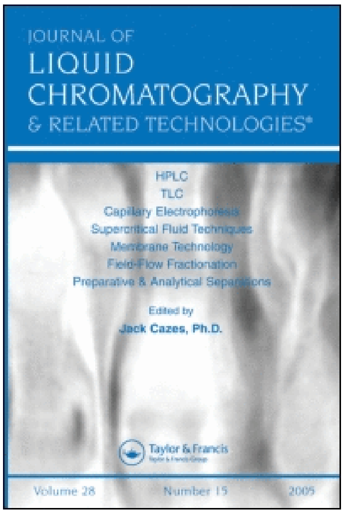

**Journal of Liquid Chromatography & Related Technologies**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

# Activity Coefficients at Infinite Dilution of Organic Compounds in Acetonitrile and Methanol by Liquid Chromatography

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**To cite this Article** Vega, Aurelio and Coca, José(1990) 'Activity Coefficients at Infinite Dilution of Organic Compounds in Acetonitrile and Methanol by Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 13: 4, 789 — 801

**To link to this Article: DOI:** 10.1080/01483919008051821
**URL:** http://dx.doi.org/10.1080/01483919008051821

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(4), 789-801 (1990)

# ACTIVITY COEFFICIENTS AT INFINITE DILUTION OF ORGANIC COMPOUNDS IN ACETONITRILE AND METHANOL BY LIQUID CHROMATOGRAPHY

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## ABSTRACT

Activity coefficients at infinite dilution of series of n-alkanes, n-alcohols, n-alkylbenzenes, cresols, $\alpha$- and $\beta$-toluidine and $\gamma$-picoline in acetonitrile and methanol were determined at 25 °C by liquid-liquid chromatography. Apiezon L and Porapak Q were used as the stationary phases. For those components for which activity coefficients were available in the literature, there is reasonably good agreement with the data reported in this work, though in some cases the literature data were obtained by other techniques.

## INTRODUCTION

Phase equilibria data are required for calculation of processes involving mass transfer operations and in solution thermodynamics. Gas-liquid chromatography (GLC) is a well-established technique for the determination of thermodynamic properties at infinite dilution [1,2,3]. However, its major limitation is that the liquid phase must be nonvolatile and therefore the activity coefficients obtained are of limited value for calculation of phase equilibria. A way of circumventing this problem is to use GLC under non-steady state conditions [4,5] which has proved a useful method for obtaining solvent selectivities in extractive distillation and activity coefficients for volatile solute-solvent systems.

The limitations of the GLC method can be overcome by determining activity coefficients by liquid-liquid chromatography (LLC) and several publications have taken this approach [6,7,8,9]. The LLC technique is suitable for solvents of practically any volatility but it also has some limitations which are summarized in Table 1.

Several stationary phases have been suggested for the determination of activity coefficients by LLC such as: squalane [10], Apiezon L [7] and polydimethylsiloxane [9]. In this work activity coefficients in acetonitrile and methanol were determined for several solutes at 25 °C following the technique described in the literature [6].

## EXPERIMENTAL

The liquid chromatograph was made of two Waters modules, i.e. a chromatographic pump (M 6000 A) and a differential refractometer detector (R 400). A Rheodyne injection valve with a 5 µl external loop was used to introduce the sample into the column.

The columns used in this work were 35 cm x 1/4 in o.d. stainless steel. A Novapack C-18 (Waters) column of 15 cm x 3.9 mm

TABLE 1

Limiting Factors in the GLC and LLC Methods for the Determination of Activity Coefficients at Infinite Dilution.

| **Gas-Liquid Chromatography** |
|---|
| . The stationary solvent phase must be nonvolatile (in conventional GLC). |
| . The pressure correction may be important for some solutes at certain operating conditions. |
| . High retention times and adsorption effects may cause inaccuracy. |
| **Liquid-Liquid Chromatography** |
| . Mobile and stationary phase must be immiscible. |
| . Only ratios of activity coefficients for the solute in the mobile and stationary phase are obtained. |
| . Retention volumes can neither be too close to the column void volume nor too large. |
| . Interfacial adsorption and mass transfer nonequilibrium may be significant. |

inserted between the pump and the injector valve was used to dampen pressure fluctuations. The column, after proper cleaning, was packed with the stationary phase which consisted of 25 wt.% Apiezon L (Hewlett-Packard) on 60-80 mesh Chromosorb P-AW (Hewlett-Packard). The column packing was prepared by dissolving a weighed amount of Apiezon L in chloroform and adding to the solution a known amount of the solid support. The slurry was gently dried in a rotavapor while nitrogen flowed above the drying stationary phase. The percentage loading of stationary phase of the packing was determined gravimetrically. Also, a Porapak Q (100-120 mesh) column was used.

