# Excess Volumes, Speeds of Sound, and Viscosities for Mixtures of 1,2-Ethanediol and Alkoxy Alcohols with Water at 308.15 K

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Excess volume, speed of sound, and viscosity data of binary liquid mixtures of water + 1,2-ethanediol, + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol have been measured at 308.15 K. The results are used to derive densities and isentropic compressibilities. The excess volumes and deviations in the compressibility are negative while deviations in the viscosity are positive for all four systems. The results are discussed in terms of molecular interactions between like and unlike components.

## Introduction

Recently there has been increasing interest (*1–4*) in the thermophysical properties of binary aqueous organic mixtures. As part of our study (*5, 6*), we report excess volumes, isentropic compressibilities, and viscosities of water + 1,2-ethanediol, + 2-methoxyethanol, + 2-ethoxyethanol, and + 2-butoxyethanol. Partial molar excess volumes of alkoxy alcohols are compared with those of aqueous solutions of 1-alcohols (*7–9*). The relative influence of the ether group in the alkoxy alcohol on molecular interactions has been investigated.

## Experimental Section

***Materials.*** AR grade (SD's make, India) samples of 1,2-ethanediol, 2-methoxyethanol, 2-ethoxyethanol, and 2-butoxyethanol were further purified by standard methods (*10*) as their densities did not initially agree with those reported in the literature (*10*). 1,2-Ethanediol was dried over dehydrated sodium sulfate and fractionally distilled. Alkoxy alcohols (2-methoxy, 2-ethoxy, and 2-butoxy) were dried over 4A molecular sieves and fractionally distilled. Deionized water was distilled twice, and the fraction boiling at 373.15 K was collected. The purity of the samples was ascertained by comparing the densities and boiling points with those reported in the literature (*10*).

***Procedure.*** Excess volumes were measured directly using the batch dilatometer technique described earlier (*11*), except that three additional dilatometers having a large difference in the size of the limbs were used to cover the lower mole fractions. The performance of the technique was established by measuring the excess volumes of the test system benzene + cyclohexane. The $V^E$ values are reproducible to ±0.003 $cm^3 \cdot mol^{-1}$. A thermostatically controlled, well-stirred water bath with temperature controlled to ±0.01 K was used for all the measurements. The composition of the mixture was obtained from the mass of the components, and the uncertainty in the mole fraction is estimated to be less than $\pm 5 \times 10^{-4}$.

The liquid mixtures were recovered from the dilatometers using a hypodermic syringe, and used to determine the speed of sound and viscosity. Speeds of sound were measured with a single-crystal ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 2 MHz. The values are reproducible to ±0.1%.

Viscosities were measured using an Ostwald viscometer and were reproducible to ±0.5%. Densities of the pure components were measured using a bicapillary pycnometer, and for mixtures, densities were computed from experimental excess volume data according to the relation

**Table 1. Excess Volumes at 308.15 K**

| $x_1$ | $V^E/(cm^3 \cdot mol^{-1})$ | $x_1$ | $V^E/(cm^3 \cdot mol^{-1})$ |
|---|---|---|---|
| | Water (1) + 1,2-Ethanediol (2) | | |
| 0.1046 | −0.092 | 0.5999 | −0.365 |
| 0.2029 | −0.184 | 0.6987 | −0.334 |
| 0.3005 | −0.245 | 0.8008 | −0.281 |
| 0.3986 | −0.309 | 0.8947 | −0.175 |
| 0.5012 | −0.341 | | |
| | Water (1) + 2-Methoxyethanol (1) | | |
| 0.1034 | −0.313 | 0.6406 | −1.005 |
| 0.1923 | −0.522 | 0.6672 | −0.998 |
| 0.2978 | −0.730 | 0.7415 | −0.916 |
| 0.3944 | −0.871 | 0.8372 | −0.693 |
| 0.5527 | −0.992 | 0.9560 | −0.209 |
| | Water (1) + 2-Ethoxyethanol (2) | | |
| 0.1041 | −0.396 | 0.6990 | −1.201 |
| 0.1994 | −0.615 | 0.7918 | −1.082 |
| 0.2993 | −0.811 | 0.8469 | −0.922 |
| 0.3997 | −0.991 | 0.8996 | −0.711 |
| 0.4988 | −1.112 | 0.9491 | −0.403 |
| 0.5964 | −1.191 | | |
| | Water (1) + 2-Butoxyethanol (2) | | |
| 0.1579 | −0.383 | 0.6970 | −0.849 |
| 0.3049 | −0.615 | 0.8047 | −0.689 |
| 0.4017 | −0.765 | 0.8972 | −0.477 |
| 0.4974 | −0.853 | 0.9497 | −0.294 |
| 0.5973 | −0.882 | | |

