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SPURIOUS ADSORPTION EFFECTS IN HEADSPACE-GAS DETERMINATION OF HYDROCARBONS IN WATER*

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SUMMARY

The adsorption of benzene, hexane, heptane and octane at the phase interfaces in a gas–water system representing those used in static headspace-gas trace analysis was investigated. The apparent bulk water–gas distribution constants, calculated from the known total amounts of the model solutes and their gas-phase contents determined analytically, true bulk water–gas distribution constants, determined directly by analysis of both the aqueous and gaseous phases, and water surface–gas adsorption distribution constants, calculated from the solute mass balance, are presented and discussed. Adsorption phenomena were shown to play a significant rôle with alkanes in gas–aqueous liquid systems.

INTRODUCTION

The properties of water at an interface differ from those of bulk water[1]. It has been shown[2-5] that water at the vapour–liquid interface constitutes a low-energy surface with the hydrogens oriented towards the vapour phase. This apparently gives rise to significant surface phenomena when a sparingly water-soluble compound is introduced into a gas–aqueous liquid system, and several interesting measurements of the adsorption of vapours of hydrocarbons and other weakly polar compounds on water surfaces have been performed, employing both classical methods[6,7] and gas chromatography (GC)[8,9]. In general, the surface phenomena that occur in headspace-gas analysis are of the same nature as those dealt with in the studies quoted above. However, since the extent to which these phenomena are manifested with a given solute and a given composition of the condensed phase depends largely on the physical characteristics of the system, their rôle in headspace-gas analysis should be studied in a representative system.

Analytes which are well soluble in the condensed phase occur almost totally in

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the bulk condensed phase and in the gaseous phase. However, sparingly soluble analytes may be adsorbed to a large extent at the phase interfaces. This spurious adsorption may cause serious errors in the determination of absolute quantitative data. The aim of this work is to evaluate these effects by measurement of the true and apparent distribution constants of hydrocarbons in gas–water systems. The true distribution constants were determined by direct analysis of samples of both phases. while the apparent ones were obtained from the known total content of the analyte in the system and the analytically determined content in the gaseous phase.

THEORETICAL

Analyte mass balance

At equilibrium. the total mass of analyte a in the system, W_a. is distributed between the gaseous phase, liquid phase and interfaces XY, the respective masses of the analyte being W_{aG}, W_{aL} and ΣW_a^{XY}. Hence:

$$W_a = W_{aG} + W_{aL} + \Sigma W_a^{XY} \tag{1}$$

Since

$$W_{aG} = c_{aG} V_G \tag{2}$$

$$W_{aL} = W_{aG} K_L V_L / V_G = c_{aG} K_L V_L \tag{3}$$

$$\Sigma W_a^{XY} = W_{aG} (\Sigma K^{XY} S_{XY}) / V_G = c_{aG} (\Sigma K^{XY} S_{XY}) \tag{4}$$

where c_{aG} is the concentration (mass/volume) of the analyte in the gaseous phase, V_G and V_L are the volumes of the gaseous and liquid phases, K_L and K^{XY} are the true bulk liquid–gas distribution constant of the analyte and a distribution constant for the adsorption of analyte at a phase interface XY and S_{XY} is the surface area of the interface XY. eqn. 1 can be rewritten as:

$$W_a = c_{aG}[V_G + K_L V_L + \Sigma(K^{XY} S_{XY})] \tag{5}$$

It is also possible to write

$$W_a = c_{aG}(V_G + K_L^* V_L) \tag{6}$$

where K_L^* is the apparent bulk liquid–gas distribution constant of the analyte. Employing eqns. 5 and 6, the quantity $\Sigma(K^{XY} S_{XY})$ can be expressed by the relation

$$\Sigma(K^{XY} S_{XY}) = W_a/c_{aG} - V_G - K_L V_L = V_L(K_L^* - K_L) \tag{7}$$

and eqn. 4 combined with the last term of relation 7 yields:

$$\Sigma W_a^{XY} = c_{aG} V_L (K_L^* - K_L) \tag{8}$$

EXPERIMENTAL

Measurement of true distribution constants

The measurement of true distribution constants of hydrocarbons in aqueous liquid–gas systems has been described in detail elsewhere[10], and only a brief outline will be given here. The instrumental arrangement employed is shown schematically in Fig. 1. A model gaseous mixture with adjusted analyte content is drawn with the aid of a pump (2) through the aqueous phase (vessel 1) until equilibrium is attained. Then a defined volume, $V_{G,s}$, of the gaseous phase is injected into the gas chromatograph, thereby recording the peak area, $A_{a,G}$, and a defined volume, $V_{w,s}$, of the liquid phase, measured in a burette (10), is drawn through a short column (8) packed with an organic adsorbent. The residual liquid is pushed out of the column by a stream of nitrogen (valve 12), and the hydrocarbon entrapped is thermally desorbed and analyzed by gas chromatography (peak area $A_{a,w}$). The value of K_L is calculated by

$$K_L = \frac{A_{a,w}}{A_{a,G}} \cdot \frac{V_{G,s}}{V_{w,s} + v} \cdot \frac{T_s}{T_a}$$

where v is a correction for residual water in the trap and connecting lines, and T_s and T_a are the absolute temperatures of the equilibration vessel and of the room, respectively.

