Journal of Chromatography, 168 (1979) 208–211

CHROM. 11,251

Note

Efficiency of polyethylene glycol containing potassium iodide as a gas chromatographic stationary phase

NAORU HAMAGUCHI, YASUYO SHIOGAI, KIYOSHI YAMAOKA, TERUMICHI NAKAGAWA and TOYOZO UNO
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606 (Japan)
(Received June 5th, 1978)

Various investigations have been reported on alkali metal halide–acid amide interactions, including isolation of the complex[1] X-ray analysis[2], infrared[3] and nuclear magnetic resonance[4] spctroscopy and measurement of electrical conductivity[5] and heat of solution[6]. Our previous studies revealed that similar interactions also take place in gas chromatographic (GC) stationary phases and some alkali metal halide-containing polyethylene glycol (PEG) columns are useful for the specific separation of acid amides[7]. The characteristics of lithium iodide-containing PEG columns have also been investigated for the GC analysis of amide drugs[8]. This paper deals with the evaluation of the efficiency of potassium iodide-containing PEG as a GC stationary phase in terms of the height equivalent to a theoretical plate (HETP) using N-methylacetamide as a test solute.

EXPERIMENTAL

Gas chromatography

The instrument used was a Hitachi K-23 gas chromatograph equipped with a thermal conductivity detector. The glass columns were packed with potassium iodide-containing PEG 20M (weight ratios of potassium iodide to PEG = 1:20, 2:20, 3:20 and 4:20) coated on Chromosorb W (60–80 mesh) so that the PEG content was 20% of the total weight. The column and detector temperatures were maintained at 150, 155, 160, 165 and 170° and the injector temperature at 200°. The linear flow-rate of the carrier gas (helium) was varied between 10 and 38 cm/sec and was measured by dividing the column length by the gas hold-up time (t_M). A minimal amount of sample was used for injection.

Reagents and materials

N-Methylacetamide (MA) and potassium iodide of analytical-reagent grade were obtained from Wako (Osaka, Japan). MA was used after distillation and KI was dried over phosphorus pentoxide and used without further purification.

Measurement of HETP and partition ratio

The elution curve of MA was measured at various weights ratio of potassium iodide to PEG, column temperature and flow-rate of the carrier gas. The HETP was calculated from the elution curve in the usual manner and the partition ratio (k) was calculated by means of the equation $t_R = t_M (1 + k)$, where t_R is the retention time of MA.

RESULTS AND DISCUSSION

The relationship between the concentration of potassium iodide in the stationary phase and the partition ratio of MA at 160° is shown in Fig. 1, indicating that k increases almost proportionately with increasing potassium iodide concentration below 10%, followed by a slight decrease in the slope with a further increase in concentration up to 20%. Such a salting-in effect in PEG solution is similar to those previously found in other combinations of alkali metal halides and acid amides[7,8].

Fig. 2 shows the HETP curves for varying potassium iodide concentrations at

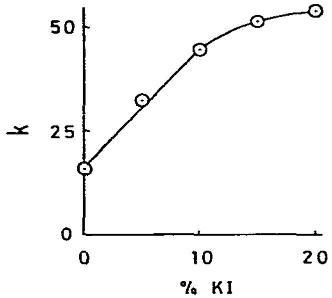

Fig. 1. Relationship between partition ratio (k) and potassium iodide concentration at 160°.

