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VAPOR SORPTION OF ORGANIC COMPOUNDS ON HUMAN SERUM ALBUMIN

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Sorption isotherms were measured for a series of organic compounds from the vapor phase on dried solid human serum albumin (HSA). Parameters of the Brunauer–Emmet–Teller (BET) isotherm were evaluated from experimental data. A nonlinear trend was observed between the volume of a filled 'monolayer' and the molar volume of organic compounds. The effective 'monolayer' volume quickly decreased with increase in sorbate molar volume. Larger molecules have less space available for sorption on solid HSA. This shows that the size of molecules is important factor determining the number of available places for sorption on HSA. The sorbate–protein interactions are sensitive also to the structural differences between *n*-and *iso*-isomeric sorbates. The Gibbs energy $RT\ln K_R$ for the sorbate transfer from the gas phase standard state to the state to the state of an infinite by diluted sorbed compound (at zero sorbate activity) with uptake 1 mol kg^{-1} was calculated from the BET parameters. This Gibbs energy of the gas phase–protein phase transfer corresponds to the distribution coefficient K_R similar to the Henry coefficient. A correlation was found between $RT\ln K_R$ values and the molar volume of sorbates. As distinct from the behavior typical for organic solvents, larger molecules are more distributed to the gas phase in comparison with smaller compounds. The positive increment of a methylene group to the gas-protein transfer Gibbs energies was also estimated from data for aliphatic alcohols. This increment is higher than the analogous value evaluated from the Gibbs energies of hydration of the same alcohols. The sorption phenomenon was interpreted in terms of dissolution of organic compounds in the protein phase. It demonstrates a superficially repulsive effect for the organic molecules sorbed in solid HSA. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Study of the gas-phase sorption of organic compounds on solid protein preparations provides direct information about the interactions of proteins with organic molecules. This study can have also potential for catalysis with enzymes suspended in non-aqueous media demonstrating various effects of organic solvents (stripping of water from a protein preparation,[1–3] competition for the enzyme reaction center,[4] activating enzymes suspended in non-aqueous media through easing the flexibility constraints imposed by protein–protein contacts,[5] affecting the enantioselectivity of suspended enzymes[6]). It was shown also that the enthalpy changes on suspending the protein in organic solvents and the ability of the suspended protein to bind water influenced by the nature of organic solvents.[7,8] Depending on the organic solvent, the suspended protein may also demonstrate a non-equilibrium state that shows up as a calorimeric exothermic peak on thermoscanning the protein suspension.[9]

Thus, in order to examine the nature of solid protein–organic solvent interactions, it would be useful to study the gas-phase sorption of various compounds on solid protein preparations.

As distinct from water vapor sorption, such data are more limited for the vapors of other substances. For instance, nitrogen sorption on fiber collagen was found[10] to be more than 100 times lower than sorption of water on the same protein. We obtained the sorption isotherms for *n*-propyl alcohol and *n*-undecane on human serum albumin (HSA) and showed large differences in the binding ability of HSA for these compounds. Small but perceptible suppression in water sorption on alcohol dehydrogenase was found in the presence of acetone in the vapor phase.[11] A linear and selective response to the concentration of partathion (antigen) in the vapor phase was demonstrated for a quartz frequency sensor coated with its antibody, but only slight sensitivity was observed for this sensor covered with bovine serum albumin and immunoglobulin G.[12]

In this study, we determined the sorption isotherms from

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the gas phase on a preparation of HSA for a series of organic compounds. The aim of this work was to estimate the effects of the size, shape and structure of organic compounds on the interactions of their vapors with solid HSA.

EXPERIMENTAL

All measurements were carried out on human serum albumin from Reanal (Budapest, Hungary; product N 01092, lyophilized, with electrophoretic purity >95%, remainder after burning <2%). A total concentration of 0.2% of fatty acids (C_{12}–C_{22}) in this protein preparation was determined by the usual technique,[13] which includes extraction with chloroform–methanol (2:1), washing of the extract with water, methylation with diazomethane in diethyl ether and gas chromatographic (GC) determination in concentrated *n*-hexane solution. Organic compounds were of reagent grade (purity >99%) and were dried by standard methods[14] before the experiments.

