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Static Dielectric Constants of Acetonitrile/Water Mixtures at Different Temperatures and Debye−Hückel *A* and a_0B Parameters for Activity Coefficients

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Static dielectric constants of acetonitrile/water mixtures in the whole composition range and within the temperature range from (15 to 60) °C have been measured. The values were fitted to a unique equation as a simultaneous function of temperature and acetonitrile composition. Densities of these mixtures at temperatures from (5 to 55) °C and different compositions have been collected from the literature. The complete data set was critically analyzed, the outliers were excluded, and the remaining values were also fitted to a unique equation as a function of temperature and acetonitrile composition. From the dielectric constants and densities, the activity coefficients of ions can be calculated by means of the Debye−Hückel approach, allowing the study of the ionic equilibria and determination of reference pH values or acidity constants in any acetonitrile/water mixture at any temperature within the studied range.

Introduction

The knowledge of solvent physical properties is fundamental in understanding the behavior of their solutions. Densities and static dielectric constants have a special interest because they are critical for solution chemistry [i.e., change of composition scales (by volume/weight), concentration scales (molal/molar), estimation of ionic activities, determination of equilibrium constants involving ions, reference pH values, reference standard potential of electrochemical cells, etc.]. For most of the pure liquids these properties are available in literature at 25 °C and for a few of them at other temperatures.[1] Alcohol/water mixtures have been used as polar solvents since early years. Then, for some mixtures of methanol, ethanol, or ethylene glycol with water, these physical properties can be found in literature.[1,2] The acetonitrile/water mixtures became of importance in the last few decades, mainly due to their extended use in reverse-phase liquid chromatography. Viscosities, densities, and dielectric constants for these mixtures have been reported in the literature for different acetonitrile/water compositions at 25 °C. Recently, the manufacture of thermally resistant HPLC columns allowed the development of chromatographic methods at higher temperatures. However, fundamental studies supporting the use of high-temperature liquid chromatography in acetonitrile/water mixtures are scarce, in part due to the lack of physical property data. For instance, for temperatures higher than 25 °C, pH reference standard values for the calibration of electrodes in acetonitrile/water are available only for 35 °C and at the specific compositions where the dielectric constants were available.[3−5] Literature data of acetonitrile/water mixture densities at several temperatures are available, but the values can be spread out due to different authors. A complete and systematic study of its dependence with both variables, solvent composition and temperature, is still lacking.

In this work, we determine the static dielectric constants of acetonitrile/water mixtures in the composition range from (0 to 100) % in steps of 10 % and for the temperature range from (15 to 60) °C in steps of 5 °C. The obtained values are compared with those available in literature, and finally, they are fitted to a unique empirical equation that allows an accurate estimation of the dielectric constant as a simultaneous function of the acetonitrile composition and temperature. In addition, densities of acetonitrile/water mixtures have been collected from literature and fitted to an empirical single equation. Previously, the complete data set was critically analyzed, and those values resulting from outliers were not considered. The obtained equation can be used not only for the estimation of the density of acetonitrile/water mixtures at any temperature and composition within the range but also for describing the change of this property with these variables.

Once density and static dielectric constants are determined, the ionic activity coefficients can be calculated at any temperature and composition of the studied range by means of the extended Debye−Hückel equation:[6]

$$-\log\ {}_s^s\gamma = \frac{z^2 A\sqrt{I}}{1 + a_0 B\sqrt{I}} \qquad (1)$$

A and a_0B are the parameters of this equation and can be calculated by using the densities and static dielectric constants reported in this paper and by adopting the Bates−Guggenheim convention, which considers a constant value of 4.56 Å for the Debye radius (a_0). Equations for these parameters are as follows:[6−8]

$$A = 1.8246 \times 10^6 \sqrt{\frac{\rho_s}{(\epsilon_s T)^3}} \qquad (2)$$

and

$$a_0B = 1.5\sqrt{\left(\frac{\epsilon_w}{\epsilon_s}\right)\left(\frac{\rho_s}{\rho_w}\right)} \qquad (3)$$

where T is the absolute temperature; ϵ is the static dielectric

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Table 1. Experimental and Literature Data of Static Dielectric Constant of Acetonitrile + Water Mixtures from (288.15 to 333.15) K

