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Publisher *Taylor & Francis*

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## Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

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Online publication date: 20 December 2000

**To cite this Article** Scott, R. P. W.(2000) 'THE THERMODYNAMIC PROPERTIES OF TETRAHYDROFURAN-WATER ASSOCIATION AND ITS INFLUENCE ON RETENTION IN LIQUID CHROMATOGRAPHY', *Journal of Liquid Chromatography & Related Technologies*, 23: 20, 3083 – 3093

**To link to this Article:** DOI: 10.1081/JLC-100102369

**URL:** <http://dx.doi.org/10.1081/JLC-100102369>

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# THE THERMODYNAMIC PROPERTIES OF Tetrahydrofuran-Water Association AND ITS INFLUENCE ON RETENTION IN LIQUID CHROMATOGRAPHY

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## ABSTRACT

Employing density data reported for a range of tetrahydrofuran-water mixtures, measured at different temperatures, the tetrahydrofuran-water association constant was calculated at each temperature, employing previously established procedures. The standard free enthalpy and entropy of association were then determined from the linear relationship that exists between the logarithm of the association constant and the reciprocal of the absolute temperature. It is shown that the standard free enthalpy is very high for simple association, viz., 1.642 Kcal/mol, and the standard free entropy of distribution was 3.00 cal/mol. These values indicate strong association and the relative low standard free entropy shows a comparatively small change in molecular freedom after association. *This suggests that the solvents are also probably strongly associated with themselves when not associating with each other.*

Using the thermodynamic parameters and molar volumes derived from the calculation, the volume fractions of unassociated

methanol, unassociated water and methanol-water associate were calculated for a range of initial methanol/water mixtures at different temperatures. The association decreased fairly rapidly with increased temperature, as would be expected. At 60°C the association constant was reduced to about half that at 25°C

## INTRODUCTION

The relationship between water concentration, tetrahydrofuran (THF), and the tetrahydrofuran-water associate has been described elsewhere<sup>1-3</sup> but, as it is central to the following calculations, it will be briefly reiterated here. The equilibrium constant for the association of water with tetrahydrofuran can be described by the following equation:

$$\frac{[W][T]}{[TW]} = K \quad (1)$$

where [W] is the molar concentration of water, [T] is the molar concentration of THF, and [TW] the molar concentration of the THF-water associate.

Assuming the original tetrahydrofuran/water mixture was made up (before mixing) with a volume fraction ( $\alpha$ ) of THF, there will be a volume fraction ( $1-\alpha$ ) of water. Then, the original molar concentration of tetrahydrofuran and water will be  $\left(\frac{\alpha}{V_T}\right)$  and  $\left(\frac{1-\alpha}{V_w}\right)$ , respectively, where ( $V_T$ ) and ( $V_w$ ) are the molar volumes of tetrahydrofuran and water, respectively. Consequently, after mixing and association has taken place to form the associate (TW),

$$[T] + [TW] = \frac{\alpha}{V_M} \quad (2)$$

$$[W] + [TW] = \frac{(1-\alpha)}{V_w} \quad (3)$$

Now equations (1), (2), and (3) are three simultaneous equations and, so, solving for [W] in the usual way

$$[W] = \frac{(-b + (b^2 + 4c)^{0.5})}{2} \quad (4)$$

$$\text{where } b = K + \frac{\alpha}{V_T} + \frac{\alpha}{V_w} \text{ and } c = K \left( \frac{1}{V_w} - \frac{\alpha}{V_w} \right).$$

Furthermore, having calculated [W] by carrying out a molar balance, it is clear that

$$[\text{TW}] = \left( \frac{(1-\alpha)}{V_w} \right) - [\text{W}] \quad (5)$$

$$\text{and } [\text{T}] = \frac{\alpha}{V_M} - [\text{TW}] \quad (6)$$

Thus, the new volume, after mixing, will be the number of moles of each component multiplied by its molar volume and, consequently, the volume after mixing will be

$$v_i = [\text{W}]V_w + [\text{T}]V_T + [\text{TW}]V_{\text{TW}} \quad (7)$$

where ( $V_{\text{TW}}$ ) is the molar volume of the methanol-water associate.

Similarly, the weight of the mixture will be the product of the number of mols of each component and its molecular weight

$$w_i = [\text{W}]M_w + [\text{T}]M_T + [\text{TW}]M_{\text{TW}} \quad (8)$$

where ( $M_w$ ), ( $M_T$ ), and ( $M_{\text{TW}}$ ) are the molecular weights of water, methanol, and the methanol-water associate, respectively.