To determine the sorption isotherm, static headspace GC analysis was carried out by measuring the sorbate concentration in the vapor phase over a solid protein preparation of HSA. For this, the equal portions of protein placed in a series of the 15 ml vials were dried in desiccator over P_2O_5 at 0·1 kPa. The content of water on the dried protein (8 ± 2 mg g^{-1}) was determined from the decrease in weight at 298 K and 1 Pa with an MGDTD-17S microthermoanalyzer (SETARAM). The final weight of the dry protein in each vial was about 300 mg. The liquid organic compound (sorbate) was carefully dosed with a microsyringe on the internal walls of the vials. The volume of the added liquid was in the range 1–20μl, depending on the organic compounds. The vials were then sealed, without stirring, with fluoropolymer and silicone rubber linings and were held at 298 K for 100 h.

An automated headspace doser of original design[15] was used to dose the vapor phase from the sealed vial into a capillary GC column. In this doser a principle of electropneumatic dosing[16] is applied. The doser does not contain any metal or unheated elements, with which the vapor sample could contact during transfer from a vial to the GC column. The total volume of all connecting paths was less than 30 μl. Hence distortions caused by sorption on internal parts of the doser were avoided. A fused silica chromatographic column (30 m × 0·4 mm i.d., Lukoprene-102) and a flame ionization detector were used.

The activity of the sorbate was determined as the ratio of the area of its chromatographic peak for the vapor phase over HSA to the area of the peak over its pure liquid. The absence of overlapped impurity peaks was checked by comparing the peak height/area ratio for peaks of the sorbate over protein and over pure liquid. In most cases the activity of the sorbate ceased to vary after the first 24 h after beginning thermostating. The errors in the activity determination were in the range from 5% for sorbate activities over 0·5 to 10% for activities below 0·1.

The volume V_s of sorbate on HSA was calculated from the difference between the total amount of a sorbate in the system and its amount in the vapor phase. For the systems studied containing methanol, acetonitrile, nitromethane and ethanol, the fraction of the organic compound in the vapor phase was less 10% of the total amount. Hence, the error of determination of V_s depending mainly on the accuracy of dosing of the liquid sorbate into the vials containing protein. For such systems the errors in V_s were 3–5%. For systems with isopropyl alcohol, acetone, propionitrile and pyridine, the fraction of sorbate in the vapor phase was larger. Hence the errors in the V_s determination were 2–3 times higher because the errors in headspace analysis were added. No volatile organic impurities were detected in the headspace over the HSA samples in the vapor sorption experiments.

RESULTS AND DISCUSSION

Presentation of sorption data

The volumes of organic compounds, V_s (μl of sorbate/g of protein), sorbed on the solid HSA preparation at 298 K are plotted in Fig. 1(A) against the sorbate activity P/P_0, where P is the vapor pressure of the sorbate above the solid HSA and P_0 is the pressure of its saturated vapor. In Figure 1(B) the same data are plotted on a different scale for better presentation. The sorption isotherm for *n*-propyl alcohol was measured earlier.[17] Data for sorption of water vapor were taken from Ref. 18. This water sorption isotherm was obtained on horse serum albumin.

Following the typical approach for the presentation of gas-phase sorption data, we approximated the sorption isotherms with the BET equation:[19]

$$V_S = \frac{P/P_0}{\left(\frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_0}\right)\left(1 - \frac{P}{P_0}\right)} \quad (1)$$

where C is the sorption constant and V_m corresponds to the volume of sorbate in a filled 'monolayer'. Approximation was performed using the non-linear regression method. Since the sorption parameters for water were obtained from the linearization of the BET equation,[18] we re-evaluated these data using the non-linear procedure. The parameters obtained for all compounds are listed in Table 1. The solid curves in Figure 1 were calculated using equation (1) from these adjusted parameters. Data for methanol sorption are shown also in Figure 2. Approximation of the methanol data with the BET equation (1) is shown in Figure 2 with curve 1. As can be seen from Figure 2, the BET equation does not represent the sorption data very well. All points corresponding to the methanol activities below 0·03 lie systematically over the calculated curve 1. Parameters of the BET equation obtained for propionitrile, isopropyl alcohol and pyridine should be considered as rough because of the low sorption of the compounds.

