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Partial Molar Volumes of C_2–C_5 Normal and Branched Nitriles in Dilute Sulfolane Solutions at 30 °C

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Partial molar volumes, $\bar{v}_2$, of acetonitrile, propionitrile, butyronitrile, valeronitrile, 2-methylpropionitrile, and 2,2-dimethylpropionitrile were determined in dilute sulfolane solutions, at 30 °C. Data were correlated with van der Waals volumes, v_w, calculated by thermal data, by an improved method proposed by one of us. The empty volumes of molecules were calculated, for the six nitriles, in the presence ($\bar{v}_2 - v_w$) and in the absence ($V_2^\circ - v_w$) of the solvent and the relative extent of interactions under the two conditions was detected. Some regularities concerning group contributions to $\bar{v}_2$ were observed.

Introduction

This research was undertaken mainly with two aims: (a) First of all, we attempted to provide a new contribution for testing the adequacy of modern theories (*1–6*) in obtaining information about solute–solvent interactions starting from determinations of solute partial molar volume, $\bar{v}_2$, in dilute solutions; (b) furthermore, as it concerns sulfolane solutions of several solutes, we attempted to supply further evidence for the supposition, drawn from our previous papers (*7–10*), that sulfolane plays the role of an almost inert diluent and this in spite of a fairly high dipole moment (μ = 4.8 D) and a moderately high dielectric constant ($\epsilon^{30°C}$ = 43.4), presumably owing to the steric hindrance of its "globular" molecule (*11*, *12*).

In the last 10 years several papers indeed (*13*, *17*) appeared, which showed how specific solvent–solute and solute–solute interactions may be detected if it is assumed that the solute partial molar volume, $\bar{v}_2$, includes an intrinsic volume, impenetrable to other molecules, and an empty volume which can be modified by interactions; the former may be equated to van der Waals volume, v_w, and the latter to the difference $\bar{v}_2 - v_w = v_e$. Moreover, Bondi proposed that v_w could be calculated by addition of the van der Waals increments for separate atoms or atomic groups making up the molecule and hence several methods (*19–22*) were proposed for calculating these increments for groups or atoms in different states of bonding. Simultaneously extensive research was developed concerning the determinations of the partial volumes, $\bar{v}_2$, of solutes in aqueous and nonaqueous dilute solutions.

In this context we present herewith the results of our own determinations of $\bar{v}_2$ concerning dilute sulfolane solutions of normal and branched (C_2–C_5) alkane nitriles. Our choice of nitriles was guided by the regular variation of molecular size of selected nitriles, with increasing carbon atom number in the molecule, without inordinate alteration in molecular structure and the effective polarity of the nitrile [the dipole moment of the nitriles is 3.57 (normal), 3.65 (branched), and 3.44 (acetonitrile)]; on the other hand, the main conclusion which may be drawn from our previous determinations of thermodynamic and physical excess properties (*23–26*) (volumes, dielectric constants, and enthalpies) on mixing sulfolane and nitriles was that the structure of nitriles was but little disturbed by the presence of sulfolane. The selected nitriles were acetonitrile, propionitrile, butyronitrile, valeronitrile, 2-methylpropionitrile, and 2,2-dimethylpropionitrile; starting from capronitrile, solubility in sulfolane is lacking.

Experimental Section

Materials. Sulfolane, kindly supplied by Shell Italia, and nitriles were carefully purified and dried, as already reported (*11*, *23*, *26*).

The primary sources of component substances as well as the physical properties of purified materials are summarized in Table I and compared with the most reliable literature data.

Solutions were made by weight (reduced to mass) in a drybox and then stored in apt containers and protected from moisture as far as possible. The composition is stated as molality of nitrile (m); the nitrile is indicated as component 2.

Densities were measured with a DMA 60 digital precision density meter (Anton Paar, Austria) which was described elsewhere (*9*). The apparatus was calibrated with standard pure liquids. The calibration was repeated before and after each run. All measurements were carried out at a temperature of 303.16 ± 0.001 K because sulfolane is a solid at temperatures below 301.61 K.

