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Temperature Behavior of Electric Relaxational Effects due to Ionic Conductivity in Liquid Lactones

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Abstract This paper concerns the studies of temperature and frequency behavior of the complex impedance, electric modulus, and electric conductivity due to an ionic current in liquid γ -butyrolactone (GBL) and γ -valerolactone (GVL). The frequency of the applied electric stimulus (500 Hz to 5 MHz) corresponds to the static dielectric regime of the lactones. The studies were performed in the temperature range of 263 K to 313 K. It was shown that in the static dielectric case, the dc ionic conductivity (σ_{DC}) and the static dielectric permittivity (ϵ_s) determine the relaxational behavior of the impedance (Z^*) and the electric modulus (M^*) of the molecular liquids and both spectra are of the Debye-type characterized by the same conductivity relaxation time (τ_σ). Both σ_{DC} and τ_σ of GBL and GVL fairly well fulfill an Arrhenius temperature dependence with very similar values of the thermal activation energy $E_{\sigma_{DC}} \approx E_{\tau_\sigma} \approx 25 \text{ kJ} \cdot \text{mol}^{-1}$. The temperature dependence of the static dielectric permittivity and its temperature derivative is analyzed and interpreted in terms of the dipolar aggregation in the studied lactones.

Keywords Electric conductivity · Electric impedance · Electric modulus · Lactones · Relaxational effects

1 Introduction

Lactones, especially γ -butyrolactone (GBL), are used as “green” solvents in various chemical engineering processes, including the production of biodegradable polymers [1–7]. However, some physical properties of GBL, such as a low melting point

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(≈ 230 K) and a low viscosity ($\eta = 1.7$ mPa·s, at 303 K), on the one hand, and a high boiling point (≈ 477 K) and relatively high static dielectric permittivity ($\epsilon_s \approx 40$, at 303 K), on the other hand, make this compound very attractive for application in Li-batteries [8–12]. In comparison to the liquid media currently used in the batteries, GBL (possibly in a mixture with an other liquid, such as ethyl carbonate [8,9], for example) can assure an enhanced solubility of ionic salts and, consequently, a higher conductivity, i.e., can improve Li-batteries remarkably including their performance at low temperatures. That aspect of GBL application makes its dielectric and conductivity temperature behavior especially important.

This paper presents results of studies on the temperature dependence of the electric and dielectric properties of GBL (and its homolog, GVL) as seen in different electric relaxation spectroscopies.

The electric relaxation methods are commonly used in studies of the ionic conductivity and molecular dynamics in different dielectric materials, such as glasses, crystals, and liquids [13–23]. The term “electric relaxation” may concern, in principle, the frequency dependence of four complex quantities: the impedance $Z^*(\omega) = Z'(\omega) + jZ''(\omega)$, the conductivity $\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega)$, the dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega)$ and the electric modulus $M^*(\omega) \equiv 1/\epsilon^* = M'(\omega) + jM''(\omega)$; $\omega = 2\pi f$ is the angular frequency of the electric stimulus, f is the linear frequency, and $j = \sqrt{-1}$. All of these complex quantities are alternative representations of the same macroscopic relaxation data and can be easily transformed to each other according to the scheme:

$$\frac{1}{\epsilon^*(\omega)} = M^*(\omega) = j\omega C_0 Z^*(\omega) = \frac{j\omega\epsilon_0}{\sigma^*(\omega)}, \quad (1)$$

where $C_0 = k\epsilon_0$ is the electrical capacity of an empty measuring cell ($k = S/l$, S and l are the electrode surface and the distance between the electrodes, respectively) and $\epsilon_0 = 8.85$ pF · m⁻¹ is the permittivity of free space. Each of the above complex functions emphasizes a different aspect of the electric phenomena occurring in conducting liquids, and the usefulness of particular function depends, in practice, on the specificity of the phenomenon.

The data presented in this paper concern a relatively simple situation: we will operate in the frequency region where the relaxation effects can be related only to the ionic current occurring in the liquid. The dielectric relaxation due to the lactone dipolar reorientation, which results in the displacement current, takes place in the much higher (gigahertz) frequency region [24], so in our experiment we are dealing with the static dielectric regime.

2 Experimental

The studied compounds— γ -butyrolactone and γ -valerolactone—of purities of $\geq 99\%$ (Sigma-Aldrich) were stored over molecular sieves (4 Å) before investigation. The electric conductivity of the lactones results only from some thermally activated ionic impurities present in the liquids. The studies were performed in the temperature range of 263 K to 313 K.

