EXPERIMENTAL MEASUREMENT OF BINARY DIFFUSION COEFFICIENT FOR PROCESS DESIGN CALCULATIONS

AMOL S. BALE[*] and N. H. SHINDE

Tatyasaheb Kore Institute of Engineering and Technology, Warananagar, KOLHAPUR (M.S.) INDIA

ABSTRACT

In present study, the arrested elution method was used for the determination of binary diffusion coefficients for nitrobenzene-hydrogen and aniline-hydrogen systems. The data are required for process design calculations for the catalytic vapor phase hydrogenation of nitrobenzene to aniline.

INTRODUCTION

Various gas chromatographic methods have been employed for the measurement of the binary diffusion coefficients of gases and vapors of volatile compounds[1]. The arrested elution method suggested by Knox and McLaren[2] bypasses most of the experimental and theoretical difficulties encountered in the continuous elution method developed by Giddings and Seager[3-5]. Cloete et al.[6] studied the binary diffusion of C_1-C_5 saturated hydrocarbons, sulphur hexa fluoride, neon, nitrogen and helium in helium, argon and nitrogen 0.85 atm and 294^0 - 483^0 C by using the peak arrest method.

EXPERIMENTAL

The chromatography was carried out on a Hewlett packed gas chromatograph with a flame-ionization detector (FID) an electro integrator. Stainless-steel columns of length 220 cm and internal cross-sectional area 0.148 cm^2, without a packing, were used. The dead volumes in the injector and column connections were reduced by introducing solid glass rods into them. The experimental arrangement was similar to that used by Knox and McLaren[2], except that hydrogen was used both as the carrier gas and as a component of the gas-vapor binary system. Separate connections to the FID were made for the carrier gas and for the fuel (hydrogen).

The hydrogen was obtained from IOL (Poona, India) and was purified by passing over palladium-alumina (0.5 %, w/w, of palladium) at 100^oC and silica gel in order to remove trace amounts of oxygen and moisture. The compounds under study, nitrobenzene and aniline, were of AR grade.

In all experiments, a sharp band of nitrobenzene or aniline vapor was introduced into the column at a particular temperature by injecting 1 µL of liquid sample and eluted at a controlled and measurable velocity. When the band was about half way down the column, the flow of carrier gas was arrested by diverting it by using a two-way stopcock for a time t, during which spreading could occur only by diffusion. The band was

_____

finally eluted from the column and its concentration profile and standard deviation were determined by using the detector.

The pressure drop across the column and the adsorption of nitrobenzene and aniline on the inner wall of the column were found to be negligible. The carrier gas velocity (v) was obtained by determining the retention time (t_R) of the compound under study without arresting the flow of carrier gas and from the column length (L) by using the equation $v = L/t_R$. The values of v and t_R were checked by measuring the volumetric gas flow-rates and the column volume directly.

The standard deviation (σ_t) of the eluted peak was obtained from the peak width (w) at the base-line by using the equation $\sigma_t = w/4$.

RESULTS AND DISCUSSION

Experimental results were obtained for the nitrobenzene-hydrogen and aniline-hydrogen systems at a pressure of 725 mm Hg and at temperatures varying from 210° to 295^oC. The standard deviations of the eluted peaks for arrest times ranging from 0 to 300 sec at different temperatures for both systems are given in Table 1.

Table 1: Standard deviations (sec.) of eluted peaks for different arrest times

Values given are averages of more than three experimental values in each instance.

Arrest Time t (Sec.)	Diffusing system					
	Nitrobenzene-hydrogen			Aniline-hydrogen		
	215°C	250ºC	295ºC	210°C	250ºC	290ºC
0	3.50	3.27	3.09	3.62	3.56	4.28
30	-	3.35	3.23	3.72	3.63	4.50
60	3.65	-	3.28	3.84	3.75	4.62
90	3.81	3.56	3.37	3.87	3.90	-
120	4.00	3.79	3.43	4.02	4.00	4.96
150	3.94	3.94	3.40	4.12	4.20	5.12
180	3.94	3.08	3.59	4.13	4.20	5.19
210	4.03	4.06	3.62	4.19	4.36	5.31
240	4.13	4.00	3.56	4.37	4.40	5.50
270	4.18	4.22	3.70	4.50	4.41	5.56
300	4.30	4.37	3.79	-	4.56	5.77
Y(cm/sec)	8.50	8.40	11.60	8.30	8.30	6.5

According to the equation

$$\frac{d\sigma_t^{\,2}}{dt} = \frac{2D_g}{v^2} \qquad\qquad …(1)$$

For diffusional spreading in an empty tube, where D_g is the inter diffusion coefficient, a plot of variance (σ_t^2) against arrest time (t) should give a straight line of slope 2 D_g/v^2, from which D_g can be calculated. As v is raised to the second power in Eq. 1, its measurement should be very accurate for this method to be precise.

