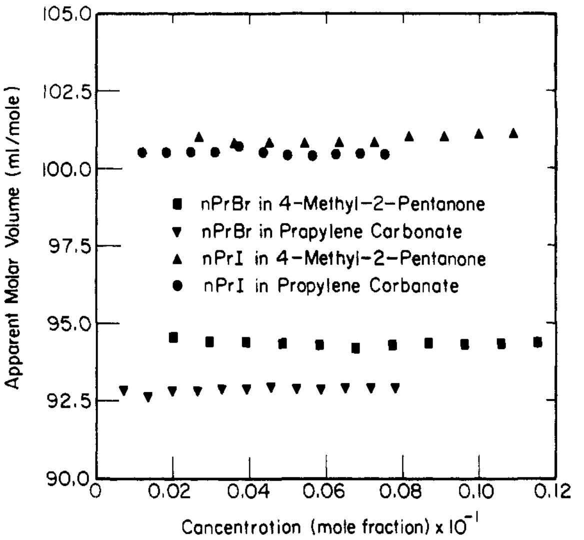

Figure 4. Apparent molar volume of nonionic solutes as a function of concentration at 25 °C.

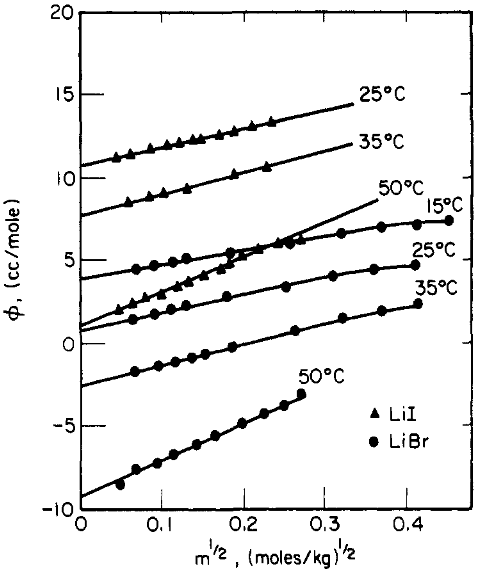

Figure 5. Apparent molar volume of some ionic solutes as a function of concentration.

futable. The nonionic solutes used in the study do not grossly change the structure of the solvents and the ionic solute can.

Substantial contractions (i.e., volumes smaller than ideal) are seen for ionic solutes in the low dielectric constant solvents. Generally contractions on mixing in dilute solutions are associated with an increase in solvent structure due to interactions with the solute (*13*, *14*). For the low dielectric constant solvents and ionic solutes, the solute-solvent interaction is much more energetic and much more long-ranged than the solvent-solvent interactions. Ionic solutes cause striking contractions of these solvents. For many salts negative partial molar volumes are observed; that is, the volume after mixing is smaller than the volume of the solvent alone before mixing. The solvent structure is grossly altered with the addition of ions.

The structure of the more polar solvents are much less affected by the addition of ions. This does not necessarily mean that the solute-solvent interactions are less energetic than in less polar solvents. In fact, one would expect that the energetics of these interactions would be larger for the more polar solvents (*15*). The solute-solvent and solvent-solvent interactions must be similar for the more polar solvents. Therefore, the structure of the more polar solvents is much more highly developed than it is for the less polar solvents.

Partial molar volumes in dilute solutions offer a unique opportunity to probe the solvent structure with macroscopic observations. The volume of a solution is related to the solvent packing geometry and the solvent polarity. This type of information is crucial in forming a mental picture of the structure of ionic solutions in nonaqueous media. The value of this information is magnified when one realizes that the solvent effect on ionic partial molar volumes is paralleled by a solvent effect on ionic activities. The ability to adjust ionic activities by choosing a solvent has ramifications in the rates and equilibrium properties of many industrial processes and reactions. Therefore, understanding and controlling these factors is very desirable.

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Density of 2-Butoxyethanol from 20 to 60 °C

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The density of purified samples of 2-butoxyethanol has been measured from 20 to 60 °C by densimetry and pycnometry. The results are well described by $d/(\mathrm{g\ cm^{-3}}) = 0.91694 - (8.149 \times 10^{-4})(t/{}^\circ\mathrm{C}) - (5.1 \times 10^{-7})(t/{}^\circ\mathrm{C})^2$ with a standard deviation of 3×10^{-5} g cm^{-3}.

