

VAPORISATION KINETICS OF ASSOCIATED AMINES

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The vaporisation rates of various hydrogen bonded amines i.e. ethylene diamine, diethylene triamine and triethylene tetramine were studied in vacuum (10^{-3} torr) at temperatures between 294-325 K. The vaporisation rates were studied by the use of RH Cahn Electrobalance system. From the experimental vaporisation rates (J_{obs}), the activation enthalpy of vaporisation, ΔH_V^* , was calculated and compared with the enthalpy of vaporisation, ΔH_V computed from the well known Langmuir equation using the equilibrium vapour pressure data from the literature. Attempt has been made to correlate ΔH_V^* with the number of H-bonds broken in the liquids during the vaporisation process. The breaking of the H-bonds between various molecules has been considered to be the rate-limiting in the vaporisation process. The results are interpreted in terms of intra- and intermolecular hydrogen bonding in amines.

Key words: Kinetics, Vaporisation, Associated amines.

INTRODUCTION

The vaporisation kinetics of various single crystal surfaces have been investigated quite extensively revealing a variety of vaporisation mechanisms [1]. The desorption of the surface species is believed to be the rate-limiting step for some solids (mostly metals) whereas for other compounds bond-breaking at surface sites, surface chemical reactions, association or dissociation are said to be the rate-limiting. In contrast, the vaporisation kinetics of liquids have not been investigated so extensively. Willie [2] has, however, measured the vaporisation rates of several liquids at a single temperature and has thus obtained the vaporisation coefficient, α_V . Somorjai [3], later on, measured the vaporisation rates of some liquids as a function of temperature and obtained the activation enthalpies of vaporisation, ΔH_V^* . The ΔH_V^* values have been correlated with the vaporisation rates of liquids such as glycerol, diethylene glycol and triethylene glycol. The number of hydrogen bonds broken at the liquid surface is considered by Afzal *et al.* [4] to be rate-limiting for vaporisation to occur in various alcohols. More recently enthalpies of vaporisation of aliphatic C_5 and C_6 alcohols has been reported by Major *et al.* [5].

Suoboda and Major [6] have recently reviewed various group contribution methods used for the estimation of vaporisation heats of pure substances. In associated liquids, the energy binding a molecule to its neighbours at the liquid surface is primarily due to attractive interactions

through dispersion forces (Vander wall forces) and secondarily owing to H-bonding

$$\Delta H_V^{Total} = \Delta H_V^{HB} + \Delta H_V^{Dis} \dots \dots \dots (1)$$

Bondi and Simkin [7] have devised a method of separating the two major contributions. The interaction energy due to dispersion forces is estimated by the heat of vaporisation of an equistructural molecule involving no hydrogen bonding (homomorph), ΔH_h . The assumption holds fairly good except in low temperature range. In this procedure, the implicit assumption is made that the dispersion energy contribution of the NH- and NH₂ groups in amines is equal to that of a methyl group. The correctness of this assumption for alcohols has been assessed previously [4].

In the present paper, the vacuum vaporisation kinetics of ethylene diamine, diethylene triamine and triethylene tetramine within a temperature range of 294-340 K has been reported. The difference in the values of the activation enthalpy of vaporisation and the enthalpy of vaporisation of an equistructural compound (homomorph) is considered to be a measure of the contribution due to hydrogen bonding. The number of hydrogen bonds broken at the liquid surface is believed to be the rate-limiting step. The "homomorph" compounds used to estimate the dispersion force contribution for amines were 3-methyl pentane (for diethylene triamine) and dipropoxy ethane (for triethylene tetramine). However, for ethylene diamine, we have a rough value derived from the heat of sublimation of butane at 0 K.

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The maximum possible rate of vaporisation, J_{max} , can be calculated using the equilibrium vapour pressure P_{eq} , data from the literature [8] and employing the well-known Langmuir equation:

$$J_{max} = P_{eq} / (2 \pi MRT)^{1/2} \dots \dots \dots (2)$$

where M is the molecular weight of the monomer and R and T have their usual meanings. The P_{eq} data for each liquid can be used to calculate the corresponding heat of vaporisation (ΔH_v) by means of Clausius-Claperon equation,

$$\frac{d(\ln P_{eq})}{dT} = \frac{-\Delta H_v}{R} \dots \dots \dots (3)$$

The number of hydrogen bonds 'n' to be broken at the vaporising surface of a liquid can be computed using a semi-empirical parameter, $\delta(NH_2)$, which is the energy per H-Bond, in the following expression:

$$n = \frac{\Delta H_v^* - \Delta H_{homo}}{\delta(NH_2)} \dots \dots \dots (4)$$

for the purpose of our analysis we may choose an average value for $\delta(NH)$ and $\delta(NH_2)$ of 14.5 kJ mol^{-1} in our calculations [9].

