

Isentropic Compressibilities of Alcohol-Water Mixtures at 25°C

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Received June 21, 1981; revised October 16, 1981

The sound velocities of aqueous solutions of methanol, ethanol, 2-propanol, tert-butanol and 2-butoxyethanol (BE) were measured over the whole mole fraction range at 25°C. The isentropic apparent and partial molar compressibilities, $\phi_{K,S}$ and $\overline{K}_{S,A}$ were derived from these data. In the case of BE, the isothermal partial molar compressibilities were also calculated. $\phi_{K,S}$ and $\overline{K}_{S,A}$ for all alcohols except BE initially decrease slightly with the mole fraction and then increase sharply, especially with the higher members, to the value of the pure liquid. In the case of BE, $\phi_{K,S}$ and $\overline{K}_{S,A}$ do not go through an initial minimum and the latter goes through a sharp maximum. The compressibilities of water in these mixtures are significantly lower than those of pure water itself. These data can be correlated with other properties and are consistent with the existence of micro-phase transitions in these aqueous organic mixtures.

KEY WORDS: Alcohols; methanol; ethanol; 2-propanol; tert-butanol; 2-butoxyethanol; ultrasonic velocities; compressibilities;

1. INTRODUCTION

It has been known for many years that alcohol-water mixtures show unusual properties in the water-rich region.⁽¹⁻⁵⁾ Systematic studies in our laboratory indicate that trends in partial molar heat capacities and volumes of alcohols such as tert-butanol,⁽⁶⁾ 2-propanol⁽⁹⁾ and 2-butoxyethanol⁽⁸⁾ are similar to those of micellar systems, suggesting that these aqueous-organic mixtures probably undergo some micro-phase transitions. These microheterogeneities may well be related to the important role of alcohols in microemulsions. As a matter of fact, even without surfactants, ternary systems of simple alcohols, water and

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hydrocarbons have some of the characteristic features⁽⁹⁻¹¹⁾ of microemulsions. For example, benzene seems to dissolve preferentially in the alcohol microphases and, by doing so, further stabilizes them.^(10,11) Surfactants also have a large effect on the thermodynamic stability of these microstructures.⁽¹²⁾

In a continuing study of the role of alcohols in microemulsions the isentropic compressibilities of various solutes in alcohol-water mixtures are being investigated. For this purpose, precise data are required for the binary alcohol-water mixtures. Such data are scarce for the alcohols we were interested in, namely 2-propanol, *tert*-butanol, and 2-butoxyethanol. They were therefore determined carefully over the whole mole fraction region. At the time this study was initiated there was also disagreement in the literature on the compressibilities of simpler alcohols such as methanol and ethanol. Since then reliable data on these two alcohols have been published.⁽¹³⁾ We will still report our data on these alcohols since they can be used as a test of the accuracy of our measurements, and they will give a better overview of the trends in the compressibilities as the size of the alcohol molecules increases.

2. EXPERIMENTAL

The isentropic compressibilities were derived from sound velocities measured with a NUSONIC velocimeter (Mapco, model 6105) based on the 'sing-around' technique.⁽¹⁴⁾ The cell was the same as described elsewhere.⁽¹⁵⁾ The temperature was controlled with a SODEV thermostat and its value measured with a Hewlett-Packard Quartz thermometer as $25.00 \pm 0.01^\circ\text{C}$.

The sound velocities u in $\text{m}\cdot\text{s}^{-1}$ are obtained from the frequencies f with the relation

$$u = A (1 + \alpha t) / (7/f - 10^{-6}B) \quad (1)$$

where A and B are the cell constants, α the coefficient of thermal expansion of the probe and t the temperature in $^\circ\text{C}$. The values of A and B were obtained by calibration of the probe with deionized, degassed and distilled water at different temperatures, using the data of Del Grosso and Mader.⁽¹⁶⁾

The isentropic compressibilities β_s in bar^{-1} were derived from

$$\beta_s = 100/u^2d \quad (2)$$

Table I. Sound Velocities and Isentropic Compressibilities of Alcohol-Water Mixtures at 25°

