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Vaporization Kinetics of Alcohols

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Summary: The vaporization kinetics of hydrogen bonded alcohols (n-butanol, iso-butanol, n-pentanol and iso-pentanol) in air have been studied at temperatures from 25 — 50°C, under atmospheric pressure conditions. From the experimental vaporization curves, the activation enthalpy of vaporization ΔH_v, was computed. A comparison between the observed vaporization rate Jobs, and the maximum possible rate Jmax, computed from the well known Langmuir equation, yielded the vaporization coefficient α_v. From Jmax curves, the enthalpy of vaporization ΔH_v, has also been calculated. Attempt has been made to correlate the activation enthalpy of vaporization ΔH_v^*, with the number of hydrogen bonds broken in the alcohol cluster during the vaporization process.

Introduction

Many investigations have been made to study the vaporization kinetics of single crystal surfaces, which have revealed a variety of vaporization mechanisms[1]. For some solids (mostly metals), the desorption of the surface species was rate limiting, whereas, for other compounds, bond-breaking at surface sites, surface chemical reactions, association or dissociation were rate limiting. In contrast, the vaporization kinetics of liquids have not been investigated so extensively. Wyllie[2], has, however, measured the vacuum vaporization rates of several liquids at one temperature and has thus obtained the values for the vaporization coefficent α_v. Any deduction of the vaporization mechanism was impossible due to the lack of information about the activation enthalpy of vaporization. Somorjai[3], later on, measured the vacuum vaporization rates of some liquids as a function of temperature and thus obtained the activation enthalpies of vaporization, ΔH_v^*, from which the vaporization kinetics of the liquids have been deduced.

The vaporization rates of methanol, ethanol, n-propanol and iso-propanol have been studied at a fixed temperature of 29.4°C, and of n-butanol, iso-butanol, n-pentanol and iso-pentanol in the temperature range 25 — 50°C, at atmospheric pressure. For the first set of liquids only the vaporization constant α_v could be calculated, which is the ratio of observed vaporization rate Jobs, and the vacuum vaporization rate Jmax. The vaporization constant α_v, indicates the magnitude of deviation of the observed vaporization rate from the maximum rate. Whereas, for the second set of liquids the vaporization constant as well as ΔH_v^* for each liquid were obtained. The values of ΔH_v^*, were compared with the corresponding heats of vaporization ΔH_v calculated from Clausius-Clapeyron equation using the literature vapour pressure data[4].

$$\frac{d(\ln p)}{d(1/T)} = - \frac{\Delta H_v}{R} \qquad (1)$$

In cases, like ours, where desorption of molecules at the vaporizing surface is not the rate limiting step, the observed vaporization rate Jobs was frequently found to be less than the maximum possible rate, Jmax, which can be calculated from the kinetic theory of gases. From the well-known Langmuir[3] equation we get,

$$J_{max} \text{ (mg. cm}^{-2} \text{ sec}^{-1}) = P_{eq} (M/2\pi RT)^{\frac{1}{2}} \qquad (2)$$

Where P_{eq} is the equilibrium vapour pressure, M, the molecular weight of the monomer and R and T have their usual meanings.

In associated liquids, the energy binding a molecule to its neighbours at the liquid surface is primarily due to i) hydrogen bonding and ii) attractive interactions through dispersion forces.

$$\Delta H_{total}^u = \Delta H_{hb}^u + \Delta H_{dis.}^u \qquad (3)$$

Bondi and Simkin[5] have devised a method of separating these two major contributions. The interaction energy due to dispersion forces is estimated by the heat of vaporization ΔH_h of a "homomorph" (molecule of similar geometry), at the same temperature as that of alcohol. This assumption holds fairly good, except in the

low-temperature range. In this procedure the implicit assumption is made that the dispersion energy contribution of the OH-group of the alcohol is equal to that of methyl group. The correctness of this assumption can be assessed as follows. If one approximates the attractive component of dispersion energy $\alpha^2 I/r^6$ (where α is the polarizability, r the intermolecular distance, and I the first ionization potential) as $R_M^2 \cdot I/V_L^2$ (where R_M = Molar refractivity, V_L = molar volume), then one requires that

