THE DETERMINATION OF ACTIVITY COEFFICIENTS AT INFINITE DILUTION FROM GAS CHROMATOGRAPHIC MEASUREMENTS

C. J. HARDY*

The University, Bristol (Great Britain)

INTRODUCTION

A number of recent papers[1-8] have shown the usefulness of gas chromatography in the study of the thermodynamics of systems involving volatile solutes and involatile solvents. PORTER *et al.*[7,8], ANDERSON AND NAPIER[1] and KWANTES AND RIJNDERS[5] have concluded that (except for polar solutes in non-polar solvents) activity coefficients at infinite dilution (γ°) derived from gas–liquid chromatographic measurements are sound and do not depend upon operational factors, *e.g.* the nature of the support, the amount of solvent, and the flow-rate. For polar solutes in non-polar solvents the polar properties of the solid support can influence the retention time of the solute; this can be overcome by using a non-polar support such as metal helices[5].

KEULEMANS[4] has recently reviewed much of the above work, suggested methods for the calculation of γ°, and tabulated values of γ° for a number of hydrocarbons and oxygenated compounds. A satisfactory agreement was found[4,5] between values of γ° calculated from (i) chromatographic data for *n*-paraffinic hydrocarbons in up to *n*-C_{16} paraffinic solvents, (ii) the relation of BRÖNSTED AND KOEFOED[9] and (iii) with those found by VAN DER WAALS[10]. However, many of the above values from chromatographic data were not regarded as highly accurate[4] since they were derived from incidental analyses carried out for other purposes. A greater accuracy can easily be achieved in experiments designed for that purpose and the necessary control and measurement of operating parameters will be considered in this paper.

In previous qualitative and quantitative analyses of halogenated hydrocarbons by gas–liquid chromatography[11,12] a large number of retention volumes were obtained, from which activity coefficients have now been calculated. These are not claimed to be highly accurate, but are useful for comparison purposes since no other thermodynamic data for these substances have been calculated from gas chromatographic measurements.

EXPERIMENTAL

The apparatus and general procedure have been described previously[11,12]. Retention times were measured from the time of injection of the sample to the time of appearance

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of the peak maxima on the recorder chart, and were corrected for the "dead-time" of the apparatus (measured by injection of a small sample of either hydrogen or helium). The flow-rate was measured with a soap-film flow-meter at atmospheric pressure at the exit of the thermal-conductivity detector.

Details of the physical properties of the solvents used are given in Table I.

TABLE I

PHYSICAL PROPERTIES OF THE SOLVENTS

Solvent	Molecular Weight	Density	Coefficient of expansion	Reference
Glycerol	92.06	1.2656 (15°)	0.00055	a
Dibutyl phthalate (DBP)	278.3	1.0465 (16°)	0.00058	b
Dinonyl phthalate (DNP)	248.3	0.9537 (16°)	0.00056	b
Silicone 702	530	1.07 (25°)	0.00086	c
Water	18.0	1.000 (4°)	—	d

a *International Critical Tables.*
b Density and coefficient of expansion measured experimentally.
c Data sheet on Silicone 702, Edwards and Co., London.
d The volume of water at the column temperature was calculated from the density at that temperature (from reference a).

The halogenated hydrocarbons were of A.R. quality wherever possible but any small amounts of impurities were separated in the gas–liquid column and did not affect the experimental retention volume. Fluoro-hydrocarbons were supplied by I.C.I. Ltd., and by the Imperial Smelting Corporation Ltd., and samples of separated cis- and trans-dichloroethylene by I.C.I. Ltd.

Vapour pressures, latent heats of vaporisation, and critical point data were taken from *International Critical Tables*, TIMMERMANS[13], and MAXWELL[14]. Antoine equations calculated from DREISBACH's data[15] were used to derive vapour pressures for those solutes for which direct vapour pressure–temperature data were not available. Fugacity coefficients were calculated from the reduced critical point data and fugacity coefficient charts[14, 16].

Method for the calculation of partition coefficients and activity coefficients

(i) The retention time was measured for 1 μl (or less than 1 μl) of liquid solutes and for 0.1 ml N.T.P. of gaseous solutes. These amounts had previously[13] been found to give retention volumes which were within 1% of the "limiting retention volume" for zero sample size, as determined by the elution of a series of samples of varying size. The sample size is indicated in the following Tables where retention data were available only for liquid samples of > 1 μl (or > 0.1 ml of gases).

