

Activity coefficients at infinite dilution determined by gas–liquid chromatography

Organic solvents in Apiezon L

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ABSTRACT

Activity coefficients at infinite dilution were determined by gas–liquid chromatography for a variety of solutes using Apiezon L as the solvent (liquid phase). Two temperature ranges (60–90 and 150–190°C) were used depending on the boiling points of the solutes. Solubility parameters were determined from retention data for Apiezon L at 90 and 150°C using regular solution theory and Flory–Huggins interaction parameters.

INTRODUCTION

Activity coefficients at infinite dilution are important for the prediction of vapour–liquid equilibria, the selection of solvents in extractive distillation, the determination of solvent–solute interaction parameters and many other applications in chemical processes. Gas–liquid chromatography (GLC) has been used extensively to obtain these coefficients [1]. A limitation of the GLC technique is that the liquid phase (solvent) must have a low volatility. When a volatile solvent is used, a major problem is the entrainment of the stationary phase from the column. This problem can be overcome, at least to some extent, by non-steady-state [2] and reversed-flow [3] techniques. Another method is to use a combination of GLC and liquid–liquid chromatography (LLC) retention data, using a high-molecular-weight compound as the liquid phase in both instances [4].

Unlike the GLC method, only ratios of the activity coefficients of a solute at infinite dilution in the mobile and stationary phases can be obtained by

LLC. To obtain solute activity coefficients in the volatile mobile phase it is necessary to use independent methods (*e.g.*, GLC) to determine the corresponding activity coefficient in the other phase.

In this work the activity coefficients for several solutes, such as aliphatic and aromatic hydrocarbons, alcohols, cresols, toluidines and picolines at infinite dilution were determined using Apiezon L as the solvent (stationary phase) in GLC. Measurements were made in two temperature ranges, 60–90 and 150–190°C, and the results are discussed with respect to regular solution theory.

These coefficients allow the determination of activity coefficients at infinite dilution in volatile solvents (such as acetonitrile or methanol) from LLC measurements [5].

THEORY

The specific retention volumes, V_g° , were determined by the following equation [6]:

$$V_g^\circ = (t_R - t_d) \left(\frac{273.15F}{T_0 w_s} \right) \left(\frac{p_0 - p_w}{p_0} \right)_j \quad (1)$$

where t_R is the retention time, t_d the dead time, F the carrier gas flow-rate, T_0 the flow meter temperature, w_s the mass of the stationary phase, p_0 the outlet pressure, p_i the inlet column pressure, p_w the vapour pressure of water at the flow meter temperature and j the James–Martin factor defined as:

$$j = \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right] \quad (2)$$

The activity coefficients at infinite dilution, γ_2^∞ , were determined from the specific retention volume V_g° [7] by the equation:

$$\ln \gamma_2^\infty = \ln \left(\frac{273.15R}{V_g^\circ M_1 p_2^\circ} \right) - \frac{P}{RT} (2B_{12} - V_2^\circ) - \frac{p_2^\circ}{RT} (B_{22} - V_2^\circ) \quad (3)$$

where M_1 is the molecular weight of the liquid phase, p_2° the saturated vapour pressure of the pure solute, P the average column pressure, V_2° the molar volume of the pure solute, B_{12} the second virial coefficient of interaction between the solute and the carrier gas, R the gas constant, T the column temperature and B_{22} the second virial coefficient of the solute at temperature T .

At moderate pressures using helium as the carrier gas, B_{12} can be safely neglected and V_2° is also negligibly small compared with B_{22} [7]. Thus eqn. 3 can be approximated by:

$$\ln \gamma_2^\infty = \ln \left(\frac{273.15R}{V_g^\circ M_1 p_2^\circ} \right) - \frac{p_2^\circ B_{22}}{RT} \quad (4)$$

Solute vapour pressures were obtained from literature data [8] for the following solutes: *n*-propanol, isopropanol, butanol, benzene, toluene, heptane, *o*-, *m*- and *p*-cresols and *o*- and *m*-toluidines. The Antoine equation was used at pressures up to 1500 mmHg and the Harlacher–Braun equation [9] for higher vapour pressures, following suggestions given by Reid *et al.* [10]. B_{22} was estimated from the Beattie–Bridgeman correlation [11]:

$$B_{22}/V_c = 0.461 - 1.158(T_c/T) - 0.503(T_c/T)^3 \quad (5)$$

where V_c and T_c are the critical volume and the critical temperature of the solute, respectively.

The activity coefficient is commonly expressed as the contribution of two effects: the thermal contribution, γ_{th}^∞ , resulting from molecular interactions of

the compounds, and the athermal contribution, γ_{at}^∞ , associated with the difference in size between the solute and solvent molecules:

$$\ln \gamma_2^\infty = \ln \gamma_{th}^\infty + \ln \gamma_{at}^\infty \quad (6)$$

The interaction parameter, χ^∞ , is, according to the Flory–Huggins theory, related to $\ln \gamma_2^\infty$ by subtracting the Flory–Huggins size correction [12,13]:

$$\chi^\infty = \ln \gamma_2^\infty - \ln (1/r) - (1 - 1/r) \quad (7)$$

where r is approximated as the molar volume ratio of solvent to solute.

