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Ostwald Concentration Coefficients of Acetonitrile in Aqueous Mixed Solvents: A New, Rapid Method for Measuring the Solubilities of Volatile Solutes

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The Ostwald concentration coefficients of acetonitrile in aqueous methanol, propan-1-ol, 2-methylpropan-2-ol (*tert*-butyl alcohol), 1,4-dioxane, and dimethyl sulfoxide have been measured by determining the acetonitrile concentrations in the liquid and vapor phases by gas chromatography. The method described is self-calibrating and allows the rapid determination of gas solubilities. It is found that the acetonitrile solubility varies nonlinearly, and nonmonotonically, in the mixed solvents, passing through maxima in the aqueous alcohol and 1,4-dioxane systems and showing a shallow minimum in the aqueous dimethyl sulfoxide mixtures.

Introduction

The effect of changes in solvent on the thermodynamics of solvation is one of the classic problems of physical chemistry. In general, enthalpies of solution can be measured directly using a suitable calorimeter. In the case of electrolytes, the Gibbs energies of solution can be determined simply from the standard emf's of electrochemical cells or from the solubilities of the solid electrolyte in the solvent of interest. In contrast, the measurement of the Gibbs energies of solution of liquid nonelectrolytes is more difficult. Typically, there are no suitable electrochemical cells and, for liquid solutes at least, the solutes are likely to be completely miscible with the solvent of interest. In these cases, the most direct route to the Gibbs energy of solution is through the liquid/vapor equilibrium. Two types of measurements can be undertaken: that of the Henry's law constant, where the pressure of the solute above a solution of known concentration is measured, or that of the Ostwald coefficient, where the amounts of solute present in the liquid and vapor phases are determined.

In the present work, we report Ostwald coefficients,[1] as Ostwald concentration coefficients, L_c, for acetonitrile in aqueous mixtures of dimethyl sulfoxide, DMSO, 1,4-dioxane, methanol, propan-1-ol, and 2-methylpropan-2-ol (*tert*-butyl alcohol, TBA). The measurements were carried out using direct determination of the concentrations of acetonitrile in the solution and vapor phases by gas/liquid chromatography. The method has the advantages of being rapid and of not requiring thorough outgassing of the solutions.

Experimental and Results

Acetonitrile,[2] dimethyl sulfoxide,[3] 1,4-dioxane,[4] methanol, propan-1-ol,[5] and 2-methylpropan-2-ol[6] (*tert*-butyl alcohol, TBA) were purified as described previously. Distilled water was used throughout. All solutions were prepared by mass with a precision of at least 0.1%.

Battino[1] has discussed the Ostwald coefficient and shown that it is equivalent to the ratio of the concentrations of the solute in the liquid and vapor phases, which was termed the Ostwald concentration coefficient, L_c, defined by

$$L_c = \frac{c_{\text{soln}}}{c_{\text{vap}}} \tag{1}$$

where c_{soln} and c_{vap} represent the solution and vapor phase concentrations of the solute, acetonitrile in this case, expressed in the same units. The L_c values of acetonitrile were measured at different solute concentrations and extrapolated to infinite dilution in the solution phase. Thus, they are reported as L_c^∞, the limiting value of L_c. In practice, the L_c values were relatively insensitive to the acetonitrile concentration over the concentration range used (typically 0.1 to 1.0 mol dm^{-3}). Measurements were carried out over a range of pressures, from the vapor pressure of the solution up to 1 atm (air or N_2), and within the experimental precision, L_c^∞ was independent of pressure.

The L_c values were determined by the direct measurement of the concentrations of acetonitrile in the solution and vapor phases by gas/liquid chromatography using a packed column and FID detection. Vapor samples were taken using a sample loop of known volume, and liquid samples were handled using syringes. Since the chromatographic peak area is directly proportional to the amount of acetonitrile present in the sample, L_c can be simply calculated as

$$L_c = \frac{c_{\text{soln}}}{c_{\text{vap}}} = \frac{A_{\text{soln}}/V_{\text{soln}}}{A_{\text{vap}}/V_{\text{vap}}} \tag{2}$$

where A and V represent the peak area and injection volumes, respectively. Measurement of the values for both the solution and vapor phases reduces any effects of variation in the sensitivity of the detection system, making it, in effect, self-calibrating.

The experimental setup comprised a 1 dm^3 flask with a side arm to allow introduction of solutions and, if necessary, extraction of liquid samples. The flask was also connected to a vacuum line. The flask was modified to include a 4

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Table 1. Ostwald Concentration Coefficients for Acetonitrile in Water (1) + Organic (2) Mixed Solvents at 298.2 K[a]

	$L_c^\infty/10^3$				
x_2	DMSO	1,4-dioxane	methanol	propan-1-ol	TBA
0.00	1.21	1.21	1.21	1.21	1.21
0.05	1.08	2.37	1.75	1.22	1.15
0.10	0.95	2.84	2.42	1.22	1.01
0.20	0.91	3.21	4.05	1.43	0.99
0.30	1.09	3.53	5.32	1.66	1.03
0.40	1.23	3.50	5.47	1.79	0.93
0.50	1.38	3.39	5.43	1.64	0.74
0.60	1.77	3.21	5.03	1.45	0.61
0.70	2.16	3.14	5.21	1.28	0.51
0.80	2.25	3.11	4.98	1.16	0.42
0.90	2.29	3.02	5.05	0.87	0.41
1.00	2.33	2.85	5.10	0.82	0.40

