of barium oxide. After twenty hours at 28°, the reaction mixture was acidified with concentrated hydrochloric acid and extracted with six 10-cc. portions of ether. Evaporation gave 0.425 g. (72.5%) of crystalline mandelic acid which was dissolved in 10 cc. of 0.5 *N* barium hydroxide. The solution was filtered, allowed to stand one hour, acidified, and extracted with ether. After repetition of the equilibration and sublimation, 0.317 g. (54.2%) of mandelic acid was obtained. Recrystallized from benzene, pure X was obtained, m. p. 118.5–119.3°, showing no depression on admixture with an authentic sample.

Anal. Calcd. for $C_8H_7D_{(7.25\%)}O_3$: D_2O, 0.906. Found: D_2O, 0.036.

The above procedure was repeated using 10.24 g. of water containing 27.6 weight per cent. (corrected for water of hydration) of deuterium oxide and 0.61 g. of phenylglyoxal hydrate. There was obtained 0.360 g. (59%) of crude mandelic acid. Recrystallization afforded 0.296 g., m. p. 118–119°.

Anal. Calcd. for $C_8H_7D_{(27.6\%)}O_3$: D_2O, 3.45. Found: D_2O, 0.039.

α-Hydroxyphenylacetic-*d* Acid.—Mandelic acid (1.470 g.) was refluxed under nitrogen for one week with 13.52 g. of 29.56% deuterium oxide and 1.23 g. of barium oxide. The deuterated mandelic acid, recovered by acidification with concentrated hydrochloric acid, extraction with ether and evaporation *in vacuo*, was equilibrated twice by refluxing for eighteen hours with 17 cc. of water under nitrogen. The recovered equilibrated acid was recrystallized from benzene giving a first crop (A) weighing 0.876 g.

Anal. Calcd. for $C_8H_7D_{(29.56\%)}O_3$: D_2O, 3.70. Found: D_2O, 3.57.

Sample A was twice reëquilibrated by treating with 23 cc. of 0.5 *N* baryta for seventy-five minutes at room temperature.

Anal. Found: D_2O, 3.57, 3.57, 3.57.

Summary

Using phenylglyoxal in which the ketone carbon is marked with C^{13}, it has been proved that there is no rearrangement of the carbon skeleton in the alkali-catalyzed conversion to mandelic acid. The failure of solvent deuterium to become attached to the alcohol carbon atom of mandelic acid prepared from phenylglyoxal in heavy water has allowed exclusion of a proton-removal mechanism and has substantiated a mechanism involving intramolecular transfer of hydrogen. The present status of the mechanism is discussed.

NEW YORK 27, N. Y. RECEIVED AUGUST 25, 1947

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Configuration and Adsorption. A Comparison of the Adsorption of the *cis* and *trans* Isomers of Dichloroethylene on Activated Carbon

BY DAVID H. VOLMAN AND LAWRENCE J. ANDREWS

In an attempt to account for the data of adsorption from the vapor phase on activated carbon adsorbates may be separated into three classifications: first, molecules which can undergo hydrogen bonding; second, molecules which do not form hydrogen bonds but which possess permanent dipole moments; third, molecules which do not form hydrogen bonds and do not have permanent dipole moments.

Only the first classification is known definitely to behave abnormally in adsorption on carbon. For this type of compound the correlation of adsorbability and condensation properties of the gas has been pointed out recently by Volman and Klotz.[1] It was proposed that the initial adsorption does not reflect the hydrogen bonding properties of the molecule even though the relative pressures do, and the apparent anomalies in adsorption are to be explained by the values assigned to the relative pressure axis for the isotherms. For both of the other classifications no anomalies comparable to those found with a compound of the first classification such as water are known. However, it seemed of interest to determine the effect of the existence of a permanent dipole moment on van der Waals adsorption on carbon. A near approach to a comparison of this nature should be obtained by studying the adsorption of molecules differing only in geometric configuration. Thus by choosing *cis*- and *trans*-dichloroethylene the principal difference in interaction effects would seem to be the large difference in dipole moment, zero for the *trans* and 1.8 debyes for the *cis* compound.[2] In addition the isomers are easily obtained in a pure state and have convenient physical properties for adsorption studies.

