J. Pharm. Pharmacol., 1964, **16**, 258–264 Received October 9, 1963

Sorption of water vapour and surface activity of ghatti gum

P. H. ELWORTHY AND T. M. GEORGE

The sorption of water vapour by three fractions of sodium ghattate has been studied at 25° and 40°. The results were fitted by Brunauer, Emmett & Teller plots at low relative vapour pressures. Calculations of the differential heats and entropies of sorption gave initially exothermic $\Delta\bar{H}$ values and negative $\Delta\bar{S}$ values. As the sorption proceeded the signs of the thermodynamic properties became positive The mechanism of sorption onto different parts of the macromolecules was discussed.

The surface tension of one sodium ghattate fraction was measured in water, 0·05 and 0·5 N sodium chloride solution, as a function of concentration, using the sessile drop method. The presence of salt enhanced the surface activity. A structure for the adsorbed film is suggested.

PREVIOUSLY (Elworthy & George, 1963) sodium ghattate was studied in water and in dilute sodium chloride solutions by light-scattering and viscosity techniques. The molecular weight was in the 2–3 × 10^6 region depending on which of the three fractions (Elworthy & George, 1963) used; a rod shaped molecule fitted the experimental results best. For fraction 2, the length of the rod was 3,680 Å in water, and 2,660 Å in 0·5N sodium chloride solution. The molecular contraction found on adding salt is characteristic polyelectrolyte behaviour.

Some idea of the interaction of water with the sodium ghattate molecules has now been gained by studying the sorption of water vapour on to the solid gum. It was also interesting to determine the effect of added salt on the surface activity at the air: water interface.

Experimental

MATERIALS

The three fractions of sodium ghattate have been described by Elworthy & George (1963). Analar sodium chloride was used, and water was twice distilled from permanganate.

SORPTION OF WATER VAPOUR

About 0·4 g of the three samples of sodium ghattate were contained in weighing bottles which fitted into wells cut in a thick brass plate. The plate rested on a glass support, 4 cm. high, inside a wide mouthed glass bottle. A layer of sulphuric acid solution, 1–2 cm deep was placed at the bottom of the bottle. The bottle was connected to a three way tap by means of ground glass joints; vacuum could be gently applied to the samples. The samples were placed in the apparatus after drying at 40° in a vacuum oven over P_2O_5, and weighing them accurately, Both the sulphuric acid and the samples were degassed at 0·01 mm Hg for 2 hr, during this process the bottle was cooled in a solid carbon dioxide/acetone mixture, although it was allowed to warm up occasionally. The apparatus

From the School of Pharmacy, Royal College of Science and Technology, Glasgow, C.1.

was immersed in a thermostated bath at 25° or 40° (±0·01°). The samples were removed and weighed every few days until their weights were constant. The concentration of sulphuric acid was determined by titration with standard alkali after equilibrium had been reached. Relative vapour pressures were obtained from the acid concentration using Stokes & Robinson's (1959a) tables for 25°, and International Critical Tables for 40°.

Adsorption experiments were commenced with samples which had been dried and degassed, while for desorption experiments degassed samples were placed over water for 2–3 days before use.

SURFACE TENSION MEASUREMENTS

Preliminary experiments using a Wilhelmy plate apparatus (Elworthy & Macfarlane, 1962) gave irreproducible results, possibly due to adsorption of solute on the platinum plate. This method was discarded, and a sessile drop apparatus based on the designs of Shotton (1955) and Andreas, Hauser & Tucker (1938) was set up. The drop of solution was placed on a glass plate made hydrophobic with a coating of hard paraffin, and the plate placed in a glass box thermostated to 20±0·1°. The drop was illuminated with light from a sodium vapour lamp (Mazda 80/H), which passed through a stop controlling the area of illumination, and a condensing lens. An ebonite rod of known diameter was suspended above the drop to enable the magnification factor to be calculated. Several small tubes filled with water were present in the glass box to give a saturated atmosphere around the drop.

The drop could be photographed with a half plate camera to give a permanent record, using a Cambridge Universal Measuring Machine to measure the image. By removing the camera lens, the drop could also be viewed through the body of the camera by a cathetometer. Both drop height and equatorial diameter could be measured. Wheeler, Tartar, & Lingafelter's (1945) corrections were used in the calculation of surface tension.