acetonitrile % w/w	x_{ACN}[a]	15 °C		20 °C		25 °C		30 °C	35 °C		40 °C		45 °C		50 °C	55 °C	60 °C
0	0	82.00[b]		80.14[b] 80.16[c] 80.18[d]		78.33[b] 78.36[c] 78.37[d]		76.5[b] 76.57[c] 76.60[d]	74.84[b]		73.15[b] 73.16[c] 73.18[d]		71.51[b]		69.90[b] 69.90[c] 69.91[d]	68.3[b]	66.79[b] 66.79[c] 66.78[d]
10	0.0465	78.61		76.80		74.92	74.7[e]	73.36	71.55		70.04		68.44		66.84	65.36	63.85
20	0.0988	73.85		72.05	73.2[f]	70.49	70.5[e] at 20.2 %[g]	68.85	67.33	67.4 at 20.2 %[g]	65.90		64.34		62.99	61.47	60.07
30	0.158	68.68		67.21		65.57	65.8[e]	64.22	62.78		61.26		59.91		58.60	57.29	55.97
40	0.226	63.44		62.00	64.8[f]	60.61	60.2[e]	59.30	58.07		56.79		55.44		54.13	53.02	51.79
50	0.305	58.11		56.92		55.69	55.7[e]	54.58	53.43		52.28		51.18		49.99	48.92	47.94
60	0.397	53.10	53.2 at 60.3 %[g]	52.20	54.6[f]	51.05	50.8[e] at 60.3 %[g]	50.07	48.88	48.9 at 60.3 %[g]	47.98		46.87		45.89	44.90	43.92
70	0.506	48.72		47.77		46.83	46.5[e]	45.89	44.99	45.3 at 69.5 %[g]	44.12		43.18		42.28	41.38	40.52
80	0.637	44.82		43.92	45.6[f]	43.10	43.2 at 79.5 %[h]	42.20	41.38		40.64		39.74		38.84	37.97	37.15
90	0.798	41.05	41.2 at 90.1 %[g]	40.39		39.41	39.3 at 90.1 %[g]	38.67	37.85	37.9 at 90.1 %[g]	37.11		36.29		35.39	34.82	34.08
100	1	37.52	37.6[g]	36.62	36.8[f]	35.88	35.9[g–k] 33.0,[l] 37.0[m]	35.15	34.45	34.8[g], 30.0[i]	33.75	33.8[j] 33.1[m]	33.01	28.0 l	32.36	31.62	31.05

[a] Acetonitrile mole fraction. [b] Values averaged from refs 9 and 10. [c] From ref 38. [d] From ref 39. [e] From ref 27. [f] From ref 29. [g] From ref 3. [h] From ref 11. [i] From ref 24. [j] From ref 23. [k] From ref 26. [l] From ref 28. [m] From ref 25.

Table 2. Parameters of Equation 6 To Calculate the Dielectric Constants of Acetonitrile/Water Mixtures at Different Temperatures in Different Solvent Composition Scales

	acetonitrile composition		
parameter	% w/w	% v/v[a]	x_{ACN}
a	87.73	87.67	87.57
b	−0.3311	−0.3009	−49.19
c	$5.144 \cdot 10^{-3}$	$4.723 \cdot 10^{-3}$	124.6
d	$-3.536 \cdot 10^{-5}$	$-3.355 \cdot 10^{-5}$	−86.09
e	−0.1867	−0.1888	−0.2410
f	$-7.583 \cdot 10^{-4}$	$-1.347 \cdot 10^{-3}$	0.4432
g	$1.736 \cdot 10^{-4}$	$1.448 \cdot 10^{-4}$	2.598
h	$-8.830 \cdot 10^{-7}$	$-5.209 \cdot 10^{-7}$	−2.108
i	$2.430 \cdot 10^{-3}$	$2.3861 \cdot 10^{-3}$	$1.528 \cdot 10^{-3}$
r^2[b]	0.99989	0.99995	0.99988
s[c]	0.1	0.1	0.2

[a] Volumes measured at 20 °C. [b] r^2, correlation coefficient. [c] s, standard deviation.

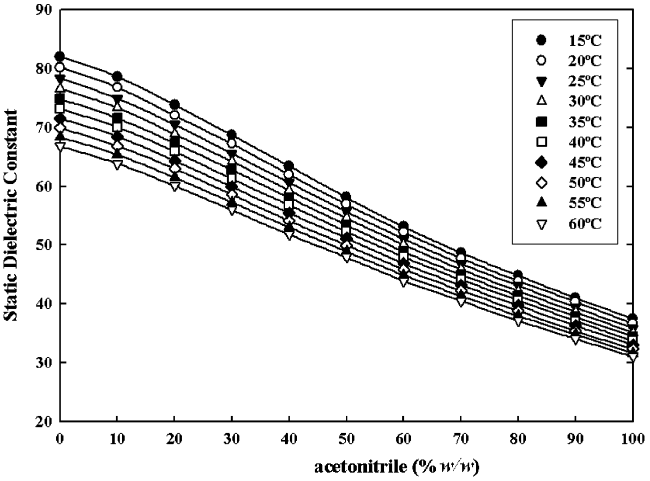

Figure 1. Static dielectric constants of acetonitrile/water mixtures at different temperatures. Symbols correspond to experimental values and lines to predictions from eq 6.

constant, and ρ is the density, all of them at the working temperature; subscript w indicates pure water; and subscript s indicates the solvent mixture.