$$\rho = \frac{x_1 M_1 + x_2 M_2}{x_1 V_1 + x_2 V_2 + V^E} \qquad (1)$$

where $M_1$ and $M_2$ are the molecular weights, $x_1$ and $x_2$ are the mole fractions, and $V_1$ and $V_2$ are the molar volumes of water (1) and 1,2-ethanediol or alkoxy alcohols (2), respectively. Density values are reproducible to $\pm 5 \times 10^{-5}$ $g \cdot cm^{-3}$.

## Results

Excess volumes are given in Table 1, and $V^E$ as a function of mole fraction is shown in Figure 1. Isentropic compressibilities, $k_s$, and deviations in isentropic compressibility, $\Delta k_s$, are calculated using the relations

$$k_s = 1/U^2\rho \qquad (2)$$

$$\Delta k_s = k_s - (\phi_1 k_{s,1} + \phi_2 k_{s,2}) \qquad (3)$$

where $k_s$, $k_{s,1}$, and $k_{s,2}$ are the isentropic compressibilities of

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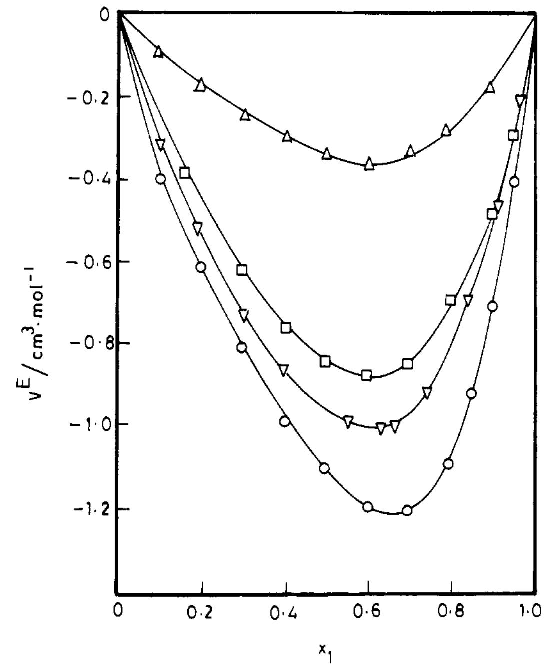


**Figure 1.** Mole fraction of water versus excess volumes for water + 1,2-ethanediol (△), + 2-methoxyethanol (▽), + 2-ethoxyethanol (○), and + 2-butoxyethanol (□) at 308.15 K.

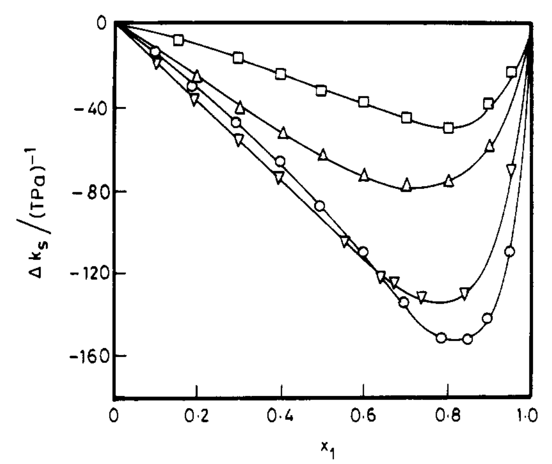


**Figure 2.** Mole fraction of water versus deviations in isentropic compressibility of water + 1,2-ethanediol (△), + 2-methoxyethanol (▽), + 2-ethoxyethanol (○), and + 2-butoxyethanol (□) at 308.15 K.

the mixture and components 1 and 2 and $\phi_1$ and $\phi_2$ are the volume fractions of components 1 and 2, respectively. Deviations in viscosity are obtained by the equation

$$\ln \eta = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (4)$$

where $\eta$, $\eta_1$, and $\eta_2$ are the viscosities of the mixture and components 1 and 2, respectively. Data on the density ($\rho$), speed of sound ($U$), isentropic compressibility ($k_s$), and viscosity ($\eta$) are included in Table 2. The variation of $\Delta k_s$ with volume fraction and of $\Delta \ln \eta$ with mole fraction is represented in Figures 2 and 3, respectively. The values of $V^E$ and $\eta$ for the system water + 2-methoxyethanol are in agreement, within experimental error, with those reported by Das and Hazra (*12*).

