

Phase Transitions in Adsorbates: Part IV—Behaviour of Acetic Acid Dioxane & *p*-Xylene Adsorbed on Silica Gel

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The vapour pressure-temperature studies on adsorbate-adsorbent systems have been carefully analysed. It is found that for a particular system the 'apparent freezing points' obtained from $\log p$ versus $1/T$ plots lie on a straight line passing through the freezing point of the pure adsorbate. Surprisingly the slopes (m) of such linear plots obtained for different adsorbate-adsorbent systems have the same order of magnitude such that $\Delta H^* = 2.303 Rm$ has an average value of 15.3 ± 1.0 kcal/mole. The studies confirm the belief that $\log p$ versus $1/T$ plots for adsorbate-adsorbent systems after commencement of freezing represent a gradual shift of the triple point. A method for the calculation of apparent depression in freezing points (ΔT) has been suggested.

OUR earlier studies¹⁻³ on phase transition of a number of adsorbates in various adsorbate-adsorbent systems have shown that the freezing point (T) of adsorbates (commencement of freezing) is invariably lower than the normal freezing point (T_0) and that the depression in freezing point ($T_0 - T$) has some functional dependence on the relative vapour pressure p/p° . The heats of phase transition (ΔH_i) were generally found to be higher (in some cases about 5-6 times) than the normal heat of fusion (ΔH_f) of the adsorbate and the ratio $\Delta H_i/\Delta H_f$ was found to depend on the value of ΔH_f . It has also been shown³ that the ratio $\Delta H_i/\Delta H_f$ decreases as the relative vapour pressure decreases and appears to converge to a zero value for p/p° of the order of 0.3-0.4. The above observations are further supported by the data on acetic acid-silica gel, dioxane-silica gel and *p*-xylene-silica gel systems, reported in this paper.

Materials and Methods

Silica gel (batch 0871-4 NCL, Poona) had a BET surface area of 631 m²/g as determined by adsorption of CO₂ at zero degree.

Acetic acid, *p*-xylene and dioxane were purified before use and the purity checked from their boiling points and by determining their vapour pressures at known temperatures.

Adsorption isotherms determined by a spring method at 35° show that capillary condensation and hysteresis occur in each case.

An oil-mercury manometer¹ was used to determine the vapour pressure of the adsorbate-adsorbent systems. The studies cover a range of relative vapour pressure of about 0.45 to almost saturation.

Results and Discussion

The plots of $\log p$ versus $1/T$ for acetic acid, dioxane and *p*-xylene adsorbed on silica gel (typical plots illustrated in Fig. 1) consist of two linear

portions in each case. The point of intersection can be considered to correspond to the temperature of inception of phase transition (T) which can be evaluated to an accuracy of $\pm 0.5^\circ$. We may define it as the apparent freezing point. The values of ΔH_i and $\Delta H_i/\Delta H_f$, obtained from the plots of $\log p$ versus $1/T$, are reported in Table 1. It may be clear from the data in Table 1 that the general features of the present systems are similar to those reported earlier¹⁻³. It may, however, be worth pointing out that unlike the gradual decrease in the values of $\Delta H_i/\Delta H_f$ with decrease in p/p° , the values of $\Delta H_i/\Delta H_f$ for the present systems are practically constant over a fairly wide range of high relative vapour pressures (p/p°).

On plotting the experimental $\Delta(1/T)$ data for an adsorbate-adsorbent system for the different values of p/p° it is observed that the 'apparent freezing points' are found to lie on a straight line passing through the freezing point of the pure adsorbate[†]. This is illustrated in Fig. 2 for a typical case of cyclohexane-charcoal system.

Still more surprising is the fact that the slopes of the straight lines passing through the 'apparent freezing points' for the various adsorbate-adsorbent systems have about the same order of magnitude except for benzene-silica gel system. Defining ΔH^* by the relation

$$\begin{aligned} \Delta H^* &= 2.303 R d \frac{\log p}{d(1/T)} \\ &= 2.303 R m \end{aligned} \quad \dots(1)$$

where m is the slope of the line joining 'apparent freezing points', the values of ΔH^* have been calculated for the various adsorbate-adsorbent systems

[†]Considering the freezing point of pure adsorbate as a fixed point on $\log p$ versus $1/T$ plot, a straight line (dotted line in Fig. 2) was drawn through the 'apparent freezing points' for each adsorbate-adsorbent system with the help of an IBM-1620 computer by the method of least squares.