$$\frac{R_M(OH). V_L(CH_3)}{V_L(OH). R_M(CH_3)} \quad \frac{I(OH)}{I(CH_3)} \sim 1 \quad (4)$$

while the group increments for R_m (Eisenlohr) and V_L (Kopp) are known, but those for I are not well established. However, ionization potentials are sufficiently similar to each other so that only a small error is made if one substitutes the ratio $I(H_2O)/I(CH_4)$ for $I(OH)/I(CH_3)$. Making these substitutions one finds that at the boiling point and at $0^\circ K$ the above ratios are about 0.8 and 0.9 respectively. Substitution of a methylene group for an ether oxygen leads to an error of the same magnitude and is in the direction of making $\delta(OH)$ a bit too small. For relatively large molecules of our interest, this error is negligible.

In our case, the interaction energy due to dispersion forces may be estimatded by the heat of vaporization of an equi-structural compound(homomorph) in which CH_3- group is substituted for OH- group. For example, the contribution forces for n-butanol may be taken to be the ΔH_v of n-pentane. The hydrogen bonding contribution may thus be accounted for using our semiempirical parameter δ OH-. For the purpose of our analysis we may choose $\delta(OH)$ = 4.3 kcal. mole^{-1}; since that is the average reported value of H-bond energies for alcohol given by Pimental[6].

Structure of Liquid Alcohols

In order to understand the structures of associated liquids several models have been proposed[7] (e.g. mixture model, interstitial model, distorted hydrogen bond model, random network model) on the basis of X-rays studies, spectroscopy and radial distribution curves. However, the state of molecular aggregation of alcohols is less well defined. But, it is believed that alcohols form indistinguishable double or otherwise multiple

molecules. Careful viscosity measurements by Bondi[8] have shown that the aggregation occurs at low temperature (t $<30^\circ C$), where specific steric effect may become important.

Thus from the above discussion we can assume that alcohols form dimers or multimers. By now it has become apparent that in order to vaporize a molecule from the surface of a liquid, certain number of hydrogen bonds may be broken. Since the molecules of different alcohols have different energy requirements which would determine the size of the multimers formed, our semi-empirical parameter $\delta OH = (\Delta H_v^* - \Delta H_h)$ seems to be a nice measure of the number of hydrogen bonds broken at the surface (assuming the additivity of H-bond energies).

Experimental

The vaporization experiments were carried out using RH CAHN Recording Electrobalance. The weight changes of the sample were displayed on a recorder as a function of time so that the weight of the vaporizing sample could be monitored continuously. The balance is sensitive upto 2.0 $\mu g \pm 1.0 \mu g$.

The liquid samples viz. methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, n-pentanol and iso-pentanol were refluxed and distilled before use.

The vaporizing liquids were maintained at a constant temperature, in the range 25 – 45$^\circ C$, within the accuracy of $\pm 0.1^\circ C$, by means of a thermostated water circulater. Reproducible steady state vaporization rates at, as many as, five different temperatures were measured and at least triplicate results were obtained for each sample.

Results

Table I depicts the vaporization rates as well as the vaporization coefficients of various alcohols in homologous series at 29.4$^\circ C$. Figures 1 and 2 show plots of the logarithm of evaporation rates (mg. cm^{-2} sec^{-1}) as a function of temperature for n-butanol, isobutanol, n-pentanol and iso-pentanol. The solid line indicates the experimental vaporization rates while the dotted line represents the maximum rate predicted by kinetic theory of gases.

