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The Structure of Aqueous Non-electrolyte Solutions (Comparative Analysis of the Thermodynamic Properties of Aqueous and Non-aqueous Binary Systems)

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A comparison of the thermodynamic properties of a large number of aqueous and alcoholic binary systems has established that the following properties are characteristic only of aqueous solutions: (1) negative enthalpies and entropies of mixing at low non-electrolyte concentrations; (2) negative partial molar entropies and enthalpies of water at moderate concentrations. The first property is evidence of the stabilisation of the water structure when the vacancies are filled. The second implies that the solution has a microheterogeneous structure owing to the presence in it of ordered regions (globules). The problem of the nature of the globules and their cooperative properties is discussed.
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1. INTRODUCTION

Concepts have recently developed as to the nature of the changes in the structure of water under the influence of a non-electrolyte dissolved in it. They reduce to the assertion that, when the vacancies in the water skeleton are filled by a non-electrolyte, the water structure is stabilised. This view explains various effects arising when small amounts of non-electrolytes are dissolved in water: the decrease of the self-diffusion coefficient, compressibility, and ion hydration and the increase of viscosity [1-5]. The filling of the vacancies in the water structure also accounts for the minima in the partial molar volumes of the non-electrolytes [6] and the anomalous variation of the solubility of gases [7,8] and certain other sparingly soluble substances [9].

Despite the abundance of studies and available data, we believe it useful to attempt to approach the problem of stabilisation from a purely thermodynamic standpoint without invoking beforehand any specific models of the water structure. Although the thermodynamic properties of aqueous non-electrolyte solutions have been discussed by Morachevskii [10,11] and Franks [12,13], we believe that one can proceed somewhat further by comparative analysis of the properties of aqueous and alcoholic binary systems. Only such analysis will make it possible to isolate the properties characteristic of aqueous solutions and justify the necessity for hypotheses concerning the collective interactions in aqueous systems. Using the method of comparative analysis, we shall also discuss, apart from stabilisation, the characteristics of the behaviour of aqueous solutions in the microheterogeneous region

(moderate concentrations of the non-electrolyte). In view of the inadequate treatment of this problem in the literature, here we will go beyond the framework of the thermodynamic description and will put forward a molecular mechanism for the phenomenon.

Sufficient experimental data have now been published to make such comparative analysis possible. However, it should be noted that, in the interpretation of the results obtained, most workers employ excess thermodynamic functions (with the usual notation H^E, S^E, and G^E) and not the functions of mixing (H^M, S^M, and G^M). We believe that such an approach is useful only when the system deviates little from ideal behaviour. For the alcoholic and aqueous solutions discussed below, this is known not to be the case. Here it is simpler to interpret directly the functions of mixing. Moreover, these functions can be used to assess the tendency of the solutions to form separate phases. In the present study we will therefore employ exclusively the thermodynamic functions of mixing.

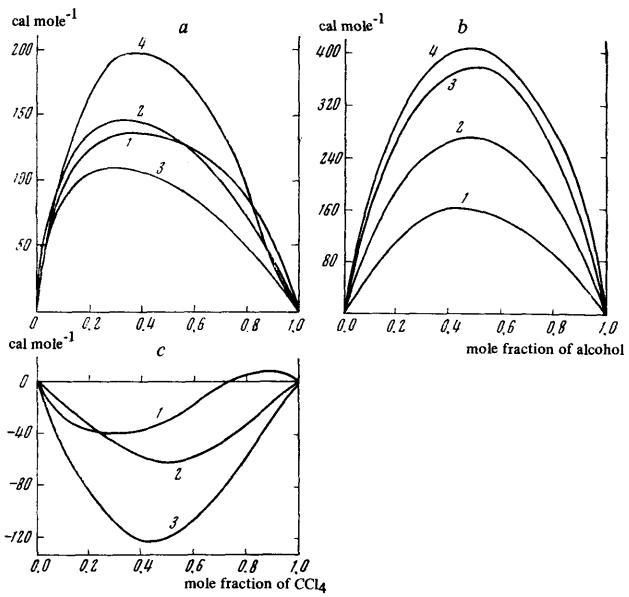


Figure 1. Enthalpy of mixing at 25°C for various systems: *a*) 1) ethyl alcohol–n-hexane; 2) n-propyl alcohol–n-hexane; 3) n-octyl alcohol–n-hexane; 4) isopropyl alcohol–n-hexane[14,15]; *b*): 1) methyl alcohol–acetone; 2) ethyl alcohol–acetone; 3) isopropyl alcohol–acetone; 4) s-butyl alcohol–ethyl methyl ketone[14,16]; *c*): 1) pyridine–carbon tetrachloride; 2) dioxan–carbon tetrachloride; 3) 3,5-dimethylpyridine–carbon tetrachloride[17,18].

