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APPLICATION OF GAS CHROMATOGRAPHIC HEADSPACE ANALYSIS TO THE CHARACTERIZATION OF CHEMICAL EQUILIBRIA IN SOLUTIONS

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SUMMARY

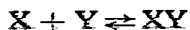
The possibility is considered of using headspace analysis in studies of chemical equilibria in solutions of volatile organic compounds. The main theoretical relationships for the determination of the constants of $X + Y \rightleftharpoons XY$ type equilibria by the gas chromatographic analysis of equilibrated vapour above a solution are derived. New methods are proposed and have been checked experimentally for the measurement of the ionization constants of volatile organic compounds, and of the stability constants of metal complexes with unsaturated and aromatic hydrocarbons.

INTRODUCTION

Because of their wide use and obvious advantages, gas chromatographic methods for the characterization of liquids and solids based on the analysis of the equilibrated vapour phase, the so-called headspace analysis (HSA), are important not only to analytical chemists working with industrial and agricultural products and biochemical and medical personnel¹, but also to chemical research workers engaged in the determination of various physico-chemical parameters. Indeed, the possibility of employing HSA for the characterization of non-ideal solutions has recently been pointed out². Binary systems exhibiting positive and negative deviations from Raoult's law have been used to illustrate the possibility of determining activity coefficients and some thermodynamic functions. In this paper, we wish to draw attention to an interesting and promising application of HSA to the determination of the constants of chemical equilibria in solutions with volatile organic compounds.

THEORETICAL

Consider the simplest case of a chemical equilibrium which is the reversible interaction of equimolecular amounts of components X and Y involving the formation of an adduct XY:



only one of the reagents (X) being volatile and thus present in the vapour above the solution.

To determine the equilibrium constant

$$K = \frac{[X][Y]}{[XY]} \quad (1)$$

it is sufficient in this instance to measure the equilibrium concentration of the volatile reagent X in the vapour above two solutions with different concentrations of the non-volatile reagent Y. Indeed, if the total amount of the volatile reagent in a heterogeneous vapour-liquid system is maintained constant while varying the concentration of the non-volatile reagent from [Y] to [Y'], then the balancing equation can be written in the form

$$C_x v_g + [X] v_l + \frac{[X][Y] v_l}{K} = C_x' v_g + [X'] v_l + \frac{[X'] [Y'] v_l}{K} \quad (2)$$

where C_x and C_x' are the equilibrium concentrations of component X in the gas phase of the corresponding solutions, and v_g and v_l are the gas and liquid phase volumes, respectively. Assuming the partition coefficient, K_p , of component X to be constant, one can take write that

$$K_p = \frac{[X]}{C_x} = \frac{[X']}{C_x'}$$

after which eqn. 2 reduced to

$$K = \frac{(C_x [Y] - C_x' [Y']) K_p v_l}{(C_x' - C_x) (v_g + K_p v_l)} \quad (3)$$

Vapour sample collection for a gas chromatographic determination of the concentrations C_x and C_x' without violating the equilibrium in the system can be performed by the technique making use of variable-volume vessels representing essentially thermostated glass hypodermic syringes developed in our laboratory³. The same technique can be employed in the determination of the partition coefficients, K_p (ref. 4).

Depending on the actual numerical values of the constants K and K_p , and on the methods of selecting (or determining) the concentrations [Y] and [Y'], the general relationship expressed in eqn. 3 can be simplified and modified to fit the study of specific chemical equilibria in solutions, *e.g.*, dissociation of volatile organic bases or complexing with volatile ligands. This will be discussed below, after giving the basic experimental data.

EXPERIMENTAL

Commercial preparations of hydrocarbons, amines and pyridine were used. The amines and pyridine were additionally purified by distillation in a rectification column.

The samples were analyzed on a Tsvet-102 chromatograph with a flame-ionization detector under the conditions specified in Table I.