Parameters of BET equation

The sorption constants C are of the same order of magnitude for different molecules. They vary from $6{\cdot}6 \pm 1{\cdot}2$ for acetone to $32 \pm 5{\cdot}2$ for methanol. No simple dependence of this parameter on the ability of molecules to undergo intermolecular interactions was found. Several reasons can cause these relatively small differences in the sorption constants. First, it should be mentioned that the sorption constants are evaluated for a broad activity range. Hence the evaluated sorption constants are, in essence, effective and averaged over the different sorption sites. For example, the sorption of methanol was determined in the activity range 0·0037–0·176 (Figure 2). As can be seen, this dependence for methanol is not smooth. It may be considered as made up two parts, corresponding to the activity regions 0·0037–0·0226 and 0·0319–0·176. Evidently, these activity intervals correspond to the filling of different populations of the sorption sites. This inhomogeneity of the sorption sites may lead to the above-noted systematic deviations of the low activity points from the curve calculated with the BET equation. We fitted the data for methanol fairly well with an equation that is the sum of two BET expressions. Curve 2 in Figure 1 corresponds to this fitting. This sum, describing the

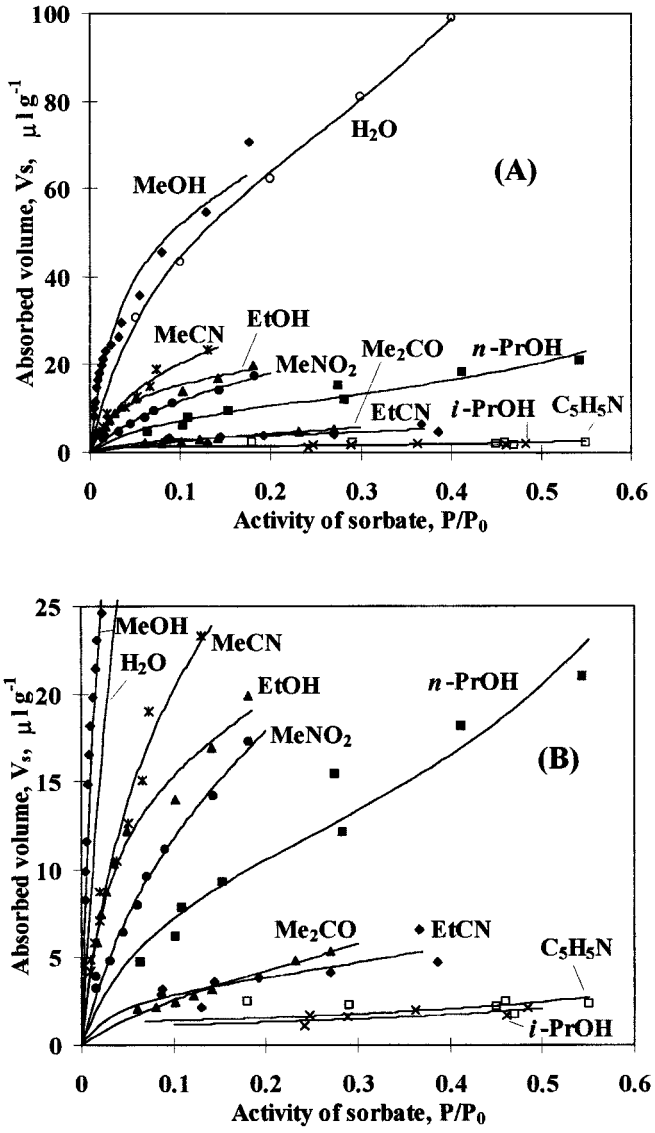

Figure 1. Volumes V_S of organic compounds sorbed on solid HSA plotted against the sorbate activity P/P_0 at 298 K