2. LOW NON-ELECTROLYTE CONCENTRATIONS

The nature of the phenomena occurring in aqueous solutions at low (up to a mole fraction of 0.1) and moderate non-electrolyte concentrations is significantly different. Therefore in a comparative analysis of aqueous and alcoholic systems it is desirable to consider these two concentration ranges separately.

a. Enthalpy and Entropy of Mixing in Alcoholic Systems

At first sight it appears that the addition of any non-polar liquid to lower alcohols should lead to positive enthalpies of mixing H^M, since dilution of an associated liquid leads to the dissociation of some of the hydrogen bonds. This view is justified for systems of the alcohol–hydrocarbon type (Figs. 1*a* and 2) and also for systems of the alcohol–ketone type (Fig. 1*b*), although one cannot exclude *a priori* the possibility that hydrogen bonds are formed between alcohols and ketones. For this reason, the finding that the mixing of lower alcohols with carbon tetrachloride, a classical inert solvent, at fairly low temperatures leads to negative values of H^M, indicating a powerful interaction between the alcohol and carbon tetrachloride (Fig. 3), is all the more surprising. This increase of H^M cannot be accounted for by the interaction of carbon tetrachloride with the hydrocarbon "tail" of the alcohol, since, first, on passing to higher alcohols, H^M increases and becomes positive (Figs. 3*a* and 3*b*) and, secondly, H^M for the mixing of hydrocarbons with carbon tetrachloride is positive[23]. The increase due to the van der Waals interaction between carbon tetrachloride and the proton of the OH group is evidently also impossible, since the replacement of a strong hydrogen bond by a van der Waals interaction cannot lead to an energy gain.

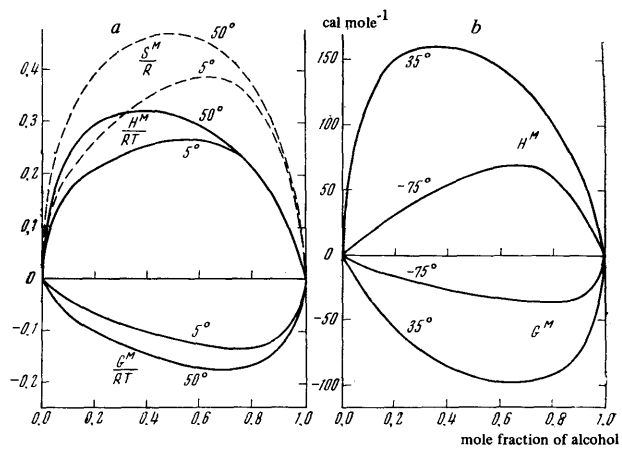


Figure 2. Thermodynamic functions of mixing for various systems:
a) ethyl alcohol–cyclohexane[19]; *b*) ethyl alcohol–methylcyclohexane[20].

Thus only one explanation remains: the increase of H^M at low carbon tetrachloride concentrations in alcohol is due to powerful van der Waals interactions between carbon tetrachloride molecules and the *p*-orbitals of the alcohol oxygen atoms not involved in hydrogen bonding. Each alcohol molecule has two possibilities of forming a hydrogen bond via oxygen and only one via hydrogen. Thus even in a completely self-associated alcohol each of its molecules retains on average one possibility of forming an additional hydrogen bond. Since hydrogen bonds in alcohols do not form a three-dimensional network but lead to

chain or ring structures[24-27], the carbon tetrachloride molecule can come into contact with the oxygen atom of the alcohol without affecting the hydrogen bond. The validity of this explanation is confirmed by the negative value of H^M in dioxan–carbon tetrachloride and pyridine–carbon tetrachloride systems (Fig. 1*c*). On the other hand, the large increase of H^M in the methanol–chloroform system (Fig. 4*a*), due to the formation of a hydrogen bond between chloroform and the alcohol, is evidence of the absence of steric hindrance to van der Waals interaction between carbon tetrachloride and the oxygen atom of the alcohol. Another system where an increase of H^M is observed below −50°C is ethanol–toluene (Fig. 5*a*). Probably this effect can also be accounted for by ready van der Waals interaction between the benzene ring and the oxygen atom.

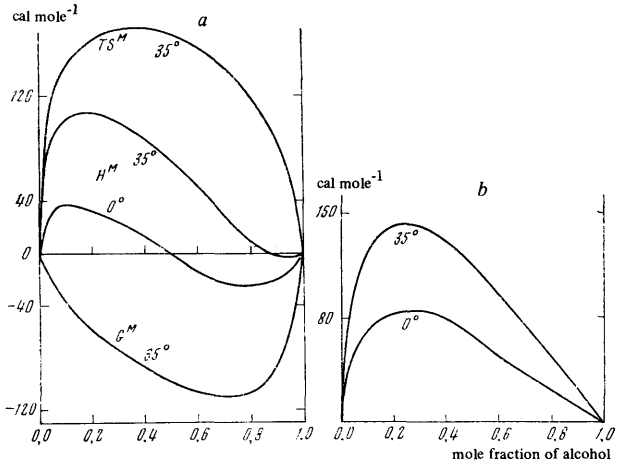


Figure 3. *a*) Thermodynamic functions of mixing for the methyl alcohol–carbon tetrachloride system[21,22]; *b*) enthalpy of mixing in the n-octyl alcohol–carbon tetrachloride system[22].

