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Solution properties of ethanol in water

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Abstract

The packing propensity of ethanol in aqueous solution is very unusual, yet ethanol finds extensive use both in the food and the pharmaceutical industry. An analysis of the solution properties of increasing concentrations of ethanol in water at 20° and 37°C reveals valuable information about its packing characteristics. Apparent molar and specific volumes provide information about the interaction of ethanol with surrounding water structure. Isentropic apparent molar and specific compressibilities indicate the extent to which the hydration layer around the ethanol molecules can be compressed. Compressibility hydration numbers show the number of water molecules that are displaced by the introduction of the ethanol to water. The enhanced packing efficiency of ethanol in water at low concentrations, is affected by the formation of cage-like structures around the hydrophobic end of the molecule. At high concentrations, however, linear chains or rings of ethanol molecules are formed which change its mode of packing within the three-dimensional structure of water. These effects may be used to help explain the mechanism of action of ethanol in food, pharmaceutical and other applications. © 1999 Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Ethanol has long been used as a powerful disinfectant in medicine and as an extraction solvent or carrier both in the pharmaceutical and food industry. It is also present in food and beverage products either naturally or added for its functional properties. Ethanol can be produced in the food itself, as in fermented foods and beverages (Birch & Lindley, 1985; Morton & Macleod, 1986) and in bakery products obtained from yeast fermentation, imparting both preservative action and flavour to the products. It is often incorporated in foods as a flavour component particularly when it is enclosed as a liqueur. Ethanol is finding increasing use as a preservative in packaged food, and can be inserted directly or released from a carrier into the atmosphere inside the pack, thereby increasing the shelf-life of the product (Ooraikul & Stiles, 1991; Seiler & Russell, 1991; Smith, Ooraikul, Koersen, van de Voort, Jackson & Lawrence, 1987). Its other uses include anti-microbial (Shapero, Nelson & Labuza, 1978) and anti-staling (Hodge, Rob & Chester, 1978; Seiler, 1979) properties. Ethanol's use as an anti-microbial agent in food comes from its ability to lower the water activity of foods as well as its effects on membrane structure and function (Ingram, 1990; Jones & Greenfield, 1987; Sinskey, 1979). Ethanol as a food source, has a high energy content, and is rapidly metabolised in the body. The ethanol molecule contains a hydrophilic hydroxyl group which is available to hydrogen-bond to water molecules, and an alkyl chain which confers a certain degree of hydrophobicity upon the molecule. These properties dictate the partitioning of the molecule between the aqueous and hydrophobic phases in the different environments that it is exposed to (Ingram, 1990). The properties, effects and mode of action of ethanol vary with the nature of the environment and the ratio of ethanol to water present in the medium. These effects are clearly demonstrated by the very unusual packing characteristics of ethanol in aqueous solution (Frank & Evans, 1945; Franks & Ives, 1966; Kappatos, Gordon & Birch, 1996). Its packing characteristics change from low to high concentrations of use, and this is reflected in its solution properties.

Solution property measurements have proved useful in understanding solute and solvent effects, and hence the packing characteristics of solutes among the solvent molecules (Birch, Park, Siertsema & Westwell, 1997; Parke & Birch, 1999; Parke, Birch, MacDougall & Stevens, 1997). Determinations of the apparent volumes, isentropic compressibilities and hydration numbers give information about ethanol-water interactions as the

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concentration of ethanol is increased in solution as well as the packing efficiency of the molecules among each other.

In the neighbourhood of a solute molecule, the nearest-neighbour water molecules are always essentially mobilised by attractive forces. This forms a hydration sheath around the solute molecule, which is comprised of different layers of water molecules, subject to varying degrees of attraction to the solute (Frank & Wen, 1957). Measurements such as the apparent molar and specific volumes have long been used as an estimate of the packing order of solute molecules among solvent molecules (Birch, Karim, Chavez & Morini, 1993). They are related to other solution measurements, one of which is the isentropic apparent compressibility. Isentropic compressibilities show the extent to which the two primary hydration layers around the solute can be compressed (Parke, Birch, Portman & Kilcast, 1999). Compressibility hydration numbers are derived from isentropic compressibility measurements, and show the number of water molecules that are disturbed by the presence of the solutes in solution. All these parameters take into account the electrostrictive or other attractive forces between solute and solvent, and the effect that these have on the organisation of the molecules in solution.

2. Materials and methods

Ethanol (99.9% reagent grade) was obtained from BDH, Lutterworth, Leicestershire. Water used for solution properties was HPLC grade. All measurements were carried out at 20°C and 37°C. Experiments were duplicated to minimise errors.