Further interest in the problem derives from the fact that no comparisons of the adsorption of *cis–trans* isomers from the vapor phase have been made. However, in recent years extensive studies directed toward the separation of *cis–trans* isomers by chromatographic adsorption have been carried out.[3] These studies have all been made from solution and primarily with stereoisomers of carotenoids. In addition the adsorption of maleic and fumaric acids from aqueous solution on activated carbon has been carried out.[4] Here the adsorption is mainly dependent on the degree of ionization of the acids in solution. It was expected that a study of gas phase adsorption of *cis-trans* isomers would yield information on the possibility of separation of such isomers by adsorption techniques.

Experimental

Preparation of Materials.—The *trans* compound was obtained by fractionation of Eastman Kodak Co. *trans*-

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[1] Volman and Klotz, *J. Phys. Chem.*, **14**, 642 (1946).

[2] *Trans. Faraday Soc.*, **30**, Appendix (1934).

[3] Zechmeister, *Chem. Rev.*, **34**, 267 (1944).

[4] Phelps, *J. Chem. Soc.*, 1724 (1929).

dichloroethylene through a four-foot column packed with glass helices. The fraction retained boiled at 48.1° at 756 mm. The *cis* compound was obtained from the *trans* by isomerization according to the method of Jones and Taylor.[5] The *cis* isomer (b. p. 60.5° at 766 mm.) was isolated from the resulting mixture by fractionation on the four foot column.

The activated carbon was obtained from the Pittsburgh Coke and Chemical Company. It was screened to 20–30 mesh, dried at 140° for twenty-four hours and stored in dry air.

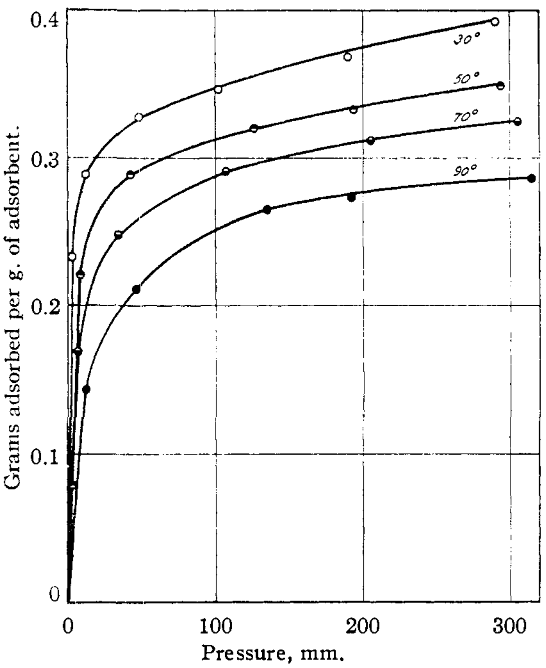

Fig. 1.—*trans*-Dichloroethylene adsorption isotherms.

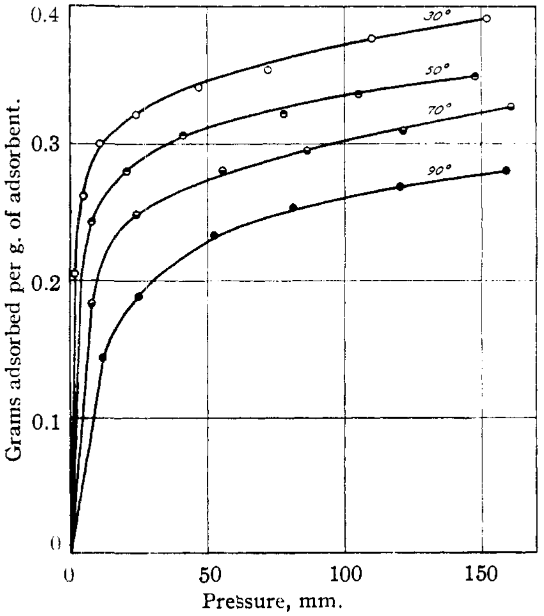

Fig. 2.—*cis*-Dichloroethylene adsorption isotherms.