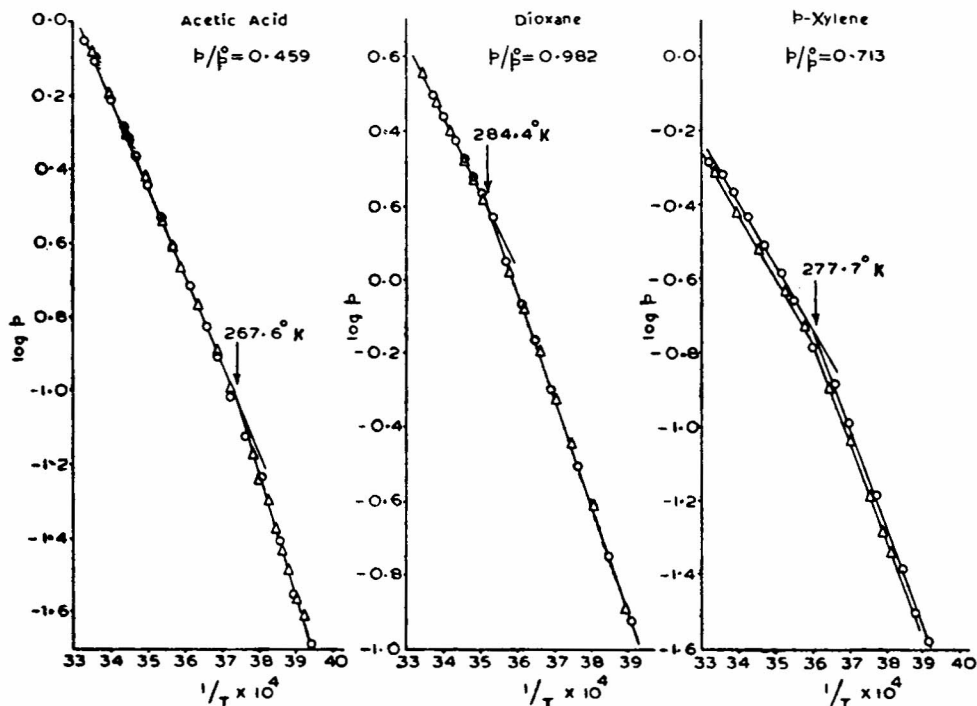

 Fig. 1 — Typical plots of $\log p$ versus $1/T$ for acetic acid, dioxane and *p*-xylene adsorbed on silica gel