The size correction is usually taken as the value of $\ln \gamma_{at}^\infty$. The interaction parameter redefined as a “residual” free energy [14] involves the enthalpy and entropy effects:

$$\chi^\infty = \chi_H^\infty + \chi_S^\infty \quad (8)$$

and from the regular solution theory:

$$\chi_H^\infty = (V_2^\circ/RT)(\delta_1 - \delta_2)^2 \quad (9)$$

Substituting eqn. 9 into eqn. 8 and rearranging leads to:

$$\left(\frac{\delta_2^2}{RT} - \frac{\chi^\infty}{V_2^\circ} \right) = \left(\frac{2\delta_1}{RT} \right) \delta_2 - \left(\frac{\delta_1^2}{RT} + \frac{\chi_S^\infty}{V_2^\circ} \right) \quad (10)$$

A plot of the left-hand side of eqn. 10 versus the solute solubility parameter, δ_2 , should yield a straight line from which the liquid phase solubility parameter, δ_1 , can be obtained [14,15].

The molar excess thermodynamic properties of the solution are given by the equation:

$$\Delta G_e^\infty = RT \ln \gamma_2^\infty = \Delta H_e^\infty - T \Delta S_e^\infty \quad (11)$$

EXPERIMENTAL

Measurements were carried out with a Hewlett-Packard 5750 G gas chromatograph equipped with a thermal conductivity detector. A glass chromatographic column, 2.4 m × 0.25 in., was packed with Apiezon L (Hewlett-Packard) as the stationary phase, supported on Chromosorb P-AW (80–100 mesh); the liquid loading was 25.3% by mass. The column packing was prepared by dissolving a weighed amount of Apiezon L in trichloromethane and adding to the solution a known amount of the solid support. The slurry was gently dried in a rotary

evaporator with nitrogen flowing above the drying stationary phase. The percentage loading of the stationary phase on the packing material was determined gravimetrically.

Samples of 0.1 μl were injected after 8 h of thermal equilibration. The elution peaks were only slightly asymmetric, which is a good indication of infinite dilution conditions [16]. Furthermore, the stationary phase is not polar and a high liquid phase loading on a highly inert support was used. It can therefore be assumed that the experimental data are reasonably unaffected by adsorption phenomena. The results reported here are the average of at least three experimental determinations.

The solutes were supplied by Romil Chemicals (UK), Fluka (Switzerland) and Ega-Chemie (Germany), and were selected because they show a variety of functional groups and some of them are important coal by-products.

The molecular mass of the Apiezon L stationary phase, 1160, was determined using a Knauer osmometer.

RESULTS

Values of specific retention volumes, V_g° , and the activity coefficients are listed in Tables I and II for the various solutes with Apiezon L as the liquid phase.

TABLE I
SOLUTE-SPECIFIC RETENTION VOLUMES AND ACTIVITY COEFFICIENTS IN APIEZON L

Solute	60°C		70°C		80°C		90°C	
	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞
Ethanol	12.7	3.45	10.0	2.75	7.9	2.34	6.7	1.90
<i>n</i> -Propanol	33.9	3.07	25.8	2.48	20.4	1.99	15.8	1.67
Isopropanol	18.9	2.87	14.6	2.29	11.8	1.85	9.6	1.53
Butanol	86.2	2.78	64.7	2.29	48.2	1.89	37.1	1.60
Benzene	134.8	0.28	101.1	0.27	75.6	0.27	57.7	0.26
Toluene	348.4	0.31	243.5	0.30	173.1	0.30	125.8	0.30
<i>n</i> -Pentane	26.6	0.36	20.4	0.36	16.1	0.35	12.9	0.34
<i>n</i> -Hexane	68.2	0.39	50.6	0.38	37.9	0.38	29.0	0.37
<i>n</i> -Heptane	171.9	0.42	122.2	0.41	87.6	0.40	65.0	0.39