The columns were immersed in a constant temperature bath and the temperature was controlled to within ± 0.1 °C. The systems were allowed to equilibrate at a given temperature under constant flow until a stable baseline was obtained.

The mobile phases acetonitrile and methanol (Romil Chemicals) with a purity of 99.9 % were saturated with the stationary phase and then degassed in an ultrasonic bath, prior to their use as eluent. The solutes were reagent-grade products (Romil Chemicals, Fluka A.G. and Ega-Chemie) and their purity and that of acetonitrile were checked by gas-liquid chromatography. Because of their purity they were used without further purification.

The chromatograms were recorded with a OmniScribe recorder, and from them the retention measurements were made. Interstitial and dead volumes in the system were measured by frequent injections of water which was not retained in the column. Retention data were taken as the average of at least three measurements and reproductibility of $V_g$ values was within 5 %.

## RESULTS AND DISCUSSION

The specific retention volume at the column temperature, $V_g$, is defined as:

$$V_g = (V_R - V_M)/w_S = K/\rho_S \qquad (1)$$

where $V_R$ is the solute volume, $V_M$ is the interstitial and dead volume in the column, $W_S$ and $\rho_S$ the weight and density respectively of the stationary phase in the column and K the solute distribution coefficient.

The ratio of activity coefficients of the solutes in the mobile phase, $\gamma_2^{m,\infty}$, obtained by LLC and in the stationary phase, $\gamma_2^{s,\infty}$, obtained by GLC is given by the equation [11, 12]:

$$\ln V_g = \ln \frac{\gamma_2^{m,\infty} M_m}{\gamma_2^{s,\infty} M_s \rho_m} + \frac{\bar{P} - 1}{R T} (\bar{V}_2^m - \bar{V}_2^s) \qquad (2)$$

where $M_m$ and $M_s$ are the molecular weights of the mobile and stationary phases respectively, $\rho_m$ is the mobile phase density at the column temperature, $\bar{P}$ is the average column pressure and $\bar{v}_2^m$ and $\bar{v}_2^s$ the solute partial molar volumes in the mobile and stationary phase respectively. The pressure correction term, unlike very often in GLC, is negligible unless at very high pressures ($10^2$ - $10^3$ atm) operation [11] and hence:

$$V_g = \frac{\gamma_2^{m,\infty} M_m}{\gamma_2^{s,\infty} M_s \rho_m} \qquad (3)$$

Activity coefficients in acetonitrile

The solute specific retention volumes in the system acetonitrile/Apiezon L and activity coefficients of the solutes in acetonitrile calculated from Eq. (3) at 25 °C are listed in Table 2.

## TABLE 2

Solute Specific Retention Volumes in Acetonitrile/Apiezon L and Activity Coefficients at Infinite Dilution in Acetonitrile at 25°C

| SOLUTE | $V_{g,ACN}$ (ml/g) | $\gamma_2^{s,\infty}$ This work | Lit. | Ref. |
|---|---|---|---|---|
| Ethanol | 0.023 | 4.07 | | |
| n-Propanol | 0.040 | 6.52 | | |
| i-Propanol | 0.033 | 5.00 | | |
| Butanol | 0.061 | 8.18 | | |
| Benzene | 0.382 | 2.66 | 2.69 | 16 |
| | | | 3.06 | 7 |
| | | | 2.77 | 7 |
| | | | 3.08 | 6 |
| | | | 2.70 * | 17 |
| Toluene | 0.514 | 3.57 | 4.51 | 6 |
| | | | 4.53 | 7 |
| | | | 4.06 | 7 |
| Ethylbenzene | 0.620 | 4.34 | 5.75 | 7 |
| | | | 6.23 | 7 |
| | | | 6.17 | 6 |
| o-xylene | 0.659 | 5.55 | 6.12 | 6 |
| m-xylene | 0.732 | 5.66 | 6.64 | 6 |
| p-xylene | 0.734 | 5.43 | 6.64 | 6 |
| n-pentane | 2.308 | 20.49 | 20.40 * | 16 |
| | | | 21.40 | 6 |
| | | | 21.33 | 7 |
| | | | 20.09 | 7 |
| n-hexane | 2.982 | 26.78 | 25.50 * | 17, 7 |
| | | | 21.40 | 6 |
| | | | 30.57 | 7 |
| n-heptane | 4.146 | 41.41 | 33.45 | 7 |
| | | | 42.10 | 7 |
| | | | 33.78 | 7 |
| | | | 42.50 | 6 |
| o-cresol | 0.047 | 2.58 | | |
| m-cresol | 0.039 | 3.53 | | |
| p-cresol | 0.042 | 4.81 | | |
| o-toluidine | 0.055 | 2.45 | | |
| m-toluidine | 0.043 | 2.39 | | |
| γ-picoline | 0.207 | 3.77 | | |
| β-picoline | 0.219 | | | |
| α-picoline | 0.246 | | | |

