Self-Diffusion in Multicomponent Liquid Systems

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1 Introduction

Self-diffusion coefficients are the simplest transport coefficients. They describe transport processes occurring in chemically uniform systems. In multicomponent solutions their values are also easily accessible in experiments. It is very important that the self-diffusion coefficient of any component can be determined independently, without any assumptions concerning other components.

For many years, in theoretical approaches and in treatments of experimental data, the self-diffusion processes occurring in liquids were considered to be like those in gases, *viz.* the result of translational, independent motions of single molecules. However, liquids are not structureless media and the motion of a molecule is affected by its nearest neighbours. The self-diffusion coefficient must therefore be considered as a 'collective quantity'.[1] In such a case, self-diffusion studies may provide information about intermolecular interactions and the local structure of the system.

2 Some Remarks about Experimental Methods

Although quasi-elastic neutron scattering offers a direct insight into the translational motions of small molecules, its application to the investigation of self-diffusion processes is very rare.[2] The most popular techniques used in self-diffusion studies are the radioactive tracer and NMR spin-echo methods. The advantages and disadvantages of these techniques are widely known.[3] In recent years the spin-echo techniques have become more popular, although their accuracy, even in very careful experiments, does not exceed ± 1%. Measurements of the self-diffusion coefficient by means of spin-echo methods are fast, compared with those using radioactive tracers, and these techniques are very suitable for studying the dependence of self-diffusion coefficients on various intensive parameters such as temperature, pressure, and concentration. The absolute value of the self-diffusion coefficient may be also obtained after the calibration of the NMR spectrometer by means of standard liquids.[3]

Techniques involving radioactive tracers are the classic methods. Among them the techniques of open-end capillary and of diaphragm-cell are widely used. The diaphragm method is precise, with an accuracy of about ±0.1%, and it is faster than the open-end capillary technique. In some cases the diaphragm itself can be a source of serious errors. Our experiments have shown that if the chemical concentration of the component under study is very low the diaphragm, even when made from glass, is able to adsorb the tracer. The diaphragm method should therefore not be used if the concentrations of the chemical components are of different orders of magnitude.

The disadvantages of the open-end capillary method are well-known: the technique is time consuming and requires rather a large volume of non-radioactive solutions. The most important advantage is the lack of any artificial boundary separating the radioactive and non-radioactive solutions. The inaccuracy of the method results mainly from (i) the small volume of the radioactive solution, and from (ii) so-called end-effects. The error due to the small volume can be significantly reduced by using a tracer of high specific radioactivity. It is worth noting that the precision of the radioactivity measurements is extremely high. Errors due to end-effects can be significantly reduced or even completely avoided by the determination of the tracer radioactivities before and after the self-diffusion processes under exactly the same experimental conditions.[4] The accuracy, usually about 0.1%, can be improved if the capillary length, usually measured by means of a projection microscope, is obtained by calibration with standard liquids.

The chemical properties of the tracer and unlabelled substance are assumed to be the same, but the masses of the labelled and unlabelled substances are not equal. Thus the self-diffusion coefficient of the unlabelled, 'light', component D_L is not exactly the same as the diffusion coefficient measured for the 'heavy' tracer D_H, but it can be obtained from equation 1,

$$\frac{D_L}{D_H} = \sqrt{\frac{M_H}{M_L}} \qquad (1)$$

where M_H and M_L are masses of the tracer and the unlabelled compound respectively. For organic compounds labelled with either ^{14}C or ^{3}H the inaccuracy due to the isotope effect should not exceed 1%. In systems with strong intermolecular interactions when the self-diffusion coefficient is a collective quantity one may expect the isotope effect to be smaller than that calculated from equation 1. Water is a case in point. For water labelled with ^{2}H, ^{3}H, or ^{18}O isotope effects of around 5% were expected, but the isotope effects determined experimentally were smaller.[5]

Some complications appear when tracer techniques are used to determine the self-diffusion coefficients in solutions containing water and a compound with labile hydrogen, such as alcohols, urea, amines. Water labelled with ^{3}H exchanges the isotope with the second component, thus the tritium diffusion coefficient D_T is due to simultaneous self-diffusion processes of both components. In such a case the value of the water self-diffusion coefficient D_W can be evaluated, but the following conditions must be fulfilled: (i) the tritium exchange reaction has to be much faster than all self-diffusion processes, and (ii) the self-diffusion coefficients of both components should be of similar order of magnitude. Under such experimental conditions the distribution of the tracer between both components remains constant and a change of the tracer radioactivity is due to the self-diffusion processes of both components. To calculate the D_W-value the self-diffusion coefficient of the second component D_2 must be obtained in an independent experiment, for example