Adsorption Method.—Adsorptions were determined by a simple gravimetric apparatus. Two grams of the activated carbon was weighed directly into an adsorption chamber. The sample was then outgassed at 100° for twenty-four hours. With proper manipulation of the stopcocks the adsorption chamber may be removed and weighed without breaking the vacuum over the carbon. The adsorption chamber is then replaced in a thermostat at the isothermal temperature, and after evacuation of the air contaminated region the carbon is allowed to come to equilibrium with enough adsorbate to give the desired pressure. The adsorption chamber may then be removed and weighed and the procedure repeated for the full range of pressures used. Although this simplified apparatus is of limited accuracy, the data are sufficiently reliable for the purposes of this experiment.

Results and Discussion

Comparison of Isotherms.—Figures 1 and 2 show the adsorption isotherms obtained for the *trans* and *cis* configurations, respectively, at temperatures 30, 50, 70 and 90°. In order to compare the area of surface covered by the two adsorbates at the same relative pressures it is necessary to determine the areas covered in adsorption. This may be calculated from a knowledge of the weight adsorbed provided the area occupied per molecule is known. A reasonable assumption is that the area occupied by an adsorbed molecule on the surface is the same as the cross section obtained by considering the molecules to be hexagonally close packed in the liquid. Then the average area per molecule is given by

$$A = 4(0.866)\left[\frac{M}{4\sqrt{2}N\rho}\right]^{2/3} \qquad (1)$$

where M is the molecular weight of the gas, N is Avogadro's number and ρ is the density of the liquefied gas.[6] Even if this is not an exact expression for the area of an adsorbed molecule, the assumption of the dependence of A on $1/\rho^{2/3}$ appears to be the significant one for comparative purposes since the exact area is not important.

The densities of the isomers were determined over a range of temperatures from 25 to 48° by means of a Westphal balance and agreed well with already published data.[7] Since the coefficient of thermal expansion is

$$\alpha = \frac{1}{V}\left(\frac{\partial T}{\partial V}\right)_p \qquad (2)$$

a plot of log density *vs.* T should yield a straight line if α is sufficiently constant in the region used. From such a linear plot, Fig. 3, the density at temperatures greater than 48° may be obtained.

To obtain the relative pressures for a comparison of adsorption it was necessary to know the saturation vapor pressures. In the region below the boiling point these values may be obtained from the data of Herz and Rathmann.[7] At higher temperatures the saturation pressures were calculated by use of the Clausius–Clapeyron equation assuming a constant heat of vaporization. The values used are shown in Table I. In Table II a

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[5] Jones and Taylor, THIS JOURNAL, **62**, 3480 (1940).

[6] Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

[7] Herz and Rathmann, *Chem. Ztg.*, **37**, 621 (1913).

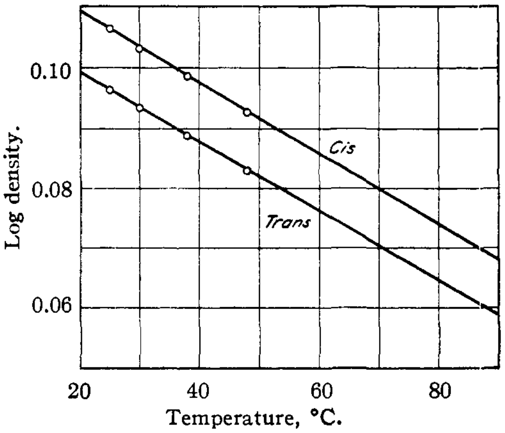

Fig. 3.—Density of *cis*- and *trans*-dichloroethylene.

comparison of the areas covered at the same relative pressures for the *cis* and *trans* isomers is given. The values are seen to be in very good agreement, especially since the P_0 values above the boiling point are of limited accuracy.

