

Verification of empirical drinking theories in binary mixtures of cervisia and vinum.

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IN HONOUR OF DR. U. KAATZE ON THE OCCASION OF HIS RETIREMENT

In order to evaluate the validity of famous German drinking laws we measured various physical parameters for the binary mixture *cervisia/vinum*. Here, the measured dependence of sound velocity, density, ultrasonic attenuation, dielectric permittivity and light scattering on the mass fraction were measured. The findings were interpreted in terms of validity of the popular laws, but also in terms of time dependent maturation or degradation of either substance. From these measurements we conclude that some of the laws prove valid while some need reformulation. Furthermore, we strongly suggest confirming our findings from *in vitro* studied to *in vivo* systems, preferably in appropriate turbid (i.e. smoky) habitats like original German Biergartens. While restrictive German legislation will restrict such experimental approaches in the near future we suggest reacting to these condition by drinking faster.

1. Introduction

It is well known in literature, that the consequences of the consumption of the substances *cervisia* and *vinum* on a single evening strongly depend on the chronological order of their intake. Therefore, most people generally accept the empirical formulas

$$\textit{Bier auf Wein, das lass sein!} \quad (1)$$

and

$$\textit{Wein auf Bier, das rat ich Dir!}, \quad (2)$$

respectively. Here *Bier* denotes *cervisia* and *Wein* is a synonym for *vinum*. Contrary to the wide acception of eq. (1) and (2), to our knowledge, there have been no attempts to either verify or disprove them experimentally so far.

Another field, where many empirical theories can be found, concerns the time dependence of the quality of both the investigated substances. The probably best known of these theories are

$$\textit{Ein Pils braucht sieben Minuten!} \quad (3)$$

and

$$\textit{Wein muss atmen!} \quad (4)$$

Here *Pils* is another common synonym for *cervisia*. While the first one of them gives a concrete

description, that the quality of *cervisia* will show a maximum at $t=7$ min, the latter one for *vinum* is rather vague. This gives an additional need for a detailed investigation of the quality-vs-time behavior of this substance.

2. Experimental

2.1 Solutions

Cervisia (*Hasseroeder*, Wernigerode, Germany, ethanol content 4.9% vol/vol) and *Vinum* (*Domkellerstolz*, Burgherrn, Bernkastel-Kues, Germany, ethanol content 9.5% vol/vol) have been purchased from *tegut*, Goettingen, Germany and have been used without further purification, as the purity was approved by *Deutsches Reinheitsgebot von 1516* in one case (*cervisia*) and *Guetesiegel der Europäischen Union* in the other case (*vinum*). Binary mixtures have been prepared by weighing appropriate amounts of the substances into flasks. Between the measurements the substances were kept cool and dark. After the measurements the substances were biodegraded by the experimentalists livers.

2.2 Auxiliary Measurements

The density ρ of the samples has been measured with the aid of a vibrating tube densitometer with built-in reference oscillator and Peltier temperature

control (Physica DMA 500, Anton Paar, Graz, Austria). The sensitivity of the method was $\Delta\rho/\rho=5\cdot 10^{-6}$. Due to imperfect wetting of the tube the error in the data may be somewhat larger, up to $\Delta\rho/\rho=5\cdot 10^{-4}$.

The specific electric (low frequency) conductivity σ of the liquids was obtained using a laboratory conductivity meter (inolab Cond 720 with cell TetraCon 325, WTW, Weinheim, Germany) that allows σ to be determined to within 0.5%, with the temperature of the cell measured with an error less than 0.1 K.

The sound velocity c_s of the samples has been determined at a frequency ν around 300 kHz by means of a fixed pathlength cavity resonator method. The liquid was contained in a small-volume cylindrical cavity the faces of which were formed by plane X-cut quartz discs. One quartz was operated as transmitter the other one as receiver. The transfer function of the cell was measured to obtain a series of resonance frequencies of the cavity from which the sound velocity was calculated. The cell was calibrated against doubly distilled, de-ionized, and degassed water with well-known sound velocity. The resolution in the sound velocity measurement was $\Delta c_s/c_s=10^{-4}$. The temperature of the resonator cell was controlled and measured with an error smaller than 0.02 K.

