MOLECULAR CLUSTERING AND SEGREGATION IN SORPTION SYSTEMS

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ABSTRACT

The clustering functions interpret adsorption, sorption, and solution thermodynamic behaviour in geometric terms; they cannot predict solution properties. The clustering functions, derived from the cluster integrals of the dilute gas method of statistical mechanics, are free energy functions which depend strongly upon the first derivatives of activities with respect to volume-fractions. Clustering functions greater than minus one are monotone, increasing functions of the tendency of like molecules to cluster. Clustering functions less than minus one denote segregation of like molecules; this segregation increases as the clustering functions become more negative. The clustering functions are applicable to any binary sorption system. This is demonstrated by considering experimental data for several solvent–polymer and gas–polymer systems, a binary solution of liquids of ordinary molecular sizes, three versions of the lattice theory of polymer solutions, monolayer and multilayer adsorption theories, and ideal solution behaviour.

I. INTRODUCTION

Two distinctly different methods of statistical mechanics have been used to develop theories of adsorption and solution for small molecule and macromolecular systems. These arise because two methods are used to approximate the function which describes the partition of energy of a system among the many, quantized energy levels accessible to the molecular moities which make up the system.

In the usual method of statistical mechanics, the grand partition function is separated into a product of partition functions describing distributions of non-interacting, independent energy levels (see, for example, ref. 1). Obviously this works quite well for individual molecules, such as those in dilute gases, if widely spaced non-interacting energies, such as electronic and translational motion energies, are considered. The separation into a product works not nearly as well for more closely spaced, interacting energies like those for vibrations and rotations. In condensed systems, intermolecular energies are spaced close to one another, and they interact. For mixtures, the intermolecular energy levels for groups of like and unlike molecules cannot be separated. The usual zeroth approximation is to assume that contributions

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due to configurations, the mixing of different kinds of molecules, and contributions due to interactions among molecules can be separated as a product in the partition function. In a sorption process, this is equivalent to assuming that the enthalpy and entropy changes for the process are invariant with temperature and the enthalpy change is that at 0 K, $\Delta H^{\circ}{}_{0\,\mathrm{K}}$. This method separates the free energy change for any process into an energy-independent configuration term and a configuration-independent energy term.

The so-called 'dilute gas method' of statistical mechanics[2], which is not limited to dilute systems, uses an expansion of the free energy in a power series in concentrations of molecules and identifies properties of single molecules, pairs, triplets, quartets, etc. with corresponding powers of concentration. This method does not separate the partition function into configuration and energy terms. However, calculation of the free energy change for a process from a given geometric model becomes impossibly complex except at high dilution. Nevertheless, the dilute gas method does give some generally applicable equations which can be used to interpret and understand sorption behaviour in geometric terms but which cannot predict sorption behaviour from a geometric model and molecular properties.

The assumption inherent in the usual method of writing the partition function as the product of partition functions for various non-interacting levels and a mixing term can be seen best by writing a partition function for a system[3]:

$$Q = \sum_{i=0}^{\text{all states}} q_i \exp\left[-(\varepsilon_i - \varepsilon_0)/kT\right] \tag{1}$$

where $\varepsilon_i - \varepsilon_0 \equiv$ energy of the energy level i above the ground state or lowest energy level ε_0

$q_i \equiv$ the multiplicity or degeneracy of the ith energy level (the number of quantum states of energy ε_i)

$k \equiv$ the Planck–Boltzmann constant.

The Gibbs free energy, the enthalpy H, and the entropy are[4]

$$G = H - TS = E^0_{0\,\mathrm{K}} + RT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V + RT\left(\frac{\partial \ln Q}{\partial V}\right)_T V - T\left[R \ln Q + RT\left(\frac{\partial \ln Q}{\partial T}\right)_V\right] \tag{2}$$

where $E^0_{0\,\mathrm{K}} \equiv$ internal energy of the system at 0 K,

$RT\left(\frac{\partial \ln Q}{\partial V}\right)_T = p \equiv$ the pressure of and on the system (in the equation of state contribution to the free energy of the system), and

$R \equiv$ the gas constant.

Writing the partition function as a product of energy and configuration terms is equivalent to saying $(\partial \ln Q/\partial T)_V = 0$ or that the heat capacity is zero ($c_p = 0$). For no real process should the change in heat capacity, Δc_p, be zero, the enthalpy change at any experimentally accessible temperature be that at 0 K, and the entropy term be energy-independent and invariant

with temperature. Nevertheless, the usual statistical derivations of sorption isotherms begin with these limitations[5]. Effects of energies of interactions on entropies and the effects of configurations are added as corrections. These corrections usually result either in mathematical complexities preventing inclusion of anything except small first order corrections[6], invoking a corresponding states assumption[7], or using empirical terms in the resulting equations. In spite of these limitations, results of derivations made with these assumptions are valuable in predicting properties of pure systems and in understanding macroscopic behaviour in molecular terms. Much of our understanding of statistical thermodynamics, including polymer solution chemistry, has been gained in spite of these limitations.

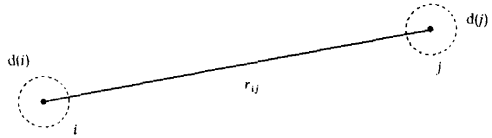
The dilute gas method of statistical mechanics does give equations which are generally applicable to any binary system at equilibrium over the whole concentration range. Calculations of thermodynamic properties from geometric models are impossibly complex; therefore these equations cannot be used to predict thermodynamic properties from molecular properties of constituents. However, these equations can interpret in geometric terms, the tendency of like molecules to cluster or to segregate, the thermodynamic properties of any binary solution or adsorption system whether the properties be measured experimentally or calculated from some model.

II. THE CLUSTERING FUNCTIONS

The molecular pair distribution function

$$\frac{1}{V_2} F_2(i,j)\mathrm{d}(i)\mathrm{d}(j)$$

is the probability that molecules i and j are each at the coordinates i and j in space and in the range of these coordinates d(i) and d(j) (where V is the volume of the system)[8]. This may be represented pictorially by



two volume elements, d(i) and d(j), each containing a molecule and separated by a distance r_{ij}. Of course, inherent in the development of dilute gas method statistical mechanics is the assumption of a centro-symmetric system. The resulting equations may not be limited by this limitation in our mathematical methods. The cluster integral is

$$G_{11} = \frac{1}{V}\iint[F_2(i,j) - 1]\mathrm{d}(i)\mathrm{d}(j) \tag{3}$$

where

$\phi_1 G_{11}/\bar{v}_1 \equiv$ the mean number of type 1 molecules in excess of the mean concentration of type 1 molecules in the neighbours of a given type 1 molecule at low concentrations of component 1,

$\phi_1 \equiv$ volume fraction of component 1, and

$\bar{v}_1 \equiv$ partial molecular volume of component 1.