(ii) The "corrected retention volume", V_R°, was obtained by multiplying the retention time (corrected for the "dead-time" of the apparatus) by the "corrected flow-rate". The latter was obtained by correcting the measured flow-rate (a) for the

vapour pressure of water at the flow-meter temperature, (b) for the pressure drop across the column (by the formula given by JAMES AND MARTIN[17]) and (c) to the temperature of the column.

(iii) The partition coefficient, k, was obtained by dividing V_R^o by the volume of the stationary liquid phase at the column temperature.

(iv) The activity coefficient at infinite dilution, γ^o, was obtained in the form of γ_p^o or γ_f^o from the formulae:

$$\gamma_p^o = \frac{N_{liq}.RT}{k.p^o} \quad \text{or} \quad \gamma_f^o = \frac{N_{liq}.RT}{k.f^o}$$

where p^o is the vapour pressure, and f^o is the fugacity, of the solute at temperature T, and N_{liq}. is the number of moles of liquid phase per unit volume at temperature T.

RESULTS

The reproducibility of γ_p^o for retention times measured at approximately the same temperature but with varying operating conditions during routine analyses is shown in Table II.

TABLE II

THE REPRODUCIBILITY OF k AND γ_p^o FOR VARYING CONDITIONS

Liquid phase	Weight of liquid phase, g	Column temperature, °C	p_i/p_0	Solute	Volume of solute, μl or ml		k	γ_p^o
Dinonyl phthalate	1.89	57.6	1.275	CH_2Cl_2	1	μl	98	0.43
	1.86	56.2	1.490		1	μl	94	0.46
	1.89	57.2	1.182	.	0.5	μl	92	0.47
	1.89	57.6	1.275	$CHCl_3$	1	μl	234	0.35
	1.86	56.2	1.490		1	μl	227	0.37
	1.89	57.2	1.182		1	μl	230	0.36
	1.89	19.1	1.172	$CFCl_3$	0.1	ml	99	0.78
	1.89	20.3	1.077		0.1	ml	98	0.76
	1.89	19.4	1.129		0.1	ml	104	0.74
Silicone 702	1.25	57.0	1.382	CCl_4	1	μl	214	0.48
	2.14	55.7	1.246		1	μl	204	0.51
	2.14	55.7	1.120		1	μl	203	0.51
	2.14	55.7	1.246	CH_2Br_2	1	μl	392	0.58
	2.14	57.6	1.316		0.1	μl	385	0.59
	2.14	55.7	1.120		1	μl	397	0.57

The mean values of k and γ_p^o for a number of halogenated hydrocarbons at a series of temperatures are given for DNP, Silicone 702, and glycerol in Tables III, IV and V respectively. Values of k and γ_p^o for three chloromethanes and methanol in water are given in Table VI and for a few hydrocarbons and oxygenated compounds in DBP, DNP, and Silicone 702 in Table VII.

TABLE III

VALUES OF k AND γ_p° FOR HALOGENATED HYDROCARBONS IN DINONYL PHTHALATE

References to sample size, (a) 0.3 ml N.T.P., (b) 5 μl, (c) 10 μl, (d) 0.4 ml N.T.P.

Temperature, °C	19.3		23.6		24.5		39.7		57.4		76.8		97.9	
Solute	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°
CH_3Cl			27.3	0.45	27.0	0.44					9.15[a]	0.45		
CH_2Cl_2	33.1[b]	0.44					170.5	0.42	98.2	0.43	55.7	0.46	32.4	0.49
$CHCl_3$							451	0.33	232	0.35	122.4	0.38	71.5	0.37
CCl_4							353	0.71	192.4	0.70	107.2	0.71	62.2	0.71
CH_2ClBr											120.5	0.49	71.0	0.48
CH_2Br_2											250	0.60	133.5	0.61
$CHBr_3$													600	0.64
cis-Dichloroethylene							366	0.38			107.7	0.42	64.5	0.42
trans-Dichloroethylene							173.5	0.52			57.8	0.58	32.6	0.60
Trichloroethylene							767[c]	0.46			187.8	0.55	100.5	0.60
Tetrachloroethylene											390	0.80	202	0.79
Ethylene dichloride											164.5	0.57		
CF_3H	10.0	1.16	9.3	1.12	1.84	0.82								
CF_3Cl					0.58	3.4								
CF_2Cl_2					9.39	0.91					3.78[d]	0.80		
$CFCl_3$	104.2	0.74	89.0	0.75	80.6	0.80					23.4	0.66		
$CFCl_2H$			139.5	0.28	130.5	0.29								
CF_2ClH			18.1	0.58	18.0	0.57								

