CHROM. 4753

COMPARISON OF ACTIVITY COEFFICIENTS MEASURED BY A STATIC AND BY A DYNAMIC METHOD

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(Received February 18th, 1970)

SUMMARY

Activity coefficients at infinite dilution were determined for various chlorinated hydrocarbons in squalane and dinonyl phthalate by two distinct chromatographic methods. The first, and well known method, involved the measurement of specific retention volumes; the second, and less common method, involved measurements obtained from the diffuse edge of a single chromatographic peak. In the latter case the injection of very large samples was necessary. The results are compared with activity coefficients obtained by the static method that uses a McBain balance. Generally, agreement between the dynamic and static methods is good. A conclusion reached is that non-linearity of the partition isotherm may be an important factor when measuring activity coefficients even at infinite dilution.

INTRODUCTION

The measurement of the activity coefficients of some chlorinated hydrocarbons in squalane and in dinonylphthalate by a static method (McBain balance) have been described elsewhere[1,2]. The object of this paper is to compare results obtained by gas chromatographic techniques with those obtained by the static method. Two distinct chromatographic methods were used to obtain values of γ_2^∞, the activity coefficient of the solute at infinite dilution. In the first, small samples of the pure solutes were injected onto a chromatographic column in which either squalane or dinonylphthalate was used as the stationary phase and, from the elution peaks obtained, γ_2^∞ was calculated using the expression:

$$\gamma_2^\infty = \frac{1.704 \times 10^7}{M p_2^0 V_g^0} - \frac{1}{RT}\{p_2^0 B_{22} - \bar{p}(2B_{23} + B_{33})\}$$

where V_g^0 is the specific retention volume, that is, the net retention volume per gram of stationary phase, at 0°; p_2^0 is the saturated vapour pressure; M is the molecular weight, and $\bar{p}$ is the mean column pressure[7]. The second term on the right hand side corrects for imperfections in the gas phase. Values of the second virial coefficients B_{22} (solute) and B_{33} (carrier gas) were calculated from the Berthelot equation and the cross term, B_{23}, from the theory of corresponding states[3]. A third term involving the molar volumes was neglected. Measurements of V_g^0 were also made from the chro-

matogram in two ways; firstly from the "air peak" to the solute peak maximum, and secondly from the "air peak" to the solute peak front. The position of the peak front was established by drawing the tangent to the point of inflection in the peak front and taking the point where it intersected the base line.

In the second method, large samples—up to 250 μl—were injected onto the column and absorption isotherms calculated from the diffuse fronts of the chromatograms, following the method of CREMER AND HUBER[4], HUBER AND KEULEMANS[5] and KNOZINGER AND SPANNHEIMER[6] as applied to the determination of adsorption isotherms from gas–solid chromatography. In the present work the term "isotherm" refers to the plot of the amount (a) of solute absorbed against the vapour pressure (p) of the solute, per gram of stationary phase (the solvent). These quantities are given by:

$$a = \frac{nW}{A} \cdot \int_{h=0}^{h=p} \lambda \mathrm{d}h$$

$$p = \frac{h}{S_p} = \frac{nRT_m xh}{AjF_m}$$

where n is the number of mole of absorbate (solute); T_m and F_m are flow meter temperature and flow rate of carrier gas respectively; x is chart recorder speed; h and A are peak height and peak area, respectively; j is the compressibility factor; W is weight of absorbent (stationary phase), S_p is detector sensitivity; and λ is given by xt_r, where t_r is the retention time.

The integration is carried out graphically from the chromatogram by measuring the area from the air peak to the peak maximum within the limits $h = 0$ to $h = p$. Both this area and the peak area were determined by cutting out the chart and weighing, the weights being compared with the weight of a known area of chart paper taken from a region close to the chromatographic peak.

HUBER AND KEULEMANS[5] have shown that the effect of sample size on the position of the peak front is small, and the present work confirmed this observation. It was therefore considered permissible to calculate an isotherm from the diffuse edge of a single large peak by taking points corresponding to different concentrations, rather than using a number of peaks of different height. A more accurate estimate of the isotherm can, however, be made from the maxima of a number of peaks of different height, provided that the runs are carried out under identical conditions, by superimposing all the chromatograms and drawing a curve through the peak maxima. This curve is then used as if it were a diffuse front boundary. In this way the effects of diffusion, convective mixing and mass transfer are minimised.

