

Phase Transitions in Adsorbates: Part III—Vapour Pressure Studies on Formic Acid, *tert*-Butyl Alcohol & Cyclohexane Adsorbed on Charcoal

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The vapour pressure studies on formic acid, *t*-butyl alcohol and cyclohexane adsorbed on charcoal have been reported. The observed behaviour regarding the depression in freezing point and its variation with relative vapour pressure is found to be similar to that for adsorbate-silica gel systems [*Indian J. Chem.*, 11 (1973), 796, 922]. The disagreement between the values of ΔH_i and ΔH_f support the earlier inference that freezing in an adsorbate-adsorbent system is not a case of first order transition. The ratio $\Delta H_i/\Delta H_f$ has been found to decrease with decrease in p/p° .

VAPOUR pressure studies on phase transitions in a number of substances adsorbed on silica gel have been reported^{1,2} earlier. It was very interesting to observe that the heats of phase transition (ΔH_i) obtained from the plots of $\log p$ versus $1/T$ were generally found to be higher (in some cases four to five times higher) than the heats of fusion (ΔH_f) of the adsorbates in the pure states. It was of interest to study whether this ratio is in some way dependent on the nature of the adsorbent. In this paper vapour pressure studies of formic acid, *t*-butyl alcohol and cyclohexane adsorbed on charcoal have been reported at temperatures above and below their normal freezing points.

Materials and Methods

Charcoal used was prepared by the carbonization of sucrose with con. sulphuric acid. The sample was freed of the sulphate ions by repeatedly washing it with hot distilled water. The charcoal thus obtained was activated with super-heated steam dried and stored for use.

Formic acid, *t*-butyl alcohol and cyclohexane were purified as reported² earlier.

Oil-mercury manometer was used for determining the vapour pressure of an adsorbate in the adsorbate-adsorbent system.

Results and Discussion

As reported earlier^{1,2} the plots of $\log p$ versus $1/T$ for these adsorbate-adsorbent systems consist of two linear portions. The point of intersection corresponds to the temperature of inception of freezing of the adsorbate. Some typical plots are illustrated in Fig. 1. The depressions in freezing point (ΔT) for the various adsorbate-adsorbent systems, reported in Table 1, show that ΔT increases regularly as the relative vapour pressure (p/p°), decreases.

Theoretical calculation of depression in freezing point—The theoretical values of ΔT were calcu-

lated as in earlier communications^{1,2} by Batchelor and Foster's method³ according to which

$$\Delta T = \frac{T_0}{\Delta H_f} \cdot \frac{2M}{r} \left[\frac{\gamma_l}{\rho_l} - \frac{\gamma_s}{\rho_s} \right] \quad \dots(1)$$

Assuming the applicability of Kelvin equation,

$$\ln p^\circ/p = \frac{2M\gamma}{r\rho RT} \quad \dots(2)$$

to both liquid and solid states of the adsorbate Eq. (1) was obtained by substituting $\ln(p_i^\circ/p_i)$ and $\ln(p_s^\circ/p_s)$ as $2M\gamma_l/r\rho_l RT$ and $2M\gamma_s/r\rho_s RT$, respectively in Eq. (3)³

$$\ln(p_i^\circ/p_i) - \ln(p_s^\circ/p_s) = -\Delta(1/T) \frac{\Delta H_f}{R} \quad \dots(3)$$

where the symbols have their usual meaning¹. While the value of γ_l/ρ_l in Eq. (1) is estimated from literature data for the pure liquid at the experimental freezing point, the value of γ_s/ρ_s is obtained using the relation (4)

$$\ln(p_i^\circ/p_i) / \ln(p_s^\circ/p_s) = \frac{\gamma_l/\rho_l}{\gamma_s/\rho_s} \quad \dots(4)$$

This method of introducing the value of γ_s/ρ_s in Eq. (1) is artificial since replacement of γ_s/ρ_s in Eq. (1) by $\ln(p_s^\circ/p_s)/\ln(p_i^\circ/p_i)$ yields Eq. (3). As $p_s = p_i$ at the freezing point, Eq. (3) is really

$$\ln(p_i^\circ/p_s^\circ) = -\Delta(1/T) \cdot \frac{\Delta H_f}{R} \quad \dots(5)$$

It is obvious that Eq. (5) is independent of the real system under examination. It may be clear that selection of $\ln(p_i^\circ/p_i)$ and $\ln(p_s^\circ/p_s)$ from experimental data is nothing but determination of $\ln(p_s^\circ/p_s)$ at a particular temperature. The agreement shown¹⁻³ between the so-called theoretical values of ΔT with the experimental values is thus meaningless. Batchelor and Foster's method³ for