TABLE 1 — FREEZING POINT DEPRESSIONS AND HEATS OF PHASE TRANSITIONS FOR DIFFERENT ADSORBATES ADSORBED ON SILICA GEL

p/p° at freezing point	$\Delta T_{\text{obs.}}$ ($^\circ\text{C}$)	$\Delta T_{\text{calc.}}$ (Eq. 3)	ΔH_f (cal/mole)	$\Delta H_i/\Delta H_f$	p/p° at freezing point	$\Delta T_{\text{obs.}}$ ($^\circ\text{C}$)	$\Delta T_{\text{calc.}}$ (Eq. 3)	ΔH_i (cal/mole)	$\Delta H_i/\Delta H_f$
ACETIC ACID					0.606 C	10.2	12.5	1517	0.49
$(T_0 = 289.8^\circ\text{K}; \Delta H_f = 2755 \text{ cal/mole})$					0.622 W	10.4	11.0	2263	0.74
0.972 C*	1.2	1.0	5671	2.06	0.593 C	16.2	13.0	3201	1.04
0.973 W	1.1	1.2	5795	2.10	0.610 W	12.3	12.3	3202	1.04
0.915 C	4.2	3.2	8432	3.06	0.540 C	17.2	15.2	1323	0.43
0.893 W	2.1	4.0	7761	2.82	0.565 W	16.4	14.1	1934	0.63
0.844 C	4.9	6.0	6807	2.47	0.493 C	20.9	17.3	2705	0.88
0.864 W	5.4	5.2	7088	2.57	0.523 W	19.4	15.8	2781	0.91
0.661 W	11.5	14.2	6755	2.45	<i>p</i>-XYLENE				
0.534 C	18.8	21.0	3878	1.40	$(T_0 = 286.5^\circ\text{K}; \Delta H_f = 4010 \text{ cal/mole})$				
0.600 W	14.1	17.3	4615	1.68	0.930 W	1.3	1.9	4061	1.01
0.520 C	17.0	21.8	3263	1.18	0.923 C	2.0	2.1	5326	1.33
0.537 W	16.6	20.8	3909	1.42	0.863 W	2.3	3.8	4656	1.16
0.510 W	19.1	22.4	4121	1.50	0.894 W	2.7	2.9	3715	0.93
0.459 C	22.2	25.6	2979	1.08	0.867 C	2.5	3.8	4528	1.13
0.492 W	21.4	23.5	3449	1.25	0.871 W	3.4	3.6	4569	1.14
0.478 C	20.0	24.4	3813	1.38	0.801 C	6.2	5.8	4528	1.13
0.472 W	22.2	24.7	2432	0.88	0.713 C	8.8	8.7	4834	1.21
DIOXANE					0.645 W	10.6	11.2	5068	1.26
$(T_0 = 284.9^\circ\text{K}; \Delta H_f = 3067 \text{ cal/mole})$					0.621 C	14.7	12.1	2965	0.74
0.995 C, W	0.24	0.12	4112	1.34	0.579 W	16.1	13.8	3018	0.75
0.982 C, W	0.49	0.47	3522	1.15	0.551 C	18.4	15.0	2463	0.61
0.935 W	1.60	1.71	3233	1.05	0.540 W	15.3	15.5	3190	0.80
0.801 W	5.0	5.71	3744	1.22	0.546 C	14.6	15.2	4324	1.08
0.775 C	7.4	6.5	3206	1.04	0.503 W	18.2	17.2	4013	1.00
0.716 W	6.7	8.4	3631	1.18	0.476 W	16.7	18.4	1112	0.28

*C and W indicate cooling and warming runs.

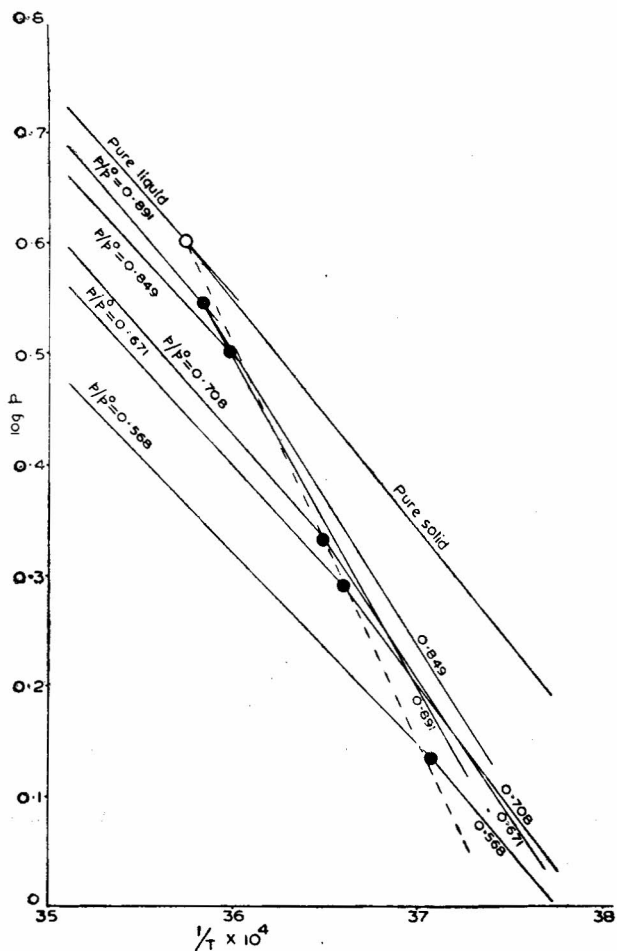


Fig. 2 — Plots of $\log p$ versus $1/T$ for cyclohexane-silica gel system corresponding to different values of p/p° [Dotted line is the least square line through the freezing points of the adsorbate with the freezing point of the pure adsorbate taken as a fixed point]

