMA 5000M, also from Anton Paar. The results from the density measurement agree with the data obtained in Graz. Only a few viscosity measurements, which also concur with the results from Graz, could be done, because afterwards different problems with the apparatus occurred. In contrast to that a rather big difference showed up, when comparing the data from the two dielectric constant measurements of the temperature mixture. The results of the dielectric constant mixture only showed a small difference for each data point[24]. Also for the latter the important part is that the dielectric constant varies, which was confirmed in Regensburg, and that the desired ε range is kept, which was still the case. The values for this mixture are listed at “4.3 Dielectric Constant Mixture”. After a few more experiments in Graz it was possible to ascertain that the problem stems from the measuring cell.

This table shows the dielectric constant values of the temperature mixture measured in Graz compared to Regensburg.

Table 6 Comparison Dielectric Constant Graz-Regensburg

T [°C]	x (AN)	x (BN)	x (PC)	ε Graz	ε Regensburg
15	0.80	0.17	0.03	40.0	35.0
25	0.69	0.25	0.06	40.3	33.5
35	0.61	0.60	0.09	39.9	32.3
45	0.43	0.46	0.11	40.1	30.8
55	0.20	0.67	0.13	39.4	27.7

---

[24] Between 0.5 and 1.2 dielectric constant units

The difference increases with temperature, but no reason for this behaviour could be ascertained yet, as shown in “Figure 25 Dielectric Constant Comparison Graz-Regensburg”.

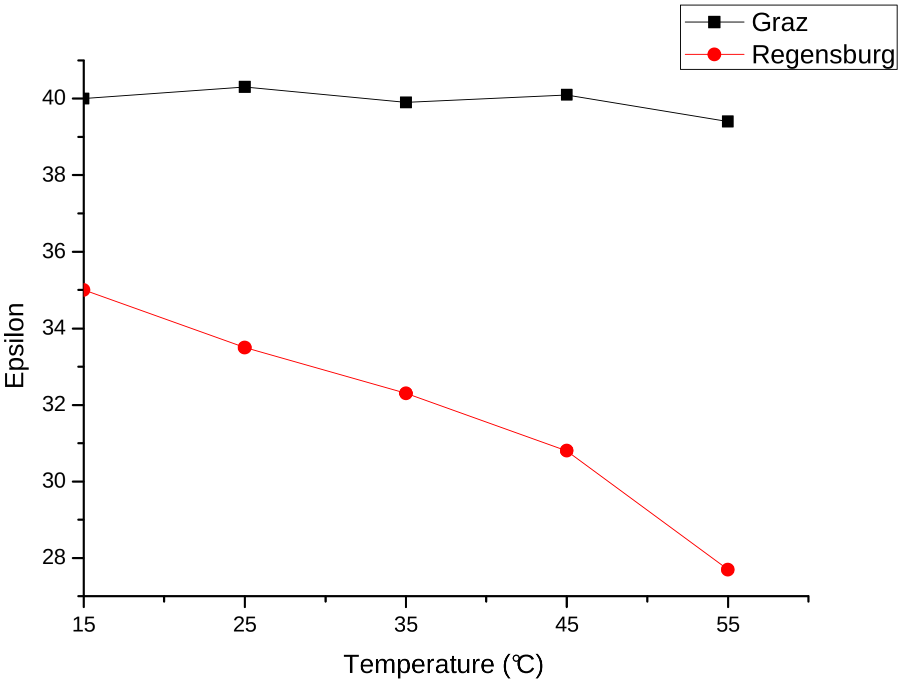


Figure 25 Dielectric Constant Comparison Graz-Regensburg

4 Results and Discussion

> *Zwei Dinge sind zu unserer Arbeit nötig: Unermüdliche Ausdauer und die Bereitschaft, etwas, in das man viel Zeit und Arbeit gesteckt hat, wieder wegzuwerfen*
>
> ALBERT EINSTEIN

4.1 Temperature Mixture

Because of the dubious data obtained in Graz a suitable ternary mixture with constant solvent properties while varying the temperature could not be devised. A new measurement cell is necessary in order to be able to start working on this mixture again.

4.2 Viscosity Mixture

The relaxation of mixtures with a high glycerol percentage occurs at low frequencies, which cannot be measured by the VNA in Regensburg. The following graphs show ε' and ε'' of all mixtures plotted against the frequency. In order to get ε_r out of these plots ε' needs to reach a plateau.