Values of $\ln\gamma_2^\infty(T,0)$ may be calculated from the expression:

$$RT\ln\gamma_2^\infty(T,0) = RT\ln\gamma_2^{\infty *} - (B_{22} - v_2^0)p_2^0 + 2(B_{23} - B_{33} - v_2^\infty)p$$

where

$$\gamma_2^{\infty *} = \lim x^L \to 0 \; (p_2/p_2^0 \cdot x_2^L)$$

$\ln\gamma_2^{\infty *}$ is obtained by plotting $\ln(p_2/p_2^0 \cdot x_2^L)$ against the mole fraction x_2, where x_2^L is the mole fraction of the solute dissolved in the absorbate, and extrapolating to $x_2 = 0$. The virial correction can then be made to give $\ln\gamma_2^\infty(T,0)$. Values of the virial

TABLE I

VALUES OF THE MIXED SECOND VIRIAL COEFFICIENTS OF THE ABSORBATES WITH HYDROGEN AT DIFFERENT TEMPERATURES

Calculated from corresponding states theory.
1,1-DCE = 1,1-dichloroethane; 1,2-DCE = 1,2-dichloroethane; 1,1,1-TCE = 1,1,1-trichloroethane; *cis*-1,2-DCEth = *cis*-1,2-dichloroethylene; *trans*-1,2-DCEth = *trans*-1,2-dichloroethylene; 1,1,2,2-TCE = 1,1,2,2-tetrachloroethane; PCE = pentachloroethane.

Absorbate	*Mixed virial coefficient* $-B_{12}$ *cm³/mole (°C)*			
	30	*40*	*50*	*60*
1,1-DCE	28	25	21	18
1,2-DCE	32	28	24	21
1,1,1-TCE	35	30	26	22
cis-1,2-DCEth	22	19	17	14
trans-1,2-DCEth	27	23	20	16
CCl_4	34	30	26	22
CH_2Cl_2	23	20	17	14
$CHCl_3$	27	23	20	17
	90	*100*	*110*	*120*
1,1,2,2-TCE	22	19	16	12

coefficient B_{22} have been given elsewhere[2]; values for the cross term B_{23} and the virial corrections are given in Tables I and II.

EXPERIMENTAL

The apparatus was based on a Griffin Mark III katharometer chromatograph. During any given determination the oven temperature remained within $\pm 0.05°$, or better, of the measured temperature, and the variation along the column length was

TABLE II

VALUES OF THE VIRIAL CORRECTION TERM USED IN CORRECTING $\log j^P$ FOR GAS IMPERFECTIONS

Absorbate	*Virial correction (°C)*			
	30	*40*	*50*	*60*
1,1-DCE	0.005	0.007	0.010	0.013
1,2-DCE	0.000	0.001	0.003	0.005
1,1,1-TCE	0.002	0.005	0.007	0.011
cis-1,2-DCEth	0.004	0.006	0.009	0.012
trans-1,2-DCEth	0.006	0.009	0.012	0.016
CCl_4	0.001	0.003	0.006	0.008
CH_2Cl_2	0.003	0.006	0.008	0.012
$CHCl_3$	0.009	0.012	0.016	0.021
	90	*100*	*110*	*120*
1,1,2,2-TCE	0.001	0.002	0.003	0.004
PCE	0.001	0.002	0.003	0.004

less than 0.1°. Hydrogen was used as carrier gas and the flow rate was measured with a soap film flow meter. Outlet pressure was atmospheric, and the column inlet pressure was measured to the nearest millimetre on a mercury manometer. Carrier gas flow rates were chosen to give acceptable retention times and near optimum column efficiency (minimum HETP). In the first method, 0.2 μl samples were injected with a Hamilton syringe and five injections were made for each determination of the solute retention volume, and each determination was done in duplicate. In the second method, the size of the sample injected was varied according to the vapour pressure of the solute, but usually it was about 250 μl. The apparatus "dead" volume was determined by injecting air and recording the retention time by means of a stop watch. Other retention times were obtained from the recorder chart.

