

# Study of Ultrasonic Speeds of $\{x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1 - x)\text{H}_2\text{O}\}$ , ( $\nu = 1$ and $2$ ) at 298.15 K

A. Pal\* and Y. P. Singh

Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, India

The speed of sound in  $\{x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1 - x)\text{H}_2\text{O}\}$  for  $\nu = 1$  and  $2$  has been measured as a function of composition at 298.15 K. These results have been combined with those of our previous results for excess molar volumes converted to densities to obtain isentropic compressibilities  $k_S$ . Deviation in the isentropic compressibility properties  $\Delta k_S$  were evaluated using volume fraction weighting of the individual component properties to estimate ideal mixture behavior.

## Introduction

In an earlier paper (Pal and Singh, 1995), we reported the results of our measurements of the excess molar volumes of  $\{a\text{-}2\text{-}[(2\text{-alkoxyethoxy})\text{ethoxy}]\text{ethanol} + \text{water}\}$  at 298.15 K. These results suggested the relative importance of hydrogen-bonding interactions between the water and the ether molecules. Since the addition of an amphiphile to water gives rise to a slight enhancement of the water lattice in the water-rich region, its magnitude increases with the size of the hydrocarbon chain.

In a continuing effort to collect other thermodynamic quantities, we report here measured values of the speed of sound in the mixtures  $\{2\text{-}[(2\text{-methoxyethoxy})\text{ethoxy}]\text{ethanol}$  and  $2\text{-}[(2\text{-ethoxyethoxy})\text{ethoxy}]\text{ethanol} + \text{water}\}$  at 298.15 K across the entire range of mole fractions. This property has not been reported previously. The molar excess volumes were converted to densities which were combined with the measured values of the speeds of sound to estimate the isentropic compressibility  $k_S$  for the mixtures. Deviation in isentropic compressibility  $\Delta k_S$  is evaluated by considering ideal solution behavior values based on volume fraction weighted adducts of the pure components. These properties for the two binary systems studied are presented and discussed.

## Experimental Section

**Materials.** 2-[(2-Methoxyethoxy)ethoxy]ethanol (Aldrich, >98 mol %) and 2-[(2-ethoxyethoxy)ethoxy]ethanol (Fluka, >99 mol %) were the same as those used in earlier studies (Pal and Singh, 1995). They were kept tightly sealed to minimize, as far as possible, the absorption of atmospheric moisture and  $\text{CO}_2$ , and carefully dried over 4A molecular sieves (Fluka, AG). The water was deionized and distilled in glass. Before the measurements, liquids were partially degassed under vacuum.

**Apparatus and Procedure.** Densities of pure solvents were measured with a bicapillary pycnometer of about 15  $\text{cm}^3$  capacity. The reproducibility of density at (298.15  $\pm$  0.01) K is 0.3  $\text{kg m}^{-3}$ . Densities of the nonaqueous components taken from our previous paper (Pal and Singh, 1995) and of water reported by Kell (1975) were used for the estimation of  $k_S$ .

The speed of sound,  $u$ , in both the pure liquids and their mixtures were measured at 298.15 K with a NUSONIC (Mapco, Model 6080 Concentration Analyser) velocimeter based on the sing-around technique (Garnsey et al., 1969),

with 4 MHz acoustic waves. Details of its calibration, experimental setup, and operational procedure have been described previously (Pal et al., 1994; Pal and Singh, 1996). The maximal error of the speed measured relative to water (1496.687  $\text{m s}^{-1}$  at 298.15 K) (Del Grosso and Mader, 1972) is estimated to be less than 0.2  $\text{m s}^{-1}$ . The mole fraction of each mixture was obtained with an accuracy of  $1 \times 10^{-4}$  from the measured apparent masses of the components. All the measurements were carried out in a thermostatically controlled, well-stirred water bath with temperature controlled to within  $\pm 0.01$  K.

## Results and Discussion

The measurements of  $u$  at 298.15 K for  $\{x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1 - x)\text{H}_2\text{O}\}$  for  $\nu = 1$  and  $2$  at various values of  $x$  are summarized in Table 1 and are graphically shown in Figure 1.

