Monatsh Chem (2011) 142:19–24
DOI 10.1007/s00706-010-0411-4

ORIGINAL PAPER

Dipole moment and self-association of acesulfame and saccharin in 1,4-dioxane solution at 298.15 K

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Received: 15 July 2010 / Accepted: 22 October 2010 / Published online: 2 December 2010

Abstract The density, refractive index, and electrical permittivity of 1,4-dioxane solutions of acesulfame [6-methyl-1,2,3-oxathiazine-4(3*H*)-one-2,2-dioxide] and saccharin [1,2-benzisothiazole-3(2*H*)-one-1,1-dioxide] were measured at 298.15 K. From the experimental data the limiting apparent specific volume, refraction, and polarization of acesulfame and saccharin were calculated. The electrical dipole moments of acesulfame and saccharin were estimated according to the Debye, Onsager, and Kirkwood approaches. The association via dipole–dipole interactions of acesulfame and saccharin was treated with the assumption that the dipole moment of dimeric species of acesulfame and saccharin is zero. The dimerization constants and dipole moments of corresponding monomeric species were evaluated. Since the fraction of monomers is close to unity it is worth mentioning that the dimerization effect is rather weak.

Keywords Volumetric properties · Dielectric properties · Self-association · Acesulfame · Saccharin · Dioxane solution

Introduction

Among the many sweeteners currently approved as food additives, a new class of sweeteners named oxathiazinone dioxides have received wide commercial use in food industry [1]. Chemically they bear some structural resemblance to saccharin. Among these compounds the alkali salts of saccharin and acesulfame are of special interest, because of their pronounced solubility in water in comparison with saccharin or acesulfame [2–4]. From the structural point of view the molecules of saccharin or acesulfame have attracted appreciable scientific attention, e.g., [5–8]. Both molecules feature the oxathiazinone moiety and thus three different groups, namely imino, sulfonyl, and carbonyl group, connected to each other (Fig. 1). In aqueous solution they are strong monobasic acids and are practically completely dissociated in water [9]. So, the pK_A value of acesulfame [10] and of saccharin [11] is ~ 2 at 298.15 K.

Measurement of electric permittivity has been used frequently as a quantitative method for studying molecular association. The procedure has been successfully employed to determine the dimerization constants of a number of carboxylic acids [12], 2-pyrrolidinone [13], alcohols [14], disubstituted amides [15], and some carbonyl compounds [16] in nonpolar solvents.

At present little is known regarding the extent and character of molecular association, and still less is known regarding the polar character of saccharin and acesulfame molecules, which are present at low concentration in nonaqueous media. In this investigation, measurement of electric permittivity was used to determine molecular dipole moments and dimerization constants of saccharin and acesulfame in 1,4-dioxane solution. Additionally, this study represents a continuation of our previous work on this matter [17].

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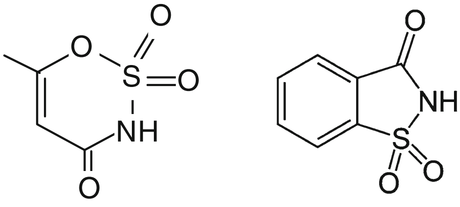

(a) (b)

Fig. 1 Structural formulae of acesulfame (**a**), and saccharin (**b**)

Results and discussion

Apparent specific quantity of solute and partial specific quantity of solute and solvent

The density ρ, refractive index n_D, and relative permittivity ε of the investigated solutions are given in Tables 1, 2, and 3 as a function of (solute/solvent) mass ratio ς_2. The partial molar quantities of solute and solvent were obtained and analyzed via corresponding apparent specific quantities as described previously [17].

Partial molar volume of acesulfame and saccharin in 1,4-dioxane

From the density of solution, given in Table 1, the apparent specific volume of solute v_Φ was calculated as

$$v_\Phi = \frac{v - v_1^0}{\varsigma_2}, \quad (1)$$

where $v = (1 + \varsigma_2)/\rho$ is the specific volume of solution and $v_1^0 = 1/\rho_1^0$ is the specific volume of pure solvent; ρ and ρ_1^0 are the density of solution and pure solvent, respectively. The uncertainty of v_Φ was calculated as in Ref. [17]. For 1,4-dioxane we used a value of $\rho_1^0 = 1.02792$ g cm^{-3}. The v_Φ values are collated in Table 1. The uncertainty of v_Φ is 2×10^{-3} cm^3 g^{-1} for acesulfame and 2×10^{-4} cm^3 g^{-1} for saccharin at the highest value of ς_2, and 1×10^{-2} cm^3 g^{-1} for acesulfame and 3×10^{-3} cm^3 g^{-1} for saccharin at the lowest ς_2 value.