The equilibrium heats of vaporization, ΔH_v, and the experimentally determined activation enthalpies, ΔH_v^*, for all the four liquids are summarized in table II along-
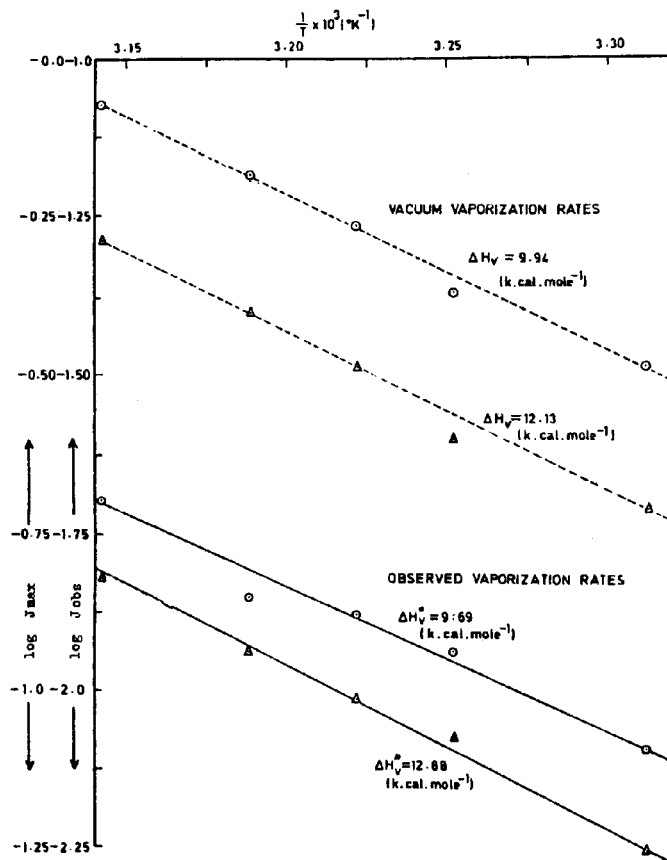
FIG. I PLOT OF THE LOGARITHMS OF Jmax. and Jobs. VS RECIPROCAL TEMP.
▲ n BUTANOL AND O Iso-BUTANOL.

Table I

The vaporization rates of various alchols in homologous series at 29.4°C.

| Alcohol	M.Wt.	b.p. (°C)	Jobs (mg. cm^{-2} sec^{-1})	Jmax. (mg. cm^{-2} sec^{-1})	α_v
Methanol	32.04	64.7	0.03374	1.75376	0.019
Ethanol	46.07	78.4	0.02097	0.98777	0.021
Iso-Propanol	60.10	82.4	0.018301	0.94426	0.019
n-Propanol	60.10	97.2	0.011645	0.46514	0.025
Iso-Butanol	74.12	108.1	0.008140	0.28207	0.028
n-Butanol	74.12	118.0	0.005645	0.16579	0.034
Iso-Pentanol	88.15	132.0	0.001475	0.10529	0.014
n-Pentanol	88.15	138.1	0.000960	0.06212	0.015
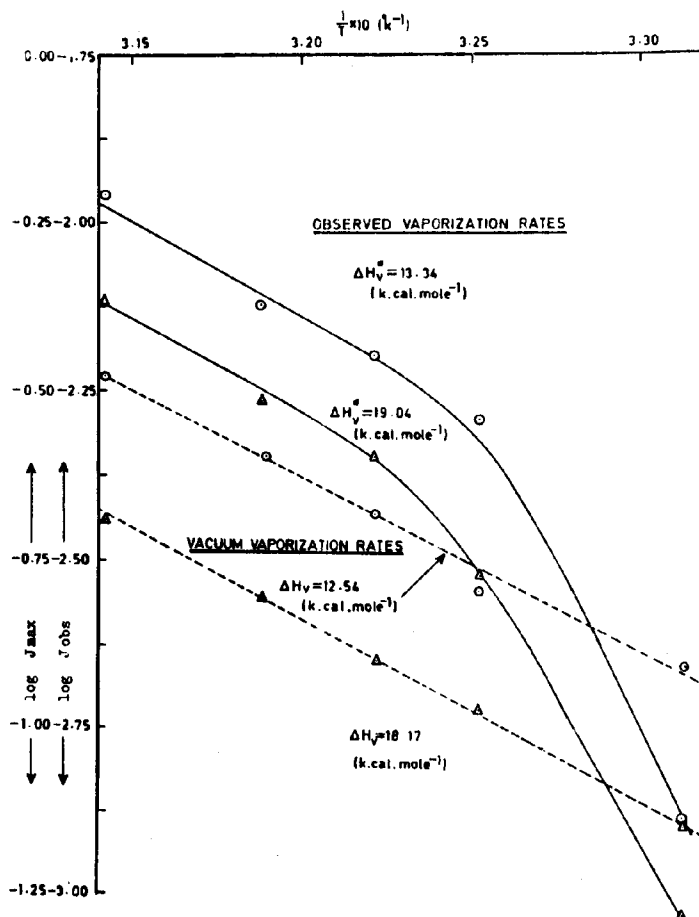
FIG. 2 . PLOT OF LOGARITHMS OF J max. AND J obs. VS. RECIPROCAL
TEMPERATURES.   ▲ n-PENTANOL AND ⊙ Iso-PENTANOL.

with the evaporation constant α_v.