Thus, the density of the mixture (d<sub>i</sub>) will be given by

$$d_i = \frac{w_i}{v_i} \quad (9)$$

It follows that, if density data was available for a series of THF-water mixtures, then both the equilibrium constant and the molar volume of the associate could be identified. This could be carried out iteratively by assuming values for the equilibrium constant, (K), and the molar volume of the associate ( $V_{\text{TW}}$ ) calculating the density of the mixture employing equations (1)-(9) and comparing the results with the data experimentally obtained. The correct values of equi-

librium constant and molar volume of the associate would be those that provide the minimum for the sum of variances of the error between the experimental data and the calculated data.

In addition, if density data was available for a range of THF-water mixtures, taken over a span of temperatures, then the standard free enthalpy and standard free entropy of association could be determined from the slope and intercept of the curve relating equilibrium constant to the reciprocal of the absolute temperature. Consequently, the relative volume fractions of tetrahydrofuran, water, and tetrahydrofuran-water associate could be calculated for any practical operating temperature. Such data could be used to optimize chromatographic separations when using tetrahydrofuran-water mixtures as the mobile phase to provide minimum analysis time and the required resolution.

### EXPERIMENTAL DATA

Suitable density data, taken over a range of temperatures, was determined by Gutierrez<sup>4</sup> as part of a Ph.D. thesis at Georgetown University, Washington, DC. The results that were obtained and taken from his thesis are shown in Table 1.

The density  $\rho$  values were plotted against volume fraction of THF and the results are shown in Figure 1.

It is seen that there is considerable scatter between the points, so to increase the precision of the equilibrium constant measurement, the experimental values were curve fitted to a third-order polynomial expression, which is included in Figure 1. This expression was used to provide more accurate experimental values in the computer program to compare with those calculated theoretically. This procedure was carried out for the experimental data obtained at each temperature. Thus, as already stated, by assuming values for the equilibrium constant and molar volume of the associate and using equations (1) to (9), the density of each mixture was calculated and compared with the smoothed data obtained from the results given in Table 1. The correct values of the equilibrium constant and molar volume of the associate were taken as those that provided the minimum error between the experimental data and the calculated data. The results obtained from these iterative calculations for the equilibrium constant and the molar volume of the associate are given in Table 2.

The logarithm of the equilibrium constant was plotted against the reciprocal of the absolute temperature, which produced the linear curve shown in Figure 2 having an index of determination of 0.985. The slope and intercept are proportional to the standard free enthalpy and standard free entropy of association, i.e.,

**Table 1****Density of Tetrahydrofuran-Water Mixtures Taken at Four Temperatures (Ref. 4)**

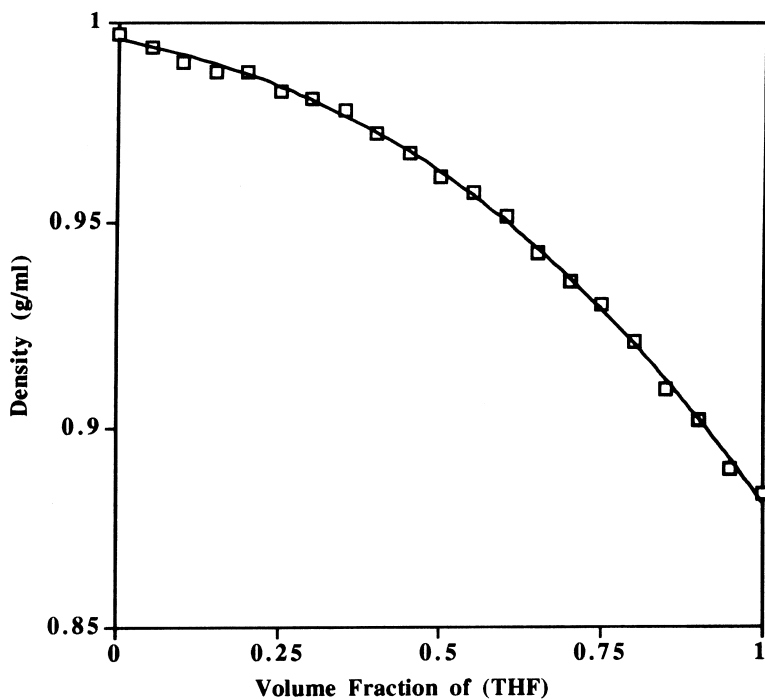
Volume Fraction of THF	Density			
	25°C	35°C	45°C	55°C
0.00	0.9971	0.9941	0.9902	0.9857
0.05	0.9934	0.9900	0.9866	0.9832
0.10	0.9897	0.9859	0.9821	0.9783
0.15	0.9870	0.9827	0.9785	0.9744
0.20	0.9872	0.9826	0.9780	0.9734
0.25	0.9824	0.9774	0.9724	0.9675
0.30	0.9806	0.9752	0.9698	0.9645
0.35	0.9778	0.9720	0.9663	0.9605
0.40	0.9720	0.9659	0.9597	0.9536
0.45	0.9672	0.9607	0.9542	0.9477
0.50	0.9614	0.9545	0.9476	0.9408
0.55	0.9575	0.9503	0.9431	0.9359
0.60	0.9517	0.9441	0.9365	0.9290
0.65	0.9430	0.9351	0.9272	0.9194
0.70	0.9362	0.9280	0.9198	0.9116
0.75	0.9304	0.9218	0.9133	0.9049
0.80	0.9209	0.9120	0.9032	0.8944
0.85	0.9096	0.9004	0.8913	0.8823
0.90	0.9020	0.8925	0.8832	0.8739
0.95	0.8900	0.8803	0.8707	0.8612
1.00	0.8834	0.8734	0.8635	0.8537