The impedance spectra of GBL were recorded with the use of an HP 4194A impedance/gain phase analyzer in the frequency range from 500 Hz to 5 MHz. A measuring capacitor consisted of three plane electrodes (surface area of about 1 cm^2): one central and two grounded on each side, with a distance between them of about 0.2 mm. The shape of the capacitor electrodes is rectangular, and they are made with gold-plated copper. The capacitance of the empty cell used (C_0) was equal to about 10 pF. The probing electric field intensity E was equal to about $1 \text{ V} \cdot \text{mm}^{-1}$. The electrical heating of high performance with the use of a “Scientific Instruments” temperature controller, Model 9700, assured very good temperature stabilization (at the millikelvin level). Such equipment allows one to determine the impedance with an uncertainty of about 0.5 %.

3 Results and Discussion

The *dielectric spectrum* ($\varepsilon^*(\omega)$), in general, contains two contributions—(i) the dipolar relaxation (represented by the dielectric relaxation time, τ_D) and (ii) the dc ionic conductivity (σ_{DC}). For molecular liquids where the dielectric relaxation can be represented by a single relaxation-time and where the dipoles relax throughout the normal Brownian rotational motion, the relaxation spectra are described with the following Debye equation [25]:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau_D} + \frac{\sigma_{DC}}{j\omega\varepsilon_0}. \quad (2)$$

ε_s and ε_∞ denote, respectively, the static and high frequency limits of the dielectric permittivity of the material under investigation.

For frequencies low enough in comparison to those where the maximum of the dielectric loss of the studied system occurs ($\omega\tau_D \ll 1$), the Debye equation reduces to a simple form where the real (ε') and imaginary (ε'') parts of the permittivity are given by

$$\varepsilon' = \varepsilon_s, \quad \varepsilon''(\omega) = \sigma_{DC}/\omega\varepsilon_0. \quad (3)$$

Figure 1 presents the (a) real and (b) imaginary parts of the dielectric spectra of GBL, recorded at different temperatures, far from the dielectric relaxation region of the compound. The spectra of GVL are quite similar to those presented in the picture. The real part of the spectra (Fig. 1a) presents the static dielectric permittivity but, as seen in figure, for frequencies lower than about 10 kHz, one observes a very strong increase of the permittivity, and in the kilohertz region, the permittivity reaches a quite high value of about 10^3 . That apparent increase of the permittivity results certainly from the ionic polarization effects occurring near the blocking electrodes of the measuring cell.

The imaginary part of the dielectric spectrum (Fig. 1b) presents, according to Eq. 3, straight lines of slope -1 (on log–log scale). Both ε_s and σ_{DC} can be obtained, in principle, from analysis of the dielectric spectra with Eq. 3, provided the electrode effects are of a moderate intensity, such as in the case presented in Fig. 1. Because quite often the effects are so high that one meets serious difficulties in analysis of the dielectric