X_A	u^a	β_S^b	$\phi_{K,S}^c$	$\phi_{K,W}^c$	X_A	u^a	β_S^b	$\phi_{K,S}^c$	$\phi_{K,W}^c$	X_A	u^a	β_S^b	$\phi_{K,S}^c$	$\phi_{K,W}^c$
MeOH					BE					Z-PrOH				
0.00167	1498.26	4.47	1.21	0.80	0.00295	1511.99	4.39	0.06	0.80	0.00243	1504.25	4.44	0.61	0.79
0.00469	1500.42	4.46	1.21	0.79	0.00589	1526.18	4.31	0.21	0.78	0.00548	1513.35	4.39	0.49	0.77
0.01016	1504.36	4.45	1.20	0.78	0.00877	1539.16	4.24	0.36	0.76	0.00965	1525.62	4.33	0.48	0.74
0.01948	1511.13	4.42	1.18	0.75	0.01166	1550.42	4.18	0.58	0.74	0.01850	1550.95	4.21	0.48	0.67
0.03684	1523.95	4.37	1.15	0.69	0.01739	1556.02	4.16	1.82	0.71	0.03140	1584.52	4.06	0.53	0.58
0.06848	1543.72	4.29	1.17	0.58	0.02337	1542.26	4.24	3.44	0.69	0.04840	1616.23	3.93	0.81	0.46
0.08962	1554.60	4.26	1.20	0.50	0.03004	1530.56	4.32	4.43	0.68	0.06930	1623.76	3.92	1.40	0.34
0.11130	1562.75	4.23	1.24	0.43	0.03948	1517.48	4.41	5.22	0.68	0.09640	1590.79	4.14	2.33	0.24
0.13980	1569.80	4.22	1.30	0.32	0.04485	1510.90	4.46	5.52	0.67	0.12060	1553.34	4.38	2.97	0.17
0.16210	1571.76	4.23	1.36	0.24	0.05101	1504.32	4.50	5.77	0.66	0.15630	1503.84	4.75	2.68	0.07
0.18250	1569.98	4.26	1.43	0.17	0.06254	1493.07	4.59	6.11	0.65	0.17630	1479.03	4.95	2.97	-0.02
0.20530	1565.72	4.31	1.50	0.09	0.06361	1492.02	4.60	6.14	0.64	0.20140	1450.75	5.20	4.29	-0.14
0.23470	1556.58	4.39	1.60	-0.02	0.08031	1492.00	4.62	6.18	0.64	0.22680	1426.13	5.44	4.56	-0.10
0.26310	1544.60	4.49	1.70	-0.12	0.09896	1466.41	4.81	6.65	0.59	0.25470	1401.36	5.70	4.83	-0.16
0.33890	1502.51	4.83	1.96	-0.39	0.10686	1461.76	4.85	6.73	0.59	0.28250	1379.87	5.94	5.06	-0.22
0.37370	1480.11	4.02	2.08	-0.51	0.12963	1450.73	4.95	6.89	0.58	0.30830	1361.44	6.14	5.22	-0.28
0.40070	1461.98	4.18	2.17	-0.61	0.15125	1441.15	5.04	7.04	0.54	0.32970	1347.88	6.30	5.33	-0.33
0.43140	1442.12	5.36	2.27	-0.73	0.19010	1426.65	5.17	7.16	0.52	0.34600	1337.79	6.42	5.42	-0.37
0.47180	1414.72	5.63	2.40	-0.88	0.27713	1401.15	5.43	7.45	0.46	0.35810	1330.76	6.51	5.49	-0.40
0.49870	1396.58	5.81	2.49	-0.99	0.29197	1397.44	5.47	7.50	0.34	0.37090	1324.22	6.60	5.55	-0.43
0.56710	1351.19	6.31	2.71	-1.27	0.31190	1392.73	5.53	7.57	0.33	0.37750	1320.79	6.65	5.59	-0.45
0.66970	1285.10	7.15	3.06	-1.71	0.33890	1386.75	5.58	7.61	0.31	0.46530	1281.84	7.21	5.97	-0.66
0.72090	1253.33	7.61	3.23	-1.94	0.38670	1377.40	5.68	7.70	0.27	0.55270	1249.62	7.71	6.28	-0.89
0.77450	1220.95	8.11	3.42	-2.19	0.41780	1371.40	5.74	7.76	0.20	0.66160	1216.85	8.29	6.63	-1.20
0.82650	1190.29	8.64	3.62	-2.43	0.49390	1358.55	5.90	7.95	0.16	0.72850	1199.11	8.62	6.84	-1.40
0.91090	1143.62	9.54	3.94	-2.83	0.61130	1341.61	6.09	8.14	0.10	0.80700	1180.33	8.99	7.05	-1.72
0.94840	1123.76	9.96	4.09	-3.00	0.74130	1325.75	6.28	8.34	-0.02	0.88230	1162.81	9.35	7.27	-2.09
0.97320	1111.02	10.24	4.19	-3.10	0.83100	1316.44	6.37	8.41	-0.13	0.96420	1143.72	9.75	7.52	-2.84
0.98620	1104.52	10.39	4.24	-3.13	0.91370	1308.86	6.49	8.57	-0.35	0.97260	1141.68	9.79	7.55	-2.99
1.00000	1097.70	10.55	4.30	0.00	1.00000	1301.96	6.58	8.67	0.00	0.98140	1139.56	9.84	7.58	-3.23
										0.99010	1137.42	9.89	7.61	-3.85
										0.99940	1134.80	9.94	7.65	-16.04
										1.00000	1134.26	10.00	7.70	0.00
t-BuOH					EtOH									
0.00014	1497.18	4.47	0.64	0.81	0.00705	1509.60	4.42	0.89	0.77					
0.00043	1498.35	4.47	0.34	0.81	0.02200	1536.52	4.29	0.84	0.70					
0.00087	1500.14	4.46	0.25	0.80	0.03835	1564.20	4.16	0.84	0.61					
0.00158	1503.00	4.45	0.36	0.79	0.05361	1584.76	4.07	0.88	0.53					
0.00246	1506.54	4.43	0.18	0.78	0.09076	1620.31	3.94	1.14	0.35					
0.00312	1509.16	4.41	0.10	0.78	0.11450	1622.44	3.96	1.40	0.24					
0.00462	1514.93	4.38	0.22	0.76	0.17180	1584.02	4.23	2.07	0.04					
0.00824	1528.83	4.31	0.23	0.73	0.20940	1547.16	4.49	2.45	-0.07					
0.01469	1556.54	4.18	0.19	0.66	0.27700	1483.49	4.99	2.98	-0.26					
0.02642	1591.69	4.02	0.31	0.56	0.33910	1433.60	5.44	3.36	-0.43					
0.03012	1599.43	3.93	0.80	0.46	0.42100	1379.69	6.01	3.75	-0.67					
0.05128	1607.03	3.99	1.86	0.37	0.49880	1335.44	6.53	4.06	-0.90					
0.06206	1583.78	4.13	2.67	0.33	0.58590	1294.13	7.08	4.37	-1.20					
0.06356	1579.21	4.17	2.81	0.32	0.70290	1246.20	7.81	4.74	-1.65					
0.08899	1522.27	4.55	4.17	0.24	0.84050	1194.94	8.70	5.19	-2.32					
0.11913	1472.43	4.95	5.06	0.15	0.92180	1165.17	9.27	5.48	-2.76					
0.13898	1442.36	5.22	5.52	0.09	0.96890	1147.99	9.62	5.66	-3.05					
0.16066	1416.01	5.47	5.88	0.03	1.00000	1136.65	9.86	5.78	0.00					
0.21499	1363.90	6.03	6.53	-0.12										
0.25680	1332.50	6.42	6.90	-0.24										
0.36890	1270.25	7.30	7.64	-0.54										
0.42690	1245.62	7.69	7.94	-0.68										
0.50520	1217.96	8.17	8.29	-0.87										
0.64630	1177.99	8.93	8.84	-1.18										
0.74040	1156.09	9.38	9.17	-1.37										
0.82490	1138.15	9.76	9.45	-1.46										
0.90470	1122.95	10.10	9.70	-1.42										
1.00000	1108.22	10.45	9.93	0.00										