(*) Literature values obtained by static methods

The solute activity coefficients in acetonitrile, $\gamma_2^{m,\infty}$, were calculated using data of $\gamma_2^{s,\infty}$ obtained by GLC, according to Eq. (3). The GLC data have been presented in a previous publication [13]. All of the GLC were obtained at temperatures exceeding 25 °C, and extrapolations from ln $\gamma_2^{s,\infty}$ *vs.* 1/T were made to evaluate at 25 °C. The extrapolation is reasonable for n-alkanes, alkylbenzenes and aliphatic alcohols as GLC data were obtained in the range 50 - 120 °C; for all the other solutes the realiability of data, and hence $\gamma_2^{m,\infty}$, is questionable as GLC data were obtained in the range of 150 - 190 °C.

As shown in Table 2 values for $\gamma_2^{m,\infty}$ in acetonitrile reported in the literature are also listed, some of the values have been obtained by static methods. A comparison of the data reported in this work with the wide spectrum of data reported in the literature shows that values for aromatic hydrocarbons tend to be lower while the agreement is quite satisfactory for the aliphatic hydrocarbons.

The aliphatic hydrocarbons show the largest values for $\gamma_2^{m,\infty}$, which would be expected because of the high polarity of the acetonitrile molecule and the poor solubility of those hydrocarbons in acetonitrile. Benzene, cresols and nitrogen compounds show the lowest $\gamma_2^{m,\infty}$ values and the xylenes and aliphatic alcohols series show intermediate values.

A similar trend is observed when the heats of mixing of acetonitrile-benzene and acetonitrile-alcohols are considered [14], which are easily explained as a result of the rupture of hydrogen bonds resulting from the mixing process. It has been suggested [6] that values of $\gamma_2^{m,\infty} > 15$ obtained by LLC have to be treated with caution because of the complications that arise from interfacial adsorption.

According to Pierotti, Deal and Derr correlation [15] the activity coefficient is related to the number of carbon atoms in the solute ($n_2$) and solvent ($n_1$) structure by the equation:

$$\ln \gamma_2^{\infty} = A_{12} + B_1\, n_2/n_1 + C_2/n_2 + D\,(n_2 - n_1)^2 + F_1/n_1 \qquad (4)$$

If the first two terms of Eq. (4) are substituted in Eq. (3) it results:

$$\ln V_g = (A_{12}-A'_{12}) - (B_1-B'_1)(n_2/n_1) + \ln M_m/M_s\, \rho_m =$$

$$k_1 + k_2\, n_2 \qquad (5)$$

This suggests that a plot of $\ln V_g$ vs. $n_2$ should give a straight line for an homologous series, as happens with retention data in GLC. This behavior is shown in Fig. 1 for the homologous series studied in this work.

This trend has also been observed when $\ln \gamma_2^{m,\infty}$ is plotted vs. the number of carbon atoms in solutes of homologous series, but large deviations are observed for the first solutes in the series.

### Activity coefficients in methanol

The previous values of the activity coefficients at infinite dilution in acetonitrile have been used in connection with LLC

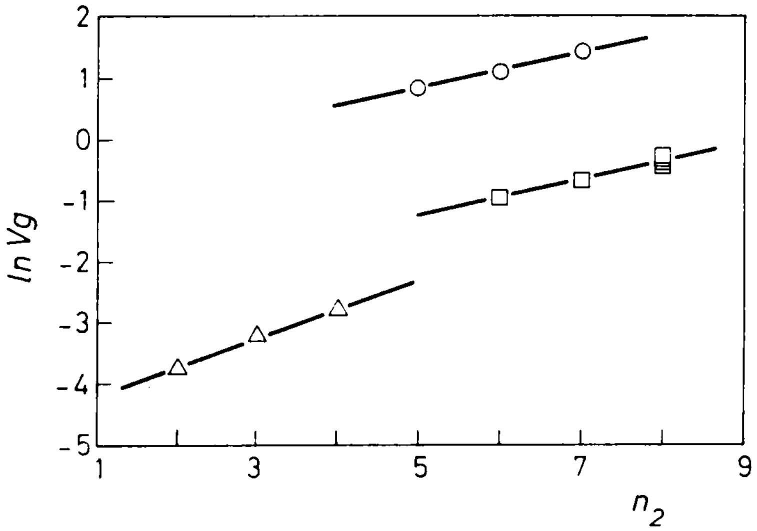

**FIGURE 1.** Specific Retention Volumes of Homologous Series at 25 °C in Acetonitrile/Apiezon L as a Function of the Number of Carbon Atoms of the Solute. Solutes: ○ n-Alkanes, □ n-Alkylbenzenes, △ Alcohols

