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Determination of infinite dilution activity coefficients and second virial coefficients using gas–liquid chromatography I. The dilute mixtures of water and unsaturated chlorinated hydrocarbons and of water and benzene

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Abstract

Specific-retention volume data from gas–liquid chromatographic measurements can be used to obtain infinite dilution activity coefficients and second cross virial coefficients for the solute–carrier gas mixtures.

The gas–liquid chromatographic measurements have been carried out for benzene and three unsaturated chlorinated hydrocarbon + water mixtures in the temperature range 285.15–323.15 K, with water as stationary phase and nitrogen as carrier gas. A gas–liquid chromatographic apparatus was used for measurements on water rich mixtures, and organic rich mixtures were studied using an isopiestic technique. The chromatographic specific retention volume data and the results from the isopiestic technique may be used to estimate group interaction parameters for the UNIFAC correlation to predict activity coefficients.

1. Introduction

The aliphatic and aromatic chlorinated hydrocarbons have many and various applications. These include use in the manufacture of products such as resin and pharmaceuticals, they also serve as aerosols solvents and as reaction media. The mutual solubilities of water and unsaturated chlorinated hydrocarbons and aromatic chlorinated hydrocarbons are very small and special techniques are required for the determination of vapour–liquid equilibria of mixtures in their miscible regions. In a previous paper [1] we reported measurements of the infinite dilution activity coefficients for mixtures of water with

benzene, chlorobenzene, trichloroethene, *trans*-1,2-dichloroethene and 1,1-dichloroethene in the temperature range 285.15–323.15 K. In this paper we report the results of the continuation of ref. 1. In particular the results reported are the estimates of the second cross virial coefficients for the solute/nitrogen mixtures. Also Henry's constants for solute–water mixtures have been derived, as well as the excess partial molar enthalpies for water at infinite dilution in the solutes for the temperature range studied. The experimental infinite dilution activity coefficients for solute–water mixtures previously reported [1], have been used to obtain updated effective UNIFAC group interaction parameters for the ACH–water, ACCl–water (where A defines the aromatic ring), C=C–water and Cl(C=C)–water

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interactions. The new parameters have been used to predict activity coefficients at infinite dilution for several chlorinated hydrocarbon–water mixtures and these have been compared with experimental values where possible.

2. Theory of gas–liquid chromatographic (GLC) technique

The technique allows the determination of activity coefficients γ_1 of a non-electrolyte solute (component 1) at very low concentrations (10^{-3} to 10^{-6} mole fraction) in a solvent (component 2). The technique is feasible to ternary systems in which component 3 is a carrier gas that is relatively insoluble in the solvent. Usually the solvent is either an involatile non-electrolyte or water. Many treatments of GLC retention theory have been reported in the literature [2–5]. These differ in the procedure used for extrapolating measured retention data to zero carrier gas pressure. The relationship between the net retention volume V_N and the carrier gas flow-rate at column outlet F_C and retention times t_R and t_M for an absorbed solute vapour and a non-absorbed maker gas, respectively, is given in Eq. 1. The factor J_3^2 allows for the pressure-drop across the chromatographic column and is defined by Eq. 2, in which p_i and p_o are the column inlet and outlet pressures, respectively

$$V_N = J_3^2 F_C (t_R - t_M) \quad (1)$$

$$J_3^2 = \frac{3}{2} \cdot \left(\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right) \quad (2)$$

Eq. 3 due to Cruickshank *et al.* [5] shows the relationship between V_N and p_o for real gases at moderate carrier gas pressures and allows for the non-ideality of the solute vapour, the solute–carrier gas molecular interactions and the pressure dependence of the partition coefficient.