The above data allow the following conclusions to be drawn: the sign and magnitude of H^M in alcoholic systems can be various and are determined by the characteristics of the interaction of the alcohol with the second component in each specific case. In contrast to the enthalpy, the entropy of mixing in all the systems considered shows the same behaviour and is positive †.

b. Entropy and Enthalpy of Mixing in Aqueous Solutions

Fig. 5*b* and Figs. 6–11 present the heats of mixing for various binary aqueous systems. A characteristic feature of all these curves is the negative sign of H^M at low concentrations of the second component (and at sufficiently low temperatures). Moreover, the enthalpy of mixing is negative also for the dissolution in water of aliphatic and aromatic hydrocarbons and even the inert gases[35,36]. Thus one may assert that the dissolution in water of the majority of non-electrolytes takes place with evolution of heat. This behaviour is an important property of aqueous systems and sharply distinguishes them from the alcoholic solutions discussed above.

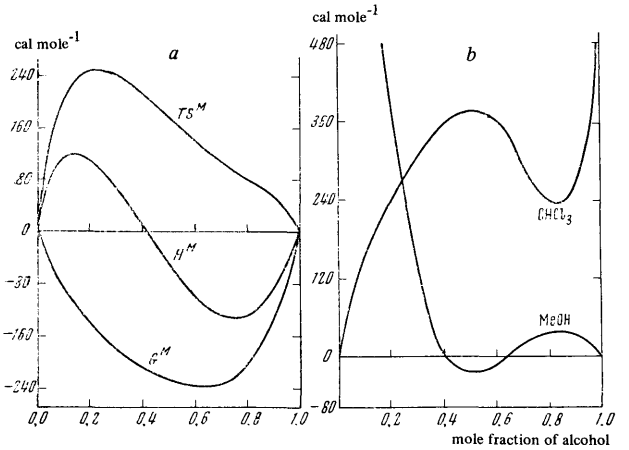


Figure 4. The methyl alcohol–chloroform system at 35°C: *a*) thermodynamic functions of mixing[21]; *b*) partial entropies $T\bar{S}_i^M$ of the components.

We shall now attempt to discover the reasons for such behaviour of H^M in the specific example of the water–acetone system. If the energy gain on mixing the two liquids is regarded as the result of only the pair interactions between their molecules, the negative value of H^M can be accounted for in two ways: (1) the formation of a hydrogen bond between acetone and water; (2) powerful van der Waals interaction between acetone and water.

However, the first hypothesis must be immediately rejected. Indeed, the formation of a hydrogen bond between acetone and water is possible only at the expense of the dissociation of the stronger water–water hydrogen bond; moreover, H^M for the mixing of acetone with alcohols is positive (Fig. 1*b*) and it would be difficult to understand why acetone associates with water but not with alcohols. This explanation is also unsatisfactory because it is not universal and is not applicable, for example, to the dissolution of hydrocarbons and noble gases in water.

The second explanation, based on a powerful van der Waals interaction, requires a more detailed examination. In the first place it is necessary to resolve the difficulty mentioned above: the different signs of H^M in the dissolution of acetone in alcohols and water. The overall heat of solution of acetone consists of the energy loss resulting from the interactions between the molecules of the solvent and the energy gain from the interactions between the solvent and acetone. However, the energy differences between the water–water and alcohol–alcohol interactions are not very great; the same may be said of the alcohol–acetone and water–acetone interactions. Therefore, in order to account for the negative sign of H^M in water, it is necessary to postulate that there is no large positive

† There is no need to quote S^M curves for all the systems in support of this assertion, since the entropy of mixing cannot be negative if $H^M > 0$ (by virtue of the relation $TS^M = H^M - G^M$ and $G^M < 0$). The positive sign of S^M for systems with $H^M < 0$ is illustrated in Figs. 3*a* and 4*a*.

contribution to H^M due to water–water dissociations. We arrive at a similar conclusion by considering other aqueous solutions. Consequently this phenomenon is not caused by the properties of the non-electrolyte but the characteristics of the water structure, i.e. it is necessary to assume that water contains fairly large cavities (vacancies) which accommodate non-electrolyte molecules on dissolution.