Table 1· Parameters of vapor sorption isotherms of organic compounds on HSA at 298 K

Sorbate	Activity range	V_m (μl g^{-1})[a]	C[a]	δ[b]	$RT\ln K_R$ (kJ mol^{-1})	ΔG_{hydr} (kJ mol^{-1})[c]	V_0 (ml mol^{-1})
Water	0·05–0·4	65·6±1·1	14·0±1·1	1·4	−18·3	−8·58	18·02
Methanol	0·0037–0·176	60·0±3·6	32·0±5·2	3·7	−13·9	−3·47	41·7
Methanol[d]	0·0037–0·176	27·8±5·8	120±40	1·2			
		173±315	1·0±2·4				
Acetonitrile	0·0096–0·130	28·0±2·7	16·8±3·4	1·2	−10·8	1·59	52·23
Nitromethane	0·015–0·182	20·0±1·3	10·1±1·5	0·6	−10·8	1·05	54·16
Ethanol	0·0177–0·181	17·7±0·8	31·3±4·6	0·8	−11·9	−3·05	58·69
n-Propyl alcohol[e]	0·064–0·543	11·1±0·8	12·9±4·5	1·6	−10·6	−2·43	74·54
Acetone	0·0602–0·271	5·4±0·4	6·6±1·2	0·2	−1·2	1·92	73·43
Propionitrile	0·130–0·367	3·6±0·5	22±18	0·8	−7·2	1·80	71·35
Isopropyl alcohol[f]	0·24–0·46	1·1±0·1	-	0·3	-	−2·01	76·56
Pyridine[f]	0·18–0·55	1·25±0·15	-	0·7	-	−1·76	80·88

[a] ± Corresponds to the standard error.
[b] Standard deviation.
[c] Data from Refs 20 and 21.
[d] Parameters from approximation by the sum of two BET equations.
[e] Parameters from Ref. 17.
[f] C is non-determinable; V_m values were calculated at $C=\infty$.

independent filling of two kinds of the sorption sites, should be considered still as a mainly empirical model approximating the experimental data. Parameters of both BET terms are also included in Table 1.

Second, the sorption constant is based on the activity scale where activity is P/P_0. This means that it corresponds to the transfer of a sorbate from its pure liquid state to the sorption site. Therefore, these sorption constants depend on the intermolecular interactions that occur in the pure liquid state of organic compounds. Therefore water and alcohols that are able to interact strongly with sorption sites on HSA are also self-associated through hydrogen bonding. Acetone or acetonitrile does not undergo hydrogen bonding, but the interactions in their pure liquid state may also be weaker in comparison with alcohols. As such, these interactions in the pure liquid state of sorbates can complicate the effect of the molecular structure on the estimated BET sorption constants. Third, we assume that the sorption process on HSA can be accompanied by the rupture of protein–protein contacts. Hence the sorbed organic compound may be