TABLE IV

VALUES OF k AND γ_p° FOR HALOGENATED HYDROCARBONS IN SILICONE 702

References to sample size, (a) 0.3 ml N.T.P., (b) 0.2 ml N.T.P., (c) 2 μl.

Temperature, °C	20.2		21.9		23.1		40.1		55.7		77.0		97.9	
Solute	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°	k	γ_p°
CH_3Cl	278	0.38			23.1	0.36					8.07ᵃ	0.37		
CH_2Cl_2							128.1	0.40	74.0	0.44	42.6	0.44	22.4	0.50
$CHCl_3$	710	0.32					288	0.37			85.8	0.40	42.4	0.45
CCl_4	891	0.45					363	0.50	203.5	0.51	109.4	0.50	55.3	0.58
CH_2ClBr	730	0.42					306	0.45	162	0.47	91.1	0.47	48.5	0.51
CH_2Br_2							797	0.52	360.5	0.59	185.0	0.59	95.8	0.61
$CHBr_3$											915	0.65		
cis-Dichloroethylene											79.0	0.42	38.6	0.51
trans-Dichloroethylene											50.0	0.46	26.6	0.53
Trichloroethylene													76.3	0.57
CH_3I	238ᶜ	0.46												
CHF_3			0.84	1.83			0.53ᵇ	1.61						
CF_3Cl							0.63	1.80						
CF_2Cl_2			10.8	0.75	10.0	0.78	6.90	0.76			4.12	0.63		
$CFCl_3$			93.1	0.56	88.8	0.56	55.0	0.53			21.8	0.52		
$CHFCl_2$					80.9	0.36	47.8	0.37			19.4ᵇ	0.38		
CHF_2Cl			10.4	0.79	10.4	0.76					3.76ᵃ	0.71		

TABLE V

VALUES OF k AND γ_p^o FOR HALOGENATED HYDROCARBONS IN GLYCEROL

Temperature, °C	25.6		28.2		40.1		77.0		
Solute	k	γ_p^o	k	γ_p^o	k	γ_p^o	k	γ_p^o	$\ln \gamma^o$
CH₃Cl			2.82	20.1	2.67	14.8			
CH₂Cl₂	17.2	33.8			13.5	25.7	7.13	17.8	2.88
CHCl₃	21.1	59.6			18.3	39.2	8.65	27.2	3.30
CCl₄	5.45	415			5.4	226	3.5	109	4.69
CH₂ClBr			48.3	31.7	31.6	29.8			
CH₂Br₂					72.3	38.7	25.4	29.7	3.39
CHBr₃							91.8	44.6	3.80
cis-Dichloroethylene					15.9	43.9	7.40	31.0	
trans-Dichloroethylene					5.9	76.7	3.87	40.6	
Trichloroethylene							6.74	76.0	4.33
Tetrachloroethylene							5.7	274	5.61
Ethylene dibromide							37.5	59.4	4.08

TABLE VI

VALUES OF k AND γ_p^o FOR CHLORO-METHANES AND METHANOL IN WATER

Solute (1 μl)	Wt. of H₂O, g*	Temperature °C	V_R^o ml	k	γ_p^o
CH₂Cl₂	1.57	23.4	30.0	19.1	140
	1.12	24.1	15.1	13.6	180
	0.48	27.3	2.85	5.94	370
CHCl₃	1.56	23.4	19.4	12.5	310
	1.05	24.1	10.4	9.94	540
	0.38	27.3	3.15	8.20	580
CCl₄	1.59	23.4	3.69	2.31	4150
	1.07	24.1	3.03	2.83	3300
	0.45	27.3	2.76	6.14	1300
MeOH	0.41	27.3	1380	3360	2.2

* Weight in g on 3 g kieselguhr (corrected for loss of water to gas phase as described previously[13]).