TABLE 2 — ΔH^* FOR VARIOUS ADSORBATE-ADSORBENT SYSTEMS

Adsorbate	ΔH^* (kcal/mole)	
	Silica gel	Charcoal
Water	15.3	—
Benzene	10.6	—
Formic acid	14.5	15.1
Cyclohexane	16.4	15.1
tert-Butyl alcohol	15.6	14.8
Acetic acid	16.4	—
Dioxane	14.8	—
p-Xylene	15.3	—

and are recorded in Table 2. Except for the benzene-silica gel system, the average value of ΔH^* is 15.3 kcal/mole with a variation of 1.0 kcal/mole. It follows from the above observations that the 'apparent freezing points' for all adsorbate-adsorbent systems (except benzene-silica gel system) should fall on a straight line on a plot of $\log p/p_T^\circ$ vs $\Delta(1/T)$ where p_T° refers to the vapour pressure of the pure adsorbate at its freezing point (T_0) in

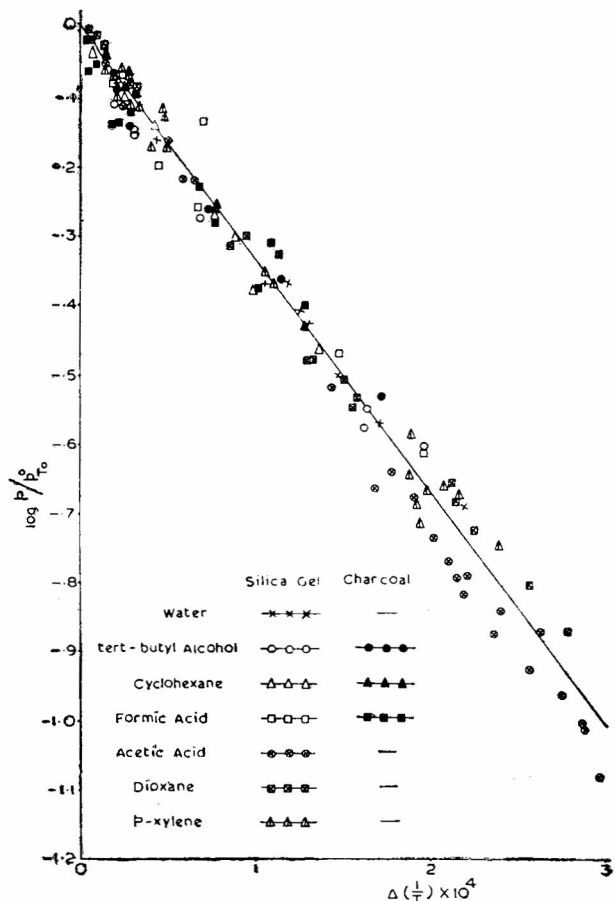


Fig. 3 — Plot of $\log p/p_T^\circ$ versus $\Delta(1/T)$ for various adsorbate-adsorbent systems

each case. This is shown in Fig. 3. This generalized behaviour observed for the adsorbate-adsorbent systems is interesting but at the same time intriguing since the systems differ widely in respect of the vapour pressure, heats of vaporization and sublimation and molecular structure of the adsorbates and different surface characteristics and adsorption potentials of the adsorbents. This regularity in behaviour is interesting since it lends clarity to our understanding of the nature of phase transition in adsorbates.

Nature of phase transition in adsorbate-adsorbent systems — Experimental data from wide range of studies¹⁻¹⁴ show that phase transition of adsorbate (from liquid to solid state) does not occur at one temperature but the solid separates gradually from liquid phase as the temperature is lowered. In other words, after the inception of freezing, the liquid and solid states of adsorbates coexist at a range of lower temperatures, although relative amounts of the two phases are significantly altered with decrease in temperature. For this phase equilibrium chemical potentials μ_l and μ_s are equal and hence vapour pressure of the liquid and the solid adsorbate must also be the same at all these temperatures. It is important to realize that the plot of $\log p$ versus $1/T$ after commencement of freezing should in fact represent a gradual shift of

