Static Dielectric Permittivity and Electric Conductivity of N-Methylacetamide + N,N-Dimethylacetamide Mixtures

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Static Dielectric Permittivity and Electric Conductivity of *N*-Methylacetamide + *N*,*N*-Dimethylacetamide Mixtures

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Impedance spectroscopy (IS) was used for the determination of the static dielectric permittivity and the electric conductivity of *N*-methylacetamide (NMA) + *N*,*N*-dimethylacetamide (DMA) mixtures over the whole concentration range and over the temperature range of 303.15 K to 393.15 K. The static permittivity values obtained with IS for both neat compounds at different temperatures are in a very good agreement with those measured with the classical dielectric methods. In NMA + DMA mixtures, the permittivity deviations ($\Delta\varepsilon$) from the concentration additive rule are strongly negative, and the $\Delta\varepsilon$ dependence on the mole fraction of NMA was fitted to the Redlich−Kister equation.

Introduction

N-methylacetamide (NMA) is one of the most self-associated liquids. Because of trans configuration of the peptide group −CO·NH−, the compound exhibits an unusual ability to form the intermolecular hydrogen bonds C═O···H−N, and, as a consequence, the linear, highly polar supramolecular polymers are formed.[1−4] The static dielectric permittivity of NMA is one of the highest among the molecular liquids, and simultaneously, the compound exhibits a high electric conductivity.[5,6] The substitution of the hydrogen atom in the peptide linkage by the methyl group makes the situation quite different, namely, the hydrogen bonds cannot be formed in neat *N*,*N*-dimethylacetamide (DMA). However, in the mixtures with NMA, because of the proton-acceptor C═O group in DMA molecules, the hydrogen bonded complexes NMA + DMA can be formed. So, the molecules of DMA can play the role of the stopper in the development of the self-association process of NMA molecules, and the efficiency of that limiting action depends on the NMA/DMA molecules ratio.

The measurement of the dielectric characteristics of materials of high electric conductivity always presents many serious problems, and for obtaining reliable dielectric data, special technical care must be taken.[7−9] In this article, we present the results of measurements of the static dielectric and electric properties of NMA + DMA mixtures performed with the use of the impedance spectroscopy (IS). The results obtained prove that the relative simple experimental method of the impedance measurements over a large frequency range allows one to get reliable static dielectric characteristics of some highly conducting molecular materials over a large temperature range.

Experimental Section

Materials. The compounds studied, *N*-methylacetamide and *N*,*N*-dimethylacetamide, from Aldrich of purity ≥ 99 % and ≥ 99.5 %, respectively, were used as supplied.

Apparatus and Procedure. The impedance spectra of studied compounds were recorded with the use of an HP 4194A impedance/gain phase analyzer in the frequency range of 100 kHz to 100 MHz and over the temperature range of 303.15 K to 393.15 K. A homemade measuring capacitor consisted of three plane electrodes (the surface of about 0.5 cm^2): one central and two grounded on each side, with a distance between them of about 0.3 mm. The shape of the capacitor electrodes is rectangular, and they are made with a gold-plated copper. The probing electric field intensity, E, was equal to about 1 $V \cdot mm^{-1}$. The electrical heating of high performance with the use of a Scientific Instruments temperature controller, model 9700, assured a good temperature stabilization (on the millikelvin level). Such equipment allows one to determine the permittivity with an uncertainty of about 0.5 %.

The procedure of the determination of the dielectric and electric characteristics of the liquids studied is as follows. Impedance (Z) of the system composed of the resistance (R) and capacitance (C) is a complex quantity given by relation

$$Z(\omega) = \mathrm{Re}(Z) + j\mathrm{Im}(Z) = R(\omega) + j\frac{1}{\omega C} \qquad (1)$$

where Re(Z) and Im(Z) stand for the real and imaginary parts of the impedance, $j \equiv \sqrt{-1}$, $\omega = 2f\pi$ is an angular frequency of electrical stimulus applied, and f is the frequency. The impedance is a fundamental concept in electrical engineering because it takes into account the phase differences; therefore, it is a more general concept than the resistance.[10]