The working temperature was checked with a platinum resistance thermometer assembled with a G2 Müller Bridge and calibrated by NBS (U.S.A.). The maximum error on density did not exceed 1.10^{-5} g cm^{-3}. For each binary system seven to nine measurements, at different molalities, were carried out. The selected molarlities ranged between 0.000 90 and 0.0250 m.

Results

The experimental values of density, $d_{1,2}^{303.16K}$, and molalities, m, of the solutions of (C_2–C_5) normal and branched nitriles are summarized in Tables II–VII, where also the averages of the measured densities, $d_1^{303.16K}$, of the solvent, before and after each run, are reported. The volumes of solutions, $V_{1,2}$ are calculated from molalities and densities and the apparent molar volumes of the solute ϕ_2, at ach composition, derived by using the following formula:

$$\phi_2 = (V_{1,2} - 1000/d_1)/m \qquad (1)$$

In the molality range studied, ϕ_2 values do not show any trend to vary with dilution; therefore, smoothed equations of the type

$$V_{1,2} = (1000/M_1)\bar{v}_1 + \bar{v}_2 m \qquad (2)$$

allow us to calculate the partial molar volume $\bar{v}_2$ of the solute on the basis of a linear dependence of $V_{1,2}$ on molalities (in eq 2, M_1 is the molecular weight of the solvent and $\bar{v}_1$ the partial molar volume of the solvent, obtained by linear extrapolation of eq 2 at m = 0).

In each table (Tables II–VII) the corresponding smoothed equation (eq 2) is also reported, which reproduces experimental values of volume and hence of density in the limits of experimental error. For the sake of comparison $\bar{v}_2$ values, calculated by smoothed eq 2, are reported in each Table. The volume V_2° of pure substances, as well as the partial molar volumes, $\bar{v}_2$, in dilute sulfolane solutions show a linear dependence on the number of CH_2 groups in the nitrile molecule, as shown in Figure 1. Therefore a constant group contribution may be assigned to CH_2 = 17.223 cm^3 in the case of pure substances

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Table I. Description and Physical Properties of Component Liquids

component	source	purification ref	$d^{303.16K}/(g\ cm^{-3})$ obsd	$d^{303.16K}/(g\ cm^{-3})$ ref	mp/K obsd	mp/K lit.
acetonitrile	J. T. Baker Chemical Co. (analyzed reagent)	*23-26*	0.771 11	0.771 20 (*27*)		
propionitrile	J. T. Baker Chemical Co. (analyzed reagent)	*23-26*	0.771 66	0.771 96 (*27*)		
butyronitrile	Aldrich Chemical Co. (analyzed reagent)	*23-26*	0.781 67	0.781 83 (*27*)		
valeronitrile	Aldrich Chemical Co. (analyzed reagent)	*23-26*	0.790 72	0.790 32 (*27*)		
2-methylpropionitrile	Aldrich Chemical Co. (analyzed reagent)	*23-26*	0.760 36	0.760 82 (*26, 27*)		
2,2-dimethylpropionitrile	Aldrich Chemical Co. (analyzed reagent)	*23-26*	0.752 00	0.752 00 (*26, 28*)		
sulfolane	Shell Italia	*11*			301.61	301.61 (*11*) 301.78 (*29*)

Table II. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-Acetonitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 30	792.202		
0.010 96	1.261 94	792.787	53.38	52.45
0.014 13	1.261 84	792.953	53.15	52.43
0.013 52	1.261 86	792.921	53.18	52.44
0.020 15	1.261 66	793.262	52.61	52.11
0.025 55	1.261 52	793.526	51.82	51.43
0.025 80	1.261 49	793.553	52.36	51.98

[a] $V_{1,2} = 792.212 + 51.94m$ (*2*). [b] Solvent = sulfolane; solute = acetonitrile.