Mixtures of ethanol, containing 5–100% ethanol, were made up in water w/w and their density and sound velocity measured. Apparent volumes, isentropic compressibilities and compressibility hydration numbers were then calculated.

2.1. Density and sound velocity

Density and sound velocity values were determined using an Anton Paar Density Sound Analyser (DSA 48) from Paar Scientific Ltd, Raynes Park, London. The density of the sample is measured from the period of oscillation of an oscillating U-tube. The sound velocity is calculated from the propagation speed of ultrasonic pulses in a known distance within the sample in the measuring cell.

Prior to taking measurements, the temperature is set and the instrument allowed to equilibriate for a few hours. Temperature was maintained at 20° or 37° ± 0.1°C. The Density Sound Analyser is then calibrated once using air and freshly boiled distilled water. Density and sound velocity measurements are accurate to $\pm 1\times10^{-4}$ g/cm^3 and ± 1 m/s, respectively.

2.2. Molar volumes

Apparent molar volumes, ϕ_v (cm^3/mol), and apparent specific volumes, V_2 (cm^3/g), of solutes in water, are calculated from density values using Eqs. (1) and (2), respectively.

$$\phi_\text{v} = 1000(d_0 - d)/mdd_0 + M_2/d \tag{1}$$

where d_0 = density of water at one temperature (g/cm^3)
d = density of solution at the same temperature (g/cm^3)
m = molality of the solution (mol/kg of water)
M_2 = molecular weight of solute (g/mol)

$$V_2 = \phi_\text{v}/M_2 \tag{2}$$

Partial molar volume ($V\phi^\text{o}$) and partial specific volume (V_2^0) values are obtained at infinite dilution. Because errors tend to occur at very low concentrations of solute, a linear extrapolation procedure was employed from the points at higher concentrations to zero concentration.

2.3. Isentropic compressibilities

Isentropic apparent molar compressibilities ($K_{\phi(\text{s})}$ cm^3/mol.bar) are calculated from both density and sound velocity values using Eq. (3).

$$K_{\phi(s)} = 1000(\beta_s - \beta_{so})/md + \beta_s\phi_\text{v} \tag{3}$$

where β_s = isentropic compressibility coefficient of solution (bar^{-1})
β_so = isentropic compressibility coefficient of water (bar^{-1})

Isentropic compressibility coefficients are calculated from

$$\beta_s = 100/u^2d \tag{4}$$

where u = sound velocity of solution (m/s)

Isentropic apparent specific compressibilities ($K_{2(\text{s})}$ cm^3/g.bar) are calculated using the equation below.

$$K_{2(s)} = K\phi(s)/M_2 \tag{5}$$

Isentropic partial molar and specific compressibility values ($K_{2(\text{s})}^0$ cm^3/mol.bar and $K_{2(\text{s})}^0$ cm^3/g.bar) are obtained at infinite dilution, by extrapolating the best fit to the curve to zero concentration.

2.4. Compressibility hydration numbers

Compressibility hydration numbers (n_h) are calculated using the following equation:

$$n_h = (n_w/n_s)(1 - \beta_s/\beta_{so}) \quad (6)$$

where n_w = number of moles of water (mol/kg solution)
n_s = number of moles of solute (mol/kg solution).

Partial compressibility hydration numbers (n_h^0) are also obtained by extrapolation of the curve to zero concentration.

3. Results and discussion

The plots of solution properties of ethanol in water at 20 and 37°C are shown Figs. 1–5. Table 1 gives a summary of the solution properties of ethanol at infinite dilution.

3.1. Apparent specific volumes

The curve for the apparent specific volume (V_2) against concentration of ethanol (Fig. 2) shows a minimum at approximately 25% ethanol w/w, a phenomenon also demonstrated by Kappatos et al. (1996) and Franks and Ives (1966). The initial fall in V_2 at lower concentrations is common to hydrophobic solutes. It is best explained using the Frank & Evans (1945) model of the formation of "icebergs" around hydrophobic solute molecules in water. When ethanol molecules are introduced to water, the water molecules around the hydrophobic end of the ethanol undergo a structural rearrangement in such a way that strong water–water hydrogen bonds are formed. It is very likely that such an arrangement may be long range [in analogy to Jeffrey's (1993) polarizability power of hydrogen bonds], so that it can be assumed that the cage-like structures normally encountered in bulk water are stabilised in the process, enabling solutes to pack within the interstitial spaces formed within them. Those icebergs, therefore, have a relatively open structure. At the minimum (25% ethanol) in the V_2 curve, all the available interstitial spaces presumably become saturated with either ethanol or water molecules, so that addition of excess ethanol only increases the apparent volume. Apparent specific volume increases rapidly as ethanol–water interactions are replaced by ethanol–ethanol hydrophobic interactions.

