Journal of Chromatography, 97 (1974) 15–18

CHROM. 7563

APIEZON L AS A STATIONARY PHASE FOR THE DETERMINATION OF ACTIVITY COEFFICIENTS BY LIQUID–LIQUID CHROMATOGRAPHY

PAOLO ALESSI and IRENEO KIKIC
Istituto di Chimica Applicata, Università di Trieste, Trieste (Italy)
(Received May 6th, 1974)

SUMMARY

The use of a stationary phase of high molecular weight in the determination of activity coefficients at infinite dilution by liquid–liquid chromatography (LLC) is described.

With Apiezon L as the stationary phase, the problem of mutual solubility with the mobile phase is overcome. Activity coefficients of hydrocarbons in acetonitrile and aniline determined by LLC are in good agreement with those reported in the literature.

INTRODUCTION

Liquid–liquid chromatography (LLC) is useful in the determination of thermodynamic quantities, for example activity coefficients, in those cases where gas–liquid chromatography (GLC) fails, that is when volatile solvents are used as the stationary phase. However, the activity coefficients obtained by LLC are higher than those found by other techniques.

In earlier work[1,2], we ascribed these discrepancies mainly to the mutual, even if slight, solubilities of the two solvents used as stationary and mobile phases. There are two means of lowering these mutual solubilities: decreasing the temperature (as discussed in previous work[2]), or changing the stationary phase. As the solubilities of the compounds of a homologous series in a pure solvent generally decrease with increasing molecular weight, in this work we have studied the variation of activity coefficients determined by LLC with changes in the molecular weight of the stationary phase.

EXPERIMENTAL

The experiments were carried out with an LLC apparatus of our own construction. The whole system was thermostatically controlled at 25 ± 0.01°. The separation columns were made of stainless steel with a length of 2 m and an I.D. of 4 mm, while the pre-columns were 1 m long. The packings for both columns were 25% (w/w) of stationary phase (*n*-hexadecane, squalane, Apiezon L) supported on 60–80 mesh Chromosorb P. The mobile phases (aniline, acetonitrile) were deaerated before use. The analyses of the fractions were carried out by GLC. As the main column pressure was close to 1 atm, the pressure term (A) in eqn. 1 (see later) was not considered because its value was negligible.

The GLC apparatus was a thermal conductivity chromatograph (Fractovap Model B, Carlo Erba, Milan, Italy). The eluent used was high-purity hydrogen. The stainless-steel pre-columns and columns were 2 m long and 4 mm I.D., packed with 25% (w/w) of stationary phase supported on 60–80 mesh Chromosorb P. The stationary phases were Apiezon L, squalane saturated with aniline and n-hexadecane saturated with aniline, saturation being achieved by equilibrating the two solvents at 25°. The various quantities appearing in eqn. 2, which gives the activity coefficients, were evaluated according to refs. 3 and 4. The solvents and solutes used in the LLC and GLC tests were reagent-grade products (Fluka, Buchs, Switzerland and BDH, Poole, Great Britain) with a minimum purity of 99.5 mole-%.

RESULTS AND DISCUSSION

By combining LLC and GLC, it is possible to determine the activity coefficients of solutes in polar solvents (mobile phase in LLC) using as the stationary phase in both GLC and LLC an apolar solvent of high molecular weight, for example, a paraffin (n-hexadecane, squalane, etc.). However, even for these solvents, the influence of the mutual solubilities is considerable, as confirmed by the results obtained using acetonitrile[5] and aniline as mobile phases (Tables I and II). In fact, the values obtained by LLC in these solvents should be considered as the activity coefficients of the solutes not in the pure solvents but rather in the saturated solvents, because the solvents as used in LLC are saturated, as shown in previous work[2].

TABLE I

COMPARISON BETWEEN ACTIVITY COEFFICIENTS IN ANILINE AT 25° DETERMINED BY LLC USING SQUALANE ($\ln \gamma_{i_{Sq}}^{\infty,A}$), n-HEXADECANE ($\ln \gamma_{i_{Hex}}^{\infty,A}$) AND APIEZON L ($\ln \gamma_{i_{AL}}^{\infty,A}$) AS STATIONARY PHASES AND THOSE IN THE LITERATURE[2] ($\ln \gamma_i^{\infty,A}$)

Compound	$\ln \gamma_i^{\infty,A}$	$\ln \gamma_{i_{Sq}}^{\infty,A}$	$\ln \gamma_{i_{Hex}}^{\infty,A}$	$\ln \gamma_{i_{AL}}^{\infty,A}$
n-Hexane	3.17	3.19	3.26	3.17
n-Heptane	3.40	3.44	3.46	3.41
n-Octane	3.67	3.68	3.70	3.67
1-Hexene	2.50	2.51	2.53	2.50
1-Heptene	2.72	3.74	2.76	2.72
1-Octene	2.94	2.99	3.01	2.93
Cyclohexane	2.54	2.56	2.59	2.55
Methylcyclohexane	2.83	2.86	2.87	2.83
Ethylcyclohexane	3.10	3.10	3.13	3.10
Benzene	0.79	0.82	1.04	0.80

In particular, Table I reports the activity coefficients of solutes in aniline as obtained by LLC in combination with the GLC determination of the activity coefficients of the same solutes in the stationary phases saturated with aniline (see eqn. 1). From this table, it can be seen that the increase in molecular weight of the stationary