In 1953, Zimm[9] derived a simple relationship between the cluster integral G_{11} and the volume fraction activity coefficient of component 1:

$$\frac{G_{11}}{\bar{v}_1} = \frac{kT\beta}{\bar{v}_1} - \phi_2\left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{p,T} - 1 \tag{4a}$$

where

$$\beta = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

is the isothermal compressibility of the system,

$$\phi_1 = (1 - n_2\bar{v}_2/n_1\bar{v}_1)^{-1} = 1 - \phi_2 = 1 - (1 - n_1\bar{v}_1/n_2\bar{v}_2)^{-1}$$

n_1 and $n_2 \equiv$ number of molecules of components 1 and 2, and
$\bar{v}_1$ and $\bar{v}_2 \equiv$ partial molecular volumes of component 1 and 2.
A similar function can be written for component 2

$$\frac{G_{22}}{\bar{v}_2} = \frac{kT\beta}{\bar{v}_2} - \phi_1\left[\frac{\partial(a_2/\phi_2)}{\partial a_2}\right]_{p,T} - 1. \tag{4b}$$

We have called these the clustering functions[5].

Equations 4a and 4b describe molecular clustering in single component and binary systems. In a pure system the activity coefficient term is zero, and the compressibility term is not dominant except for gases at pressures below one atmosphere, in the critical region, and for vapour and liquid coexisting at equilibrium. At the critical point and for vapour and liquid coexisting at equilibrium, the compressibility increases without bound; so must the clustering function. In a liquid–gas region, gaseous molecules can and do condense to form clusters of molecules large enough to be recognized as a macroscopic phase.

For binary systems far from the gas–liquid critical region, the compressibility terms can be neglected; $kT\beta/\bar{v}$ is about 0.02 to 0.06 for ordinary liquids[10]. Neglecting the compressibility terms, the clustering functions for components 1 and 2 are

$$\frac{G_{11}}{\bar{v}_1} \simeq -\phi_2\left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{p,T} - 1 = -\frac{\phi_2}{\phi_1} + \frac{\phi_2}{\phi_1}\frac{a_1}{\phi_1}\left(\frac{\partial\phi_1}{\partial a_1}\right)_{p,T} - 1 \tag{5a}$$

and

$$\frac{G_{22}}{\bar{v}_2} \simeq -\phi_1\left[\frac{\partial(a_2/\phi_2)}{\partial a_2}\right]_{p,T} - 1 = -\frac{\phi_1}{\phi_2} + \frac{\phi_1}{\phi_2}\frac{a_2}{\phi_2}\left(\frac{\partial\phi_2}{\partial a_2}\right)_{p,T} - 1 \tag{5b}$$

Behaviour of the clustering functions for a binary system in the critical miscibility region and where two liquid phases coexist is exactly analogous to behaviour of the clustering function of a single component in the critical and liquid–vapour regions. Since activity–volume fraction isotherms have zero slope ($\partial a_1/\partial\phi_1 = 0$ and $\partial a_2/\partial\phi_2 = 0$) at the critical miscibility point and in the region where two phases coexist, the clustering functions increase without bound. This is consistent with sufficient clustering to form macroscopic phases.

For pure condensed systems, the clustering functions have values of minus one. In a pure system a molecule excludes to another molecule only its own molecular volume and has no other effect on the system.

A clustering function decreasing without bound corresponds to segregation increasing without bound. Infinite segregation of like molecules probably is not physically reasonable even in the limit of zero concentration. Therefore, in the limits of zero concentrations, the clustering functions should be finite.

The values of the clustering functions at limiting concentrations and at phase separations are:

	$G_{11}/\bar{v}_1$	$G_{22}/\bar{v}_2$
$\phi_1 = 1, \phi_2 = 0$	-1	finite
$\phi_1 = 0, \phi_2 = 1$	finite	-1
phase separation	$+\infty$	$+\infty$

The clustering functions of the two components of a binary system are related; $G_{11}/\bar{v}_1$ can be calculated from $G_{22}/\bar{v}_2$ and vice versa. The Gibbs–Duhem equation[11a] for activities holds for any system at equilibrium; thus, for a binary system

$$x_1 \mathrm{d} \ln a_1 + x_2 \mathrm{d} \ln a_2 = 0 \tag{6}$$

where $x_1 = (1 + n_2/n_1)^{-1} = 1 - x_2 = 1 - (1 + n_1/n_2)^{-1}$ and x_1 and x_2 are mol fractions of components 1 and 2.

Substituting equation 5b and 6 into equation 5a, and equations 5a and 6 into equation 5b. along with definitions of mol and volume fractions, gives for the clustering functions, neglecting compressibility:

$$\frac{G_{11}}{\bar{v}_1} = \frac{\bar{v}_2}{\bar{v}_1}\left(\frac{\phi_2}{\phi_1}\right)^2\left[\frac{G_{22}}{\bar{v}_2} + \frac{1}{\phi_2}\right] - \frac{1}{\phi_1} \tag{7a}$$

and

$$\frac{G_{22}}{\bar{v}_2} = \frac{\bar{v}_1}{\bar{v}_2}\left(\frac{\phi_1}{\phi_2}\right)^2\left[\frac{G_{11}}{\bar{v}_1} + \frac{1}{\phi_1}\right] - \frac{1}{\phi_2} \tag{7b}$$

For systems of very different molecular volumes, the larger molecules will be segregated, that is the average concentration of the larger molecules in the neighbourhood of a given larger molecule will be less than the mean concentration of larger molecules. This can be seen easily by taking $\bar{v}_2 \gg \bar{v}_1$ and noting that even if $G_{11}/\bar{v}_1 > 0$ the $-1/\phi_2$ form of equation 7b will dominate and $G_{22}/\bar{v}_2$ will be less than minus one over most of the concentration range (even as $\phi_2 \to 1$ because of the rapid decrease in $(\phi_1/\phi_2)^2$ as $\phi_2 \to 1$). For $\bar{v}_2 \gg \bar{v}_1$, the first term of equation 7a predominates; the clustering function can be greater than minus one indicating clustering of molecules of component 1, or less than minus one denoting segregation of molecules of component 1.

III. EXPERIMENTAL MEASUREMENTS OF CLUSTERING FUNCTIONS

The clustering functions for the system *n*-perfluoroheptane–2,2,4-tri-

methylpentane calculated from slopes of a_1/ϕ_1 *versus* a_1 plots using activity, volume and concentration data of Mueller and Lewis[12] at 30°C are given in *Figure 1*. This system has a critical miscibility temperature of 23.78°C at $\phi_1 \simeq 0.45$ perfluoroheptane[13]. The clustering function of *n*-perfluoroheptane is a maximum of $G_{11}/\bar{v}_1 \simeq +14$ at $\phi_1 \simeq 0.28$; that for 2,2,4-trimethylpentane has a maximum of $G_{22}/\bar{v}_2 > +17$ between $\phi_1 \simeq 0.56$ and $\phi_1 \simeq$