Table 1 Density (ρ) of 1,4-dioxane solutions of acesulfame and saccharin, and the apparent specific volume (v_Φ) of acesulfame and saccharin as a function of the (solute/solvent) mass ratio (ς_2) at 298.15 K

ς_2	ρ (g cm^{-3})	v_Φ (cm^3 g^{-1})
Acesulfame		
0.00078	1.02823	0.65
0.00139	1.02844	0.66
0.00188	1.02860	0.66
0.00248	1.02882	0.65
0.00316	1.02906	0.65
0.00395	1.02931	0.65
0.00466	1.02955	0.65
0.00554	1.02985	0.65
0.00630	1.03013	0.65
Saccharin		
0.00477	1.02958	0.66
0.00911	1.03109	0.65
0.01291	1.03236	0.65
0.01770	1.03398	0.65
0.02721	1.03716	0.65
0.03612	1.04011	0.65
0.04565	1.04320	0.65
0.05473	1.04609	0.65
0.06415	1.04904	0.65
0.07146	1.05133	0.65
0.08066	1.05418	0.65
0.08952	1.05688	0.65
0.09562	1.05874	0.65

The apparent specific volume of acesulfame can be represented with a linear form of Eq. 4 as in Ref. [17], where v_ϕ^∞ is the limiting apparent specific volume of solute, equal to the limiting partial specific volume of solute, $v_2^0 = (0.6543 \pm 0.0007)$ cm^3 g^{-1}, and the regression constant, $a_v = -(0.96 \pm 0.14)$ cm^3 g^{-1}, calculated by a weighted least-squares procedure. The apparent specific volume of saccharin was found to be independent of (solute/solvent) mass ratio, ς_2 (see Table 1); its average value, calculated as a weighted mean, amounts to $v_\phi^\infty = (0.6489 \pm 0.0005)$ cm^3 g^{-1}. From the limiting apparent specific volume of solute, the partial molar volume of acesulfame and saccharin at infinite dilution was calculated and amounts to $V_2^0 = (106.75 \pm 0.12)$ cm^3 mol^{-1} for acesulfame and $V_2^0 = (118.86 \pm 0.09)$ cm^3 mol^{-1} for saccharin.

The partial specific volume of acesulfame v_2 was calculated according to Eq. 6 in Ref. [17]. The v_2 values slightly decrease with increasing mass ratio (from 0.653 to 0.642 cm^3 g^{-1}).

Partial molar refraction of acesulfame and saccharin

From the given refractive index of 1,4-dioxane solutions of acesulfame and saccharin (Table 2), the specific refraction of the solution, i.e., $r = (n_D^2 - 1)v/(n_D^2 + 2)$ and of pure solvent, $r_1^0 = [(n_D^0)^2 - 1]v_1^0/[(n_D^0)^2 + 2]$, was calculated, and the apparent specific refraction of the solutes by Eq. 1 in Ref. [17]. The apparent specific refraction of acesulfame and saccharin is given in Table 2. The uncertainty of r is given by the relation

$$(\delta r)^2 = \left(\frac{6n_D}{(n_D^2 + 2)^2}v\right)^2 (\delta n_D)^2 + \left(\frac{n_D^2 - 1}{n_D^2 + 2}\right)^2 (\delta v)^2, \quad (2)$$

Table 2 Refractive index (n_D) of 1,4-dioxane solutions of acesulfame and saccharin, and the apparent specific refraction (r_Φ) of acesulfame and saccharin as a function of the (solute/solvent) mass ratio (ς_2) at 298.15 K