$$\text{Log}(K) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} = \frac{-826.39}{T} + 1.512 \quad (10)$$

$$\text{Thus, } \frac{-\Delta H}{R} = 826.39 \text{ or } \Delta H = 826.39R,$$

$$\text{and } \frac{\Delta S}{R} = 1.512 \text{ or } \Delta S = 1.512R.$$

Taking a value of R of 1.987 Kcal/°/mol, the standard free enthalpy and standard free entropy of distribution are 1642 cal/mol and 3.00 cal/°/mol, respectively. Bearing in mind that, in the pure state, water is strongly associ-



$$y = -0.029419x^3 - 0.051987x^2 - 0.032826x + 0.995255$$

$$r = 0.999303$$

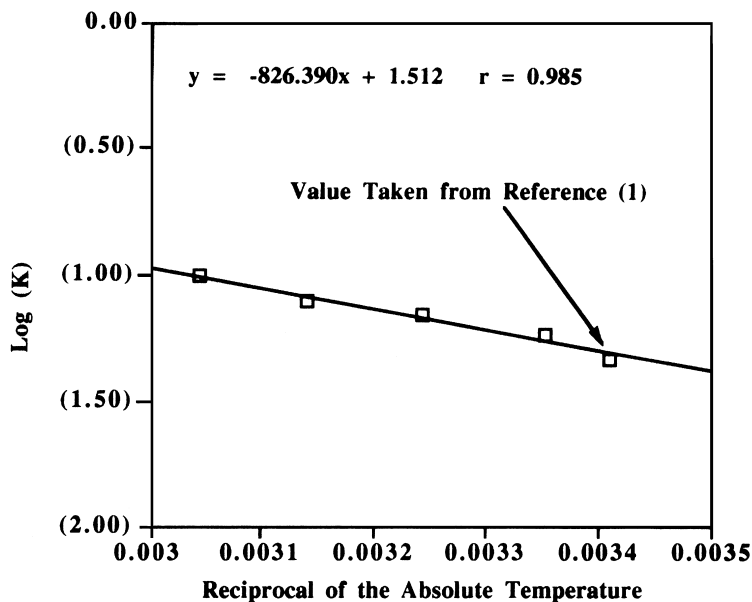
**Figure 1.** Graph of density of water/THF mixtures against volume fraction of THF before mixing.

**Table 2**

**Data Generated by the Iteration Program to Determine the Equilibrium Constant of Tetrahydrofuran-Water Association and the Molar Volume of the Associate**

Temp. (°C)	Reciprocal of Equilibrium Absolute Temp.	Equilibrium Constant	Log Equil. Constant	Molar Vol. of Associate
20*	0.003408	0.0468	-1.3298	88.89
25	0.003351	0.0591	-1.2284	86.50
35	0.003243	0.0695	-1.1580	85.83
45	0.003141	0.0792	-1.1013	85.14
55	0.003045	0.0999	-1.0004	82.58

\* All data for 20°C from ref. (1).