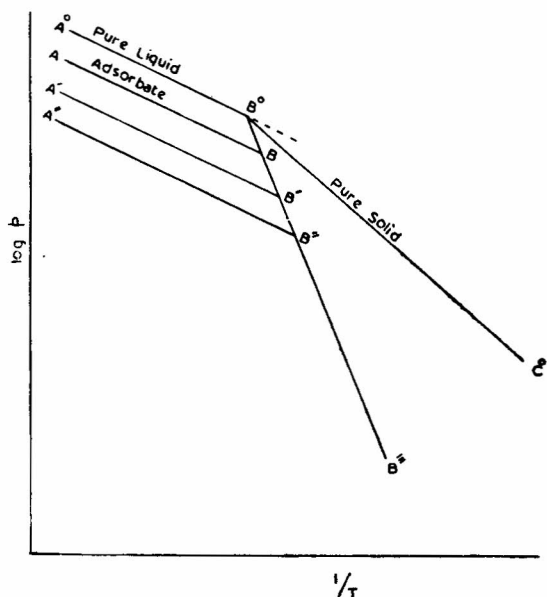


Fig. 4 — Hypothetical plot of $\log p$ versus $1/T$ showing the process of freezing of the adsorbate

the triple point since the three phases of the adsorbate are simultaneously present all along the temperature range.

In the light of the above, under ideal experimental conditions, $\log p$ vs $1/T$ plots (corresponding to different values of p/p°) after commencement of freezing, should follow the line joining the 'apparent freezing points', as depicted in Fig. 4. In that case both $\Delta H_i/\Delta H_f$ should be independent of p/p° . A reference to Fig. 2 (which is typical of the adsorbate-adsorbent systems) will show that the above conditions are not strictly fulfilled by the experimental data, although the plots after commencement of freezing are found to be much more close to the line joining the 'apparent freezing points' (dotted line in Fig. 2) than to the line for the pure solid adsorbate. It follows that $\log p$ vs $1/T$ plots after commencement of freezing certainly do not represent the sublimation curves of the adsorbate. This, in fact, explains the abnormal experimental values of ΔH_i for adsorbate-adsorbent systems. The observed deviations of $\log p$ vs $1/T$ plots after commencement of freezing from ideal behaviour (Fig. 3) and the dependence of $\Delta H_i/\Delta H_f$ on p/p° may become understandable in view of the fact that attainment of true equilibrium conditions between the liquid and solid phases of the adsorbate cannot be easily realized. In order to decide the issue unambiguously, there is need for more carefully obtained experimental data.

Although the experimental data for the various adsorbate-adsorbent systems is in agreement with the mechanism of gradual shift of the triple point, the following questions remain unexplained. Why should the line joining the 'apparent freezing points'

be linear? Why should the lines joining the 'apparent freezing points' for the different adsorbate-adsorbent systems have the same slope? Why does benzene-silica gel system deviate from generalized behaviour?

Theoretical calculation of depression in freezing point (ΔT)—It has been shown earlier^{1,3} that Clausius-Clapeyron equation

$$\ln p/p^\circ = \frac{\Delta H_f}{R} \cdot \frac{\Delta T}{TT_0} \quad \dots(2)$$

and Batchelor and Foster's equation

$$\Delta T = \frac{T_0}{\Delta H_f} \cdot \frac{2M}{r} \left[\frac{\gamma_l}{\rho_l} - \frac{\gamma_s}{\rho_s} \right]_T \quad \dots(3)$$

are inadequate for theoretical calculation of ΔT . However, the fact that the lines joining the 'apparent freezing points' (B° , B, B'.....etc. in Fig. 4) of almost all adsorbate-adsorbent systems have almost the same slope and hence the same value of ΔH^* can be utilized for the calculation of ΔT for these systems. Since ΔH^* has an average value of 15.3 kcal/mole, the relations

$$\ln p/p^\circ = \frac{15300 - \Delta H^*}{R} \cdot \Delta(1/T) \quad \dots(4)$$

and

$$\ln p = \frac{15300}{R} \cdot \Delta(1/T) + \ln p^\circ \quad \dots(5)$$

should yield the theoretical value of ΔT . The values of ΔT calculated from Eq. (4) for the present systems are reported in Table 1. The agreement of the theoretical value with the experimental values should be considered fairly good in view of the uncertainty ($\pm 0.5^\circ$) in the experimental determination of ΔT .

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