^aUnits, m-s⁻¹. ^bUnits, 10⁻⁵ bar⁻¹. ^cUnits, 10⁻³ cm³-bar⁻¹-mol⁻¹.

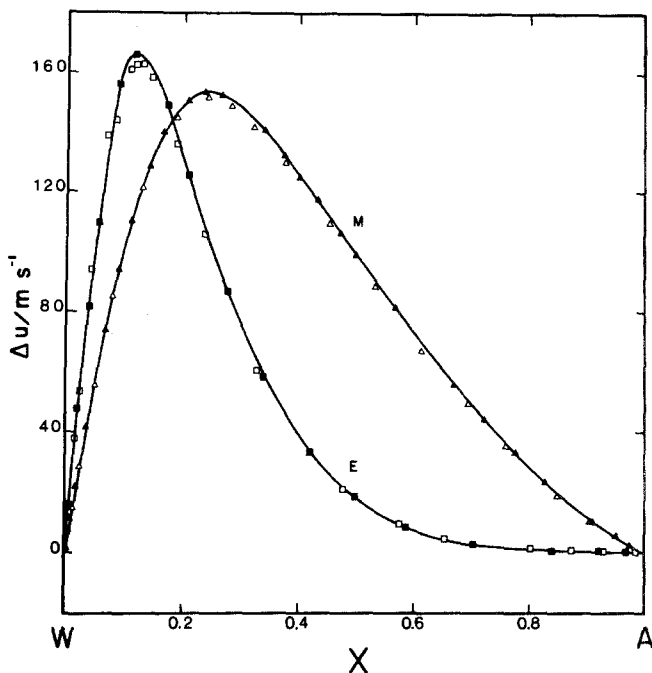


Fig. 1. Excess sound velocities of methanol- and ethanol-water mixtures at 25°C: ■ and ▲, present data; □ and △, Kiyohara and Benson⁽¹⁰⁾.

where d is the solution densities in $\text{g}\cdot\text{cm}^{-3}$. These densities were generally available from previous studies⁽⁶⁻⁸⁾ or else were determined with a SODEV flow densimeter.