Figure 1 presents, as an example, the impedance spectrum of NMA recorded at 363.15 K. Part a of the Figure presents the real and imaginary parts of the cell impedance as a function of the frequency of the stimulus applied, and part b presents the results in the complex plane. As can be seen, the complex plane representation has a form of a quite perfect semicircle showing a formal similarity to the Debye behavior of the complex dielectric permittivity observed in some liquids. Such type of the electric response, as presented in Figure 1, means that the equivalent circuit of our molecular system is the capacitor, C_0, connected in parallel to the resistor, R_0.[10] It is the simplest possible experimental result that can be recorded with the IS.

As depicted in Figure 1, at the point $\omega = 0$, the real part of the impedance corresponds to the static value of the electric resistance, R_0, whereas at the maximum of the semicircle, the

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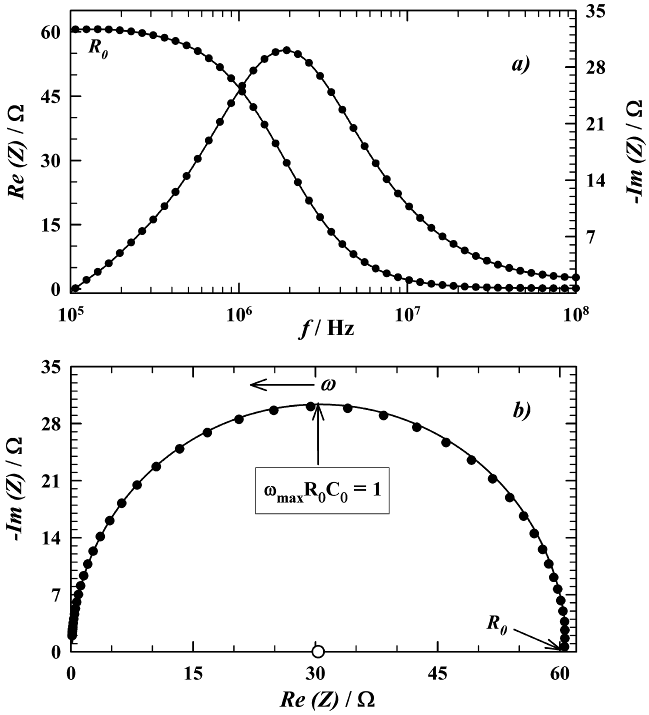

Figure 1. Frequency dependence of (a) the real (Re) and imaginary (Im) parts of the impedance recorded for *N*-methylacetamide at 363.15 K and (b) the complex plane representation. The solid lines represent the best fit of the Debye-like dependence to the experimental data.

relation $\omega_{max}\tau = 1$ is fulfilled, where the relaxation time, τ, for our equivalent circuit is equal to $\tau = R_0C_0$. Therefore, the static dielectric permittivity of the liquid studied, at different temperature, T, can be calculated with the following equation

$$\varepsilon(T) \equiv \frac{C_0(T)}{C_{emp}} = \frac{1}{C_{emp}\omega_{max}(T)R_0(T)} \tag{2}$$

where C_{emp} is the capacity of the empty measuring cell. We obtained the value of C_{emp} from the calibration procedure with the use of liquids of known dielectric permittivity (air, cyclohexane, carbon tetrachloride, acetone, and chloroform). In our experiment, $C_{emp} = (12.98 \pm 0.02)$ pF, and the measured C_{emp} change on the temperature is less that 1 % per $\Delta T \approx 100$ K.

The static electric conductivity of the sample studied can be calculated from the simple relation

$$\sigma_0(T) = \frac{l}{SR_0(T)} \tag{3}$$

where l and S are the distance between electrodes of the measuring cell and the surface of the electrode, respectively.