2.3 Ultrasonic spectrometry

At frequencies between 100 kHz and 300 MHz the ultrasonic attenuation coefficient α of the samples has been measured using two different frequency domain methods. At frequencies below 15 MHz, where α is small, a cavity method has been applied in which the pathlength of interactions of the sonic field with the liquid was virtually increased by multiple reflections. The complex resonator transfer function has been recorded in a frequency range around a principal resonance peak in order to carefully consider the effects from higher order modes. The half-power bandwidth of the principal resonance without disturbances by higher order satellite modes has been used to calculate the quality factor Q_{total} of the liquid-filled resonator. Intrinsic cell losses contributing to Q_{total} have been considered by the common relation

$$Q_{liquid}^{-1} = Q_{total}^{-1} - Q_{cell}^{-1} \quad (5)$$

that is based on energy arguments. The quality factor Q_{cell} representing the intrinsic losses has been obtained from reference measurements using liquids with well-known attenuation coefficient and with matched sound velocity and density. Two resonator cells have been used. At $f < 1.9$ MHz the faces of the cell were concavely shaped, in order to reduce diffraction effects. In the frequency range between 1.9 and 15 MHz plane quartz transducer discs have been used as faces. They were, however, mounted in a way that they were slightly bent, thus featuring favourable properties of biconcave cells.

At frequencies above 3 MHz absolute α measurements have been performed by transmitting pulse-modulated sonic waves through a cell of variable length. At each frequency of measurement the transfer function of the liquid-filled cell has been recorded as a function of sample length and α has been obtained by fitting the corresponding analytical form to the data. Two cells have been used, one at lower ($3 \leq f \leq 60$ MHz) and another one at higher ($30 \leq f \leq 400$ MHz) frequencies. The former was equipped with X-cut quartz transducers, the latter with 36° Y-cut lithium niobate transducer discs. Both types of transducers were operated at odd overtones of their fundamental frequency of thickness vibrations.

The experimental errors in the α data as following from repeated measurements, including all cleaning and refilling procedures between different runs, are those given below: $\Delta\alpha/\alpha=0.1$, 0.1-3 MHz; $\Delta\alpha/\alpha=0.02$, 3-25 MHz; $\Delta\alpha/\alpha=0.01$, 25-300 MHz; $\Delta\alpha/\alpha=0.02$, 300-400 MHz. The temperature of the cells was controlled to within ± 0.03 K by circulating thermostate fluid through suitable channels in the cells and also through an additional thermostatic coat. Errors from such temperature fluctuations were negligibly small in the attenuation coefficient data. Also omitted were the small errors from fluctuations in the frequency f of measurements ($\Delta f/f < 10^{-4}$).

2.4 Dielectric Spectroscopy

The complex permittivity $\epsilon(f)$ of the sample liquids has been measured as a function of frequency between 0.5 MHz and 1.5 GHz using a frequency domain method. Within this frequency range the wavelength of the electromagnetic field within the samples was sufficiently large to enable a quasistatic approach. Reflection coefficient measurements on a coaxial cell from the cutoff variety were performed, utilizing a computer-controlled network analyzer (HP 8753A) combined with a suitable reflection test set (HP 85044A). The specimen cell essentially consisted of a coaxial line/circular waveguide transition. The waveguide, filled with the sample, was excited below the cutoff frequency of its fundamental TM_{01} field mode so that an evanescent electromagnetic field was set up in the waveguide section. In order to match the cell capacity to the measuring range, a device with geometrical length $l=10$ mm of the coaxial line part, containing the liquid under test, was used. A model analysis of this type of sample cell resulted in a rather simple lumped element equivalent circuit representation. The parameters of this equivalent circuit have been determined using the empty cell and the cell filled with suitable reference liquids, such as water or acetone.

The temperature of the samples was controlled during measurements to within 0.05 K and was measured with an error less than 0.02 K. The error in the frequency f of the electromagnetic field was negligibly small. The experimental errors in the

permittivity data at $f \leq 1$ GHz were smaller than 1.5% in both $\epsilon'(f)$ and $\epsilon''(f)$. Above 1 GHz errors were 5% in $\epsilon'(f)$ and 7% in $\epsilon''(f)$.