All aqueous solutions were prepared by weight using deionized distilled water (Continental Deionizer).

The alcohols, methanol (M) (Fisher Spectra Analyzed), ethanol (E) and 2-propanol (P), both from Fisher ACS certified, and *tert*-butanol (*t*-B) (Baker analyzed reagent) were used as such after drying over 4 Å molecular sieves (Davidson Chemicals). 2-Butoxyethanol (BE) (Baker Chemicals) was redistilled and kept over molecular sieves. The water content of all of the alcohols was determined by Karl Fischer titration.

3. RESULTS

The sound velocities and derived isentropic compressibilities are given in Table I. It is customary to express the sound velocities as excess functions, *i.e.*

Table II. Isentropic Compressibilities of Alcohol-Water Mixtures at 25°C

Solute	$10^3 \bar{K}_{S,A}^0$ cm ³ -bar ⁻¹ -mol ⁻¹	$10^3 A_{K,S}$ cm ³ -bar ⁻¹ -mol ⁻² -kg	$10^3 K_{S,A}^*$ cm ³ -bar ⁻¹ -mol ⁻¹
M	1.25	-0.031	4.30
	1.26 (14)		(4.24) (21)
	1.26 (21)		4.30 (13)
	1.25 (13)		
	1.26 (22)		
E	0.99	-0.22	5.78
	0.99 (20)		5.74 (13)
	1.00 (21)		
	0.98 (13)		
	1.00 (22)		
P	0.62	-0.31	7.70
	0.61 (23)		(7.61) (17)
	1.10 (20)		
	0.61 (22)		
t-B	0.38	-1.44	9.93
	0.75 (20)		9.55 (3)
	0.55 (24)		
BE	-0.12	1.05	8.67
	-0.04 (19)	1.25 (19)	

$$\Delta u = u - X_A u_A - (1 - X_A) u_W \quad (3)$$

where A and W stand for alcohol and water. Our data for M and E are compared in Fig. 1 with the precise values of Kiyohara and Benson.⁽¹³⁾ Except in the region of the maximum, where differences of about 2 percent are observed, the agreement is inside the experimental uncertainty which can be evaluated as $\pm 0.05 \text{ m-s}^{-1}$ on Δu . The values of u for pure M and E were found to be 1097.70 and 1136.65 m-s^{-1} , which can also be compared with those of Kiyohara and Benson, 1097.57 and 1141.20 m-s^{-1} .

The Δu data for P, t-B and BE are shown in Fig. 2. Some literature data are available, mostly below $X_p = 0.2$, for P⁽¹⁷⁾ and reasonably good agreement is observed. For pure P, $u = 1134.26$ compared with

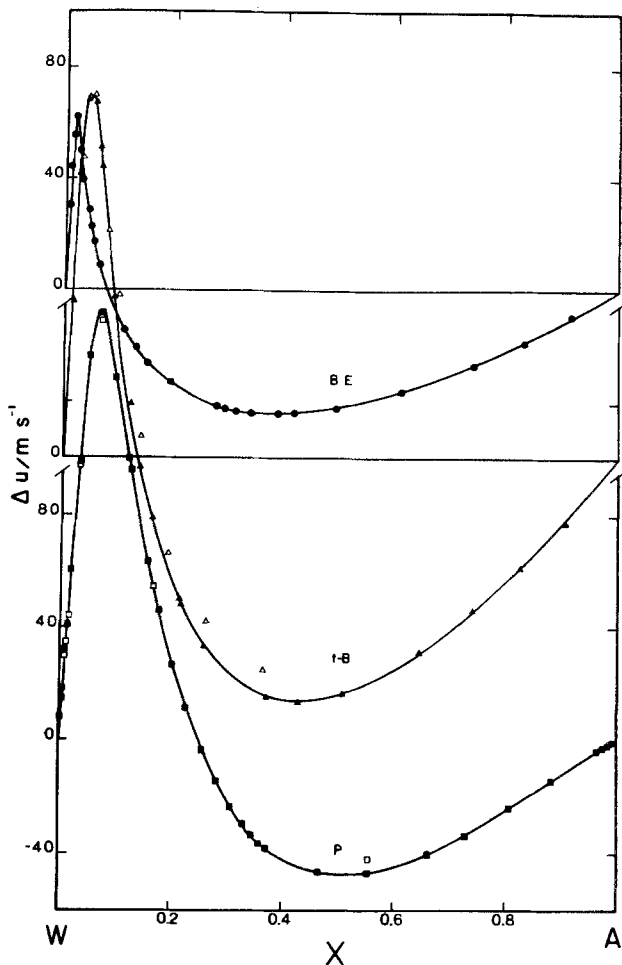


Fig. 2. Excess sound velocities of 2-propanol-, *tert*-butanol-, and 2-butoxyethanol-water mixtures at 25°C: ●, ■ and ▲, present data; △, Tamura *et al.*⁽¹³⁾; □, Brunn *et al.*⁽¹⁷⁾