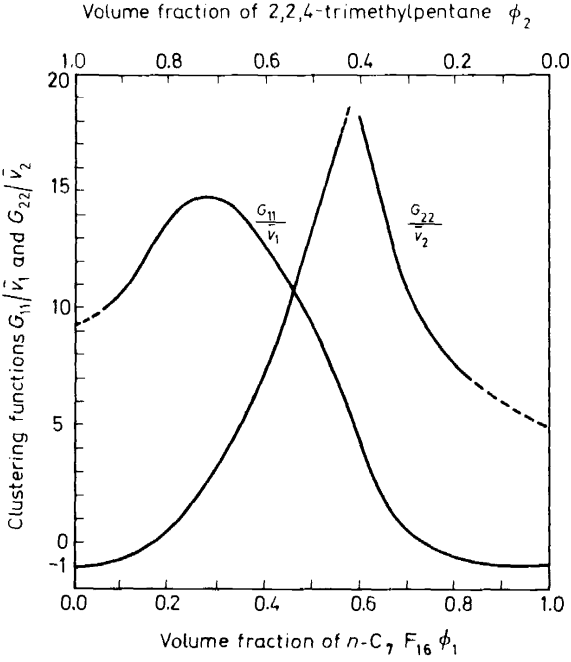


Figure 1. Plot of clustering functions *versus* concentration for *n*-perfluoroheptane (ϕ_1) and 2,2,4 trimethylpentane (ϕ_2) at 30°C from data of Mueller and Lewis[12]

0.62. As the temperature of this system is decreased from 30°C to T_c = 23.78°C, the maxima in the clustering functions should increase becoming infinite at T_c and should shift with concentration toward $\phi_1 \simeq 0.45$. This system at a temperature more than six degrees from the critical miscibility temperature has clustering functions substantially greater than minus one. This indicates that like molecules are clustered. Unfortunately, we have no calibration of the degree of clustering from other experiments.

The clustering functions for the systems, benzene–rubber at 25°C[14], benzene–polyethylene at 109°C[15], cyclohexane–polyisobutylene at 15°C[16], toluene–polystyrene at 25°[17] and 27°C[18], and water–collagen at 25° and 40°C[19] are shown in *Figure 2*. These are calculated by graphical differentiation and/or by differentiating activity–concentration functions given by investigators to represent their data.

The clustering functions for most nonpolar solvents in solution with nonpolar polymers probably are positive, usually about plus one or two except in solutions dilute in polymer, and perhaps in very concentrated solutions. This arises from the concavity downward of the plot of activity, a_1, *versus* volume fraction ϕ_1, and the dominance of the $(\partial\phi_1/\partial a_1)_{p,T}$ term of equation 5a. Examples of polymer solutions for which $G_{11}/\bar{v}_1$ of solvent is about plus one to plus two are benzene–polyethylene at 109°C[15], toluene–polystyrene ($\bar{M}_n \simeq 300000$) at 25°C[10], and benzene–rubber at 25°C[14]. The clustering function of cyclohexane in polyisobutylene at 15 C[16] is larger than those in the three examples cited rising to $G_{11}/\bar{v}_1 \simeq 4$ at $\phi \simeq 0.8$ (*Figure 2*).

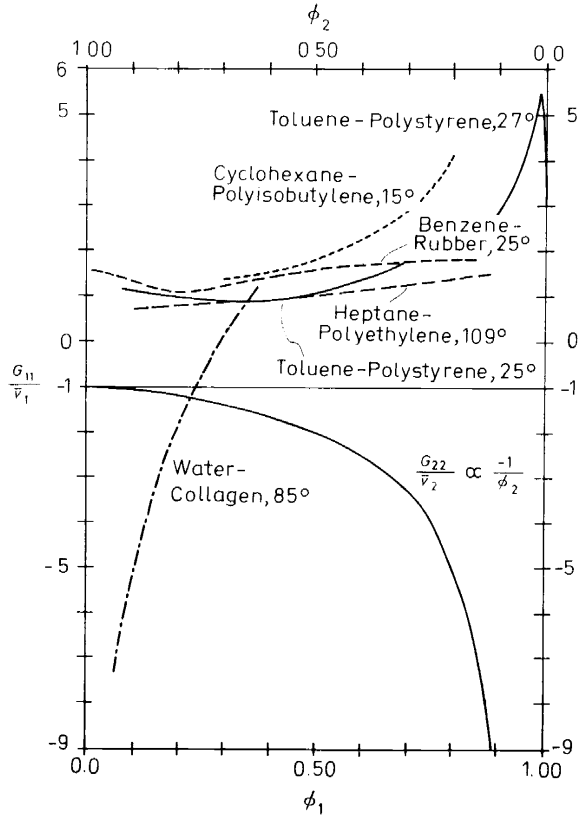


Figure 2. Plot of clustering functions *versus* solvent (ϕ_1) and polymer (ϕ_2) concentration for benzene–polyethylene at 109°C[15], toluene–polystyrene at 25°C[17] and 27°C[18], benzene–rubber at 25°C[14], cyclohexane–polyisobutylene at 15°C[16], and water–collagen at 25°C[19]

Since clustering functions greater than minus one are evidence of the tendency for like molecules to cluster, solvent molecules in these four systems are clustered. The cyclohexane–polyisobutylene system is more heterogeneous than are the other three systems.

The clustering function of toluene in dilute solutions of polystyrene ($\bar{M}_n \simeq 500000$) at 27°C[18] has a maximum value of $G_{11}/\bar{v}_1 \simeq +5.5$ at $\phi_1 \simeq 0.99$ and decreases to $G_{11}/\bar{v}_1 = -1$ at $\phi_1 = 1$ as it must for pure solvent. This increase in $G_{11}/\bar{v}_1$ to a maximum in dilute solutions is consistent with the increase in heterogeneity of a polymer solution upon dilution as polymer molecules begin to disentangle. A detailed description of the clustering function of toluene in polystyrene at high dilution is given in *Figure 3* where the osmotic pressure data of Bawn and colleagues[20] and those of Schick, Doty, and Zimm[18] are plotted. Virial-type equations given by the

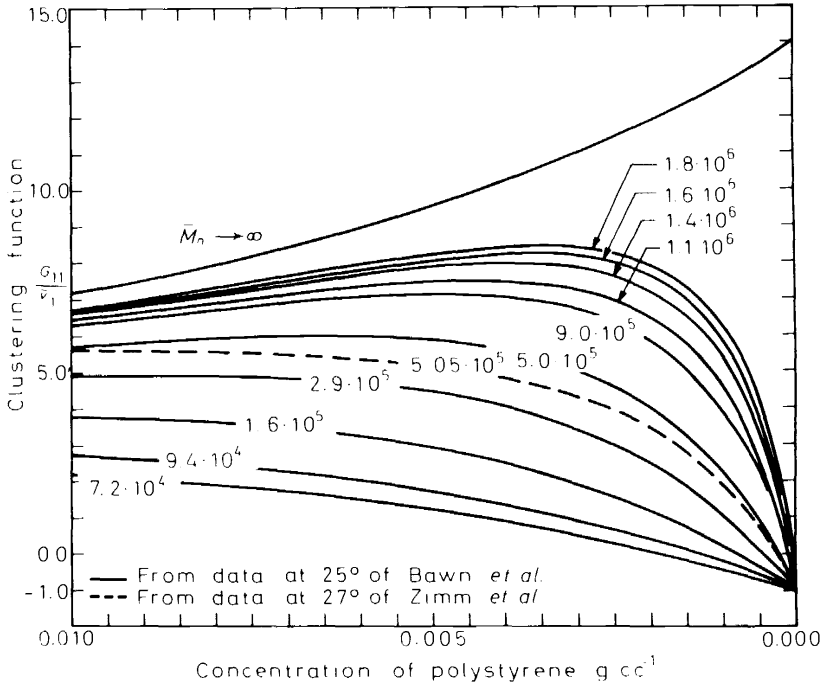


Figure 3. Plot of clustering functions *versus* concentration for toluene in dilute solutions of various fractions of polystyrene at 25°C[20] and 27°C[18]. (Reprinted from ref. 36, p. 706, by courtesy of Marcel Dekker, Inc.)