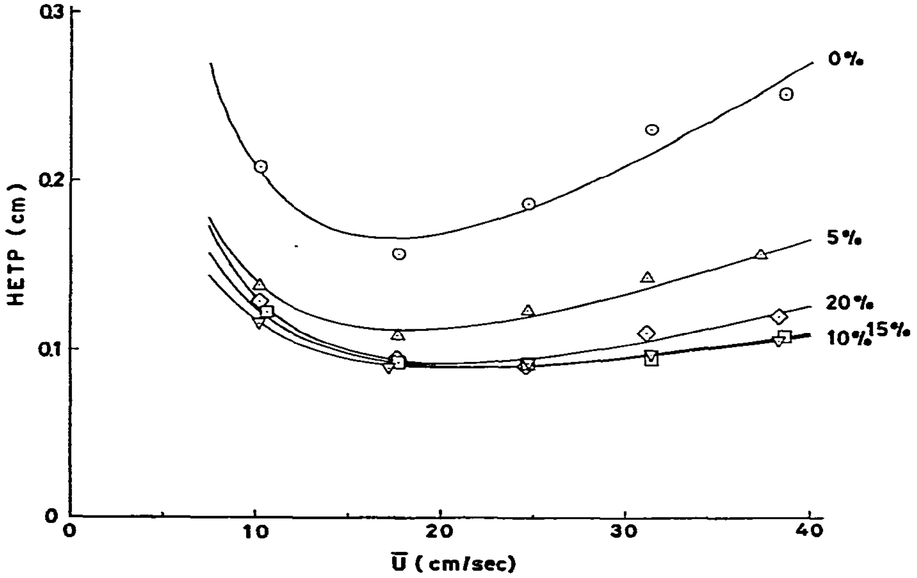

Fig. 2. HETP curves for various concentration of potassium iodide at 160°: ⊙, 0%; △, 5%; ▽, 10%; ⊡, 15%; ◇, 20%.

160°. The points indicate the experimental values and the curves were fitted to these points by means of least-squares method using the Van Deemter equation[9]:

$$H = A + B/\bar{U} + C\bar{U} \tag{1}$$

where H (cm) is HETP, $\bar{U}$ (cm/sec) is the linear flow-rate of carrier gas and A (cm), B (cm^2/sec) and C (sec) are coefficients relevant to the column characteristics.

It was found that an increase in potassium iodide concentration from 0 to 10% gives rise to (i) a decrease in HETP, (ii) a decrease in the flow-rate of carrier gas at which the HETP is at a minimum ($H_{\min}$, $\bar{U}_{\min}$) and (iii) a decrease in the convexity of the curve towards the abscissa, which results in a wide range of carrier gas flow-rates giving small HETP values. A further increase in potassium iodide concentration up to 20% yields slightly contrary effects, and consequently 10% of potassium iodide in PEG gives the smallest HETP.

Such changes in HETP obviously appear to be dependent on the C coefficient in eqn. 1, that is, the addition of potassium iodide causes C to decrease. Van Deemter *et al.*[9] gave the equation

$$C = \frac{8}{\pi^2} \cdot \frac{d_f^2}{D_L} \cdot \frac{k}{(1+k)^2} \tag{2}$$

where d_f and D_L are the effective thickness of the stationary liquid film and the diffusion coefficient of the solute in the stationary phase, respectively. Plots of C *versus* $k/(1+k)^2$ for the present data are given in Fig. 3, where C is due to the curve in Fig. 2. It is found that C is a linear function (correlation coefficient 0.9526) of $k/(1+k)^2$. This, in turn, means that d_f^2/D_L is almost independent of potassium iodide concentration. Therefore, it follows that the addition of potassium iodide leads to an increase in the partition ratio and a subsequent decrease in HETP, thus enhancing the column efficiency.

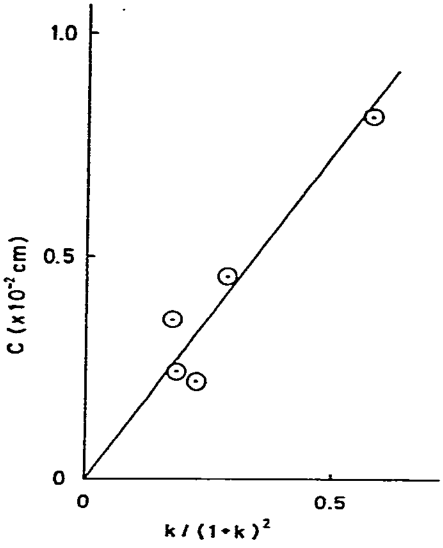

Fig. 3. Plots of C *versus* $k/(1+k)^2$ at 160°.