1138.09 $\text{m}\cdot\text{s}^{-1}$.⁽¹⁷⁾ With *t*-B some difficulties arise in calculating Δu since pure *t*-B is a solid at 25°C, and $u_{t\text{-B}}$ has to be obtained by extrapolation. This can account for the large differences with the data⁽³⁾ of Tamura *et al.* at high $X_{t\text{-B}}$. Their $u_{t\text{-B}}$ is 1129.00 compared with our value of 1108.22 $\text{m}\cdot\text{s}^{-1}$. With the exception of the dilute region,⁽¹⁹⁾ and a few points in the intermediate region,⁽¹⁸⁾ no literature data could be found for Δu of BE. Our u_{BE} is 1301.96 $\text{m}\cdot\text{s}^{-1}$ for the pure liquid.

The apparent molar isentropic compressibilities $\phi_{\text{K,S}}$ of the alcohol can be calculated from β_{S} in the usual way from

$$\phi_{K,S} = \beta_S \phi_V + 1000 (\beta_S - \beta_{S,0}) / m_A d_0 \quad (4)$$

or

$$\phi_{K,S} = \beta_S \phi_V + X_W M_W / X_A (\beta_S - \beta_{S,0}) \quad (5)$$

where ϕ_V is the apparent molar volume, $\beta_{S,0}$ the isentropic compressibility of pure water, m_A the molality of A and M_W the molecular weight of water. These $\phi_{K,S}$ can be converted into isentropic compressibilities of mixing $\Delta K_{S,m}$ by

$$\Delta K_{S,m} = X_A (\phi_{K,S} - K_{S,A}^*) \quad (6)$$

where $K_{S,A}^*$ is the molar isentropic compressibility of the pure alcohol. Also, $\phi_{K,S}$ can be converted into partial molar isentropic compressibilities from

$$\bar{K}_{S,A} = \phi_{K,S} + X_W X_A (\partial \phi_{K,S} / \partial X_A)_{T,P} \quad (7)$$

or from a plot of $\Delta(\phi_V X_A / X_W) / \Delta(X_A / X_W)$ against the mean mole fraction of A.

The values of $\phi_{K,S}$ are given in Table I and are shown in the dilute region for the five alcohols in Fig. 3. The $\phi_{K,S}$ data can be extrapolated to infinite dilution, $\phi_{K,S}^0 = \bar{K}_{S,A}^0$, from a linear regression using the relation

$$\phi_{K,S} = \phi_{K,S}^0 + A_{K,S} m \quad (8)$$

A summary of the parameters $\bar{K}_{S,A}^0$, $A_{K,S}$ and $K_{S,A}^*$ is given in Table II. The agreement with the available literature values is generally good considering that some of these data were extrapolated from relatively high concentrations. From this comparison, our $\phi_{K,S}^0$ values can probably be considered reliable to $\pm 10^{-5} \text{ cm}^3 \cdot \text{bar}^{-1} \cdot \text{mol}^{-1}$.

4. DISCUSSION

4.1. Sound Velocities

The excess sound velocities in Fig. 1 and 2 go through a maximum, and this maximum becomes sharper and moves towards the water-rich region as the hydrophobic character of the alcohol increases. These maxima occur at 0.016, 0.045, 0.058, 0.125, and 0.166 mole frac-

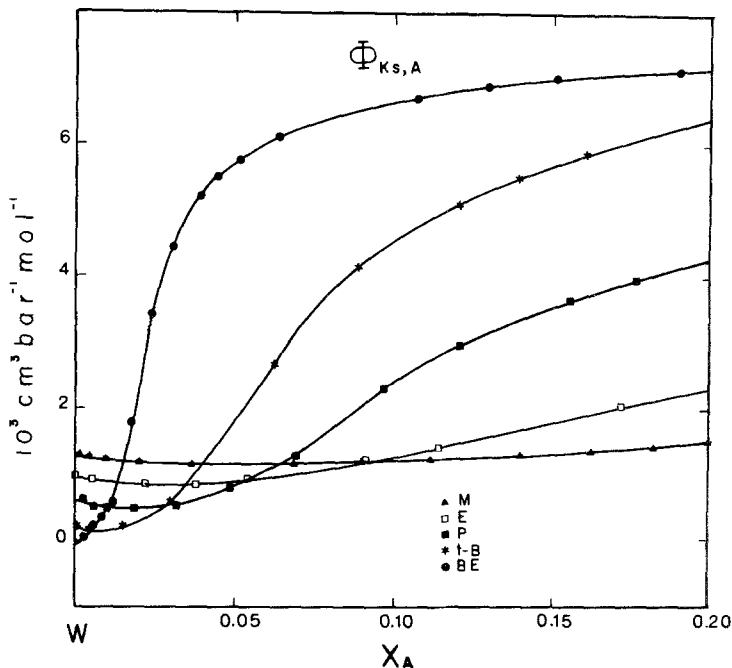


Fig. 3. Apparent molar isentropic compressibilities of alcohols in water at 25°C.