Columns (4 ft. $\times$ $\frac{1}{4}$ in. O.D. copper) were packed with 44–60 mesh acid-washed Embacel (May & Baker) loaded with 20% (w/w) squalane or dinonylphthalate. Silanised and non-silanised supports were tried. Neither showed any significant tailing with the solutes used, but results obtained with silanised supports showed better agreement with the static results and were used henceforth.

RESULTS AND DISCUSSION

Values of $\log\gamma^{\infty}$ determined at various temperatures are shown in Tables III(a) and III(b). The values given include those obtained from retention volume measurements—both from the peak front (PF) and from the peak maximum (PM)—together with the values from the isotherms obtained by the chromatographic method (GCI), and those previously reported from the static isotherms (SI).

Some workers[7,8] have found that the initial retention volume (V_{RI}) gives better agreement with the results obtained by the static method, others[9], that retention data calculated from the peak maxima give better agreement. In the present work no definite trend was observed, but the peak front usually gave the better agreement when squalane was used as the solvent. With dinonylphthalate, on the other hand, peak maximum values are slightly favoured. It is well known that in non-linear chromatography with isotherms of the "anti-Langmuir" type the peak will tend to show the phenomenon of fronting and the retention volume measured to the peak maximum will increase as the sample size increases. It is usually assumed that if the sample size is small enough the concentrations of absorbate involved will lie on that part of the isotherm that is effectively linear, and that within this range the retention volume will be independent of the sample size. With strongly curved isotherms, however, peak distortion will still tend to be present even at very low solute concentration, consequently the retention volume, if measured to the peak maximum will be too large and the value of γ^{∞} thus derived will be too small. In many cases the value of γ^{∞} from the peak maximum is smaller than the value from the static measurements, and this is particularly marked in the case of solutions of 1,1,1-trichloroethane in both squalane and dinonylphthalate, and it is significant that the curvature of the isotherms for these systems is greater than that of any other system studied in the present work. Thus there seems to be a third effect, in addition to the two mentioned by CRUICKSHANK *et al.*[9], that may be important even at low concentrations of solute, namely, non-linearity of the isotherm.

In Fig. 1(a) and 1(b) isotherms obtained by the chromatographic method are

TABLE III(a)

VALUES OF $\log \gamma^{\infty}$ FROM GLC MEASUREMENTS AND COMPARISON WITH STATIC RESULTS.

PF = peak front; PM = peak maximum; GCI = gas chromatographic isotherm; SI = static isotherm.
Solutions in squalane.

Solute	*30°*				*40°*				*50°*				*60°*			
	PF	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*
1,1-DCE	$\bar{1}$.986	$\bar{1}$.949	$\bar{1}$.968	$\bar{1}$.961	$\bar{1}$.961	$\bar{1}$.914	–	$\bar{1}$.938	$\bar{1}$.955	$\bar{1}$.919	$\bar{1}$.938	$\bar{1}$.930	$\bar{1}$.927	$\bar{1}$.886		
1,2-DCE	0.120	0.090	0.102	0.114	0.088	0.058		0.076	0.052	0.027	0.029	0.047	0.033	$\bar{1}$.997		
1,1,1-TCE	$\bar{1}$.819	$\bar{1}$.787	$\bar{1}$.802	$\bar{1}$.840	$\bar{1}$.800	$\bar{1}$.768	$\bar{1}$.777	$\bar{1}$.830	$\bar{1}$.781	$\bar{1}$.752	$\bar{1}$.767	$\bar{1}$.814	$\bar{1}$.767	$\bar{1}$.734		
1,1,2,2-TCE					$\bar{1}$.842	$\bar{1}$.812		~0.06	$\bar{1}$.842	$\bar{1}$.812		~0.06				
PCE	$\bar{1}$.710	$\bar{1}$.695			$\bar{1}$.723	$\bar{1}$.705			$\bar{1}$.734	$\bar{1}$.714						
cis-1,2-DCEth	$\bar{1}$.913	$\bar{1}$.880	$\bar{1}$.910	$\bar{1}$.902	$\bar{1}$.903	$\bar{1}$.868	$\bar{1}$.893	$\bar{1}$.892	$\bar{1}$.880	$\bar{1}$.847	$\bar{1}$.883	$\bar{1}$.885	$\bar{1}$.864	$\bar{1}$.827		
trans-1,2-DCEth	$\bar{1}$.805	$\bar{1}$.773	$\bar{1}$.809	$\bar{1}$.793	$\bar{1}$.744	$\bar{1}$.713	$\bar{1}$.710	$\bar{1}$.741	$\bar{1}$.743	$\bar{1}$.712	$\bar{1}$.716	$\bar{1}$.733	$\bar{1}$.738	$\bar{1}$.706		
CCl_4	$\bar{1}$.753	$\bar{1}$.722	$\bar{1}$.736	$\bar{1}$.733	$\bar{1}$.744	$\bar{1}$.713	$\bar{1}$.710	$\bar{1}$.741	$\bar{1}$.743	$\bar{1}$.712	$\bar{1}$.716	$\bar{1}$.733	$\bar{1}$.738	$\bar{1}$.706		
CH_2Cl_2[a]	$\bar{1}$.992	$\bar{1}$.956	$\bar{1}$.959	0.032	$\bar{1}$.968	$\bar{1}$.919		0.022	$\bar{1}$.943	$\bar{1}$.897	–	$\bar{1}$.980	$\bar{1}$.918	$\bar{1}$.866		
$CHCl_3$[a]	$\bar{1}$.843	$\bar{1}$.811	$\bar{1}$.833	$\bar{1}$.815	$\bar{1}$.833	$\bar{1}$.797	$\bar{1}$.800	$\bar{1}$.806	$\bar{1}$.820	$\bar{1}$.784	$\bar{1}$.796		$\bar{1}$.796	$\bar{1}$.760		