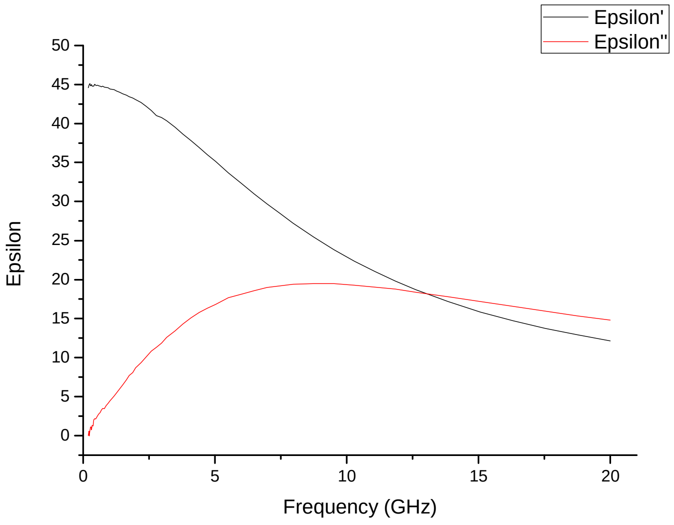


Figure 26 1.0 DMSO - 0.0 Glycerol

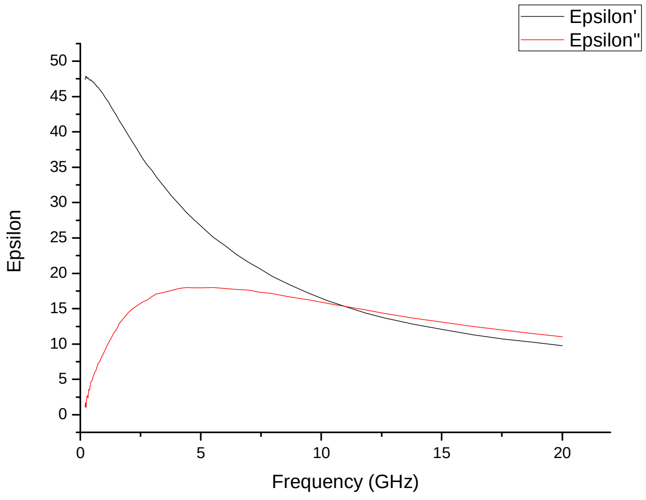


Figure 27 0.9 DMSO - 0.1 Glycerol

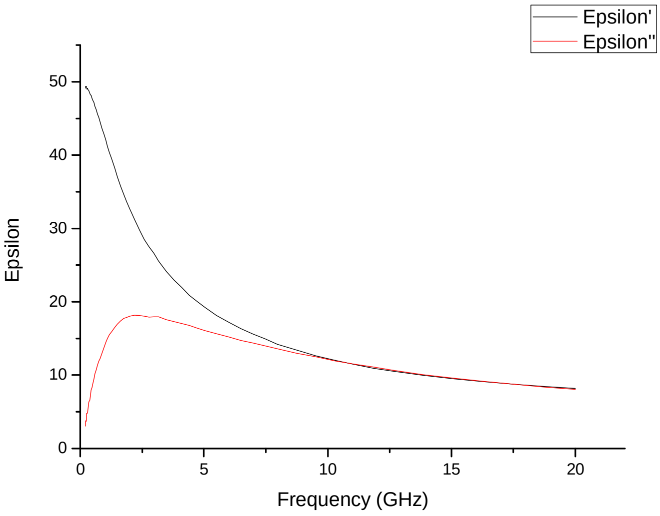


Figure 28 0.8 DMSO - 0.2 Glycerol

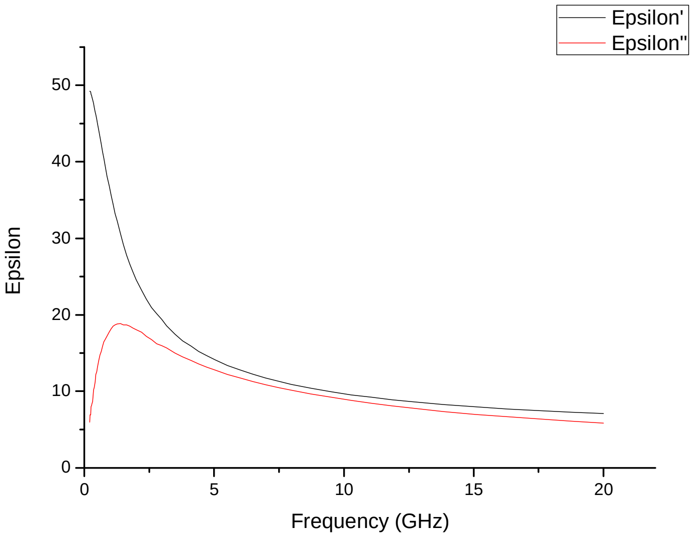


Figure 29 0.7 DMSO - 0.3 Glycerol

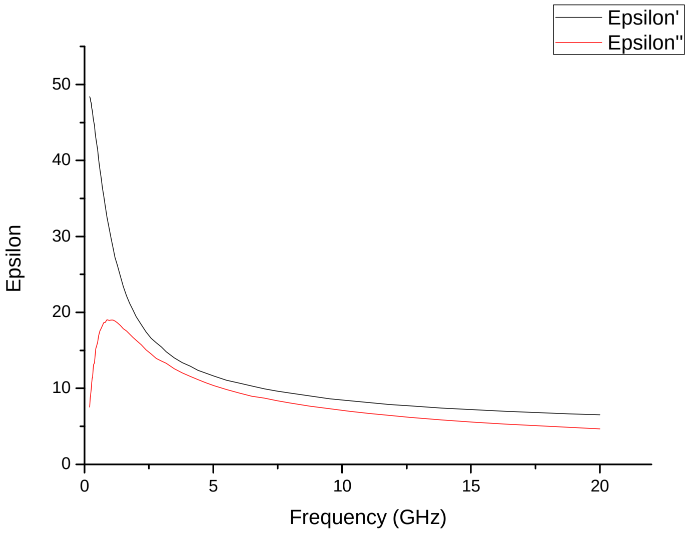


Figure 30 0.6 DMSO - 0.4 Glycerol

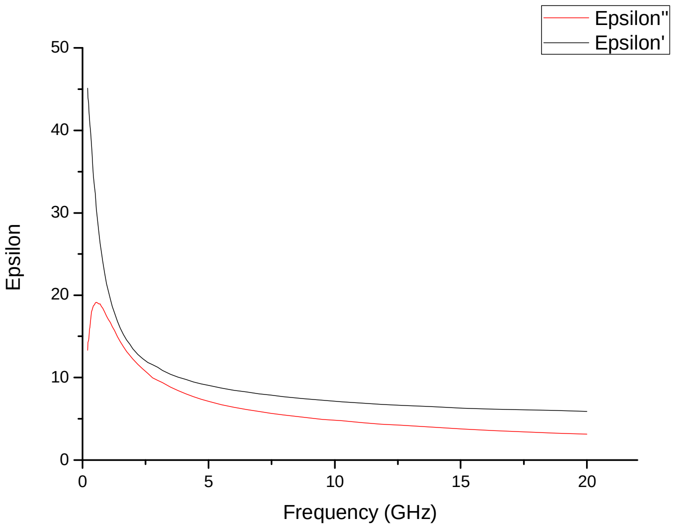


Figure 31 0.5 DMSO - 0.5 Glycerol

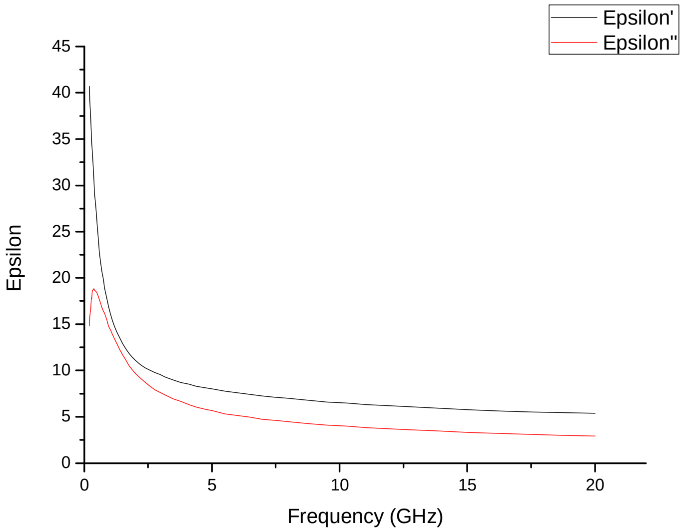


Figure 32 0.4 DMSO - 0.6 Glycerol