Table III. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-Propionitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 28	792.217		
0.006 09	1.262 02	792.646	70.44	70.11
0.008 90	1.261 91	792.838	69.78	69.55
0.011 74	1.261 79	793.037	69.85	69.68
0.013 85	1.261 70	793.186	69.96	69.82
0.016 50	1.261 59	793.371	69.94	69.82
0.018 61	1.261 51	793.513	69.64	69.53
0.020 24	1.261 44	793.629	69.76	69.66

[a] $V_{1,2} = 792.219 + 69.70m$ (*2*). [b] Solvent = sulfolane; solute = propionitrile.

Table IV. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-Butyronitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 28	792.217		
0.001 21	1.262 22	792.321	85.95	80.17
0.002 62	1.262 13	792.455	90.84	88.17
0.004 94	1.262 01	792.657	89.07	87.65
0.014 52	1.261 54	793.477	86.76	86.29
0.016 98	1.261 40	793.700	87.34	86.93
0.020 68	1.261 26	793.991	85.78	85.44
0.020 69	1.261 25	793.996	86.11	85.77

[a] $V_{1,2} = 792.224 + 86.01m$ (*2*). [b] Solvent = sulfolane; solute = butyronitrile.

and = 16.70 cm^3 in the case of dilute solutions of nitriles (data refer to T = 303.16 K).

Table V. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-Valeronitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 08	792.343		
0.000 94	1.262 02	792.442	105.32	101.06
0.002 49	1.261 92	792.607	106.02	104.42
0.012 72	1.261 34	793.646	102.44	102.12
0.014 44	1.261 24	793.822	102.42	102.15
0.017 08	1.261 09	794.091	102.34	102.11
0.019 82	1.260 92	794.378	102.67	102.47
0.023 26	1.260 74	794.719	102.15	101.98

[a] $V_{1,2} = 792.347 + 102.16m$ (*2*). [b] Solvent = sulfolane; solute = valeronitrile.

Table VI. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-2-Methylpropionitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 23	792.248		
0.004 41	1.262 00	792.635	87.76	87.53
0.007 22	1.261 86	792.876	86.98	86.84
0.009 49	1.261 75	793.070	86.62	86.51
0.011 91	1.261 62	793.284	86.99	86.90
0.018 27	1.261 30	793.834	86.81	86.75
0.020 91	1.261 16	794.067	86.99	86.94
0.022 49	1.261 08	794.204	86.97	86.93

[a] $V_{1,2} = 792.249 + 86.90m$ (*2*). [b] Solvent = sulfolane; solute = 2-methylpropionitrile.

Table VII. Densities ($d_{1,2}$) and Total Volumes ($V_{1,2}$)[a] of Sulfolane (1)-2,2-Dimethylpropionitrile (2) Solutions[b] and Apparent Molar Volumes (ϕ_2) and Partial Molar Volumes ($\bar{v}_2$) of Solute at 303.16 K

m	$d_{1,2}$	$V_{1,2}$	ϕ_2	$\bar{v}_2$
0.000 00	1.262 33	792.183		
0.004 91	1.262 07	792.674	100.00	101.83
0.007 42	1.261 90	792.945	102.70	103.91
0.009 83	1.261 76	793.190	102.44	103.36
0.012 18	1.261 60	793.444	103.53	104.27
0.014 99	1.261 44	793.732	103.34	103.94
0.017 52	1.261 30	793.989	103.08	103.60
0.020 18	1.261 11	794.284	104.11	104.56
0.020 21	1.261 14	794.264	102.97	103.41

[a] $V_{1,2} = 792.174 + 103.84m$ (*2*). [b] Solvent = sulfolane; solute = 2,2-dimethylpropionitrile.

Discussion

Current theories on solutions ascribe to first approximation spherical envelopes to molecular force fields, affording sometimes corrections for the nonsphericity in the case for example, of cylindrical molecules.