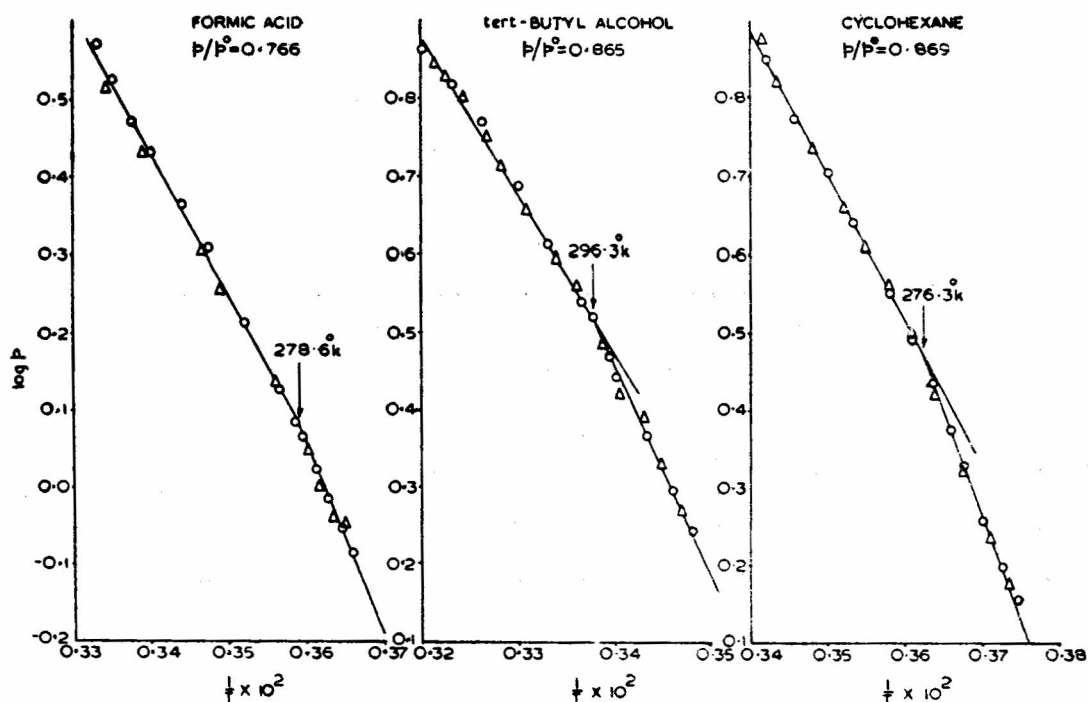


Fig. 1 — Typical plots of $\log p$ versus $1/T$ for formic acid, *t*-butyl alcohol and cyclohexane, adsorbed on charcoal [Circles (—○—○—) and triangles (—△—△—) represent cooling and warming runs]

TABLE 1 — FREEZING POINT AND HEAT OF PHASE TRANSITION DATA FOR VARIOUS ADSORBATES ADSORBED ON CHARCOAL

Freezing point (T) (°K)	p/p° at freezing point	Expt. freezing point depression (ΔT) (°C)	ΔH_i (cal/mole)	$\Delta H_i/\Delta H_f$
FORMIC ACID ($\Delta H_f = 3038$ cal/mole)				
280.9	0.879	0.8	2870	0.94
280.3	0.873	1.4	3754	1.23
278.6	0.796	3.1	2650	0.87
277.6	0.750	4.1	2502	0.82
275.3	0.711	6.4	2355	0.78
274.0	0.668	7.7	2282	0.75
<i>t</i> -BUTYL ALCOHOL ($\Delta H_f = 1629$ cal/mole)				
297.2	0.977	1.5	4406	2.70
297.0	0.933	1.7	3680	2.26
296.3	0.865	2.4	3036	1.86
292.4	0.832	6.3	2944	1.81
287.1	0.832	11.6	3404	2.08
284.2	0.764	14.5	2484	1.52
CYCLOHEXANE ($\Delta H_f = 627$ cal/mole)				
278.9	0.942	0.8	4160	6.63
276.3	0.869	3.4	3220	5.13
274.0	0.738	5.7	3220	5.13
270.3	0.601	9.4	2075	3.31

calculation of depression in freezing point has hence been abandoned. At the same time, in view of the characteristic behaviour observed for the adsorbate-adsorbent systems after the commencement of freezing, there can really be no way for theoretical calculation of ΔT unless the nature of phase transition is better understood.