The apparatus was tested by measuring the surface tension of water, giving 72·9 dynes cm^{-1} at 20° and 72·0 dynes cm^{-1} at 25°, compared with literature figures of 72·8 and 72·0 dynes cm^{-1} respectively (Harkins, 1959). The readings on water were constant over the time period necessary for equilibrium of solutions.

Results and Discussion

SORPTION OF WATER VAPOUR

The adsorption and desorption isotherms for sodium ghattate are shown in Fig. 1a, b, and c, as plots of 'a' (g water/100g material) against 'x' (relative vapour pressure). No hysteresis loops were observed for any of the samples at either temperature. Each sample sorbed more water vapour at low x values at 25° than at 40°, but at higher relative vapour pressures the situation was reversed.

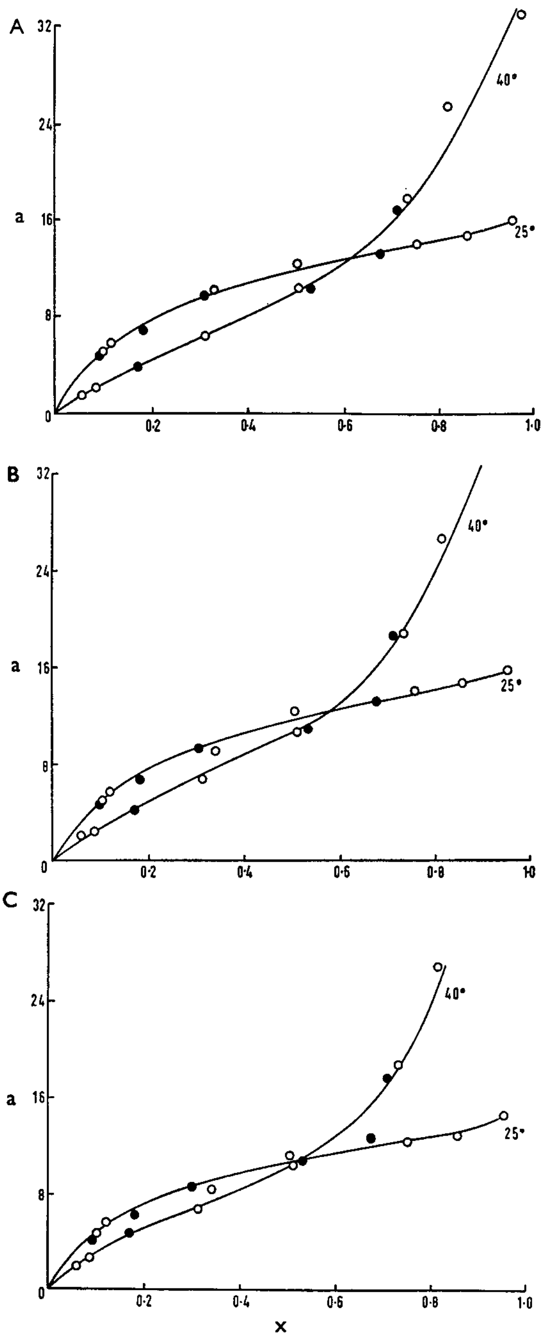

FIG. 1. Sorption isotherms for water vapour on sodium ghattate. A. Fraction 1. B. Fraction 2. C. Fraction 3. ○ = adsorption. ● = desorption. See p. 259 for symbols.

Good B.E.T. plots (Brunauer, Emmett & Teller, 1938) were obtained for all samples below $x = 0{\cdot}4$. The values of the amount of water sorbed in the first layer, a_1, and the B.E.T. constant, C, were calculated from the slopes and intercepts of the plots. The values of a_2 and a_S, the amount of water sorbed in the second layer and at saturation respectively, were determined from graphs of a/x against x; a_2 being calculated from the minimum in the curves, and a_S from the intercept on the a/x axis at $x = 1$ (see Elworthy, 1961).