TABLE VII

VALUES OF k AND γ_p^o FOR VARIOUS SOLUTE–SOLVENT SYSTEMS

Solvent	Temperature °C	Solute	Amount of solute μl	k	γ_p^o
DNP	57.2	H₂O	< 0.01	51	8.27
		H₂O	1	28	15.0
DNP	56.5	MeOH	2	39.9	2.55
		EtOH	2	85.5	2.14
		iso-PrOH	2	120.6	1.83
DNP	57.6	Acetone	< 0.01	69.3	0.99
	57.2	Acetone	2.5	62.5	1.13
DNP	39.5	Acetone	2.5	114.8	1.10
DBP	17.7	MeOH	< 0.01	268	2.99
		EtOH	< 0.01	571	3.14
Silicone 702	16.8	Isopentane	0.5	78.9	0.92
		n-Pentane	1.5	112.1	0.88
		2-Me-pentane		241	1.02
		3-Me-pentane	< 0.01	288	0.96
		n-Hexane		368.6	0.95
		2,4-Di-Me-pentane	1	546.3	1.00

DISCUSSION

Comparison of γ_p^o values for halogenated hydrocarbons with those for other substances in polar and non-polar solvents

For the solvents DNP and Silicone 702, γ_p^o values for halogenated hydrocarbons are < 1, with only three exceptions, *viz*: $\gamma_p^o = 1.1$–1.2 for CF_2Cl_2 at 20°, $\gamma_p^o = 1.6$–1.8 for CF_3Cl and CF_3H at 20–30°. However, the last two substances gave very low retention volumes, which were therefore difficult to measure accurately. CF_2Cl_2 gave the value $\gamma_p^o = 0.8$ at 77°, and from the limited data available appears to have $\gamma_p^o < 1$ at temperatures $> 40°$. With glycerol as the solvent all the halogenated hydrocarbons gave $\gamma_p^o \gg 1$. The few results with chloromethanes in H_2O as solvent gave $\gamma_p^o > 100$ and the values depended upon the amount of solvent.

In general therefore for halogenated hydrocarbons γ_p^o is < 1 in non-polar or relatively non-polar solvents, and $\gg 1$ in highly polar solvents. These results are very similar to those found for a wide range of hydrocarbons in polar and non-polar solvents, *e.g.* in non-polar hydrocarbon solvents γ^o is < 1, in the relatively non-polar di-isodecyl phthalate γ^o is $<$ or $\simeq 1$, and in highly polar polyglycol solvents aliphatic hydrocarbons have large values of γ^o (17–1.3) and aromatic hydrocarbons have values ranging from 2.3–0.5.

The relationship of γ^o to the transport of solutes through gas–liquid columns

Values of $\gamma^o < 1$ are found if the components of the solution are similar in polarity but have a large difference in molecular magnitude, or if the components tend to form transient adducts[4], and "negative" deviation from Raoult's law usually results. The value of k is lower for a concentrated part of a zone of solute than for a dilute part. Hence the leading edge of a zone is sharpened as it travels through a column, and the tail is dispersed. The retention volume of the maximum of a relatively concentrated zone is therefore less than that of an infinitely dilute zone. A graphical example of this effect has previously been given[12] for a zone of $CHCl_3$ eluted through a column containing DNP. This effect applies for all the above halogenated hydrocarbons in DNP and in Silicone 702.

Values of $\gamma^o > 1$ are found if there is a large difference in the polarity of the solute and the solvent. The value of k is greater in the more concentrated part of a zone than in dilute parts. The elution curve has a sharpened tailing edge and a diffuse front, and the retention volume of the zone maximum is greater than in the limiting case of "zero" concentration.

The above effects are most important in the first part of a column where the concentration of a solute is highest, and they become smaller as the column length is increased and the sample size is reduced. Hence for the measurement of accurate values of γ^o, small samples and long columns (3–6 m) are recommended[4].