However, all theories agree with the statement that only empty volumes, v_e, are responsible for interactions of any kind

Table VIII. Molar Volumes of Pure Substances at 298.16 K, Vaporization Enthalpies at 298.16 K ($\Delta H_v^{298.16K}$) and at the Boiling Point ($\Delta H_v^{T_B}$), and van der Waals Volumes (v_w) for C_2-C_5 Normal and Branched Nitriles

substance	$V_2°$/(cm^3 mol^{-1})	$\Delta H_v^{298.16K}$/(kJ mol^{-1})	$\Delta H_v^{T_B}$/(kJ mol^{-1})		v_w/(cm^3 mol^{-1}) eq 8	v_w/(cm^3 mol^{-1}) Bondi
CH_3CN	52.868 (*9*)	32.94 (*30, 31*)	29.82	(T_B = 353.66 K) (*27*)	27.75	28.37
CH_3CH_2CN	70.928 (*23*)	36.03 (*30, 31*)	30.96	(T_B = 370.57 K) (*27*)	38.15	38.60
$CH_3(CH_2)_2CN$	87.890 (*23*)	39.33 (*30, 31*)	32.56	(T_B = 391.10 K) (*27*)	48.08	48.83
$CH_3(CH_2)_3CN$	104.615 (*23*)	43.60 (*30, 31*)	33.39	(T_B = 414.46 K) (*27*)	59.24	59.08
$(CH_3)_2CHCN$	90.355 (*26*)	37.11 (*30, 31*)		(T_B = 377.01 K) (*27*)		48.83
$(CH_3)_3CCN$	109.860 (*26*)	37.36 (*30, 31*)		(T_B = 379.16 K) (*28*)		59.08

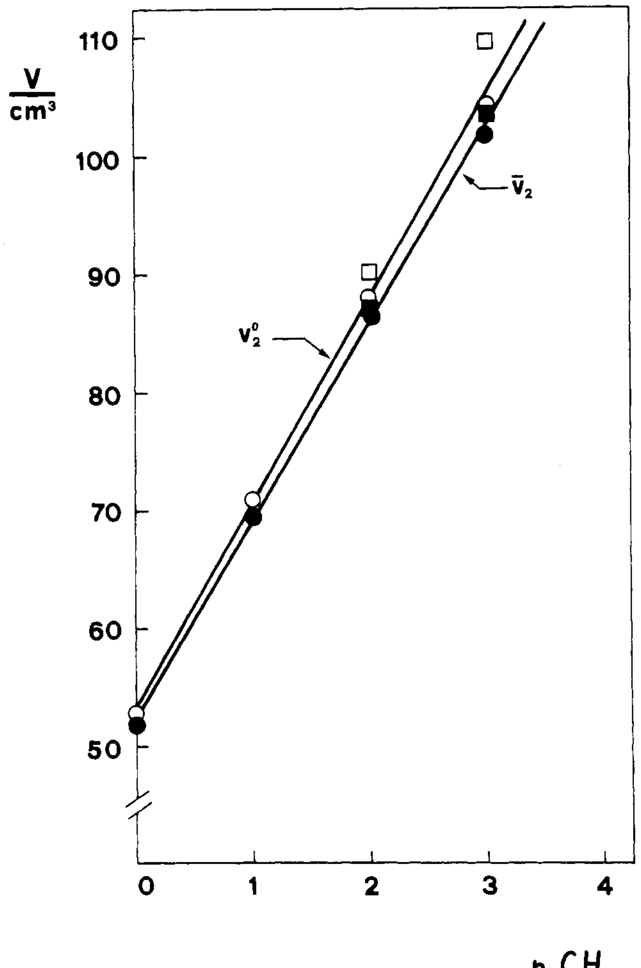

Figure 1. Molar volumes $V_2°$ (open circles) and partial molar volumes $\bar{v}_2$ (full circles) vs. the number of CH_2 groups for C_2–C_5 normal nitriles at 303.16 K; for the sake of comparison also molar volumes (open squares) and partial molar volumes (full squares) for branched nitriles are reported.