[a] Static results due to FREEGUARD.

TABLE III(b)

VALUES OF $\log \gamma^{\infty}$ FROM GLC MEASUREMENTS AND COMPARISON WITH STATIC RESULTS

Solutions in dinonylphthalate.

Solute	*30°*				*40°*				*50°*				*60°*			
	PF	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*	*PF*	*PM*	*GCI*	*SI*
1,1-DCE	$\bar{1}$.682	$\bar{1}$.639	$\bar{1}$.611	$\bar{1}$.636	$\bar{1}$.700	$\bar{1}$.656	$\bar{1}$.628	$\bar{1}$.656	$\bar{1}$.694	$\bar{1}$.650	$\bar{1}$.641	$\bar{1}$.649	$\bar{1}$.696	$\bar{1}$.649		
1,2-DCE	$\bar{1}$.688	$\bar{1}$.653	$\bar{1}$.663	$\bar{1}$.668	$\bar{1}$.698	$\bar{1}$.663	$\bar{1}$.628	$\bar{1}$.656	$\bar{1}$.694	$\bar{1}$.658	$\bar{1}$.637	$\bar{1}$.679	$\bar{1}$.697	$\bar{1}$.658	$\bar{1}$.668	$\bar{1}$.744
1,1,1-TCE	$\bar{1}$.732	$\bar{1}$.686	$\bar{1}$.710	$\bar{1}$.723	$\bar{1}$.733	$\bar{1}$.690	$\bar{1}$.682	$\bar{1}$.728	$\bar{1}$.721	$\bar{1}$.675	$\bar{1}$.693	$\bar{1}$.728	$\bar{1}$.718	$\bar{1}$.672	$\bar{1}$.693	
1,1,2,2-TCE					$\bar{1}$.381	$\bar{1}$.360		$\bar{1}$.542	$\bar{1}$.413	$\bar{1}$.392		$\bar{1}$.545				
PCE	$\bar{1}$.516	$\bar{1}$.486			$\bar{1}$.544	$\bar{1}$.514			$\bar{1}$.569	$\bar{1}$.639						
cis-1,2-DCEth	$\bar{1}$.497	$\bar{1}$.461	$\bar{1}$.458	$\bar{1}$.476	$\bar{1}$.515	$\bar{1}$.479	$\bar{1}$.458	$\bar{1}$.508	$\bar{1}$.530	$\bar{1}$.494		$\bar{1}$.533	$\bar{1}$.544	$\bar{1}$.502		
trans-1,2-DCEth	$\bar{1}$.678	$\bar{1}$.640	$\bar{1}$.694	$\bar{1}$.611	$\bar{1}$.689	$\bar{1}$.659		$\bar{1}$.624	$\bar{1}$.690	$\bar{1}$.646		$\bar{1}$.639	$\bar{1}$.698	$\bar{1}$.648		
CCl_4[a]	$\bar{1}$.810	$\bar{1}$.767	$\bar{1}$.746	$\bar{1}$.778	$\bar{1}$.805	$\bar{1}$.764	$\bar{1}$.740	$\bar{1}$.774								
CH_2Cl_2[a]	$\bar{1}$.559	$\bar{1}$.517		$\bar{1}$.579	$\bar{1}$.567	$\bar{1}$.522		$\bar{1}$.580	$\bar{1}$.564	$\bar{1}$.516						
$CHCl_3$[a]	$\bar{1}$.445	$\bar{1}$.410	$\bar{1}$.407	$\bar{1}$.400	$\bar{1}$.468	$\bar{1}$.430	$\bar{1}$.435	$\bar{1}$.425								