Variation of γ^o with temperature

The variation of γ_p^o with temperature for halogenated hydrocarbons depends upon the particular hydrocarbon and upon the solvent. Values of γ_p^o in glycerol decrease

with increase in temperature. With DNP, γ_p° increases with temperature for CH_2Cl_2, trichloroethylene, and *trans*-dichloroethylene, remains approximately constant for CCl_4, CH_2Br_2, CH_2ClBr, CH_3Cl, $CHCl_3$, *cis*-dichloroethylene, and tetrachloroethylene, and decreases with increase in T for CF_2Cl_2 and $CFCl_3$. With Silicone 702, γ_p° increases with T for CH_2Br_2, CH_2Cl_2, $CHCl_3$, CCl_4 and CH_2ClBr, remains constant for CH_3Cl, $CFCl_2H$ and $CFCl_3$, and decreases for CF_2Cl_2 and CF_2ClH.

KEULEMANS[4] and KWANTES AND RIJNDERS[5] find that γ_f° varies very little with T, and that γ_p° varies to a greater extent, as would be expected since γ_p° is a measure of the combined imperfections in the gas and liquid phases. However, for the majority of the halogenated hydrocarbons under the conditions studied the calculated fugacity coefficients are close to unity and therefore $\gamma_p^\circ \simeq \gamma_f^\circ$. For several solutes γ° shows a large variation with T, and since this effect is not in agreement with results for non-halogenated hydrocarbons a more accurate determination of γ° as a function of T would be desirable.

It is of interest to note the difference between the temperature-variation of k, and of γ°. For all the substances studied k is approximately linearly dependent on $1/T$, where T is the absolute temperature, whereas γ° shows the above-mentioned complex dependence on T. The tabulation of retention data as plots of k against $1/T$ or log V_g against $1/T$ is therefore more convenient than plots of γ° as a function of T. Considerably more experimental data of higher accuracy than have already been reported will be required before the temperature dependence of γ° can be satisfactorily explained.

The accurate determination of γ° by gas–liquid chromatography

The requirements for the accurate evaluation of γ° from measurements with gas–liquid columns can be summarised as follows:

(a) Very small sample size, or extrapolation to zero size from a range of small samples (the latter is recommended).

(b) Long columns (explained previously).

(c) Accurate measurement of retention time, dead-volume of apparatus, temperature and pressure of flow-meter, inlet and outlet pressures at the column, and column temperature.

(d) Accurate determination of the mass of the solvent and, if k is also required, the volume of the solvent at each column temperature, which requires a knowledge of the coefficient of expansion of the solvent.

(e) The molecular weight of the solvent, which implies that γ° values cannot be accurately evaluated for solvents which contain a mixture of substances in unknown proportion (unless they are isomers) or for polymers for which accurate molecular weights cannot be determined.

For the values of γ° to be fundamentally sound they should be independent of specific parameters that determine the column efficiency. Whereas this is usually the case[5,8] (provided that the amount of solvent on an adsorptive support such as Celite is at least 15% by weight[5]) it should be confirmed for the particular solute–solvent

combination for which γ° is to be determined. With chloromethanes in water on Celite the values of k and γ° are not independent of the amount of water and further work is required to elucidate the interactions in this system. The use of a non-polar support, *e.g.* fine metal helices, is recommended[5], particularly for polar solutes in non-polar solvents. The basic method can be extended to solvents of relatively high volatility by presaturating the carrier-gas with the vapour of the solvent, and the value of γ° for a n-hydrocarbon in its next higher homologue can then be determined.

Highly accurate values of γ° can be evaluated if the above requirements are satisfied. Gas–liquid chromatography will then be applicable to the detailed study of the thermodynamics of volatile solutes in volatile and involatile solvents, for which it is difficult to derive γ° by the classical vapour-pressure measurements.

SUMMARY

Activity coefficients at infinite dilution, γ°, have been calculated for a series of halogenated hydrocarbons in dinonyl phthalate, glycerol, and Silicone fluid 702 over the range 20–100°. Values of γ° for several aliphatic hydrocarbons and oxygenated compounds have also been calculated.

The values of γ° for halogenated hydrocarbons are compared with those for other substances in polar and non-polar solvents and are discussed in relation to the transport of solutes through gas–liquid columns. Considerable deviations from ideality have been found for halogenated hydrocarbons in highly polar solvents, *e.g.* for halogenated methanes at 25° $\gamma^0 > 10$ in glycerol and > 100 in water. The variation of γ° with temperature has been shown to depend upon the particular solute and upon the solvent.

A summary is given of the experimental requirements for the accurate determination of γ° by gas–liquid chromatography.

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