Table IX. Molar Volumes ($V_2°$) of Pure Substances, Partial Molar Volumes ($\bar{v}_2$) in Dilute Sulfolane Solutions at 303.16 K, and Ratios (*r* and *R*) for C_2-C_5 Normal and Branched Nitriles

substance	$V_2°$/ cm^3 mol^{-1})	$\bar{v}_2$/ (cm^3 mol^{-1})	$r^{a,b}$	R^c
CH_3CN	53.239 (*9*)	51.94	0.94_9	0.97_3
CH_3CH_2CN	71.387 (*23*)	69.70	0.94_9	0.97_2
$CH_3(CH_2)_2CN$	88.418 (*23*)	86.01	0.94_1	0.96_7
$CH_3(CH_2)_3CN$	105.190 (*23*)	102.16	0.93_4	0.96_2
$(CH_3)_2CHCN$	90.921 (*26*)	86.90	(0.90_4)	(0.94_6)
$(CH_3)_3CCN$	110.551 (*26*)	103.84	(0.87_0)	(0.92_6)

[a] $r = (v_2 - v_w)/(V_2° - v_w)$. The scarcely noticeable, if any, change of v_w with temperature has been disregarded in the calculations. [b] Data in parentheses refer to calculations with Bondi's v_w values. [c] $R = r(V_2°/\bar{v}_2)$.

which result in an increase or shrinkage of empty volumes.

Therefore, we prefer to disregard, for the present, any consideration of the shape of the molecules and focus our efforts on calculating correct values of empty volumes of nitriles.

At this point we would like to underline an improved method (*32*) proposed by one of us for calculating van der waals volumes of molecules apart from theoretical considerations of the different states of bonding of component atoms. This method is based on the supposition that the vaporization enthalpy, ΔH_v^T, which includes all energetic effects of the structural destruction of a liquid, depends on the ratio v_w/v_e, which may be related to the packing density, $v_w/V°$, after King (*13*):

$$\Delta H_v^T = K(v_w/v_e) \tag{3}$$

On the other hand, from a review of literature data on vaporization enthalpies for several classes of substances, the conclusion may be drawn that the empty volume of a molecule amounts to 50% of the total volume, $V_2°$, at the boiling point, T_B: therefore, at T_B, eq 3 reduces to

$$\Delta H_v^{T_B} = K \tag{4}$$

Hence, we may derive from eq 3 and 4 the expression

$$\Delta H_v^T = \Delta H_v^{T_B}(v_w/v_e) \tag{5}$$

and hence

$$v_w = V_2^{°,T}/(1 + \Delta H_v^{T_B}/\Delta H_v^T) \tag{6}$$

Equation 6 allows us to calculate the van der Waals volumes of molecules from thermal data only.

The calculated values of v_w for all normal C_2–C_5 nitriles are compared in Table VIII with Bondi's data. The deviations between the two series of data in no case exceed 0.6 cm^3 mol^{-1}; although the agreement may be judged satisfactory, nevertheless we would think that our own values, which are drawn directly from experimental data of ΔH_v^T, reflect more faithfully the real energetic situation of the molecule; for example, Bondi's value for CH_3CN does not take into account, doubtless, the inductive effect of CH_3 toward the $-C^+{=}N^-$: group (it should be responsible for the observed decrease in the dipole moment of the molecule with respect to higher members of the nitrile series).

Data on vaporization enthalpy, at T_B, for branched nitriles are lacking in the literature; therefore, we could not apply our method in calculating v_w for branched nitriles.

Data in Table IX ($V_2°$, $\bar{v}_2$, and v_w) allow the empty volumes of nitriles in the absence ($V_2° - v_w$) and in the presence ($\bar{v}_2 - v_w$) of sulfolane at 303.16 K to be calculated.

Then the ratio $(\bar{v}_2 - v_w)/(V_2° - v_w) = r$ may be indicated as a valid criterium for calculating the relative extent of solute–solvent and solute–solute interactions and, on the whole, characterizing the solvent as structure making or breaking.

In Table IX the ratio, normalized to the effective volumes $V_2°$ and $\bar{v}_2$, is also reported: $r(V_2°/\bar{v}_2) = R$.