tion respectively for BE, *t*-B, P, E, and M, respectively. Andrea *et al.* proposed that this maximum in the velocity could be a measure of the breakdown of the water structure around the solute.⁽²⁵⁾ This is somewhat consistent with the light scattering studies of Iwasaki and Fujiyama,⁽⁵⁾ from which the authors suggest that a clathrate of average composition *t*-B (H₂O)₂₁ exists at concentrations $X_{t-B} < 1/22$. This critical concentration corresponds to that of the maximum sound velocity. Therefore, if we accept that the maximum corresponds to the maximum concentration where all the water is held in clathrate-like structures on a time average, then the ratio of alcohol to water in these complexes would be 1/5, 1/7, 1/16, 1/21, and 1/61, respectively, when going from M to BE. At higher concentrations, the hydrocarbon chains of any additional alcohol are essentially unsolvated. These ratios therefore give some idea of the extent of hydrophobic hydration of these solutes.

4.2. Apparent and Partial Molar Isentropic Compressibilities

The molar isentropic compressibilities $K_{S,A}^*$ of the pure alcohols,

given in Table II, increase as the size of the alcohol increases. On the other hand, the values of $\bar{K}_{S,A}^0$ decrease as the number of carbon atoms increase. The same general observation has been made for the corresponding *n*-alcohols.^(21,23) The difference $\bar{K}_{S,A}^0 - K_{S,A}^*$ is always negative, and its magnitude increases significantly with the size of the solute. This difference can be taken as a measure of the contribution of hydrophobic hydration to this property. Most clathrate or 'iceberg' models for hydrophobic hydration can account for the sign and trends of these differences.^(21,26,27)

As seen from Fig. 3 and Table II, except for BE, $\phi_{K,S}$ in the water-rich region decreases initially with increasing mole fraction. This, however, is not generally true. While $\bar{K}_{S,A}^0$ for *n*-propanol and for *n*-butanol^(21,25) have approximately the same values as P and *t*-B, $\phi_{K,S}$ of these normal alcohols initially increases with mole fraction. BE would fall in this latter category. To understand these trends in the initial slopes, a comparison should be made with apparent molar volumes ϕ_V and heat capacities ϕ_C . In the case of volumes $\bar{V}_A^0 - V_A^*$ are negative and $d\phi_V/dX_A$ are also negative. This negative initial slope can be interpreted with various models, such as the cosphere overlap concept.⁽²⁸⁾ Since the origin of the negative sign of $\bar{K}_{S,A}^0 - K_{S,A}^*$ and $\bar{V}_A^0 - V_A^*$ is essentially the same, *i.e.* loss of free space due to hydrophobic hydration, the negative sign of $d\phi_{K,S}/dX_A$ could also be interpreted through the cosphere overlap model. Or else, since $\phi_K = -(\partial\phi_K/\partial P)$, it can be concluded that the structural interactions leading to the negative $d\phi_V/dX_A$ are decreasing with increasing pressure. It is generally admitted that pressure breaks down the structure of water. The observed negative initial slope with some of the alcohols is therefore the normal expected behavior.

In the case of heat capacities $d\phi_C/dX$ are sometimes positive and sometimes negative depending on the hydrophobic solute. The positive slope is generally attributed to the relaxational contribution to ϕ_C ,^(6,7,8,29,30) *i.e.* the shift in equilibrium when the temperature is increased by one degree. There will also be a relaxational contribution to ϕ_K which would be positive. The positive values of $d\phi_{K,S}/dX_A$ for BE and the larger normal alcohols is probably a consequence of the predominance of the relaxational contribution. It is not clear however why this contribution would be more important for straight chain alcohols than branched ones.

The values of $\phi_{K,S}$ of M change very gradually over the whole mole fraction range. This is often taken as evidence that M forms hydrogen bonds with water and thus participates in the water

