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GAS-LIQUID CHROMATOGRAPHIC STUDIES OF ELECTRON-DONOR-ACCEPTOR SYSTEMS

V. SOLUTE ADSORPTION AT THE GAS-LIQUID INTERFACE

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SUMMARY

A study of solute adsorption for two typical donor amines at the gas-liquid interface of a stationary phase containing an acceptor as additive has shown that relationships between activity coefficients and complexing power do not arise as a result of such adsorption. A very small surface effect may be present when primary amines are used as solutes but this can be minimised by using column loadings greater than ten per cent.

INTRODUCTION

Our earlier investigations of the role of charge-transfer (CT) interactions in gas-liquid chromatography (GLC), using an electron-acceptor stationary phase, have indicated that these interactions are important in the elution of aromatic donors¹. Further, the values of the apparent activity coefficients for the donors, as determined by the GLC method, show reasonable correlations with spectroscopically determined equilibrium constants for these donor-acceptor complexes even though such equilibrium constants have to be measured in some inert solvent². Assuming that mole fraction association constants for CT complexing are measures of the relative complexing powers of the donors, a linear relationship between these values and the reciprocals of the apparent activity coefficients should be obtained. When this was examined using substituted anilines as electron donors and 2,4,7-trinitrofluorenone as the electron-acceptor stationary phase, it was found that separate approximately linear relationships were obtained, depending upon whether the donors were primary, secondary or tertiary amines, and these results suggested that there is some additional interaction between the stationary phase and the primary and secondary amines.

However, the ability to demonstrate that CT interactions are operative in the

GLC systems does not imply that these effects provide the greatest contribution to the solute-solvent interactions. If the acceptor is present in the stationary phase as a complexing additive, any "association constant" between donor and acceptor determined by GLC measures contributions from solvent-donor and solvent-acceptor interactions, size effects and the fit of solute molecules into the solvent lattice, polar, dipolar, and hydrogen bonding interactions etc. in addition to the CT interaction, and PURNELL³ has recently shown that favourable solute interaction with a solvent matrix can more than offset any enhanced interaction by CT forces in some systems. CT interactions will thus be relatively small when compared with the normal solution forces which are always present in GLC. This implies that association constants measured by partition methods will be considerably larger than those measured by spectroscopic methods. This has been shown to be true for distribution measurements of association constants for picrate formation⁴ and for GLC measurements of aniline-2,4,7-trinitrofluorenone interactions⁵. One possibility for these high association constants is that they arise mainly from surface effects, the polar 2,4,7-trinitrofluorenone being concentrated at the surface of the stationary phase and giving rise to adsorption rather than partition chromatography. If this were so there might well be strong hydrogen-bonding interactions between primary and secondary amines and the acceptor which would account for the differences in behaviour noted earlier² for primary, secondary and tertiary amines. We have now investigated the possibility of solute absorption at the gas-liquid interface using aniline and *N,N*-dimethylaniline as typical donor amines and 2,4,7-trinitrofluorenone dissolved in tritolyl phosphate (TTP) as the acceptor stationary phase. Such liquid surface excess effects may be observed with polar solute-polar solvent systems in which the measured solute activity coefficients are close to unity⁶. As activity coefficients of this magnitude were found for substituted anilines dissolved in 2,4,7-trinitrofluorenone as the bulk liquid² we considered it necessary to ensure that such adsorption effects did not give rise to the observed relationships between association constants and activity coefficients etc.

EXPERIMENTAL

The apparatus and technique for measuring retention data have been described elsewhere². One-metre glass columns of 4 mm I.D. were packed with hexamethyl-disilazane-treated Celite (40-60 mesh) coated with 10-15% w/w TTP containing 2,4,7-trinitrofluorenone (0.2 *M*). The evenness of the liquid phase deposition was checked by visual examination of random samples of the Celite particles under magnification. The weight of the stationary phase was calculated from the weight increase of the support after treatment. The amount of additive on the column support was measured spectroscopically. Retention measurements were made relative to a reference donor to measure the loss of stationary phase and thus true retention volumes were obtained. It was found that the solvent loss for a 0.5 *M* trinitrofluorenone-TTP column at 150° was less than 0.1% per operating hour.