EXPERIMENTAL

The liquid samples viz ethylene diamine, diethylene triamine and triethylene tetramine (all E. merck) were refluxed for several hours and were carefully distilled before use.

The vaporisation experiments were carried out using RH CAHN Recording Electrobalance which was connected to a vacuum line. The details of the experimental procedure is given elsewhere [4]. For the study of the rate of vaporisation in vacuum, the balance was connected to the vacuum line evacuated at 10^{-3} torr and the liquid was allowed to vaporise into the evacuated vacuum line. The initial vaporisation rates were therefore considered.

RESULTS

Table 1 depicts for the three amines the computed values of ΔH_{homo} and ΔH_v (theoretical) alongwith the values of the activation enthalpies of vaporisation, ΔH_v^* , obtained for vaporisation in vacuum. The corresponding plots for $\log_{10} J_{obs}$ as well as $\log_{10} J_{max}$ versus $1/T$ were constructed where from the values of ΔH_v and ΔH_v^* have been calculated.

The plots for the three amines have been shown in Fig. (1) and the computed values of ΔH_v , ΔH_v^* etc. are shown in Table 1. The values of ΔH_v and ΔH_v^* when compared indicate a breaking of 2 H-bonds in the case of ethy-

Table 1. Comparison the heat of the vaporisation, ΔH_v , and the activation enthalpies of vaporisation in vacuum, $\Delta H_v^* \text{ vac}$, with the enthalpy of vaporisation of the "homomorph" ΔH_{homo} assuming the additivity of H-bond contribution.

Liquids	ΔH_{homo} kJ mol^{-1}	ΔH_v (kJ mol^{-1})	$\Delta H_v^* \text{ vac}$ (kJ mol^{-1})	n	$\alpha_v^{305 \text{ K}}$
Ethylene diamine	30.33	41.55	61.13	2	0.001
Diethylene triamine	36.40	54.81	80.37	3	0.065
Triethylene tetramine	42.44	75.56	85.06	3	0.181

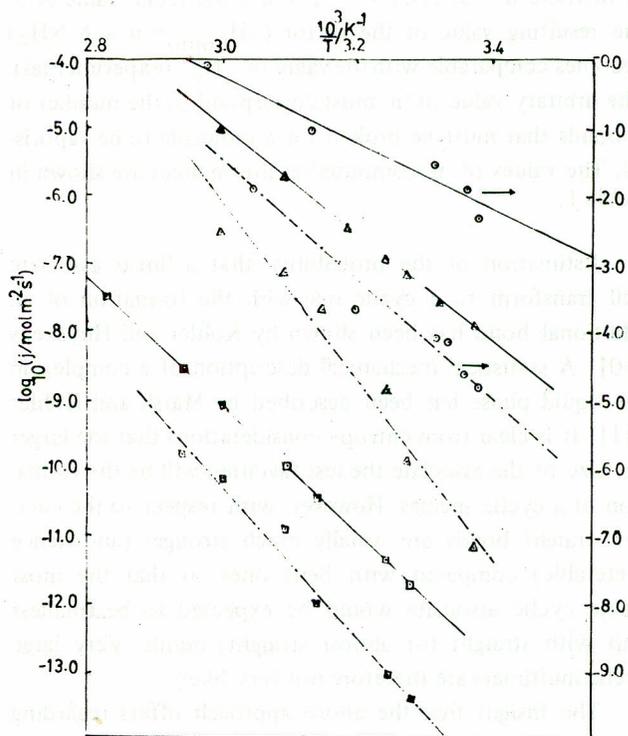


Fig. 1. Plots of the logarithms of J_{max} and J_{obs} versus reciprocal temperatures for: \circ Ethylene diamine, Δ Diethylene triamine, \square Triethylene tetramine, - - - corresponding theoretical plots.

lene diamine and 3 H-bonds in the case of ethylene diamine and 3 H-bonds in the cases of both diethylene triamine and tri-ethylene tetramine. The plots of $\log_{10} J_{\text{Obs}}$ as well as of $\log_{10} J_{\text{max}}$ VS $1/T$ give straight lines in all the samples indicating that the Arrhenius equation is obeyed throughout the temperature range under investigation.