The specific compression of solution is defined as the partial derivative of specific volume  $V$  with respect to pressure  $p$  under isentropic conditions:  $k_S = -(\partial V/\partial p)_S$ . Then, the isentropic compressibility  $k_S$  values can be estimated from the relation

$$k_S = (\rho u^2)^{-1} \quad (1)$$

where  $\rho$  is the density of the mixture.

Defining the ideal isentropic solution property  $k_S^{\text{id}}$  is not as straightforward as for the ideal molar volumes  $V_m^{\text{id}}$  (Douch et et al., 1992). In general, the ideal mixing rules are defined by the following equation (Douch et et al., 1985; Douch et and Davis, 1993)

$$k_S^{\text{id}} = \sum_i x_i f_i (k_{S,i}^*) \quad (2)$$

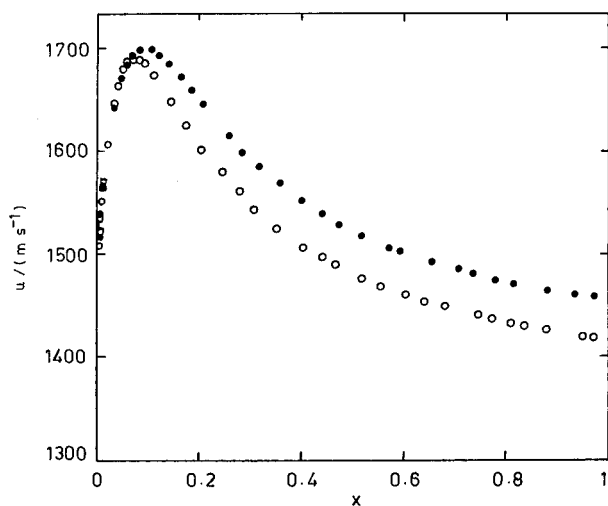
where  $x_i$  is an explicit weighting coefficient such as mole or volume fraction,  $k_{S,i}^*$  is the isentropic compressibility of pure component  $i$ ,  $f_i$  is a multiplying factor which is a function of  $A_p = (\partial V/\partial T)$ , and  $C_p$  is the molar isobaric heat capacity. To the best of our knowledge, the values of  $A_p$  and  $C_p$  for the systems are not available in the literature. However, one may write a defining equation in terms of the volume fraction average (Benson and Kiyohara, 1979; Baumgartner and Atkinson, 1971; Masood et al., 1977).

$$k_S^{\text{id}} = \sum_i (k_{S,i}^*) \phi_i \quad (3)$$

\* To whom correspondence should be addressed.

**Table 1.** Speeds of Sound  $u$ , Isentropic Compressibilities  $k_S$ , and Deviation in Isentropic Compressibilities  $\Delta k_S$ , for  $[x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}]$  at 298.15 K