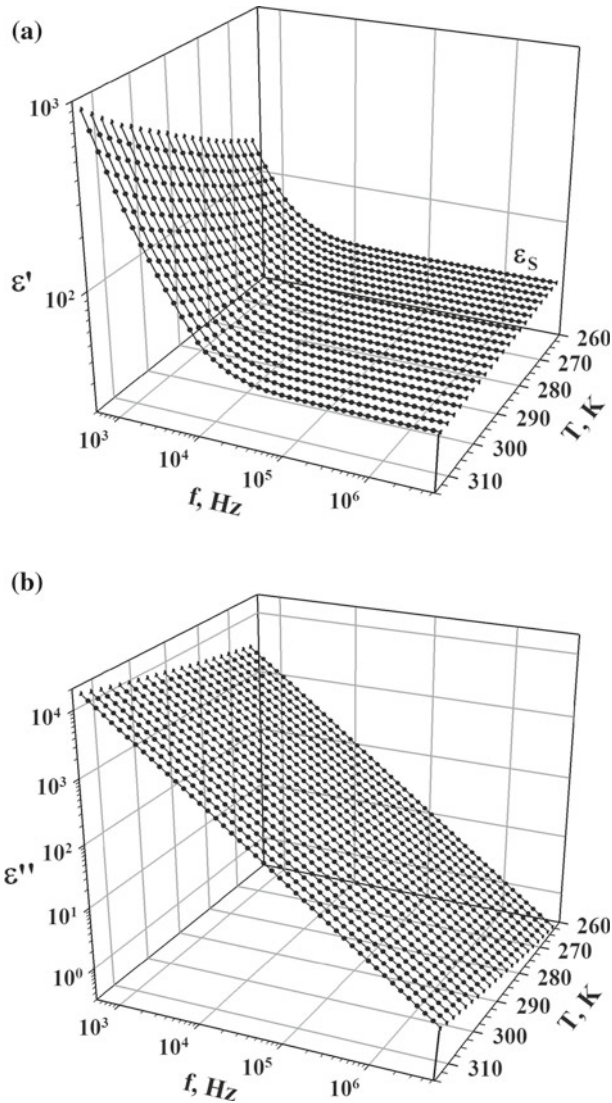


Fig. 1 Real (ϵ') and imaginary (ϵ'') parts of the dielectric spectra $\epsilon^*(\omega)$ of GBL, recorded at different temperatures

spectrum [26–28], it was proposed to transform the dielectric spectrum into the *electric modulus spectrum* defined as $M^*(\omega) = 1/\epsilon^*(\omega)$. So, the frequency dependence of the real (M') and imaginary (M'') parts of the electric modulus have, in general, the following form:

$$M'(\omega) = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2}, \quad M''(\omega) = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}. \quad (4)$$

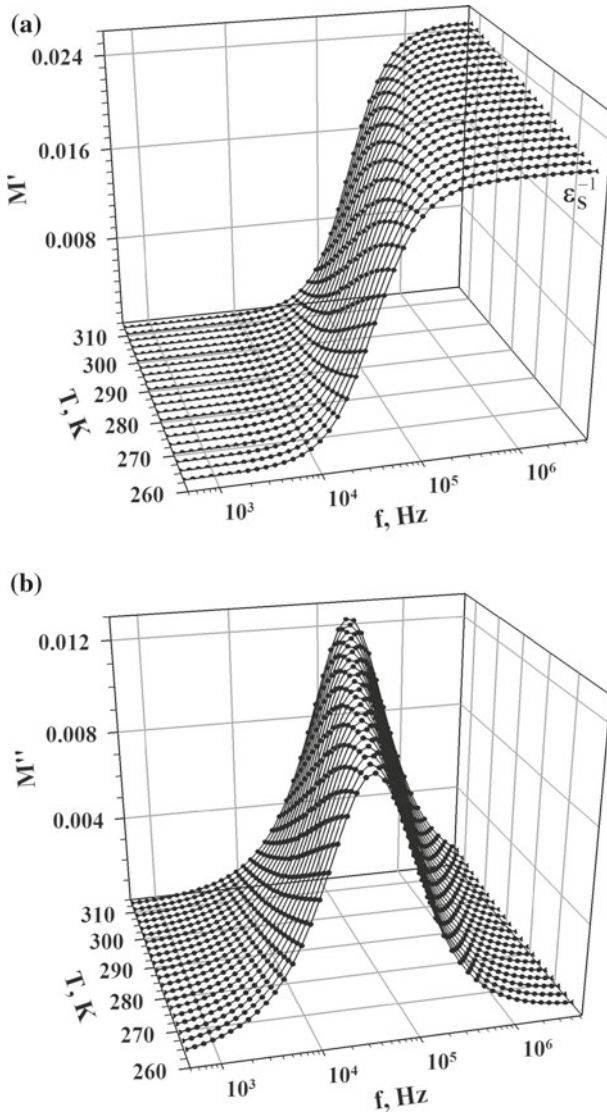


Fig. 2 Electric modulus spectra, $M^*(\omega) = 1/\varepsilon^*(\omega)$, of GBL, corresponding to the dielectric spectra from Fig. 1: (a) real M' and (b) imaginary M'' parts. *Solid lines* represent the best fit of Eq. 5 to the experimental data (*points*)

Figure 2 presents the electric modulus spectra of GBL at different temperatures, corresponding to the dielectric spectra from Fig. 1, and Fig. 3 presents the modulus spectra in the complex plane. Indeed, as can be seen in Fig. 2a, at low frequencies the parasitic effects vanish when one operates with the electric modulus spectra.