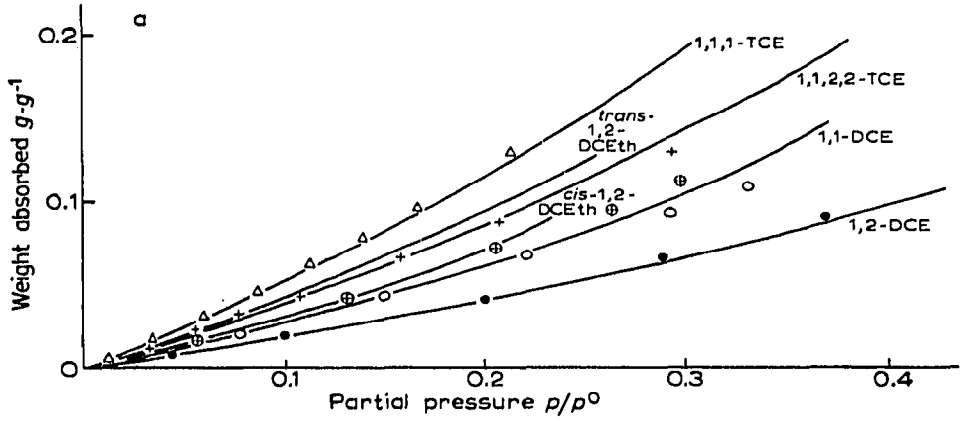

Fig. 1(a). Comparison of static and gas chromatographic isotherms. Solutions in squalane at 30°. ○ = 1,1-DCE; ● = 1,2-DCE; △ = 1,1,1-TCE; ⊕ = *cis*-1,2-DCEth; + = *trans*-1,2-DCEth. Static isotherms are shown as full lines.

compared with those from the static method. The chromatographic measurements tend to give lower values of the absorption, especially at higher relative pressures. At lower relative pressures agreement is surprisingly good and this is reflected in the agreement between the activity coefficients obtained by the two methods.

In order to obtain data over as wide a pressure range as possible in the chromatographic method it was necessary to use very large samples. When the sample concentration is high, non-ideality, non-linearity and sorption effects should be taken into account as shown by HAARHOFF AND VAN DER LINDE[10]. Under such circumstances the sign of an empirical parameter, called by these authors the "characteristic number", determines whether the chromatogram shall have a diffuse front or a diffuse rear boundary. It is further predicted that when the distribution coefficient is relatively large, tailing peaks should be found above a certain column temperature, and