TABLE 1. SORPTION OF WATER VAPOUR ON SODIUM GHATTATE

Fraction	Temp. ° C	a_1	a_2	a_S	C	a_1 moles/polar group
1	25	7·69	15·35	19·70	13·0	7·13
1	40	6·58	8·99	36·75	4·75	
2	25	7·66	15·44	18·75	12·32	7·80
2	40	7·35	10·08	39·30	4·39	
3	25	7·50	13·77	18·00	11·80	7·73
3	40	7·95	9·00	45·00	5·09	

At 25° the values of a_2 for all fractions were approximately twice the a_1 values. In general there is little difference between the a_1 values for the three fractions. By analogy with the sorption of water vapour on proteins and phosphatides (Bull, 1944; Mellon, Horn & Hoover, 1949; Altman & Benson, 1960; Elworthy, 1961, 1962) it would be expected that the polar groups in the sodium ghattate molecule would be responsible for the initial sorption; there is also the possibility of interactions between additionally sorbed water and the hydroxy groups of the sugar residues present in the macromolecules. The thermodynamics of sorption gives some aid in distinguishing between these effects.

The differential heats and entropies of sorption were determined from the isotherms, assuming $\Delta\bar{H}$ to be linear over the 25–40° temperature interval, using (Barrer & Kelsey, 1961):

$$\Delta\bar{H} = \bar{H}_S - \tilde{H}_1 = R\left(\frac{d\ln.x}{d(1/T)}\right)_{p,\,N_1,\,N_2}$$

$$\Delta\bar{S} = \bar{S}_S - \tilde{S}_1 = (1/T)(\Delta\bar{H} - RT\ln.x)$$

where $\bar{H}_S$ and $\bar{S}_S$ are the partial molar enthalpies and entropies of sorbate, $\tilde{H}_1$ and $\tilde{S}_1$ are the molar enthalpies and entropies of water, and N_1 and N_2 are the number of moles of sorbate and sorbent respectively. The values of $\Delta\bar{H}$ and $\Delta\bar{S}$ are plotted against a in Figs 2 and 3.

All three fractions show roughly the same thermodynamic behaviour. Both $\Delta\bar{H}$ and $\Delta\bar{S}$ are negative at low values of a, but become increasingly positive as more sorption takes place. This implies that during the initial stages of sorption there is a distinct ordering of the water molecules on the sodium ghattate compared with their state in liquid water. This could well be a result of interactions with the polar groups and counter ions of the macromolecules. For $\Delta\bar{S}$ to become positive with further sorption a second process must be postulated, which may well be a mixing process between the sorbent and the hydroxy groups of the macromolecule. The

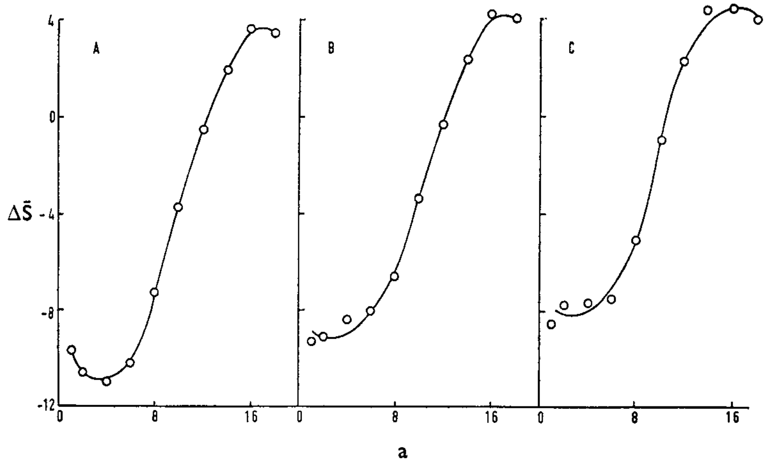

FIG. 2. Differential entropy of sorption, ΔS̄, against amount of water vapour sorbed, a. A. Fraction 1. B. Fraction 2. C. Fraction 3.