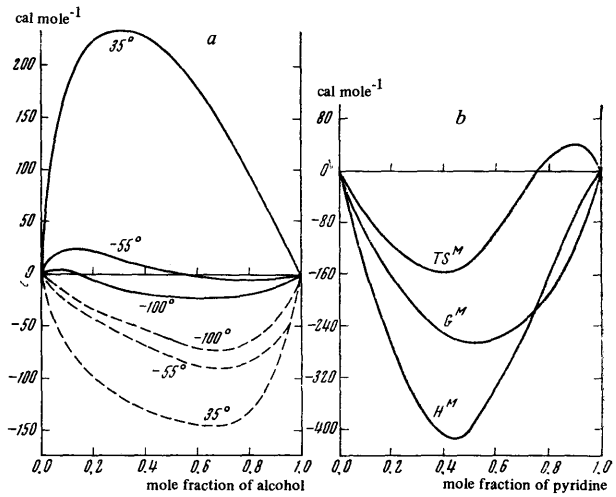


Figure 5. Thermodynamic functions of mixing for various systems:
a) ethyl alcohol–toluene[20] (continuous line—H^M; dashed line—G^M); *b*) water–pyridine at 20°C[28].

The existence of cavities, which is a distinctive feature of the structure of water, may be confirmed by considering the partial molar enthalpies of non-electrolytes on infinite dilution $\bar{H}^M_{H,O}$. In the majority of the systems examined (Figs. 5*b*, 6–9, and 11) $\bar{H}^M_{H,O}$ amounts to 1–3 kcal mole^{-1} in absolute magnitude. This exceeds by several hundred cal mole^{-1} not only the values of $\bar{H}^M_{i,O}$ observed in systems with powerful van der Waals interaction between the components [for example, carbon tetrachloride–dioxan, carbon tetrachloride–pyridine, and carbon tetrachloride–methanol (Figs. 1*c* and 3*a*)], but even the $H^M_{i,O}$ in certain systems with hydrogen bonds [for example, chloroform–dioxan[37], chloroform–acetone[38], and chloroform–methanol (Fig. 4*a*)]. Clearly such a large negative heat change could be accounted for by van der Waals interactions only if it is assumed that water–water bonds are not dissociated on mixing.

However, it is doubtful if these large heat changes are completely determined by van der Waals pair interactions. Indeed, comparison of the values of $\bar{H}^M_{H,O}$ on dissolution in water of alcohols, ketones, hydrocarbons, and the inert gases shows that the heat change is virtually independent of the polarity of the second component although a dependence would be expected for van der Waals interactions.

The inadequacy of the hypothesis of van der Waals interactions alone becomes evident when the entropy of mixing is considered. Comparison of Figs. 5*b* and 6–11 shows that S^M is as a rule negative for all aqueous systems at low concentrations of the second component and at low temperatures, while for all other liquids (see, for example, Fig. 1–4 and 5*a*) S^M is positive even if the mixing is exothermic. The negative sign of S^M is an important characteristic of aqueous solutions, which distinguishes them from other binary systems.

Nevertheless, when water and a non-electrolyte are mixed, a positive contribution to the entropy of the system appears, as for any other two liquids, owing to the interchange of molecules of water and of the second component. The van der Waals interaction between the components leads to a decrease of S^M compared with S^M_{id} but its sign still remains positive. These considerations are fully confirmed by experimental data: we are not aware of a single system without hydrogen bonds where a negative entropy of mixing is observed.

A negative contribution to entropy in the pair interaction between species can arise only if they form a complex, say via hydrogen bonding. However, we have already rejected this possibility for water–non-electrolyte systems. Therefore one must assume that the negative entropy of mixing in these systems is not caused by pair interaction between water and non-electrolyte molecules, but by collective changes in the water structure towards greater order. In such a process the enthalpy of the system should also fall ($\Delta H = \Delta G + T\Delta S < 0$) which makes a contribution to the heat change, additional to the van der Waals interactions. All these collective phenomena have come to be referred to as the stabilisation of the water structure. The energy gain on stabilisation implies that the dissolution in water of small amounts of non-electrolytes does not lead to the dissociation of some of the hydrogen bonds, as in all other highly self-associated liquids, but in fact results in the formation of a certain number of water–water hydrogen bonds or in their strengthening ‡.

Although the conclusion that the concept of stabilisation must be introduced is not based on any particular model of the water structure, it is useful to illustrate the significance of this term with reference to a specific model, for example that of Samoilov[39,40], according to which water consists of molecules forming an ice-like framework blurred by thermal motion and of molecules partially filling the vacancies in the framework. When a non-electrolyte is added to water, it enters the cavities within the framework (without dissociating the hydrogen bonds or disrupting the van der Waals water–water interactions) and displaces some of the "cavity" water molecules to the framework, since by filling part of the cavities it displaces the dynamic equilibrium between the "cavity" and "framework" water molecules[41]. Since this involves the formation of new water–water hydrogen bonds, the enthalpy of mixing should be negative. On the other hand, the transfer of some water molecules to the more ordered phase (the framework) leads to a negative entropy of mixing.

The water–pyridine system requires special consideration. Although here too negative values of S^M are observed (Fig. 5*b*), they cover an unduly wide concentration range. One cannot postulate that the effect associated

‡ The effects associated with stabilisation should evidently decrease with temperature owing to the breakdown of the water structure. This is in fact observed (Figs. 7 and 9).

with stabilisation can be observed up to a pyridine concentration of 50 mole %, where the water structure is certainly disrupted. Probably the explanation of the negative values of S^M for this system consists in the fact that pyridine forms very strong hydrogen bonds with water. Indeed, H^M for this system is high and negative over the entire pyridine concentration range. This explanation is also confirmed by vibrational spectra [42,43]. Probably the behaviour of thermodynamic functions in the water–dimethyl sulphoxide [44,45] and water–diethylformamide systems [46] should be explained similarly.