authors were used. The second virial coefficients of Bawn and coworkers were smoothed by a linear, least squares fit with $\bar{M}_n^{-1}$. The clustering function $G_{11}/\bar{v}_1$ of toluene passes through a maximum which is greater and occurs at higher dilution the greater is the molecular weight of the dissolved polystyrene. The maxima occur at polymer concentrations which are greater than the maximum concentrations at which solutions of discrete polymer molecules can exist based on estimates of molecular dimensions in solution from measurements of scattered light[21].

The clustering functions for nonpolar gases in nonpolar polymers are considerably less than minus one at high concentrations of polymer[22]. In the concentration range $\phi_1 = 0$ to $\phi_1 \simeq 0.04$, the clustering functions of nitrogen in polyethylene melt increases from $G_{11}/\bar{v}_1 \simeq -11$ at 126°C to $G_{11}/\bar{v}_1 \simeq -7$ at 226°C. From $\phi_1 = 0$ to $\phi_1 \simeq 0.1$, the clustering function of methane in branched and linear polyethylene rises from $G_{11}/\bar{v}_1 \simeq -5$ at 125° and 140°C to $G_{11}/\bar{v}_1 \simeq -3$ at 227°C. Clustering functions are more negative for methane in polyisobutylene, $G_{11}/\bar{v}_1 \simeq -8$ at 101°C increasing to $G_{11}/\bar{v}_1 \simeq -4$ at 189°C in the $\phi_1 = 0$ to $\phi_1 \simeq 0.05$ concentration range. Even lower values of the clustering function are found for methane in polystyrene, $G_{11}/\bar{v}_1 \simeq -17$ at 100°C rising to $G_{11}/\bar{v}_1 \simeq -7$ at 189°C for $\phi_1 = 0$ to $\phi_1 \simeq 0.03$[22]. As the pressures of these gases are increased, the polymers should become miscible in the gases over wide ranges of concentration; this expectation is based upon the measurements of Ehrlich of the solubilities of polyethylene in ethane, ethylene, and higher alkanes[23]. In these ranges of great miscibility, the activity–concentration plot should be concave downwards giving clustering functions for the gaseous solvents greater than minus one, probably about plus one like the nonpolar systems in *Figure 2*. Estimating from Ehrlich's data for polyethylene solubility in the higher alkanes[23] and the methane–polymer solutions cited[22], the region of negative functions less than minus one, $G_{11}/\bar{v}_1 < 1$, which requires concave upwards activity–concentration plots, may be limited to low concentrations of solvent, and temperatures close to or above the critical temperature of the solvent in the case of nonpolar solvent–polymer systems. The concentration range over which the clustering function is less than minus one in these hydrocarbon systems appears to be broader the higher is the temperature of the system above the critical temperature of the solvent gas.

For polar solvents in polar polymers or polyelectrolytes, the clustering function $G_{11}/\bar{v}_1$ of solvent is negative in the lower concentration ranges of solvents. It rises to values characteristic of ordinary nonpolar solvents (in nonpolar polymers) as the polar polymers or polyelectrolytes are swelled and become more dilute solutions. Bull's data for water in collagen are characteristic of water in several proteins[19] and cellulose[24]. The first water to enter the collagen is widely dispersed; at $\phi_1 \simeq 0.07$ each molecule of water excludes on the average about seven times its molecular volume to another molecule (*Figure 2*). Such segregation of like molecules is neither unusual nor extreme as Bull's data for other proteins attest[19]. This segregation is not limited to systems with strong interactions between solvent and polymer molecules. In the essentially athermal mixtures of gases in molten polymers previously cited[22], gas molecules are segregated.

A clear picture of the general behaviour of the clustering function for solvent in a polymer–solvent system emerges from the foregoing observations. The $(\mathrm{d}\ln\phi_1/\mathrm{d}\ln a_1)_{p,T}$ term of equation 5a dominates in determining $G_{11}/\bar{v}_1$; other terms involve only concentration. Therefore, requirements upon functional dependence of activity and concentration can be outlined. Any comprehensive theory of polymer solutions must satisfy these criteria. Behaviour of the clustering function generally is as follows. (1). At $\phi_1 = 0$, the clustering function for solvent may be very much less than minus one and rise at low concentrations of solvent to the about plus one to plus two

or more range characteristic of ordinary, nonpolar solvent–polymer systems. Alternatively, at $\phi_1 = 0$ the clustering function may be about the value it has over most of the concentration range for ordinary, nonpolar solutions. (2). In the concentrated solution range ($\phi_1 \simeq 0.2$ to $\phi_1 \simeq 0.8$), the clustering function of solvent will be about plus one to plus two or more with a tendency to increase at lower concentrations. (3). In the dilute solution range, the clustering function for solvent will rise to a maximum which increases with molecular weight and might be in the plus 3 to plus 15 or more range. (4). The clustering function of solvent will decrease to minus one, $G_{11}/\bar{v}_1 = -1$, at $\phi_1 = 1$. The activity–concentration equation which can give a good representation of experimentally observed behaviour of the clustering function (which is dominated by the first derivative of activity with respect to concentration) probably is a multiple term equation containing more than two and, perhaps, four or more adjustable parameters. The probability of deriving such an equation from first principles, without the inherent empiricism of an assumption of corresponding states, is not great.

The clustering functions for polymer, $G_{22}/\bar{v}_2$, calculated from equation 7b using the values of $G_{11}/\bar{v}_1$ of solvent from activity of solvent data for the solvent–polymer systems in *Figure 2*, are almost indistinguishable from $-\phi_2^{-1}$. This must be the case because of the dominance of the $\bar{v}_1/\bar{v}_2$ and $(\phi_1/\phi_2)^2$ terms of equation 7b. The clustering function for polymer $G_{22}/\bar{v}_2$ at low concentrations of polymer will pass through a minimum, increase becoming greater than zero, and pass through a maximum if $G_{11}/\bar{v}_1$ is positive and then decreases. The clustering function $G_{22}/\bar{v}_2$ does not decrease without bound as $\phi_2 \to 0$. The limiting value of the clustering function for polymer may be of the order of $-\bar{v}_2/\bar{v}_1$ as predicted by some theories.