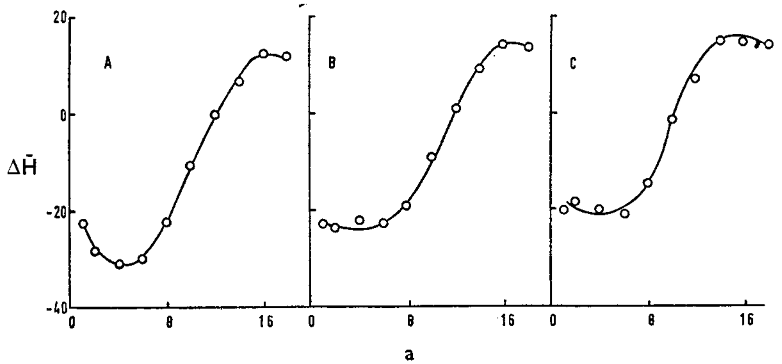

FIG. 3. Differential enthalpies of sorption, ΔH̄, against amount of water vapour sorbed, a. A. Fraction 1. B. Fraction 2. C. Fraction 3.

observed value of ΔS̄ will be a resultant of both processes, and presumably at large relative vapour pressures, the mixing process predominates.

The values of ΔH̄ and ΔS̄ at a_1 are given in Table 2.

TABLE 2. ΔH̄ (K.CAL. MOLE^{-1}) AND ΔS̄ (CAL. MOLE^{-1} DEG^{-1}) AT MONOLAYER COVERAGE

Fraction	ΔH̄	ΔS̄	Equiv wt
1	−8·7	−22·9	1,750
2	−6·8	−18·3	1,800
3	−5·4	−16·4	2,040

Fraction 1, containing the largest number of polar groups, gives the greatest negative values of ΔH̄ and ΔS̄, indicating that the polar groups might be responsible for the first stage of the sorption. The lowest points in Figs 2 and 3 occur before monolayer coverage, so the mixing process begins before sorption on to the polar group is complete. Table 1 shows that 7–8 water molecules were sorbed to each -COONa group, (assuming in the calculation that all water molecules at a_1 are associated with the polar groups). This number is larger than that required to solvate one sodium plus one carboxyl ion, estimates varying from 3–5 molecules (Stokes & Robinson 1959b; Elworthy, 1963); again there is the indication that several processes are responsible for sorption.

The polar groups are present on the side-chains in the sodium ghattate molecule, and would thus be expected to readily sorb water vapour. The hydroxyl groups are distributed throughout the molecular structure; at high temperatures the molecule may be more expanded and permit greater interactions to take place between hydroxyl groups and sorbate, provided x is large enough. This may explain why the 40° isotherm crosses the 25° one as x is increased.

In previous work (Elworthy, 1961: Elworthy & Macfarlane, 1964), water vapour sorption isotherms have been used to give an idea of particle hydration, the method being to determine the value of a at $x = 1$ by extrapolation, i.e. a_S. The method is empirical but has been succesful for a number of systems. The results obtained at 25° for fractions 1 and 2 (Table 1) were used in the calculation of molecular volume (Elworthy & George, 1963).

SURFACE ACTIVITY

The surface tensions of fractions 2 in water, 0·05 and 0·5 N sodium chloride solution were studied. Considerable surface-ageing effects were noted, 24–36 hr being required for the equilibrium surface tension to develop (see Fig. 4). The ageing effects may be due to slow diffusion of solute into the surface region, and to the possibility that considerable orientation of the macromolecules is necessary at the surface. Equilibrium was obtained more rapidly when salt was present in the solutions. The results are given in Fig. 5, the surface tension decreasing with increasing sodium ghattate concentration until a roughly constant value was reached,

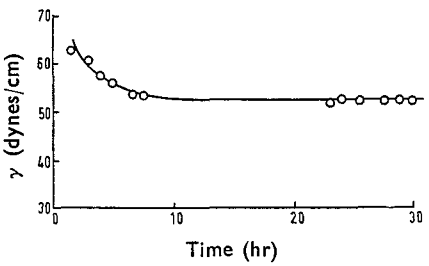

FIG. 4. Surface-ageing for 1·66 % sodium ghattate in water.

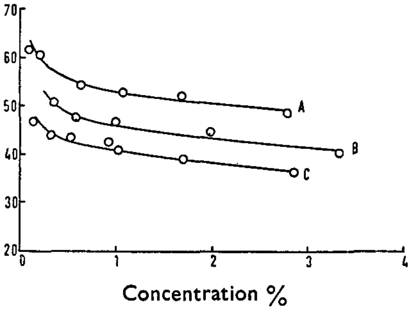

FIG. 5. Surface tension, γ, against concentration of sodium ghattate (fraction 2) in: A. Water. B. 0·05 N NaCl. C. 0·5 N NaCl.

at which the surface layer should be fairly closely packed with adsorbed molecules.