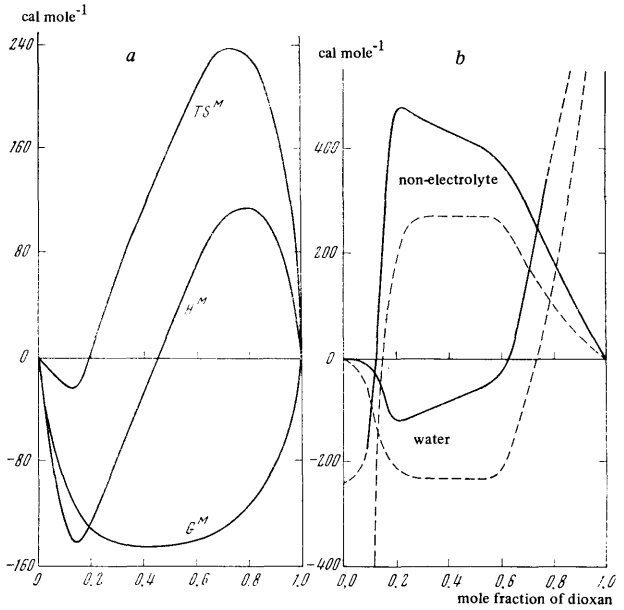


Figure 6. The water–dioxan system at 25°C; *a*) thermodynamic functions of mixing [29]; *b*) partial entropies $T\overline{S}_i^M$ (continuous line) and enthalpies $\overline{H}_i^M$ (dashed line) of the components.

The stabilising effect of the non-electrolyte entering the cavities in the water structure should be reduced with increase of the non-electrolyte concentration. This accounts for the characteristic S shape of the plots of S^M and H^M in aqueous systems against concentration: the negative contributions to S^M and H^M owing to stabilisation are replaced at high non-electrolyte concentrations by positive contributions from the dissociation of water–water hydrogen bonds. It would be extremely interesting to establish the concentration corresponding to maximum stabilisation or, what amounts to the same thing, to the optimum filling of the cavities. The minima in H^M, S^M, or the excess partial volume $\overline{V}_H^E$ are usually compared with this concentration. However, there is a difficulty here. If the stabilising effect of the non-electrolyte and the disruption of the structure are described by fairly smooth concentration functions, the extrema in H^M, S^M, and $\overline{V}_H^E$ need not coincide, since they are a consequence of the superposition of different functions varying in the opposite sense. Then the significance of the term "maximum stabilisation" becomes extremely indefinite. This situation in fact obtains. For example in the water–dioxan system at 25°C a minimum in the excess partial volume of dioxan is observed at a non-electrolyte mole fraction of 0.04, [47] while the minima in H^M and S^M occur at mole fractions of 0.13 and 0.12 respectively (Fig. 6*a*). The extrema in all the functions should coincide only when the stabilisation varies sharply with concentration, for example, when one can speak of the exact instant when the cavities are filled. However, in such a case it would be necessary to seek additional explanations of the observed differences in the positions of the extrema. This dilemma cannot be resolved solely on the basis of thermodynamic data. The first view appears more prudent. Having adopted it, one can assume that the stabilising effect of the non-electrolyte hardly extends beyond concentrations where its mole fraction is 0.10–0.15.

Summarising the above discussion, one may assert that (1) at low non-electrolyte concentrations aqueous solutions exhibit unique properties, which consist in the fact that, regardless of the nature of the second component, the entropy and enthalpy of mixing are negative and (2) these facts provide evidence of a collective stabilisation of the hydrogen bond lattice on addition of a non-electrolyte to water due to an increase in the energy of the hydrogen bonds or in their number.

3. MODERATE CONCENTRATIONS

We shall now consider the behaviour of the thermodynamic functions of mixing for non-electrolyte concentrations corresponding to a mole fraction of 0.2 and above, i.e. in the region where the water structure is disrupted. In the first place we must note that the G^M–concentration curve has sections with low curvature, which are particularly distinct in the water–dioxan system for dioxan mole fractions in the range 0.25–0.6 (Fig. 6*a*). These indicate that the system tends to form two layers, i.e. microheterogeneity of the structure of the solution. Such behaviour of G^M is not in itself an exclusive characteristic of aqueous mixtures, since sections with low curvature on G^M–x curves are encountered fairly frequently in binary systems with positive deviations from ideality (see, for example, Figs. 2, 3*a*, 4*a*, and 5*a*). The particular properties of aqueous solutions are shown in the unusual behaviour of the partial enthalpies and entropies of mixing in the region of microheterogeneity, namely (1) in all systems (with the exception of water–methanol mixtures) $\overline{H}_{water}^M$ and $\overline{S}_{water}^M$ are negative over a considerable concentration range at not unduly high temperatures (see Fig. 6*b*; similar behaviour follows from Figs. 5*b* and 6–11) and (2) in a series of aqueous systems there is a rigorously linear relation between H^M and concentration with corresponding horizontal sections in H_i^M–x curves (Figs. 6, 7*a*, and 9*b*)§.