Measurement of apparent distribution constants

A schematic representation of the apparatus for the measurement of apparent distribution constants is shown in Fig. 2. The procedure is as follows. A volume of distilled water is transferred by means of injection syringe 4 from container 5 to a 254-ml flask (1) placed in a thermostatted water-bath (3) and provided with a magnetic stirrer (2). The flask is partially evacuated via septum 6, a 10-ml charge (v_G^0) of a model gaseous mixture of known analyte concentration, c_{aG}^0, is introduced by a 50-ml injection syringe (Chirana, Brno, Czechoslovakia), the pressure inside the flask is
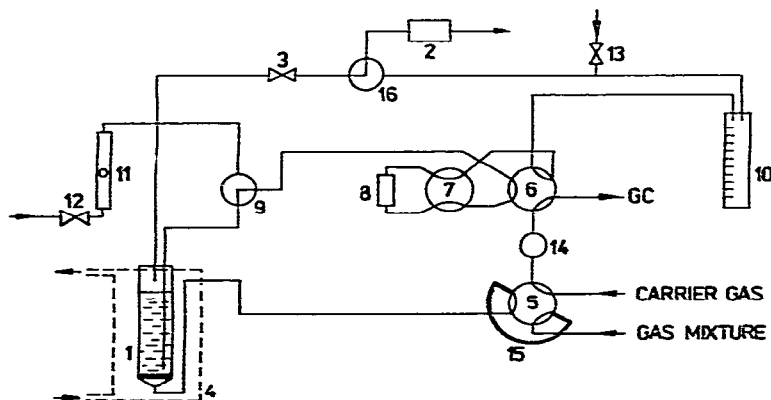

Fig. 1. Schematic representation of the arrangement for measuring the true water–nitrogen distribution constants. 1 = Equilibrium vessel; 2 = pump; 3, 12, 13 = needle valves; 4 = thermostatted water-jacket; 5, 6, 7, 9, 16 = valves; 8 = adsorption tube; 10 = burette; 11 = flow meter; 14 = injection port; 15 = sampling loop.
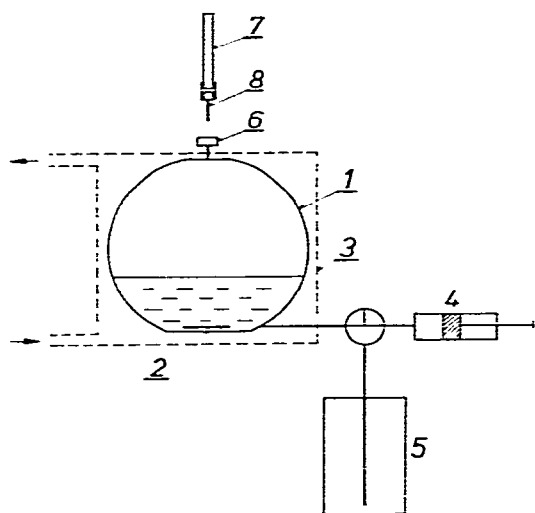
Fig. 2. Schematic representation of the arrangement for measuring the apparent water–air distribution constants.

brought to atmospheric pressure and several hours are allowed to equilibrate the system while continuously stirring the liquid phase. Another 10-ml charge (v_G^0) of the model gaseous mixture is drawn through a trap packed with Tenax GC. The deposit entrapped is thermally desorbed and introduced into the gas chromatograph, thereby recording the peak area, A_a^0. The same Tenax trap (7) is connected, via injection needle 8 drawn through the septum, with the gas phase inside the flask. When the system is at equilibrium, a 30-ml volume ($v_{G,s}$) of the gaseous phase is pushed out through the trap by distilled water supplied gently from syringe 4, and the deposit entrapped is again analyzed by GC, thereby recording the peak area, $A_{a,s}$. The apparent distribution constant is calculated on the basis of the mass balance

$$c_{aG}^0 v_G^0 = c_{aG} V_G + c_{aL} V_L \qquad (9)$$

where c_{aG} and c_{aL} are the equilibrium concentrations of the analyte in the gaseous and liquid phases of the system containing the total mass $W_a = c_{aG}^0 v_G^0$ of the analyte added, and V_G and V_L are the volumes of the gaseous and liquid phases. Since $c_{aL} = K_L^* c_{aG}$, the apparent distribution constant can be expressed as:

$$K_L^* = \frac{V_G}{V_L}\left(\frac{v_G^0}{V_G} \cdot \frac{c_{aG}^0}{c_{aG}} - 1 \right) \qquad (10)$$