The magnitudes of the two parameters *r* and *R* for all nitriles studied, noticeably close to unity, supply further evidence for our previous (*7*, *10*, *23–26*) statement of the role of sulfolane as an almost inert diluent. The observed regularities (Table IX and Figure 1), concerning the behavior of V_2° and $\bar{v}_2$ as a function of the number of CH_2 groups in nitrile molecules, would prompt us to enter into a discussion on the suitability of one or another theory, based on group-contribution models, in interpretating experimental data. Moreover, our measurements were carried out at 303.16 K, as reported above, whereas most of the literature data on the subject refer to measurements, on aqueous solutions, at 298.16 K. Therefore, we think that, for a more detailed discussion and a more complete and self-consistent review of literature data, for the sake of comparison, measurements on dilute aqueous nitrile solutions are needed, at 298.16 K, which will be the subject of the next paper.

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Registry No. Sulfolane, 126-33-0; acetonitrile, 75-05-8; propionitrile, 107-12-0; butyronitrile, 109-74-0; valeronitrile, 110-59-8; 2-methylpropionitrile, 78-82-0; 2,2-dimethylpropionitrile, 630-18-2.

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Partial Molar Volumes of C_2–C_6 *n*-Alkanenitriles and Octanenitrile in Dilute Aqueous Solutions at 298.16 K

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Partial molar volumes, $\bar{v}_2$, of acetonitrile, propionitrile, butyronitrile, valeronitrile, and hexane- and octanenitriles were measured in dilute aqueous solutions, at 298.16 K. Experimental data were correlated to van der Waals volumes, v_w, calculated from thermal data. Equations of the kind $V = av_w + b$ ($a \simeq 1.55$) were found to be suitable in reproducing both volumes of pure substances and partial molar volumes of solutes in dilute solutions within the limits of experimental errors. The above correlation may be interpreted in terms of an impenetrable volume larger than v_w, presumably because of intrinsic geometrical factors, which result in reducing the empty volume involved in interactions. Data on nitriles are analyzed in the light of current theories based on group-contribution models.

Introduction

In a previous note (*1*) we presented data on partial molar volumes, $\bar{v}_2$, of normal and branched C_2–C_5 alkanenitriles in dilute sulfolane solutions, at 303.16 K. Some regularities were observed concerning the CH_2 and CH_3 group contributions both to volume V_2° of pure nitriles and to $\bar{v}_2$ of nitriles as solutes, as expected.

Furthermore, on the basis of the supposition that only the empty volume of a molecule, v_e ($\simeq V^\circ - v_w$, to first approximation), could be modified by interactions of any kind, we calculated the van der Waals volumes, v_w, from thermal data by means of an improved method proposed by one of us (*2*).

We suggested as well a possible criterion for evaluating the relative extent of solute–solvent interactions and solute–solute interactions and hence for classifying the solvent as structure making or breaking. We preferred however, at that time, not to enter into a discussion on the suitability of one or another of current theories (*3–5*) based on group-contribution models. We proposed the interpretation of experimental data, after the completion of the picture of nitrile series behavior by means of analogous measurements on aqueous solutions. This is the subject of the present note.

Experimental Section

Conductivity water was obtained by repeated distillations over $KMnO_4$ after passage through a mixed-bed ion-exchange-resin column. The conductance of samples collected and stored after degassing, in all-Pyrex glassware, routinely ranged between 0.4×10^{-6} and 1×10^{-6} Ω^{-1} cm^{-1}.

C_2–C_5 n-Alkanenitriles (J. T. Baker Chemical Co.) were purified as reported previously (*6*). Hexane- and octanenitriles (Aldrich Chemical Co.) were purified by repeated distillation over P_2O_5.

The properties (density, dielectric constants, melting points) of the samples agreed with the most reliable literature data (*7*).

Solutions were made by weight (reduced to mass) and stored in dark containers. In the case of octanenitrile, because of its

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