**Figure 2.** Graph of log. equilibrium constant against the reciprocal of the absolute temperature.

ated with water and THF is also probably strongly associated with itself, it would appear that the energy involved in the association of water with THF is much greater than either. This would mean, from the point of view of chromatography, that the interactive potential of both the THF and the water with any dissolved solute is reduced by removing a significant proportion of both, in the formation of the strongly bound and, consequently, less interactive associate. The net effect is to reduce the overall eluting capacity of the solvent. It is also interesting to note that the standard free entropy of association is relatively small, indicating that the molecules are probably equally restrained when associated with themselves, as when they are associated with each other, i.e., their random character changes on association are not great.

Values for ( $V_{MW}$ ), the molar volume of the associate, were calculated simultaneously with the equilibrium constants ( $K$ ) at each temperature and the values obtained plotted against the temperature ( $t$ ), in  $^{\circ}\text{C}$ , are shown in Figure 3.

Again, it is seen that, as the density of the associate suffers a relatively small change over the temperature range examined, the change in the molar vol-



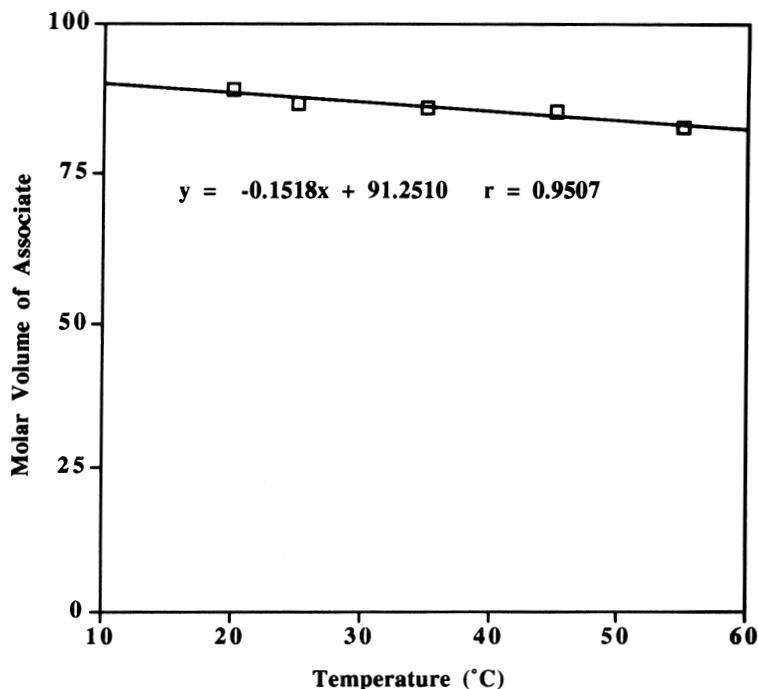


Figure 3. Graph of molar volume of THF/water associate against temperature.

ume with temperature is also relatively small. The curve in Figure 3 gives an expression for ( $V_{MW}$ ) which can be used in calculating the relative distribution of the components of the solvent mixture at any temperature, viz., i.e.,

$$V_{MW} = 91.251 - 0.1518t \quad (11)$$

where ( $t$ ) is the temperature in ( $^{\circ}\text{C}$ ).

This expression, together with the equation for ( $K$ ), will allow the volume fractions of methanol, water, and methanol-water associate to be calculated for any known solvent mixture (expressed in volume fractions before mixing) and at any experimentally practical temperature. The relative volume fractions of unassociated THF, unassociated water, and the THF-water associate at  $25^{\circ}\text{C}$  are given in Table 3.

Table 3

**Volume Fractions of Methanol, Water, and Methanol-Water Associate for Different Initial Methanol-Water Mixtures at 20°C**

<b>Vol Fraction of THF Before Mixing</b>	<b>Volume Fraction of THF</b>	<b>Volume Fraction of Water</b>	<b>Volume Fraction of THF- Water Assoc.</b>
0	0.0000	1.0000	0.0000
0.1	0.0063	0.8655	0.1282
0.2	0.0151	0.7295	0.2554
0.3	0.0278	0.5928	0.3794
0.4	0.0475	0.4567	0.4958
0.5	0.0809	0.3241	0.5951
0.6	0.1432	0.2022	0.6547
0.7	0.2642	0.1053	0.6305
0.8	0.4654	0.0459	0.4886
0.9	0.7223	0.0156	0.2621
1.0	1.0000	0.0000	0.0000