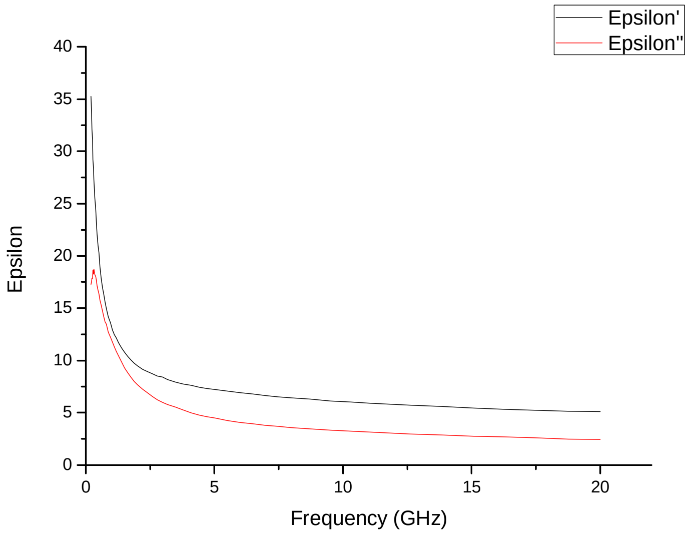


Figure 33 0.3 DMSO - 0.7 Glycerol

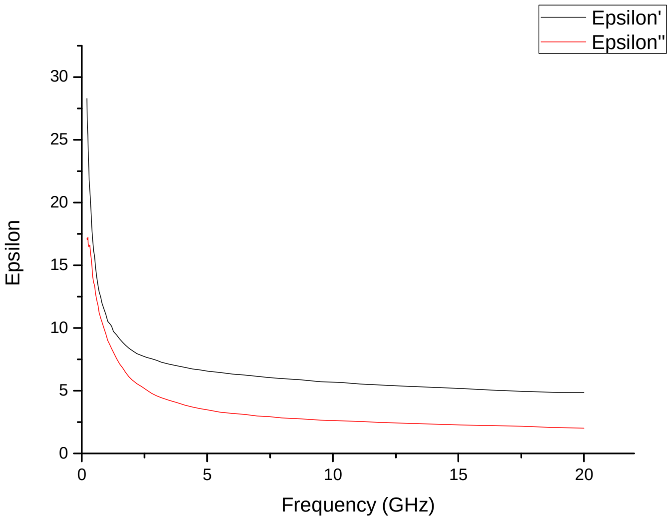


Figure 34 0.2 DMSO - 0.8 Glycerol

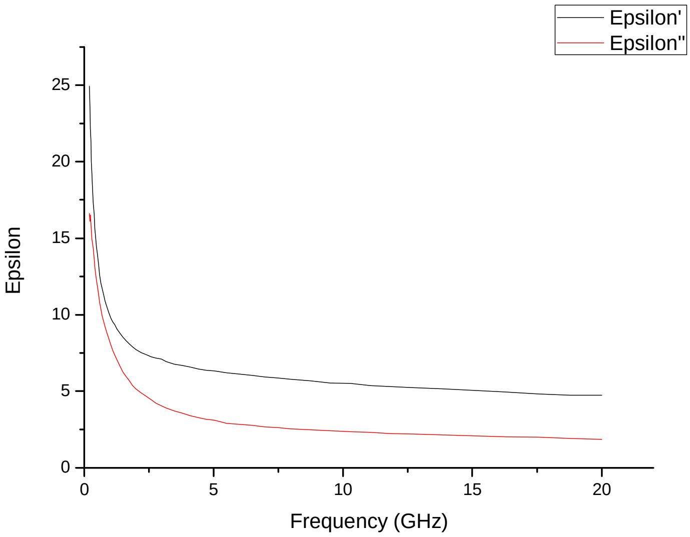


Figure 35 0.1 DMSO - 0.9 Glycerol

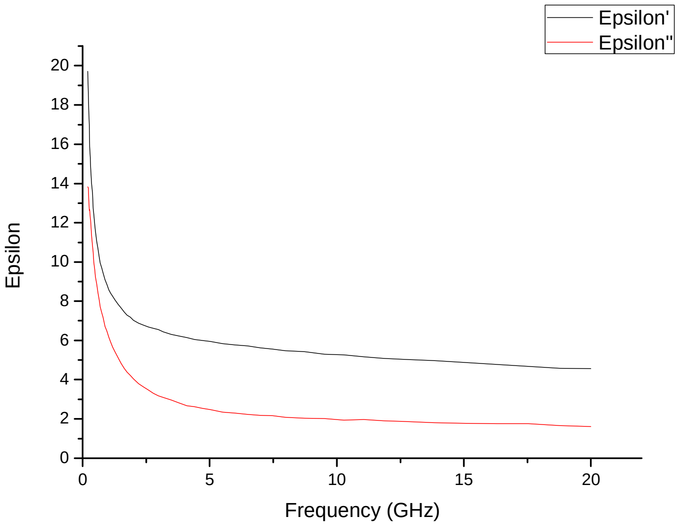


Figure 36 0.0 DMSO - 1.0 Glycerol

These diagrams still show that τ_L, which is the x value of the inflection point of the ε' plot, changes. This correlates with the theory explained later on at "5.1 Temperature Mixture", as there is definitely a viscosity change in these mixtures.