$x$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{GPa}^{-1}$	$\Delta k_S/\text{GPa}^{-1}$	$x$	$u/\text{m}\cdot\text{s}^{-1}$	$k_S/\text{GPa}^{-1}$	$\Delta k_S/\text{GPa}^{-1}$
[ $x\text{CH}_3\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}$ ]							
0.0000	1496.687	0.4477	0	0.2890	1599.5	0.3705	-0.0806
0.0010	1502.2	0.4440	-0.0038	0.3191	1585.2	0.3774	-0.0737
0.0025	1509.3	0.4391	-0.0087	0.3583	1568.5	0.3858	-0.0654
0.0040	1516.8	0.4342	-0.0137	0.4019	1552.7	0.3941	-0.0572
0.0082	1537.4	0.4209	-0.0271	0.4415	1539.8	0.4011	-0.0503
0.0147	1565.6	0.4037	-0.0446	0.4719	1529.4	0.4069	-0.0450
0.0380	1642.6	0.3612	-0.0877	0.5187	1519.1	0.4128	-0.0388
0.0514	1669.8	0.3473	-0.1017	0.5754	1507.2	0.4199	-0.0319
0.0609	1683.2	0.3406	-0.1087	0.5898	1504.3	0.4215	-0.0302
0.0711	1692.5	0.3357	-0.1137	0.6561	1492.7	0.4285	-0.0232
0.0854	1699.3	0.3318	-0.1178	0.7082	1485.1	0.4332	-0.0186
0.1098	1698.5	0.3306	-0.1194	0.7359	1481.0	0.4356	-0.0162
0.1217	1694.7	0.3315	-0.1185	0.7820	1475.8	0.4391	-0.0127
0.1415	1685.3	0.3346	-0.1157	0.8142	1472.2	0.4414	-0.0105
0.1640	1672.2	0.3393	-0.1111	0.8802	1466.0	0.4455	-0.0064
0.1852	1659.1	0.3444	-0.1062	0.9349	1461.4	0.4486	-0.0033
0.2063	1645.9	0.3497	-0.1009	0.9739	1458.3	0.4507	-0.0012
0.2565	1616.2	0.3627	-0.0882	1.0000	1456.5	0.4520	0
[ $x\text{C}_2\text{H}_5\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}$ ]							
0.0000	1496.687	0.4477	0	0.2463	1580.1	0.3867	-0.0931
0.0004	1499.7	0.4456	-0.0021	0.2278	1563.1	0.3957	-0.0853
0.0016	1506.8	0.4411	-0.0073	0.3085	1544.8	0.4057	-0.0763
0.0021	1509.6	0.4392	-0.0094	0.3551	1525.0	0.4171	-0.0661
0.0041	1521.6	0.4315	-0.0178	0.4041	1508.0	0.4274	-0.0570
0.0066	1535.7	0.4227	-0.0276	0.4405	1497.2	0.4341	-0.0509
0.0099	1553.7	0.4119	-0.0396	0.4693	1489.3	0.4392	-0.0464
0.0144	1576.1	0.3989	-0.0541	0.5172	1477.9	0.4466	-0.0397
0.0215	1607.1	0.3819	-0.0733	0.5556	1469.5	0.4522	-0.0345
0.0337	1645.8	0.3618	-0.0966	0.6038	1460.8	0.4581	-0.0291
0.0418	1664.3	0.3526	-0.1077	0.6420	1454.8	0.4623	-0.0254
0.0525	1680.3	0.3446	-0.1179	0.6811	1449.0	0.4664	-0.0216
0.0613	1687.2	0.3410	-0.1231	0.7486	1440.7	0.4724	-0.0161
0.0714	1690.7	0.3388	-0.1269	0.7756	1437.7	0.4746	-0.0141
0.0827	1689.3	0.3387	-0.1287	0.8113	1432.7	0.4782	-0.0108
0.0914	1686.2	0.3396	-0.1290	0.8352	1430.3	0.4799	-0.0092
0.1127	1672.7	0.3445	-0.1265	0.8804	1426.4	0.4829	-0.0065
0.1437	1649.0	0.3541	-0.1198	0.9549	1420.3	0.4876	-0.0022
0.1746	1624.9	0.3648	-0.1113	0.9740	1418.7	0.4888	-0.0010
0.2059	1602.5	0.3754	-0.1026	1.0000	1417.3	0.4899	0

**Figure 1.** Variation of speed of sound,  $u$  for  $\{x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}\}$  at 298.15 K: ●,  $\nu = 1$ ; ○,  $\nu = 2$ .

Then the deviations in isentropic compressibility,  $\Delta k_S$ , from the ideal mixing values can be estimated from the following equation

$$\Delta k_S = k_S - \sum_i (k_{S,i}^*) \phi_i \quad (4)$$

The values of  $k_S$  and  $\Delta k_S$  are reported in Table 1.