Figure 2 presents the dielectric permittivity results obtained with the procedure described above (eq 2). Many published papers are devoted to the measurements of the permittivity of NMA and DMA.[11−15] The high value of the permittivity together with a relatively high conductivity was really a challenge for the dielectric studies of NMA with the use of the classical dielectric spectroscopy. The results on the static dielectric permittivity of NMA published in numerous papers are gathered,[6] and the following empirical formula for $\varepsilon(T)$ dependence is proposed

$$\varepsilon(T) = 17.51 - 4.6146(10^4/T) + 2.884(10^7/T^2) \tag{4}$$

where T is the absolute temperature in kelvins.

The solid line in Figure 2a is traced according to eq 4. The results obtained with IS (full points) perfectly agree with an empirical relation (eq 4). Similarly, for DMA (Figure 2b), our results are in a good agreement with those obtained with the dielectric spectroscopy measurements.[11,12] At the highest temperatures used in our experiments, both NMA and DMA show no chemical decomposition effects that would influence the static permittivity value of the compounds.

Results and Discussion

The results of the static permittivity measurements performed with the use of IS for the mixtures of NMA + DMA are summarized in Table 1 and Figure 3. The temperature dependence of the permittivity of the mixtures was described with an equation analogous to eq 4

$$\varepsilon(T) = A + B/T + C/T^2 \tag{5}$$

The solid lines in Figure 3 correspond to the best fit of this equation to the experimental data. The values of the fitting parameters A, B, and C are gathered in Table 2, and their dependence on NMA mole fraction is depicted in Figure 4. Table 2 also contains the standard deviations, σ^*, calculated with the formula

$$\sigma^* = \left(\frac{\sum_i (\varepsilon_{i\text{exptl}} - \varepsilon_{i\text{calcd}})^2}{n_d - n_p}\right)^{1/2} \tag{6}$$

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

Figure 5 presents the permittivity dependence on NMA mole fraction (x) in the mixtures with DMA at several temperatures. The dependence is strongly nonlinear, and the results seem to be a good example for illustration of a possible error extension in the estimation (even rough) of the permittivity value of liquid

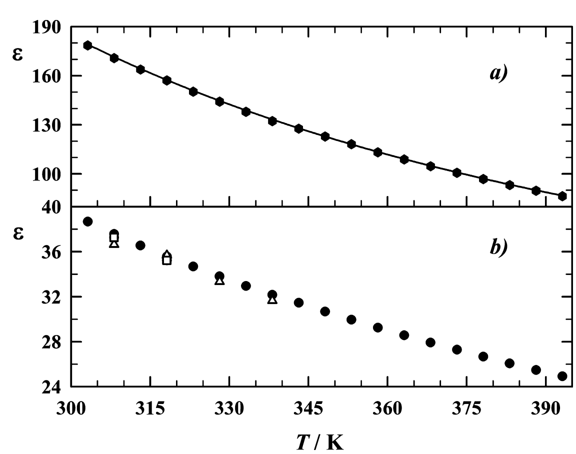

Figure 2. Static dielectric permittivity of (a) NMA and (b) DMA determined with the use of the impedance spectroscopy (full points). The solid line in part a is traced according to eq 2,[6] representing numerous experimental values published in the literature of the permittivity of NMA obtained with the classical dielectric methods. In part b, the literature data for DMA are presented by open points: □,[11] △.[12]

Table 1. Static Permittivity, ε, Permittivity Deviations, $\Delta\varepsilon$, and Electric Conductivity, σ_0, for the Binary Mixtures of (x)N-Methylacetamide + $(1-x)$N,N-Dimethylacetamide at Different Temperatures