4.3 Dielectric Constant Mixture

This mixture did not suffer from the defect measuring cell, because the dielectric constant changes here and only a certain dielectric constant range covered is wanted, which is still the case.
The mole fraction of each mixture can be found in the following table:

Table 7 Dielectric Constant Mixture Results

T [°C]	x (PA)	x (BN)	x (DEP)	ε	η [cP]	n_D
15	1.00	0.00	0.00	6.0	0.6287	1.3875
	0.80	0.20	0.00	8.9	0.6277	1.3871
	0.60	0.40	0.00	12.2	0.6270	1.3868
	0.40	0.60	0.00	16.0	0.6287	1.3868
	0.20	0.80	0.00	20.3	0.6261	1.3870
	0.00	1.00	0.00	25.2	0.6298	1.3877
25	0.97	0.00	0.03	5.9	0.6135	1.3884
	0.78	0.195	0.025	8.6	0.6055	1.3890
	0.585	0.39	0.025	11.6	0.6062	1.3883
	0.39	0.585	0.025	15.1	0.6108	1.3894
	0.20	0.78	0.02	18.7	0.6064	1.3885
	0.00	0.98	0.02	23.4	0.6054	1.3886
35	0.96	0	0.04	5.5	0.6005	1.3871
	0.77	0.19	0.04	8.0	0.5918	1.3879
	0.58	0.38	0.04	10.8	0.5985	1.3883
	0.38	0.575	0.045	14.0	0.5922	1.3900
	0.19	0.765	0.045	17.8	0.6056	1.3910
	0.00	0.95	0.05	21.5	0.6118	1.3920
45	0.90	0.00	0.10	5.5	0.6151	1.3952
	0.73	0.18	0.09	7.7	0.5990	1.3954
	0.55	0.36	0.09	10.1	0.6007	1.3952
	0.36	0.55	0.09	12.9	0.6043	1.3960
	0.18	0.73	0.09	15.9	0.6099	1.3969
	0.00	0.91	0.09	19.3	0.6121	1.3980
55	0.86	0.00	0.14	5.5	0.6017	1.3982
	0.69	0.17	0.14	7.5	0.6027	1.4011
	0.52	0.345	0.135	9.6	0.6051	1.4007
	0.35	0.52	0.13	12.1	0.6089	1.4010
	0.175	0.70	0.125	14.8	0.6051	1.4016
	0.00	0.88	0.12	17.9	0.6087	1.4016

As can be seen the dielectric constant per temperature is between ~6 and ~20, while the viscosity and the refractive index stay in a reasonable close range, especially considering "Figure 1 Temperature Dependence Viscosity", which shows the big influence of temperature. So this mixture, with such a small variation range of η, is a big improvement and should be usable for small activation energy measurements.

5 Outlook

Das Geheimnis aller Erfinder ist,
nichts für unmöglich anzusehen.
JUSTUS VON LIEBIG

5.1 Temperature Mixture

A stable and working measurement method for the dielectric constant has to be established. In order to fulfil this, plans for a new measuring cell are being considered. An application idea for this mixture would be an in-depth analysis of the adiabatic case of electron transfer reactions. During the electron transfer process the nucleus coordinate is influenced by vibrations and by the longitudinal relaxation time (τ_L) of the solvent. With these two together the coordinate can increase and decrease. If the energy hill is broad, then the time, for crossing this barrier[25], is long enough for τ_L to influence the coordinate. As a result the following scenario is possible:

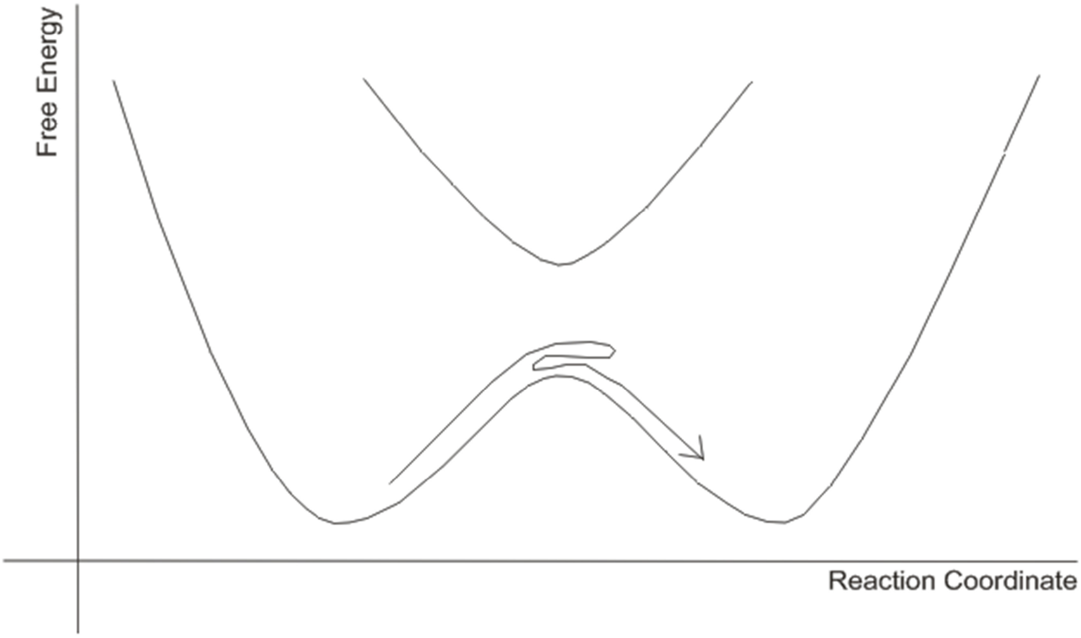


Figure 37 Adiabatic Energy Diagram

As “Figure 37 Adiabatic Energy Diagram” shows the nucleus coordinate increases and decreases while crossing the barrier. That means that for this case not only the height but also the form of the hill[26] is important.