Nature of phase transition — The heats of phase transition (ΔH_i) determined from experimental curves of $\log p$ versus $1/T$ and the ratio $\Delta H_i/\Delta H_f$ for adsorbate-charcoal systems are given in Table 1. It is worth mentioning that ΔH_f values used for the calculation of $\Delta H_i/\Delta H_f$ are those reported in literature⁴ and have not been determined from vapour pressure-temperature data, as was done earlier². Since the values of ΔH_f determined from these two sources differ considerably from each other in some cases, it has been felt that calorimetric values of ΔH_f should be more reliable. Keeping this in view, the values of $\Delta H_i/\Delta H_f$ for adsorbate-silica gel systems, wherever necessary, have been revised and are given in Table 2.

It is interesting to note that the values of ΔH_i differ considerably from the corresponding values of ΔH_f for almost all the adsorbates whether adsorbed on charcoal or silica gel (Tables 1 and 2). The values of $\Delta H_i/\Delta H_f$ generally vary from 2 to 7, the notable exception being formic acid for which the $\Delta H_i/\Delta H_f$ values are nearly unity or even less. A careful examination of $\Delta H_i/\Delta H_f$ values for all the adsorbate-adsorbent systems (Tables 1 and 2) makes it abundantly clear that the ratio is dependent on the value of ΔH_f . At present, we do not see any reason for the observed dependence and an explanation for this behaviour may not be possible unless

TABLE 2 — REVISED VALUES OF $\Delta H_i/\Delta H_f$ FOR FORMIC ACID, *t*-BUTYL ALCOHOL, CYCLOHEXANE AND BENZENE ADSORBED ON SILICA GEL

p/p° at freezing point	ΔH_i (cal/mole)	$\Delta H_i/\Delta H_f$	p/p° at freezing point	ΔH_i (cal/mole)	$\Delta H_i/\Delta H_f$
FORMIC ACID ($\Delta H_f = 3038$ cal/mole)			BENZENE ($\Delta H_f = 2375$ cal/mole)		
0.946	2439	0.80	0.908	4850	2.04
0.885	4012	1.32	0.904	4850	2.04
0.834	3894	1.28	0.887	4805	2.02
0.787	2778	0.91	0.771	4233	1.78
0.640	613	0.20	0.867	3318	1.39
0.640	2439	0.80	0.851	4956	2.08
0.580	1524	0.50	0.838	4461	1.87
<i>t</i> -BUTYL ALCOHOL ($\Delta H_f = 1629$ cal/mole)			0.832	6237	2.62
0.908	4107	2.52	0.828	3967	1.67
0.885	3208	1.96	0.817	5188	2.18
0.869	2974	1.82	0.826	4730	1.99
0.791	3052	1.87	0.809	6022	2.53
0.673	2540	1.56	0.736	5185	2.17
0.596	2066	1.26	0.803	5111	2.15
CYCLOHEXANE ($\Delta H_f = 627$ cal/mole)			0.785	4118	1.73
0.891	4732	7.55	0.716	4942	2.08
0.849	3510	5.60	0.773	7473	3.14
0.723	2468	3.93	0.667	7166	3.01
0.696	3299	5.26	0.724	5994	2.52
0.671	1904	3.03	0.705	6713	2.82
0.600	458	0.73	0.689	6782	2.84
0.582	1776	2.83	0.637	3638	1.52
			0.612	3853	1.62

