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Abstract

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ON THE GAS-CHROMATOGRAPHIC DETERMINATION OF THE SOLUBILITY OF GASES AND VAPORS IN LIQUIDS

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In the work that opened gas-liquid chromatography [1], James and Martin noted the possibility of using it for physicochemical investigations, in particular for determining solubility. Later, in works [2–5], the solubilities of volatile substances in nonvolatile liquids were determined using analytical chromatographs. In the present work, simple apparatus is proposed, specially intended for absolute measurements of the solubility of gases and vapors both in low-volatile and in highly volatile liquids, and an estimate is given of the accuracy and possibilities of the chromatographic method.

The apparatus differs from the usual one [6] by the use of sealed columns (Fig. 1). A filled column is closed with self-sealing rubber stoppers (used for preserving sterile medical preparations, for example penicillin) and is connected to the system by means of injection needles. Columns of this construction can be connected to one another in any combinations within a few seconds, connected in the required sequence to the chromatograph, and disconnected for weighing, while remaining sealed. For thermostating the columns, a liquid thermostat (Fig. 1) is used instead of the customarily used air thermostat; this makes it possible to manipulate the columns without disturbing the thermal equilibrium in the system. The installation may be independent or may serve as an attachment to an analytical chromatograph*; the working procedure is the usual one (see, for example, [6]), except for the filling of the columns.

With the usually employed filling of columns, the losses of liquid, judging from the values of K, reach $\sim$ 10%. To eliminate this error, the packing of the columns, of precisely known composition, was prepared in a closed vessel with an outlet. The packing was poured through the outlet into the column, taking into account (by weight balance) the amount of liquid that evaporated during the process of filling the column.

An example of a chromatogram is given in Fig. 2. The calculation is carried out according to the formula:

$$K = \frac{t'_g \cdot V_0}{\rho W}, \tag{1}$$

where K is the distribution coefficient between the liquid and gas phases at equal phase volumes; ρ, W are the density and weight of the liquid phase in the column; V_0 is the mean volumetric flow rate of the carrier gas, taking into account the pressure drop in the column [6]; t'_g is the retention time from the "air" peak (Fig. 2). Determination of K is possible in the region of applicability of Henry' s law, where the value of K does not depend on concentration [6].

The use of columns whose construction is shown in Fig. 1 makes it possible to control accurately the amount of stationary liquid in the column and, consequently, to work with volatile liquids, such as, for example, acetone at 25°. By weighing the column before and after the experiment, it is easy to deter–

* We used KhL-3 chromatographs with a thermal-conductivity detector, Khrom-1 with a flame-ionization detector, and a homemade combustion-heat detector.

measure the losses of liquid in the column during the experiment and take this into account in the calculation. The usual design of the column would not make it possible to obtain absolute values of the distribution coefficients for volatile liquids. Without precise control of the weight of the liquid, for comparatively low-volatility liquids the absolute values obtained may be inaccurate. Thus, for N,N-dimethylformamide with a vapor pressure of 3.7 mm Hg (at 25°), the losses of liquid during the experiment reached 3%.

Fig. 1. Cross section of a liquid thermostat with columns. 1—Dewar vessel; 2—saturator; 3—columns: *a*—self-sealing stoppers, *b*—glass capillaries, *v*—clamp; 4—holder.

Another advantage of the column design is the ease of checking the uniformity of the filling of the column along its length (which is necessary when using equation (1)). For this it is sufficient to interchange the inlet and outlet of the column and make sure that the time t'_g remains unchanged.

In our work, a series of experiments showed that the values of the distribution coefficients obtained by the chromatographic method do not systematically depend on the amount of stationary phase, the carrier-gas flow rate, the length of the column, the nature of the solid support, or the carrier gas. This is in complete agreement with the data of work (3), obtained on other objects. In addition, the influence of these parameters on the accuracy of the results obtained was investigated. It turned out that the accuracy of the chromatographic values depends to the greatest extent on the losses of the deposited liquid during filling of the column. This is evident from the fact that the reproducibility of measurements (on one co-

Table 1

Accuracy of absolute and relative measurements of the distribution coefficients (K) of acetylene hydrocarbons at 25°

Component	Solvent	K^*_{abs}	Mean deviation, %, one column	Mean deviation, %, different columns	K^{**}_{rel}	Mean deviation, %, relative
Acetylene	N,N-Dimethylformamide	35.5	0.55	2.1		
Methylacetylene	N,N-Dimethylformamide	68.0	0.50	1.8	67.9	0.43
Ethylacetylene	N,N-Dimethylformamide	143	0.24	1.9	142.8	0.80
Vinylacetylene	N,N-Dimethylformamide	274.6	0.48	2.2	274.6	1.12
Acetylene	N-Methylpyrrolidone	43.2	0.80	2.0		
Allene	N-Methylpyrrolidone	27.7	–	2.2	28.2	0.80
Methylacetylene	N-Methylpyrrolidone	73.0	0.50	–	73.4	0.94
Vinylacetylene	N-Methylpyrrolidone	342	0.90	–	341.4	1.10

* Calculated by formula (1).
** Calculated from the ratio of times t'_g and the known value of K of another component.