TABLE I

SATURATION VAPOR PRESSURES AND AVERAGE ADSORBED MOLECULAR AREAS OF *cis*- AND *trans*-DICHLOROETHYLENE

Temp., °C.	Saturation vapor pressure, mm. *Cis*	*Trans*	Molecular areas, sq. Å. *Cis*	*Trans*
30	251	380	27.5	27.9
50	537	776	28.0	28.4
70	1050	1440	28.5	28.9
90	1900	2570	29.0	29.4

TABLE II

COMPARISON OF ADSORPTION OF *cis*- AND *trans*-DICHLOROETHYLENE AT THE SAME VALUES OF RELATIVE PRESSURE

Temp., °C.	Relative pressure, P/P_0	Area of surface covered, sq. m./g. *cis*	*trans*
30	0.1	561	567
	.2	603	602
	.3	632	626
	.4	653	647
	.5	667	663
	.6	680	678
50	.1	543	532
	.2	587	580
	.3	613	608
70	.1	532	532

The close correspondence for area covered at the same relative pressures in the above data indicates that the forces important in adsorption are the same as those which account for condensation even at low relative pleasure values. Brunauer, Emmett and Teller[8] have derived a theory of adsorption isotherms on the assumption that the same forces that produce condensation are also responsible for adsorption. Our findings indicate that this is valid where the principal intermolecular forces are van der Waals with or without a contribution due to the existence of a permanent dipole moment. On the basis of the discussion of Volman and Klotz,[1] molecules which form hydrogen bonds in the liquid but not in the vapor state are excluded from the above generalization.

Surface Area and Heat of Adsorption.—The shape of the adsorption isotherms and the exten-

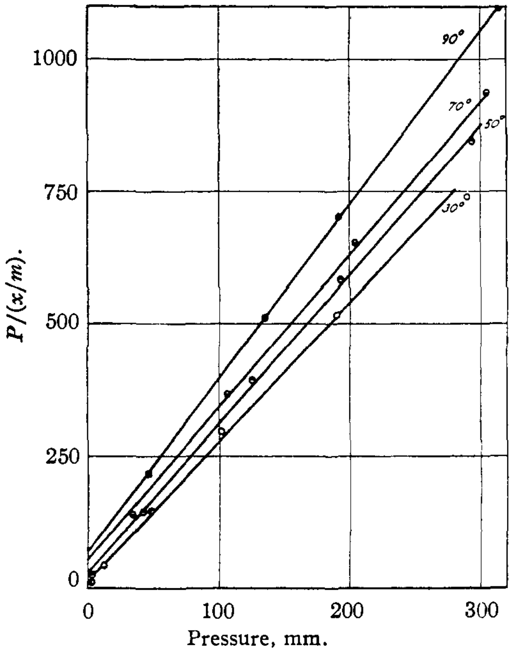

Fig. 4.—Adsorption isotherms of *trans*-dichloroethylene, plotted according to the Langmuir equation x/m in grams per g. of adsorbent.

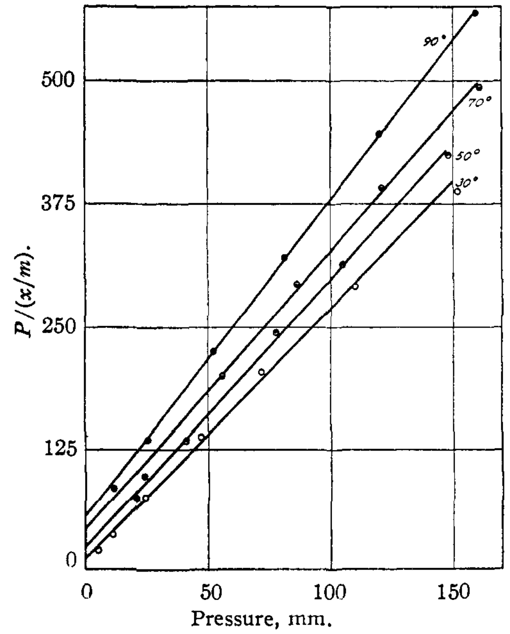

Fig. 5.—Adsorption isotherms of *cis*-dichloroethylene, plotted according to the Langmuir equation x/m in grams per g. of adsorbent.