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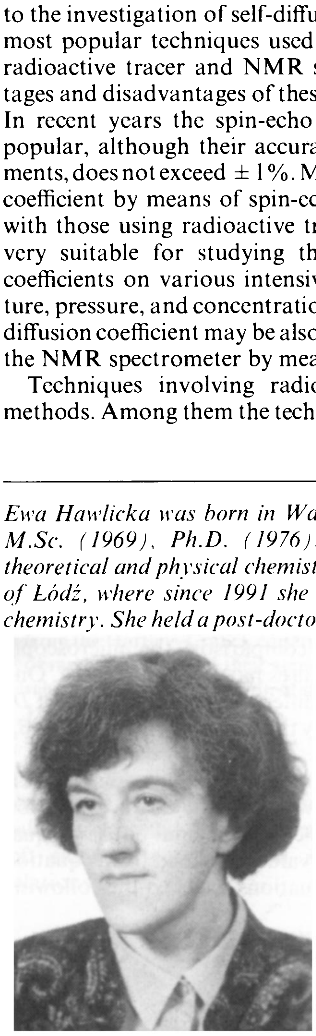

using that component labelled with ^{14}C or with ^{3}H in the non-labile position. The relationship between the values of D_T, D_2, and D_W must be derived for the technique used in the experiment.

The diaphragm techniques are based on Fick's first law and it is easy to show[6] that the experimentally determined tritium diffusion coefficient D_T is the weighted sum of the self-diffusion coefficient of water D_W and of the second component D_2:

$$D_T = x_W D_W + \alpha_T(1 - x_W)D_T \qquad (2)$$

where x_W is the mole fraction of water and α_T denotes the tritium fractionation factor.

Calculation of the water self-diffusion coefficient is not performed *via* equation 2 if the open-end capillary method is used. In that case, solution of Fick's second law and the self-diffusion coefficient of the tracer can be obtained from the following series:

$$\frac{A(t)}{A(0)} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} (2n + 1)^{-2} \exp[-(2n + 1)^2 \beta D t] \qquad (3)$$

with $\beta = \frac{\pi^2}{4l^2}$.

$A(t)$ and $A(0)$ denote the total radioactivities of the solution in a capillary of length l after diffusion time t, and at the beginning of the experiment, respectively. In such a case the relationship between the values of the experimentally determined tritium diffusion coefficient D_T, the self-diffusion coefficients of water D_W, and of the second component D_2, respectively, valid for the time of experiment long enough to neglect higher terms of the series (equation 3), has been derived[7] in the simplest form (equation 4):

$$[(1 - \alpha_T)x_w + \alpha_T] \exp(-\beta t D_T) = x_w \exp(-\beta t D_w) + \alpha_T(1 - x_w) \exp(-\beta t D_2) \qquad (4)$$

Thus water labelled with tritium can be used to determine the water self-diffusion coefficient in the presence of substances containing labile hydrogen. One has to remember, that if the content of water decreases the inaccuracy of the determination of the self-diffusion coefficients decreases too. In water-deficit mixtures tritium can be used to measure D_W values, but only to investigate the influence of various parameters on the self-diffusion processes. In order to measure the water self-diffusion coefficient itself, water labelled with ^{18}O is required.

3 Theoretical Approaches of Self-Diffusion Processes

Several theories have been proposed to describe self-diffusion processes in liquids on the molecular level, but in recent years attention has been focused mainly on time correlation function methods and hydrodynamic approximations. The commonly used approaches based on time correlation methods have been developed by Hertz and co-workers,[8] who introduced the velocity cross-correlation f_{cc}, and by Friedmann and co-workers,[9] who proposed a distinct diffusion D^d coefficient. There is a simple relationship between these quantities, but distinct diffusion coefficients seem to be more informative. The definition of the distinct diffusion coefficient is given in equation 5,

$$D^d = \frac{N}{3} \int_0^{\infty} dt \langle v^{\alpha}(t) v^{\beta}(0) \rangle \qquad (5)$$

and it is very similar to that of the self-diffusion coefficient D^S (equation 6.)

$$D^S = \frac{1}{3} \int_0^{\infty} dt \langle v^{\alpha}(t) v^{\alpha}(0) \rangle \qquad (6)$$

The difference between the distinct diffusion and the self-diffusion coefficients is that the former coefficient results from correlated motions of the distinct molecules α and β, either of the same or of different components, whereas the latter is due to the independent motions of single molecules. Thus the D^d values are a measure of intermolecular interactions. The D^d coefficients are expected to be positive if attractive interactions exceed the repulsive ones, whereas for strong repulsion between molecules negative values of D^d are expected.