x	ε	$\Delta\varepsilon$	$\sigma_0 \cdot 10^{-4}$/S·cm^{-1}	x	ε	$\Delta\varepsilon$	$\sigma_0 \cdot 10^{-4}$/S·cm^{-1}
		T = 303.15 K				T = 313.15 K	
0.0000	38.67	0.00	1.49	0.0000	36.55	0.00	1.95
0.1041	43.95	−9.27	1.08	0.1041	41.48	−8.32	1.31
0.2077	50.51	−17.20	1.73	0.2077	47.77	−15.22	2.01
0.3056	58.27	−23.12	1.62	0.3056	54.99	−20.45	1.92
0.4019	66.66	−28.19	2.03	0.4019	62.67	−25.02	2.41
0.5060	76.95	−32.46	2.39	0.5060	72.11	−28.82	2.87
0.6088	90.55	−33.23	2.15	0.6088	84.67	−29.34	2.62
0.6985	103.31	−33.01	3.28	0.6985	96.29	−29.14	4.00
0.7974	122.24	−27.90	3.14	0.7974	113.52	−24.49	3.90
0.9001	148.24	−16.27	3.29	0.9001	137.33	−13.75	4.21
1.0000	178.47	0.00	3.25	1.0000	163.79	0.00	4.47
		T = 323.15 K				T = 333.15 K	
0.0000	34.68	0.00	2.40	0.0000	32.95	0.00	3.07
0.1041	39.28	−7.43	1.51	0.1041	37.29	−6.59	1.75
0.2077	45.14	−13.55	2.30	0.2077	42.73	−12.02	2.61
0.3056	52.07	−17.93	2.29	0.3056	49.35	−15.68	2.73
0.4019	58.92	−22.21	2.85	0.4019	55.45	−19.69	3.35
0.5060	67.68	−25.49	3.40	0.5060	63.64	−22.44	3.97
0.6088	79.19	−25.86	3.15	0.6088	74.15	−22.72	3.73
0.6985	89.86	−25.56	4.85	0.6985	83.96	−22.33	5.84
0.7974	105.50	−21.35	4.77	0.7974	98.21	−18.46	5.71
0.9001	127.11	−11.61	5.28	0.9001	117.28	−10.17	6.45
1.0000	150.27	0.00	6.14	1.0000	137.94	0.00	7.75
		T = 343.15 K				T = 353.15 K	
0.0000	31.46	0.00	4.00	0.0000	29.95	0.00	4.62
0.1041	35.46	−6.01	2.02	0.1041	33.74	−5.40	2.34
0.2077	40.50	−10.93	2.99	0.2077	38.54	−9.73	3.49
0.3056	46.70	−14.14	3.31	0.3056	43.90	−13.00	4.03
0.4019	52.38	−17.72	3.94	0.4019	49.59	−15.80	4.64
0.5060	59.93	−20.18	4.59	0.5060	56.55	−18.03	5.32
0.6088	69.54	−20.46	4.36	0.6088	65.50	−18.13	5.10
0.6985	78.62	−20.00	6.88	0.6985	73.78	−17.77	7.98
0.7974	91.73	−16.40	6.66	0.7974	85.69	−14.58	7.60
0.9001	108.75	−9.26	7.78	0.9001	101.11	−8.22	9.29
1.0000	127.62	0.00	10.49	1.0000	118.13	0.00	12.89
		T = 363.15 K				T = 373.15 K	
0.0000	28.58	0.00	5.08	0.0000	27.29	0.00	5.34
0.1041	32.15	−4.78	2.69	0.1041	30.74	−4.20	3.05
0.2077	36.74	−8.52	4.13	0.2077	35.02	−7.52	4.90
0.3056	41.56	−11.55	4.96	0.3056	39.45	−10.28	6.00
0.4019	46.96	−13.88	5.48	0.4019	44.54	−12.27	6.46
0.5060	53.46	−15.74	6.19	0.5060	50.49	−13.96	7.14
0.6088	61.69	−15.76	5.98	0.6088	58.20	−13.80	7.02
0.6985	69.23	−15.42	9.22	0.6985	65.03	−13.56	10.57
0.7974	80.16	−12.43	8.54	0.7974	75.04	−10.81	9.48
0.9001	94.17	−6.66	10.95	0.9001	87.71	−5.69	12.71
1.0000	108.85	0.00	16.48	1.0000	100.73	0.00	19.16
		T = 383.15 K				T = 393.15 K	
0.0000	26.07	0.00	5.44	0.0000	24.92	0.00	5.18
0.1041	29.28	−3.79	3.44	0.1041	27.87	−3.45	3.96
0.2077	33.34	−6.68	5.67	0.2077	31.71	−5.97	6.42
0.3056	37.46	−9.14	7.08	0.3056	35.57	−8.12	8.10
0.4019	42.23	−10.83	7.50	0.4019	40.04	−9.57	8.51
0.5060	47.73	−12.32	8.13	0.5060	45.14	−10.86	9.07
0.6088	54.87	−12.08	8.16	0.6088	51.74	−10.58	9.34
0.6985	61.11	−11.87	11.88	0.6985	57.41	−10.42	13.07
0.7974	70.28	−9.34	10.53	0.7974	65.87	−8.04	11.78
0.9001	81.70	−4.81	14.60	0.9001	76.14	−4.07	16.73
1.0000	93.22	0.00	21.93	1.0000	86.35	0.00	24.72