Experimental Section

Instrumentation. Static dielectric constants of the solvent mixtures have been determined by measuring the capacitance of a thermostated cylindrical capacitance WTW cell (model MFL-3). Measured capacitance of this cell empty was 6.05 pF. The cell was connected to a Selecta Tectron Bio water bath to control the temperature within the range of ± 0.2 °C of the desired temperature. The measurements have been done with a Boonton 7200 capacitance meter using a potential of 100 mV alternating at 1 MHz frequency. The precision of the measurements was about 0.2 %. All the capacitances were measured by duplicate.

Chemicals. Solutions were prepared with water supplied by a Milli-Q system, acetonitrile, and methanol Merck LiChroSolv (HPLC grade). The resistance of the ultrapure water was of more than 18 MΩ, and the organic solvents are provided with less than 0.02 % water. All necessary safety cautions have been considered for solvent handling and waste disposal.

Procedures. The capacitance meter system was calibrated by measuring the capacitances of pure water at different temperatures from (15 to 60) °C (see Table 1), pure methanol at 25 °C ($\epsilon = 32.62$ and 32.63 from refs 11 and 12, respectively), and pure acetonitrile at 25 °C ($\epsilon = 35.87$, 35.90, 35.95, 35.84, and 35.95, from refs 13, 24, 23, 26, and 11, respectively).[9−13] Reliability of the capacitance meter was tested adding resistances of decreasing values from (20, 2, and 0.5) kΩ between terminals in the conditions of temperature and solvent composition of maximum conductivity: pure water at 60 °C. We verified that the loss increased intentionally did not affect the capacitance measured by the bridge. The calibration of the measured capacitance versus dielectric constant is a straight line in which the intercept is a residual capacitance of the whole system (wires, connections, Faraday box, cell in vacuum, etc.),and the slope is a constant involving the geometry of the cell and the dielectric constant of vacuum.

Selection of the best mathematical function from a large collection of equations (more than 3000) was done by using the Akima procedure.[14−18] The choice of the empirical equation

Table 3. Parameters of Equation 7 To Calculate Densities of Acetonitrile/Water Mixtures at Different Temperatures in Different Solvent Composition Scales

	acetonitrile composition		
parameter	% w/w	% v/v[a]	x_{ACN}
a	1.0012	1.0023	1.0033
b	$7.8397 \cdot 10^{-3}$	$8.9890 \cdot 10^{-4}$	0.0901
c	$-1.0718 \cdot 10^{-2}$	$-6.6075 \cdot 10^{-3}$	$-6.5659 \cdot 10^{-3}$
d	$3.5274 \cdot 10^{-5}$	$2.6672 \cdot 10^{-5}$	$2.7135 \cdot 10^{-5}$
e	$8.9212 \cdot 10^{-3}$	1.8311.10−3	0.4693
f	$3.3215 \cdot 10^{-5}$	$1.7501 \cdot 10^{-5}$	−0.1088
g	$-1.0614 \cdot 10^{-2}$	$-6.4850 \cdot 10^{-3}$	$-6.4543 \cdot 10^{-3}$
h	$3.6539 \cdot 10^{-5}$	$2.9337 \cdot 10^{-5}$	$3.0034 \cdot 10^{-5}$
r^2 [b]	0.99988	0.9998	0.9997
s [c]	0.0009	0.0011	0.002

[a] Measured at 20 °C. [b] r^2, correlation coefficient. [c] s, standard deviation.

was based on the stabilization of the standard deviation at a minimum value as the number of parameters of the equations was increased. After the selection of the best empirical equation of the set, the single fitting of the experimental data was carried out with the software Sigma Plot v4 for Windows, which uses the Marquardt−Levenberg algorithm.[19]

