Temperature Dependence of Speeds of Sound for Solutions of Some Tetraalkylammonium Bromides in H_2O and D_2O at Temperatures in the Range (283.15 to 338.15) K†

Evgeniy V. Ivanov,* Elena Yu. Lebedeva, and Vladimir K. Abrosimov

Laboratory of Thermodynamics of Non-electrolyte Solutions, Institute of Solution Chemistry of Russian Academy of Sciences, 1 Akademicheskaya Str., Ivanovo, Russian Federation 153045

The speeds of sound in both H_2O and D_2O solutions of Me_4NBr and n-Bu_4NBr have been measured at molalities up to 3.0 mol·kg^{-1} at temperatures of (283.15, 298.15, 318.15, and 338.15) K and at a pressure of 0.1 MPa with a single-crystal variable-path interferometer of uncertainty ± 0.5 m·s^{-1}.

1. Introduction

In this paper, we report the measurements of the sound speed of solutions with molality up to 3 mol·kg^{-1} of two tetraalkylammonium bromides Me_4NBr and n-Bu_4NBr with solvents of both H_2O and D_2O at temperatures from (283.15 to 338.15) K at a pressure of 0.1 MPa. The solutes have been investigated with solvents of H_2O and D_2O elsewhere.[1−5] The structure is discussed in terms of Frank and Wen's model[6] that indicates n-Bu_4NBr is an overall structure maker, while Me_4NBr is a net structure breaker. However, to the authors knowledge, no ultrasonic measurements have been performed as a function of temperature between (283.15 and 338.15) K and molality up to 3 mol·kg^{-1}.

2. Experimental Section

2.1. Materials. Me_4NBr and n-Bu_4NBr were supplied by Merck as puriss p.a. with mass fraction purity ≥ 99 %. These materials were recrystallized using a procedure described by Conway and Laliberté.[1] Prior to our measurements, both salts were dried under vacuum at room temperature for several days. The ordinary water of natural isotope composition was redistilled from an alkaline permanganate solution in a quartz still, and its conductance κ was found to be (1.2 to 1.4)·10^{-5} S·m^{-1}. The heavy water, D_2O, was supplied by Isotope Co., St. Petersburg, with $\kappa = 1.0 \cdot 10^{-5}$ S·m^{-1} and a deuterium mass fraction of 99.90 % and used without further analysis or purification.

2.2. Apparatus and Procedure. The isotopically distinguishable solutions were prepared by mass without exposure to air to give molality with an uncertainty of ± 1·10^{-3} mol·kg^{-1}. The speeds of sound were measured, with an estimated uncertainty of less than ± 0.5 m·s^{-1}, with a single-crystal variable-path ultrasonic interferometer operating at a frequency of 2 MHz. In these measurements, the reproducibility in u was found to be better than ± 0.1 m·s^{-1} at each temperature. The reproducibility in the temperature measurement provided by the precise mercury-in-glass thermometer was less than ± 0.01 K on ITS-90. The temperature of the brass thermostatic jacket surrounding the apparatus was controlled to within ± 0.05 K when immersed in a Julabo-type thermostat by recirculating water from a thermostatted bath. The path length of the ultrasonic cell was determined by calibration measurements with deionized, double-distilled, and degassed water at each temperature. For this calibration, the speeds of sound in water were taken from the work of Del Grosso and Mader.[7] For the measurements with D_2O to reduce the D to H isotope exchange with atmospheric water vapor, dry N_2(g) was flushed through the upper compartment of the cell. Further details of the experimental apparatus and procedure have been published elsewhere.[8,9]

3. Results and Discussion

The speeds of sound determined D_2O at each temperature studied are listed in Table 1. For comparison, the literature values of the speed of sound for heavy and ordinary water are also included in the table as a function of temperature. Table 1 shows that our measurements of $u(H_2O)$ differ fractionally by less than 2·10^{-4} from the data reported by Kell[10] and Greenspan et al.[11] For $u(D_2O)$, the relative fractional difference of our measurements from the literature values are less than 2·10^{-3} in the worst case at $T = 298.15$ K. It is plausible these differences arose from variations in the chemical composition of the D_2O particularly the deuterium content and variations in the experimental procedure.

