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Odd−Even Effects in the Static Dielectric Permittivity of a Homologous Series of Liquid Cycloalkanones, $(CH_2)_{n-1}C{=}O$, $n = 4$ to 8

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ABSTRACT: Electric modulus spectra were used for the analysis of the static dielectric properties of liquid cycloalkanones: cyclobutanone, cyclopentanone, cyclohexanone, and cycloheptanone, studied in the temperature range from (243 to 313) K, and cyclooctanone, studied from (303 to 343) K. Odd−even effects with respect to the number of carbon atoms in the molecular ring of the compounds were found in the static dielectric permittivity value and in the dipolar aggregation ability, represented by the Kirkwood correlation factor.

1. INTRODUCTION

Cyclic ketones are important intermediates in the synthesis of many organic compounds important for the chemical industry, pharmacy, and cosmetics. In the liquid state these polar compounds are widely used as relatively safety solvents. In the solid state, due to the globular shape of the molecules, cycloalkanones form one or more orientational disordered phases, also known as rotor or plastic phases.[1−7] The physicochemical properties of cycloalkanones are the subject of numerous studies,[1,3,8−12] but a literature survey reveals only a few studies on the dielectric properties of the compounds.[13−18] In general, the studies were not systematic. In this paper we present the results of systematic experimental studies which discovered a very peculiar behavior of the static dielectric permittivity of cycloalkanones in relation to the size of the rings of these compounds.

2. EXPERIMENTAL SECTION

The studied compounds—cyclobutanone, cyclopentanone, cyclohexanone and cycloheptanone (mass purity of 99 %) and cyclooctanone (98 %)—were supplied from Sigma-Aldrich. The liquids were stored over the molecular sieves of 4 Å (Sigma-Aldrich) before measurements.

The impedance spectra 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 (the surface 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 a gold-plated copper. The capacity of the empty cell used (C_0) was equal to about 10 pF. The probing electric field intensity E was equal to about 1 V·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 less than 1 %.

The measurements were performed (two times for each sample) with decreasing temperature. For cycloheptanone ($n = 7$) and cyclooctanone ($n = 8$) with the melting points of about (252 and 317) K, respectively, the measurements were performed also for supercooling liquids up to the appearance of the solid phase of the compounds.

The frequencies of the measuring electric stimulus used in our experiment are relatively low in comparison to the frequency range where the orientational dipolar relaxation occurs in cycloalkanones (gigahertz region[13]), and therefore, the results obtained in this paper concern the static dielectric properties of these compounds.

3. RESULTS AND DISCUSSION

For determination of the static dielectric permittivity (ε_s) of cycloalkanones, the impedance spectra, $Z^*(\omega) = Z'(\omega) + jZ''(\omega)$, recorded in our experiments, have been transformed into the electric modulus spectra:[19]

$$M^*(\omega) \equiv 1/\varepsilon^* = M'(\omega) + jM''(\omega) \tag{1}$$

according to the relation:

$$M^*(\omega) = j\omega C_0 Z^*(\omega) \tag{2}$$

where the real (M') and imaginary (M'') parts of the electric modulus are equal:

$$M'(\omega) = \omega C_0 Z''(\omega) \quad \text{and} \quad M''(\omega) = \omega C_0 Z'(\omega) \tag{3}$$

$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$ is the complex dielectric permittivity, $\omega = 2\pi f$ is the angular frequency of the electric stimulus, f is the linear frequency, and $j = (-1)^{1/2}$. $C_0 = k\varepsilon_0$ is the electric capacity of empty measuring cell, $k = S/l$, S and l are the electrode surface and the distance between the electrodes, respectively, and ε_0 = 8.85 pF·m^{-1} is the permittivity of free space.