IV. CLUSTERING FUNCTIONS CALCULATED FROM PREDICTIVE THEORIES

1. Small molecule solutions

If on a volume fraction basis the activity of one component of a binary mixture follows the ideal or perfect solution equation (Raoult's law)[11b]

$$a_1 = \phi_1 \tag{8}$$

or the regular solution equation (Henry's law)[11c]

$$a_1 = k_1'\phi_1 \tag{9}$$

where k_1' is constant, the activity of the other component is

$$a_2 = \phi_2^{\bar{v}_2/\bar{v}_1} \tag{10}$$

as a consequence of the Gibbs–Duhem equation (equation 6). The clustering functions are

$$G_{11}/\bar{v}_1 = -1 \tag{11a}$$

and

$$G_{22}/\bar{v}_2 = \frac{\phi_1}{\phi_2}\left(\frac{\bar{v}_1}{\bar{v}_2} - 1\right) - 1 \tag{11b}$$

Similarly, if on a mol fraction basis the activity of component 1 of a binary system follows the ideal or perfect solution equation (Raoults law)[11b]

$$a_1 = x_1 \tag{12}$$

or the regular solution equation (Henry's law)[11c]

$$a_1 = k_1 x_1 \tag{13}$$

where k_1 is a constant, the Gibbs–Duhem equation requires that the activity of component 2 be given by the ideal solution equation[11d]

$$a_2 = x_2. \tag{14}$$

The clustering functions are

$$G_{11}/\bar{v}_1 = -\phi_2\left[1 - \frac{\bar{v}_2}{\bar{v}_1}\right] - 1 \tag{15a}$$

and

$$G_{22}/\bar{v}_2 = -\phi_1\left[1 - \frac{\bar{v}_1}{\bar{v}_2}\right] - 1 \tag{15b}$$

The clustering functions, equations 11a, 11b, 15a, and 15b, show clearly and unambiguously the necessary requirement for ideal or perfect solution behaviour over the whole concentration range, that the partial molecular volumes of both components be equal ($\bar{v}_1 = \bar{v}_2$). Only if $\bar{v}_1 = \bar{v}_2$ can both $G_{11}/\bar{v}_1$ and $G_{22}/\bar{v}_2$ be minus one. In an ideal or perfect solution, one molecule of a given component excludes only its own volume to another molecule and has no other effect on the system. This statement defines an ideal or perfect solution.

Of course, in binary systems where Henry's law holds for the minor component, Raoult's law applies to the major component[11d]. For real systems, this behaviour is approached in the limit of pure, major component. The clustering functions for ideal solutions, the major component at infinite dilution, and pure compounds are identical and have the value $G_{11}/\bar{v}_1 = -1$ as they must.

Equations 15a and 15b show the effect of molecular size upon molecular distributions. In the absence of either net repulsive or attractive interactions between molecules of components 1 and 2 in a binary system, the smaller molecules are clustered and the larger molecules are segregated. In equations 15a and 15b, if $\bar{v}_1 < \bar{v}_2$, $G_{11}/\bar{v}_1 > -1$ and $G_{22}/\bar{v}_2 < -1$.

Adding a van Laar or Scatchard–Hildebrand type partial molal heat of mixing term[25] to equation 8

$$a_1 = \phi_1 \exp(\alpha_1 \phi_2^2) \tag{16}$$

where $\Delta\bar{H}_1 = RT\alpha_1{\phi_2}^2 \equiv$ partial molal heat of solution of component 1 and $\alpha_1 \equiv$ a constant,
and substituting in equation 5a and this result into equation 7b, confirms

that positive heats of dilution and clustering of like molecules, and negative heats of dilution and segregation of like molecules, accompany one another[10]. Of course, the solution model described by equation 16 is idealized to a degree which limits its application to few systems over limited ranges of concentration. Nevertheless, the regular solution equations, on a volume fraction basis (equation 16) or on a mol fraction basis for which the clustering functions are more complicated but depend similarly on parameters $\bar{v}_2/\bar{v}_1$ and heats of mixing[10], demonstrate the interplay of molecular volumes and heats of mixing in determining the kind and give a relative measure of molecular association in solutions.

2. Polymer solutions

The athermal solution theories or ideal solution theories for polymer solutions, which assume ideal mixing of chain-like molecules and no heat effects or volume changes on mixing, were developed from lattice or free volume models by many investigators including Flory[26], Huggins[27], Guggenheim[28], Hildebrand[29], Miller[30], Orr[31], and others. These theories, which we have called the Flory–Huggins–Guggenhein (F–H–G) theory[5], may be summarized by writing the activity equation for the solvent (in closed form):

$$a_1 = \phi_1 \left(1 - \frac{2}{z'}\phi_1\right)^{-(1 - \bar{v}_1/\bar{v}_2)z'/2} \tag{17}$$

where z' is the 'effective coordination number' defined by Huggins and is very nearly equal to the coordination number of the assumed lattice.

Hildebrand's free volume derivation[29] is equivalent assuming an infinite coordination number in equation 17. Flory made this approximation first[26], apparently because the kindred expressions which Flory derived and equation 17 are not strong functions of z' for $z' \geqslant 6$. In effect, taking $z' \to \infty$ assumes that polymer molecules are infinitely flexible and can pass through themselves. This assumption of super-flexibility and no exclusion of volume should and does result in an over estimate of the partial molal entropy of dilution corresponding to an underestimate of the heterogeneity of the system. In the limit of $z' \to \infty$, equation 17 simplifies to

$$a_1 = \phi_1 \, \mathrm{e}^{(1 - \bar{v}_1/\bar{v}_2)\phi_2} \tag{18a}$$

The clustering functions for Flory's and Hildebrand's equation 18a are

$$\frac{G_{11}}{\bar{v}_1} = \frac{-1}{\bar{v}_2/\bar{v}_1 - (\bar{v}_2/\bar{v}_1 - 1)\phi_1} \tag{18b}$$

and

$$\frac{G_{22}}{\bar{v}_2} = \frac{-\bar{v}_2/\bar{v}_1}{\bar{v}_2/\bar{v}_1 - (\bar{v}_2/\bar{v}_1 - 1)\phi_1} \tag{18c}$$

In the limit of very high molecular weight polymer these become

$$\lim_{\bar{v}_2/\bar{v}_1 \to \infty} \frac{G_{11}}{\bar{v}_1} = 0 \tag{18d}$$

and

$$\lim_{\bar{v}_2/\bar{v}_1 \to \infty} \frac{G_{22}}{\bar{v}_2} = -\frac{1}{\phi_2} \tag{18e}$$

For Flory's and Hildebrand's equation 18a, the clustering function for solvent as a function of concentration is described by an envelope of curves between minus one and zero. Of course for $\bar{v}_2 = \bar{v}_1, G_{11}/\bar{v}_1 = -1$; at $\bar{v}_2/\bar{v}_1 \to \infty, G_{11}/\bar{v}_1 = 0$ for $0 \leqslant \phi_1 < 1$. For all values of $\bar{v}_2/\bar{v}_1, G_{11}/\bar{v}_1 = -1$ at $\phi_1 = 1$ and $G_{11}/\bar{v}_1 = -\bar{v}_1/\bar{v}_2$ at $\phi_1 = 0$; $G_{11}/\bar{v}_1 \sim -\bar{v}_1/\bar{v}_2$ over most of the concentration range and decreases to $G_{11}/\bar{v}_1 = -1$ as $\phi_1 \to 1$. Clearly, the Flory–Hildebrand form of the equation underestimates the heterogeneity of the system. To agree with experiment the clustering function for solvent should have a value from about one to two or more.