Jorgensen & Strauss (1961) studied the surface tension of solutions of coiled polyelectrolytes, and found very little surface activity. Sodium ghattate and sodium arabate are both surface-active. It may be significant that the two molecules have fairly stiff structures, with the polar groups on flexible side chains. Adsorption of a detergent at the air: water interface gives a film structure with the hydrocarbon chains remote from the water and the polar groups in contact with it. An explanation of the surface activity of sodium ghattate may lie in the molecule arranging itself in two regions at the interface, with the flexible side-chains and polar groups in the water, and the main backbone excluded from the surface. Elworthy & George (1963) have shown that the backbone was capable of some flexibility. This type of arrangement is difficult to visualise for the coiled type of polyelectrolyte, as the energy required to untangle the coil and orientate it at an interface would be considerable.

Like sodium arabate (Shotton & Wibberly, 1959), sodium ghattate has been found to give denatured films at the benzene/water interface; the films formed could be manipulated with a platinum wire. No evidence of a denatured film could be found at the air: water interface.

The presence of sodium chloride in the solutions reduces the surface tension at any particular sodium ghattate concentration e.g. for a 2·5% solution, γ fell from 50·6 dynes cm^{-1} in water to 37·2 dynes cm^{-1} in 0·5 N sodium chloride. The previous paper also showed that an increase in ionic strength causes the molecules to contract, and this effect may give rise to a more closely packed film at the interface.

Acknowledgements. We thank Evans Medical Ltd. for the award of an Evans Medical Research Fellowship to T.M.G., and for the gift of ghatti gum.

References

Altman, R. L. & Benson, S. W. (1960). *J. phys. Chem.*, **64**, 851–855.
Andreas, J. M., Hauser, E. A. & Tucker, W. B. (1938). *Ibid.*, **42**, 1001–1019.
Barrer, R. M. & Kelsey, K. E. (1961). *Trans. Faraday Soc.*, **57**, 452–462.
Brunauer, S., Emmett, P. H. & Teller, E. (1938). *J. Amer. chem. Soc.*, **60**, 309–319.
Bull, H. B. (1944). *Ibid.*, **66**, 1499–1507.
Elworthy, P. H. (1961). *J. chem. Soc.*, 5385–5389.
Elworthy, P. H. (1962). *Ibid.*, 4897–4900.
Elworthy, P. H. & Macfarlane, C. B. (1964). *Ibid.*, 311–315.
Elworthy, P. H. & Macfarlane, C. B. (1962a). *J. Pharm. Pharmacol.*, **14**, 100*T*–102*T*.
Elworthy, P. H. (1963). *J. chem. Soc.*, 388–392.
Elworthy, P. H. & George, T. M. (1963). *J. Pharm. Pharmacol.*, **15**, 781–793.
Harkins, W. D. (1959) in *Physical Methods of Organic Chemistry*, Editor, Weissberger, A., Vol. 1., Part 1, p. 772. New York: Interscience.
International Critical Tables, (1928). Vol. 3, p. 303. New York: McGraw-Hill.
Jorgensen, H. E. & Strauss, U. P. (1961). *J. phys. Chem.*, **65**, 1873–1877.
Mellon, E. F., Horn, A. H. & Hoover, S. R. (1949). *J. Amer. chem. Soc.*, **71**, 2761–2764.
Shotton, E. (1955). *J. Pharm. Pharmacol.*, **7**, 990–1003.
Shotton, E. & Wibberly, K. (1959). *Ibid.*, **11**, 120*T*–126*T*.
Stokes, R. H. & Robinson, R. A., (1959). *Electrolyte Solutions*, (*a*) p. 477; (*b*) p. 126. 2nd ed., London: Butterworths.
Wheeler, O. L., Tartar, H. V. & Lingafelter, E. C. (1945). *J. Amer. chem. Soc.*, **67** 2115–2119.