$$\ln V_N = \ln (k^0 V_2) + \beta p_o J_3^4 + \xi (p_o J_3^4)^2 \quad (3)$$

where

$$J_3^4 = \frac{3}{4} \cdot \left(\frac{(p_i/p_o)^4 - 1}{(p_i/p_o)^3 - 1} \right) \quad (4)$$

and V_2 is the volume of solvent on the chromatographic support material. The three coefficients k^0 , β and ξ in Eq. 3, are defined as follows

$$\ln k^0 = \ln \frac{RT}{\gamma_1^\infty v_2^0 p_1^0} - \frac{B_{11} - v_1^0}{RT} \cdot p_1^0 \quad (5)$$

$$\beta = (2B_{13} - \bar{v}_{12}^\infty) / RT \quad (6)$$

$$\xi = (3C_{133} - 4B_{13}B_{33}) / 2(RT)^2 \quad (7)$$

Here, k^0 is the zero pressure partition coefficient which is related to γ_1^∞ through Eq. 5. B_{11} is the solute second virial coefficient, p_1^0 the vapour pressure of pure solute, v_1^0 is the molar volume of pure solute and v_2^0 is the molar volume of pure solvent. B_{33} is the second virial coefficient of carrier gas and \bar{v}_{12}^∞ is the partial molar volume of the solute infinitely dilute in the solvent (where \bar{v}_{12}^∞ is not available then v_1^0 is used instead as an approximation). B_{13} and C_{133} are, respectively, the second and third cross virial coefficients between the solute and carrier gas. Pemberton and Mash [6] stated that if the carrier gas pressure $p_o < 2$ MPa and the carrier gas is not appreciably soluble in the solvent at the column temperature, and also if $(p_i - p_o) < 200$ kPa and $|B_{13}| < 180$ cm³ mol⁻¹, then for solute samples of < 2 μ mol admitted to packed columns of 4 mm internal diameter, Eq. 3 can be reduced to Eq. 8.

$$\ln V_N = \ln (k^0 V_2) + \beta p_o J_3^4 \quad (8)$$

The selection of nitrogen as carrier gas for the mixtures investigated in this work permits the use of Eq. 8. Thus a plot of $\ln (V_N/V_2)$ versus $p_o J_3^4$ should give a straight line from which γ_1^∞ and B_{13} can be found.

3. Experimental

The measurements for water-rich mixtures were carried out using a GLC apparatus, and for organic-rich mixtures an isopiestic technique was used. Both of these techniques have been described in detail previously [1,6–8]. Only a brief

description is given here for the gas–liquid chromatograph.

3.1. The gas–liquid chromatograph

A schematic diagram of the apparatus was shown previously [7]. A typical chromatogram is shown in Fig. 1, from which the retention time is obtained. The sharp peak of the methane marker gas is followed by a broader solute peak. To obtain an accurate measurement of $(t_R - t_M)$, the solute retention time corrected for gas hold-up, it is necessary to measure the times t_n and t'_n at a displacement height h_n on the leading and trailing edges of the solute peak, respectively. Then $(t_R - t_M)$ can be found, by extrapolation of $(t_n + t'_n)/2$ to maximum solute peak height.

The chromatographic columns were made from 1.2 m lengths of soft annealed 7 mm copper tubing. They were packed with diatomaceous earth (Diatomite S, 60–72 BSS mesh) supplied by JJ's Chromatography. They were prepared in a similar manner to those used previously [1,7].

3.2. Materials

The water used was doubly-distilled tap water. Benzene and trichloroethene was supplied by

Fisons and chlorobenzene, 1,1-dichloroethene and *trans*-1,2-dichloroethene by BDH. All of these had purities in excess of 99%.

4. Group interaction parameters

In this paper we also report the results of an analysis of the new measurements in terms of one of the modifications of the UNIFAC group contribution model, the effective UNIFAC model. The detailed form of the UNIFAC equation of Fredenslund *et al.* [9], has been previously reported [7]. However, the effective UNIFAC method reported here has been developed by Nagata and Koyabu [10]. The combinatorial term of the effective UNIFAC equation is the same as in the UNIFAC and is given by Eq. 9

$$\ln \gamma_i^c = \left(\ln \left(\frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i} \right) - \frac{1}{2} \cdot Zq_i \left(\ln \left(\frac{\phi_i}{\theta_i} \right) + 1 - \frac{\phi_i}{\theta_i} \right) \quad (9)$$

where γ_i^c is the combinatorial activity coefficient, q_i is the pure component surface area parameter, x_i is the mole fraction of component i , θ_i is the