Table 2

Comparison of distribution constants of acetylenic hydrocarbons obtained by chromatographic and static* methods

Solvent	C_2H_2			C_3H_4			C_4H_4		
	K_{chr}	K_{st}	ΔK, %	K_{chr}	K_s	ΔK, %	K_{chr}	K_{st}	ΔK, %
NN-Dimethylformamide	35.5	34.2 (7)	−3.7	68.0	65 (10)	−4.4	275	227 (11)	−17.5
NN-Dimethylformamide	35.5	34.2 (10)	−3.7	68.0	65 (10)	−4.4	275	227 (11)	−17.5
NN-Dimethylformamide	35.5	36.6 (8)	+3.7	68.0	65 (10)	−4.4	275	227 (11)	−17.5
NN-Dimethylformamide	35.5	33.1 (9)	−6.8	68.0	65 (10)	−4.4	275	227 (11)	−17.5

Solvent	C_2H_2	C_3H_4	C_4H_4						
NN-Dimethylformamide + 10% water**	19.7	20.3 (11)	+3.0	38.9	37.7 (11)	−3.0	130.6	111 (11)	−10
N-Methylpyrrolidone**	43.2	39.8 (9)*	−7.9						
Acetone	21.7	22 (12)	−1.4						

* Henry constants from the original works were recalculated as distribution-coefficient values.
** Chromatographic values were obtained by the usual column-packing procedure.

lies within 0.5–1%, while the absolute values of K obtained for different columns deviate from the mean by 2%. At the same time, no such difference is observed for the relative values, and their scatter is close to the reproducibility of measurements on a single column (Table 1).

The values of the distribution coefficients obtained chromatographically were compared with values calculated from static measurements of solubility. As can be seen from the data in Table 2, the chromatographic values either do not differ from the static ones (within the limits of the data of different authors), or are higher than the latter.

Distribution coefficients are the principal quantity determining the behavior of substances in the column; they enter directly into the equation given by the theory. Therefore the values of the distribution coefficients obtained from the chromatogram are more correct than those calculated from static data.

(Figure: Fig. 2. Chromatogram of a mixture of air (1), allene (2), acetylene (3), and methylacetylene (4). The arrows indicate retention times according to formula (1).)

Fig. 2. Chromatogram of a mixture of air (1), allene (2), acetylene (3), and methylacetylene (4). The arrows indicate retention times according to formula (1).

In a number of cases chromatography makes it possible to determine the effect of a third volatile component on the solubility of a gas in a liquid. The measurement procedure remains the same; only the carrier gas is changed, the role of which is to be played by the third component under study. We, for example, investigated the effect of acetylene on the solubility of higher homologues when acetylene was used as the carrier gas. Such ternary systems can be studied chromatographically in the region of any pressures, with appropriate changes in the apparatus.

Distribution coefficients were determined for some of the acetylenic hydrocarbons in N,N-dimethylformamide with the addition of 10% water. For chromatography here it seemed possible to obtain overestimated—

results if the water molecules are adsorbed by the support and "drop out" of the exchange. However, the agreement of the obtained values with the data of static measurements was quite satisfactory. The most important advantage of the chromatographic method over the static one proves to be its speed and the possibility of working with impure substances and mixtures of substances. For example, we measured K for allene only because the methylacetylene used in the work contained it as an impurity. At the same time, for static measurements the purity of the gas is of primary importance.

The chromatographic determination of the distribution coefficient (Henry' s constant) of a single substance, or the simultaneous determination of Henry' s constants for a series of substances, takes 1–3 hours. If the value of K is known for at least one of the components, then the determination for the others is faster and simpler.

The chromatographic method, in its present form, is suitable only in the linear region of the absorption isotherm; but if, in the operating pressure range (usually up to 10 mm Hg), the isotherm is nonlinear, this is evident from the asymmetry of the peak and from the dependence of its position on the sample volume. To obtain a complete picture of the behavior of a given system, the chromatographic and static methods should be combined: the chromatographic method for determining Henry' s constant, and the static method for the isotherm in the nonlinear region.

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REFERENCES

1. A. T. James, A. J. P. Martin, *Biochem. J.*, **50**, No. 5, 679 (1955).

2. A. B. Littlewood, C. S. G. Phillips, D. T. Price, *J. Chem. Soc.*, **1955**, 14.

3. P. E. Porter, C. H. Deal, F. H. Stross, *J. Am. Chem. Soc.*, **78**, No. 13, 2999 (1956).

4. E. R. Adlard, *Symp. on Vapour Phase Chromatography* Inst. of Petr., London, 1956.

5. A. Kvantes, G. Reinders, in: *Gas Chromatography*, IL, 1961.

6. A. Keulemans, *Gas Chromatography*, IL, 1959.

7. W. B. Howard, E. P. Schoch, F. P. Mayforth, *Petrol. Refiner.*, **33**, No. 1, 143 (1954).

8. A. C. McKinnis, *Ind. and Eng. Chem.*, **47**, 850 (1955).

9. P. Hölemann, R. Hasselmann, *Forschungsber. des Wirtschaft- und Verkehrminist.*, Nordheim—Westfalie, 1954.

10. E. Haidegger, I. Szebenyi, A. Szekely, *Magyar kém. folyóirat*, **64**, No. 10, 365 (1958).

11. G. E. Braude, M. A. Leites, I. V. Dedova, *Khim. prom.*, No. 4, 232 (1961).

12. A. Seidell, *Solubilities of Organic Compound*, **2**, III Ed., N. Y., 1941.

Note: Figure translations are in progress. See original paper for figures.