Comparison of experimental and theoretical entropies for esters adsorbed on graphitized thermal carbon black

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By comparing theoretically calculated and experimental standard entropies of adsorption it is proved that the state of esters adsorbed on graphitized thermal carbon black corresponds quite well to the model of an ideal two-dimensional gas.

It is well known that the gas-chromatographic method is quite suitable for the determination of thermodynamic adsorption characteristics in the Henri region where the linear isotherm equation is valid:

$$\Gamma = K_{1,c}c, \qquad (1)$$

where Γ is the adsorption (in mmol m^{-2}), c is the concentration of gaseous adsorbate (in mmol cm^{-3}) and $K_{1,c}$ is the so-called Henri constant (in cm^3 m^{-2}). The basic assumption that permits us to connect chromatographic data (principally non-equilibrium) with thermodynamics of adsorption lies in the equalization of $K_{1,c}$ with the corresponding retention volume $V_{A,1}$.[1] According to this assumption the following approximate equation for the temperature dependence of $V_{A,1}$ is usually used:

$$\ln V_{A,1} \equiv \ln K_{1,c} = \frac{B}{T} + A = \frac{\bar{q}_{\mathrm{dif,1}}}{R} \cdot \frac{1}{T} + \left(\frac{\Delta \bar{S}_{1,c}^{s^o}}{R} + 1 \right), \qquad (2)$$

where $\bar{q}_{\mathrm{dif,1}}$ is the so-called differential heat of adsorption, $\Delta \bar{S}_{1,c}^{s^o} = \bar{S}_1^{s^o} - \tilde{S}_g^o$, where $\bar{S}_1^{s^o}$ is the standard differential entropy of adsorbed substance, $\tilde{S}_g^o$ is the standard molar entropy of adsorbate in gaseous phase, and R is the gas constant. The coefficients A and B and also $\bar{q}_{\mathrm{dif,1}}$ and $\Delta \bar{S}_{1,c}^{s^o}$ in the accepted approximation do not depend on T and can be determined from routine chromatographic data. The following expression will be useful:[2]

$$\bar{S}_1^{s^o} = \tilde{S}_1^{s^o} - R, \qquad (3)$$

where $\tilde{S}_1^{s^o}$ is the standard integral entropy of the adsorbed substance. Standardisation of entropies is connected with the dimension of $K_{1,c}$, the standard states being $\Gamma = 1$ and $c = 1$. This is another system of standardisation as compared with that accepted in traditional studies,[3,4] our system being more convenient when the use of chromatographic (and not adsorption) data is intended. The index 1 at different quantities refers to the Henri region and the index s is ascribed to the characteristics of the adsorbed substance.

Some attempts to represent the physical state of the adsorbed substance at the surface as a two-dimensional gas have already been made earlier in studies on adsorption (see, *e.g.* ref. 5). In the present paper we have used the well known model of an ideal two-dimensional gas. The essential point of the model consists of a supposition that the whole change in entropy that accompanies the transfer under equilibrium conditions of 1 mole of substance from the gas phase to the adsorbed state is equal to its change at the loss of one translational degree of freedom. It follows from molecular statistics[6] that

$$\tilde{S}_{\mathrm{tr}}^{(3)} = R\left[-\ln c - \ln N_{\mathrm{A}} + \frac{5}{2} + \ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{\frac{3}{2}} \right] \qquad (4)$$

$$\tilde{S}_{\mathrm{tr}}^{(2)} = R\left[-\ln \Gamma - \ln N_{\mathrm{A}} + 2 + \ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right) \right], \qquad (5)$$

where N_{A} is the Avogadro number, k_{B} is the Boltzmann constant, h is the Planck constant and m is the mass of the molecule. $\tilde{S}_{\mathrm{tr}}^{(3)}$ and $\tilde{S}_{\mathrm{tr}}^{(2)}$ are translational contributions to the integral molar entropies for a three-dimensional and a two-dimensional gas, respectively. For the standard integral translational entropies we have

$$\tilde{S}_{\mathrm{tr}}^{(3)^o}(c = 1) = R\left[-\ln N_{\mathrm{A}} + \frac{5}{2} + \ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{\frac{3}{2}} \right] \qquad (6)$$

$$\tilde{S}_{\mathrm{tr}}^{(2)^o}(\Gamma = 1) = R\left[-\ln N_{\mathrm{A}} + 2 + \ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right) \right] \qquad (7)$$

For $\Delta \bar{S}_{1,c}^{s^o}$ (theor.), in accordance with the accepted model and taking into account the relation (3) we obtain:

$$-\Delta S_{1,c}^{s^o}(\text{theor.}) = \tilde{S}_{\mathrm{tr}}^{(3)^o} - \tilde{S}_{\mathrm{tr}}^{(2)^o} + R = R\ln\sqrt{MT} + 56.95 + R, \quad (8)$$

where M is the molecular mass of adsorbate substance and the number 56.95 accumulates all the constants present.

The quantities $\Delta \bar{S}_{1,c}^{s^o}$ (theor.) calculated using equation (8) are now to be compared with experimental values $\Delta \bar{S}_{1,c}^{s^o}$ (exp.) obtained from coefficient A. In the present work the comparison has been done with $\Delta \bar{S}_{1,c}^{s^o}$ (exp.) for 30 esters adsorbed on graphitized thermal carbon black (GTCB).