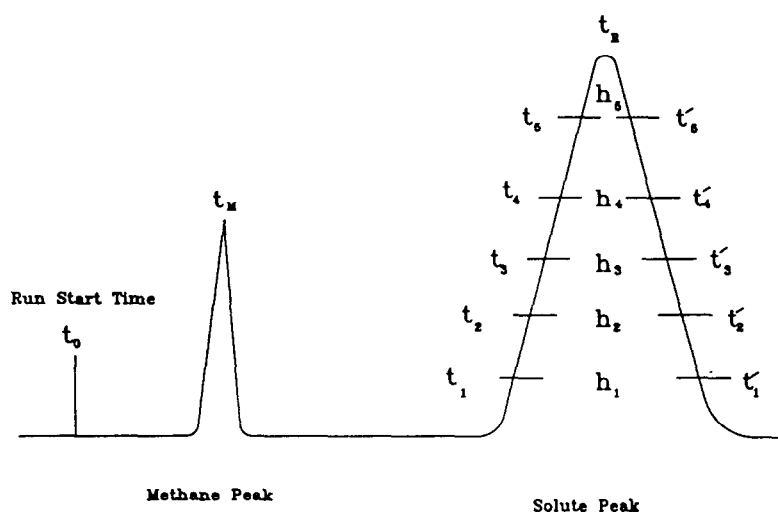


Fig. 1. A typical GLC chromatogram.

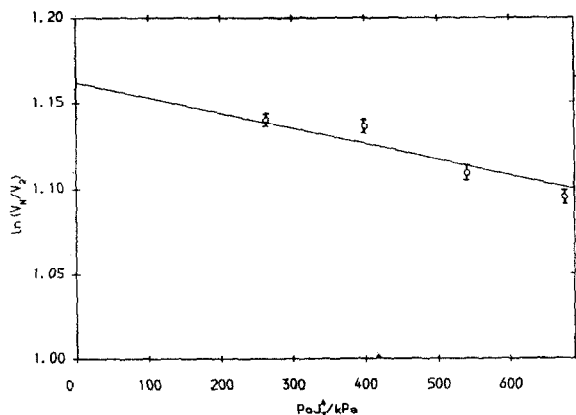


Fig. 2. A plot of $\ln(V_N/V_2)$ against $\rho_0 J_3^4$ for trichloroethene + water system at 293.15 K.

area fraction and ϕ_i is the segment fraction which is similar to the volume fraction. The coordination number Z is taken as 10 [9]. But the main modification has been made in the residual activity coefficients, by adding a term that is a function of the area fraction.

Thus

$$\ln \gamma_i = \ln \gamma_i^c + \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) - \left(\ln \left(\frac{\theta_i}{x_i} \right) + 1 - \frac{\theta_i}{x_i} \right) \quad (10)$$

and

$$\ln \Gamma_k = 1 - \ln \left(\sum_m X_m \psi_{mk} \right) - \sum_m \left(\frac{X_m \psi_{km}}{\sum_n X_{nn} \psi_{nm}} \right) \quad (11)$$

where Γ_k is the group residual activity coefficient, Γ_k^i is the residual activity coefficient of group k in a reference liquid containing only molecules of type i and X_m is the mole fraction of group m . The group interaction parameters are given by

$$\psi_{mn} = \frac{Q_m}{Q_n} \exp \left[- \left(\frac{a_{mn}}{T} \right) \right] \quad (12)$$

where Q is the group surface area parameter, a_{mn} is the group interaction parameter and T is the temperature (K).