Materials

Tritolyl phosphate. This was May and Baker "Embaphase" grade, used without further purification.

2,4,7-Trinitrofluorenone. This was a commercial product recrystallized twice from glacial acetic acid and dried at 100°; m.p. 175°.

Amines. These were commercial samples, purified in accordance with literature procedures, redistilled and collected at their reported boiling points.

RESULTS AND DISCUSSION

In the absence of support adsorption, and following the notation of MARTIN⁷, the corrected net retention volume/g of packing, V_{Rg}^0 , is given by

$$V_{Rg}^0 = k_s V_L + k_a A_L \quad (1)$$

where k_s is the bulk liquid partition coefficient, k_a is the adsorption coefficient for the gas-liquid interface and V_L and A_L are the volume and surface area of the liquid/g of packing. V_{Rg}^0 is related to the specific retention volume by

$$V_{Rg}^0 = \frac{V_g W_L T}{273} \quad (2)$$

where W_L is the weight percentage of liquid phase. Rearrangement of eqn. 1 leads to

$$\frac{V_{Rg}^0}{A_L} = \frac{k_s V_L}{A_L} + k_a \quad (3)$$

whence values of k_s and k_a may be determined. The quantitative values of these partition coefficients will be meaningful provided that the liquid interfacial adsorption can be separated from the bulk liquid partition effects. This is possible when sufficient solvent is present on the support to act as a bulk liquid with a depth much greater than the depth of the gas-liquid adsorbed phase. As long as solvent-support ratios are in excess of 5%, independence of liquid interface and bulk liquid effects will be maintained⁸.

In Table I are shown the retention data etc. for aniline and N,N-dimethylaniline on 0.2 M 2,4,7-trinitrofluorenone-TTP column under various conditions of column loading. The values of V_{Rg}^0/A_L are plotted against V_L/A_L in Fig. 1. PECOK *et al.*⁸ have shown that, within experimental error, A_L is independent of the liquid phase but does depend on the support. Using hexadecane or β,β' -thiodipropionitrile as liquid phase on Chromosorb W or firebrick they obtained identical plots of W_L against A_L for the same solid. Values of A_L could be interpolated from their data. Values of V_L were obtained from density measurements at the operating temperature. From these data it can be seen that k_a for N,N-dimethylaniline is zero whereas a small value of 50×10^{-6} cm is obtained for aniline. The corresponding k_s values are thus 637 and 645. MARTIRE⁶ has observed that in systems in which k_a and thus k_a/k_s are zero there is no discernible variation of specific retention volume with column loading and this is also evident from Table I.

Two types of adsorption at the gas-liquid interface may be distinguished. The first is characterised by large deviations from Raoult's law — the greater the activity coefficient the less ideal is the solution. Large positive deviations indicate that solute molecules are being forced from the bulk liquid to the surface or into the vapour phase, primarily because solvent-solvent interactions are much greater than

solute-solvent interactions. The solute cannot compete with a solvent molecule for interaction with a neighbouring solvent molecule, has therefore minimal solubility in the bulk phase, and this results in a high activity coefficient and a large value of k_a/k_g .

The second type of adsorption occurs when the solutes are of comparable polarity to the solvent molecules. This results in solution of the solute molecules in the bulk solvent and adsorption of solute caused by dipole-dipole interactions or hydrogen bonding between the solute and the liquid surface⁶.

In the systems studied here the second type of effect may be anticipated when aniline is the solute as there is the possibility of adsorption on the liquid surface by hydrogen bonding. This possibility does not exist for *N,N*-dimethylaniline. The