The data on $V^E$, $\Delta k_s$, and $\Delta \ln \eta$ are fitted to a general empirical equation of the form (*13*)

$$X^E = \frac{x_1 x_2 [a_1 + a_2(x_2 - x_1) + a_3(x_2 - x_1)^2]}{[1 + a_0(x_2 - x_1)]} \qquad (5)$$

**Table 2. Density, $\rho$, Speed of Sound, $U$, Isentropic Compressibility, $k_s$, and Viscosity, $\eta$, at 308.15 K**

| $x_1$ | $\rho$/(g·cm$^{-3}$) | $U$/(m·s$^{-1}$) | $k_s$/TPa$^{-1}$ | $\eta$/(MPa·s) |
|---|---|---|---|---|
| Water (1) + 1,2-Ethanediol (2) | | | | |
| 0.000 | 1.105 35 | 1629 | 341 | 10.473 |
| 0.1046 | 1.103 26 | 1641 | 337 | 9.207 |
| 0.2029 | 1.101 42 | 1647 | 335 | 8.051 |
| 0.3005 | 1.097 73 | 1661 | 330 | 6.899 |
| 0.3986 | 1.093 42 | 1675 | 326 | 5.846 |
| 0.5012 | 1.088 03 | 1683 | 324 | 4.779 |
| 0.5999 | 1.082 14 | 1690 | 324 | 3.798 |
| 0.6987 | 1.069 99 | 1689 | 328 | 2.866 |
| 0.8008 | 1.054 30 | 1672 | 339 | 1.998 |
| 0.8947 | 1.032 29 | 1624 | 367 | 1.315 |
| 1.0000 | 0.994 12 | 1522 | 434 | 0.719 |
| Water (1) + 2-Methoxyethanol (2) | | | | |
| 0.0000 | 0.952 90 | 1327 | 596 | 1.189 |
| 0.1034 | 0.958 03 | 1348 | 574 | 1.452 |
| 0.1923 | 0.962 43 | 1374 | 551 | 1.477 |
| 0.2978 | 0.968 35 | 1402 | 526 | 1.629 |
| 0.3944 | 0.973 52 | 1429 | 504 | 1.768 |
| 0.5527 | 0.983 33 | 1494 | 456 | 1.918 |
| 0.6406 | 0.989 55 | 1538 | 427 | 2.023 |
| 0.6672 | 0.991 53 | 1549 | 420 | 2.023 |
| 0.7415 | 0.996 05 | 1583 | 401 | 2.002 |
| 0.8372 | 0.999 93 | 1623 | 379 | 1.768 |
| 0.9560 | 0.997 53 | 1600 | 392 | 1.085 |
| 1.0000 | 0.994 12 | 1522 | 434 | 0.719 |
| Water (1) + 2-Ethoxyethanol (2) | | | | |
| 0.0000 | 0.917 97 | 1266 | 680 | 1.370 |
| 0.1041 | 0.923 65 | 1280 | 661 | 1.418 |
| 0.1944 | 0.928 13 | 1297 | 640 | 1.621 |
| 0.2933 | 0.933 75 | 1320 | 615 | 1.785 |
| 0.3997 | 0.940 59 | 1347 | 586 | 1.954 |
| 0.4988 | 0.947 94 | 1380 | 554 | 2.148 |
| 0.5964 | 0.956 96 | 1421 | 518 | 2.307 |
| 0.6990 | 0.968 46 | 1481 | 471 | 2.385 |
| 0.7918 | 0.980 02 | 1546 | 427 | 2.320 |
| 0.8469 | 0.986 37 | 1586 | 403 | 2.111 |
| 0.8976 | 0.992 91 | 1621 | 383 | 1.787 |
| 0.9491 | 0.995 33 | 1623 | 381 | 1.279 |
| 1.0000 | 0.994 12 | 1522 | 434 | 0.719 |
| Water (1) + 2-Butoxyethanol (2) | | | | |
| 0.0000 | 0.888 73 | 1283 | 684 | 2.193 |
| 0.1579 | 0.894 37 | 1292 | 670 | 2.327 |
| 0.3047 | 0.900 41 | 1306 | 651 | 2.388 |
| 0.4017 | 0.905 65 | 1313 | 640 | 2.477 |
| 0.4974 | 0.912 12 | 1327 | 622 | 2.624 |
| 0.5973 | 0.918 96 | 1341 | 605 | 2.835 |
| 0.6970 | 0.928 73 | 1364 | 579 | 2.955 |
| 0.8047 | 0.941 97 | 1394 | 546 | 2.873 |
| 0.8972 | 0.961 06 | 1429 | 510 | 2.245 |
| 0.9497 | 0.977 45 | 1458 | 481 | 1.576 |
| 1.0000 | 0.994 12 | 1522 | 434 | 0.719 |