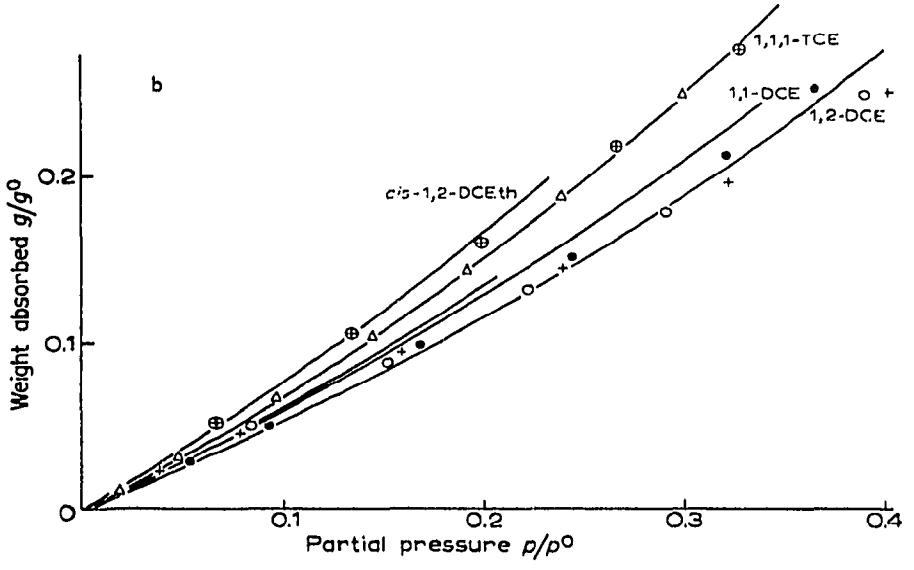

Fig. 1(b). Comparison of static and gas chromatographic isotherms. Solutions in dinonylphthalate at 30°. For key to GLC points, see Fig. 1(a).

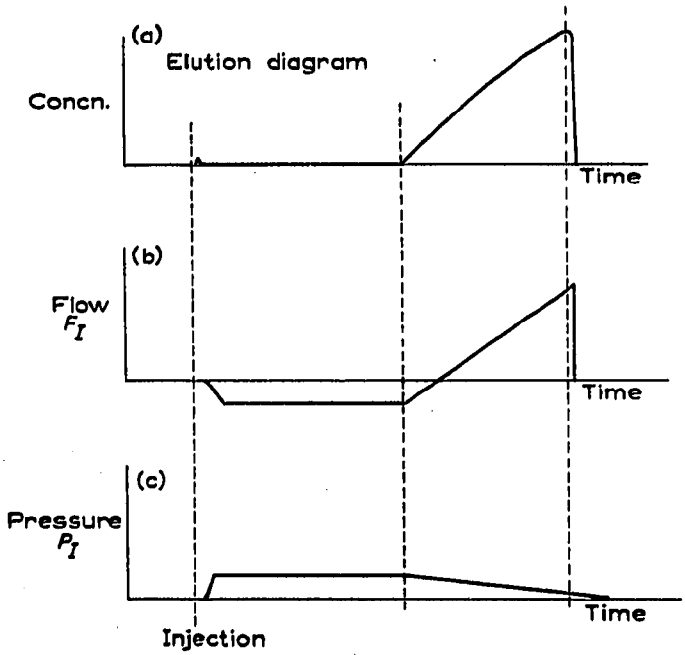

Fig. 2. Effect of high solute concentration on flow rate and inlet pressure. F_I = flow of pure carrier gas; P_I = pressure of pure carrier gas.

fronting peaks below this temperature. Such behaviour was in fact observed in the systems: dichloromethane–squalane and *trans*-1,2-dichloroethylene–squalane, as well as dichloromethane–dinonylphthalate and *cis*- and *trans*-1,2-dichloroethylene–dinonylphthalate. When a tailing peak was found it was not possible to calculate an isotherm from it.

It was observed that during the elution of a large peak from the column there was a change in the flow rate of the carrier gas as measured at the column outlet, and there was a corresponding increase in the column inlet pressure. Pressure changes caused by variations in the viscosity and flow rate when an increase in flow velocity is observed have been discussed by several workers[11–13]. In the present work the flow was monitored at the column outlet and the pressure drop across the column was observed from the change in inlet pressure. Results for 1,1,1-trichloroethane on a dinonylphthalate column maintained at 50° are shown in Fig. 2. Fig. 2(a) shows the chromatogram and Fig. 2(b) and 2(c) the corresponding flow and pressure changes. Readings were taken after the initial pressure fluctuations caused by sample injection had subsided. The sharp increase in flow as the peak is eluted is the so-called "surge effect" described by VAN DER CRAATS[11] and is caused by the fraction of the component in the stationary phase being transferred into the gaseous phase at the end of the column. The size of the change naturally depends on the size of the sample, but is relatively insensitive to the nature of the solute and the column temperature. Pressure changes were about 0.5 to 1.0% of the column pressure, and flow changes about 6.0 to 10.0% of the normal flow rate, according to the sample size (50–150 μl). An explanation is that a back pressure is produced causing a reduction in gas flow; as the solute is eluted the back pressure drops and the normal surge effect is then observed. The most important consequence of this is on the calculation of the column pressure and hence of the concentration, of the solute. For example, if the flow rate used in

the calculation is the one taken with pure carrier gas only through the column, then the calculated pressure term is too low. The change in the column pressure also has an effect on the solute pressure term and in the same sense as the flow rate change.