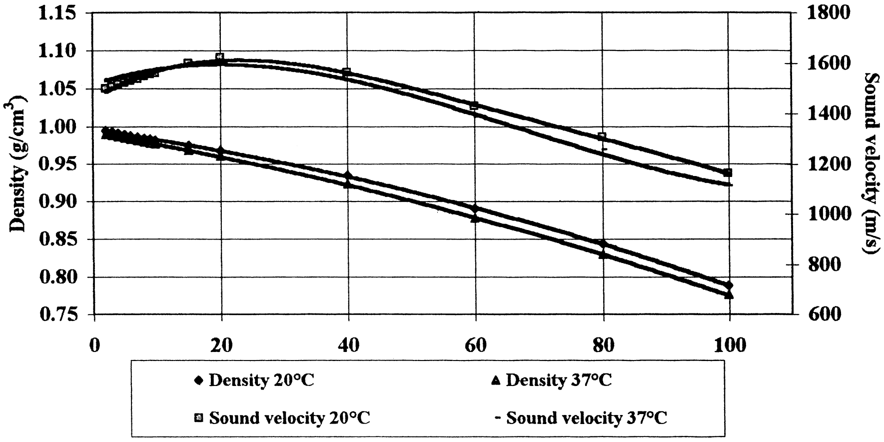

Fig. 1. Plots of density and sound velocity of increasing concentrations of ethanol in water.

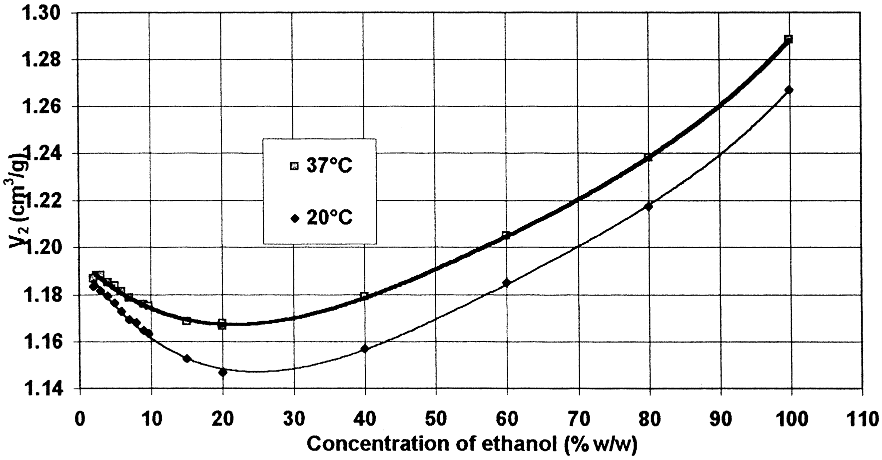

Fig. 2. Apparent specific volume vs concentration of ethanol in water.

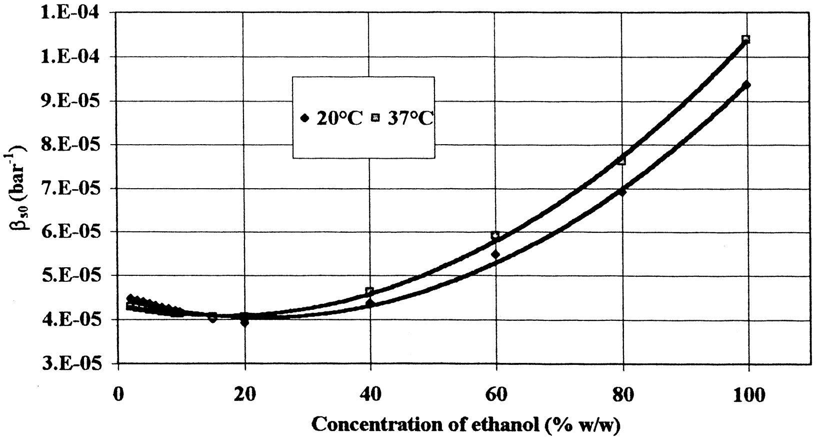

Fig. 3. Plots of isentropic compressibility coefficient of increasing concentrations of ethanol in water.