Results and Discussion

The experimentally measured dielectric constants of acetonitrile/water mixtures at different temperatures are shown in Table 1. Values for pure water included in the table are from the literature and are those used for the calibration of the cell. The acetonitrile composition is given in weight percent (% w) because the experimental work was conducted using this composition scale, although it can be easily converted in volume percent at 20 °C (% v) or mole fraction (x_{ACN}) by using the following equations:

$$\%\,\mathrm{w} = \frac{100}{1 + \left(\frac{M_w}{M_{\mathrm{ACN}}}\right)\left(\frac{1 - x_{\mathrm{ACN}}}{x_{\mathrm{ACN}}}\right)} \quad \text{or} \quad x_{\mathrm{ACN}} = \frac{1}{1 + \left(\frac{M_{\mathrm{ACN}}}{M_W}\right)\left(\frac{100 - \%\,\mathrm{w}}{\%\,\mathrm{w}}\right)} \tag{4}$$

where $M_{\mathrm{ACN}} = 41.05$ and $M_W = 18.015$ are the molar weights of the solvent indicated in the subscript, and

$$\%\,\mathrm{w} = \frac{100}{1 + \left(\frac{\rho_w^{20°}}{\rho_{\mathrm{ACN}}^{20°}}\right)\left(\frac{100 - \%\,\mathrm{v}}{\%\,\mathrm{v}}\right)} \quad \text{or} \quad \%\,\mathrm{v} = \frac{100}{1 + \left(\frac{\rho_{\mathrm{ACN}}^{20°}}{\rho_w^{20°}}\right)\left(\frac{100 - \%\,\mathrm{w}}{\%\,\mathrm{w}}\right)} \tag{5}$$

where $\rho_{\mathrm{ACN}}^{20°} = 0.78186$ and $\rho_w^{20°} = 0.99821$ are the densities of the pure solvents at 20 °C obtained from the literature.[20−22] The obtained dielectric constants are in good agreement with that reported in literature by refs 3, 11, 12, and 23−26. A few values reported by Niazi and Ali[27] show small but clear differences, and values of the refs 28 and 29 are markedly far from our values.

The empirical equation used to fit the dielectric constant values determined experimentally is expressed as follows:

$$\epsilon_s = \frac{(a + bX + cX^2 + dX^3 + eY)}{(1 + fX + gX^2 + hX^3 + iY)} \tag{6}$$

where ϵ is the static dielectric constant; X is the acetonitrile content in the mixture, which can be expressed as % w, % v,

Table 4. Parameter *A* of the Debye−Hückel Equation 1[a]

acetonitrile % w/w	x_{ACN}[b]	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C
0	0	0.507	0.511	0.515	0.52	0.524	0.529	0.534	0.539	0.544	0.503
10	0.0465	0.536	0.54	0.545	0.55	0.555	0.56	0.565	0.571	0.576	0.532
20	0.0988	0.581	0.586	0.59	0.595	0.6	0.606	0.611	0.617	0.623	0.577
30	0.158	0.642	0.646	0.651	0.655	0.66	0.666	0.671	0.677	0.683	0.638
40	0.226	0.716	0.72	0.724	0.729	0.734	0.739	0.744	0.75	0.756	0.712
50	0.305	0.802	0.806	0.81	0.814	0.819	0.824	0.829	0.835	0.841	0.799
60	0.397	0.901	0.904	0.907	0.911	0.915	0.92	0.925	0.931	0.937	0.898
70	0.506	1.011	1.014	1.017	1.02	1.024	1.029	1.034	1.04	1.046	1.009
80	0.637	1.135	1.138	1.141	1.144	1.148	1.153	1.158	1.164	1.171	1.134
90	0.798	1.278	1.28	1.284	1.287	1.292	1.297	1.303	1.31	1.318	1.276
100	1	1.447	1.45	1.455	1.459	1.465	1.472	1.48	1.488	1.498	1.445

[a] Values given in molal scale. [b] Acetonitrile mole fraction.

Table 5. Parameter a_0B of the Debye−Hückel Equation 1[a]

acetonitrile % w/w	x_{ACN}[b]	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C
0	0	1.500	1.500	1.500	1.500	1.500	1.500	1.500	1.500	1.500	1.500
10	0.0465	1.521	1.520	1.520	1.520	1.519	1.519	1.519	1.518	1.518	1.518
20	0.0988	1.553	1.552	1.551	1.550	1.549	1.548	1.547	1.546	1.545	1.544
30	0.158	1.594	1.592	1.590	1.588	1.586	1.584	1.582	1.581	1.579	1.578
40	0.226	1.640	1.637	1.634	1.631	1.629	1.626	1.623	1.620	1.618	1.616
50	0.305	1.691	1.686	1.682	1.678	1.674	1.670	1.667	1.663	1.660	1.657
60	0.397	1.742	1.737	1.732	1.727	1.722	1.717	1.713	1.708	1.704	1.701
70	0.506	1.795	1.789	1.783	1.777	1.771	1.766	1.761	1.756	1.751	1.747
80	0.637	1.850	1.843	1.836	1.829	1.823	1.817	1.811	1.805	1.800	1.796
90	0.798	1.907	1.900	1.892	1.885	1.878	1.871	1.865	1.859	1.854	1.849
100	1	1.970	1.962	1.954	1.947	1.940	1.933	1.927	1.921	1.916	1.911

