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Speed of Sound in Concentrated Aqueous KCl Solutions from 278.15 to 338.15 K

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The speed of sound in aqueous KCl is measured up to high concentration in the temperature range (273.15 to 338.15) K. The sound speed data are analyzed with the specific ion-interaction theory of Pitzer with an average standard deviation of 0.31 m·s^{-1} in the temperature range studied.

Introduction

During our theoretical and experimental investigations on the effect of electrolytes on the thermodynamic properties of amino acids,[1] we faced a problem of lack of sound speed data of aqueous KCl up to high concentrations in the temperature range (278.15 to 338.15) K. Accurate densities of concentrated KCl solutions at different temperatures, including at 298.15 K, are available in the literature.[2] Reports are available on the measurements of speed of sound of aqueous KCl up to high concentrations at 298.15 K.[3,4] With respect to other temperatures other than 298.15 K, the speed of sound in very dilute KCl solutions has been reported at some discrete temperatures by Japanese workers.[5−7] In view of the above, we present the speed of sound of aqueous concentrated KCl from (278.15 to 338.15) K with 10 K intervals.

Experimental Section

KCl (Baker analyzed) was dried at 423 K in an oven and stored in a desiccator prior to use. The solutions were prepared by mass in deionized water (with 0.055 μS·cm^{-1} conductivity, 18.2 MΩ·cm resistance from Elga PURELAB classic model) on a single pan Mettler balance within the accuracy of 0.01 mg. The molalities were accurate to within 2×10^{-4} mol·kg^{-1}.

An ultrasonic interferometer (Mittal Enterprises) was used to measure the speeds of sound in solutions at 2 MHz. The quartz crystal was fixed at the bottom of the measuring cell of the interferometer. The crystal was excited at its resonance frequency to produce sound waves of 2 MHz frequency in the test solution inside the cell using a high-frequency generator. A micrometer supplied by Mitutoyo Manufacturing Company Limited Japan with a resolution of 1×10^{-4} cm was provided at the top of cell. A metallic reflector plate held parallel to the quartz crystal could be raised or lowered through a known distance in the test solution, and the wavelength of the sound waves was determined by noting the distance covered by the reflector plate between successive resonance peaks. The interferometer was calibrated against the literature data on NaCl solutions.[8] The sound speeds of the solutions were measured relative to those in water to a precision of 0.10 m·s^{-1} and an estimated accuracy of 0.60 m·s^{-1}. The temperature for all the measurements was kept constant to within 0.005 K.

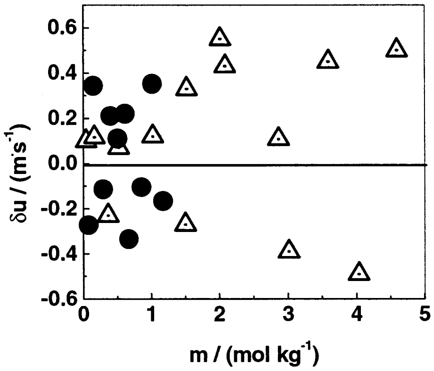

Figure 1. δu (our values minus literature values) as a function of molality of KCl at 298.15 K: ●, ref 3; △, ref 4.

Results and Discussion

In Table 1 is listed the relative sound speed, Δu ($\Delta u = u - u°$, where u and $u°$ are the sound speeds in solution and in pure water, respectively), as a function of molality of KCl at different temperatures. We do not present sound speeds at 298.15 K, as these data at 298.15 K are well established and our data agree to within 0.05% with the literature data.[3,4] In Figure 1 are shown the differences, δu, between our measured speeds of sound and those reported by others.[3,4] These differences are random and are within 0.05% of our values of speed of sound at 298.15 K.

The speeds of sound, Δu, in aqueous KCl as a function of molality at different temperatures were fitted by a nonlinear least-squares method using commercially available ORIGIN v 5.0 supplied by Microcal Inc. USA to the equation

$$\Delta u = Q_1 m^{1/2} + Q_2 m + Q_3 m^{3/2} + Q_4 m^2 \qquad (1)$$

where Q_1, Q_2, Q_3, and Q_4 are the adjustable parameters, the temperature-dependence of which is given by the following equation:

$$Q_1 = q_{11} + q_{12}(T - 273.15) + q_{13}(T - 273.15)^2 \qquad (2)$$

with analogous definitions for Q_2, Q_3, and Q_4.