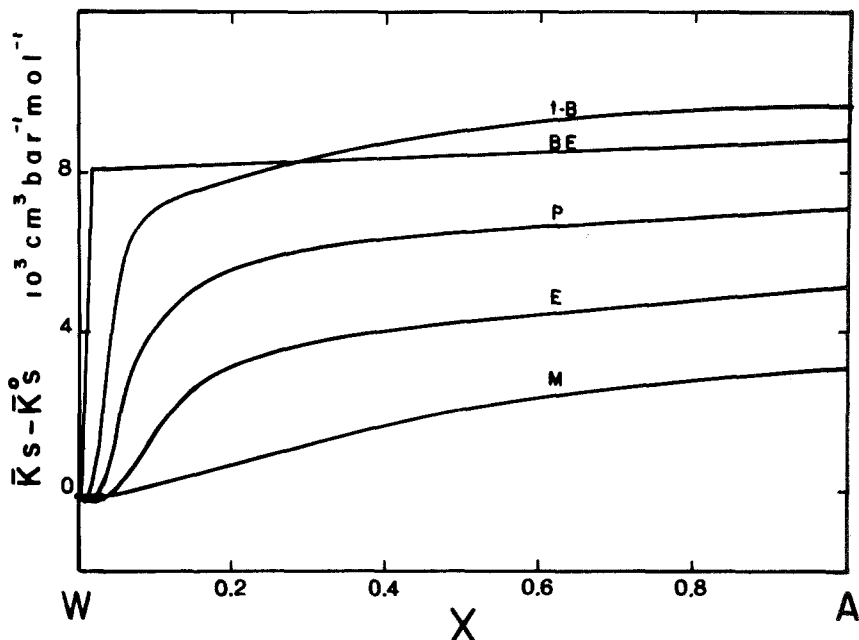


Fig. 4. Excess partial molar isentropic compressibilities of alcohols in water at 25°C.

structure.^(1,20) For the larger alcohols, $\phi_{K,S}$ increases rapidly with X_A beyond a certain concentration. These trends become evident if $\bar{K}_{S,A}$ is plotted against X_A , as shown in Fig. 4. As the hydrophobic character increases, the transition becomes very well defined. A careful analysis of the data for BE shows that $\bar{K}_{S,A}$ goes through a sharp maximum in the transition region as shown in Fig. 5. The possibility that this maximum could be an artifact resulting from the data fitting of $\phi_{K,S}$ cannot be excluded and the trends drawn in Fig. 4 were those corresponding to the dotted line in Fig. 5. However, recent theoretical calculations of thermodynamic functions based on an association model⁽³¹⁾ do in fact predict such a sharp maximum for $\bar{K}_{S,A}$ resulting from the relaxational contribution. The recent sound velocities of Nishikawa *et al.*⁽¹⁸⁾ although less precise than the present ones, also seem to support the existence of such a maximum for $\bar{K}_{S,A}$ of BE in water. The sharp increase in $\bar{K}_{S,A}$ is strong evidence for the existence of a microphase transition for the higher members of these alcohols, as previously suggested from volume and heat capacity studies.⁽⁶⁻⁸⁾ Beyond the transition zone, the values of $\bar{K}_{S,A}$ are essentially those of the pure alcohols. This implies that the hydrophobic part of the alcohol 'sees' only other alcohol molecules, in agreement with the existence of microphases.

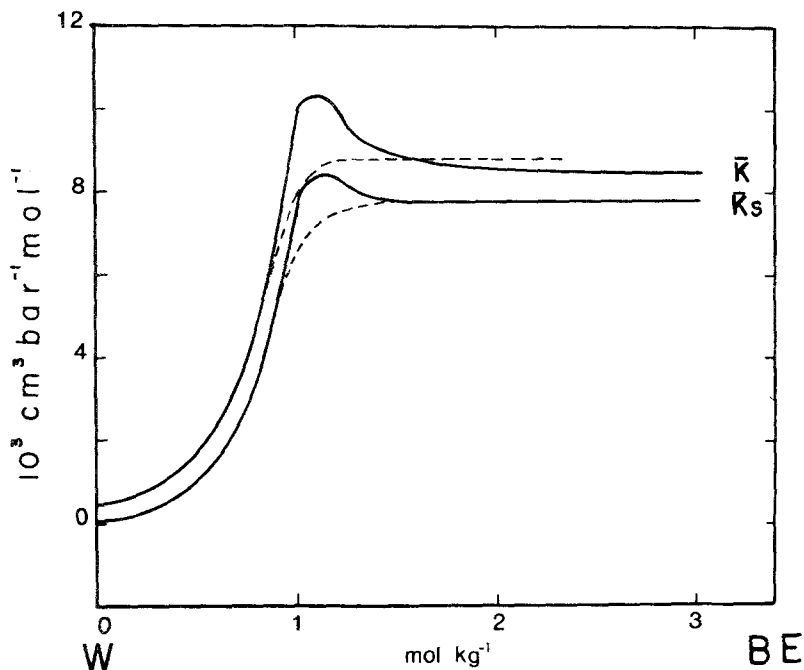


Fig. 5. Partial molar isentropic and isothermal compressibilities of 2-butoxyethanol in water at 25°C.