ς_2	n_D	r_Φ (cm^3 g^{-1})
Acesulfame		
0.00078	1.42002	0.203
0.00139	1.42006	0.199
0.00188	1.42010	0.201
0.00248	1.42014	0.201
0.00316	1.42018	0.198
0.00395	1.42024	0.200
0.00466	1.42029	0.199
0.00554	1.42036	0.200
0.00630	1.42042	0.200
Saccharin		
0.00281	1.42036	0.236
0.00466	1.42061	0.245
0.01608	1.42208	0.232
0.02451	1.42317	0.232
0.03231	1.42425	0.233
0.04448	1.42573	0.232
0.05051	1.42647	0.232
0.05930	1.42754	0.232
0.06763	1.42855	0.232
0.07758	1.42970	0.232
0.08810	1.43088	0.231
0.09650	1.43186	0.231

and the uncertainty of r_1^0 by an analogous relation. The total uncertainty of the apparent specific refraction of acesulfame and saccharin was obtained as in Ref. [17]. The uncertainty in the value of r_Φ at the lowest mass ratio is 0.014 cm^3 g^{-1} for acesulfame and 0.003 cm^3 g^{-1} for saccharin, while at the highest value it is 0.002 cm^3 g^{-1} for acesulfame and 0.0001 cm^3 g^{-1} for saccharin. In the calculation of the r_Φ values, a value of $n_D^0 = 1.41999$ was used for the refractive index, which is somewhat higher than the literature value [18]. The apparent specific refractions of acesulfame and saccharin (Table 2) do not show any dependence on mass ratio, so we calculated their weighted average values, using the reciprocal value of the squared error of r_Φ, i.e., $1/(\delta r_\Phi)^2$, as the weight. They amount to $r_\Phi^0 = (0.1998 \pm 0.0002)$ cm^3 g^{-1} for acesulfame and $r_\Phi^0 = (0.2318 \pm 0.0004)$ cm^3 g^{-1} for saccharin. The corresponding limiting partial molar refractions are $R_2^0 = (32.597 \pm 0.033)$ cm^3 mol^{-1} for acesulfame and $R_2^0 = (42.461 \pm 0.073)$ cm^{3}mol^{-1} for saccharin. Additionally, the molar refractions of both solutes, calculated from the respective atomic or atomic group refractions given by Vogel [19, 20], amount to 32.89 cm^3 mol^{-1} for acesulfame and 40.65 cm^3 mol^{-1} for saccharin.

Partial molar polarization of acesulfame and saccharin

The polarization of solution and consequently the apparent specific polarization of solute depends on the theoretical model used [21]. The Debye model, applied to homogeneous fluid mixtures, gives the following expression for the specific polarization of solution p:

$$p = \frac{(\varepsilon - 1)}{(\varepsilon + 2)} v, \tag{3}$$

and an analogous relation is valid for the specific polarization of pure solvent. The Onsager model, which can be used for solutions in polar solvents and which takes into account the reaction field, yields for the specific polarization of solution p^*:

$$p^* = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} v, \tag{4}$$

and an analogous relation for the specific polarization of pure solvent. The Onsager theory becomes inaccurate for solutions in which there is molecular complexing between solute and solvent. For such systems, Kirkwood derived a general theory which allows for coupling of dipoles due to molecular complexing. His expression for the polarization of solution, $p^\dagger$, is formally identical to Onsager's equation, i.e., $p^* \equiv p^\dagger$ [21].

From the relative permittivity data of 1,4-dioxane solutions of acesulfame and saccharin (Table 3) and the specific volume, the apparent specific polarization of solute was calculated through Eq. 1 in Ref. [17], using for the specific polarization of solution Eq. 3 (Debye model) and Eq. 4 (Onsager's model). In the calculation of the apparent specific polarization of solute we used a literature value of $\varepsilon_0 = 2.2090$ for the relative permittivity of 1,4-dioxane [18]. The uncertainty of specific polarization of solution due to the Debye model is given by the relation

$$(\delta p)^2 = \left(\frac{3}{(\varepsilon + 2)^2} v \right)^2 (\delta\varepsilon)^2 + \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right)^2 (\delta v)^2, \tag{5}$$

and that for the Onsager model by

$$(\delta p^*)^2 = \left(\frac{v}{9} \right)^2 \left(\frac{2\varepsilon^2 + 1}{\varepsilon^2} \right)^2 (\delta\varepsilon)^2 + \left(\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \right)^2 (\delta v)^2. \tag{6}$$

Analogous relations are valid for the uncertainty of the specific polarization of pure solvent due to the Debye (Eq. 3) and Onsager (Eq. 4) model. The uncertainty of the apparent specific polarization of acesulfame and saccharin was obtained as in Ref. [17]. The uncertainty for the p_Φ