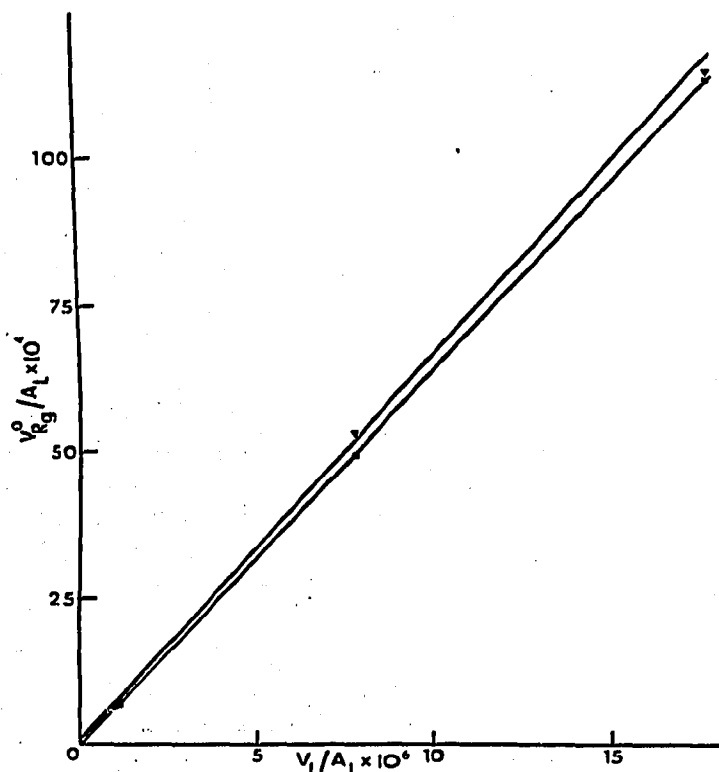


Fig. 1. Values of $V_{R_g}^0/A_L$ plotted against V_L/A_L for aniline and *N,N*-dimethylaniline on a 0.2 *M* 2,4,7-trinitrofluorenone-TTP column at 130°. Values are taken from Table I. ▼, aniline; ●, *N,N*-dimethylaniline.

TABLE I

COLUMN LOADINGS W_L , VOLUME OF LIQUID/g OF PACKING V_L , SURFACE AREA/g OF PACKING A_L AND RETENTION VOLUMES FOR ANILINE AND *N,N*-DIMETHYLANILINE ON A 0.2 *M* 2,4,7-TRINITROFLUORENONE-TTP COLUMN AT 130°

W _L (%)	V _L (ml)	A _L (m ² /g)	V _g		V _{Rg} ⁰	
			Aniline	<i>N,N</i> -Dimethyl- aniline	Aniline	<i>N,N</i> -Dimethyl- aniline
0.02	0.1195	0.67	414.2	393.9	79.61	75.82
0.05	0.0537	0.75	422.6	396.7	39.89	37.45
0.12	0.0124	1.05	416.9	392.2	7.67	7.20

surface effect produced in this way should be considerably smaller than that characterised by large solute activity coefficients and the observed results in Table I may arise as a result of such interactions. However, effects are secondary and cannot account for the observed relationships between activity coefficients and complexing power.

Failure to use a surface correction can introduce⁶ an error greater than 1% in the bulk partition coefficient when

$$\frac{k_a}{k_s} > \frac{V_L}{100A_L} \quad (4)$$

but this correction is only necessary at the lowest column loading of Table I. Any effect of surface can thus be ignored as long as column loadings greater than 10% are used and this condition has been employed in all our studies of complexing systems.

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REFERENCES

- 1 A. R. COOPER, C. W. P. CROWNE AND P. G. FARRELL, *J. Chromatogr.*, 29 (1967) 1.
- 2 A. R. COOPER, C. W. P. CROWNE AND P. G. FARRELL, *Trans. Faraday Soc.*, 62 (1966) 2725.
- 3 S. H. LANGER AND J. H. PURNELL, *J. Phys. Chem.*, 70 (1966) 964.
- 4 P. G. FARRELL AND J. V. WESTWOOD, *J. Chem. Soc. (B)*, (1970) 1518.
- 5 C. W. P. CROWNE, M. F. HARPER AND P. G. FARRELL, unpublished results; see also C. W. P. CROWNE, J. M. GROSS, M. F. HARPER AND P. G. FARRELL, *Proc. V Symposium on Chromatography and Electrophoresis*, P.A.E. Brussels, 1969, p. 153.
- 6 D. E. MARTIRE, *Anal. Chem.*, 38 (1966) 244.
- 7 R. L. MARTIN, *Anal. Chem.*, 33 (1961) 347.
- 8 R. L. PECSOK, A. DE YLLANA AND A. ABDUL-KARIM, *Anal. Chem.*, 36 (1964) 452.

J. Chromatogr., 61 (1971) 1-5