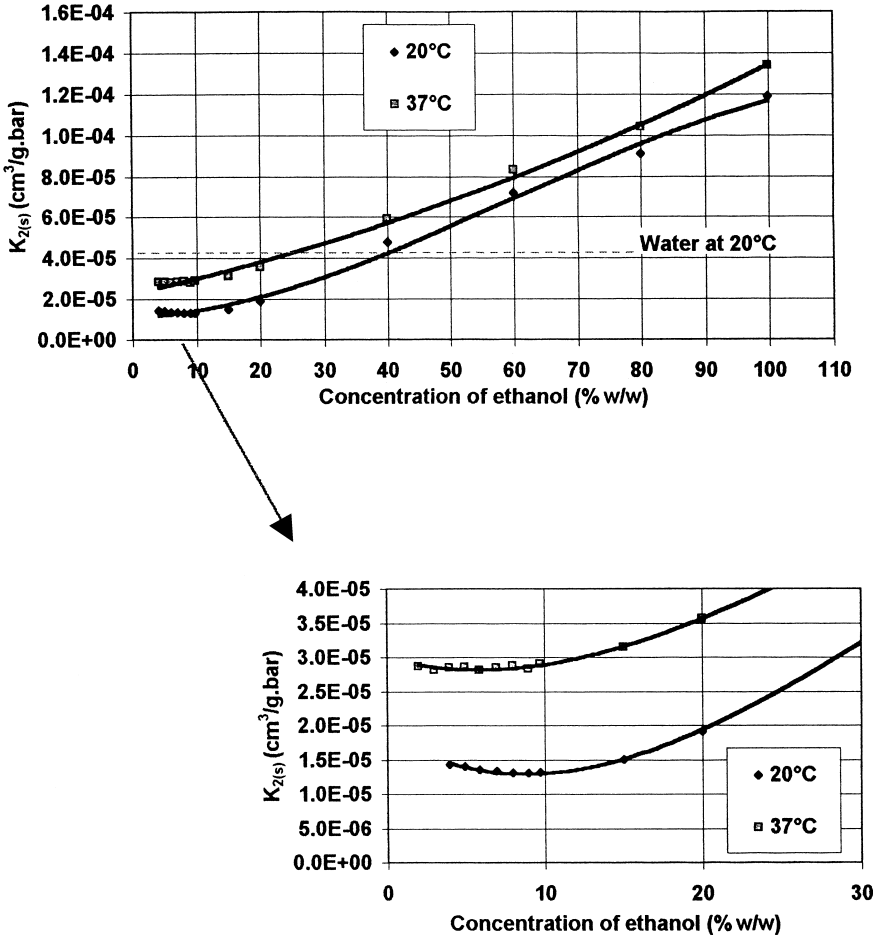

Fig. 4. Isentropic apparent specific compressibility vs concentration of ethanol in water.

Fig. 1 shows an increase in the packing efficiency of the ethanol molecules in water which results in a maximum in the sound velocity curve; this tallies with the idea of hydrophobic packing and iceberg formation. However, at concentrations higher than 25%, ethanol molecules pack less efficiently among water molecules and hence the speed of sound in water falls.

3.2. Isentropic apparent compressibilities

Isentropic compressibility coefficients are calculated from density and sound velocity measurements. The curve of isentropic compressibility coefficient against concentration (Fig. 3) also exhibits a minimum at around 25% ethanol in accordance with the packing propensity

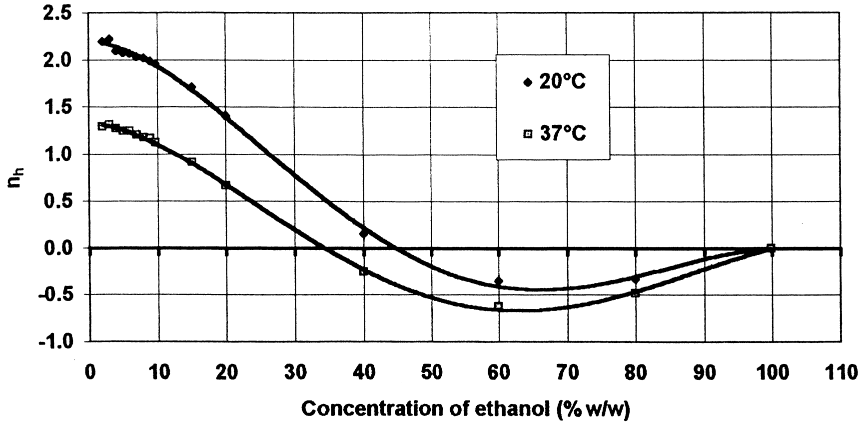

Fig. 5. Compressibility hydration number vs concentration of ethanol in water.