The peak areas recorded when analysing the model gas mixture and the gaseous phase of the equilibrated system are, respectively

$$A_a^0 = k c_{aG}^0 v_G^0 \qquad (11)$$

$$A_{a,s} = k c_{aG} v_{G,s} \qquad (12)$$

where k is a calibration factor, and combination of eqns. 10–12 yields:

$$K_L^* = \frac{V_G}{V_L}\left(\frac{A_a^0}{A_{a,s}}\cdot\frac{v_{G,s}}{V_G} - 1\right)$$ (13)

The concentration c_{aG} can readily be calculated with the aid of eqns. 10 and 13:

$$c_{aG} = \frac{A_{a,s}}{A_a^0}\cdot\frac{v_G^0}{v_{G,s}}\cdot c_{aG}^0$$ (14)

The Tenax trap was a 6 cm × 3 mm I.D. glass tube packed with about 60 mg of Tenax GC (30–60 mesh) (Applied Science Labs., State College, PA, U.S.A.). The desorption of the analytes entrapped was carried out at 170°C. The equipment and procedure for transferring the concentrate from the trap into the gas chromatograph has been described in detail elsewhere[11]. The GC analyses were carried out on a Hewlett-Packard 402 gas chromatograph (Hewlett-Packard, Avondale, PA, U.S.A.) equipped with a flame ionization detector and a 180 cm × 3 mm I.D. glass column packed with 10 wt. % Apiezon K (AEI, Manchester, Great Britain) on Chromaton NAW DMCS (90–120 mesh) (Lachema, Brno, Czechoslovakia) and kept at 130°C. The peak areas were measured with an Infotronics CRS 101 integrator (Infotronics, Shannon Airport, Ireland). The distilled water was boiled before use. The model solutes were analytical grade benzene, hexane, heptane and octane (Lachema).

RESULTS AND DISCUSSION

The apparent distribution constants of benzene at 25.1°C, together with data on the corresponding gas-phase concentrations and mass distribution of benzene in the system at different volumes of water in the 254-ml flask, are summarized in Table I. The true water–nitrogen distribution constant of benzene at 25.1°C is 4.320.

It is supposed that the adsorption of solute at the glass–liquid water interface is negligible. Further, since the glass surface in the gas-phase compartment of the flask is exposed to saturated water vapour, it can be supposed that this glass surface will be largely covered and deactivated by a layer of water. Hence, there is actually only a gas–water interface, i.e., the gas–bulk water plus gas–water layer-on-glass interface.

TABLE I

APPARENT WATER–AIR DISTRIBUTION CONSTANTS OF BENZENE AT 25.1°C AND THE CORRESPONDING GAS-PHASE CONCENTRATIONS AND MASS DISTRIBUTIONS AT DIFFERENT VOLUMES OF WATER

$K_L = 4.320$.

V_L (ml)	K_L^*	c_{aG}^0 (µg/ml)	c_{aG} (µg/ml)	W_a (µg)	W_{aG} (µg)	W_{aL} (µg)	$\Sigma W_a^{\gamma\gamma}$ (µg)
100	4.80 ± 0.10	0.984	0.0156	9.84	2.402	6.74	0.749
150	4.71 ± 0.04	0.992	0.0125	9.92	1.300	8.10	0.731
200	4.59 ± 0.13	0.914	0.00937	9.14	0.506	8.10	0.506

TABLE II

APPARENT (K_L^*) AND TRUE (K_L) DISTRIBUTION CONSTANTS OF HEXANE, HEPTANE AND OCTANE AT 25.1°C AND THE CORRESPONDING GAS-PHASE CONCENTRATIONS AND MASS DISTRIBUTIONS AT 100 ml OF WATER