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(8) Brunauer, Emmett and Teller, THIS JOURNAL, 60, 309 (1938).

sive evidence of Brunauer and Emmett[9] for unimolecular adsorption on activated carbon suggested the advisability of Langmuir equation plots of the adsorption data. Figures 4 and 5 show the results obtained.

Using the B.E.T.[8] equation for unimolecular adsorption in the form

$$\frac{p}{(x/m)} = \frac{p_0}{c(x/m)_M} + \frac{p}{(x/m)_M} \qquad (3)$$

where $(x/m)_M$ is the weight adsorbed per g. of adsorbent equivalent to a monolayer, the area corresponding to a monolayer may be determined from the slopes of the plots in Figs. 4 and 5. Since c in the above equation is defined by

$$c = \frac{a_1b_2}{b_1a_2} e^{(E_1 - E_L)/RT} \qquad (4)$$

where $E_1 - E_L$ is the difference between the heat of adsorption and the heat of liquefaction, $E_1 - E_L$ may be determined from the intercepts of the curves if a_1b_2/b_1a_2 is assumed unity as is customary.

Although it has been common to use the unimolecular adsorption equation for isotherms which are not approximated by the $n = \infty$ form of the B.E.T. equation, it has been pointed out[10] that the limiting B.E.T. equation for $n = 1$ is not valid except for isotherms which have an n value very close to unity. Joyner, Weinberger and Montgomery[10] have shown that the B.E.T. equation may be written

$$\frac{\Phi(n,X)}{(x/m)} = \frac{1}{c(/x/m)_M} + \frac{\theta(n,X)}{(x/m)_M} \qquad (5)$$

where

$$\Phi(n,X) = \frac{X(1 - X^n) - nX^n(1 - X)}{(1 - X)^2}$$

and

$$\theta(n, X) = \frac{X(1 - X^n)}{1 - X}$$

X is the relative pressure and n is the number of layers to which the gas is limited.

For the proper choice of n, a plot of $\Phi(n,X)/(x/m)$ *vs.* $\theta(n,X)$ should yield a straight line. Figures 6 and 7 show the results obtained when $n = 1.60$ is used. The plots are seen to be linear and are superior to the $n = 1$ plots, especially for the 30° data which cover the greatest relative pressure region. The area and $E_1 - E_L$ values obtained for $n = 1$ and $n = 1.60$ are presented in Table III. The use of the more correct $n = 1.60$ in place of $n = 1$ results in considerably lower and more constant monolayer areas. However, the $E_1 - E_L$ values are not appreciably altered.

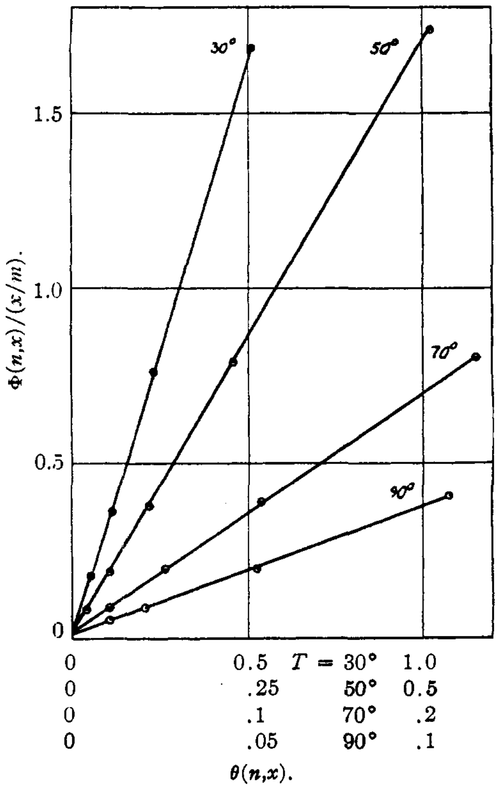

Fig. 6.—Adsorption isotherms of *trans*-dichloroethylene according to B. E. T. theory for $n = 1.60$.