[a] x_2 represents the mole fraction of the organic component; DMSO and TBA represent dimethyl sulfoxide and *tert*-butyl alcohol, respectively; precisions are ±5% or better.

mm tube projecting into the vapor space; this was connected to the sample loop via a three-way tap. This connected the sample loop to the vacuum line, the sampling tube, or the gas chromatograph. Thus, the loop was evacuated and then filled with the vapor sample; finally the sample was injected onto the gas chromatograph in the carrier gas flow. The flask was immersed in a thermostat, and measurements were made at 298.2 ± 0.2 K. Since the cosolvents are in large excess, it is necessary to have good separation of the solute peak, and a variety of column packings and temperatures were used. In principle, the FID is insensitive to water vapor; however, it was found that some quenching of the signal resulted with injections of highly aqueous liquid samples. This was overcome by adding an auxiliary heater to the detection system.

This method has several advantages for the measurement of gas solubilities. Thus, while it is undoubtedly less precise than the most accurate methods available,[7−9] it allows the rapid accumulation of data, of reasonable precision, with a minimum of sample manipulation. It also avoids the difficulties associated with outgassing samples and with direct pressure measurements. In practice, L_c values were reproducible to around 5%. This represents the accumulation of errors in the sample volumes and in the determination of the peak areas. Of these, the volume of the vapor sample is undoubtedly the most reproducible.

The L_c^∞ values for acetonitrile in the different solvent systems studied are listed in Table 1 and are shown as a function of solvent composition in Figure 1.

Discussion

The present paper serves to describe the experimental technique and to present the measured Ostwald coefficients, and we will reserve detailed discussion of the data to a later paper.

Two features of the acetonitrile solubilities, shown in Figure 1, are noteworthy. First, it is clear that there are very marked differences in the solubilities in the pure solvents, with acetonitrile being substantially more soluble in methanol, 1,4-dioxane, and dimethyl sulfoxide than in water, 1-propanol, and *tert*-butyl alcohol. The reasons for these variations in solubility are not immediately clear. Among the alcohols, the L_c^∞ decreases with increasing molar volume of the alcohol, so that it may simply reflect variations in the available free volume on the solvents, but other factors such as the interaction energies between acetonitrile and the alcohols may also be significant.

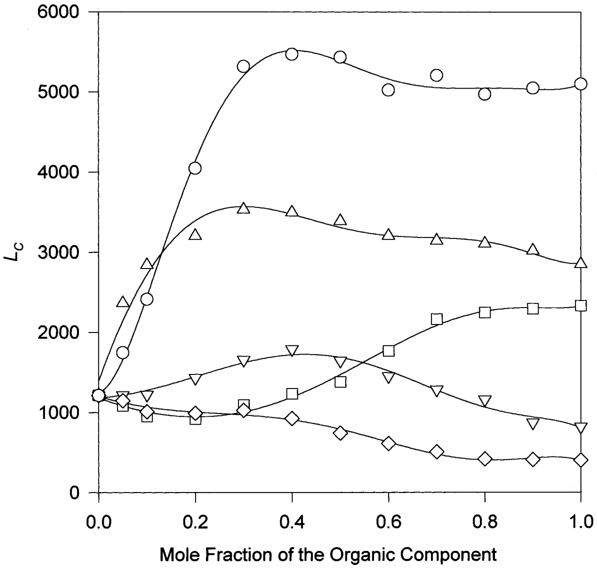

Figure 1. Ostwald concentration coefficients, L_c^∞, of acetonitrile in aqueous methanol (○), propan-1-ol (▽), TBA (◇), 1,4-dioxane (△), and DMSO (□) at 298.2 K.

The second point of interest is that the solubilities vary nonlinearly with solvent composition. In the aqueous methanol and 1,4-dioxane systems, there is a rapid increase in L_c^∞ with the addition of the organic component and then a leveling off or even a slight decrease in solubility at higher organic concentrations. For higher alcohols, the curves are qualitatively similar in shape but the magnitudes of the changes are much less, reflecting the much smaller change in L_c^∞ in these systems. In contrast, L_c^∞ varies only slightly at low DMSO concentrations and then increases above a DMSO mole fraction of around 0.3, before reaching a plateau at higher DMSO concentrations. Interestingly, the minimum in the excess enthalpy of the aqueous DMSO mixtures occurs at close to a DMSO mole fraction of 0.33, where the ratio of DMSO to water OH protons is 1:1. The addition of the alcohols to water leads, of necessity, to the development of a solvent that is less structured than water, and this is likely to be the cause of the initial increase in L_c^∞ with the addition of alcohol. The same may be true for 1,4-dioxane, which is not expected to hydrogen bond strongly to water. In contrast, the addition of DMSO clearly leads to a differently structured solvent system, with strong water−DMSO hydrogen bonding at low DMSO concentrations and a less structured solvent when there are excess DMSO molecules. This excess of DMSO over the water OH protons, of course, occurs at a DMSO mole fraction of 0.33.

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