Equation 23 Longitudinal Relaxation Time[27]

$$\tau_L = \frac{\varepsilon_\infty}{\varepsilon_r} \tau_D$$

---

[25] = the distance the nucleus coordinate has to increase

[26] the energy necessary for the reaction

[27] See (26)

Equation 24 Debye Relaxation Time[28]

$$\tau_D = \frac{3V_M\eta}{RT}$$

τ_L = longitudinal relaxation time
τ_D = Debye relaxation time
ε_r = dielectric constant measured at infinite low frequency
ε_∞ = dielectric constant measured at infinite high frequency
V_M = molar volume
R = universal gas constant
T = temperature in Kelvin

As can be seen the longitudinal relaxation time is dependent on the Debye relaxation, which in turn is proportional to the viscosity. This correlation can also be observed in the dielectric loss spectra shown in 4.2 Viscosity Mixture. So if measurements at different temperatures are made, the viscosity is changed and as a consequence τ_L is not the same, which has a direct influence on the rate constant. If these values are now used to calculate the activation energy, then the change of $\tau_{L,}$ which has influenced the rate constant, has not been accounted for, which leads to a wrong result for the energy. The error increases percental as the activation energy decreases. In order to measure without this influence, the viscosity and the ratio of ε_∞ and ε_r have to stay the same over the measured temperature region.
As the whole process is also dependent on the Pekar factor[29], another prerequisite is for the dielectric constant and the refractive index to stay constant. All of these conditions are met with the temperature mixture, which should enable measurement and calculation of small activation energies.
Another idea for application would be the standard electrode potentials. They are defined for 25°C. At the moment the temperature dependence of these potentials is not really defined. For the calculation of this dependency the system is heated. Then the potential is measured and from this potential, ΔS is calculated. This form of calculation completely ignores the changes in the solvent, which should be included in the calculated ΔS:

Equation 25 Temperature Dependence of Potentials[30]

$$\left(\frac{\delta E}{\delta T}\right)_p = -\frac{1}{nF}\left(\frac{\delta\Delta_r G}{\delta T}\right)_p = \frac{\Delta_r S}{nF}$$

The unit of ΔS is J/(K*mol). This means for a measurement above or below 25°C, the difference in temperature is multiplied to ΔS in order to calculate the energy difference. This is then converted to V by dividing by nF. The result is added to the standard electrode potential. The bigger the temperature difference is, the bigger is the impact on the solvent properties and as a consequence the bigger is the error.
The influence of the solvent properties is in the value of $\Delta_r G$. The exact correlation can be seen from Equation 6 to Equation 9. The temperature mixture would have constant solvent properties while changing the temperature. This would ensure that the solvent stays the same and has no influence on ΔS.
The problem, that would still remain, is the association constant in organic solvents. The ion pair formation increases rapidly with increasing concentration in organic solvents.[31] As the

---

[28] See (27)
[29] The influence comes from the activation energy necessary to cross the barrier = height of the barrier
[30] See (28)
[31] See (23) for experiments showing this

electron standard potentials are defined for an activity of 1M, which probably cannot be achieved in this mixture, an alternative aqueous system, that keeps all solvent properties constant, should be considered. In aqueous systems the solubility should not pose a problem.

5.2 Viscosity Mixture

In order to start working on this mixture a proper environment for measurements has to be created. For viscosity measurement a gas box has been built which should enable measurements in inert gas atmosphere. For dielectric constant measurements: the inlet of the cell in planning should be large enough so that it allows faster filling for mixtures with high viscosity.

An application would be given by photoinduced electron transfer reactions. If the electron transfer is very fast that means that $k_{ET} >> k_{-diff}$ then the reaction would be diffusion controlled. As a consequence every collusion of an excited particle with another particle would result in an electron transfer. Taking a common version of Smoluchowski's relation[32] into account, the diffusion would be viscosity and temperature dependent:

Equation 26 Smoluchowski Relation[33]

$$k_{diff} = \frac{8RT}{3000\eta}$$

As the name photoinduced electron transfer already indicates, activation energy in the form of light is necessary to start this kind of reaction. Of course the wavelength of the light has to agree with the absorption band of one of the particles. Otherwise the energy could not be transferred to the system. Due to the solvatochromic effect this is dependent on the polarity respectively the dielectric constant of the solvent. With increasing dielectric constant a bathochromic or a hypsochromic shift, depending on the particle, is possible.[34] Keeping everything constant, except for the viscosity, to eliminate the above discussed influences of the other properties, systematic measurements of the influence of the viscosity on the experiment could be observed. Of course the temperature mixture could also be used for this application, to observe the influence of temperature.

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[32] Only valid for neutral acceptor and donor before the electron transfer

[33] See (27)

[34] This is not the same dependency as for redox potentials, as these always decrease with increasing dielectric constant

5.3 Dielectric Constant Mixture

This mixture could be used in MARY measurements. MARY is a spectroscopy where a photoinduced electron transfer reaction is influenced by a magnetic field. The following figure shows the most important reaction pathways for this:

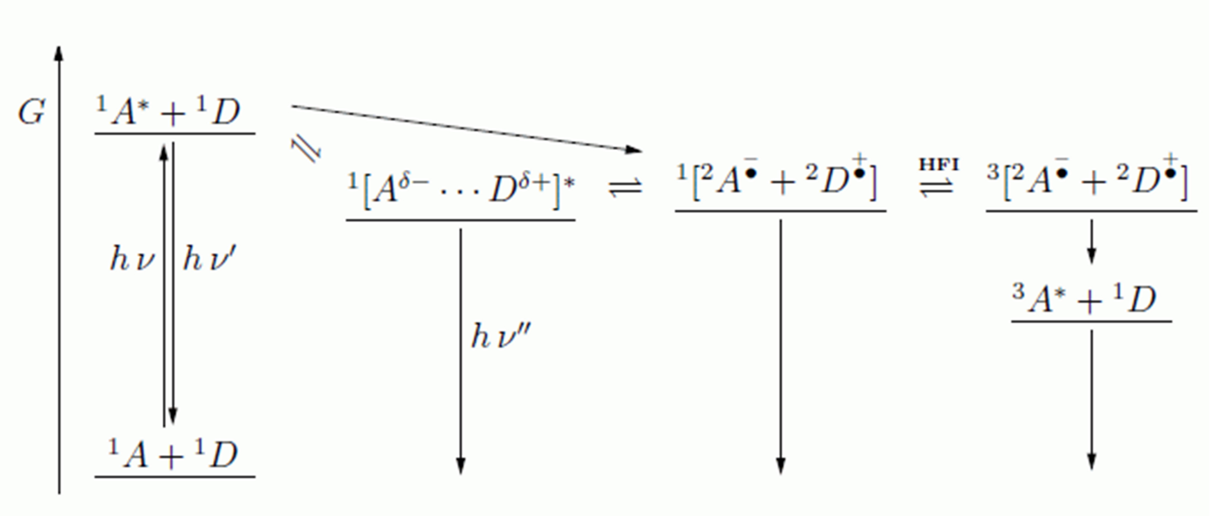

Figure 38 Photoinduced Electron Transfer[35]

The part influenced by the magnetic field is the intersystem crossing of the radical ion pair, which leads from a singlet to a triplet state. So in order to observe this influence at first the singlet radical ion pair is needed. The conversion can only happen when the ions diffuse slightly apart[36], because the spin must be able to reverse itself. This is not possible at small distances, because the energy of the spin pairing, that has to be overcome, is a function of the distance. As a consequence a certain distance has to be achieved between the two ions before intersystem crossing can occur.