2.5 Dynamic light scattering

The mutual diffusion coefficient

$$D = q^{-2} \cdot \Gamma_l(q, T) \quad (6)$$

of the liquids has been derived from the decay rate $\Gamma_l(q, T)$ of the normalized autocorrelation function

$$S_l(q, T, t) = \exp\{-t \cdot \Gamma_l(q, T)\} \quad (7)$$

of the light quasielastic scattered from the sample. A self-beating digital photon-correlation spectrometer has been used for this purpose which was provided with a goniometric system and with a special planar-window cell to enable variations of the scattering angle Θ and thus of the wave vector \vec{q} selected by the scattering geometry. The amount of this vector

$$q = \frac{4 \cdot \pi \cdot n}{\lambda_l} \cdot \sin\left(\frac{\Theta}{2}\right) \quad (8)$$

depends on the refractive index, measured with the aid of a refractometer (Zeiss, Überkochen, Germany), and on the wavelength λ_l of the incident light. A frequency-doubled Nd:YAG laser has been used as light source with $\lambda_l = 532$ nm. S_l was obtained from a real-time analysis of the scattered light using a digital correlator board (ALV-500/E, Laser, Langen, Germany) which allows for correlation function measurements within a time-scale ranging from $2 \cdot 10^{-7}$ s to $3.4 \cdot 10^3$ s. The experimental error in the diffusion coefficient values was smaller than 5%. The temperature of the sample was controlled to within ± 0.02 K and was measured with an error less than 0.01 K.

From the diffusion coefficient (eq. (6)), the particle radius R of the investigated samples can be calculated with the Einstein-Stokes relation:

$$D = \frac{k_B \cdot T}{6 \cdot \pi \cdot \eta_S \cdot R} \quad (9)$$

Here η_S is the shear viscosity of the sample. As we were lazy to measure it separately, it was assumed to be similar to that of pure water for both substances. This seems to be a rather good approximation as filling a glass of water takes exactly the same time as filling one of cervisia or vinum, respectively.

3. Results

3.1 Auxiliary Measurements

The conductivity and the density of the binary mixtures cervisia-vinum are given in Fig.1 and Fig.2, respectively. It is obvious, that for both measured quantities an increasing behavior with increasing volume fraction of vinum and a decreasing behavior with increasing volume fraction of cervisia can be observed. As the former

case corresponds to the drinking tactics given in eq. (2) and the latter case to that given in eq. (1) there is strong evidence that these tactics are not only drinking myths but can well be verified with the present results. Using the additional, well-accepted formula

$$Dichter \text{ is ' besser!} \quad (10)$$

that gives us a direct relationship between density and quality, it can be easily concluded from the density measurements, that eq. (1) and eq. (2) are valid.

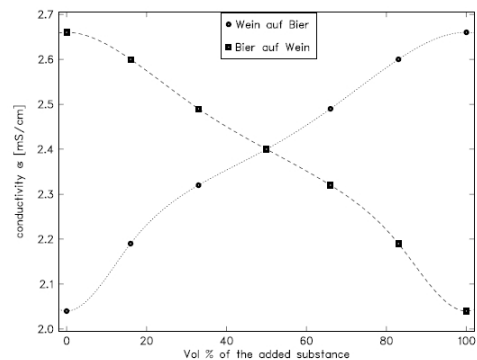


Fig.1: Conductivity of binary mixtures of cervisia and vinum plotted versus the volume fraction of the added substance. Lines are drawn to irritate the eyes.

The analysis of the conductivity measurements is somewhat more complicated, as there is no direct relationship between conductivity and quality to our knowledge. We mention however, that we found a hidden hint for such a relation – an older word for conductivity is conductibility. This word includes the word ability and it is doubtless, that more ability means higher quality.

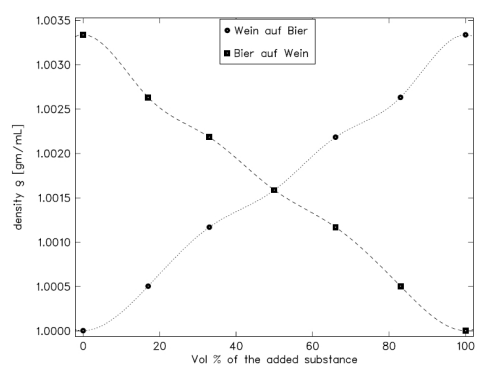


Fig.2: Density of binary mixtures of cervisia and vinum plotted versus the volume fraction of the added substance. Lines are drawn to irritate the eyes.