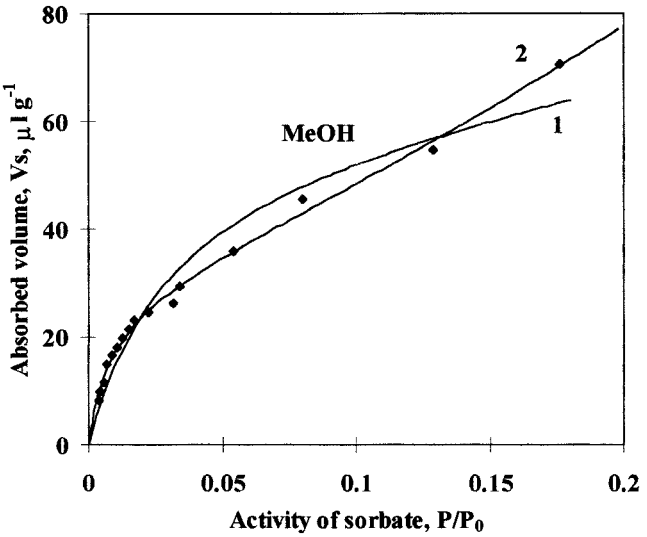

Figure 2. Sorption of methanol on HSA plotted against its activity at 298 K. Curve 1 was drawn according to equation (1). Curve 2 corresponds to the two BET fittings (see text)

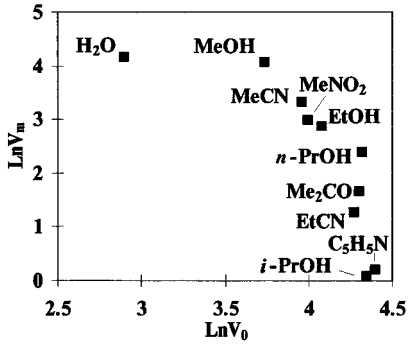

Figure 3. Volumes of sorbate V_m in filled monolayer plotted against molar volumes of organic compounds V_0

'dissolved' in the protein phase. Therefore, this rupture of protein–protein interactions is also able to contribute to the BET sorption constants. As a result of imposing different factors, this parameter *C* is a small difference between large values, and its dependence on the molecular structure may be asked.

It is also obvious from the plots in Figure 1 that the sorption isotherms are generally higher for substances with lower molecular weight. This effect would be even more significant if one compared the sorption of organic compounds on a molar basis. As can be derived from Table 1, this tendency results from the variation of the volumes of the 'monolayer', V_m.

In figure 3 we compared the V_m values with the molar volumes V_0 of compounds in a logarithmic scale. Since the parameters of the 'sum of two BET equations' model for methanol were evaluated with a large uncertainty, the V_m value from the simplest BET equation model was taken as an approximation. There is a definite trend in the variation of the V_m values. The change in V_m with the size of molecules of organic compounds shows clearly that the solid HSA preparation cannot be considered as a macroporous sorbent. For example, when considering the sorption of *n*-propyl alcohol and *n*-octane on the macroporous sorbent Cabosil M5,[17] V_m for *n*-propyl alcohol is virtually equal to that of *n*-octane (70 ± 10 and 69 ± 5 μl g^{-1}, respectively), despite the significant difference in molar volumes and the ability to undergo hydrogen bonding for these two compounds. The decrease in V_m with the molar volume indicates also that the number of the effective sorption sites is not constant for different organic compounds. When the size of a sorbate is increased, the available number of sorption sites is decreased. It appears that in this series of sorbates the molar volume of organic compounds is an important factor determining for each molecule the number of places accessible for sorption.

It is well known[22] that the surfaces of many materials are very porous and their areas depend on the size of the sorbed molecular probes. In a series of sorbates of the similar nature, the molar amount *n* of a sorbed substance is connected with its cross-sectional area σ by the relationship $n \sim \sigma^{-D/2}$, where *D* is the surface fractality. Hence one would expect that $V_m \sim V_0^{1-D/3}$. In particularly, the sorption of the first five aliphatic alcohols on silica gel was used in order to evaluate the fractality of this material.[21] The maximum value of *D* is 3. In this case, the material surface is so porous that the 'monolayer' has the properties of three-dimensional space.[22] However, the curvature of the dependence in Figure 3 is so great that it could be interpreted as a result of the porosity of the HSA preparation. As an example, we estimated the empirical coefficient *D* from data for methanol, ethanol and *n*–propyl alcohol. The value obtained was 11·9. This exceeds significantly the above *D* threshold. Hence one can assume that the reason for the dependence in Figure 3 is the possible porosity of the preparation. The trend observed in Figure 3 rather reflects dissolution of the studied substances in the bulk of the HSA preparation. The dissolution may be accompanied by some rupture of the protein–protein contacts. The thermodynamic cost of this rupture is likely to be greater for larger molecules. Hence organic compounds with larger molar volumes will have less places accessible for sorption. The data in figure 3 also show 'exclusion effect.' At some critical molar volume of an organic compound (71–75 ml mol^{-1}), the number of sorption sites decreases sharply, which may make the sorption of larger molecules negligible.