The initial ligand concentration in solution when studying the complex stability

TABLE I
CONDITIONS OF GAS CHROMATOGRAPHIC ANALYSIS

Chromatographic parameters	Compounds to be analyzed				
	Olefins	Aromatic hydrocarbons	Amines		
			Trimethylamine and pyridine	Diisopropylamine	Aromatic
Stationary phase	Triethylene glycol butyrate	Polyethylene glycol adipate	Polyethylene Polyox-100 + Na ₃ PO ₄	Pennwalt 223 + KOH	Polyethylene Polyox-100 + Na ₃ PO ₄
Amount of stationary phase (%)	30	20	10/1	28/4	10/1
Support, particle diameter (mm)	Spherochrome-1, 0.25-0.375	Spherochrome-1, 0.20-0.25	Chromosorb W, 0.20-0.25	Gas-Chrom R, 0.16-0.20	Chromosorb W, 0.20-0.25
Column length (m)	6	2	2	2	2
Column temperature (°C)	30	90	100	100	135
Carrier gas	Argon	Argon	Nitrogen	Nitrogen	Helium
Carrier gas flow-rate (ml/min)	55	60	60	60	60
Gas sample valve temperature (°C)	40	100	130	130	130
Sample volume (ml)	1	1	1.5	1.5	1.5

constants was 10^2 – 10^{-3} %. Such concentrations of gaseous hydrocarbons in solution were prepared by introducing 0.3–0.8 ml of the compound of interest into the reaction vessel with the known gas-to-liquid volume ratio ($V_g/V_l = 0.5$ – 2). The values of the liquid–gas partition coefficients required to calculate the stability constant and the pre-set olefin concentration in solution were determined by the method based on measuring the change in the concentration of a compound in the gas phase with the equilibrated gas replaced with pure gas³. Liquid substances were introduced into the reaction vessel in the form of a solution, its concentration being adjusted to the required level by diluting a saturated aqueous solution of the corresponding hydrocarbon.

To determine the stability constants of weak complexes, the reaction vessel, after introducing the ligand, was thermostated to within $\pm 0.1^\circ\text{C}$ for 30–40 min under continuous stirring. Next, the gas phase was injected into the chromatograph (5–10 samples) and the peak area corresponding to C_g° was determined.

The complexing agent was introduced into the reaction vessel in the form of a solution of known concentration by means of a hypodermic syringe. The amount of the solution introduced was determined by weighing it to ± 0.3 %. After the injection of the complexing agent, the system was shaken periodically for 1–1.5 h. Next, the gas phase was chromatographed and the peak area corresponding to C_g' measured.

The value of pK was determined in the following way. Some of a buffer solution containing the compounds under study at concentrations of 0.07–0.5% was introduced into the reaction vessel³ thermostated at $25 \pm 0.1^\circ$. The system was shaken periodically for 30 min to establish equilibrium, after which the equilibrated gas was injected into the chromatographic column by means of a thermostated gas

sample valve⁴. The peak areas were measured with a Takeda-Riken TR-2213 digital integrator.

It should be pointed out that in order to exclude errors associated with the strong sorption of amines, the tubes admitting the gas under study to the chromatograph were saturated, prior to the analysis of the equilibrated gas phase, with an auxiliary gas sample containing the amines of interest in concentrations close to those encountered in the gas to be analyzed.

STUDY OF SPECIFIC CHEMICAL EQUILIBRIA IN SOLUTIONS

Determination of ionization constants of volatile organic compounds by the HSA method

The basicity of a volatile compound B can be characterized by the dissociation constant of the conjugated acid BH⁺:

$$K_{\text{BH}^+} = \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} \quad (4)$$