TABLE II

COMPARISON BETWEEN ACTIVITY COEFFICIENTS IN ACETONITRILE AT 25° DETERMINED BY LLC USING SQUALANE[5] (ln $\gamma_{i_{Sq}}^{\infty,ACN}$) AND APIEZON L (ln $\gamma_{i_{AL}}^{\infty,ACN}$) AS STATIONARY PHASES AND THOSE IN THE LITERATURE[6,7] OBTAINED BY OTHER METHODS (ln $\gamma_i^{\infty,ACN}$)

Compound	*ln* $\gamma_i^{\infty,ACN}$	*ln* $\gamma_{i_{Sq}}^{\infty,ACN}$	*ln* $\gamma_{i_{AL}}^{\infty,ACN}$
n-Pentane	3.01 (ref. 6)	3.06	3.00
n-Hexane	3 24 (ref. 6)	3.42	3.24
n-Heptane	3.51 (ref. 7)	3.74	3.52
n-Octane		4.11	3.96
1-Pentene	2.24 (ref. 6)	2.24	2.24
1-Hexene		2.66	2.52
1-Heptene	2.70 (ref. 7)	3.00	2.73
1-Octene		3.37	3.04
Cyclohexane		3.20	3.05
Methylcyclohexane		3.46	3.34
Ethylcyclohexane		3.78	3.62
Benzene	0.99 (ref. 6)	1.12	1.02
Toluene		1.51	1.40
Ethylbenzene		1.83	1.75

phase has a positive influence: the discrepancy between the experimental results and those reported in the literature decreases on passing from *n*-hexadecane to squalane.

Therefore, a stationary phase with a higher molecular weight must be chosen, such as paraffin waxes, greases and polymers. When polymers are employed, the adsorption phenomena and the risk of swelling by the action of the mobile phase give rise to some difficulties.

For all the above substances, however, there is the problem of the lack of a well defined molecular weight (M_s), which interferes in the determination both of the ratios of activity coefficients by LLC[5] and of the activity coefficients of the stationary phase by GLC[8]:

$$\ln \left(V_{g_i}^0\right)_{\mathrm{LLC}} = \ln \left(\frac{\gamma_i^{m,\infty}}{\gamma_i^{s,\infty}}\right) + \ln \left(\frac{M_m}{M_s \varrho_m}\right) + A \tag{1}$$

$$\ln \gamma_i^{s,\infty} + \ln M_s = \ln \omega_s = \ln \left(\frac{273\ R}{(V_{g_i}^0)_{\mathrm{GLC}}\ P_i^0}\right) + B \tag{2}$$

where $V_{g_i}^0$ is the retention volume, M_m and M_s are the molecular weights of the mobile and stationary phase, ϱ_m is the density of the mobile phase, P_i^0 is the vapour pressure of pure solute, A is the pressure correction term and B is the correction for nonideality in gas phase.

This difficulty can be overcome by determining, by GLC, the quantities $\gamma_i^{s,\infty} M_s = \omega_s$ instead of the activity coefficients ($\gamma_i^{s,\infty}$). Considering eqns. 1 and 2 and taking into account $\gamma_i^{s,\infty} M_s = \omega_s$, we obtain

$$\ln \gamma_i^{m,\infty} = \ln (V_{g_i}^0)_{\mathrm{LLC}} - A + \ln \left(\frac{\varrho_m}{M_m}\right) + \ln \omega_s \tag{3}$$

Consequently, as the retention quantities are known from LLC and the term $\ln \omega_s$ from GLC, it is possible to calculate the activity coefficients of the solutes in the mobile phase.

According to eqn. 3, the activity coefficients of different hydrocarbons in aniline were determined by LLC using Apiezon L as stationary phase in GLC and LLC (Table I). The results obtained by LLC agree exactly with those found by GLC or by other methods[3], as confirmed by the complete insolubility between Apiezon L and aniline.

Apiezon L was then used for the determination of activity coefficients in acetonitrile, for which only a few values have been reported in the literature. The values so determined were compared with the "apparent activity coefficients" obtained by Locke[5] using squalane as the stationary phase and, where possible, with the values in the literature that had been obtained by other methods[6,7]. The agreement between the literature values and the values obtained by LLC using Apiezon L as stationary phase was very good.

It follows that an increase in the molecular weight of the solvent used as the stationary phase has the same effect as a decrease in the operating temperature: in both instances the mutual solubility decreases so that the activity coefficients in pure solvents can be determined directly.

It can therefore be stated that Apiezon L can be used successfully as a stationary phase in LLC with all polar solvents that are insoluble in it: this opens a new and interesting method, complementary to GLC, for the determination of activity coefficients.

ACKNOWLEDGEMENT

This work was supported by the National Research Council (C.N.R.), Centro di Chimica Analitica Strumentale, Bari, Italy.

REFERENCES

1 P. Alessi and I. Kikic, *Chromatographia*, 7 (1974) 299.
2 P. Alessi and I. Kikic, *Gazz. Chim. Ital.*, in press.
3 D. H. Desty and W. T. Swanton, *J. Phys. Chem.*, 65 (1961) 766.
4 P. Alessi, I. Kikic and G. Tlustos, *Chim. Ind. (Milan)*, 52 (1970) 1197.
5 D. C. Locke, *J. Chromatogr.*, 35 (1968) 24.
6 J. A. Gerster, J. A. Gorton and R. Eklund, *J. Chem. Eng. Data*, 5 (1960) 423.
7 I. Kikic and P. Alessi, in preparation.