Another interesting fact is the significant difference in the sorption of *n*-propyl alcohol and isopropyl alcohol. The isotherm of *n*-propyl alcohol lies much higher than that of iospropyl alcohol. The monolayer volumes V_m for these compounds differ 10-fold. The selectivity of the solid protein preparation with respect to the alcohol structure means that not only the size but also the shape of the molecule influences its sorption. The possible cause of this selectivity may result from the sensitivity of the sorbate–protein interactions to steric hindrance caused by the protein–protein contacts in the solid preparation of HSA.

Gas-phase→solid HSA transfer Gibbs energies

Let us consider the initial slopes of the sorption dependences in Figure 1. According to equation (1), this initial slope equals $V_m C$ (in μl g^{-1}). We calculated the coefficient $K_R = P_0 V_0 / V_m C$) (atm kg mol^{-1}). Data for P_0 at 298 K were taken from Ref. 23. In this way, the above initial slope was converted into the reciprocal of the initial slope of the 'sorption (mol kg^{-1}) *vs* sorbate pressure (atm)' dependence. Evidently, this K_R parameter describes the distribution of a sorbate between the gas phase and solid HSA at infinitely low vapor pressure. Correspondingly, $RT\ln K_R$ should be considered as the Gibbs energy of transfer of a compound from the gas phase standard state at 1 atm to the standard state of an infinitely diluted sorbed compound with an uptake 1 mol kg^{-1}. Calculated $RT\ln K_R$ values are presented in Table 1.

Let us consider some formal points.

1. Typically, such solvation Gibbs energies are defined

for the transfer processes 'gas-phase standard state at unit pressure→infinitely dilute solution at unit mole fraction' or 'gas-phase standard state at unit molar concentration→infinitely dilute solution at unit molar concentration.' These two accepted definitions of the transfer Gibbs energy correspond to the Henry and Ostwald coefficients, respectively. When considering infinite dilution for a series of solutes at a given temperature, the choice of the standard states does not affect the changes in the Gibbs energies in this series. The K_R value is proportional to the Henry coefficient with the molar mass of HSA as the proportionality factor. Therefore, the change in the calculated Gibbs energies in the series of organic compounds should be the same for all three kinds of distribution coefficients.

2. An important point is that the calculated $RT\ln K_R$ values do not depend on the current interpretation of the C and V_m parameters. The latter values are above all else the parameters of the model approximating the sorption data.
3. 'Infinite dilution' in the definition of K_R should be referred to the population of sorption sites that make a main contribution to the sorption in the studied activty range. The situation is not excluded when stronger and not numerous sorption sites on HSA do not contribute to the sorption of organic compounds in the considered activity range but they influence significantly the K_R values at extremely low activities of sorbates.

In figure, 4 we compare the $RT\ln K_R$ values with the molar volumes V_0 of sorbates. It can be seen that there is a definite trend in the change of the $RT\ln K_R$ value with molar volume. It is worth noting that an increase in the molar volume causes an increase in the Gibbs energy of the sorbate transfer from the gas phase to the solid phase. This tendency is opposite to the well known correlations between the Gibbs energy of solvation of organic compounds in non-aqueous solvents and the size of solutes (molar volumes, molar refraction, number of methylene groups and molecular surface area may be considered as a measure of the molecule size in various cases).[15, 20, 21, 24–28] Therefore, when considering the solvation of organic molecules in non-aqueous solvents, the larger molecules usually have more negative values of the Gibbs energy of solvation defined in terms of the above-mentioned transfer processes.