Table 3 Relative permittivity (ε) of 1,4-dioxane solutions of acesulfame and saccharin, and the apparent specific polarization (p_Φ, ρ^*_Φ) according to the Debye and Onsager models, respectively, as a function of the (solute/solvent) mass ratio (ς_2) at 298.15 K

ς_2	ε	p_Φ (cm^3 g^{-1})	ρ^*_Φ (cm^3 g^{-1})
Acesulfame			
0.00078	2.223	3.13	4.53
0.00139	2.235	3.18	4.55
0.00188	2.243	3.17	4.54
0.00248	2.254	3.15	4.53
0.00316	2.266	3.14	4.54
0.00395	2.279	3.06	4.44
0.00466	2.289	2.97	4.30
0.00554	2.304	2.96	4.31
0.00630	2.316	2.91	4.25
Saccharin			
0.00281	2.227	1.25	1.76
0.00466	2.239	1.25	1.76
0.01608	2.312	1.23	1.76
0.02451	2.365	1.22	1.75
0.03231	2.416	1.22	1.76
0.04448	2.491	1.20	1.76
0.05051	2.530	1.19	1.76
0.05930	2.584	1.18	1.76
0.06763	2.641	1.18	1.78
0.07758	2.705	1.18	1.79
0.08810	2.780	1.18	1.82
0.09650	2.833	1.18	1.82

value for the Debye model at the lowest mass ratio is 0.30 cm^3 g^{-1} (acesulfame) and 0.06 cm^3 g^{-1} (saccharin), and at the highest mass ratio is 0.04 cm^3 g^{-1} (acesulfame) and 0.002 cm^3 g^{-1} (saccharin). The uncertainty for the p^*_ϕ value for the Onsager model at the lowest mass ratio is 0.4 cm^3 g^{-1} (acesulfame) and 0.12 cm^3 g^{-1} (saccharin), and at the highest mass ratio is 0.05 cm^3 g^{-1} (acesulfame) and 0.004 cm^3 g^{-1} (saccharin).

The apparent specific polarization of solute as a function of mass ratio for acesulfame can be expressed by Eq. 4 in Ref. [17] in a linear form, and for saccharin in a quadratic form. The values of the parameters calculated by a least-squares procedure are given in Table 4; the limiting apparent specific or molar polarization of solute for the Onsager model are substantially higher than those of the Debye model for both compounds. Consequently, partial specific values of solute p_2 or p^*_2 are also higher for the Onsager model. The initial decrease of p_2 or p^*_2 values with increasing mass ratio may be ascribed to the disappearance of strongly polar monomeric species and to the appearance of nonpolar or slightly polar species.

Electrical dipole moment of acesulfame and saccharin

According to the Debye model, the partial molar polarization of solute at infinite dilution is given by [21]

$$P^0_2 = \frac{4\pi N_A}{3}\left(\alpha_e + \frac{\mu_2^2}{3kT}\right), \tag{7}$$

where μ_2 is the permanent molecular electric dipole moment, k is Boltzmann's constant, N_A is Avogadro's number, α_e is the electronic polarizability of solute, and T is the absolute temperature. When calculating μ_2 via Eq. 7 the electronic polarizability was multiplied by a factor of 1.05 to allow for atomic polarization [22]. The electronic polarization was calculated from the limiting partial molar refraction of solute R^0_2 as $\alpha_e = 3R^0_2 \cdot 1.05/4\pi N_A$ and amounts to 1.36×10^{-23} cm^3 for acesulfame and 1.77×10^{-23} cm^3 for saccharin. The values of the permanent molecular dipole moment amount to $\mu_2 = (1.654 \pm 0.001) \times 10^{-29}$ C m for acesulfame and $\mu_2 = (1.006 \pm 0.001) \times 10^{-29}$ C m for saccharin.