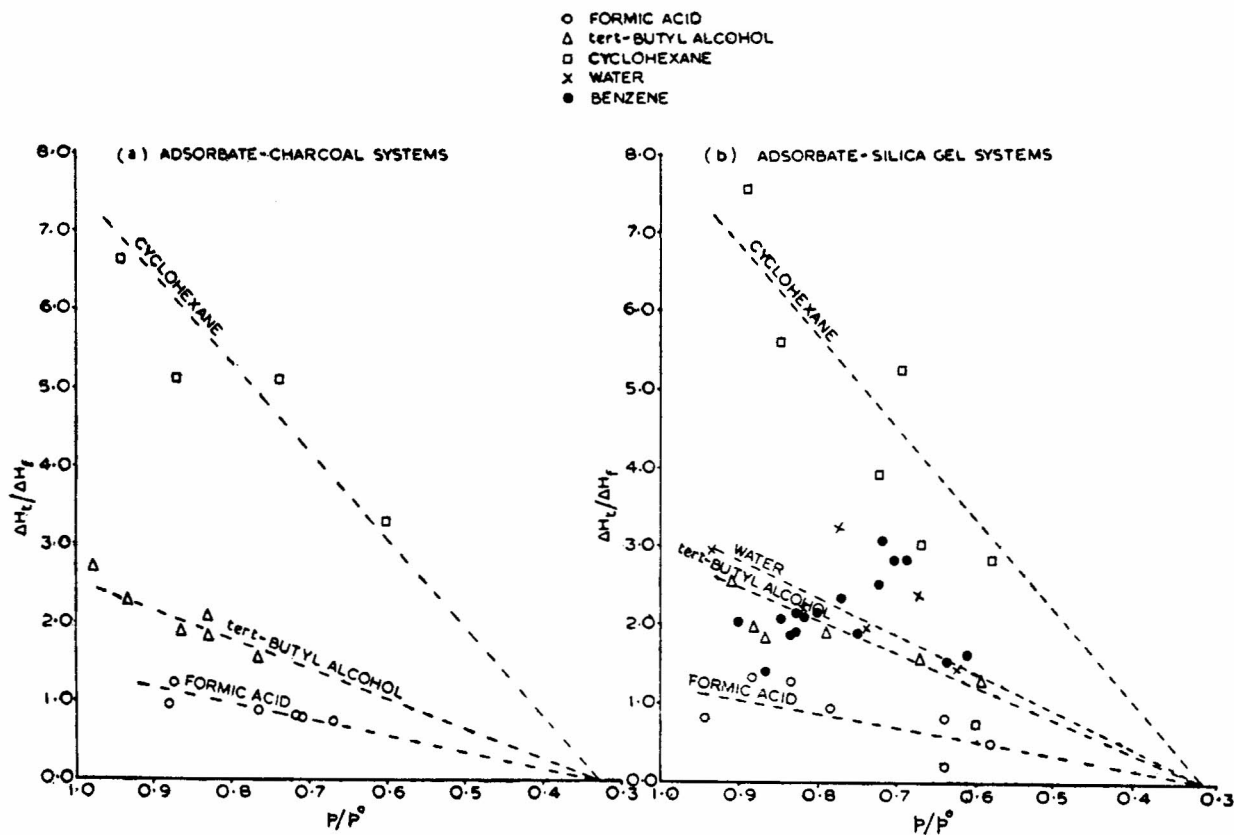


Fig. 2 — Plots of $\Delta H_i/\Delta H_f$ versus p/p° for various adsorbate-adsorbent systems

a meaningful appreciation of the difference between ΔH_i and ΔH_f is available.

As pointed out earlier², the ratio $\Delta H_i/\Delta H_f$ also shows some dependence on relative vapour pressure (p/p^0) of the adsorbate-adsorbent systems. This has been illustrated in Fig. 2(a) for adsorbate-charcoal systems and in Fig. 2(b) for adsorbate-silica gel systems. Although a fair amount of scatter (which may be due to experimental difficulties) is observed but, in general, the values of $\Delta H_i/\Delta H_f$ seem to decrease with decrease in p/p^0 , as indicated by the dotted lines in Fig. 2. It is interesting to observe that, except in the case of benzene-silica gel systems, the lines indicating the trend of variation of $\Delta H_i/\Delta H_f$ with p/p^0 appear to converge, in almost all the cases, to zero value at a relative vapour pressure somewhere between 0.3 and 0.4. This range of p/p^0 may be imagined to correspond to a few adsorbed layers which on account of their being in close vicinity of the adsorbent surface, may show no phase transition. This inference is supported by calorimetric studies carried out by Morrison *et al.*^{5,6} on multilayer adsorption of argon on rutile where the authors report that phase transition in adsorbate is noticeable only after one or two adsorbed layers.

It is abundantly clear from the observed lowering of vapour pressure of solid adsorbates and from the

differences between the values of ΔH_i and ΔH_f that phase transitions in adsorbates are not cases of first order phase transition. It is tempting to suggest tentatively that the linear portion of the plot of $\log p$ versus $1/T$ after the commencement of freezing (usually considered to be the curve for solid adsorbate) may represent the gradual shift of the triple point where the chemical potential of the liquid adsorbate (μ_l) equals the chemical potential of the solid adsorbate (μ_s). The process of phase transition of adsorbates is such that the solid phase is being continually separated from the liquid phase as the temperature is gradually lowered. It may only be a coincidence that all the points for plots of $\log p$ versus $1/T$ lie on a linear curve.

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