The first characteristic is indeed an exclusive property of aqueous solutions. In all the non-aqueous systems examined, the partial molar entropies of mixing of both components always proved to be positive. We succeeded in finding only one system which is an exception to this rule, namely methanol–chloroform (Fig. 4*b*).

§ The linearity of the H^M–x relation has been established very reliably. Thus in the water–dioxan system 7 experimental points lie on a straight line [29] and in the system water–t-butyl alcohol 5 points [32].

Here, the negative values of $\bar{H}^{M}_{meth}$ and $\bar{S}^{M}_{meth}$ can evidently be explained by the formation of hydrogen bonds between methanol and chloroform, which can occur without the dissociation of alcohol–alcohol hydrogen bonds, i.e. the reason for the anomalous behaviour of the thermodynamic functions for this system consists in the unusual nature of the proton donor–acceptor properties of the alcohol, to which attention has already been drawn in the first section of the review. Thus the negative partial entropy of mixing is typical only for aqueous systems and therefore must be associated with the characteristics of the water structure.

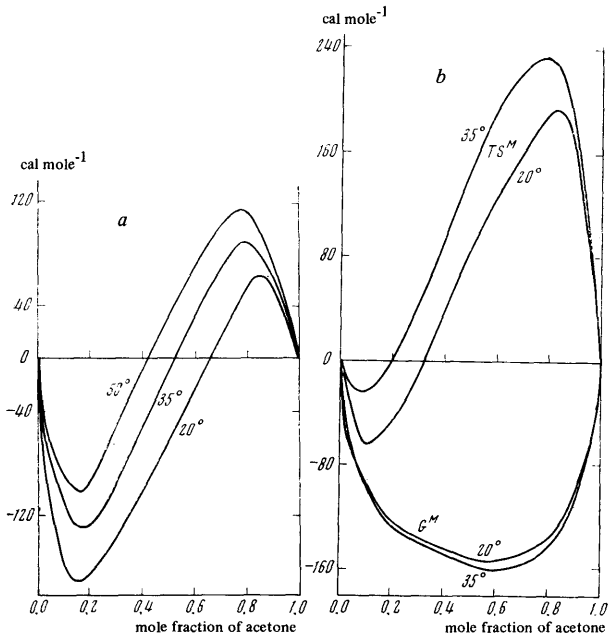


Figure 7. The water–acetone system: *a*) enthalpies of mixing[30]; *b*) entropies and free energies of mixing[31].

The retention of the negative sign of H^{M}_{water} and S^{M}_{water} over a wide range of concentrations, up to a non-electrolyte mole fraction of 0.7, is evidence of the existence in solution at these concentrations of regions where water molecules exhibit a fairly high degree of order. Indeed, by definition, the partial molar entropy of water is the entropy of mixing of a large volume of solution at a given concentration with one mole of water. If the solution is a homogeneous mixture of association complexes of water and the non-electrolyte, the degree of order in water should decrease when it is added to the solution, since water–non-electrolyte complexes are weaker than water–water complexes. Contrary to experiment, this leads to positive values of $\bar{H}^{M}_{water}$ and $\bar{S}^{M}_{water}$. Consequently we are obliged to attribute to this solution a microheterogeneous structure which contains regions (globules) where water exists in an even more ordered state than in pure water. When the added water enters these regions, negative values of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$ are in fact obtained. However, in a heterogeneous system of this kind there is another possible mechanism leading to the negative signs of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$: the added water can displace the equilibrium between the globules and the disordered phase towards the former. Therefore the assertion that globules are more ordered than pure water is not justified.

We must emphasise that the conclusion that ordered regions (globules) exist in aqueous solution is a fact. It follows logically from two factors: (1) the negative sign of $\bar{S}^{M}_{water}$ and $\bar{H}^{M}_{water}$ and (2) the assertion that water–non-electrolyte association complexes are less stable than the water–water complexes. The first is an experimental fact in the systems investigated; the validity of the second follows from the endothermic heat of solution of water in pure electrolytes (n-propyl alcohol, t-butyl alcohol, acetone, and dioxan) and has also been demonstrated spectroscopically for the case where the non-electrolyte is acetone or dioxan[42,43]. According to this reasoning, we are not justified in assuming that the globules are present in the water–pyridine system, where the second factor does not apply[42,43], and in alcohol–non-electrolyte systems, where the first factor does not hold.