The interesting part concerning the dielectric constant mixture is the formation of the ion pair, which is dependent on the dielectric constant. If an ion pair is formed, the overall charge is still zero, but a charge separation has taken place. This means that the solvent adjusts itself around the ion pair according to the idea for the outer reorganisation energy. This is illustrated in the following graph:

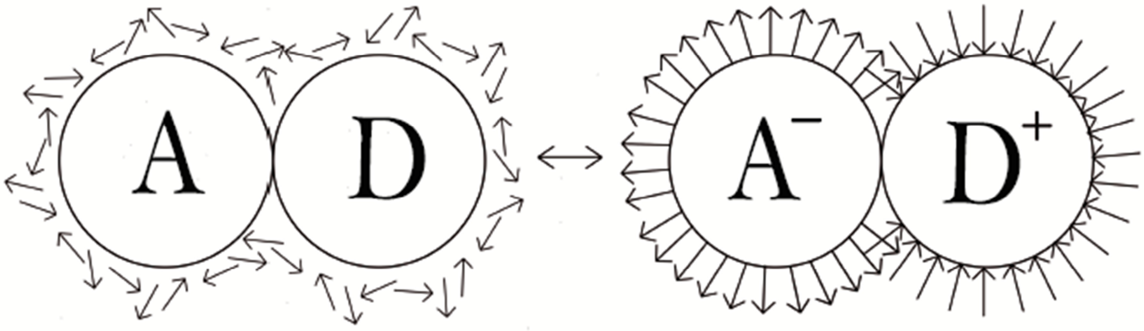

Figure 39 Solvent Reorganization

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[35] Figure taken from (22) page 7

[36] although it says “apart” the distance between the ions is still in the range where they can be considered an ion pair

A high dielectric constant promotes ion formation. As a consequence the magnetic field effect increases with the dielectric constant, as the number of radical ion pairs increases. At the same time a high dielectric constant also promotes dissociation of ion pairs.
A simple explanation of this effect can be given by looking at Coulomb's law:

Equation 27 Coulomb's Law[37]

$$F = \frac{q_1 q_2}{\varepsilon_0 \varepsilon_r d^2}$$

F = force
q_i = magnitudes of the electrical charge of particle i
ε_0 = static dielectric constant
ε_r = relative dielectric constant
d = distance between the two particles

The bigger F is the stronger is the force that keeps the two differently charged ions together. If ε or the distance between the two ions is increased, the force decreases. When the force falls under a certain value it is too weak to keep the ions together and the ion pair is broken. This means that with a high dielectric constant the distance, that is necessary to break the ion pair, decreases, or that the distance, which is needed between two free ions to become an ion pair, is decreased. The reason for the movement of the ion pair and the possible breaking of it, due to movement, is diffusion. So ion pairs are less favoured in solvents with a high dielectric constant.[38]
Combining both effects means that, until a dielectric constant of about 13 is reached, the magnetic field effect should increase with the dielectric constant. After that, if ε is further increased, the effect slowly decays. This is the reason that, for this mixture, a dielectric constant range of 5 to 20 has been aimed at.
The refractive index has to be kept constant, because it also influences the outer reorganisation energy like the dielectric constant, while the temperature and the viscosity must stay constant, because both influence the diffusion rate. With the dielectric constant mixture this is the case and the above described effect of the dielectric constant on the magnetic field effect can be observed using this mixture.

5.4 Conclusion

Although only the mole fractions for one mixture could be successfully determined, this thesis shows that it is definitely possible to create such mixtures. It is also possible to find the values for the viscosity and the temperature mixture, if the work is continued. The application ideas discussed at "5 Outlook" are only examples. These kinds of mixtures are useful for everyone, who works with electron transfer reactions, as certain dependencies can be eliminated or controlled. This allows conducting experiments that were not possible before, and alleviate many of the already established experiments.
Further research in this field will definitely be conducted.

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[37] See (28)
[38] For further information on ion pair formation in organic solvents along with experimental values see (23)