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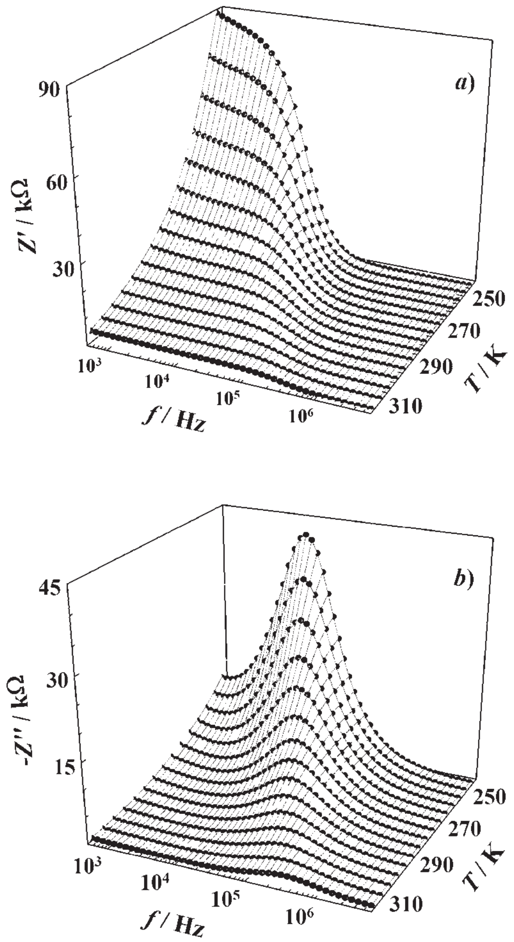

Figure 1. Real (Z') and imaginary (Z'') parts of the impedance spectra $Z^*(\omega)$ of cyclopentanone recorded at different temperatures.

Figures 1 and 2 present, respectively, the impedance and the electric modulus spectra (resulting from the transformation, eq 2) for cyclopentanone, as an example. The profiles are similar for other cycloalkanones under investigation.

As the frequency range of the electric stimulus used in our experiments corresponds to the static dielectric regime of the compounds, the real and imaginary parts of the dielectric permittivity are given by:

$$\varepsilon' = \varepsilon_s \quad \text{and} \quad \varepsilon''(\omega) = \sigma_{DC}/\omega\varepsilon_0 \tag{4}$$

where σ_{DC} denotes the dc (direct current) ionic conductivity in the liquid. In such static dielectric cases, the electric modulus spectra are described with the following equations:

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

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

where $\tau_\sigma = \varepsilon_0\varepsilon_s/\sigma_{DC}$ is known as the conductivity relaxation time.[20] As can be seen in Figure 2, eq 5 perfectly reproduces (the solid lines) the electric modulus spectra of cyclopentanone and also other cycloalkanones studied.

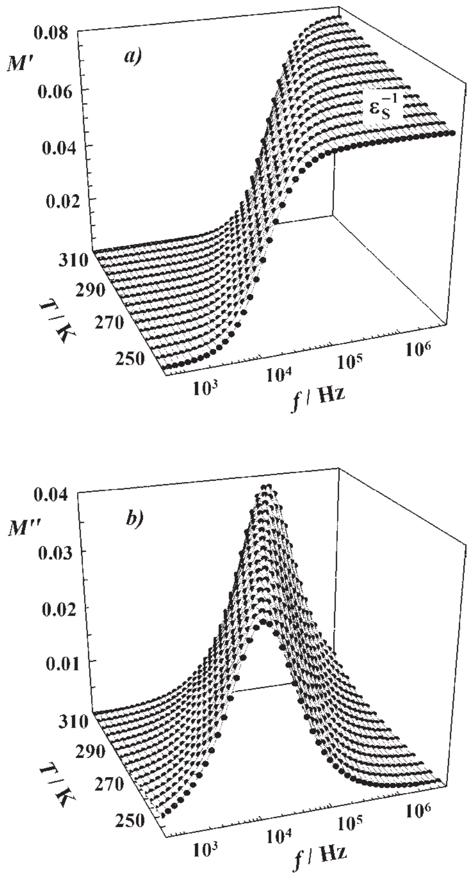

Figure 2. Electric modulus spectra, $M^*(\omega) = 1/\varepsilon^*(\omega)$, of cyclopentanone resulting from transformation of the impedance spectra according to eq 2. The solid lines represent the best fit of eq 5 to the experimental data (points).

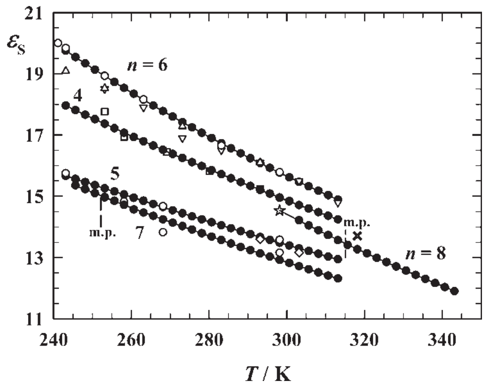

Figure 3. Temperature dependences of the static dielectric permittivity of cycloalkanones of a different number n of carbon atoms in the ring. For $n = 7$ and 8, the ε_s values measured for supercooled liquids are shown. The solid points represent the results obtained in our experiments, and the open ones represent the literature data: ○, ref 13; □, ref 14; ▽, ref 15; △, ref 16; ◇, ref 17; ×, ref 18. For $n = 8$, the permittivity value (14.54) extrapolated to 298 K is denoted as ☆.