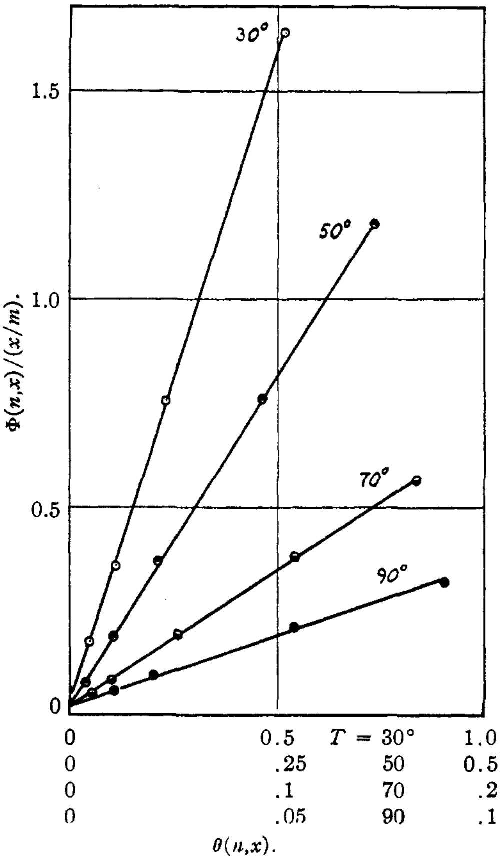

Fig. 7.—Adsorption isotherms of *cis*-dichloroethylene according to B.E.T. theory for $n = 1.60$.

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[9] Brunauer and Emmett, This Journal, 59, 2682 (1937).

[10] Joyner, Weinberger and Montgomery, *ibid.*, 67, 2182 (1945).

TABLE III

COMPARISON OF MONOLAYER AREAS AND DIFFERENCE BETWEEN HEAT OF ADSORPTION AND VAPORIZATION FOR *cis* AND *trans*-DICHLOROETHYLENE.

Temp., °C.	Area of monolayer, sq. m./g.				$E_1 - E_L$, kcal./mole			
	cis		*trans*		*cis*		*trans*	
	$n = 1$	$n = 1.6$	$n = 1$	$n = 1.6$	$n = 1$	$n = 1.6$	$n = 1$	$n = 1.6$
30	6.8×10^2	5.6×10^2	6.9×10^2	5.6×10^2	2.5	2.7	2.7	2.7
50	6.4	5.6	6.6	5.6	2.7	2.7	2.8	3.0
70	6.4	5.6	6.4	5.4	2.9	3.3	3.0	3.3
90	5.7	5.6	5.7	5.2	3.4	3.2	3.5	3.3

The differential heat of adsorption is ordinarily considered to be given by the Clausius–Clapeyron type equation

$$\frac{q}{R} = \left(\frac{\partial \ln p}{\partial(1/T)}\right)_a \qquad (6)$$

where the amount of adsorbate on the surface is the same. Then the heat of adsorption may be calculated from isosteres constructed on the basis of constant amount adsorbed. However, Wilkins[11] has correctly pointed out that the above equation should be applied to isosteres based on a constant area of surface covered rather than constant weight adsorbed.

In Fig. 8 plots of log p *vs.* $1/T$ are shown for equal areas covered in the temperature range 30–70°. The q values found are 8.5 kcal./mole for the *trans* and 9.0 kcal./mole for the *cis* compound. Using 7.0 and 7.4 kcal./mole as the heats of vaporization for the *trans* and *cis* compounds, respectively,[7] these differences are seen to be about the same as for the heats of vaporization. The values of $q - E_L$ obtained are correspondingly 1.5 and 1.6 kcal./mole. If the calculation is made on the basis of constant amount adsorbed, one obtains values of 3.9 and 3.8 kcal./mole, respectively. Wilkins[11] has predicted that the values based on constant weight should be lower than those based on constant area covered. However, it may be readily seen that the slope of curves constructed on the basis of constant weight adsorbed would be steeper than the ones shown in Fig. 8. For example if the point corresponding to the highest temperature were the same for both methods of calculation, then at a common lower temperature the pressure corresponding to an equal area covered must be greater than the pressure corresponding to an equal weight absorbed if the density of the adsorbate decreases with increasing temperature.