As eqn. 4 is only a special case of eqn. 1 at X = B, Y = H⁺ and XY = BH⁺, one can use eqn. 3 to calculate K_{BH⁺}. The partition coefficient of volatile organic bases between water and air is usually sufficiently high so that K_p ≫ v_g/v_l. If the magnitude of K_p is unknown, the constancy of [B] with the equilibrium gas being replaced with a pure gas may serve as a criterion for meeting this condition. In this case, neglecting the possibility of ionization of the base in the gas phase, eqn. 3 reduces to a simpler equation:

$$K_{\text{BH}^+} = \frac{\frac{C_{\text{B}}}{C'_{\text{B}}} [\text{H}^+] - [(\text{H}^+)]'}{1 - \frac{C_{\text{B}}}{C'_{\text{B}}}} \quad (5)$$

If equal volumes of the vapour samples are injected into a gas chromatograph at different pH values of the solutions, the concentration ratio of the free base in the vapours, C_B/C'_B, can be replaced with the ratio of the areas of the corresponding peaks in the chromatograms, S_B and S'_B, or simply by the ratio of the integrator readings:

$$K_{\text{BH}^+} = \frac{\frac{S_{\text{B}}}{S'_{\text{B}}} [\text{H}^+] - [(\text{H}^+)]'}{1 - \frac{S_{\text{B}}}{S'_{\text{B}}}} \quad (6)$$

The proposed method of determining the basicity constants of volatile organic compounds thus reduces to measuring the peak area ratio for the free bases in the vapour chromatograms of solutions with different hydrogen ion concentrations. The latter can be measured directly with a hydrogen electrode or can simply be fixed by employing buffer solutions with accurately known values of pH. In this simplest version, the proposed method of the basicity constant determination consists in injecting equal amounts of the base-containing compound of interest into a pre-determined volume of buffer solutions with different values of pH, chromatographing the equilibrated vapours of these solutions and calculating K_{BH⁺} with eqn. 6.

It should be stressed that such a determination of the basicity constants can be

carried out in complex mixtures of compounds of different nature and different volatility, even if the total quantitative and qualitative compositions of these mixtures remain unknown. However, in order to obtain sufficiently accurate results, it is essential to select the pH value of the solutions under study such that the peak areas S_B and S'_B are determined with the maximum accuracy possible and that the operating pH range lies in the region of maximum sensitivity of the areas S_B to the change in pH. The quantity pK_{BH^+} corresponds to the centre of this region, and therefore solutions with $pH \approx pK_{BH^+} \pm 1$ will be optimal for the measurement of K_{BH^+} . The magnitudes of pK_{BH^+} for most volatile organic bases (amines, hydrazines, nitrogen heterocyclic compounds) lie from 4 to 11, and all of this range can be covered by four or five buffer solutions with pH 3–12. It is these four or five solutions that should be used in determining the basicity constants by the proposed version of the gas chromatographic method.

The results of these determinations, listed in Table II, indicate that the accuracy of pK_{BH^+} of the order of ± 0.2 pK units reached is sufficient for the purposes of qualitative analysis and classification. The method proposed can also be used when known techniques of determining the basicity constants cannot be employed (e.g., the characterization of complex mixtures of unknown composition) and represent an additional useful tool.

TABLE II

DETERMINATION OF BASICITY CONSTANTS BY THE GAS CHROMATOGRAPHIC HSA METHOD

Base	pH and pH'	Base peak area (\bar{S}) on vapour chromatogram (integrator reading)	Values of pK_{BH^+}		Error, I–II
			By eqn. 6 (I)	Literature data (II)	
Diisopropylamine	11.27	175,657	11.30	11.05 ⁵	+ 0.25
	11.58	238,234			
Trimethylamine	8.82	22,241	9.65	9.80 ⁶	– 0.15
	10.10	127,709			
Aniline	4.45	68,063	4.65	4.61 ⁶	+ 0.04
	6.15	169,726			
Diethylamine	5.42	7117	6.66	6.56 ⁶	+ 0.10
	6.80	75,910			
Pyridine	4.45	20,541	5.51	5.25 ⁵	+ 0.26
	6.80	242,494			