mixtures, assuming the additivity of the permittivity of the mixture partners.

The problem can be formally presented in the form of the permittivity deviations, $\Delta\varepsilon$, from the concentration additive rule

$$\Delta\varepsilon(x) = \varepsilon_{\text{exptl}} - [x\varepsilon_1 + (1-x)\varepsilon_2] \tag{7}$$

where $\varepsilon_{\text{exptl}}$ is the static dielectric permittivity measured for a given solution and ε_1 and ε_2 are the permittivities of neat NMA and DMA, respectively. The values of $\Delta\varepsilon$ are gathered in Table 1, and Figure 6 presents $\Delta\varepsilon$ dependences on NMA mole fraction at several temperatures. The dependences were fitted to the Redlich−Kister polynomial equation[16]

$$\Delta\varepsilon(x) = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \tag{8}$$

where A_i represents adjustable parameters. The solid lines in Figure 6 represent the best fit of eq 8 to the experimental $\Delta\varepsilon(x)$ data. The fitting parameters (A_i) as well as the corresponding standard deviations (σ^*) are gathered in Table 3. Figure 7 presents the

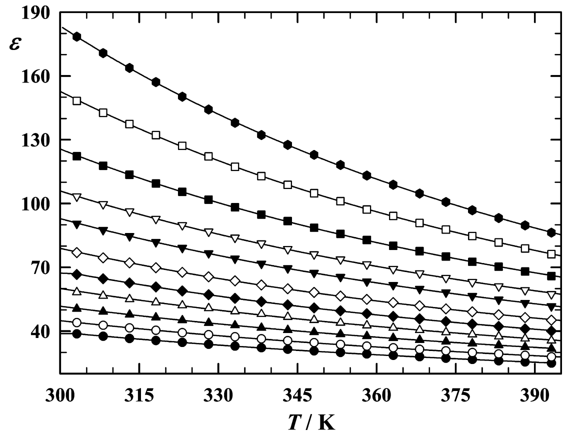

Figure 3. Temperature dependence of the static dielectric permittivity measured with the impedance spectroscopy for the NMA + DMA mixtures of different mole fraction (x) of NMA: ⬢, pure NMA, $x = 1.0$; □, $x = 0.9$; ■, $x = 0.8$; ▽, $x = 0.7$; ▼, $x = 0.6$; ◇, $x = 0.5$; ◆, $x = 0.4$; △, $x = 0.3$; ▲, $x = 0.2$; ○, $x = 0.1$; ●, pure DMA, $x = 0$. The solid lines are the best fit of eq 5 to the experimental data.

Table 2. Coefficients of Equation *5* and the Standard Deviation, σ^*, for Permittivity Temperature Dependence of the Binary Mixtures of *N*-Methylacetamide + *N*,*N*-Dimethylacetamide

x	A	$B \cdot 10^4$/K	$C \cdot 10^7$/K^2	σ^*
0.0000	7.378	−0.1646	0.3384	0.092
0.1041	8.623	−0.2800	0.4109	0.103
0.2077	9.488	−0.3554	0.4868	0.110
0.3056	10.223	−0.5627	0.6175	0.295
0.4019	11.468	−0.7055	0.7231	0.123
0.5060	12.580	−0.9578	0.8846	0.163
0.6088	13.426	−1.280	1.099	0.134
0.6985	14.500	−1.620	1.309	0.228
0.7974	15.549	−2.234	1.661	0.187
0.9001	16.707	−3.248	2.197	0.231
1.0000	17.702	−4.604	2.873	0.255

temperature dependence of the parameters obtained for the solutions studied.