These adjustable parameters together with the standard errors are listed in Table 2. The above equation can

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Table 1. Speeds of Sound in Aqueous KCl from (278.15 to 338.15) K

m/mol·kg^{-1}	Δu/m·s^{-1}	m/mol·kg^{-1}	Δu/m·s^{-1}	m/mol·kg^{-1}	Δu/m·s^{-1}
T = 278.15 K		T = 288.15 K		T = 308.15 K	
0.0905	6.12	0.1058	6.40	0.0858	4.40
0.1623	10.84	0.3983	23.38	0.3364	18.69
0.3595	23.14	0.8585	48.59	0.5275	27.39
0.7294	44.79	1.2483	68.67	0.9595	45.68
1.1888	71.92	2.0058	104.18	1.1122	52.41
1.7806	102.01	2.9535	143.30	2.0853	90.85
2.3750	131.86	3.7878	172.34	3.0499	121.95
3.0293	160.52	4.0355	180.91	4.0057	146.52
3.6081	184.26			4.3850	155.96
4.0201	205.43				
T = 318.15 K		T = 328.15 K		T = 338.15 K	
0.2619	12.32	0.2525	11.17	0.3015	12.76
0.4815	22.13	0.5135	22.21	0.6815	28.29
0.7813	35.13	1.0222	42.88	0.9989	41.11
1.0515	46.12	2.0598	86.77	1.9959	80.81
2.0101	82.43	3.0055	112.21	3.0085	117.48
3.0159	112.13	3.7853	132.41	4.0198	146.64
3.9958	135.42	4.0211	138.73	4.2795	153.33
4.1899	139.56	4.1998	143.25		

Table 2. Parameters of Eq 2 for Calculation of Sound Speeds in Aqueous KCl

parameter	value	parameter	value
q_{11}/m·kg$^{0.5}$·s^{-1}·mol$^{-0.5}$	-6.954 ± 0.052	q_{31}/m·kg$^{1.5}$·s^{-1}·mol$^{-1.5}$	-21.48 ± 0.45
q_{12}/m·kg$^{0.5}$·s^{-1}·mol$^{-0.5}$·K^{-1}	0.3852 ± 0.0047	q_{32}/m·kg$^{1.5}$·s^{-1}·mol$^{-1.5}$·K^{-1}	0.7915 ± 0.0190
q_{13}/m·kg$^{0.5}$·s^{-1}·mol$^{-0.5}$·K^{-2}	-0.0295 ± 0.0005	q_{33}/m·kg$^{1.5}$·s^{-1}·mol$^{-1.5}$·K^{-2}	-0.0030 ± 0.0001
q_{21}/m·kg·s^{-1}·mol^{-1}	91.85 ± 0.95	q_{41}/m·kg^{2}·s^{-1}·mol^{-2}	8.525 ± 0.150
q_{22}/m·kg·s^{-1}·mol^{-1}·K^{-1}	-1.705 ± 0.040	q_{42}/m·kg^{2}·s^{-1}·mol^{-2}·K^{-1}	-1.085 ± 0.019
q_{23}/m·kg·s^{-1}·mol^{-1}·K^{-2}	0.0149 ± 0.0005	q_{43}/m·kg^{2}·s^{-1}·mol^{-2}·K^{-2}	0.0388 ± 0.0010