The above values are to be compared with the $E_1 - E_L$ values reported in Table III, approximately 3.0 kcal./mole. The discrepancy is not unexpected since the E_1 values are integral values while the isosteric values are differential ones. Actually the isosteres were taken near a monolayer where the differential heat of adsorption would be expected to be lower than the integral heat of adsorption since the differential heat of adsorption generally decreases with increasing adsorption even within a monolayer.[12]

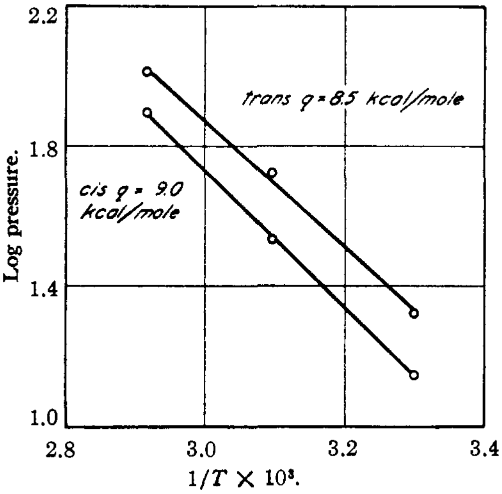

Fig. 8.—Isosteric heat of adsorption of the dichloroethylenes: area covered equal to 531 sq. m./g.

Note on the Separation of *cis–trans* Isomers by Adsorption.—It is of interest to speculate on the possibilities of separation of the *cis–trans* isomers by adsorption on activated carbon from the gas phase. A separation factor for a single stage in adsorption may be defined by

$$\gamma = (x_c/X_t)/(p_c/p_t) \qquad (7)$$

where x_c/x_t is the ratio of weights of *cis* and *trans* isomers on the adsorbent and p_c/p_t is the ratio of partial pressures of *cis* and *trans* isomers in the gas phase in equilibrium with the adsorbent. This equation is analogous to the separation factor usually defined for isotopic separation.

Let us now consider the separation factor obtained for an equimolar gas phase mixture of *cis* and *trans*-dichloroethylenes. Assume that in the mixed adsorption the individual adsorptions are in the same ratio what would obtain if they were adsorbed singly at a pressure equal to the total. For a pressure of 5.0 mm. for each isomer this leads to a value of $\gamma = 1.07$ for data from the 30° isotherms. This value is in the same general range usually obtainable in single stage separations of isotopic mixtures and implies that separation of most *cis–trans* isomers by gas phase adsorption would be a multi-stage process. The recent results of Isom and Hunt[13] obtained in an attempt to separate diastereoisomers by gas phase adsorption on activated carbon confirm this conclusion. However, it may be observed that Claesson,[14] has obtained considerable success in gas phase separations by using the displacement development techniques of chromatography.

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[11] Wilkins, *Proc. Roy. Soc.* (*London*), **A164**, 496 (1938).

[12] Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947).

[13] Isom and Hunt, *J. Phys. Chem.*, **50**, 28 (1946).

[14] Claesson, *Arkiv Kemi, Mineral Geol.*, **23A**, 1 (1946).

Summary

1. Adsorption isotherms on activated carbon were determined for *cis* and *trans*-dichloroethylene over a range of temperatures in the gas phase.

2. The adsorption for both isomers followed the B.E.T. theory if the number of layers possible in adsorption was taken as 1.6. The surface areas and heats of adsorption based on the theory were determined.

3. Isosteric heats of adsorption based on a constant fraction of the surface covered rather than constant weight adsorbed were calculated.

4. The adsorption of the *cis* and *trans* isomers were found to be the same when a comparison of surface area covered at fixed relative pressures was made.

5. It was concluded that the condensation properties of molecules adequately determine the adsorption where the only intermolecular forces are van der Waals with or without permanent dipole interaction.