The values of the static conductivity, σ_0, of the mixtures studied, calculated with eq 3, are gathered in Table 1, and $\sigma_0(T)$ dependences for different mole fractions of NMA in the mixtures with DMA are presented in Figure 8. Both NMA and DMA exhibit quite high electric conductivity, but the ratio $\sigma_0^{NMA}/\sigma_0^{DMA}$ strongly depends on the temperature from

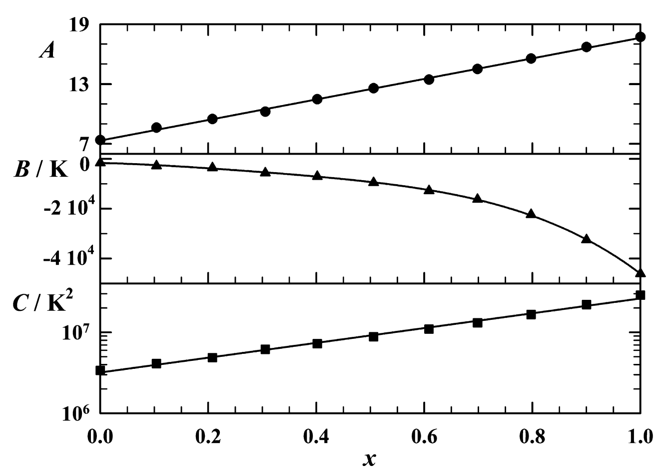

Figure 4. Coefficients A, B, and C resulting from the best fit of eq 5 to the experimental $\varepsilon(T)$ dependences of NMA + DMA mixtures as a function of NMA mole fraction.

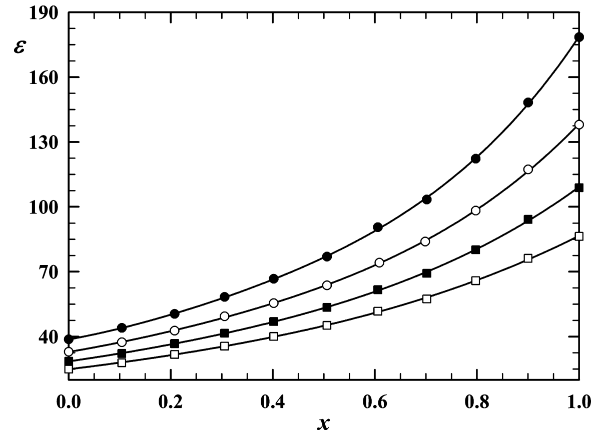

Figure 5. Static dielectric permittivity dependence on the mole fraction of NMA in the NMA + DMA mixtures at different temperatures: ●, 303.15 K; ○, 333.15 K; ■, 363.15 K; □, 393.15 K.

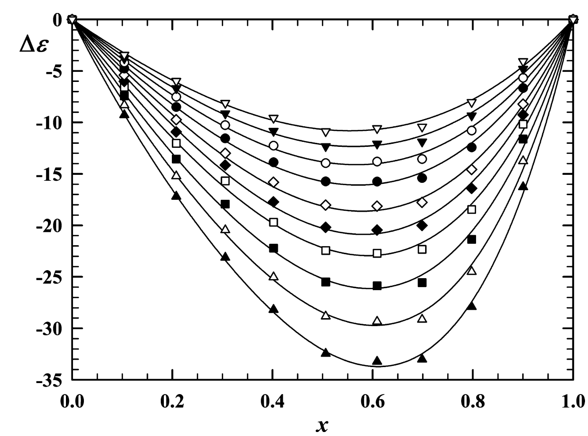

Figure 6. Deviation of the static dielectric permittivity of NMA + DMA mixtures from the additive concentration rule (eq 7) at different temperatures: ▲, 303.15 K; △, 313.15 K; ■, 323.15 K; □, 333.15 K; ◆, 343.15 K; ◇, 353.15 K; ●, 363.15 K; ○, 373.15 K; ▼, 383.15 K; ▽, 393.15 K. The solid lines are the best fit of the Redlich−Kister polynomial (eq 8).