Table 3. Adjustable Parameters of Eq 3 for Calculation of Density, ρ, of Aqueous KCl Solutions from (278.15 to 368.15) K from Dedick et al.[a]

parameter	value	parameter	value
a_{11}/kg^{2}·m^{-3}·mol^{-1}	$50.161\,32 \pm 0.281\,922$	a_{32}/kg^{4}·m^{-3}·mol^{-3}·K^{-1}	$0.089\,12 \pm 0.000\,76$
a_{12}/kg^{2}·m^{-3}·mol^{-1}·K^{-1}	$-0.196\,88 \pm 0.010\,27$	$10^{5}a_{33}$/kg^{4}·m^{-3}·mol^{-3}·K^{-2}	$-3.528\,97 \pm 0.023\,42$
a_{13}/kg^{2}·m^{-3}·mol^{-1}·K^{-2}	$0.002\,88 \pm 0.000\,5$	a_{41}/kg^{5}·m^{-3}·mol^{-4}	$-0.037\,92 \pm 0.001\,02$
$10^{5}a_{14}$/kg^{2}·m^{-3}·mol^{-1}·K^{-3}	$-1.355\,7 \pm 0.025\,4$	a_{42}/kg^{5}·m^{-3}·mol^{-4}·K^{-1}	$0.003\,53 \pm 0.000\,07$
a_{21}/kg^{3}·m^{-3}·mol^{-2}	$-3.503\,13 \pm 0.176\,54$	$10^{4}a_{43}$/kg^{5}·m^{-3}·mol^{-4}·K^{-2}	$-1.295\,75 \pm 0.102\,35$
a_{22}/kg^{3}·m^{-3}·mol^{-2}·K^{-1}	$0.064\,12 \pm 0.002\,33$	$10^{7}a_{44}$/kg^{5}·m^{-3}·mol^{-4}·K^{-3}	$9.282\,23 \pm 0.121\,02$
a_{23}/kg^{3}·m^{-3}·mol^{-2}·K^{-2}	$-0.001\,53 \pm 0.000\,03$	a_{51}/kg^{6}·m^{-3}·mol^{-5}	$-0.011\,65 \pm 0.000\,12$
$10^{6}a_{24}$/kg^{3}·m^{-3}·mol^{-2}·K^{-3}	$9.631\,64 \pm 0.120\,35$	$10^{4}a_{52}$/kg^{6}·m^{-3}·mol^{-5}·K^{-1}	$5.065\,63 \pm 0.205\,32$
a_{31}/kg^{4}·m^{-3}·mol^{-3}	$0.110\,35 \pm 0.000\,28$	$10^{6}a_{53}$/kg^{6}·m^{-3}·mol^{-5}·K^{-2}	$-3.266\,62 \pm 0.010\,43$

[a] The average RMSD of the fits = 24×10^{-3} kg·m^{-3}.

reproduce the sound speeds in aqueous KCl up to high concentrations in the given temperature range with a root-mean-square deviation, RMSD, of 0.25 m·s^{-1}.

The solution density, ρ, and u were used to calculate adiabatic compressibility, β, by the Laplace equation ($\beta = 1/(u^2\rho)$). Highly accurate ρ values of KCl solutions at different temperatures were taken from Dedick et al.[2] These authors have measured densities of aqueous KCl from dilute solutions to saturation at different temperatures (278.15 K to 368.15 K) using a Mettler/Paar DMA 602 HT static vibrating densimeter. Though the raw density data at each temperature are given in their original report, they were calculated at the desired molality and temperature by the equation and its constants given below:

$$\rho - \rho^{o} = A_1 m + A_2 m^2 + A_3 m^3 + A_4 m^4 + A_5 m^5 \quad (3)$$

where A_1, A_2, A_3, and so forth are adjustable parameters, the temperature dependence of which is expressed by

$$A_1 = a_{11} + a_{12}(T - 273.15) + a_{13}(T - 273.15)^2 + a_{14}(T - 273.15)^3 \quad (4)$$

with analogous expressions for A_2, A_3, and so forth. ρ^{o} is the density of pure water.

Table 4. Density, ρ^{o}, and Speed of Sound, u°, of Water at Different Temperatures (refs 9 and 10)

T/K	ρ°/kg·m^{-3}	u°/m·s^{-1}
278.15	999.967	1426.16
288.15	999.101	1465.94
308.15	994.036	1519.81
318.15	990.216	1536.39
328.15	985.695	1547.38
338.15	980.558	1553.44

The values of these adjustable parameters together with their standard errors are recorded in Table 3.