For each mixture, the values of  $k_S$  were fitted by an equation of the form

$$k_S = \sum_{i=0}^n a_i x^i \quad (5)$$

while the dependence of  $\Delta k_S$  on volume fraction is expressed by an equation of the type

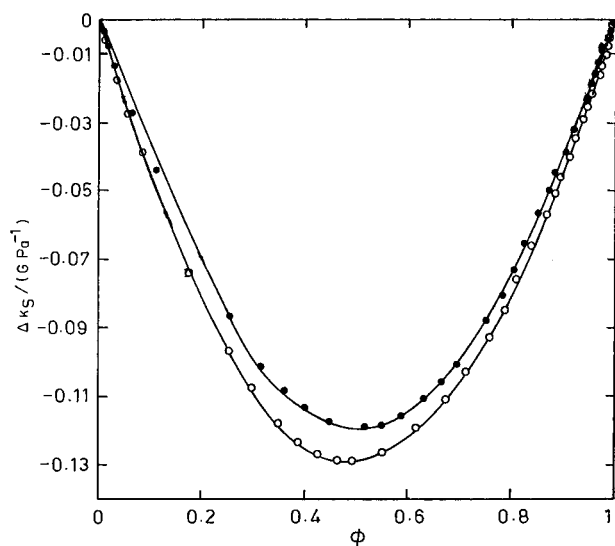
$$\Delta k_S = \phi(1-\phi) \sum_{i=0}^n a_i (2\phi-1)^i \quad (6)$$

Values of the coefficients  $a_i$  calculated by the method of least squares with all points weighted equally and standard deviations  $s$  are given in Table 2.

From Figure 1 it is seen that there is a maximum in speed of sound in the water-rich region. Its magnitude increases in the sequence  $(\nu = 1) > (\nu = 2)$ . In fact, we observe similar characteristics for  $u$  as in  $\{x\text{H}(\text{CH}_2)_\nu\text{OCH}_2\text{OH} + (1-x)\text{H}_2\text{O}\}$  (Douhéret et al. 1990) and  $\{x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_2\text{OH} + (1-x)\text{H}_2\text{O}\}$  (Pal and Singh, 1996; Douhéret et al., 1992), a large positive value and the maximum shifted toward low values of  $x$  with the chain length of the amphiphile, but there is a marked increase in  $u$  here. As the amphiphile is added to water, thereby causing a breakdown of the less dense hydrogen-bonded structures of water or a breakdown of self-associated amphiphile aggregates or both, and hence contributing to a denser packing of the molecules through intermolecular

**Table 2. Parameters of Eqs 5 and 6 and the Standard Deviation at 298.15 K**

	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$s$
			[ $x\text{CH}_3\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}$ ]				
$k_S/\text{GPa}^{-1}$	0.4350	-1.9829	11.9269	-27.3129	27.5402	-10.1816	0.0090
$\Delta k_S/\text{GPa}^{-1}$	-0.4791	-0.0118	0.0537	0.0121	0.512		0.0004
			[ $x\text{C}_2\text{H}_5\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}$ ]				
$k_S/\text{GPa}^{-1}$	0.4300	-1.8886	12.3219	-28.9021	29.3837	-10.8801	0.0115
$\Delta k_S/\text{GPa}^{-1}$	-0.5165	0.0153	0.0316	-0.0259			0.0005



**Figure 2.** Deviations in isentropic compressibility,  $\Delta k_S$ , for  $\{\phi\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-\phi)\text{H}_2\text{O}\}$  at 298.15 K: ●,  $\nu = 1$ ; ○,  $\nu = 2$ ; —, calculated from eq 6.

hydrogen bonding, the speed of sound  $u$  increases and the compressibility  $k_S$  decreases at low amphiphile concentrations. The behavior of these systems can be better explained in terms of the deviation in isentropic compressibility  $\Delta k_S$ .

Since the compressibility coefficient is a measure of the relative change in volume with pressure, it seems appropriate to examine the variation of  $\Delta k_S$  as a function of the volume fraction of amphiphile in the binary mixtures. Figure 2 shows the variation of  $\Delta k_S$  with volume fraction of amphiphile. The values of the  $\Delta k_S$  are negative for the mixtures throughout the volume fraction range. This behavior is qualitatively similar to that of the  $V_m^E$  (Pal and Singh, 1995). We suggested previously (Pal and Singh, 1995) that the volume behavior of (amphiphile + water) is the result of hydrogen bond association between water and amphiphile molecules. This leads to a more compact structure and tends to decrease the  $\Delta k_S$  relative to the pure components. The result of excess volume studies were interpreted as indicating that in the intermediate composition stronger hydrogen bonding is believed to occur between water molecules as opposed to weaker bonding between the water and the ether molecules. Hence, a slight enhancement of the three-dimensional water lattice exists in the

water-rich region as opposed to pure water itself. The present results for  $\Delta k_S$  is consistent with the conclusions drawn from our previous studies on  $V_m^E$ .