Solute	K_L^*	K_L	c_{aG}^0 ($\mu g/ml$)	c_{aG} ($\mu g/ml$)	W_a (μg)	W_{aG}' (μg)	W_{aL}' (μg)	ΣW_a^{XY} (μg)
Hexane	0.13 ± 0.02	0.0142	0.982	0.0586	9.82	9.024	0.0832	0.679
Heptane	0.096 ± 0.014	0.0099	1.032	0.0631	10.32	9.717	0.0625	0.543
Octane	0.076 ± 0.022	0.0069	0.674	0.0411	6.74	6.329	0.0285	0.284

at which the solute will be adsorbed along with its dissolution in the bulk water. Owing to the round shape of the flask, the K_L^* as well as ΣW_a^{XY} values do not change (decrease) significantly on increasing the amount of water until about a third of the flask is filled. Upon further increase of the amount of water in the flask both K_L^* and ΣW_a^{XY} rapidly decrease, approaching the value of K_L and zero, respectively, as the flask becomes filled completely with water. Owing to the appreciable solubility of benzene in water, the differences between the K_L^* values and that of K_L are relatively small.

Table II gives the apparent and true distribution constants of hexane, heptane and octane at 25.1°C, together with the corresponding gas-phase concentrations and mass distributions, for 100 ml of water in the flask. It is seen that the apparent distribution constants of the alkanes studied are about ten times as large as the true distribution constants. This follows from the fact that the amounts of alkanes adsorbed at the surface are much larger compared with the amounts dissolved in the bulk water. Whereas with benzene at $V_L = 100$ ml the $\Sigma W_a^{XY}/W_{aL}$ ratio is 0.111, with C_6, C_7 and C_8 alkanes these ratios are 8.16, 8.69 and 9.96, respectively.

Table III shows the water–gas adsorption distribution constants, K, of benzene and C_6, C_7 and C_8 alkanes at 25.1°C. K is defined as the equilibrium ratio $(\Sigma W_a^{XY}/S)/c_{aG}$ where the value of the surface area, S, was determined as the sum of the areas of the gas–bulk water and gas–glass (supposed to be covered with water) surfaces at $V_L = 100$ ml and amounted to 184.8 cm². Also given are data on the solute concentrations, c_{aL}, in bulk water and the corresponding surface concentrations, $\Sigma W_a^{XY}/S$, illustrating the surface excess with the alkanes. It is interesting that the K values of alkanes also decrease, similarly to the corresponding K_L values, with increasing solute carbon number (cf., Fig. 3).

TABLE III

WATER–AIR ADSORPTION DISTRIBUTION CONSTANTS (K) OF BENZENE, HEXANE, HEPTANE AND OCTANE AT 25.1°C

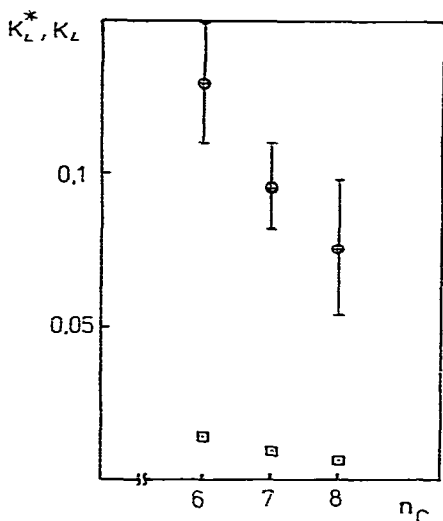| Solute	K (cm)	$\Sigma W_a^{XY}/S$ (ng/cm^2)	c_{aL} (ng/ml)
Benzene	0.260	4.050	67.400
Hexane	0.063	3.670	0.832
Heptane	0.047	2.940	0.625
Octane	0.037	1.540	0.285

Fig. 3. Plots of the apparent (⊖) and true (□) water–gas distribution constants of hexane. heptane and octane *versus* their carbon numbers.

CONCLUSIONS

There may be significant spurious adsorption of analytes in headspace-gas analysis systems. With alkanes in gas–aqueous liquid systems, the amounts of alkanes adsorbed are usually much larger than their amounts dissolved in bulk liquid. These surface phenomena constitute a significant contribution to the matrix effects ensuing from the distribution of the analytes between the gas and bulk condensed phases. Hence, with techniques of quantitative headspace-gas analysis involving the use of a reference model system, not only it is necessary that the composition of the matrix of the reference condensed material be the same as that of the matrix of the material under analysis, but also the internal characteristics and dimensions of both systems must be the same in order to obtain accurate results. It can be recalled in this context that the techniques of standard addition and multiple gas extraction provide an efficient elimination of all kinds of matrix effects in headspace-gas trace analysis. Owing to the significant rôle of adsorption effects in headspace-gas analysis, care must be exercised when attempting to determine liquid–gas distribution constants from the known total amounts of analytes added and their equilibrium gas-phase contents determined analytically.

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