The density, ρ^{o}, and speed of sound, u^{o}, of water at different temperatures used in the above calculations were taken from the literature and are listed in Table 4 for ready use.[9,10]

In the least-squares method, the degree of polynomials was optimized by the F-test. The RMSD values were obtained from the calculated property, y_{cal}, and the experimental property, y_{exp}, by

$$\text{RMSD} = \left(\sum_{i=1}^{n_{\text{DAT}}} (y_{\text{exp}} - y_{\text{cal}})^2/(n_{\text{DAT}} - (N + 1))\right)^{1/2}$$

where the denominator is the number of degrees of freedom. This is the difference between the number of experimental data, n_{DAT}, and the number of adjustable parameters, $N + 1$.

The ϕ_K data for these solutions can be analyzed by the specific interaction theory of Pitzer.[11] Though the details of the Pitzer equations are given elsewhere,[12,13] they are summarized below for prompt use. The simplified Pitzer equation for ϕ_K of KCl can be written as

$$\phi_K = \phi_K{}^o + (A_K/b)\ln(1 + bI^{0.5}) + 2mRT[\beta^{(0)K} + \beta^{(1)K}[1 - (1 + 2I^{0.5})]\exp(-2I^{0.5}) + 0.5C^{\phi K}m] \quad (5)$$

In eq 5, $\phi_K{}^o$ is the apparent molar compressibility of KCl at infinite dilution (equivalent to the partial molar compressibility at infinite dilution). The second term on the right-hand side of the equation denoted long-range interactions in terms of the Debye–Huckel expression. The Pitzer–Debye–Huckel limiting slope, A_K, was taken as (-2.3819×10^{-15}, -3.0689×10^{-15}, -3.7784×10^{-15}, -5.4505×10^{-15}, -6.4936×10^{-15}, and -7.7332×10^{-15}) $\text{m}^3\cdot\text{kg}\cdot\text{mol}^{-2}\cdot\text{Pa}^{-1}$ at (278.15, 288.15, 308.15, 318.15, 328.15, and 338.15) K, respectively.[14] The last term on the right-hand side of eq 5 encompasses the virial coefficients, known as the Pitzer coefficients specific to a cation–anion pair. In the case of ϕ_K, the $\beta^{(0)K}$, $\beta^{(1)K}$, and $C^{\phi K}$ coefficients are defined as $(\partial^2\beta^{(0)}/\partial P^2)_T$, $(\partial^2\beta^{(1)}/\partial P^2)_T$, and $(\partial^2 C^{\phi}/\partial P^2)$, where $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} are the Pitzer coefficients from the Gibbs free energy of an electrolyte solution. b is set to 1.2. The ionic strength, I, of an electrolyte is equal to the molality of KCl. R and T have the usual meanings.

We applied eq 5 for analyzing ϕ_K data at all the temperatures with appropriate weighting considering the errors in molality, density, and sound speed. As noted in earlier investigations, the $\beta^{(1)K}$ term was not required to improve the quality of fits. The resultant $\beta^{(0)K}$ and $C^{\phi K}$ at temperature T, denoted by $(\beta^{(0)K})_T$ and $(C^{\phi K})_T$ in the above temperature range can be accurately described by

$$(\beta^{(0)K})_T/\text{kg}\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1} = (9.8688 \pm 0.0302) \times 10^{-15}\ \text{kg}\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1} + [(4.1494 \pm 0.0424) \times 10^{-16}\ \text{kg}\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}\cdot\text{K}^{-1}]\Delta T - [(4.6465 \pm 0.1753) \times 10^{-18}\ \text{kg}\cdot\text{mol}^{-1}\cdot\text{Pa}^{1-}\cdot\text{K}^{-2}]\Delta T^2 \quad (6)$$

$$(C^{\phi K})_T/\text{kg}^2\cdot\text{mol}^{-2}\cdot\text{Pa}^{-1} = (2.2150 \pm 0.1120) \times 10^{-15}\ \text{kg}^2\cdot\text{mol}^{-2}\cdot\text{Pa}^{-1} - [(7.7578 \pm 0.2276) \times 10^{-17}\ \text{kg}^2\cdot\text{mol}^{-2}\cdot\text{Pa}^{-1}\cdot\text{K}^{-1}]\Delta T \quad (7)$$

where ΔT is $T - 298.15$ K.