[a] Values given in molal scale. [b] Acetonitrile mole fraction.

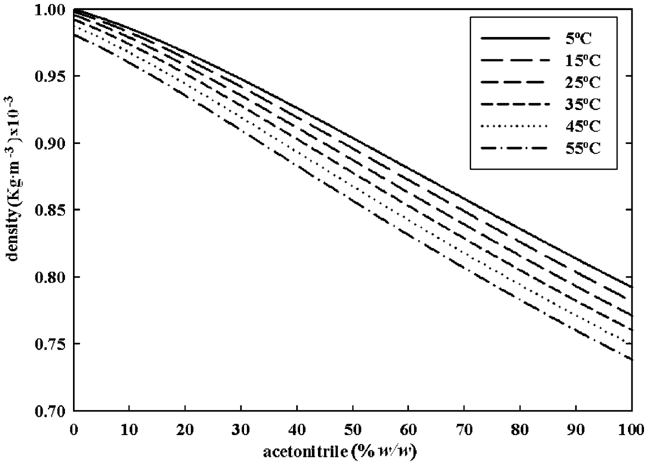

Figure 2. Densities of acetonitrile/water mixtures at different temperatures predicted with eq 7 using the coefficients obtained from the fittings.

or x_{ACN}; and Y is the temperature (Celsius). Parameters of the fitting of eq 6, coefficients, standard deviations, and correlation coefficients in different acetonitrile content scales, are listed in Table 2, and the results are shown in Figure 1.

A literature search of densities of acetonitrile/water mixtures at different temperatures gave 904 values within the temperature range from (0 to 55) °C.[4,11−13,20−22,27,30−37] In order to avoid a change of the slope due to the known maximum density of the pure water at 4 °C, we use only the values given at temperatures higher than 5 °C. Obviously, extrapolations of the fitted equation to temperatures lower than 4 °C are not recommended. The best empirical equation we have found to fit the data set is the following:

$$\rho_s = \frac{(a + bX + cY + dY^2)}{(1 + eX + fX^2 + gY + hY^2)} \qquad (7)$$

where X and Y have the same meaning than in eq 6. Outliers exceeding the range of two standard deviations (34 values) have been rejected. Parameters and standard deviations of these fittings are shown in Table 3. Standard deviations of the fittings in the acetonitrile composition by volume and mole fraction are slightly higher than those in weight percent; then, eqs 4 and 5 can be used to convert the acetonitrile composition scale to obtain density with eq 7 in the acetonitrile composition by weight. Density values calculated with eq 7 for acetonitrile/water mixtures at some different temperatures are represented in Figure 2. Relative errors for estimations with eq 7 are quite acceptable (± 0.1 %). Therefore, the estimated density is accurate enough to convert solvent compositions (% v − % w) to convert analytical concentrations (molar/molal) and also to estimate the activity coefficients by means of the Debye−Hückel theory. The parameters A and a_0B used to calculate the activity coefficients with eq 1 using the dielectric constants and densities reported in this work are listed in Tables 4 and 5.

Conclusions

Dielectric constants of acetonitrile/water mixtures within the complete range of compositions and at temperatures from (15 to 60) °C were determined. The values were fitted to a unique equation as a function of both parameters: temperature and composition. A data compilation of densities for acetonitrile/water mixtures was also carried out. The values were analyzed, and the data for temperatures higher than 5 °C were fitted to an empirical equation to represent the behavior of the densities as a function of the temperature and acetonitrile composition. With the values obtained from the fitted equations, ionic activity coefficients in acetonitrile/water mixtures of any composition and temperature of the studied ranges can be easily calculated from to the Debye−Hückel theory to be used in determinations involving ionic activities.

Acknowledgment

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Supporting Information Available:

Densities of acetonitrile/water mixtures at several compositions and from (273.15 to 328.15) K compiled from literature. This material is available via Internet at: http://pubs.acs.org.

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