Gas chromatographic measurements were carried out using a Pye chromatograph with a β-ionisation argon detector. Argon was used as a carrier gas at a flow rate of 25–35 cm^3 min^{-1} and excess pressure at the inlet of column equal to 300–380 mmHg. The chromatographic column was a straight glass tube with dimensions 120×0.25 cm. As an adsorbent GTCB 'Sterling FTG-D5' with a specific surface area $s = 11.8$ m^2 g^{-1} was used. The pellets of GTCB were prepared by shaking without binding material and had a diameter 0.25–0.50 mm. To eliminate the oxygen-containing compounds on the surface of the carbon black the pellets underwent thermal treatment at 1273 K in a flow of hydrogen gas during 4 h. The average temperatures T_{av} of the intervals in which the measurement of $V_{A,1}$ were performed, as well as the values of $\bar{q}_{\mathrm{dif,1}}$ and $\Delta \bar{S}_{1,c}^{s^o}$ (exp.), are presented in Table 1. The latter quantities were calculated using equation (2) (linear dependence $\ln V_{A,1} - 1/T$) and a standard procedure.[1] In the same Table 1 the corresponding $\Delta \bar{S}_{1,c}^{s^o}$ (theor.) values for the temperatures $T = T_{\mathrm{av}}$ are given. The agreement between $\Delta \bar{S}_{1,c}^{s^o}$ (theor.) and $\Delta \bar{S}_{1,c}^{s^o}$ (exp.) values is on the whole quite good, *i.e.* the experimental data are not in contradiction with the simple model of an adsorbed state as a two-dimensional ideal gas. The correspondence becomes a little worse with more heavy molecules for which the temperatures of the chromatographic experiment are higher, and presumably systematic experimental errors are also higher. This is probably the reason why in all cases, except for two, the following inequality is fulfilled: $\left|\Delta \bar{S}_{1,c}^{s^o}(\text{exp.})\right| > \left|\Delta \bar{S}_{1,c}^{s^o}(\text{theor.})\right|$.

It should be remembered that the molecular model used here is very a simplified one. First of all, strictly speaking, the third translational degree of freedom does not completely vanish but transforms itself into a vibration of low frequency perpendicular to the adsorbing surface that can give a significant contribution to $\tilde{S}_1^s$, the integral entropy of adsorbed substance, and thus diminish $\left|\Delta \bar{S}_{1,c}^{s^o}(\text{theor.})\right|$.[2] This change in entropy is probably compensated by a partial hindering of the

Table 1 Experimental values $\bar{q}_{\mathrm{dif},1}$ (kJ mol^{-1}), $\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$(exp.) (J mol^{-1} K^{-1}) and $\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$(theor.) (J mol^{-1} K^{-1}), calculated by equation (8) for esters adsorbed on the surface of GTCB.

N	Substance	M	$T_{\mathrm{av}}/°C$	$-\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$(exp.)	$-\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$(theor.)	$\bar{q}_{\mathrm{dif},1}$
1	Ethyl formate	74	326.6	110	107	29.3
2	Methyl acetate	74	344.2	110	107	29.6
3	Vinyl acetate	86	361.7	113	108	34.9
4	Ethyl acetate	88	356.7	112	108	34.1
5	Methyl propionate	88	360.7	112	108	33.3
6	Methyl acrylate	86	361.7	113	108	35.5
7	Propyl formate	88	359.2	111	108	33.7
8	Isopropyl acetate	102	385.2	112	109	36.9
9	Propyl acetate	102	395.2	114	109	39.0
10	Methyl isobutyrate	102	400.0	109	109	35.5
11	Methyl butyrate	102	392.4	113	109	38.4
12	Butyl formate	102	400.8	109	109	36.7
13	Methyl isovalerate	116	411.0	114	110	41.8
14	Isoamyl formate	116	411.0	115	110	42.2
15	Ethyl butyrate	116	457.0	114	110	42.5
16	Propyl propionate	116	455.0	113	110	43.3
17	Butyl acetate	116	435.6	119	110	44.7
18	Methyl caproate	130	458.4	117	111	48.1
19	Ethyl valerate	130	458.4	113	111	46.0
20	Propyl butyrate	130	455.7	118	111	47.5
21	Butyl propionate	130	462.4	118	111	48.2
22	Butyl acrylate	128	457.0	121	111	49.8
23	Amyl acetate	130	458.4	121	111	49.7
24	Isoamyl acetate	130	462.8	117	111	46.7
25	Ethyl caproate	144	470.6	128	112	55.9
26	Butyl butyrate	144	470.6	126	112	59.9
27	Amyl propionate	144	462.4	124	111	54.9
28	Amyl butyrate	158	476.8	127	112	59.2
29	Isoamyl butyrate	158	476.8	123	112	56.3
30	Isoamyl isobutyrate	158	459.5	118	112	53.3

rotations of the adsorbed molecules, so that the values $\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$ (theor.) become very close to $\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$ (exp.). However, the temperature dependence of $\Delta\bar{s}_{1,c}^{\mathrm{s}\circ}$ (theor.), as presented in equation (8), is inverse to the true one, because the heat capacity of an adsorbed substance is always higher than that of a gas. This is the main shortcoming of the model considered above.

References

1 A. V. Kiselev, *Mezhmolekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* (*Intermolecular interactions in adsorption and chromatography*), Vysshaya shkola, Moscow, 1986 (in Russian).
2 A. A. Lopatkin, *Teoreticheskie osnovy fizicheskoi adsorbtsii* (*Theoretical foundations of physical adsorption*), Izdatel'stvo Moskovskogo Universiteta, Moscow, 1983 (in Russian).
3 C. Kemball, *Advances in Catalysis and Related Subjects*, Academic Press, New York, London, 1952, vol. 2, pp. 233–250.
4 J. H. de Boer, *The Dynamic Character of Adsorption*, Oxford at the Clarendon Press, 1953.
5 E. Hückel, *Adsorption und Kapillarkondensation*, Akademische Verlagsgesellschaft M. B. H., Leipzig, 1928 (in German).
6 E. Hála and T. Boublik, *Einführung in die Statistische Thermodinamik*, Academia, Prague, 1970 (in German).