as a function of mole fraction where $a_0$ is the skewing parameter, which is included to take into account the skewing behavior and is represented as

$$a_0 = \frac{-2(1 - 2x_{expt})}{[1 + (1 - 2x_{expt})^2]} \qquad (6)$$

where $x_{expt}$ is the mole fraction which corresponds to maximum $X^E$. The parameters $a_1$, $a_2$, and $a_3$ in eq 5 are obtained by the method of least squares and are given in Table 3 along with the standard deviation, $\sigma(X^E)$. Partial molar excess volumes ($\bar{V}_i^E$) have been calculated using the differential form (*14*) of eq (5). The results of $\bar{V}_i^E$ are given in Figure 4.

## Discussion

The results given in Table 1 and in Figures 1–to 3 indicate that $V^E$ and $\Delta k_s$ are negative whereas $\Delta \ln \eta$ values are positive for the four systems over the entire range of mole fraction. The variation of excess properties with mole fraction is highly unsymmetrical and skewed toward the water-rich region in

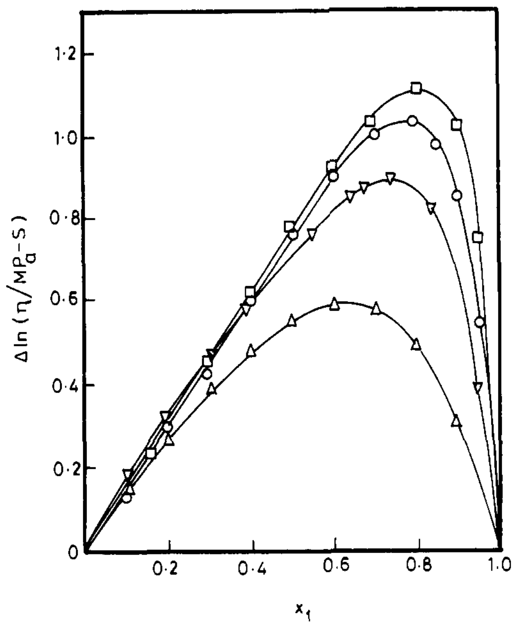


**Figure 3.** Mole fraction of water versus deviations in viscosity for water + 1,2-ethanediol (△), + 2-methoxyethanol (▽), +2-ethoxyethanol (○), and + 2-butoxyethanol (□) at 308.15 K.

**Table 3. Values of the Parameters of Eq 5 and the Standard Deviation at 308.15 K**

| $X^E$ | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma(X^E)$ |
|---|---|---|---|---|---|
| Water (1) + 1,2-Ethanediol (2) | | | | | |
| $V^E/(cm^3{\cdot}mol^{-1})$ | 0.3846 | −1.3912 | 0.0134 | 0.1313 | 0.006 |
| $\Delta k_s/TPa^{-1}$ | 0.7373 | −248.31 | 8.36 | −41.17 | 2.7 |
| $\Delta \ln(\eta/(mPa{\cdot}s))$ | 0.3846 | 2.2275 | 0.1874 | 0.0228 | 0.003 |
| Water (1) + 2-Methoxyethanol (2) | | | | | |
| $V^E/(cm^3{\cdot}mol^{-1})$ | 0.5505 | −3.9779 | 1.1795 | 0.2924 | 0.025 |
| $\Delta k_s/TPa^{-1}$ | 0.8824 | −374.16 | −24.79 | 47.09 | 3.7 |
| $\Delta \ln(\eta/(mPa.s))$ | 0.8021 | 2.8242 | 0.5181 | −0.5271 | 0.022 |
| Water (1) + 2-Ethoxyethanol (2) | | | | | |
| $V^E/(cm^3{\cdot}mol^{-1})$ | 0.6897 | −4.4746 | 1.6600 | −0.6122 | 0.009 |
| $\Delta k_s/TPa^{-1}$ | 0.9081 | −363.74 | −122.51 | 47.12 | 2.6 |
| $\Delta \ln(\eta/(mPa{\cdot}s))$ | 0.8186 | 2.7858 | 0.9433 | −0.4119 | 0.035 |
| Water (1) + 2-Butoxyethanol (2) | | | | | |
| $V^E/(cm^3{\cdot}mol^{-1})$ | 0.3846 | −3.3555 | 0.0527 | −0.6239 | 0.023 |
| $\Delta k_s/TPa$ | 0.8824 | −129.44 | −35.61 | 60.21 | 1.7 |
| $\Delta \ln(\eta/(mPa{\cdot}s))$ | 0.9081 | 2.9424 | 0.2643 | −0.0324 | 0.062 |