Table 1
Summary of solution properties of ethanol at infinite dilution at 20° and 37°C

	20°C	37°C
Partial molar volume (cm^3/mol)	54.89	55.10
Partial specific volume (cm^{3}g)	1.192	1.194
Isentropic partial molar compressibility (cm^3/mol.bar)	6.769×10^{-4}	1.347×10^{-3}
Isentropic partial specific compressibility (cm^3/g/bar)	1.469×10^{-5}	2.924×10^{-5}
Partial compressibility hydration number	2.23	1.33

of ethanol molecules in water. Compressibility measurements measure the changes in the first two layers of solvent around the ethanol molecule (Parke et al., 1999) and assume that the ethanol itself is incompressible.

In dilute solutions of ethanol, on the other hand, the packing structures are more varied. The solution is predominantly composed of water–water interactions, which form the typical three-dimensional cage-like structures and, which probably embed both monomers of water or ethanol. The collapse of water structure when ethanol molecules are introduced in water is reflected in the specific compressibility values at 20°C, which fall from 4.54×10^{-5} cm^3/g.bar (for pure water) to 1.469×10^{-5} cm^3/g.bar (for ethanol). A more compact hydration layer is formed as strong hydrogen bonds are formed between ethanol and water, which explains the minimum observed (at 12% ethanol) in the curve of isentropic apparent specific compressibility plot against concentration (Fig. 4). Above this concentration, presumably all energy of the system is concentrated on fitting the ethanol molecules into the cavities formed by the water structure around them rather than increased ethanol–water interactions. The hydration layer around the ethanol is, therefore, not greatly affected. At concentrations above 12% ethanol, compressibility starts to rise. The cage-like structure of water is increasingly disturbed by the introduction of more ethanol molecules to the solution. Presumably these same arguments apply to other alcohols, such as ethylene glycol and propylene glycol, used in antifreeze and food applications, as they exhibit similar minima in their solution parameter-concentration curves (Chavez Lopez & Birch, 1997).

At 42% w/w ethanol in water (at 20°C), the isentropic apparent specific compressibility of ethanol equals that of pure water (4.54×10^{-5} cm^3/g.bar at 20°C) (refer to Fig. 4). This shows that at that particular concentration, the hydration layer around the ethanol molecules possesses a similar packing arrangement as that in pure water, whereas at higher concentrations ethanol has a more open structure than water, so that its compressibility becomes higher than that of water. At very high concentrations of ethanol in solution, linear chains or rings of ethanol molecules have been proposed to exist (Arnett, Bentrude, Burke & Duggleby, 1965; Franks & Ives, 1966), the packing of which is likely to contribute to the large volume of the solution. As ethanol–ethanol interactions replace ethanol–water interactions, there is a weakening of ethanol–water hydrogen-bonds which could be used to explain the increase in compressibility of the hydration layer.

3.3. Compressibility hydration numbers

The equation used for calculating compressibility hydration numbers assumes that the hydration layer around the ethanol molecule is incompressible, which is not the case; However, it provides an approximate overall picture of the extent of interaction of the ethanol with water. Compressibility hydration numbers are derived from isentropic compressibility coefficient measurements and therefore, account for the first two layers of water around the solute (Parke et al., in press); The numbers obtained cannot be compared with those from literature which account for only one layer of hydration water.

Falling compressibility hydration numbers (Fig. 5) indicate that fewer water molecules are displaced by increasing ethanol concentration in solution. At the concentration (42% ethanol at 20°C) where the compressibility of ethanol equals that of water, hydration number is close zero. At higher concentrations of ethanol, negative hydration numbers reflect strong ethanol–ethanol interactions and less water–ethanol interactions. This effect has been ascribed to water-solute hydrogen bond lifetimes being shorter than water-water hydrogen bond lifetimes (Mathlouthi, Bressan, Portmann & Serghat, 1993)

3.4. *Effect of temperature on solution properties*

When the temperature is increased from 20° to 37°C, there is a corresponding rise in the specific volumes and isentropic compressibilities as would be expected from the thermal expansion of the solutes in solution, and therefore a decrease in entropy of the system. At the higher temperatures, hydration numbers are lower, in accordance with an increased rate of exchange of water from the hydration layer to the surroundings.

4. Conclusion

Ethanol shows very unusual packing characteristics in water. The maxima and minima observed in its curves of solution parameters against concentration of ethanol show different packing mechanisms as the concentration is changed. At low concentrations, ethanol–water interactions are influenced by the formation of cage-like structures, commonly known as "icebergs", formed around the hydrophobic ends of the ethanol. At higher concentrations, the formation of chains or rings of ethanol dictates packing characteristics. An understanding of the solution behaviour of aqueous ethanol at different concentrations will help illuminate its mechanism of action in various applications.

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