Onsager's model leads to the partial molar polarization of solute at infinite dilution as [21]

$$P^{0*}_2 = \frac{4\pi N_A}{3}\left(\alpha^*_e + \frac{\left(\mu^*_2\right)^2}{3kT}\right), \tag{8}$$

where α^*_e is the effective polarizability of solute and μ^*_2 is Onsager's dipole moment. The effective polarizability of solute was calculated from Onsager's relationship [17, 21] and amounts to $\alpha^*_e = 1.58 \times 10^{-23}$ cm^3 for acesulfame and 2.12×10^{-23} cm^3 for saccharin. These values are substantially higher than corresponding α_e, as is Onsager's electric dipole moment, which amounts to $\mu^*_2 = (2.039 \pm 0.002) \times 10^{-29}$ C m for acesulfame and $\mu^*_2 = (1.232 \pm 0.002) \times 10^{-29}$ C m for saccharin.

The partial molar polarization of solute at infinite dilution on the basis of Kirkwood's theory is expressed as [21]

$$P^{0\dagger}_2 = \frac{4\pi N_A}{3}\left(\alpha_e + \frac{g_2\left(\mu^\dagger_2\right)^2}{3kT}\right), \tag{9}$$

in which $\mu^\dagger_2$ is Kirkwood's molecular dipole moment in solution, including any enhancement due to the reaction field, and g_2 is a correlation factor whose deviation from unity allows for coupling between the orientation of the given dipole and the surrounding dipoles. Generally, g_2 will deviate substantially from unity if such coupling is quite strong [23]; ordinary dipole–dipole coupling alone is not enough. The calculated product $g_2^{1/2} \times \mu^\dagger_2$ for acesulfame amounts to $g_2^{1/2} \times \mu^\dagger_2 = (1.998 \pm 0.002) \times 10^{-29}$ C m and $g_2^{1/2} \times \mu^\dagger_2 = (1.232 \pm 0.002) \times 10^{-29}$ C m for saccharin. Since Onsager's electric dipole moment and Kirkwood's

Table 4 Values of the parameters of Eq. 4 in Ref. [17] of 1,4-dioxane solutions of acesulfame and saccharin (p_{Φ}^{∞}, a_p, a_{pp}, $p_{\Phi}^{\infty *}$, a_{p^*}, $a_{p^*p^*}$), and the partial molar polarization of acesulfame and saccharin at infinite dilution (P_2^0, P_2^{0*}) according to the Debye and Onsager models, respectively, at 298.15 K

Compound	p_{Φ}^{∞} (cm^3 g^{-1})	$-a_p$ (cm^3 g^{-1})	a_{pp} (cm^3 g^{-1})	$p_{\Phi}^{\infty *}$ (cm^3 g^{-1})	$-a_{p^*}$ (cm^3 g^{-1})	$a_{p^*p^*}$ (cm^3 g^{-1})	P_2^0 (cm^3 mol^{-1})	P_2^{0*} (cm^3 mol^{-1})
Acesulfame	3.290 ± 0.005	60.5 ± 1.0	–	4.700 ± 0.009	73 ± 2	–	536.74 ± 0.85	766.79 ± 1.50
Saccharin	1.259 ± 0.003	1.8 ± 0.1	10.2 ± 1	1.765 ± 0.004	0.80 ± 0.20	15 ± 2	230.57 ± 0.46	323.24 ± 0.78

product are equal within experimental error for saccharin, it may be assumed that coupling between a given dipole and surrounding dipoles is not strong. In the case of acesulfame, this difference amounts to 0.041×10^{-29} C m and can be ascribed to coupling of surrounding dipoles.

Self-association of acesulfame and saccharin

If association of solute species occurs, the volume polarization should increase less rapidly with increasing concentration than would be observed in the case of no interaction between the solute dipole moments. The decrease of the partial specific polarization of acesulfame and saccharin with increasing mass ratio can be interpreted according to the association of polar solute species. An interaction of this sort could be described by

$$2B_{\mathrm{m}} \leftrightarrow B_{\mathrm{d}} \tag{10}$$

and

$$K_{\mathrm{D}} = \frac{[B_{\mathrm{d}}]}{[B_{\mathrm{m}}]^2} = \frac{(1-\gamma)}{2\,c\gamma^2}, \tag{11}$$