In the studied case of the ionic conductivity in the liquid being in the dielectric static regime (Eq. 3), Eq. 4 take the following particular form:

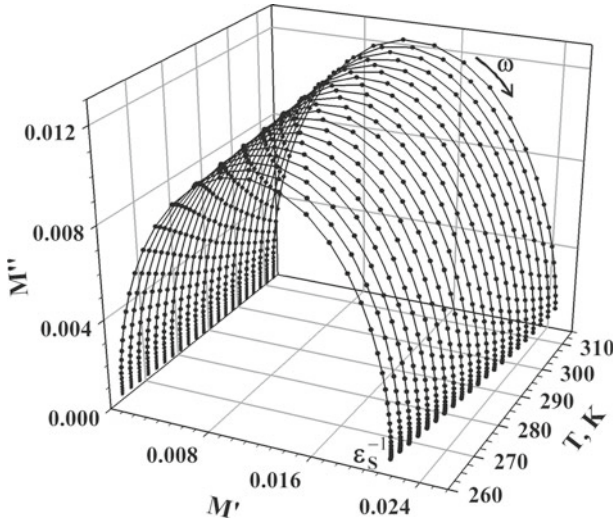


Fig. 3 Electric modulus spectra of GBL in the complex plane at different temperatures

$$M'(\omega) = \varepsilon_s^{-1} - \frac{\varepsilon_s^{-1}}{1 + \omega^2 \tau_\sigma^2}, \quad M''(\omega) = \frac{\varepsilon_s^{-1} \omega \tau_\sigma}{1 + \omega^2 \tau_\sigma^2}, \quad (5)$$

or in the complex notation:

$$M^*(\omega) = \varepsilon_s^{-1} - \frac{\varepsilon_s^{-1}}{1 + j\omega \tau_\sigma}. \quad (6)$$

The quantity

$$\tau_\sigma = \frac{\varepsilon_0 \varepsilon_s}{\sigma_{DC}} \quad (7)$$

is known in the literature as the conductivity relaxation time [14].

In Eqs. 5 and 6 one can easily recognize a frequency dependence of the Debye-type. In Fig. 2a, b, as well as in Fig. 3, the solid lines represent the best fit of Eq. 5 to the experimental electric modulus data (points) and it should be emphasized that the fit is perfect. The fitting procedure provides us with quite precisely determined values of the quantities ε_s and τ_σ .

For an easy and precise determination of the dc conductivity, the dielectric data presented in Fig. 1 are usually transformed into the *impedance spectra* $Z^*(\omega) = 1/j\omega C_0 \varepsilon^*(\omega)$. Then, the real (Z') and imaginary (Z'') parts of the complex impedance, have the following general form:

$$Z'(\omega) = \frac{1}{\omega C_0} \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}, \quad Z''(\omega) = -\frac{1}{\omega C_0} \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}. \quad (8)$$

Figure 4 presents the (a) real and (b) imaginary parts of the impedance spectra of GBL obtained according to Eq. 8. Figure 5 presents the impedance spectra of GBL in the complex plane. In our particular case, where the frequency range of the electric