The HETP curves at various column temperature are shown in Fig. 4, where the points were selected from the data obtained with 15% potassium iodide–PEG and potassium iodide-free columns and the curves were fitted to these points. The curves obtained from the same column exibit a decrease in HETP with decreasing column temperature, and this temperature dependence of HETP is apparently reduced by the addition of potassium iodide to PEG. This suggests that C is the most involved of the coefficients that participate in the temperature dependence of HETP in the high $\bar{U}$ region. Assuming that d_f is little dependent on column temperature between 150 and 170°, an increase in the column temperature should exert an opposite effect on C; an increase in D_L with decreasing viscosity of PEG leads to a decrease in C and a decrease in k has the opposite effect. The results in Fig. 4 indicate that the latter effect dominates the temperature dependence of HETP in the region above $\bar{U}_{min}$.

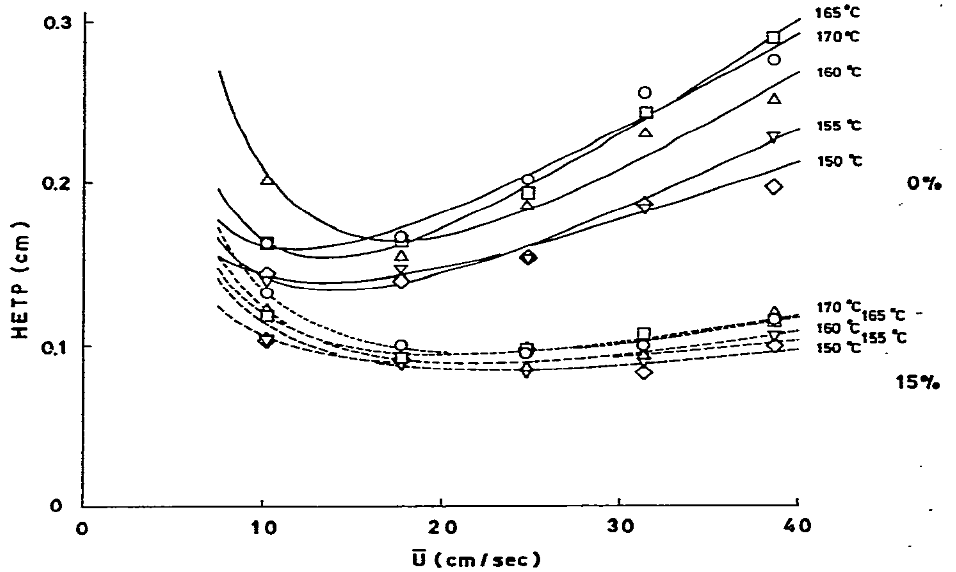

Fig. 4. Temperature dependence of HETP curve for 15% potassium iodide–PEG column (below) and potassium iodide-free column (above). ○, 170°; □, 165°; △, 160°, ▽, 155°; ◇, 150°.

Combined with the discussion given in the previous papers[7,8], the present results suggest that alkali metal iodide-containing PEG could have high column efficiencies and wide applicability to a variety of acid amides.

REFERENCES

1 A. W. Titherley, *J. Chem. Soc., London*, 79 (1901) 413.
2 P. Piret, L. Rodrique, Y. Gobillon and M. van Meerssche, *Acta Crystallogr.*, 20 (1966) 482.
3 T. Uno, K. Machida and I. Hamanaka, *Bull. Chem. Soc. Jap.*, 34 (1961) 1448.
4 N. Hamaguchi, T. Nakagawa and T. Uno, *Bull. Chem. Soc. Jap.*, submitted for publication.
5 L. R. Dawson, E. D. Wilhoit, R. R. Holms and P. G. Sears, *J. Amer. Chem. Soc.*, 79 (1957) 3004.
6 G. Somsen and L. Weeda, *Rec. Trav. Chim. Pay-Bas*, 90 (1971) 81.
7 N. Hamaguchi, T. Nakagawa and T. Uno, *J. Chromatogr.*, 147 (1978) 151.
8 N. Hamaguchi, T. Nakagawa and T. Uno, *J. Chromatogr.*, 170 (1979) in press.
9 J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.