TABLE II
SOLUTE-SPECIFIC RETENTION VOLUMES AND ACTIVITY COEFFICIENTS IN APIEZON L

Solute	150°C		160°C		170°C		180°C		190°C	
	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞	V_g° (ml/g)	γ_2^∞
<i>o</i> -Xylene	58.1	0.30	46.6	0.29	37.4	0.29	30.4	0.29	25.0	0.28
<i>m</i> -Xylene	49.8	0.31	40.3	0.30	32.5	0.30	26.5	0.30	21.8	0.30
<i>p</i> -Xylene	49.5	0.30	40.1	0.30	32.3	0.30	26.4	0.30	21.7	0.30
<i>o</i> -Cresol	98.8	0.68	77.6	0.63	60.3	0.59	48.2	0.55	38.7	0.52
<i>m</i> -Cresol	107.2	0.87	84.2	0.80	67.3	0.73	53.1	0.68	42.8	0.63
<i>p</i> -Cresol	104.9	0.95	83.0	0.85	64.4	0.78	51.2	0.71	40.6	0.67
<i>o</i> -Toluidine	135.1	0.61	104.5	0.59	85.4	0.53	65.4	0.51	52.0	0.48
<i>m</i> -Toluidine	134.3	0.71	104.0	0.68	84.9	0.61	64.9	0.59	51.4	0.55
γ -Picoline	42.0	0.42	34.3	0.41	28.6	0.39	23.0	0.38	19.3	0.37

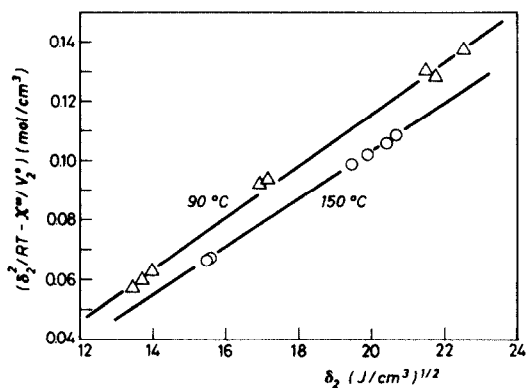


Fig. 1. Evaluation of the solubility parameters at 90 and 150°C for the solutes in Table I.

Two temperature ranges were selected based on the boiling point of the solutes. For the high-boiling-point compounds the temperature range 150–190°C was selected to obtain reasonable retention times; the retention times would have been too high in the range 60–90°C and would have been difficult to measure with the accuracy needed for thermodynamic calculations.

All the aliphatic and aromatic compounds used, with the exception of the aliphatic alcohols, showed very low activity coefficients ($\gamma_2^\infty < 1$), indicating the good solvation of these solutes in Apiezon L. The aliphatic alcohols have high γ_2^∞ values ($\gamma_2^\infty > 1$), which result from repulsive interaction due to the high polarity of the alcohols. This is also reflected by the high excess enthalpies, ΔH_e^∞ , in Apiezon L (in the range 18.4–20.9 kJ/mol) compared with the values for aliphatic hydrocarbons (in the range 2.1–2.4 kJ/mol).

Fig. 1 shows the plot of the terms in eqn. 10 for the evaluation of the solubility parameters at 90 and 150°C. The values of the estimated solubility parameters for Apiezon L are 13.3 (J/cm³)^{1/2} at 90°C and 14.1 (J/cm³)^{1/2} at 150°C. Some workers [14,15] have reported similar results using different solvents.

SYMBOLS

- B_{12} second virial coefficient of interaction between the solute and carrier gas (cm³/mol)
 B_{22} second virial coefficient for the pure solute (cm³/mol)

- F carrier gas flow-rate (cm³/min)
 ΔG_e^∞ excess partial molar Gibbs free energy at infinite dilution of the solute (J/mol)
 ΔH_e^∞ excess partial molar enthalpy at infinite dilution of the solute (J/mol)
 j James–Martin factor
 M_1 molecular weight of stationary phase (g/mol)
 p_i inlet column pressure (atm)
 p_o outlet column pressure (atm)
 p_w vapour pressure of water at the flow meter temperature (atm)
 p_2° vapour pressure of the pure solute (atm)
 P average column pressure (atm)
 R gas constant (82.05 cm³ atm/mol K in eqns. 3 and 4; 8.3144 J/mol K in eqns. 9–11)
 r molar volume ratio of solvent to solute (V_1°/V_2°)
 ΔS_e^∞ excess partial molar entropy at infinite dilution of the solute (J/mol K)
 t_R retention time (min)
 t_d dead time (min)
 T column temperature (K)
 T_c critical temperature of the solute (K)
 T_0 flow meter temperature (K)
 V_c critical volume of the solute (cm³/mol)
 V_g° specific retention volume (cm³/g)
 V_1° molar volume of the stationary phase (cm³/mol)
 V_2° molar volume of the solute (cm³/mol)
 w_s mass of stationary phase (g)

Greek letters

- γ_2^∞ activity coefficient at infinite dilution of the solute
 γ_{at}^∞ athermal contribution to the activity coefficient at infinite dilution of the solute
 γ_{th}^∞ thermal contribution to the activity coefficient at infinite dilution
 χ^∞ interaction parameter at infinite dilution
 χ_H^∞ enthalpic contribution to the interaction parameter
 χ_S^∞ entropic contribution to the interaction parameter
 δ_1 solubility parameter of the solvent (stationary phase) [(J/cm³)^{1/2}]
 δ_2 solubility parameter of the solute [(J/cm³)^{1/2}]

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