Table 1

Second cross virial coefficients (B_{13}) for benzene or chlorinated hydrocarbon (1)-nitrogen (3) mixtures and group assignments for benzene and chlorinated hydrocarbons

Solvent	T (K)	B_{13} ($\text{cm}^3 \text{mol}^{-1}$)	Group assignment
Benzene	293.15	-118.95	6ACH
	303.15	14.15	
	313.15	76.96	
	323.15	113.81	
Chlorobenzene	293.15	202.56	5ACH · 1ACCI
	303.15	175.38	
	313.15	142.07	
	323.15	-15.67	
Trichloroethene	293.15	-66.23	3Cl(C=C) · 1CH=C
	303.15	-24.83	
	313.15	-10.15	
	323.15	102.60	
<i>trans</i> -1,2-Dichloroethene	293.15	-27.64	2Cl(C=C) · 1CH=CH
	303.15	152.55	
	313.15	169.30	
	323.15	177.51	
1,1-Dichloroethene	285.15	-	2Cl(C=C) · 1CH ₂ =C
	293.15	-	

5. Results and discussion

Specific retention volumes were measured for column inlet pressures in the range 200–700 kPa at four different temperatures (293.15, 303.15, 313.15 and 323.15 K) for each solute studied. Typical results for trichloroethene + water system are shown in Fig. 2, where $\ln(V_N/V_2)$ is plotted against $p_0 J_3^4$. Each point on the plot represents the average value of up to seven measurements. The slope of the plot allows estimation of the second cross virial coefficient of the solute and carrier gas, and the derived values are given in Table 1. Unfortunately, because of a serious lack of literature data, the comparison with the values of B_{13} cannot be made. The pure component properties required for calculating these quantities were taken from different sources (vapour pressures [11,12]; molar volumes [13,14] and virial coefficients [15]). For the

systems studied Henry's law can be applied, and the derived constants from the activity coefficients ($k_i = \gamma_i^\infty p_i^0$) are given in Table 2 where some values quoted by Kavanaugh and Rhodes-Trussell [16] are also included. As can be seen the agreement is good. The estimation of the absolute accuracy of the experimental results is difficult. But an examination of the likely experimental errors leads to the following estimates: B_{13} , $\pm 10\%$; γ_1^∞ , $\pm 1\%$; γ_2^∞ , $\pm 2\%$. Since the excess partial molar enthalpy of solution at infinite dilution is related to infinite dilution activity coefficient as follows

$$d \ln \gamma_i^\infty / d(1/T) = (\bar{H}_i^\infty - H_i^0) / R = \Delta \bar{H}_i^\infty / R \quad (13)$$

where \bar{H}_i^∞ is the partial molar enthalpy of component i in the solution at infinite dilution and H_i^0 is the pure component molar enthalpy. One would expect an almost linear relationship

Table 2
Henry's law constants (k_i) for benzene or chlorinated hydrocarbon (1)–water (2) mixtures

	T (K)	$k_1 \cdot 10^{-4}$ (Pa)	$k_2 \cdot 10^{-4}$ (Pa)	$k_1 \cdot 10^{-4}$ (Pa)
Benzene	293.15	2512.65	57.25	2330.92
	303.15	4013.57	–	3737.70
	308.15	–	95.65	–
	313.15	6065.12	–	5879.09
	323.15	8914.52	166.50	8987.11
Chlorobenzene	293.15	1549.90	76.90	–
	303.15	2156.07	–	–
	308.15	–	136.68	–
	313.15	2619.42	–	–
	323.15	2809.97	247.84	–
Trichloroethene	293.15	4312.96	93.52	5452.08
	303.15	7640.23	–	8532.08
	308.15	–	199.09	–
	313.15	11532.00	–	12982.62
	323.15	17072.58	347.74	19230.20
<i>trans</i> -1,2-Dichloroethene	285.15	–	53.90	–
	293.15	4418.50	50.25	–
	303.15	7770.78	–	–
	308.15	–	104.05	–
	313.15	11572.75	–	–
	323.15	16514.26	–	–
1,1-Dichloroethene	285.15	–	124.72	–
	293.15	–	107.80	–