6. It was shown that the separation of *cis–trans* isomers by adsorption on charcoal from the gas phase could be effected only in a multi-stage apparatus.

DAVIS, CALIFORNIA RECEIVED MAY 14, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Partial Molal Volume of Acetic Acid in Sodium Acetate and in Sodium Chloride Solutions[1]

BY HENRY E. WIRTH

It has been shown[2] that the partial molal volumes of certain electrolytes depend on the total (volume) ionic strength of the solution as predicted by the Debye–Hückel theory. Redlich and Klinger[3] and Gucker[4] have shown experimentally that the apparent molal volumes of certain non-electrolytes are linear functions of the volume concentration. Redlich and Nielsen[5] found that the apparent molal volume of acetic acid (Φ_3)[6] could be represented by the equation

$$\Phi_3 = 51.8397 + 0.14184m_3 \qquad (1)$$

in the range 0.2–5 *m*, where *m* is the molality. Since the partial molal volume ($\overline{V}_3$) can be obtained from the apparent molal volume by the relation

$$\overline{V}_3 = \Phi_3 + m_3 \partial\Phi_3/\partial m_3 \qquad (2)$$

$\overline{V}_3$ is also a linear function of the molality in this concentration range. In this paper the effects of electrolytes on the partial molal volume of acetic acid are reported.

Methods.—Densities at 25° were determined by the sinker method using apparatus described previously.[2] A stock solution of acetic acid was analyzed by adding a weighed excess of standard carbonate-free sodium hydroxide solution and titrating the excess base with dilute hydrochloric acid solution using phenolphthalein as the indicator. The stock solution contained 0.37584 ± 0.00004 g. of acetic acid per gram of solution.

Solutions for the density determination were prepared by weight from the stock acetic acid. Sufficient anhydrous salt (sodium chloride or sodium acetate, previously dried at 200° for six hours) was added to give the required concentration of electrolyte.

The observed density differences were used to calculate the volume of solution containing 1000 grams of water (V) and the apparent molal volume of acetic acid in each of the solutions investigated. The partial molal volumes were obtained from the apparent molal volumes by use of equation 2.

Results

The equation

$$V = 1002.935 + 51.832m_3 + 0.1394m_3^2 \qquad (3)$$

which represents the experimental values of V in an aqueous acetic acid solution (Table I) with an average deviation of ±0.004 ml. can be arranged to give $\Phi_3 = 51.832 + 0.1394m_3$. The values of Φ_3 reported here average 0.013 ml. per mole less than those reported by Redlich and Nielsen.[5] This compares to the probable experimental error of 0.008 ml. per mole due to errors in concentration alone quoted by these authors.

Differentiation of equation 3 gives

$$\overline{V}_3 = 51.832 + 0.2788m_3 \qquad (4)$$

which agrees with the values of $\overline{V}_3$ calculated directly from the data with an average deviation of ±0.008 ml. per mole. Equations 2, 3 and 4 are valid only in the concentration range 0.16–2.5 molal, since in solutions less than 0.16 *m* the increased ionization of acetic acid causes Φ_3 and $\overline{V}_3$ to decrease toward the limiting value (40.68) characteristic of H^+ and $C_2H_3O_2^-$ at infinite dilution.

For aqueous sodium chloride solutions the equation

$$V = 1002.935 + 16.670m_2 + 1.6363m_2^{3/2} + 0.1705m_2^2 \qquad (5)$$

represents the experimental results with an aver-

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[1] Presented at the Chicago meeting of the American Chemical Society, September, 1946.

[2] Wirth, THIS JOURNAL, **59**, 2549 (1937).

[3] Redlich and Klinger, *Sitzb. Akad. Wiss. Wien, Abt. IIb*, **143**, 489 (1934).

[4] Gucker, Gage and Moser, THIS JOURNAL, **60**, 2582 (1938).

[5] Redlich and Nielsen, *ibid.*, **64**, 761 (1942).

[6] In this paper the subscript 3 refers to acetic acid, the subscript 2 to sodium chloride or sodium acetate.