Determination of stability constants of complexes with volatile ligands

If we introduce into a heterogeneous gas–liquid system containing a volatile ligand X without a complexing agent ($[Y] = 0$), a non-volatile complexing agent in an amount corresponding to its concentration in the liquid phase $[M]$, the ligand concentration in the vapour will decrease from the original value C_x to C'_x . For low stability constants $K_{st} = 1/K$ (< 100) and low ligand concentrations in solution (10^{-3} – $10^{-4}\%$), one can assume $[Y']$ to be approximately equal to $[M]$, so that eqn. 3 will become

$$K_{st} = \left(\frac{C_x}{C'_x} - 1 \right) \cdot \frac{v_g + K_p v_l}{K_p v_l [M]} \quad (7)$$

or, replacing the ligand concentration ratio by the ratio of the peak areas on chromatograms obtained from equal samples of vapour over the solution,

$$K_{st} = \left(\frac{S_x}{S'_x} - 1 \right) \cdot \frac{v_g + K_p v_l}{K_p v_l [M]} \quad (8)$$

Thus, as for the basicity constants, the problem of determining the stability constants of complexes reduces to the measurement of the peak area ratio on the vapour chromatograms of two solutions, one of which does not contain the complexing agent while the other contains it at a concentration [M].

The applicability of the proposed method and of eqn. 8 was checked on well studied cases of complexing of silver salts with olefins and aromatic hydrocarbons in aqueous solutions.

Table III presents a comparison of the stability constants obtained by this method for silver complexes of four simple olefins and two aromatic hydrocarbons with the data available in the literature. The comparison shows a fairly good agreement with the results obtained by both static and dynamic methods. A larger disagreement with the results obtained by the dynamic method for *α*- and *cis*-butenes can be attributed to the poor accuracy inherent in the dynamic determination of small partition coefficients of olefins in volatile solvents ($K_p < 0.1$).

TABLE III

STABILITY CONSTANTS OF SILVER AND THALLIUM NITRATE COMPLEXES WITH HYDROCARBONS IN AQUEOUS SOLUTION AT 25°

Ligand	Silver nitrate		Thallium nitrate	
	Obtained by injection of complexing agent into system	Literature data		Obtained by injection of complexing agent into system
		Static method	Dynamic method	
Ethylene	88.9 ± 4.0	85.3 ⁹	85 ⁵	7.6 ± 3.1
Propylene	70.8 ± 4.2	87.2 ⁹	79 ⁵	5.1 ± 2.3
<i>α</i> -Butene	121.8 ± 8.7	119.4 ⁹	110 ⁵	7.7 ± 3.0
<i>cis</i> -Butene	65.9 ± 2.8	62.3 ⁹	83 ⁵	4.7 ± 1.4
Benzene	2.67 ± 0.13	2.41 ⁷	1.58 ^{*a}	0.65 ± 0.04
Toluene	3.19 ± 0.16	2.95 ⁷	1.19 ⁵	0.93 ± 0.04

* Data for calculation obtained at 23.2°.

The application of the proposed method in the study of weak interactions ($K_{st} < 10$) is illustrated by the data on the silver nitrate complexes with benzene and toluene, which agree well with the results of the static method based on spectrographic analysis⁷ while differing considerably from the constants obtained by the dynamic method⁵. Good agreement between the results obtained by static methods based on different principles permits one to consider the values of the constants of weak complexes obtained under static conditions to be more reliable and accurate. Such weak interactions apparently do not permit one to use the dynamic gas chromatographic method successfully in this case.

The possibilities offered by the proposed method in the determination of the K_{st} values of weak complexes are also illustrated by the results of a study of thallium

nitrate complexes with hydrocarbons. The data listed in Table III show that even for fairly weak complexes with aromatic hydrocarbons a good agreement is obtained, relative variations in the value of the constant not exceeding 5%. The relative error of K_{st} depends, however, essentially on the values of K_p , so that for olefin complexes it reaches a few tens percent despite the considerably larger absolute value of K_{st} .

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