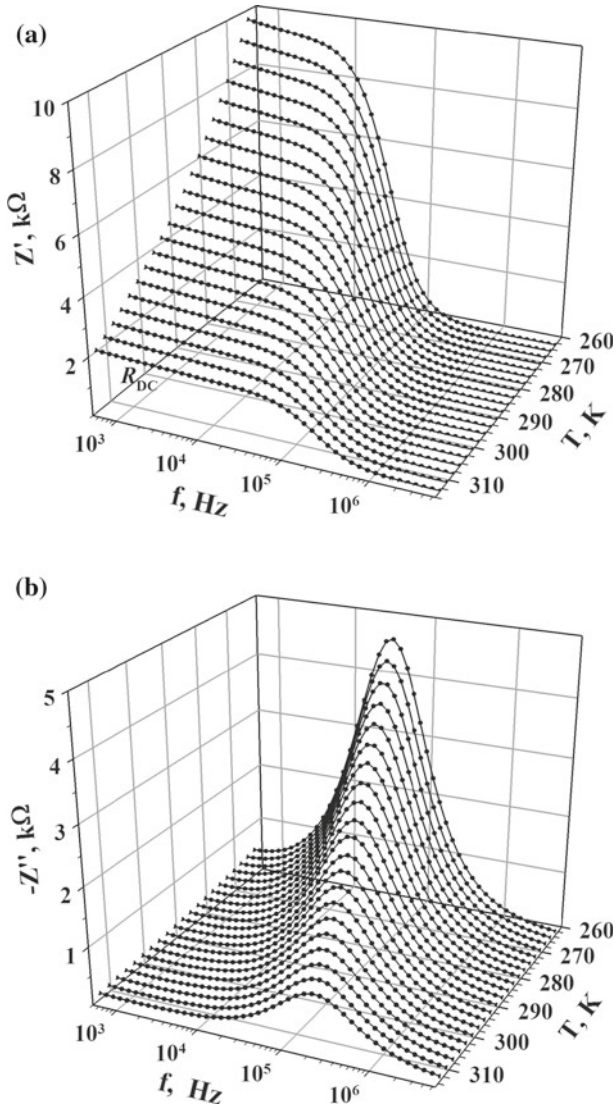


Fig. 4 Impedance spectra, $Z^*(\omega) = [j\omega C_0 \varepsilon^*(\omega)]^{-1}$, of GBL, corresponding to the dielectric spectra from Fig. 1: (a) real Z' and (b) imaginary Z'' parts. *Solid lines* represent the best fit of Eq. (9) to the experimental data (*points*)

stimulus corresponds to the static dielectric behavior of the liquid, one obtains, taking into account Eq. 1, the following form of Eqs. 8

$$Z'(\omega) = \frac{R_{DC}}{1 + \omega^2 \tau_\sigma^2}, \quad Z''(\omega) = -\frac{R_{DC} \omega \tau_\sigma}{1 + \omega^2 \tau_\sigma^2}, \quad (9)$$

or in the complex notation:

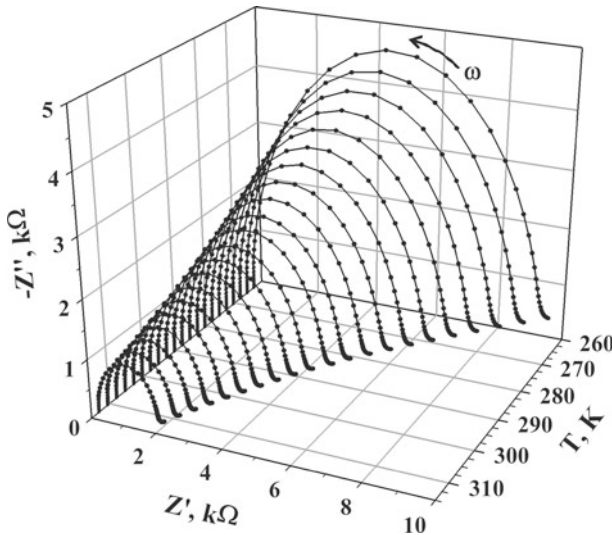


Fig. 5 Impedance spectra of GBL in the complex plane at different temperatures

$$Z^*(\omega) = \frac{R_{DC}}{1 + j\omega\tau_\sigma} \tag{10}$$

R_{DC} denotes the dc resistivity of the sample and τ_σ is given by Eq. 7. So, the relaxation of both quantities: the electric modulus $M^*(\omega)$ and the impedance $Z^*(\omega)$, is running with the same relaxation time, τ_σ . The quantities R_{DC} ($= 1/k\sigma_{DC}$) and τ_σ , resulting from the best fit of Eqs. 9 to the experimental impedance spectra, (solid lines in Figs. 4 and 5), can be used, according to Eq. 7, for determination of the static dielectric permittivity [29,30]

Finally, the complex conductivity ($\sigma^* = j\omega\varepsilon_0\varepsilon^*$), where, in general, the real (σ') and imaginary (σ'') parts have the form:

$$\sigma'(\omega) = \omega\varepsilon_0\varepsilon'', \quad \sigma''(\omega) = \omega\varepsilon_0\varepsilon', \tag{11}$$

for the discussion here of the static dielectric case are reducing themselves to a simple form:

$$\sigma' = \sigma_{DC}, \quad \sigma''(\omega) = \omega\varepsilon_0\varepsilon_s. \tag{12}$$

Figure 6 presents the conductivity spectra for GBL, at different temperatures. It seems to be important to notice in the figure, that the electrode polarization effects, resulting in the anomalously strong increase in the static permittivity, manifest themselves here as a deviation of the conductivity imaginary part from the linear frequency dependence.