Speeds of sound in ($Me_4NBr + H_2O$), {n-$Bu_4NBr + H_2O$}, {$Me_4NBr + D_2O$}, and {n-$Bu_4NBr + D_2O$} obtained at temperatures between (283.15 and 338.15) K are listed in Table 2. The experimental values of u reported in this table are mean values from three independent determinations. The results were fit by an unweighted least-squares polynomial regression to

$$u(m) = \sum_{i=0}^{k-1} a_i m^i \qquad (1)$$

where m is the molality; a_i is the adjustable parameters; and k is the number of a_i used in eq 1 determined by the F-test[24] at a 95 % confidence interval. In each case, k was found to be 4. Table 3 lists the parameters a_i obtained in the regression, together with the standard deviations, σ, defined by[24]

$$\sigma(u) = \left[\frac{1}{n-k}\sum \{u(\text{calc}) - u(\text{expt})\}^2\right]^{1/2} \qquad (2)$$

where n is the number of direct experimental values (see in Table 2).

* Corresponding author. Fax: +7-4932-336246. E-mail: evi@isc-ras.ru. Tel.: +7-4932-351859.

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Table 1. Comparison of Experimental Speeds of Sound, u, in Ordinary Water H_2O and Heavy Water D_2O at Temperatures T from (283.15 to 338.15) K and at Pressure $p = 0.1$ MPa

	u/m·s^{-1}			
	H_2O		D_2O [a]	
T/K	this work[b]	lit.	this work[b]	lit.
283.15	1447.270	1447.236,[c] 1447.594,[d] 1447.0[e]	1347.5 (99.90)	1352.0(100),[e] 1347.51(99.8),[f] 1347.51(99.81),[g] 1347.32(100) [h]
298.15	1496.687	1496.614,[c] 1497.001,[d] 1498.2,[e] 1496.58,[i] 1494.0,[j] 1497.33[k]	1399.5 (99.90)	1400.4(100),[e] 1399.59(99.8),[f] 1399.29(99.81),[g] 1398.86(100),[h] 1395.7(100),[j] 1400.13(99.75),[k] 1398.96 (99.76),[l] 1401(100),[m] 1402(100),[n,o] 1399.24(100),[p] 1403.31(100),[q] 1399.27(99.8),[r]
318.15	1536.409	1536.345,[c] 1536.723,[d] 1538.5[e]	1441.1 (99.90)	1441.8(100),[e] 1441.29(99.8),[f] 1440.80(99.81),[g] 1440.63(100)[h]
338.15	1553.437	1553.379,[c] 1553.756,[d] 1553.9[e]	1459.9 (99.90)	1460.1(100),[e] 1459.90(99.81),[g] 1459.83(100)[h]

[a] The deuterium mass fraction in % is given in brackets. [b] For H_2O, values were taken from ref 7 (del Grosso et al.) and used as the calibrant; for D_2O, values from Table 2. [c] Ref 10. [d] Ref 11. [e] Values calculated from the temperature-dependent experimental data of ref 12. [f] Ref 8. [g] Ref 9. [h] Ref 13. [i] Ref 14. [j] Ref 15. [k] Ref 16. [l] Ref 17. [m] Ref 18. [n] Ref 19. [o] Ref 20. [p] Ref 21. [q] Ref 22. [r] Ref 23.

Table 2. Selected Data of Speeds of Sound, u/(m·s^{-1}), for the Studied Isotopically Distinguishable Solutions ($Me_4NBr + H_2O$), (n-$Bu_4NBr + H_2O$), ($Me_4NBr + D_2O$), and (n-$Bu_4NBr + D_2O$) at Temperatures T