The clustering function for polymer calculated from Flory's and Hildebrand's formulation of the theory departs little from equation 18e. Since equation 7b holds for all cases, $G_{22}/\bar{v}_2$ must be very nearly equal to $-1/\phi_2$ unless $G_{11}/\bar{v}_1$ departs from zero by the order of $\bar{v}_2/\bar{v}_1$. Over most of the concentration range, the clustering function for polymer according to equation 18c follows $-\phi_2^{-1}$. As $\phi_2 \to 0$, $G_{22}/\bar{v}_2$ continues to decrease but is greater than $-\phi_2^{-1}$ and reaches the limit $G_{11}/\bar{v}_1 = -\bar{v}_2/\bar{v}_1$ at $\phi_2 = 0$ and $\phi_1 = 1$.

Huggins[27] and Guggenheim[28] took the coordination number of the lattice as a finite parameter. Indeed Huggins stated explicitly that for a hydrocarbon polymer solution z' should be about four 27c. The clustering functions for equation 17 are for solvent

$$\frac{G_{11}}{\bar{v}_1} = \frac{2(\bar{v}_2/\bar{v}_1)\phi_2 - z'}{(\bar{v}_2/\bar{v}_1)z'\phi_2 - 2(\bar{v}_2/\bar{v}_1)\phi_2 + z'\phi_1} \tag{19a}$$

and for polymer

$$\frac{G_{22}}{\bar{v}_2} = -\frac{(\bar{v}_2/\bar{v}_1)(z' - 2) + 2\phi}{(\bar{v}_2/\bar{v}_1)z'\phi_2 - 2(\bar{v}_2/\bar{v}_1)\phi_2 + z'\phi_1} \tag{19b}$$

In the limit of very high molecular weight polymer, equations 19a and 19b simplify to

$$\lim_{\bar{v}_2/\bar{v}_1 \to \infty} \frac{G_{11}}{\bar{v}_1} = \frac{2}{z' - 2} \tag{19c}$$

and to equation 18e, respectively.

For Huggins' and Guggenheim's equation, the clustering function for solvent as a function of concentration is given by an envelope of curves between

$$G_{11}/\bar{v}_1 = (2 - z'\bar{v}_1/\bar{v}_2)/(z' - 2)$$

and $G_{11}/\bar{v}_1 = 2/(z' - 2)$ for $0 \leqslant \phi_1 < 1$ and $G_{11}/\bar{v}_1 = -1$ at $\phi_1 = 1$. The clustering function is approximately

$$G_{11}/\bar{v}_1 \simeq (2 - z'\bar{v}_1/\bar{v}_2)/(z' - 2)$$

over most of the concentration range $0 \leqslant \phi_1 \lesssim 0.9$ for $\bar{v}_2 \gg \bar{v}_1(\bar{v}_2/\bar{v}_1 > \sim 10^3)$ and $z' \geqslant 3$; as $\phi_1 \to 1$, $G_{11}/\bar{v}_1$ decreases to minus one at $\phi_1 = 1$. With $z' = 3$ to $z' = 4$ for which equations 19a and 19c become $G_{11}/\bar{v}_1 \simeq +2$ and $G_{11}/\bar{v}_1 \simeq +1$, respectively, the lattice theory gives remarkably good agreement with experiment for nonpolar solvent–polymer systems. If chain stiffness and bulky side groups decrease the number of configurations which a polymer molecule can assume, the effective coordination number of such a chain may be less than four giving clustering functions of solvent greater than one.

The clustering function is a first derivative function; therefore it provides a means for rigorous test of agreement between predictive theories and experiments. Not only must predictive theory give a good representation of activity–concentration data, it must give correct first derivatives with respect to concentration. This examination of the first derivative shows clearly that the combinatorial term in the partition function given by considering reasonable, small lattice-numbers represents experimental data much better than does the infinite lattice number approximation.

Flory[26b] and Huggins[27c, 32a] wrote equations 18a and 17 respectively in logarithmic form, expanded the second logarithmic term neglecting powers of concentration greater than ϕ_2^2, and added a Scatchard–Hildebrand heat term. This expanded equation, which is often called 'the Flory–Huggins equation', written in exponential form gives for the activity of solvent

$$a_1 = \phi_1 e^{(1 - \bar{v}_1/\bar{v}_2)\phi_2 + \chi\phi_2^2} \tag{20a}$$

where in Huggins' derivation

$$\chi = (1 - \bar{v}_1/\bar{v}_2)/z' + \alpha_1' \tag{20b}$$

Equation 20a is a regular solution-type equation, the product of an athermal entropy of mixing and a configuration-independent heat of mixing term. Such separation of configuration and energy terms is not possible; therefore taking χ as an empirical parameter corrects in part for the errors made in separating the partition function into a product in this way. The empirical nature of χ, the dependence of z' in equation 20b on temperature, the improbable values of z' and α_1', and the concentration dependence of χ, has been recognized since the early tests of the lattice theory were made[17, 32].

The clustering functions for the expanded form of the Huggins–Guggenheim equation are

$$\frac{G_{11}}{\bar{v}_1} = \frac{2\chi\phi_2 - \bar{v}_1/\bar{v}_2}{\phi_2 - 2\chi\phi_1\phi_2 + \phi_1\bar{v}_1/\bar{v}_2} \tag{20c}$$

and

$$\frac{G_{22}}{\bar{v}_2} = \frac{2\chi\phi_1 - 1}{\phi_2 - 2\chi\phi_1\phi_2 + \phi_1\bar{v}_1/\bar{v}_2} \tag{20d}$$

In the limits of very high molecular weight polymer these reduce to

$$\lim_{\bar{v}_2/\bar{v}_1 \to \infty} \frac{G_{11}}{\bar{v}_1} = \frac{2\chi}{1 - 2\chi\phi_1} \tag{20e}$$

for solvent and to equation 18e for polymer.