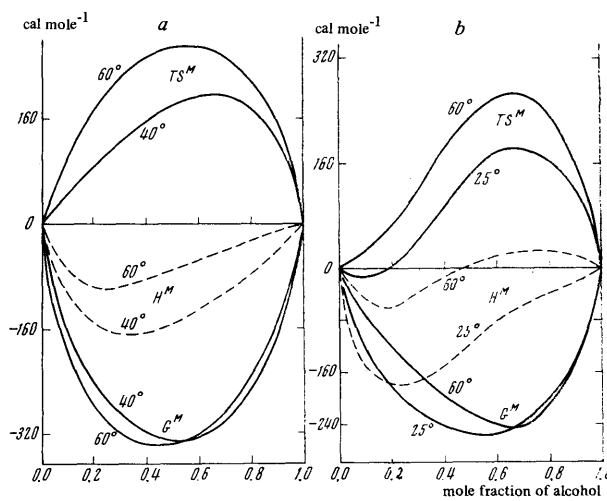


Figure 8. Thermodynamic functions of mixing for t-butyl alcohol systems[32].

We shall now examine the nature of the ordered globules in aqueous solutions. Here we cannot afford to remain at the factual level and must proceed to hypothetical considerations. The following situation is extremely probable. We have seen that a small amount of non-electrolyte leads to definite changes in the water structure, which entails a gain in stabilisation energy as a result of the collective interactions of water molecules. When the electrolyte begins to disrupt water–water hydrogen bonds after filling the cavities, a continuous disintegration of their three-dimensional lattice proves to be more difficult than the fragmentation of the water structure into fairly large structured regions in which collective stabilisation is still possible. In other words, at moderate concentrations the electrolyte can be more readily accommodated in the

interstices between the globules. Then a kind of separation into different phases takes place in the solution: into the "phase" of structured water which contains also a small amount of non-electrolyte (for example in the cavities within the structure) and a disordered "phase" consisting of non-electrolyte molecules and individual water molecules associated with them. We shall refer to such separation into microphases as microlayer formation.

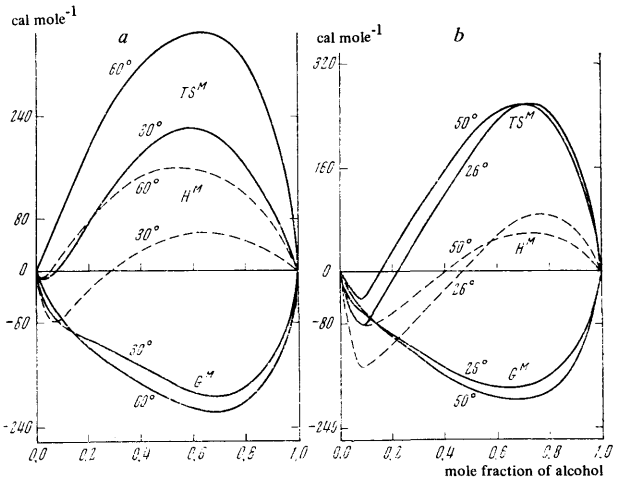


Figure 9. Thermodynamic functions of mixing for various systems:
a) n-propyl alcohol–water [10]; *b*) t-butyl alcohol–water [32].

It is important to emphasise yet again that the reason for the formation of globules is the energy gain due to the collective interactions of water molecules and made possible by the particular structure of the globules¶. The presence of stabilisation energy implies that the globules are thermodynamically stable species and cannot be regarded as fluctuations. Therefore the microlayer formation described here is a very special case of the tendency of solutions to form separate phases, which is usually understood as resulting from the development of concentrations fluctuations.

We shall now attempt to explain the significance of the second characteristic of the behaviour of the thermodynamic functions of mixing of aqueous systems in the region of microlayer formation. The constancy of the partial enthalpies can be most simply accounted for if it is assumed that the non-electrolyte (or water) added to the system always enters an identical molecular environment, which happens, for example, in true phase separation. In the case of microlayer formation, this condition will be fulfilled if the composition of the microphases (globules and disordered regions of the solution) remains constant in the concentration range considered. The composition of the microphases should then correspond to the boundary points of the linear section in the H^M plot. For example, in the water–dioxan system the microphases have the composition (in mole fractions) 0.25 dioxan + 0.75 water and 0.6 dioxan + 0.4 water.

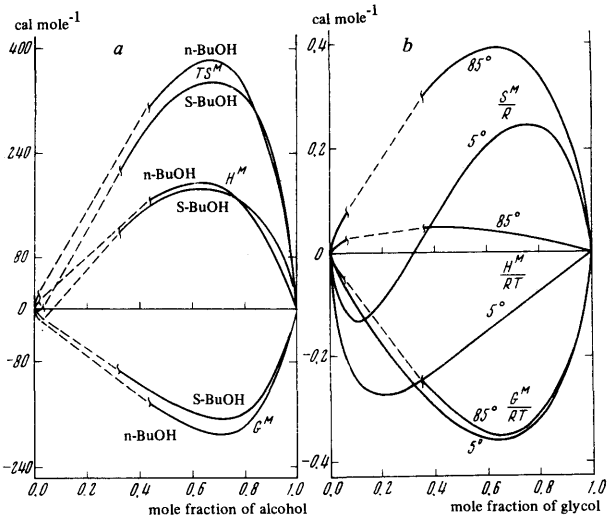


Figure 10. Thermodynamic functions of mixing for various systems:
a) n-butyl alcohol–water and s-butyl alcohol–water at 60°C [10] (dashed line—layer formation region); *b*) water–butane glycol [33].