Correspondingly, the increment of a methylene group to the Gibbs energy of transfer calculated from data for alcohols is positive: 1·7 kJ mol^{-1}. A positive increment of a methylene group to the Gibbs energy of transfer is typical of aqueous solutions of organic compounds. Its value in aqueous solutions for the same alcohols is 0·5 kJ mol^{-1}.[21] Usually, such a positive increment is interpreted as evidence for the hydrophobic effect repulsing a non-polar molecule from aqueous solution.[20] The relationship between the methylene increment for the transfer Gibbs energy to HSA and the methylene increment in water shows that the repulsive effect in the solid protein surrounding may be even stronger than in aqueous solution.

In figure 5, we compare the $RT\ln K_R$ values with the Gibbs energies of hydration ΔG_{hydr} for the compounds under study. The Gibbs energies of hydration corresponding to the transfer from the standard state of an ideal gas at 1 atm to an infintiely dilute solution at unit molar fraction of solute were taken from Refs 20 and 21. There is some correlation between the Gibbs energies of transfer from the gas phase to the solid HSA and water. This correlation shows the extent to which an aqueous solution may be a model for the sorption of the considered compounds on HSA.

It is interesting that the hydrophobic effect may be an important factor affecting the interactions of organic molecules with proteins dissolved in water. The repulsion of non-polar moieties of an organic molecule and protein from water has to be an additional reason for their interaction. Hence such hydrophobic interactions were considered to govern the entropy-driven complexation of some drugs with HSA.[29] Our results show that the opposite situation may be expected for interactions of organic molecules with the solid protein preparation suspended in organic solvents. In this

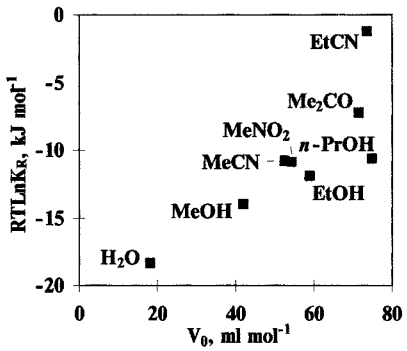

Figure 4. Transfer Gibbs energies $RT\ln K_R$ of compounds from the gas phase to the protein phase at 298 K plotted against molar volumes V_0 of organic compounds

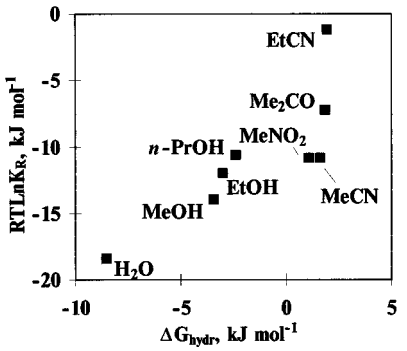

Figure 5. Transfer Gibbs energies $RT\ln K_R$ of compounds from the gas phase to the protein phase plotted against the Gibbs energies ΔG_{hydr} of hydration at 298 K

case, as distinct from the aqueous phase, the protein phase demonstrates the repulsive effect which is increased for larger molecules. Correspondingly, it is reasonable to say that this effect may counteract the binding of organic molecules with a sorption site or reaction center of a solid suspended protein.

In general, we conclude that the size of an organic compound is an important factor determining the number of sites available for sorption. Larger molecules have fewer possibilities for interaction with HSA. The sorbate–protein interactions are sensitive also to the structural differences between *n*- and *iso*-isomeric sorbates. The dependence of the Gibbs energy of the phase–protein phase transfer on the molar volume of sorbates indicates that as distinct from the behavior typical of organic solvents, larger molecules are more distributed to the gas phase in comparison with smaller compounds. This phenomenon may be interpreted in terms of dissolution of organic compounds in the protein phase and demonstrates superficially some repulsive effect for the organic molecules sorbed on solid HSA.