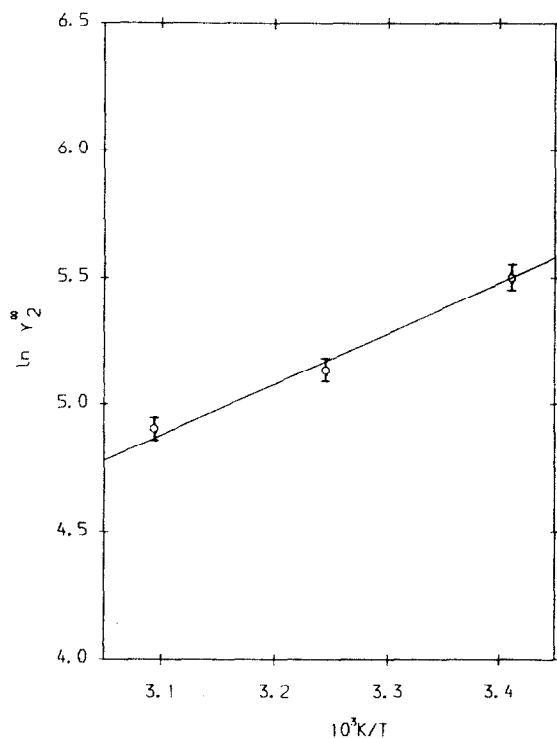


Fig. 3. Infinite dilution activity coefficients as a function of temperature for the benzene (1)–water (2) system.

between $\ln \gamma_2^\infty$ and $1/T$. This is indeed the case for γ_2^∞ , as can be seen from Fig. 3, where $\ln \gamma_2^\infty$ has been plotted against $1/T$ for benzene–water mixtures. Similar linearity has been obtained for

Table 3

Excess partial molar enthalpies for water at infinite dilution in benzene or chlorinated hydrocarbon for the temperature range 285.15–323.15 K

	$\Delta \bar{H}_2^\infty$ (kJ mol ⁻¹)
Benzene	15.48
Chlorobenzene	12.81
Trichloroethene	09.15
<i>trans</i> -1,2-Dichloroethene	19.30
1,1-Dichloroethene	57.58

the remaining systems. The derived values of $\Delta \bar{H}_2^\infty$ are given in Table 3. Group assignments for the five organic solvents investigated whose mixtures with water are given in Table 1. It can be seen that all these solvents contain two types of groups and their mixtures with water, therefore, constitute ternary mixtures of groups, except benzene which is composed by only one group. Water is considered as a single group. The group interaction parameters were estimated by minimization of the following objective function:

$$F = \sum_i \sum_j (\ln \gamma_i^\infty(\text{experimental}) - \ln \gamma_i^\infty(\text{UNIFAC}))_j^2 \quad (14)$$

The summations are taken over all binary data sets j and components i . The minimization was done by using a sequential search procedure first

Table 4

Effective UNIFAC group interaction parameters for benzene and unsaturated chlorinated hydrocarbon–water mixtures

	H ₂ O	ACH	ACCl	C=C	Cl(C=C)
H ₂ O	0.0	324.7 (327.8)	436.7 (525.5)	946.0 (1156.0)	205.9
ACH	1006.0 (1193.0)	0.0			
ACCl	1565.0 (1471.0)		0.0		
C=C	1489.0 (5008.0)			0.0	
Cl(C=C)	1148.0				0.0

The group parameters a_{mn} are in K, m is the row and n is the column of the matrix. The values in parentheses are those of Nagata and Koyabu [10].