The $\phi_K{}^o$ values were fitted to the following equation:

$$(\phi_K{}^o)_T/\text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1} = -(44.20 \pm 0.08) \times 10^{-15}\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1} + [(5.887 \pm 0.082) \times 10^{-16}\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}\cdot\text{K}^{-1}]\Delta T - [(9.208 \pm 0.425) \times 10^{-18}\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}\cdot\text{K}^{-2}]\Delta T^2 \quad (8)$$

The Pitzer equation (eq 5) can accurately describe the ϕ_K data up to high concentrations of KCl at all the temperatures studied here. In Figure 2 are plotted the differences, $\partial\phi_K$, obtained from the experimental and correlated values of ϕ_K (by eq 5 in conjunction with eqs 6–8) as a function of the molality of KCl at different temperatures. The plots show a random distribution of the $\partial\phi_K$ values. Similarly, the differences in sound speeds, ∂u ($=u_{\text{exp}} - u_{\text{corr}}$), shown as a function of molality of KCl at different temperatures are depicted in Figure 3. An examination of Figures 2 and 3 shows that apparent molal compressibilities and sound speeds in aqueous KCl can be correlated with the Pitzer equations with RMSDs of $0.05 \times 10^{-15}\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$ and $0.31\ \text{m}\cdot\text{s}^{-1}$, respectively, from (278.15 to 338.15) K. The values of $\phi_K{}^o$ are obtained from the plots of ϕ_K versus $m^{1/2}$ and by extrapolating the ϕ_K values to $m = 0$. Though our measurements are not extended to very dilute solutions, it may be noted that the $\phi_K{}^o$ values of aqueous KCl at different temperatures are in reasonable agreement with those reported in the literature.[6] During the fitting exercise, we attempted to treat $\phi_K{}^o$ both first as a freely adjustable parameter and then as a fixed parameter, as reported in the literature.[6] The $\phi_K{}^o$ values obtained as freely adjustable parameters in the Pitzer equation at different temperatures agreed to within $0.45\ \text{m}^3\cdot\text{mol}^{-1}\cdot\text{Pa}^{-1}$ with the reported values of Uedaira and Suzuki.[6]

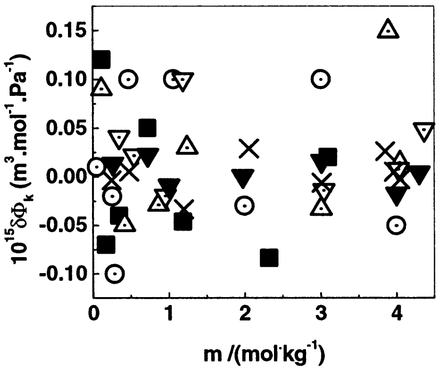

Figure 2. Differences $\partial\phi_K$ as a function of molality of KCl at different temperatures: ■, 278.15 K; △, 288.15 K; ▽, 308.15 K; ○, 318.15 K; ×, 328.15 K; ▼, 338.15 K.

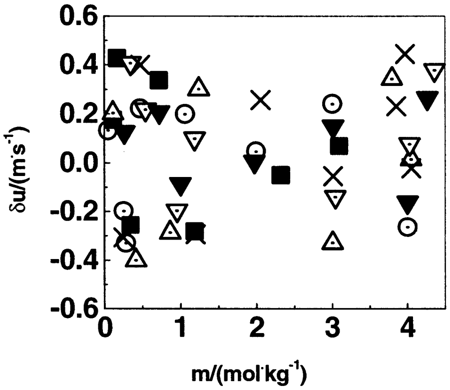

Figure 3. Differences ∂u ($=u_{\text{exp}} - u_{\text{corr}}$) versus molality of KCl at different temperatures: ■, 278.15 K; △, 288.15 K; ▽, 308.15 K; ○, 318.15 K; ×, 328.15 K; ▼, 338.15 K..

In summary, the speeds of sound in KCl in water have been measured up to saturation from (278.15 to 338.15) K and have been analyzed using the Pitzer equations.

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