data obtained for the same solutes using acetonitrile (ACN)/Porapak Q and methanol (MET)/Porapak Q as mobile-stationary phases in the chromatographic experiment. The $\gamma^{*,\infty}_{2,MET}$ for the solutes-methanol systems were evaluated from the following expression:

$$\frac{V_{g,MET}}{V_{g,ACN}} = \frac{\gamma^{*,\infty}_{2,MET} \quad M_{MET} \quad \rho_{ACN}}{\gamma^{*,\infty}_{2,ACN} \quad M_{ACN} \quad \rho_{MET}} \qquad (6)$$

The specific retention volumes $V_g$ for 21 solutes at 25 °C in acetonitrile/Porapak Q and methanol/Porapak Q systems are listed

**TABLE 3**

Specific Retention Volumes $V_g$ in Acetonitrile/Porapak Q and Methanol/Porapak Q and Activity Coefficients at Infinite Dilution in Methanol at 25 °C

| SOLUTES | $V_{g,ACN}$ | $V_{g,MET}$ | $\gamma_{2,MET}^{*,\infty}$ |
|---|---|---|---|
| Ethanol | 0.187 | 0.158 | 4.47 |
| n-propanol | 0.261 | 0.217 | 7.04 |
| i-propanol | 0.229 | 0.177 | 5.02 |
| Butanol | 0.339 | 0.278 | 8.72 |
| Benzene | 0.983 | 1.932 | 6.79 |
| Toluene | 1.225 | 2.565 | 9.70 |
| Ethylbenzene | 1.393 | 3.045 | 12.32 |
| o-xylene | 1.371 | 3.217 | 16.92 |
| m-xylene | 1.433 | 3.395 | 17.41 |
| p-xylene | 1.399 | 3.269 | 16.47 |
| n-pentane | 1.404 | 1.841 | 34.90 |
| n-hexane | 1.727 | 2.282 | 45.96 |
| n-heptane | 2.115 | 2.807 | 71.38 |
| o-cresol | 0.531 | 0.729 | 4.60 |
| m-cresol | 0.471 | 0.664 | 6.47 |
| p-cresol | 0.467 | 0.688 | 9.20 |
| o-toluidine | 0.645 | 1.069 | 5.28 |
| m-toluidine | 0.612 | 0.978 | 4.95 |
| γ-picoline | 0.811 | 1.028 | 6.20 |
| β-picoline | 0.842 | 1.098 | ---- |
| α-picoline | 0.868 | 1.034 | ---- |

in Table 3. Also, activity coefficients at infinite dilution in methanol, $\gamma_{2,MET}^{*,\infty}$ as determined by Eq. (6) are given in Table 3 for 19 solutes.

The activity coefficients are all greater than unity. The lowest value was obtained for ethanol as corresponds to a similar solute-solvent pair and the highest values were obtained for the n-alkanes which corresponds to the poor solubility of those compounds in methanol. Values of $\gamma_{2,MET}^{m,\infty}$ for the aromatic hydrocarbons are much lower than for the aliphatic ones as corresponds to their solubility in all the range of concentration with methanol. It has been suggested that the formation of charge-transfer complexes is the reason for the higher solubility of aromatic hydrocarbons [18].

In conclusion, it is possible to evaluate activity coefficients at infinite dilution by LLC when data are available for the solutes with another solvent. Only retention data of the solutes using both solvents as eluents in any stationary phase are needed. A proper selection of the stationary phase may substantially reduce the time needed for experimentation.

## SYMBOLS

A = Parameter of Pierotti, Deal and Derr correlation

B = Parameter of Pierotti, Deal and Derr correlation

C = Parameter of Pierotti, Deal and Derr correlation

D = Parameter of Pierotti, Deal and Derr correlation

F = Parameter of Pierotti, Deal and Derr correlation

k = Parameter of Eq. (5)

K = Solute distribution coefficient

M = Molecular weight

$n$ = Number of carbon atoms

$\bar{P}$ = Average column pressure

$V_g$ = Specific retention volume at the column temperature

$V_R$ = Solute volume

$V_M$ = Interstitial and dead volume in the column

$\bar{v}_2$ = Partial molar volume of the solute

$w_s$ = Weight of stationary phase in the column

$\rho$ = Density at the column temperature

$\gamma$ = Activity coefficient

Subscript

ACN = in acetonitrile

MET = in methanol

m = mobile phase

s = stationary phase

1 = solvent

2 = solute

Superscript

m = in mobile phase

s = in stationary phase

$\infty$ = at infinite dilution

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