It should be noted that α_v = Jobs/Jmax is almost constant throughout the studied temperature range except for the values for n-pentanol and iso-pentanol at lower temperature.

Discussion

Table I depicts the evaporation rates of various alcohols at a fixed temperature alongwith the calculated vaporization coefficient α_v. It is noted that α_v is not constant for all the systems studied due to the difference in ΔH_v and ΔH_v^*. The less than unity evaporation coefficient indicates that the surface population of molecules that may vaporize is less than their surface population at equilibrium.

The predicted enthalpies of vaporization for alcohols with varying hydrogen bonding contributions (if the additivity of the hydrogen bond energies be assumed) are shown in table III, alongwith the enthalpes and activation enthalpies of vaporization.

Table II.

The heat of vaporiation ΔH_v, the activaton enthalpy of vaporization ΔH_v^* and the evaporation coefficient α_v.

	ΔH_v (K. cal. mole^{-1})	ΔH_v (K. cal. mole^{-1})	α_v
Iso-Butanol	9.9350	9.6926	0.024
n-Butanol	12.1306	12.8783	0.030
Iso-Pentanol	12.5394	16.6935	0.027
n-Pentanol	18.9239	21.1925	0.030

Table III.

Comparison of enthalpies and activation enthalpies with the enthalpies of vaporization calculated by adding different H-Bond contributions to the enthalpies of vaporization of homomorph molecules ΔH_h.
All values in K cal/mole.

	ΔH_h	ΔH_h $+ 1\,\delta$ (OH)	ΔH_h $+ 2\,\delta$ (OH)	ΔH_h $+ 3\,\delta$ (OH)	ΔH_v	ΔH_v^*	t^oC
Iso-Butanol	5.84	10.14	14.44	18.14	9.93	6.69	(29-50)
n-Butanol	6.16	10.46	14.74	19.06	12.13	12.88	(29-50)
Iso-Pentanol	6.76	11.06	15.66	19.66	12.54	13.34	(36 50)
n-Pentanol	7.71	12.01	16.31	20.61	18.17	19.04	(36-50)

Inspection of table III reveals that the four liquids studied have distinctly different energy requirements for vaporization to occur. For iso-butanol, which exhibits the weakest total hydrogen bonding, the activation enthalpy of vaporization is almost equal to the enthalpy of vaporization $\Delta H_v^* = \Delta H_v$. It is, however, apparent that the enthalpy of vaporization as well as the activation enthalpy corresponds to the breaking one hydrogen bond.

For vaporization of n-butanol it is quite evident that its total enthalpy of vaporization as well as activation enthalpy corresponds to the breaking of almost two hydrogen bonds and thus it is assumed that n-butanol vaporizes breaking two hydrogen bonds.

Much more revealing, indeed surprising, are the log Jobs. vs 1/T curves obtained for n-pentanol and iso-pentanol. They show a regular linear behaviour at temperature between $(36 - 50^oC)$ where the enthalpy and activation enthalpy of vaporization are almost equal showing the breaking of three and two hydrogen bonds in n-pentanol and iso-pentanol molecules respectively. However, at lower temperatures $(< 36^oC)$ the linear slopes reach a sudden inflection point where log Jobs decreases, therefore ΔHv^* increases, to a great extent, showing the breaking of 10–12 hydrogen bonds in these alcohol molecules for the vaporization to occur.

It appears from Fig. 2, that n-pentanol and iso-pentanol at equilibrium with their vapours have a surface population of some mobile species which are hydrogen bonded to the nearest neighbours. These molecules are the source of vapour flux leaving the surface. At low temperature the vaporization rates are low enough and it seems that the equilibrium surface population

is significantly lowered due to the formation of multimers. Similar behaviour has also been reported for ice single crystal[9] and for alcohols[10], showing that the physical properties deviate from their normal behaviour at lower temperature with the variation of hydrogen bonded associations.

Acknowledgement

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