m/mol·kg^{-1}	T = 283.15 K	T = 298.15 K	T = 318.15 K	T = 338.15 K	T = 283.15 K	T = 298.15 K	T = 318.15 K	T = 338.15 K
		$H_2O + Me_4NBr$				$D_2O + Me_4NBr$		
0[a]	1447.3	1496.7	1536.4	1553.4	1347.5	1399.5	1441.1	1459.9
0.0500	1451.0	1499.7	1538.7	1555.6	1352.0	1403.0	1443.9	1462.3
0.0750	1452.9	1500.3	1540.0	1556.2	1354.7	1405.2	1445.4	1463.6
0.100	1455.0	1502.5	1541.1	1556.9	1357.5	1407.4	1447.1	1465.1
0.200	1462.1	1508.1	1545.8	1560.9	1366.7	1414.7	1452.9	1469.8
0.300	1469.5	1513.7	1550.4	1564.6	1376.5	1422.2	1458.6	1474.5
0.500	1483.1	1524.7	1559.3	1571.0	1393.7	1436.4	1469.8	1484.1
0.750	1499.8	1537.9	1569.3	1579.2	1414.4	1453.8	1483.7	1495.7
1.00	1515.7	1550.8	1578.6	1587.3	1433.4	1470.2	1496.9	1506.9
1.50	1544.7	1575.1	1596.6	1602.0	1469.8	1500.5	1521.2	1527.4
2.00	1571.1	1597.2	1613.1	1615.7	1502.4	1528.0	1543.6	1546.4
2.50	1595.4	1617.0	1628.8	1628.9	1532.1	1552.9	1564.3	1564.2
3.00	1617.4	1633.7	1644.7	1641.3	1560.4	1575.5	1583.5	1580.8
		$H_2O + n$-Bu_4NBr				$D_2O + n$-Bu_4NBr		
0[a]	1447.3	1496.7	1536.4	1553.4	1347.5	1399.5	1441.1	1459.9
0.0500	1463.0	1508.4	1544.6	1558.6	1366.8	1414.0	1451.5	1466.8
0.0750	1470.4	1514.2	1548.4	1561.2	1375.9	1421.1	1456.5	1470.5
0.100	1477.8	1520.2	1552.9	1564.2	1384.4	1427.4	1461.4	1474.3
0.200	1506.2	1541.4	1567.4	1573.6	1419.1	1453.9	1479.9	1486.6
0.300	1532.5	1561.0	1580.7	1582.4	1450.2	1478.2	1497.1	1498.1
0.500	1579.0	1596.3	1604.7	1597.0	1506.0	1519.9	1525.8	1518.2
0.750	1628.2	1632.7	1627.3	1610.3	1562.5	1562.4	1554.8	1536.6
1.00	1667.1	1661.2	1644.1	1619.5	1605.4	1594.2	1576.2	1550.2
1.50	1718.2	1697.4	1663.3	1626.6	1658.6	1634.9	1601.0	1563.5
2.00	1743.4	1713.7	1669.5	1625.0	1680.5	1652.1	1610.0	1566.4
2.50	1752.2	1718.0	1668.5	1619.5	1686.3	1657.0	1611.3	1563.7
3.00	1753.9	1717.6	1668.3	1615.4	1688.9	1661.4	1615.2	1564.0

[a] For H_2O, values from Table 1 of ref 7 were used.

Table 3. Regression Coefficients, a_i, and Standard Deviations, σ, from Equations 1 and 2 for ($Me_4NBr + H_2O$), (n-$Bu_4NBr + H_2O$), ($Me_4NBr + D_2O$), and (n-$Bu_4NBr + D_2O$) at Temperatures T

T	a_0	a_1	$-a_2$	a_3	σ	a_0	a_1	$-a_2$	a_3	σ
K	m·s^{-1}	m·kg·s^{-1}·mol^{-1}	m·kg^2·s^{-1}·mol^{-2}	m·kg^3·s^{-1}·mol^{-3}	m·s^{-1}	m·s^{-1}	m·kg·s^{-1}·mol^{-1}	m·kg^2·s^{-1}·mol^{-2}	m·kg^3·s^{-1}·mol^{-3}	m·s^{-1}
		$Me_4NBr + H_2O$					$Me_4NBr + D_2O$			
283.15 K	1447.3	75.67	7.967	0.549	0.13	1347.6	98.18	13.16	1.36	0.34
298.15 K	1496.6	57.43	2.870	−0.346	0.24	1399.4	78.00	7.690	0.418	0.15
318.15 K	1536.4	48.65	7.142	0.988	0.14	1441.0	60.70	5.230	0.277	0.13
338.15 K	1553.5	36.94	3.609	0.351	0.19	1459.8	50.90	4.303	0.258	0.14
		n-$Bu_4NBr + H_2O$					n-$Bu_4NBr + D_2O$			
283.15 K	1447.3	315.9	109.2	12.7	0.25	1347.5	386.8	148.2	19.1	0.30
298.15 K	1496.7	240.5	86.63	10.3	0.21	1399.5	293.8	113.7	15.0	0.24
318.15 K	1536.4	168.2	69.87	9.49	0.25	1441.2	210.1	87.34	12.2	0.17
338.15 K	1553.4	111.5	53.05	7.59	0.21	1460.0	146.1	65.31	9.39	0.27