Figure 3 presents temperature dependences of the static dielectric permittivity of cyclooctanones obtained from the best fit of eq 5 to the electric modulus spectra. The figure contains also

Table 1. Static Dielectric Permittivity (ε_s) of Cycloalkanones of Different Numbers n of Carbon Atoms in the Ring

	ε_s				
	n				
T/K	4	5	6	7	8
243.15	17.96 ± 0.01	15.66 ± 0.02	19.75 ± 0.01		
245.65	17.81 ± 0.01	15.56 ± 0.02	19.54 ± 0.01	15.35 ± 0.01	
248.15	17.66 ± 0.01	15.46 ± 0.02	19.34 ± 0.01	15.22 ± 0.01	
250.65	17.51 ± 0.01	15.36 ± 0.02	19.13 ± 0.01	15.09 ± 0.01	
253.15	17.37 ± 0.01	15.26 ± 0.02	18.93 ± 0.01	14.97 ± 0.01	
255.65	17.22 ± 0.01	15.15 ± 0.02	18.73 ± 0.01	14.85 ± 0.01	
258.15	17.07 ± 0.01	15.05 ± 0.02	18.54 ± 0.01	14.72 ± 0.01	
260.65	16.93 ± 0.01	14.95 ± 0.02	18.34 ± 0.01	14.57 ± 0.01	
263.15	16.79 ± 0.01	14.85 ± 0.02	18.15 ± 0.01	14.47 ± 0.01	
265.65	16.65 ± 0.01	14.75 ± 0.02	17.96 ± 0.01	14.36 ± 0.01	
268.15	16.51 ± 0.01	14.65 ± 0.02	17.78 ± 0.01	14.25 ± 0.01	
270.65	16.37 ± 0.01	14.55 ± 0.02	17.60 ± 0.01	14.14 ± 0.01	
273.15	16.24 ± 0.01	14.45 ± 0.02	17.42 ± 0.01	14.03 ± 0.01	
275.65	16.11 ± 0.01	14.35 ± 0.02	17.24 ± 0.01	13.91 ± 0.01	
278.15	15.98 ± 0.01	14.25 ± 0.02	17.07 ± 0.01	13.80 ± 0.01	
280.65	15.85 ± 0.01	14.15 ± 0.02	16.90 ± 0.01	13.69 ± 0.01	
283.15	15.72 ± 0.01	14.06 ± 0.02	16.73 ± 0.01	13.58 ± 0.01	
285.65	15.58 ± 0.01	13.96 ± 0.02	16.56 ± 0.01	13.46 ± 0.01	
288.15	15.46 ± 0.01	13.86 ± 0.02	16.40 ± 0.01	13.35 ± 0.01	
290.65	15.33 ± 0.01	13.77 ± 0.02	16.24 ± 0.01	13.25 ± 0.01	
293.15	15.20 ± 0.01	13.67 ± 0.02	16.08 ± 0.01	13.14 ± 0.01	
295.65	15.08 ± 0.01	13.58 ± 0.02	15.92 ± 0.01	13.03 ± 0.01	
298.15	14.96 ± 0.01	13.49 ± 0.02	15.77 ± 0.01	12.92 ± 0.01	
300.65	14.84 ± 0.01	13.39 ± 0.02	15.62 ± 0.01	12.82 ± 0.01	
303.15	14.72 ± 0.01	13.30 ± 0.02	15.46 ± 0.01	12.72 ± 0.01	14.22 ± 0.02
305.65	14.60 ± 0.01	13.22 ± 0.02	15.32 ± 0.01	12.62 ± 0.01	14.05 ± 0.02
308.15	14.48 ± 0.01	13.13 ± 0.02	15.17 ± 0.01	12.51 ± 0.01	13.89 ± 0.02
310.65	14.37 ± 0.01	13.04 ± 0.02	15.03 ± 0.01	12.41 ± 0.01	13.74 ± 0.02
313.15	14.25 ± 0.01	12.95 ± 0.02	14.89 ± 0.01	12.32 ± 0.01	13.57 ± 0.02
315.65					13.42 ± 0.02
318.15					13.27 ± 0.02
320.65					13.14 ± 0.02
323.15					12.99 ± 0.02
325.65					12.85 ± 0.02
328.15					12.71 ± 0.02
330.65					12.58 ± 0.02
333.15					12.44 ± 0.02
335.65					12.30 ± 0.02
338.15					12.17 ± 0.02
340.65					12.04 ± 0.02
343.15					11.90 ± 0.02