mixtures containing alkoxy alcohols. The algebraic values of $V^E$ and $\Delta k_s$ fall in the sequence 2-ethoxyethanol < 2-methoxyethanol < 2-butoxyethanol < 1,2-ethanediol. The results of $\Delta$ ln $\eta$ are in the following order: 1,2-ethanediol < 2-methoxyethanol < 2-ethoxyethanol < 2-butoxyethanol. The order in $\Delta \ln \eta$ is in accordance with the size of the noncommon components but different from that observed in $V^E$ and $\Delta k_s$. The negative $V^E$ and $\Delta k_s$ and positive $\Delta$ ln $\eta$ over the entire range of mole fraction may be attributed to the dominance of molecular association between unlike molecules over the dissociation in like molecules.

The behavior of 1,2-ethanediol and alkoxy alcohols in the water-rich region has been investigated by calculating partial molar excess volumes of both the components and is represented in Figure 4. Partial molar excess volumes of component 2, $\bar{V}_2^E$ decrease steadily with increasing $x_1$, and the decrease is rapid beyond $x_1 \approx 0.8$. Further, values of $\bar{V}_1^E$ for water vary with mole fraction. The variation of $\bar{V}_2^E$ with $x_1$ in the region $x_1 > 0.8$ is comparable with that in water + ether systems (*6, 15–18*) but different from that in water + alcohol systems (*7–9, 19*) in which a sharp discontinuity has been observed. The results may be attributed to the association between unlike molecules through hydrogen bond formation and enhancement of water–water interactions. The

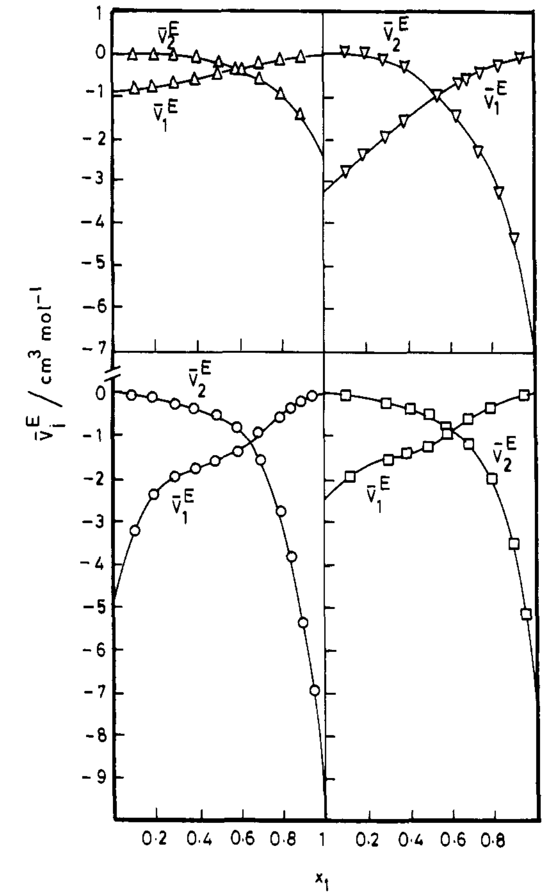


**Figure 4.** Mole fraction of water versus partial molal excess volumes for water + 1,2-ethanediol (△), and + 2-methoxyethanol (▽), + 2-ethoxyethanol (○), and + 2-butoxyethanol (□) at 308.15 K.

possibility of interaction between alkoxy alcohol molecules may be negligible in such high concentrations of water.

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