### Acknowledgment

The authors gratefully acknowledge the financial support (01(1428)/96/EMR-11) of the Council of Scientific and Industrial Research (CSIR), New Delhi, and award of a Senior Research Fellowship to one of the author (Y.P.S.).

### Literature Cited

- Baumgartner, E. K.; Atkinson, G. Ultrasonic Velocity in Non-electrolyte-Water Mixtures. *J. Phys. Chem.* **1971**, *75*, 2336-2340.
- Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061-1064.
- Davis, M. I. Thermodynamic and Related Studies of Amphiphile-Water Systems. *Chem. Soc. Rev.* **1993**, *22*, 127-134.
- Del Grosso, V. A.; Mader, C. W. Speed of Sound in Pure Water. *J. Acoust. Soc. Am.* **1972**, *52*, 1442-1446.
- Douhéret, G.; Morean, C.; Viillard, A. Excess Thermodynamic Quantities in Binary Systems of Nonelectrolytes. I. Different Ways of Calculating Excess Compressibilities. *Fluid Phase Equilib.* **1985**, *22*, 277-287.
- Douhéret, G.; Pal, A.; Davis, M. I. Ultrasonic speeds and isentropic functions of (a 2-alkoxyethanol + water) at 298.15 K. *J. Chem. Thermodyn.* **1990**, *22*, 99-108.
- Douhéret, G.; Salgado, C.; Davis, M. I.; Loya, J. Ultrasonic speeds and isentropic functions of 2-(2-alkoxyethoxy)ethanol + water at 298.15 K. *Thermochim. Acta* **1992**, *207*, 313-328.
- Douhéret, G.; Davis, M. I. Measurement, Analysis, and Utility of Excess Molar  $-(\partial V/\partial p)_S$ . *Chem. Soc. Rev.* **1993**, *22*, 43-50.
- Garnsey, R.; Boe, R. J.; Mahoney, R.; Litovitz, J. A. Determination of electrolyte apparent molar compressibilities at infinite dilution using a high-precision ultrasonic velocimeter. *J. Chem. Phys.* **1969**, *50*, 5222-5228.
- Kell, G. S. Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150 °C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale. *J. Chem. Eng. Data* **1975**, *20*, 97-105.
- Masood, A. K. M.; North, A. M.; Pethrick, R. A.; Towland, M.; Swinton, F. L. Compressibility studies of benzene + hexafluorobenzene mixtures. *J. Chem. Thermodyn.* **1977**, *9*, 133-137.
- Pal, A.; Singh, Y. P.; Singh, W. Excess volumes and ultrasonic velocities of some amide + water systems at 298.15 K. *Indian J. Chem.* **1994**, *33A*, 1083-1087.
- Pal, A.; Singh, Y. P. Excess molar volumes and apparent molar volumes of  $[x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}]$ , ( $\nu = 1, 2$ , and 4), at the temperature 298.15 K. *J. Chem. Thermodyn.* **1995**, *27*, 1329-1336.
- Pal, A.; Singh, Y. P. Speeds of sound and isentropic compressibilities of  $[x\text{H}(\text{CH}_2)_\nu\{\text{O}(\text{CH}_2)_2\}_3\text{OH} + (1-x)\text{H}_2\text{O}]$ , ( $\nu = 1, 2$ , and 4) at the temperature 298.15 K. *J. Chem. Thermodyn.* **1996**, *28*, 143-151.

Received for review February 25, 1997. Accepted March 20, 1997.®

JE970049T

® Abstract published in *Advance ACS Abstracts*, May 1, 1997.