the literature permittivity data obtained from classical dielectric measurements. The numerical data of the permittivities are presented in Table 1. The solid lines in Figure 3 represent the best fit of the empirical equation:

$$\varepsilon_s(T) = A + \frac{B}{T} + \frac{C}{T^2} \tag{6}$$

to the experimental permittivity data. The values of the fitting parameters A, B, and C are presented in Table 2. Table 2 contains also the standard deviations σ^*, calculated with the formula:

$$\sigma^* = \left(\frac{\sum_i (\varepsilon_{i\mathrm{exp}} - \varepsilon_{i\mathrm{calc}})^2}{n_\mathrm{d} - n_\mathrm{p}} \right)^{1/2} \tag{7}$$

where n_d and n_p denote the number of the experimental points and the number of the parameters, respectively.

Table 2. Values of the Parameters of Equation 6 Corresponding to Cycloalkanones of Different *n* Values and Standard Deviations Calculated with Equation 7

n	A	B/K	C/K^2	σ*
4	−5.075	$7.620 \cdot 10^3$	$-4.908 \cdot 10^5$	0.0029
5	−3.941	$7.096 \cdot 10^3$	$-5.663 \cdot 10^5$	0.0024
6	−5.398	$7.169 \cdot 10^3$	$-2.559 \cdot 10^5$	0.0024
7	−4.709	$6.810 \cdot 10^3$	$-4.629 \cdot 10^5$	0.0089
8	−6.953	$6.904 \cdot 10^3$	$-1.470 \cdot 10^5$	0.0069

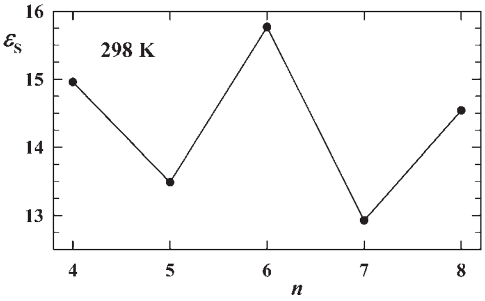

Figure 4. Odd−even effects in the static permittivity dependence on the number *n* of carbon atoms in the ring of cycloalkanones.

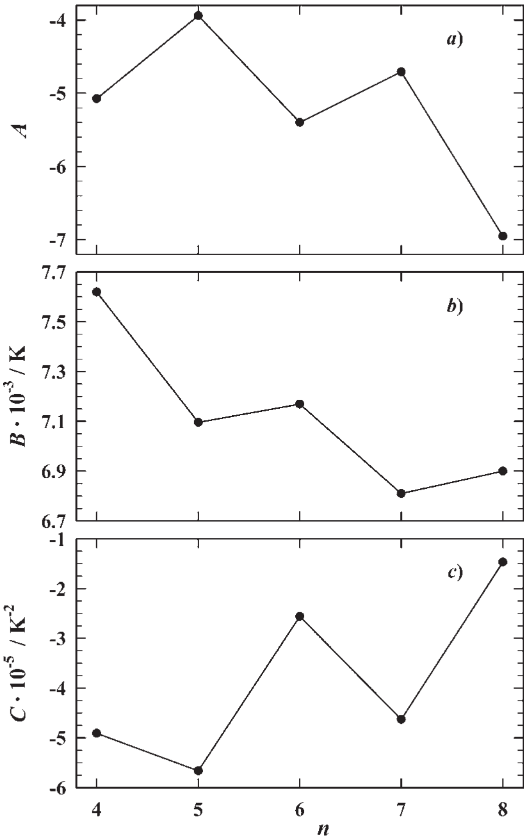

Figure 5. Odd−even effects in the dependence of the fitting parameters of eq 6 on *n*.

The most interesting feature of the static dielectric permittivity of the homologous series of cycloalkanones is its dependence on the number *n* of carbon atoms in the ring of the molecules.

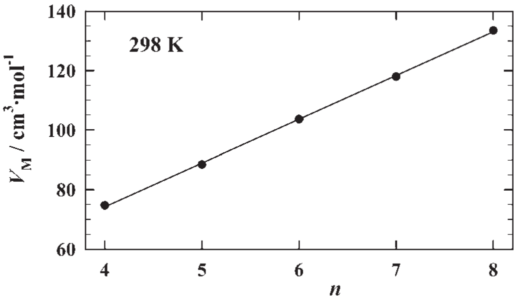

Figure 6. Dependence of the molar volume of cycloalkanones on *n*.