The plots of σ_t^2 versus t for both systems were linear and shown in Fig. 1 and 2. The values of the binary diffusion coefficients D_g obtained from the slopes of the plots and those predicted from the theoretical equation based on the kinetic theory and the Lennard-Jones expression for the intermolecular forces and from the expression developed by Fuller et al.[7] for both systems are presented in Table 2. It can be seen that the experimental values of D_g for both systems are smaller than the values predicted from both expressions, the deviation of the predicted from the experimental value being 3.4-9.4 % (average 5.6 %) for the Lennard-Jones method and 2.3-8.6 % (average 4.6 %) for the Fuller et al. method[7]. The latter method predicted the values of D_g more accurately than the former.

The arrested flow method is of high precision because the variance produced by the injector, column connections, detector and elution along the column are the same for all arrest times and accordingly cancel out. A fairly short column can be used for the pulse-broadening experiments. The main disadvantage of this method is the requirement of repeating the experiments at various arrest times. The continuous elution methods require the experiments to be carried out in a long column at very low flow-rates. Precise and accurate results can also be obtained by the method by making corrections for the end-effects and the variance produced in the instrument dead volume and by controlling the experimental conditions precisely.
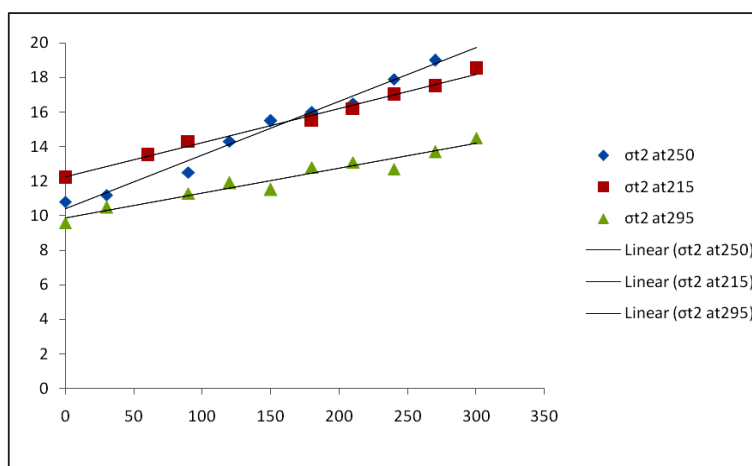

Fig. 1: Plots of σ_t^2 versus arrest time at different temperatures for the nitrobenzene-hydrogen system
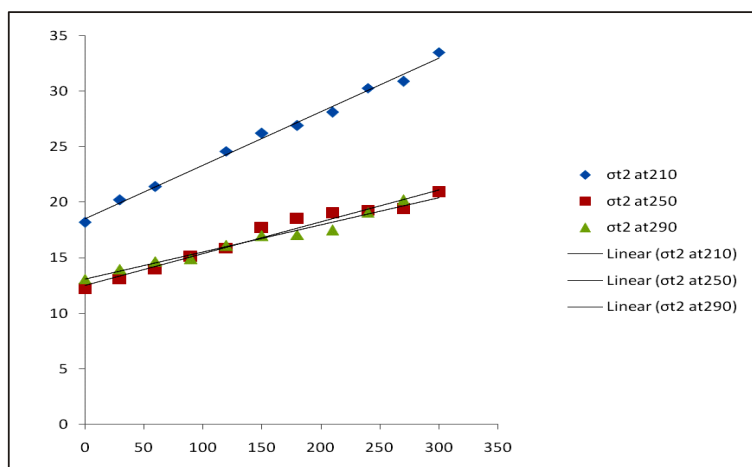

Fig. 2: Plots of σ_t^2 versus arrest time at different temperatures for the Aniline-hydrogen system

Table 2: Results of binary diffusion of nitrobenzene and aniline in hydrogen

System	Temp.	D_g (cm^2/sec)			Deviation (%)[**]	
		Exp.[*]	Predicted by Lennard-Jones Expt.	Predicted by Fuller et al. Expt.	Lennard Jones method	Filler et al. method
Nitrobenzene-hydrogen	215	0.75	0.82	0.814	9.4	8.6
	250	0.889	0.929	0.919	3.4	2.3
	295	1.014	1.068	1.062	5.4	4.8
Aniline-hydrogen	210	0.805	0.84	0.83	4.3	3.1
	250	0.926	0.973	0.954	5.0	3.0
	290	1.027	1.089	1.085	6.0	5.6

Pressure: 1 atm
[*]Experimental value reduced to 1 atm pressure.
[**]Deviation of the predicted from the experimental value.

REFERENCES

1.   V. R. Choudhary, J. Chromatogr, **98**, 491 (1974).

2.   J. H. Knox and L. Mclaren, Anal. Chem., **36**, 1477 (1964).

3.   J. C. Giddings and S. L. Seager, J. Chem. Phys., **33**, 1579 (1960); **35**, 2242 (1961).

4.   J. C. Giddings and S. L. Seager, Ind. Eng. Chem. Fundam., **1**, 1477 (1962).

5.   J. C. Giddings and S. L. Seager, J. Chem. Eng. Data, 8 919630 168.

6.   C. E. Cloete, T. W. Smuts and K. De Clerk, J. Chromatogr., **120**, 17 (1976).

7.   E. N. Fuller, P. D. Schettler and J. C. Giddings, Ind. Eng. Chem., **58**, 3679 (1966).