The clustering function for solvent given by equation 20c has the value

$$G_{11}/\bar{v}_1 = (2\chi - \bar{v}_1/\bar{v}_2)$$

at $\phi_1 = 0$; it increases to a maximum value of

$$(G_{11}/\bar{v}_1)_{max} = 2\chi/(1 - 2\chi + \bar{v}_1/\bar{v}_2)$$

at

$$\phi_2 = [\bar{v}_1/\bar{v}_2 + (\bar{v}_1/\bar{v}_2)^{\frac{1}{2}}]/2\chi$$

and decreases to $G_{11}/\bar{v}_1 = -1$ at $\phi_1 = 1$. The numerical values of the clustering function derived from the expanded form of the F–H–G equation can represent experimental results for nonpolar solvent–polymer systems quite well. For values of χ,

$$0.375 \lesssim \chi < [\tfrac{1}{2} + (\bar{v}_1/\bar{v}_2)/2 + (\bar{v}_1/\bar{v}_2)^{\frac{1}{2}}]$$

it rises from

$$0.75 \lesssim G_{11}/\bar{v}_1 \leqslant [1 + 2(\bar{v}_1/\bar{v}_2)^{\frac{1}{2}}]$$

at $\phi_1 = 0$ to a maximum of $3 \lesssim G_{11}/\bar{v}_1 \lesssim \bar{v}_2/\bar{v}_1$ at concentrations somewhat less dilute in polymer than those at which maxima in $G_{11}/\bar{v}_1$ are observed experimentally for $\bar{v}_2/\bar{v}_1 \lesssim 10^4$. The clustering function for polymer decreases from $G_{22}/\bar{v}_2 = -1$ at $\phi_1 = 1$ almost as rapidly as ϕ_2^{-1} to approximately $\phi_2 \simeq (\bar{v}_1/\bar{v}_2)^{\frac{1}{2}}$. At higher dilutions it decreases less rapidly and passes through a minimum at

$$\phi_1 = [1 - (\bar{v}_1/\bar{v}_2)^{\frac{1}{2}}]/2\chi$$

if this $\phi_1 < 1$, or it continues to decrease; the limiting value at $\phi_1 = 1$ is

$$G_{22}/\bar{v}_2 = (2\chi - 1)(\bar{v}_2/\bar{v}_1).$$

That this expanded form, an approximation to the F–H–G equations, should give better representation of experimental data than do the exact forms of these equations is not merely surprising irony. Using the expanded form adds an empirical, concentration-dependent parameter χ which is dependent upon configuration and heat of mixing in such a manner as to correct in part for separating the partition function into a product.

3. Adsorption systems

Langmuir used a mass-action type kinetics argument for adsorption and desorption of a monolayer of gas on a continuous surface to derive his adsorption isotherm[33]. Adsorption of single molecules on a limited number of sites, n_s, yields the same equation for the activity, a_1, of n_1 adsorbed molecules[34]

$$a_1 = \frac{c\, n_1}{n_s - n_1} \tag{21a}$$

where c is a constant. If each site has a partial molecular volume $\bar{v}_s$, the concentration can be written in terms of a volume fraction

$$\phi_1 = (1 + n_s\bar{v}_s/n_1\bar{v}_1)^{-1} \tag{21b}$$

These equations with equation 5a give

$$\frac{G_{11}}{\bar{v}_1} = -2 + \frac{\bar{v}_s}{\bar{v}_1} + \phi_1\left(1 + \frac{\bar{v}_s}{\bar{v}_1}\right) \tag{21c}$$

for the clustering function for adsorbed gas. Substituting equation 21c into equation 7b yields for the adsorbent

$$\frac{G_{22}}{\bar{v}_2} = \frac{\bar{v}_s}{\bar{v}_1}\phi_1 - \frac{\phi_1^2}{\phi_2} - \frac{1}{\phi_2} \tag{21d}$$

In the limit of zero adsorption ($\phi_1 \to 0$), $G_{11}/\bar{v}_1 = -2 - \bar{v}_s/\bar{v}_1$. Since the volume of an adsorption site is usually larger than the volume of an adsorbed molecule, the clustering function for adsorbed molecules at low coverage usually is substantially less than minus three. At low coverages an adsorbed molecule excludes an average of $2 + \bar{v}_s/\bar{v}_1$ times its own molecular volume to another molecule of adsorbate. In monolayer or Langmuir adsorption, adsorbed molecules are segregated. The Langmuir adsorption equation is limited to fairly low coverages; in these ranges the clustering functions, $G_{11}/\bar{v}_1$ and $G_{22}/\bar{v}_2$, have reasonable values and reasonable limiting values at $\phi_1 = 0$.

The solubilities of at least some nonpolar gases in melts of nonpolar polymers follow the Langmuir adsorption isotherm over significant ranges of concentration. These are, nitrogen in branched polyethylene, and methane in branched and linear polyethylene, polyisobutylene, and polystyrene[22]. The clustering functions of these gases in these polymers, which range from $G_{11}/\bar{v}_1 \simeq -3$ to $G_{11}/\bar{v}_1 \simeq -17$, were cited in Section III. These clustering functions can be interpreted quite literally by stating that one molecule of sorbed gas excludes to the next molecule of gas from 3 to 17 times its molecular volume. These gas–polymer systems are athermal or almost athermal in their behaviour. We usually associate the Langmuir isotherm with relatively strong binding between adsorbed molecules and adsorbing sites. Nothing in the derivation of the Langmuir isotherm restricts it to strong binding systems. The configuration or combinatorial term in the partition function merely states that as each molecule of gas is adsorbed one site is occupied or used up and no site is added to the system. In the limit of an athermal system, adsorption or solution behaviour is purely entropic. In these nearly athermal gas–polymer systems, the adsorption sites may be nothing more than unoccupied volumes in the polymer melt, volumes which can accommodate an average of one gas molecule in each void or unoccupied volume.

In monolayer adsorption, the adsorbed molecules are segregated. If molecules are adsorbed on molecules in the first layer, molecules involved in adsorption in two or more layers are clustered. Therefore, in multilayer adsorption molecular segregation at low coverages (considerably less than one monolayer) going over to clustering at higher coverages (multilayer adsorption) should be reflected by the clustering function for adsorbed molecules increasing from much less than minus one to values greater than minus one, perhaps greater than plus one.

The multilayer adsorption isotherm of Brunauer, Emmett, and Teller[35] (B–E–T) is

$$\frac{a_1}{n_1(1-a_1)} = \frac{1}{n_s c} + \frac{c-1}{n_s c} a_1 \tag{22a}$$

where $a_1 \equiv$ activity of adsorbed molecules
$n_1 \equiv$ number of adsorbed molecules
$n_s \equiv$ number of adsorption sites and
$c \equiv$ constant.