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REFERENCES

1. P. A. Fitzpatrick, A. C. U. Steinmetz, D. Ringe and A. M. Klibanov, *Proc. Natl. Acad. Sci. USA.* **90**, 8653–8657 (1993).
2. L. A. S. Gormann and J. S. Dordick, *Biotechnol. Bioeng.* **39**, 392–397 (1992).
3. P. J. Halling, *Biochim. Biophys. Acta* **1040**, 225–228 (1990).
4. T. C. de Sampaio, R. B. Melo, T. F. Moura, S. Michel and S. Barreiros, *Biotechnol. Bioeng.* **50**, 257–264 (1996).
5. O. Almarsson and A. M. Klibanov, *Biotechnol. Bioeng.* **49**, 87–92 (1996).
6. P. A. Fitzpatrick and A. M. Klibanov, *J. Am. Chem. Soc.* **113**, 3166–3171 (1991).
7. V. A. Sirotkin, M. D. Borisover and B. N. Solomonov, *Thermochim. Acta* **256**, 175–183 (1995).
8. M. D. Borisover, V. A. Sirotkin and B. N. Solomonov, *Thermochim. Acta* **284**, 263–277 (1996).
9. D. V. Zakharychev, M. D. Borisover and B. N. Solomonov, *Zh. Fiz. Khim.* **69**, 175–179 (1995).
10. K. Boki, N. Kawasaki, K. Minami and H. Takahashi, *J. Colloid Interface Sci.* **157**, 55–59 (1993).
11. F. Yang and A. J. Russell, *Biotechnol. Bioeng.* **49**, 700–708 (1996).
12. J. Ngeh-Ngwainbi, P. H. Foley, S. S. Kuan and G. G. Guilbault, *J. Am. Chem. Soc.* **108**, 5444–5447 (1986).
13. M. Keits, *Technique of Lipidology*, Mir, Moscow (1975) (in Russian).
14. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*. Pergamon Press, Oxford (1980).
15. V. V. Gorbatchuk, S. A. Smirnov, B. N. Solomonov and A. I. Konovalov, *Zh. Obsch. Khim.* **60**, 1200–1205 (1990).
16. B. Kolb, P. Pospisil, T. Borath and M. Auer. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **2**, 283–287 (1979).
17. V. V. Gorbatchuk and B. N. Solomonov, *Zh Fiz. Khim.* **70**, 723–727 (1996).
18. H. B. Bull, *J. Am. Chem. Soc.* **66**, 1499–1507 (1944).
19. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.* **60**, 309–319 (1938).
20. M. H. Abraham, J. Andonian-Haftvan, G. S. Whiting, A. Leo and R. S. Taft, *J. Chem. Soc., Perkin Trans. 2* 1777–1791 (1994).
21. M. H. Abraham, *J. Chem. Soc., Faraday Trans. 1* **80**, 153–181 (1984).
22. J. Feder, *Fractals*, pp. 232–236, Mir, Moscow (1991) (in Russian).
23. T. Boublik, V. Hala and E. Fried, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam (1973).
24. B. N. Solomonov, V. V. Gorbatchuk and A. I. Konovalov, *Zh. Obsch. Khim.* **52**, 2688–2693 (1982).
25. V. V. Gorbatchuk, S. A. Smirnov, B. N. Solomonov and A. I. Konovalov, *Dokl. Akad Nauk SSSR* **300**, 1167–1169 (1988).
26. V. V. Gorbatchuk, S. A. Smirnov, B. N. Solomonov and A. I. Konovalov, *Zh. Obsch. Khim.* **60**, 1441–1446 (1990).
27. M. S. Abraham, G. S. Whiting, R. Fuchs and E. J. Chambers, *J. Chem. Soc., Perkin Trans. 2* 291–300 (1990).
28. A. J. Dallas and P. W. Carr, *J. Phys. Chem.* **98**, 4927–4939 (1994).
29. H. Aki, M. Goto and M. Yamamoto, *Thermochim. Acta* **251**, 379–388 (1995).