6 Appendix

6.1 VBA Code

```
Sub Epsilon_DE()
Dim F As Single
Dim CR As Single
Dim G As Integer
Dim NP As Integer
Dim Agent(150, 12) As Double
Dim New_Generation(150, 12) As Double
Dim Mutation(12) As Double
Dim Trial(12) As Double
Dim r1 As Integer 'Random Index 1
Dim r2 As Integer 'Random Index 2
Dim r3 As Integer 'Random Index 3
Dim rI As Integer 'Random Index for Crossover
Dim Ausgabe(12) As Double

Dim e_BN As Double
Dim e_AN As Double
Dim e_PC As Double
Dim x1 As Double
Dim x2 As Double
Dim x3 As Double
Dim i As Integer
Dim j As Integer
Dim Epsilon As Double
Dim wDK As Worksheet
Dim Zwischenspeicher As Double

Set wDK = ThisWorkbook.Sheets("DK")

'Parameter Setting
F = 0.8
CR = 0.9


'Initialization
NP = 0
Do
    Randomize
    Agent(NP + 1, 1) = (5000 + 5000) * Rnd - 5000
    Agent(NP + 1, 2) = (20000 + 5000) * Rnd - 5000
    Agent(NP + 1, 3) = (CDbl(30000) + 5000) * Rnd - 5000
    Agent(NP + 1, 4) = (40000 + 5000) * Rnd - 5000
    Agent(NP + 1, 5) = (CDbl(200000) + CDbl(5000)) * Rnd - CDbl(5000)
    Agent(NP + 1, 6) = (1 + 100000) * Rnd - 100000
    Agent(NP + 1, 7) = (50000 + 1000) * Rnd - 1000
    Agent(NP + 1, 8) = (1000 + 50000) * Rnd - 50000
    Agent(NP + 1, 9) = (50000 + 50) * Rnd - 50
    Agent(NP + 1, 10) = (5000 + 5000) * Rnd - 5000
    Agent(NP + 1, 11) = (5000 + 5000) * Rnd - 5000
    Agent(NP + 1, 12) = (5000 + 5000) * Rnd - 5000
```

```
    For j = 7 To 41
        x1 = wDK.Cells(j, 6).Value
        x2 = wDK.Cells(j, 7).Value
        x3 = wDK.Cells(j, 8).Value
        e_AN = x1 * Log(wDK.Cells(j, 2).Value)
        e_BN = x2 * Log(wDK.Cells(j, 3).Value)
        e_PC = x3 * Log(wDK.Cells(j, 4).Value)
        Epsilon = Exp(e_AN + e_BN + e_PC + ((x1 * x2) / wDK.Cells(j,
                   1).Value) * (Agent(NP + 1, 1) + Agent(NP + 1, 2) * (x1 -
                   x2) + Agent(NP + 1, 3) * (x1 - x2) ^ 2) + ((x1 * x3) /
                   wDK.Cells(j, 1).Value) * (Agent(NP + 1, 4) + Agent(NP +
                   1, 5) * (x1 - x3) + Agent(NP + 1, 6) * (x1 - x3) ^ 2) +
                   ((x2 * x3) / wDK.Cells(j, 1).Value) * (Agent(NP + 1, 7)
                   + Agent(NP + 1, 8) * (x2 - x3) + Agent(NP + 1, 9) * (x2
                   - x3) ^ 2) + ((x1 * x2 * x3) / wDK.Cells(j, 1).Value) *
                   (Agent(NP + 1, 10) + Agent(NP + 1, 11) * (x1 - x2 - x3)
                   + Agent(NP + 1, 12) * (x1 - x2 - x3) ^ 2))
        Agent(NP + 1, 0) = Agent(NP + 1, 0) + Sqr((Epsilon - wDK.Cells(j,
10).Value) ^ 2)
    Next j
    NP = NP + 1
Loop Until NP = 150

Do
    For NP = 1 To 150

        'Selection Random Indizes
        Randomize
        Do
            r1 = CInt((150 - 1) * Rnd + 1)
        Loop Until r1 <> NP
        Do
            r2 = CInt((150 - 1) * Rnd + 1)
        Loop Until r2 <> NP And r2 <> r1
        Do
            r3 = CInt((150 - 1) * Rnd + 1)
        Loop Until r3 <> NP And r3 <> r2 And r3 <> r1

        'Mutation
        For i = 1 To 12
            Mutation(i) = Agent(r1, i) + F * (Agent(r2, i) - Agent(r3, i))
        Next i

       'Crossover
       Randomize
       rI = CInt((12 - 1) * Rnd + 1)
        For i = 1 To 12
            Randomize
            If i = rI Then
                Trial(i) = Mutation(i)
            ElseIf Rnd <= CR Then
                Trial(i) = Mutation(i)
            Else
                Trial(i) = Agent(NP, i)
            End If
        Next i

        Trial(0) = 0

        For j = 7 To 41
            x1 = wDK.Cells(j, 6).Value
```

```
            x2 = wDK.Cells(j, 7).Value
            x3 = wDK.Cells(j, 8).Value
            e_AN = x1 * Log(wDK.Cells(j, 2).Value)
            e_BN = x2 * Log(wDK.Cells(j, 3).Value)
            e_PC = x3 * Log(wDK.Cells(j, 4).Value)
            Epsilon = CDbl(Exp(e_AN + e_BN + e_PC + ((x1 * x2) /
                     wDK.Cells(j, 1).Value) * (Trial(1) + Trial(2) * (x1 -
                     x2) + Trial(3) * (x1 - x2) ^ 2) + ((x1 * x3) /
                     wDK.Cells(j, 1).Value) * (Trial(4) + Trial(5) * (x1 -
                     x3) + Trial(6) * (x1 - x3) ^ 2) + ((x2 * x3) /
                     wDK.Cells(j, 1).Value) * (Trial(7) + Trial(8) * (x2 -
                     x3) + Trial(9) * (x2 - x3) ^ 2) + ((x1 * x2 * x3) /
                     wDK.Cells(j, 1).Value) * (Trial(10) + Trial(11) * (x1
                     - x2 - x3) + Trial(12) * (x1 - x2 - x3) ^ 2)))
            On Error Resume Next
            If Epsilon - wDK.Cells(j, 10).Value >= 0 Then
                Trial(0) = Trial(0) + (Epsilon - wDK.Cells(j, 10).Value)
            Else
                Trial(0) = Trial(0) + (Epsilon - wDK.Cells(j,10).Value)*-1
            End If
        Next j

        'Selection
        If Trial(0) < Agent(NP, 0) Then
            For i = 0 To 12
                New_Generation(NP, i) = Trial(i)
            Next i
        Else
            For i = 0 To 12
                New_Generation(NP, i) = Agent(NP, i)
            Next i
        End If
    Next NP

    'Save New Generation values to Agent
    For NP = 1 To 150
        For i = 0 To 12
            Agent(NP, i) = New_Generation(NP, i)
        Next i
    Next NP

    'Output
    For i = 0 To 12
        Ausgabe(i) = Agent(1, i)
    Next i
    For i = 2 To 150
        If Agent(i, 0) < Ausgabe(0) Then
            For j = 0 To 12
                Ausgabe(j) = Agent(i, j)
            Next j
        End If
    Next i

    For i = 1 To 12
        wDK.Cells(2, i + 1).Value = Ausgabe(i)
    Next i
    wDK.Cells(3, 2).Value = Ausgabe(0)

Loop Until Ausgabe(0) < 15

End Sub
```