DISCUSSION

The values of the vaporisation rates observed and those calculated theoretically (shown in dotted lines in Fig. 1) for all the liquids under investigation are noted to be different. The less than unity vaporisation coefficients, α_v , indicate that the surface population of molecules that may vapourise is less than their surface population at equilibrium. This reveals that the molecules at the surface are strongly interacting with the molecules in the bulk of the liquid. Since the molecules of different amines have different energy requirement for vaporisation to occur the values of ΔH_v^* could be an indicative of the size of the multimer (eq. (4)).

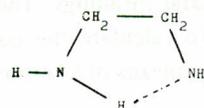
Assuming that the H-bond energies are additive in nature, the chosen value for the H-bond contribution, $\delta(\text{NH}_2)$, towards the total enthalpy of amines i.e. 14.5 kJ mol^{-1} is added to the value of ΔH_{homo} as a multiple of n (where $n = 0, 1, 2, 3 \dots$). For a particular value of n , the resulting value of the factor ($\Delta H_{\text{homo}} + n \times \delta \text{NH}_2$) becomes comparable with the value of ΔH_v^* (experimental). The arbitrary value of 'n' must correspond to the number of H-bonds that must be broken for a molecule to be vaporised. The values of 'n' computed in this manner are shown in Table 1.

Estimation of the probability that a linear associate will transform to a cyclic one with the formation of an additional bond has been shown by Kohler and Huyskens [10]. A statistical mechanical description of a complex in the liquid phase has been described by Marsh and Kohler [11]. It is clear from entropy considerations that the larger the size of the associate the less favoured will be the formation of a cyclic species. However, with respect to the energy, straight bonds are usually much stronger (and hence preferable) compared with bent ones so that the most stable cyclic associate would be expected to be smallest unit with straight (or almost straight) bonds. Very large cyclic multimers are therefore not very likely.

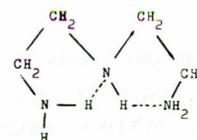
The insight that the above approach offers regarding the thermodynamic behaviour of the various species allow us to consider that the surface species (monomers) are hydrogen bonded to the nearest molecules in the liquid. To vapourise the surface species the breaking of the hydro-

gen bonds is necessary. The values of ΔH_v^* in the case of ethylene diamine corresponds to the breaking of 2 H-bonds, whereas for diethylene triamine as well as for tri-ethylene tetramine the value of ΔH_v^* is such that the breaking of 3 H-bonds is evident (Table 1).

These amines may form intra-molecular H-bonds in order to attain a stable structural configuration as shown below for ethylene diamine.

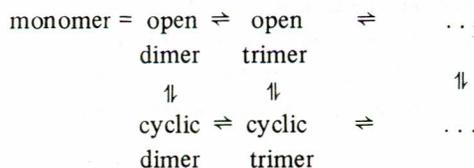


or for diethylene triamine as:



Both primary and secondary amines are weakly associated and thermodynamically they show similar behaviour since usually only one of the two hydrogen atoms of the amino group is involved in hydrogen bonding. Because the amine monomer is not very polar, chain association takes place as in alcohols, as the constants for addition of a monomer to a chain is larger than the constant for dimerisation of the two monomers [12]. Since the bonds are not strong, long chains are not readily formed and in pure amines the mole fraction of monomers is of the order of 0.5 [11]. Large cyclic associates, if existing at all, have little or no significance with respect to the thermodynamic properties.

Finally, it can be concluded that the associated liquids are a mixture of monomers, dimers and multimers grouped together through various intermolecular forces (i.e. H-bonding). A general scheme for association can be represented as :-



Depending on the monomer structure and on the strength of the H-bond, only part of this scheme will be realized. For example, for amines only cyclic species of a relatively small size having straight H-bond can be expected. In amines of larger size, the hydrogen bond is not sufficiently strong for cyclic structures to be formed in significant quantities.

However, in addition to the intra-molecular H-bonding the amine molecules would also form inter-molecular H-bonding due to the presence of larger groups (e.g. ethylene, diethylene, triethylene) in the vicinity of the amino groups. The distortion of the bonds into bent ones in order to attain the configuration shown above (which in turn allows for the intra-molecular H-bonding to take place) may become less likely. Hence, the amine monomer would have more of the species having straight bonds rather than the bent ones. If such a behaviour is expected the presence of one or more H-bonds between the amine monomer can be visualized. This suggestion fits pretty well with the calculated values of ΔH_v^* for the three amines. Since the intermolecular H-bonds have to be broken for the vaporisation to occur.

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