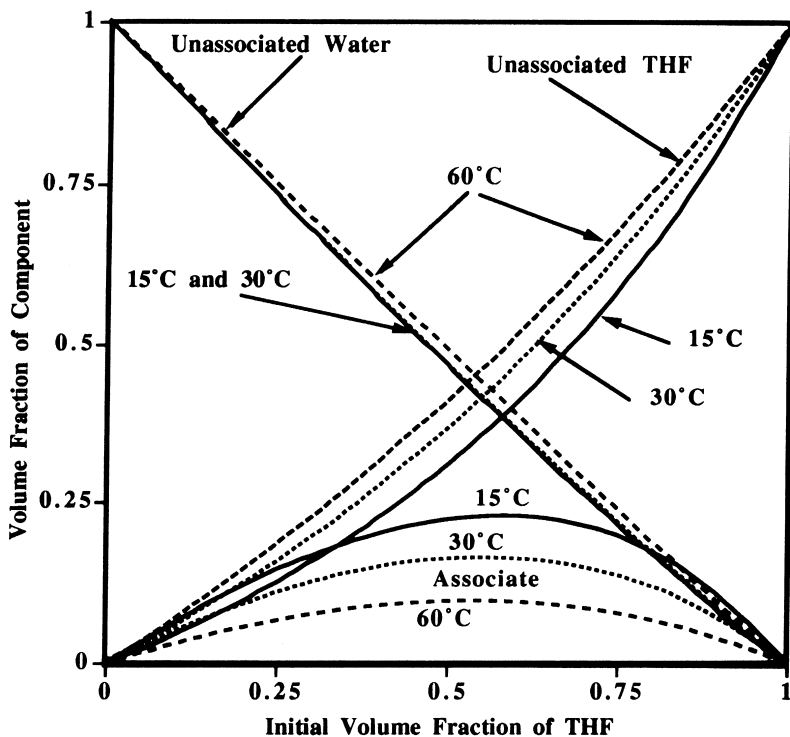
### CALCULATIONS AND DISCUSSION OF RESULTS

Employing equations (10) and (11) to calculate the equilibrium constant and molar volume of the associate at different temperatures, the volume fraction of each associate was calculated for a range of initial volume fractions of THF before mixing, using equations (9)-(11). In this way, curves relating volume fraction of each component against initial volume fraction of methanol before mixing could be obtained for temperatures of 5°C, 30°C, and 60°C, respectively. The results obtained are shown in Figure 4.

The curves follow the form previously reported.<sup>2</sup> It is seen that, at each temperature, there are three ranges of solvent composition that have quite distinct and different interactive properties. Between 0 and 0.3 volume fraction of THF before mixing, there is a restricted amount of free THF to interact with the solute as a significant amount of the THF that is present is associated with water. Between initial volume fractions of THF of 0.3 and 0.7, the solvent mixture is clearly ternary in nature, containing THF, water, and THF-water associate, all present in significant proportions. Between initial volume fractions of THF of 0.7 and 1.0, the mixture is again largely binary in nature, containing mostly THF and the THF associate with only a small proportion of water present unassociated with THF.

It is clear that raising the temperature increases the association constant as defined in equation (1) and, thus, reduces the amount of association. As a consequence, at any given THF content, there is more THF unassociated with water to interact with the solute at the higher temperatures. As the THF is, in most cases, the stronger eluting solvent, raising the temperature increases the elution rate of the solutes in two ways. Firstly, it increases the interaction between the solutes and the THF by increasing the concentration of unassociated THF; secondly, it reduces the standard free enthalpy of distribution of the solute between the two phases, reducing its distribution in the stationary phase and, consequently, its retention and elution time.

The effect of THF-water association on solute retention, however, can be more complicated. If the solute is largely dispersive, the unassociated THF will be the component that largely controls elution. As a consequence, the elution



**Figure 4.** Graphs showing the volume fraction of water, tetrahydrofuran and the water-tetrahydrofuran associate.

is controlled in the manner stated. If, however, the solute is strongly polar, then the water and, possibly, the THF-water associate will be the components of the mobile phase that largely control retention. If the solute has both strong dispersive and polar interactive centers, then all three components may play a significant part in controlling retention. Under these circumstances, the net effect of temperature change is more difficult to predict.

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Received July 31, 2000  
Accepted August 20, 2000

Author's Revisions August 5, 2000  
Manuscript 5345