During an investigation of the physical properties of its aqueous mixtures (*1*) we have measured the density of 2-butoxyethanol at 11 temperatures from 20 to 60 °C. The starting material was supplied by Cambrian Chemicals Ltd. with a quoted purity of 99 mol %. It was further purified by four fractionations in a stream of nitrogen in a 70-cm glass column

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Table I. Densities d of 2-Butoxyethanol at Different Temperatures t

	$d/(\mathrm{g\ cm^{-3}})$			
t/°C	densimeter	eq 1	pycnometer	lit.
20.00		0.9004	0.9005	0.900 75[a]
27.00		0.8946		0.894 60[b]
29.99	0.892 07	0.8920		
30.00		0.8920	0.8920	0.892 36[a]
40.00		0.8835	0.8835	0.883 89[a]
40.01	0.883 51	0.8835		
44.98	0.879 30	0.8793		
45.00		0.8792	0.8792	
49.99	0.874 92	0.8749		
50.00		0.8749	0.8750	
54.00		0.8715	0.8715	
60.00		0.8662	0.8662	0.866 59[a]

[a] Reference *7*. [b] Reference *5*.

packed with Raschig rings. The organic impurity level, as estimated by gas–liquid chromatography using an FFAP column and flame ionization detection, was less than 0.03 mol %; the major contaminants were 1-butanol and 1,2-ethanediol. The water impurity level, as estimated by gas–liquid chromatography using a Polypak column and thermal conductivity detection, was less than 0.02 mol %. The refractive index n^{20}_{D} was found to be 1.419 81 ± 0.000 05, in excellent agreement with the value 1.4198 quoted in ref *2* but slightly higher than the values reported for two different samples by Schneider and Wilhelm, 1.4194 and 1.4196 (*3*).

Two sets of density measurements were carried out. For the first set an Anton Paar 02C densimeter was used. It was calibrated by using water and air. The water was distilled, passed through an ion-exchange column, and degassed by vigorous boiling; its density was taken from the work of Kell (*4*). The density of air was obtained from tables (*2*), its temperature, pressure, and relative humidity being known. The temperature was measured to ±35 mK by using a thermistor calibrated against a platinum resistance thermometer bearing a certification from the British Calibration Service. Scatchard and Wilson (*5*) found that air-saturated 2-butoxyethanol has a rather higher density than the degassed liquid and thus our samples were boiled vigorously before measurement to expel dissolved gas. Our results therefore correspond to essentially 1-atm pressure. Column 2 of Table I contains the results of this set of measurements; we estimate their precision to be ±0.000 03 g cm^{-3}. The second set of measurements was made by using a Pyrex pycnometer having a bulb of about 6.5-cm^3 capacity and a capillary of bore 1.500$_4$ mm; it was calibrated by using mercury whose density was taken from ref *6*. The temperature was determined to ±3 mK by using the platinum resistance thermometer mentioned above. The liquid was sealed under its own vapor pressure by a grease-free stopcock sealed to the top of the capillary. Our densities from this set of measurements are thus orthobaric. They are listed in column 4 of Table I; we estimate their precision to be ±0.0001 g cm^{-3}. Although the results of the two series of determinations refer to slightly different pressures, they are equally well described by

$$d/(\mathrm{g\ cm^{-3}}) = 0.91694 - (8.149 \times 10^{-4})(t/{}^{\circ}\mathrm{C}) - (5.1 \times 10^{-7})(t/{}^{\circ}\mathrm{C})^2$$

$$\sigma = 3 \times 10^{-5}\ \mathrm{g\ cm^{-3}} \qquad (1)$$

where d is the density at temperature t. Values calculated from eq 1 are listed in column 3 of Table I. The good agreement with the experimental values demonstrates the concordance of both data sets. Column 5 contains literature data. The single value at 27 °C reported by Scatchard and Wilson is in excellent agreement with our value interpolated by using eq 1; these authors used essentially the same purification procedure as we used. The four values of Onken (*7*) are in poor agreement with our values. This discrepancy in d and the previously mentioned discrepancy in n^{20}_{D} are consistent with the presence of a small amount of water contamination in his samples. The effect of this would be to lower the refractive index and raise the density in the way observed.

Glossary

d	density, g cm^{-3}
t	temperature, °C
σ	standard deviation

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Limiting Activity Coefficients of Nonpolar and Polar Solutes in both Volatile and Nonvolatile Solvents by Gas Chromatography

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Limiting activity coefficients were measured for 35 solutes in 34 different solvents by gas chromatography. The data cover industrially important compounds with wide ranges of polarity, polarizability, and degree of association. Both volatile and nonvolatile solvents were studied. The data compare well with those determined from ebulliometry, those extrapolated from classical vapor–liquid equilibrium (VLE) studies, and those of other researchers using similar techniques.

Introduction

Infinite-dilution activity coefficients (γ^{∞}) have found numerous applications in characterizing solution behavior. They can be used to generate accurate binary parameters for several solution models (*1*–*3*), to predict the existence of an azeotrope (*4*), and to estimate mutual solubilities. In addition they can be used to calculate kinetic solvent effects with the Bronsted–Bjerrum relationship (*5*) as well as to provide incisive information for the statistical thermodynamicist in the absence of so-

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