where B_{m} and B_{d} are the monomeric and dimeric species, K_{D} is the association constant, c is the concentration in mol dm^{-3}, and γ is the fraction of solute present as monomer. In Eq. 11 it is assumed that activity coefficients of monomer and dimer species are approximated by unity. According to Treiner et al. [24], the dimerization constant and Debye electric dipole moment of the monomeric species μ_{m} can be calculated from the volume polarization of solution, which was applied previously for cyclohexylsulfamic acid in 1,4-dioxane solution [17]. The dimerization constant K_{D} and electric dipole moment of the monomeric species amount to $K_{\mathrm{D}} = 1.46 \pm 0.62$ and $\mu_{\mathrm{m}} = (1.64 \pm 0.01) \times 10^{-29}$ C m for acesulfame and $K_{\mathrm{D}} = 0.076 \pm 0.007$ and $\mu_{\mathrm{m}} = (9.95 \pm 0.02) \times 10^{-30}$ C m for saccharin. The calculated dipole moment of the monomeric species of acesulfame and saccharin is about 1×10^{-31} C m lower than those calculated from the Debye procedure. The dimerization constants of both compounds are of the expected order of magnitude for polar species in 1,4-dioxane [24]. The fractions of monomer γ calculated from Eq. 11 are high for both solutes investigated. At the lowest concentration they amount to 0.986 (acesulfame) and 0.998 (saccharin) and $\gamma = 0.905$ (acesulfame) and $\gamma = 0.932$ (saccharin) at the highest concentration studied.

According to X-ray diffraction studies [6–8, 25], infrared spectra, and ab initio force field calculations [5], except for the sulfonic group oxygen atoms and hydrogen atoms of methyl group (acesulfame), the molecules of acesulfame and saccharin are almost planar (Fig. 1). The monomeric units in dimeric species are linked by a combination of N–H···O=C and C–H···O hydrogen bonds in which all oxygen atoms act as acceptors. The N–H···O=C hydrogen bond, which utilizes a carbonyl O-atom as acceptor, generates a centrosymmetric dimer [6, 7]. The nonpolar dimeric arrangement of the acesulfame and saccharin molecule in 1,4-dioxane solution may be assumed as a discrete arrangement of monomeric polar molecules in antiparallel side-by-side configuration without further interactions [21]. Beside dipole–dipole interaction in a dimer species, strong hydrogen bonds between monomeric units and solvent molecules take place. Consequently, owing to the relatively low values of the dimerization constant, most of the molecules of acesulfame and saccharin are in 1,4-dioxane solution in monomeric form solvated by 1,4-dioxane molecules.

Experimental

Materials

Commercially available saccharin was purchased from Fluka and 1,4-dioxane (p.a.) from Kemika. The compounds were used as delivered without further purification and stored in a desiccator over P_2O_5. Acesulfame was produced from the potassium salt (acesulfame-K, purchased from

Fluka) by ion exchange of the cation of the salt with the hydrogen ion (Dowex, Type 50 WX8); water as a solvent was efficiently removed from the sample by means of a rotary evaporator. Like saccharin and 1,4-dioxane, the prepared acesulfame was kept in a vacuum desiccator over P_2O_5. The purity of acesulfame and saccharin was checked by titration with sodium tetraborate and also by analysis of the elements C, H, and N (Perkin Elmer, 2400 Series II CHNS/O Analyser); both compounds were found to be 99.9% pure. The purity of 1,4-dioxane was checked by comparing its experimental density and refractive index with data reported earlier ($n_D = 1.42025$) [18], and the agreement was found to be within experimental uncertainty ($\pm 2 \times 10^{-5}$). The investigated solutions were prepared at (solute/solvent) mass ratio ς_2 (i.e., grams of solute per gram of solvent [26]) by precise weighing, using a digital balance (model AT201; Mettler Toledo, Switzerland) accurate to within $\pm 1 \times 10^{-5}$ g.

Apparatus and procedure

The density ρ (g cm^{-3}) of 1,4-dioxane solutions of acesulfame and saccharin was measured by a vibrating-tube density meter (model DMA 60; Anton Paar, Graz, Austria) equipped with a measuring cell (type 602; Anton Paar) and a digital thermometer (DT 100-20; Anton Paar) with precision of ±0.01 K as before [17]. The density of pure 1,4-dioxane is 1.02792 g cm^{-3}, which is close to the literature value, $\rho = 1.02797$ g cm^{-3} [18].

The refractive index was measured with a model DUR-W2 Schmidt-Haensch refractometer with uncertainty of 1×10^{-5}. All measurements were performed at 298.15 K and at 589 nm wavelength.

Electric permittivities were measured by a WTW dipole meter (model DM 01) using a DFL 1 cell at constant frequency of 2 MHz as already described [17].

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