The physical quantities, σ_{DC} and τ_σ , obtained in our experiment, which correspond, respectively, to the static and dynamic behavior of the ionic conductivity in two liquid lactones, GBL, and GVL, are presented in Fig. 7 as a function of temperature. As expected, these two liquids, composed of the molecules which differ from each other only by the methyl substituent ($-CH_3$) in the C–O–C linkage of the lactone

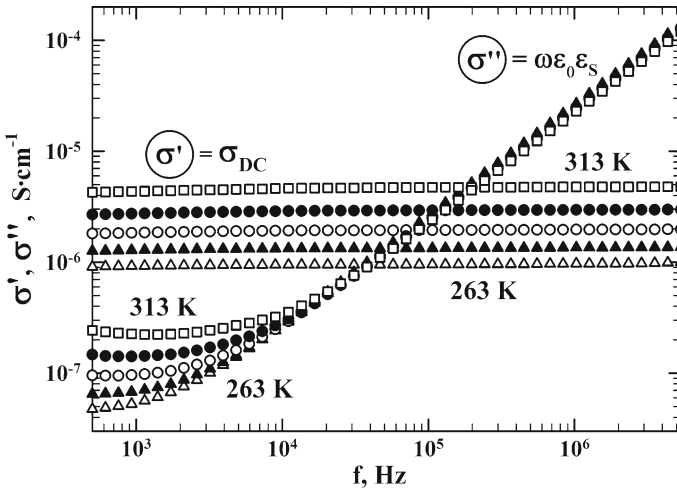


Fig. 6 Electrical conductivity spectra, $\sigma^*(\omega) = j\omega\epsilon_0\epsilon^*(\omega)$, of GBL, corresponding to the dielectric spectra from Fig. 1: real σ' and imaginary σ'' parts Eq. 12

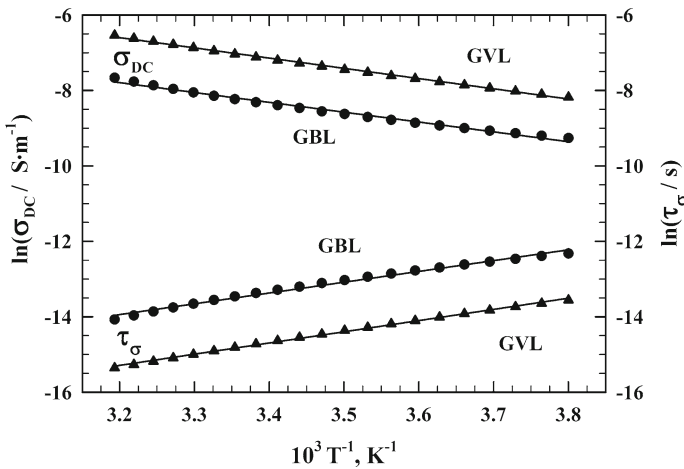


Fig. 7 Arrhenius plots for dc electrical conductivity (σ_{DC}) and conductivity relaxation time (τ_σ) for GBL and GVL. The (absolute) value of thermal activation energy $25 \text{ kJ} \cdot \text{mol}^{-1} \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ is common for all dependences presented in the figure

ring, exhibit quite similar temperature behavior. Both σ_{DC} and τ_σ fulfill the Arrhenius dependence very well and, besides, the thermal activation energy for the static conductivity as well as for the conductivity relaxation time are very close to each other: $E_{\sigma_{DC}} \approx E_{\tau_\sigma} = 25 \text{ kJ} \cdot \text{mol}^{-1} \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$, for both studied lactones.

The temperature dependences of the static dielectric permittivity, obtained for GBL and GVL, are presented in Fig. 8a. The difference in the permittivity values of GBL and GVL results from the different dipole densities in both liquids [31], namely, the ratio of the molar volumes $V_M^{GBL}/V_M^{GVL} \approx 0.81$ corresponds quite well to the ratio of