Table 3. Coefficients of the Redlich−Kister Equation *8* and Standard Deviation, σ^*, for Permittivity Deviations, $\Delta\varepsilon(x)$, for Binary Mixtures of *N*-Methylacetamide + *N*,*N*-Dimethylacetamide at Several Temperatures

T/K	A_0	A_1	A_2	σ^*
303.15	−128.320	−55.714	−23.453	0.411
313.15	−113.787	−46.786	−16.273	0.506
323.15	−100.705	−38.691	−10.719	0.544
333.15	−88.672	−32.741	−7.889	0.469
343.15	−81.141	−28.460		0.456
353.15	−72.503	−24.625		0.369
363.15	−62.940	−19.021		0.330
373.15	−55.320	−15.847		0.305
383.15	−48.567	−12.540		0.299
393.15	−42.696	−9.711		0.297

about 2 at 303 K to about 5 at 393 K. The dielectric permittivity temperature behavior is quite different: the ratio $\varepsilon^{NMA}/\varepsilon^{DMA}$ is equal to 4.6 at 303 K and decreases to 3.4 at 393 K.

The results presented in this article show that the static dielectric permittivity of high-conducting molecular liquids determined with the IS are quite reliable and precisely correspond to the permittivity values obtained with the classical dielectric methods. The impedance method allows one to extend the temperature range of the permittivity measurement toward the much higher temperatures, where

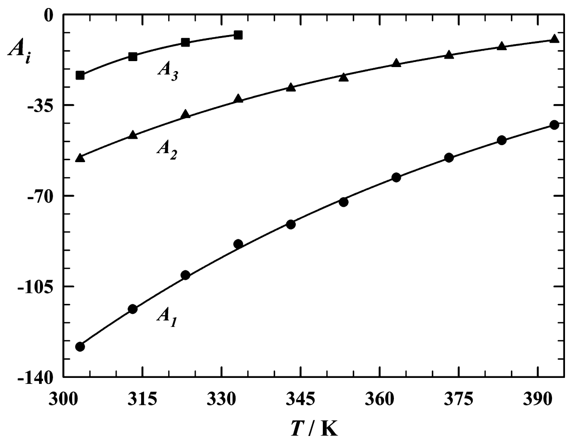

Figure 7. Temperature dependence of the coefficients A_i of Redlich−Kister eq 8 for mixtures of NMA + DMA.

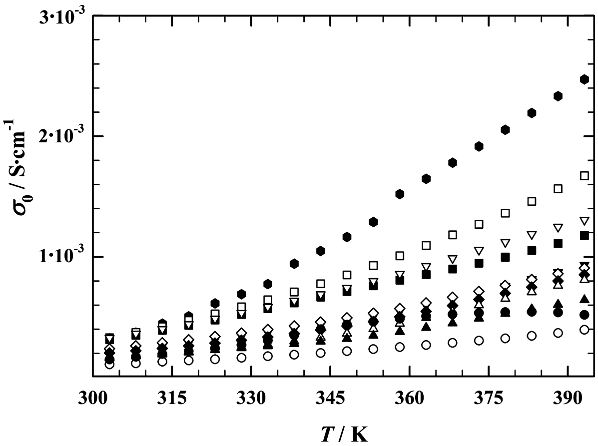

Figure 8. Static electric conductivity, σ_0, of the NMA + DMA mixtures as a function of temperature for different mole fractions of NMA: ⬢, neat NMA; □, $x = 0.9$; ■, $x = 0.8$; ▽, $x = 0.7$; ▼, $x = 0.6$; ◇, $x = 0.5$; ◆, $x = 0.4$; △, $x = 0.3$; ▲, $x = 0.2$; ○, $x = 0.1$; ●, neat DMA.

an essential increase in the liquid conductivity actually makes the dielectric measurements extremely difficult.

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