The ratios, u(solu)/u(solv), of the solution and solvent sound speed, respectively, are shown as a function of molality for {$Me_4NBr + H_2O$}, {n-$Bu_4NBr + H_2O$}, {$Me_4NBr + D_2O$}, and {n-$Bu_4NBr + D_2O$} and temperature in Figures 1 and 2 that show the sound speed increases with solution molality. For solvents of H_2O and D_2O of solute Me_4NBr, the ratio u(solu)/u(solv) is essentially linear, whereas for (H_2O + n-Bu_4NBr) and (D_2O + n-Bu_4NBr) the variations are parabolic with molality with a maximum at temperatures greater than 298.15 K. At 308.15 K, this maximum is at a molality of 2.0 mol·kg^{-1} and decreases in molality as the temperatures increases. Similar concentration dependence of u was found for the H/D isotopically distinguishable aqueous solutions of solutes HMPT,[16] DMF, and DMSO.[23] The molality dependence of u(solu)/u(solv) shown in Figures 1 and 2

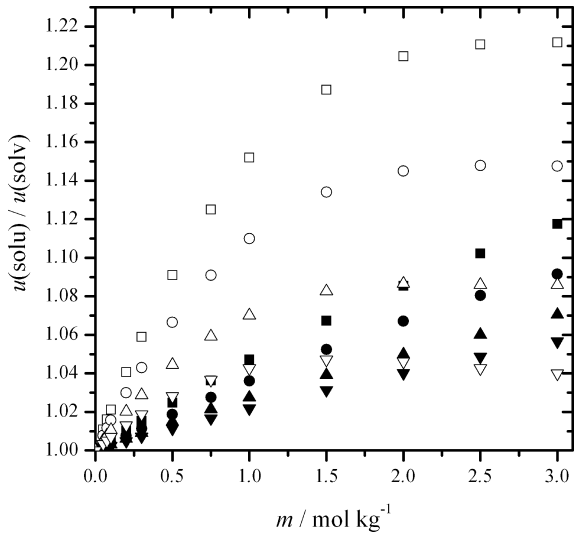

Figure 1. Ratio between the speed of sound u in (H_2O + Me_4NBr) (solid symbols) or (H_2O + n-Bu_4NBr) (open symbols) and speed of sound in H_2O as a function of solution molality at temperature T: squares, $T = 283.15$ K; circles, $T = 298.15$ K; upward pointing triangles, $T = 318.15$ K; and downward pointing triangles, $T = 338.15$ K.

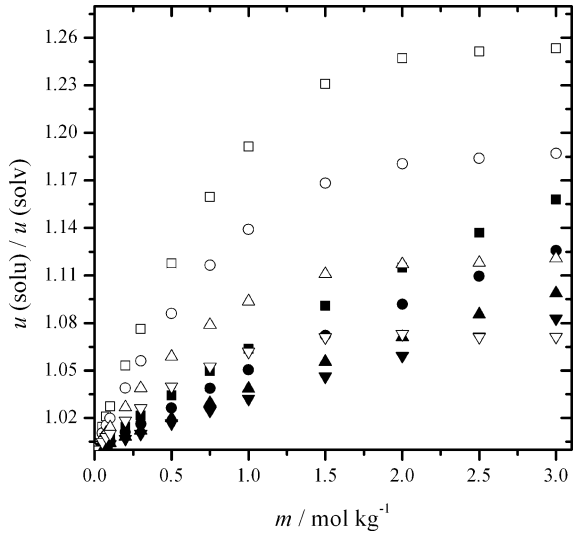

Figure 2. Ratio between the speed of sound u in (D_2O + Me_4NBr) (solid symbols) or (D_2O + n-Bu_4NBr) (open symbols) and speed of sound in D_2O as a function of solution molality at temperature T: squares, $T = 283.15$ K; circles, $T = 298.15$ K; upward pointing triangles, $T = 318.15$ K; and downward pointing triangles, $T = 338.15$ K.

for (D_2O + Me_4NBr) and (H_2O + Me_4NBr) is as expected for aqueous solutions of alkali halides.[14,25]

Figure 1 shows for the substances studied an intersection of the curves at $T = 338.15$ K and at $m \approx 2.25$ mol·kg^{-1} for solvent H_2O, and Figure 2 shows for solvent D_2O the same intersection but at $m \approx 2.5$ mol·kg^{-1}.

4. Conclusion

The speed of sound in {$Me_4NBr + H_2O$}, {n-$Bu_4NBr + H_2O$}, {$Me_4NBr + D_2O$}, and {n-$Bu_4NBr + D_2O$} has been measured at molalities up to 3.0 mol·kg^{-1} at temperatures of (283.15, 298.15, 318.15, and 338.15) K and at a pressure of 0.1 MPa.

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