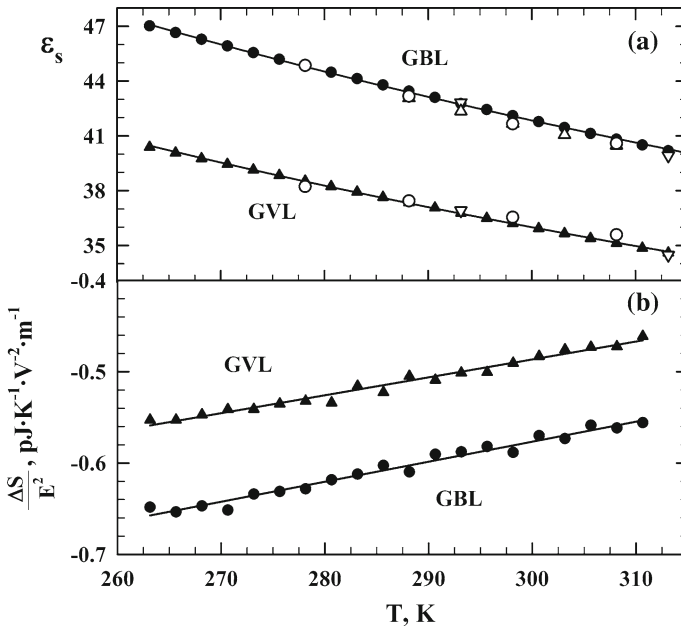


Fig. 8 Temperature dependences of (a) the static dielectric permittivity of GBL and GVL (*full points*) resulting from the best fit of Eq. 5 to the experimental electrical modulus spectra; *open points* represent the literature data \circ [24], ∇ [31], Δ [32], (b) the orientational entropy increment for GBL and GVL. *Solid lines* in (a) represent the best fit of empirical Eq. 13 to the experimental data

the values of the static permittivity of both compounds $\epsilon_s^{\text{GVL}}/\epsilon_s^{\text{GBL}} \approx 0.86$ (at 298 K). The $\epsilon_s(T)$ dependence for GBL and GVL, together with the literature data [24, 31, 32], can be well reproduced (solid lines in Fig. 8a) with the following empirical equation:

$$\epsilon_s = A + \frac{B}{T}, \quad (13)$$

with the values of the constants: $A = 4.217$ and $B = 11.29 \times 10^3$ K, for GBL and $A = 4.095$ and $B = 9.570 \times 10^3$ K, for GVL. T is the absolute temperature.

The molecular dipole moment of the studied lactones is high ($\mu \approx 4.20$ D [31, 32]), so one may expect here rather strong short-range orientational correlations, such as observed in some liquids composed of molecules with similar dipole moments, as in acetonitrile, for example [33]. However, experimental data for the Kirkwood correlation factor, g , give evidence for very weak dipole-dipole correlations in GBL and GVL ($g \approx 1$) [31]. For comparison, in the case of acetonitrile, which is quoted as a typical liquid with strong antiparallel dipolar correlation, the g -factor amounts to about 0.75 [34, 35]. The different abilities for intermolecular self-association of strongly polar molecules certainly results from the difference in the structure of the molecules. In the case of studied lactones molecules, where the dipole moment centers are formed by two oxygens (carbonyl and ether), linked with the carbon atoms in the lactone ring, the low ability for dipolar coupling must result from the steric hindrance created by the

saturated lactone ring. The lack of intermolecular dipolar coupling in GBL and GVL reflects itself also in the temperature dependence of the static dielectric permittivity of both lactones. As was shown by Fröhlich [36], the slope of the permittivity dependence on the temperature, $\varepsilon_s(T)$, is proportional to the orientational entropy increment ΔS caused by the probing electric field of intensity E :

$$\frac{\Delta S}{E^2} \equiv \frac{S(T, E) - S_0(T)}{E^2} = \frac{\varepsilon_0}{2} \frac{\partial \varepsilon_s}{\partial T}. \quad (14)$$

S_0 is the value of the entropy (per unit volume) in the absence of the electric field. As was shown recently, the $\Delta S(T)$ dependence reflects molecular self-association such as, for example, dipolar coupling in isotropic mesogenic liquids in the vicinity of the transition to the nematic phase [37–40] or hydrogen bond formation in liquid amides [30]. The negative values of ΔS (Fig. 8b) reflect the ordering action of the probing electric field with respect to the lactone molecular dipoles. The difference between the entropy effects observed in GBL and GVL is a consequence of the different dipole densities in both liquids. The temperature dependences of the entropy increment (Fig. 8b) correspond to an increase of the molar volumes of both lactones with increasing temperature. It is normal behavior of dipolar liquids where the dipole–dipole aggregation meets significant steric hindrances.

4 Conclusions

The experimental data concerning the studied lactones show that the electric and dielectric properties of these liquids exhibit foreseeable behavior in a large temperature range—an important feature for their practical uses. It was shown that the specific structure of GBL and GVL molecules, essentially reduces the possibilities for their antiparallel dipolar coupling resulting in liquids of a relatively high-dielectric permittivity—a crucial property for practical applications of liquid lactones.

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