Table 5

Comparison of experimental (Expt.) and calculated infinite dilution activity coefficients using the new and updated parameters for benzene and chlorinated hydrocarbon (1)–water (2) mixtures

Chlorinated hydrocarbon	Source	T (K)	$\gamma_1^\infty \times 10^{-4}$		γ_2^∞	
			Expt.	I	Expt.	I
Benzene	VLE	293	0.251	0.253(0.277)	245.0	246.8(472.7)
Chlorobenzene	VLE	293	1.296	1.133(1.890)	329.0	301.4(608.9)
1,2-Dichlorobenzene	LLE	293	6.089	7.340(14.24)	–	449.8(758.2)
1,3-Dichlorobenzene	LLE	293	7.350	7.340(14.24)	–	449.8(758.2)
1,4-Dichlorobenzene	LLE	293	11.656	7.340(14.24)	–	449.8(758.2)
1,2,3-Trichlorobenzene	LLE	298	31.872	34.542(87.987)	–	556.0(823.2)
1,2,4-Trichlorobenzene	LLE	298	1.007	34.542(87.987)	–	556.0(823.2)
1,2,3,4-Tetrachlorobenzene	LLE	298	277.40	173.113(584.357)	–	742.0(944.6)
1,2,3,5-Tetrachlorobenzene	LLE	298	341.43	173.113(584.357)	–	742.0(944.6)
1,2,4,5-Tetrachlorobenzene	LLE	298	2011.1	173.113(584.357)	–	742.0(944.6)
Pentachlorobenzene	LLE	298	2472.4	814.795(3645.35)	–	1010.9(1059.5)
Hexachlorobenzene	LLE	298	316200.0	3629.32(21520.7)	–	1452.4(1169.7)
1,1-Dichloroethene	LLE	293	1.076	0.0438(–)	461.0 ^a	248.6(–)
cis-1,2-Dichloroethene	LLE	298	0.154	1.576(–)	35.0	351.8(–)
trans-1,2-Dichloroethene	VLE	293	0.122	1.576(–)	215.0	381.0(–)
Trichloroethene	VLE	293	0.545	0.089(–)	400.0	227.0(–)
1,1,2,2-Tetrachloroethene	LLE	298	6.136	0.141(–)	35.6	182.2(–)

The experimental values were determined either from vapour–liquid equilibria (VLE) or liquid–liquid equilibria (LLE); I = effective UNIFAC, values of γ_i^∞ in parentheses are calculated from the parameters of Nagata and Koyabu [10].

^a From VLE.

developed by Nelder and Mead [17] and later used by Fredenslund *et al.* [18]. The new and updated parameters are given in Table 4, where they are compared with the values given by Nagata and Koyabu [10]. The derived parameters were obtained from the experimental results at 293.15 K. It can be seen from Table 4, that the only major change in the parameters occurs for C=C–water interaction. The new and updated parameters and also the parameters of Nagata and Koyabu have been used to predict the infinite dilution activity coefficients for several solvents and these are shown in Table 5. The calculated values have been compared with the experimental values of γ_i^∞ reported in ref. 1 and with the activity coefficients for the remaining solvent–water mixtures which were estimated from the liquid–liquid mutual solubilities. Table 6 gives a comparison of errors for the effective UNIFAC model for the original and updated parameters. It can be seen that the updated parameters give a significant improvement in the

predictions for this particular set of chlorinated hydrocarbon–water mixtures. It can be concluded that GLC is a very useful technique for the estimation of the second cross virial coefficients and UNIFAC group interaction param-

Table 6

Comparison of errors in calculated activity coefficients for the original and the new and updated parameters

Error range (%), effective UNIFAC	Data points in error range (%)	
	Original parameters	Updated parameters
0–20	7.0	29.0 (50.0)
20–50	21.4	25.0 (29.0)
50–100	43.0	29.0 (14.0)
100–200	21.6	0.0 (0.0)
200 ⁺	7.0	17.0 (7.0)

The quoted errors are $[\gamma_i^\infty(\text{expt.}) - \gamma_i^\infty(\text{calc})]/\gamma_i^\infty(\text{expt.})$. Values in parentheses refer to the same set of data as for the original parameters.

eters. However, the results obtained from GLC are subject to some systematic measurement errors, in flow, pressure and retention time. Furthermore, it is well known that the UNIFAC equations give poor predictions in the very dilute region. Consequently, these interaction parameters are probably not as accurate as those obtained from reduction of vapour–liquid equilibria data only.

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