Hence both the density and the conductivity measurements clearly verify eq. (1) and eq. (2) as the most successful succession of drinking.

We claim all rights on this equation – no unauthorized publication and use without permission!

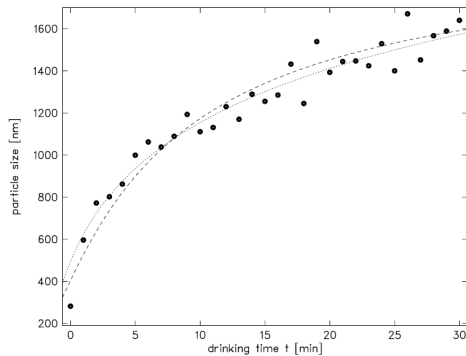


Fig.6: Time dependent particle size in cervisia at 25 °C. The lines are the exponential (dashed line) and the logarithmic (dotted line) descriptions given in the text.

It should be mentioned, that a logarithmic function can be used to describe the data as well (see Fig.6) – therefore we also claim all rights on the brand name *logarithmic beer*.

3.4 Dielectric spectroscopy

Measurement of the real and the imaginary part of the dielectric permittivity of cervisia, vinum and a 1:1-mixture of both the substances makes no sense to us without any fundamental background knowledge. We did it anyway, because the spectra look really cool and professional and it strongly increases the measuring diversity of this publication. Additionally, there is another reason, why we performed these measurements: We did it, because we are able to!

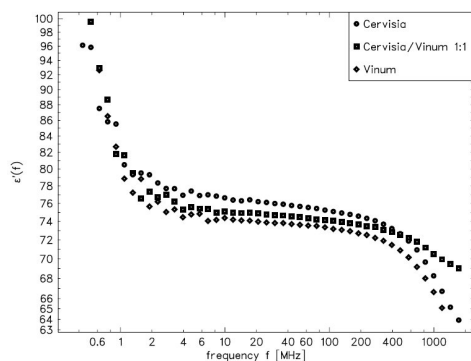


Fig.7: Real part $\epsilon'(f)$ of the dielectric permittivity of cervisia, vinum and a mixture. For explanation see text (but not this one).

As Fig. 7 and Fig. 8 show the real part and imaginary part, respectively, of the dielectric permittivity, it is obvious that the analysis of this complex quantity is a very complex problem.

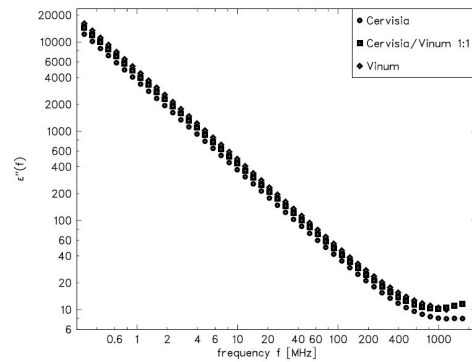


Fig.8: Negative imaginary part $\epsilon''(f)$ of the dielectric permittivity of cervisia, vinum and a mixture. For explanation see text (but not this one).

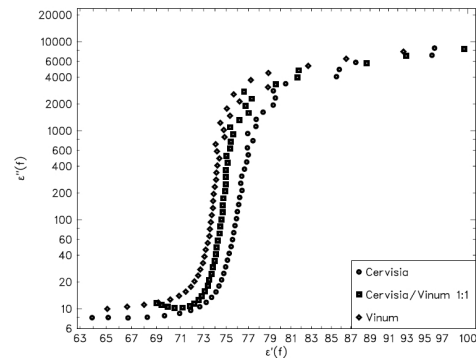


Fig.9: Cole-Cole-Plot of the dielectric spectra of cervisia, vinum and a mixture. For explanation see text (but not this one).

3. Conclusions

Prost! Cheers! Na zdrowie! Santé! Op uw gezondheid! Skål! Serefe!

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References

- (1) The Bible.
- (2) Der Volksmund.
- (3) Die innere Stimme.
- (4) Das Dschungelbuch.
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