BECHTOLD[14] has suggested a graphical method for obtaining a correction for the effect of diffusion. The shapes of the elution peaks obtained indicate, however, that diffusion of the solute band was slight except with the chloroform–dinonylphthalate system, even so the results obtained for this system are in good agreement with the static measurements. In those cases where a change from fronting to tailing occurs the absence of diffusion is only established when a vertical edge to the peak is obtained. When a symmetrical, or near-symmetrical peak is obtained the two effects, that is, diffusion and the change from a fronting to a tailing peak, are inseparable as they both tend to enhance peak symmetry.

Values for activity coefficients taken from the literature are given in Table IV. The results of MARTIRE AND POLLARA[15] were obtained at temperatures higher than those used in the present work, hence the values given were obtained by extrapolating the graph of $\log \gamma^{\infty}$ against $1/T$ to values of T corresponding to those used in the present work. MARTIRE AND POLLARA's results were obtained from specific, corrected retention volumes, that is, using peak maxima. YOUNG's[16] values were obtained from

TABLE IV

COMPARISON OF VALUES OF $\log \gamma^{\infty}$ WITH RESULTS FROM OTHER SOURCES

a = Results of this work; b = results of MARTIRE AND POLLARA; c = results of YOUNG; d = results of HARDY. SQ = squalane; DNP = dinonyl phthalate.

System	*Temperature (°C)*			*Reference*
	30	*40*	*50*	
1,1-DCE/SQ		$\bar{1}$.914	$\bar{1}$.919	a
		$\bar{1}$.922	$\bar{1}$.911	b
1,2-DCE/SQ		0.058	0.027	a
		0.037	0.023	b
cis-1,2-DCEth		$\bar{1}$.868	$\bar{1}$.847	a
		$\bar{1}$.887	$\bar{1}$.877	b
trans-1,2-DCEth		$\bar{1}$.776	$\bar{1}$.751	a
		$\bar{1}$.774	$\bar{1}$.765	b
CCl_4–SQ	$\bar{1}$.722	$\bar{1}$.713	$\bar{1}$.712	a
		$\bar{1}$.742	$\bar{1}$.742	b
	$\bar{1}$.732			c
CH_2Cl_2–SQ	$\bar{1}$.956	$\bar{1}$.919	$\bar{1}$.897	a
		$\bar{1}$.917	$\bar{1}$.901	b
	$\bar{1}$.860			c
$CHCl_3$–SQ	$\bar{1}$.811	$\bar{1}$.797	$\bar{1}$.784	a
		$\bar{1}$.818	$\bar{1}$.813	b
	$\bar{1}$.723			c
CCl_4–DNP	$\bar{1}$.767	$\bar{1}$.764		a
	$\bar{1}$.776			c
		$\bar{1}$.851		d
CH_2Cl_2–DNP	$\bar{1}$.517	$\bar{1}$.522		a
	$\bar{1}$.513			c
		$\bar{1}$.623		d
$CHCl_3$–DNP	$\bar{1}$.410	$\bar{1}$.430		a
	$\bar{1}$.407			c
		$\bar{1}$.519		d

retention volumes measured to peak maxima at a series of pressures (2–12 atmospheres) and the values extrapolated to zero pressure. YOUNG's results for chloroform and dichloromethane in squalane would appear to be low, and in a series of experiments using longer columns, from 6 ft. upwards in length, he has obtained values approaching those found in this work. He also used a McBain balance to determine $\log \gamma^{\infty}$ for dichloromethane in squalane at 30° and obtained a value of 1.99. Finally, it would appear that the value obtained by FREEGUARD[1] for dichloromethane in squalane is too high and that this system should have an activity coefficient less than 1.0 at all temperatures in the range studied. The early results of HARDY[17] would also appear to be in error.

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