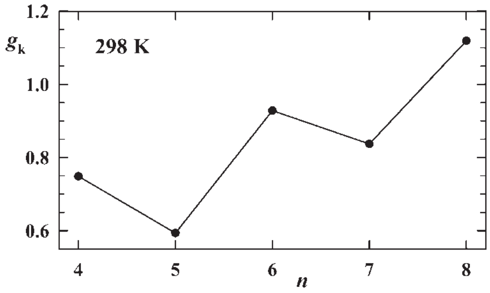

Figure 7. Odd−even effect in the dependence of the Kirkwood correlation factor g_k on the number *n* of carbon atoms in the ring of cycloalkanones.

As presented in Figure 4, the $\varepsilon_s(n)$ dependence shows an odd−even effect in which cycloalkanones composed of the molecules with an even number of *n* are characterized by a higher permittivity value than "odd" compounds. Besides, Figure 5 shows that also the coefficients *A*, *B*, and *C* of eq 6 exhibit behavior of the same type.

In general, the permittivity odd−even behavior such as depicted in Figure 4 may result from two main reasons: (i) from essentially different molecular packing for odd and even homologues or (ii) from the essential difference in the intermolecular dipolar coupling occurring in these two groups of compounds. The first possibility can be quite easily verified by the determination of the molar volume dependence on *n*. The density data for all cycloalkanones under investigation are available at 298 K (Aldrich data), so the further discussion presented in this paper concerns that temperature. Figure 6 shows that the cycloalkanone molar volume dependence on *n* shows no anomalies and each elementary increase in the *n* value represents an increase of the molar volume of about 14.7 $\text{cm}^3 \cdot \text{mol}^{-1}$, which corresponds to the volume of the CH_2 group. So, the reason of the permittivity odd−even effect should result from different abilities for the dipolar coupling of cycloalkanone molecules of different *n* values, that is, of different sizes of the molecular ring.

The dipolar aggregation ability of a given member of the homologous series of cycloalkanones can be estimated with the use of the Kirkwood correlation factor, calculated from the Onsager relation:[21]

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{\varepsilon_\infty(\varepsilon_\infty + 2)^2} \frac{9kT}{4\pi N_A} V_M = \mu_1{}^2 g_k \tag{8}$$

where μ_1 is the dipole moment of single molecule (determined in gaseous phase of the compound or in diluted solutions in nonpolar solvent), *k* is Boltzmann's constant, N_A is Avogadro's

Table 3. Values of the Dipole Moments of Cycloalkanone Molecules (μ_1) and the Kirkwood Correlation Factor (g_k) Calculated with Equation 8 for Liquid Cycloalkanones of Different Numbers *n* of the Carbon Atom in the Ring

n	4	5	6	7	8
μ_1/D	2.89[23]	3.30[24]	3.08[11]	3.07[25]	2.96[25]
g_k	0.75	0.59	0.93	0.84	1.12

number, V_M is the molar volume, T is the absolute temperature, and ε_∞ is the dielectric permittivity measured in so high frequencies to prevent the dipolar reorientation and ε_∞ often is taken as the refractive index squared. The factor g_k was introduced by Kirkwood[22] for expressing the intermolecular dipolar coupling in liquids; namely, the fractional values of the factor, $g_k < 1$, correspond to the antiparallel dipolar self-association leading to the reduction of the effective dipole moment of molecule, $g_k > 1$ corresponds to parallel association leading to the increase of the effective moment, and $g_k = 1$ indicates a lack of dipolar coupling in the liquid studied.

Figure 7 and Table 3 present the Kirkwood correlation factor as a function of *n*, calculated for the dipole moment μ_1 values presented in the table. The high-frequency permittivity value was taken as $\varepsilon_\infty = 2.6$ for all cycloalkanones studied.[18] The odd−even effect observed in $g_k(n)$ dependence shows that the polar cycloalkanone molecules of different sizes of the ring exhibit different abilities for the dipolar coupling. The compound with the ring composed of four and (especially) five carbons show a quite important tendency for antiparallel dipolar coupling ($g_k \approx 0.7$). An important conclusion resulting from Figure 7 is that the cycloalkanone molecules of the odd number of *n* exhibit an essentially higher ability to antiparallel coupling of molecular dipoles than those with the even *n* number.

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