These microphases could be essentially non-solvated alcohol molecules, as suggested by Iwasaki and Fujiyama,⁽⁵⁾ or could be aggregates similar to micelles.^(4,12)

4.3. Isothermal Compressibilities

The more fundamental thermodynamic quantity is the isothermal rather than the isentropic compressibility. The isothermal ϕ_K can readily be calculated from the isentropic values if volumes, ϕ_V , expansibilities, ϕ_E , and heat capacities, ϕ_C , are available.⁽³²⁾

$$\phi_K = \phi_{K,S} + (\delta/\alpha) (1 + \alpha/d\alpha) \phi_E - (\delta/d\sigma) \phi_C + (\delta_0 - \delta\alpha/d\alpha) \phi_V \quad (9)$$

where $\delta = \alpha^2 T/\sigma$, α is the coefficient of thermal expansion, σ is the heat capacity per unit volume and d is the density. The subscript 0 refers to the pure solvent. All these data are now available for most alcohols. Kiyohara and Benson⁽¹³⁾ have already discussed these differences between \bar{K}_A and $\bar{K}_{S,A}$ for normal alcohols. Therefore, only one example will be given here for BE. The required data for the calcu-

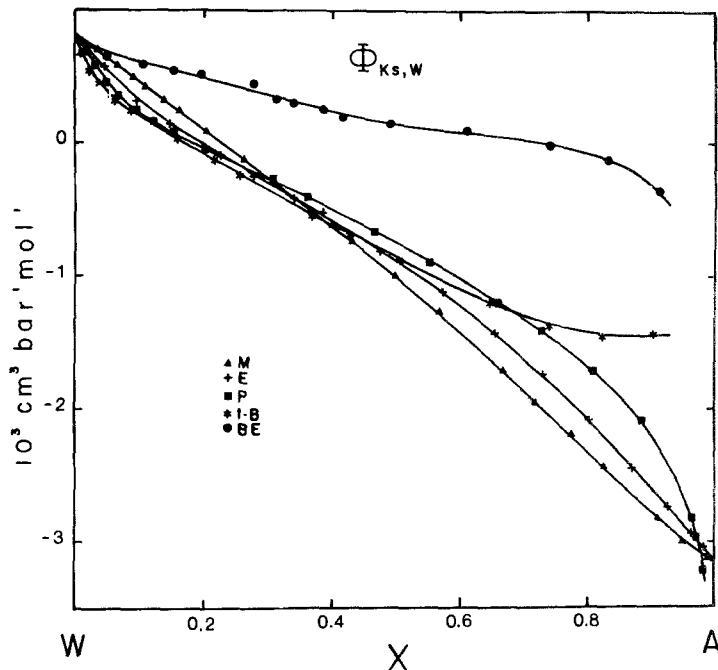


Fig. 6. Apparent molar isentropic compressibilities of water in alcohols at 25°C.

lations were taken from Roux *et al.*⁽⁸⁾ and from Fortier *et al.*⁽³³⁾ The two functions ϕ_K and \bar{K}_A were calculated, and \bar{K}_A is compared with the isentropic value in the water-rich zone in Fig. 5. The dotted line is for the same functions if it is assumed that the maximum is an artifact. It is obvious from Fig. 5 that the isothermal and isentropic compressibilities are quite similar and reflect the same kind of interactions.

4.4. Compressibilities of Water

Since compressibility data were obtained over the whole mole fraction range, it is possible to calculate the apparent and partial molar isentropic compressibilities of water in the alcohol, *i.e.* $\phi_{K,S,W}$ and $\bar{K}_{S,W}$. The values of $\phi_{K,S,W}$ are shown in Fig. 6. In all cases $\phi_{K,S,W}$ decreases when going from pure water to infinite dilution in the alcohol. With M the change is nearly linear as we would expect from the trends in $\phi_{K,S,M}$. Water has an open structure and it is therefore not unexpected that water surrounded by M would have a more compact spatial arrangement. Deviations from linearity are observed for E and P. Partial and apparent molar quantities of a component are always

much more sensitive to interactions and structure in the region where its mole fraction tends to zero. Therefore the large changes in $\phi_{K,S,A}$ and $\bar{K}_{S,A}$ in the water-rich region appear only as a slight negative deviation for $\phi_{K,S,W}$. On the other hand we can see that water is having an effect on the structure of the alcohol in the alcohol-rich region. Presumably, $\phi_{K,S,W}$ of *t*-B and BE decrease sharply as X_A tends to unity. Transitions similar to inverse micellization are probably occurring in this region. Data at very low X_W would be required to confirm this but such experiments were not possible with the present technique. It is interesting to note that $\phi_{K,S,W}$ in BE does not change much up to relatively high X_{BE} . This could indicate that the water molecules are in contact with very few hydrophobic groups and that the interactions between the -OH group of BE and H₂O are somewhat similar to H₂O-H₂O interactions. Similarly, the apparent molar heat capacities of water in BE did not show very large changes in the same concentration region.⁽⁸⁾

ACKNOWLEDGMENT

We are grateful to the Quebec Ministry of Education and to the National Science and Engineering Research Council for financial support.

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