6.2 Circuit Diagrams

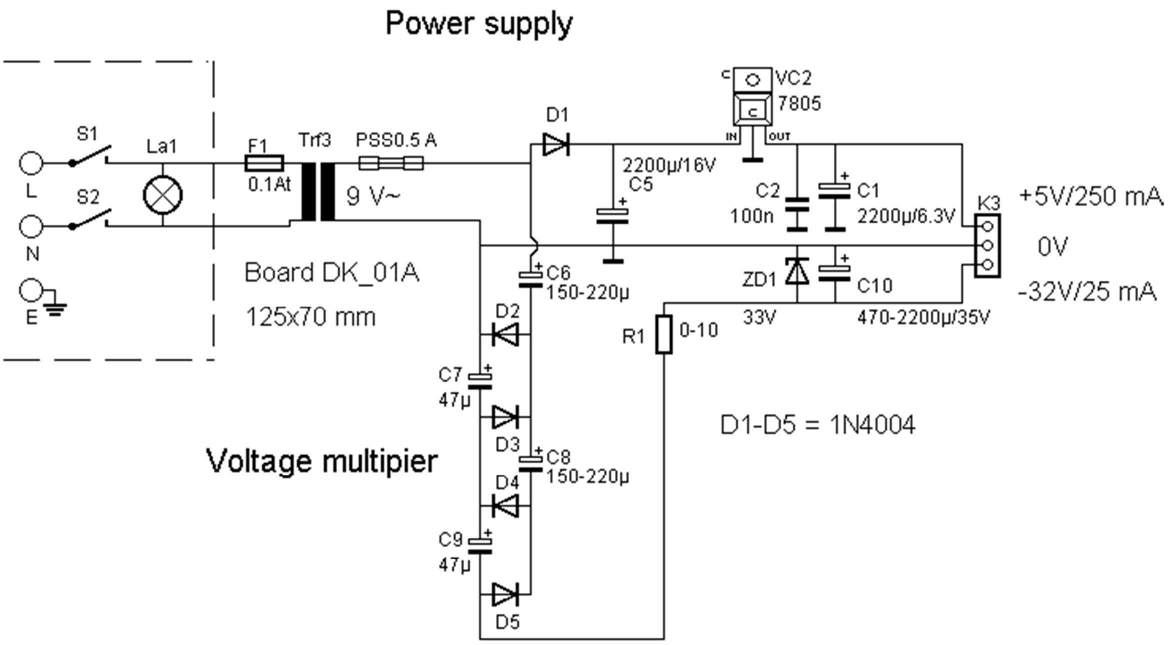

Figure 40 Circuit Diagram

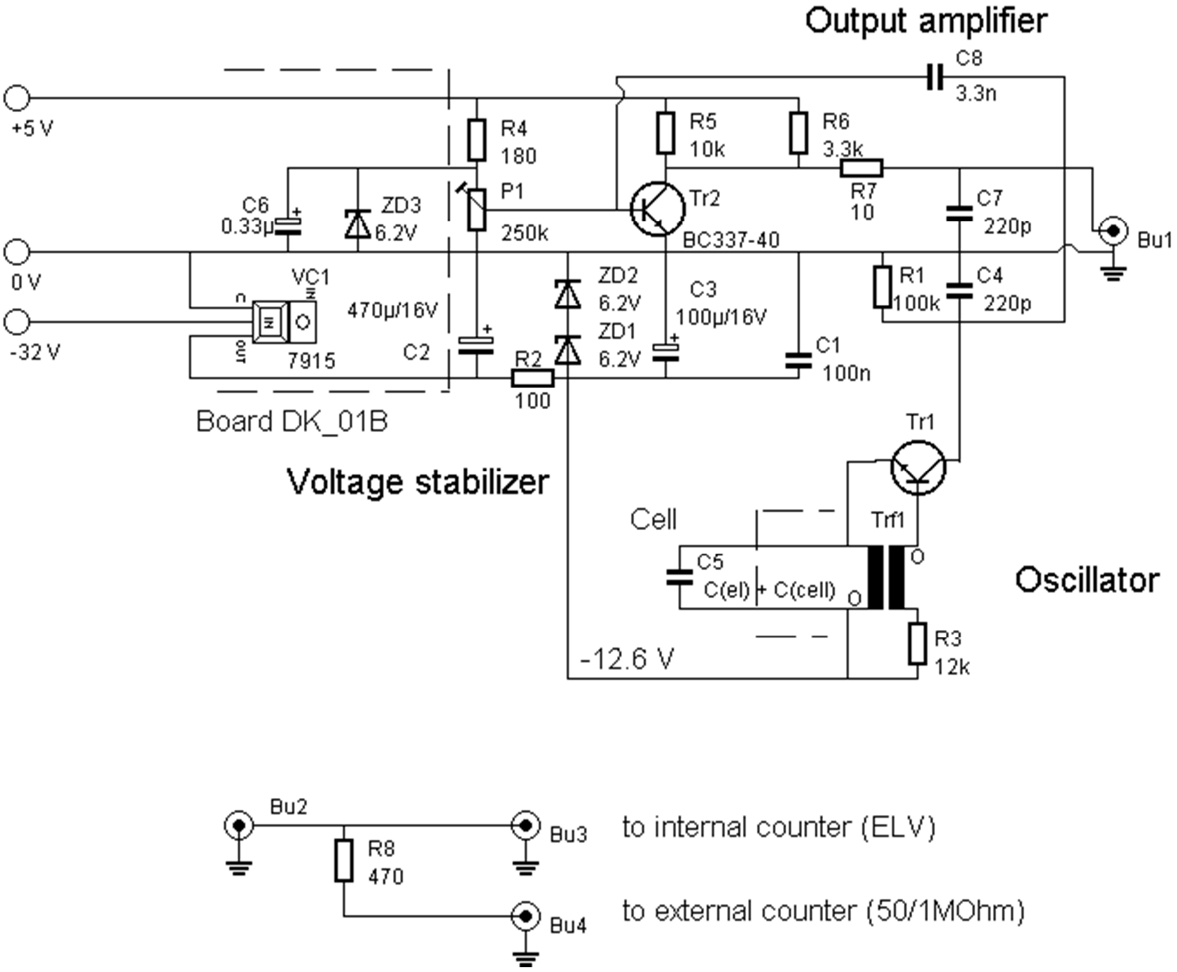

Figure 41 Circuit Diagram

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6.6 Bibliography

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