However, the constancy of the composition of the microphases in microlayer formation is not yet sufficient to ensure the linearity of the variation of H^M. In addition, one must assume that, when the concentration of the solution changes, the dimensions of the globules remain constant and only their number changes. Indeed the enthalpy of the system considered consists of three terms: (1) the enthalpy of the molecules in the disordered phase; (2) the enthalpy of the molecules in the globules; (3) the enthalpy of the interaction of these two "phases". If it is assumed that the dimensions of the globules change, the last two terms will not vary linearly with concentration and special hypotheses are necessary to ensure the linearity of their sum. At the same time the constancy of the dimensions of the globules automatically entails the linearity of the $H^M - x$ relation. Such constancy does not appear strange if account is taken of the above hypothesis that the microphases have constant composition. It therefore follows that, when the concentration of the solution is altered, the molecular environment of the globule remains unchanged. Only the distances between the globules alter, and this should not affect their dimensions.

It is also possible to account for the constancy of the composition of the microphases. The constancy of the composition of the globule is associated with the limited number of the cavities in it. On the other hand, the constancy of the composition of the second "phase" is ensured by the fact that, when the concentration of water in it exceeds a certain critical value, a new globule separates.

¶ We shall not specify the mechanism of the collective interaction. Frank [48,49], who was the first to introduce the hypothesis of the globules (in pure water), believed that this involved the mutual polarisation of water molecules, leading to a strengthening of the hydrogen bonds.

This becomes understandable if we recall that the dimensions of the globules remain constant in the region of microlayer formation, i.e. the globule decomposition processes and hence the globule formation processes are cooperative.

The suggested hypothetical mechanism explains in a natural manner why microlayer formation is revealed more clearly by H^M than by G^M: the curvature in the plot of G^M arises from the entropy of mixing, which contains a non-linear contribution from the exchange of the microphases. This factor makes it possible to estimate roughly the number of molecules in the globule. It it is assumed that the dimensions of both microphases are equal, the maximum energy of their exchange is S_{id}/ν, where S_{id} is the maximum entropy of mixing of the ideal solution and ν is the number of molecules in the globule. This quantity must be set equal to the maximum deviation of the S^M-x relation (or, what amounts to the same thing, the $G^M/T-x$ relation) from linearity in the region of microlayer formation. For the three systems water–dioxan, water–acetone, and water–t-butyl alcohol, ν is approximately 40–80 molecules.

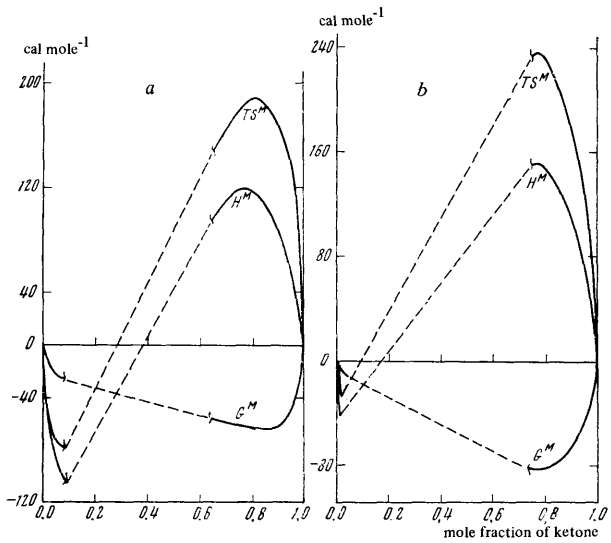


Figure 11. Thermodynamic functions of mixing for various systems:
a) water–ethyl methyl ketone at 20°C[34]; *b*) water–cyclohexanone at 20°C[34] (dashed line–layer formation region).

The experimental finding that the excess volume of the solution V^E is not a linear function of concentration in the region of microlayer formation[47] (in contrast to true phase separation) is also consistent with our microlayer formation model. The point is that the free volume in the packing of particles of different kinds makes a significant contribution to V^E. It is reasonable to suppose that the free volume in the packing of two different microphases in aqueous solution differs from the free volume in the packing of water and non-electrolyte molecules. This in fact leads to the non-linearity of the V^E-x relation.

Thus, at moderate concentrations aqueous solutions also show unusual properties, which must be attributed to the presence in the solution of regions with a high degree of order (globules). Globules probably arise from the mutual stabilisation of water molecules and probably possess (over a concentration range) cooperative properties.

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