This gives the clustering functions for adsorbed molecules

$$\frac{G_{11}}{\bar{v}_1} = -\phi_2\left\{\left[1 - \frac{2}{c} - 2a_1\left(1 - \frac{1}{c}\right)\right]\frac{\bar{v}_s}{\bar{v}_1} + 1\right\} - 1 \tag{22b}$$

and for adsorbent

$$\frac{G_{22}}{\bar{v}_2} = \frac{\phi_1^2}{\phi_2}\left[\frac{2}{c} - 1 + 2a_1\left(1 - \frac{1}{c}\right)\right] + \frac{\bar{v}_1}{\bar{v}_s}\phi_1 - \frac{1}{\phi_2} \tag{22c}$$

These clustering functions have reasonable limiting values

$$\lim_{\phi_1 \to 0} \frac{G_{11}}{\bar{v}_1} = -2 - \frac{\bar{v}_s}{\bar{v}_1} + \frac{2}{c}\frac{\bar{v}_s}{\bar{v}_1} \tag{22d}$$

and

$$\lim_{\phi_2 \to 0} \frac{G_{22}}{\bar{v}_2} = -2 + \frac{\bar{v}_1}{\bar{v}_s} \tag{22e}$$

For pure component 1 (adsorbate) and pure component 2 (adsorbent) the respective clustering functions have values of minus one. Equation 22d shows clearly that the B–E–T equation combines a Langmuir type adsorption with a term that accounts for clustering, multilayer adsorption, at higher concentrations.

The water–collagen system, the twelve other water–protein systems studied by Bull[19], water sorption by nylon, silk, and wool[19], and water sorption in cellulose[24] follow the B–E–T adsorption isotherm at least as well as any other two-parameter equation. The clustering functions for water in collagen, calculated by taking the slopes of a plot of experimental values of a_1/ϕ_1 *versus* a_1 are shown as points and those from Bull's best fit of the B–E–T isotherm as the solid line in *Figure 4*. Considering that the clustering function varies as the first derivative of the concentration as a function of activity, the agreement between clustering functions determined from a plot of experimental data and those calculated from the B–E–T equation is remarkably good. Each of the first molecules of water added to collagen excludes from 7 to 9 times its molecular volume to the next molecule of water to be added. As more water is added, 'sites' begin to be used up and water is sorbed on water; multilayer adsorption or water clustering begins to occur. As the activity of water rises to $a_1 \simeq 0.95$ at $\phi_1 \simeq 0.4$, the water in collagen behaves like that in an ordinary polymer solution with $G_{11}/\bar{v}_1 \simeq +1.3$. As more water is added to this collagen solution the system may be expected to behave somewhat like an ordinary, nonpolar solvent–polymer system with $G_{11}/\bar{v}_1 \simeq 1$ to 2 up to $\phi_1 \simeq 0.9$ and $G_{11}/\bar{v}_1 > \simeq 2$ at a maximum at $\phi_1 \simeq 0.98$ or $\phi_1 \simeq 0.99$.

The foregoing example of the applicability of the B–E–T equation to a strong-binding polymer–solvent system and the expectation from the gas-in-polymer-melt data[22] and the solubility-in-polymer data of Ehrlich[23] that the B–E–T equation is applicable to nonpolar systems, indicates that

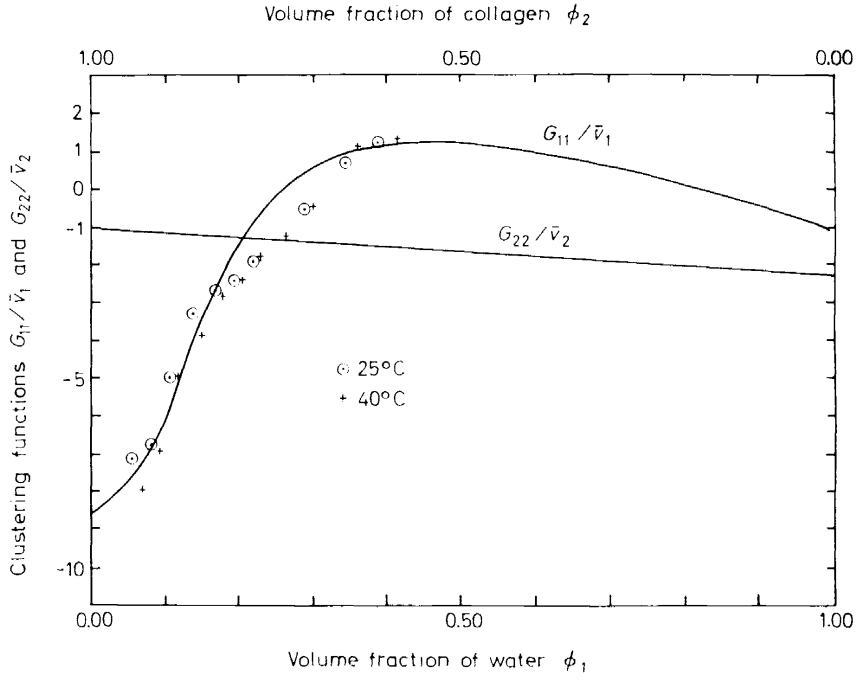


Figure 4. Plot of clustering functions *versus* concentration for water (ϕ_1) and collagen (ϕ_2) at 25° and 40 °C[19] by graphical integration, and calculated from the Brunauer, Emmett, and Teller adsorption equation[35] which represents the data.

the B–E–T adsorption isotherm may be one of the best—if not *the* best—two-parameter equations for describing polymer solutions. 'Site adsorption' going over to usual polymer solution behaviour may be much more common behaviour for solvent–polymer systems than has been realized in the past.

V. SUMMARY AND CONCLUSIONS

The clustering functions cannot predict thermodynamic properties of mixtures. They do interpret in geometric terms, the probability that similar molecules occupy adjacent volumes in space, the activity-concentration behaviour of any binary adsorption, sorption, or solution system.

The clustering function is a free energy function derived without separating the partition function into a product of terms including an energy-independent combinatorial term and a configuration-independent energy term. Therefore, the clustering function should be applicable to any binary system at equilibrium over the whole concentration range of the system.

The clustering functions are derived from the cluster integrals of dilute gas method statistical mechanics which assumes a centrosymmetric system in its development. On a molecular basis a chain-like polymer molecule is not symmetric about another polymer molecule or any given solvent molecule. This lack of radial symmetry of polymer molecules seems to have no effect on the efficacy of the clustering function in describing solvent clustering or segregation. The cluster integral for polymer molecules may not describe the segregation of polymer molecules at some small range of concentrations at high dilution.

In spite of the serious consequences of splitting the partition function into a product of terms in developing predictive theories, real differences in combinatorial terms do appear. Examples are the much better representation of experimental results by the F–H–G theory with small values of the coordination number than with z′ approaching infinity and the need for an adsorption-on-sites combinatorial term in some nonpolar as well as polar systems.

The B–E–T adsorption isotherm and the F–H–G theory in its expanded, empirical form are the best two-parameter polymer solution equations over the whole range of concentration. Only the B–E–T equation, among the common adsorption and solution equations, can describe activity–concentration behaviour where activity is concave upwards at low concentrations and concave downwards at higher concentrations.

The non-uniqueness of models is demonstrated by the fine fit of some polymer solution and sorption data by equations derived for adsorption of one or several layers of gas molecules on a continuous surface.

Calibration of the clustering functions, for example by measuring sizes of average clusters by scattering experiments, is needed.

Clustering functions provide a method for rigorously testing any adsorption theories with other theories or experimental data. Further, the clustering functions provide an easily understood, unified treatment of thermodynamics of solutions, sorptions, and adsorptions.

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