Molecular interactions in binary mixtures of non-electrolytes can be described *via* three distinct diffusion coefficients, which can be evaluated from the experimentally determined coefficients of mutual diffusion D^M and self-diffusion D^S. The D^d coefficients, like D^M coefficients, depend on the choice of the reference frame. For binary mixtures the number fixed reference frame is very convenient, and using that distinct diffusion coefficients can be evaluated as follows (equations 7):[10]

$$D_{ij}^d = D_{ji}^d = -\frac{D^M}{\beta_a} \qquad (7a)$$

$$D_{ii}^d = \frac{x_j D^M}{x_i \beta_a} - \frac{D_i^S}{x_i} \qquad (7b)$$

with the thermodynamic factor $\beta_a = 1 + \frac{\partial \ln f_i}{\partial \ln x_i}$ where x_i and f_i denote the component mole fraction and its thermodynamic activity coefficient, respectively.

Equations 7 show that over the whole range of the mixture composition, D^d coefficients for unlike molecules, i ≠ j, must be negative, whereas for molecules of the same component, i = j, they become negative in net component, $\lim_{x_i \to 1} D_{ii}^d = = D_i^S$. As mentioned above, negative values of the distinct diffusion coefficients are expected to be a feature of intermolecular repulsion. Therefore the values of D^d, calculated from equations, cannot serve as a probe of the molecular interactions, but they must be compared with the standard values. In such a case the interpretation of the experimental data depends on the choice of the standard distinct diffusion coefficients $(D^d)^o$.

For ideal solutions the experimental data for D^M and D^S are expected to fulfil the Hartley–Cranck equation (equation 8):

$$D_{ideal}^M = x_1 D_2 + x_2 D_1 \qquad (8)$$

thus standard distinct diffusion coefficients have been obtained[10] from equations 7 by incorporating the Hartley–Cranck relationship (equation 8):

$$(D)_{ij}^o = -D_{ideal}^M \qquad (9a)$$

$$(D^d)_{ii}^o = -x_j(D_i^S - D_j^S) - D_i^S \qquad (9b)$$

If attractive interactions between molecules either of the same or of different components dominate over repulsive ones, the values of D^d should be less negative than the standard $(D^d)^o$ coefficients. Based on such a comparison the microscopic properties of several binary mixtures have been discussed. One should, however, notice that the difference between values of D^d and of $(D^d)^o$ may be dominated by the thermodynamic factor β_a, as shown below.

Self-association of the component molecules, *i.e.* i = j, is expected to cause a positive deviation of the distinct diffusion coefficient D^d, calculated from the experimental data *via* equation 7b, from the standard $(D^d)^o$ value, obtained from equation 9b. The comparison of these equations leads to the following inequality:

$$D_{ii}^d - (D^d)_{ii}^o = \frac{D^M}{\beta_a} - D_{ideal}^M > 0 \qquad (10a)$$

If attractive interactions between unlike molecules exceed the

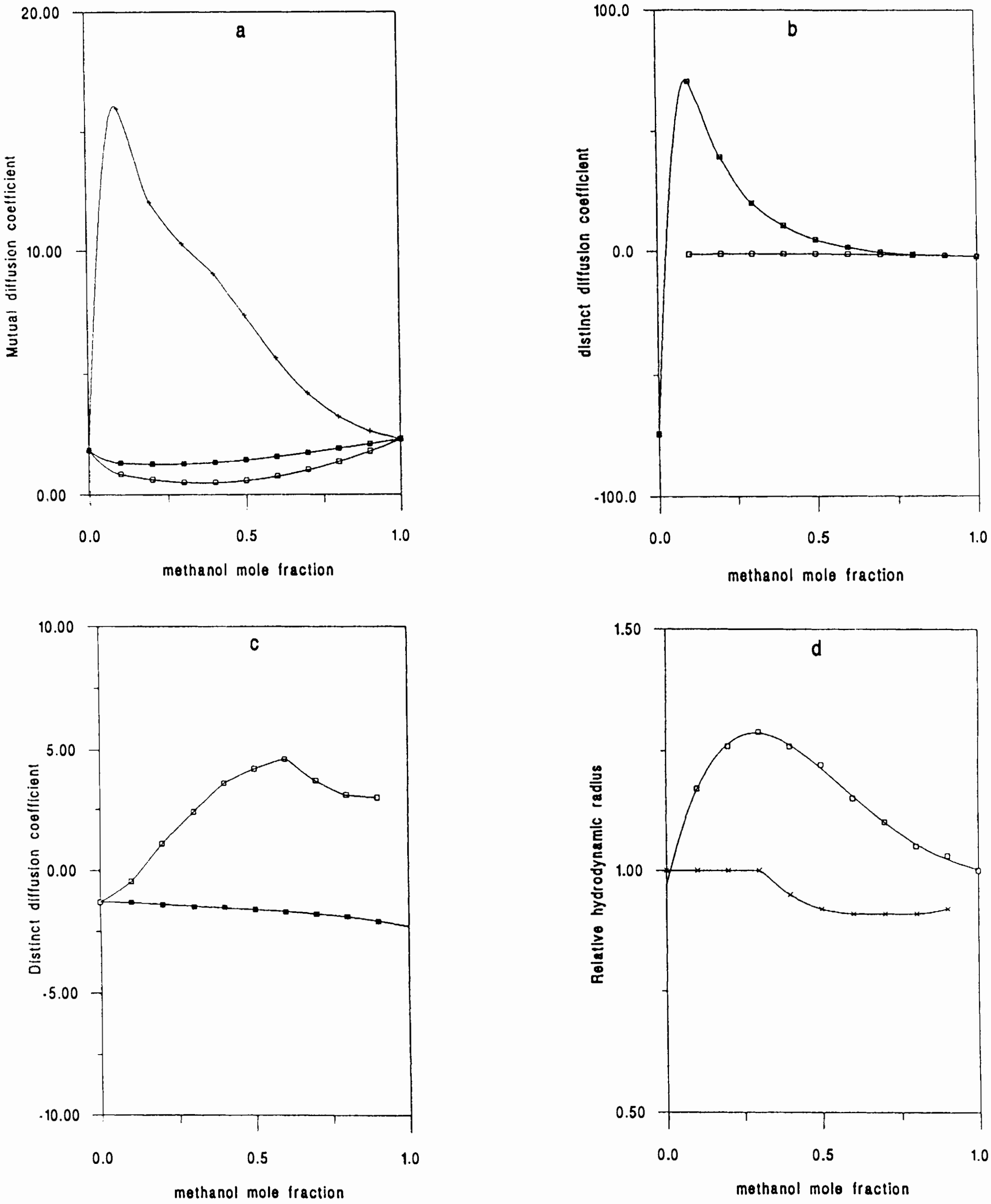

Figure 1 Diffusional behaviour in methanol – carbon tetrachloride mixtures: (a) mutual diffusion coefficient D^M experimental values (□), calculated from the Hartley–Cranck equation (■), experimental data corrected with the thermodynamic activity coefficient β; (b) distinct diffusion coefficients of methanol (■) and their standard values (□); (c) distinct diffusion coefficients of carbon tetrachloride (□) and their standard values (■); (d) relative hydrodynamic radii of methanol (□) and of carbon tertachloride (×). Data for mutual and self-diffusion coefficients taken from reference 11.

repulsive ones a positive difference between the distinct diffusion coefficients obtained from equation 7a and their standard $(D^d)^o$ values is expected. In such a case the positive difference between left sides of equations 7a and 9a leads to the following relationship:

$$D^d_{ij} - (D^d)^o_{ij} = \frac{D^M}{\beta_a} - D^M_{ideal} > 0 \tag{10b}$$

The above relationships show that deviations of the D^d coefficients from their standard values depend heavily on the thermodynamic factor β_a. The data for β_a are rather scarce and sometimes inaccurate, because they are computed from the excess Gibbs free energies *via* the first and second derivatives. For several non-ideal mixtures the β_a factor becomes close to zero. These very small β_a values can lead to overestimation of the differences between D^d and $(D^d)^o$ values. As an example the results obtained for methanol–carbon tetrachloride[11] are shown in Figure 1.

As can be seen, the experimentally determined mutual diffusion coefficients D^M are smaller than those $(D^M)_{ideal}$ calculated from the Hartley–Cranck equation 8. Such behaviour is observed over the whole range of the mixture composition, but the difference between them does not exceed 40%. In a methanol-deficit mixture the thermodynamic factor β_a is close to zero, thus correcting the experimental data for the mutual diffusion coefficient changes the character of the function D^M *vs.* methanol mole fraction and its shape results mostly from the concentration dependence of β_a. For both components the distinct diffusion coefficients and their standard values calculated from equations 7 and 9, respectively, are shown in Figures 1b and 1c. It can be seen that the D^d values for molecules of the same component, of CH_3OH and CCl_4, respectively, exhibit positive deviations from the standard $(D^d)^\circ$ coefficients. This was taken to indicate self-association of both components.[11] For methanol the D^d values became positive, suggesting strong attractions between molecules. It should be noted, however, that the construction of equations 7 results in the thermodynamic factor β_a having a stronger effect on the D^d value of the component of lower concentration.

A disadvantage of the analysis of experimental data *via* distinct diffusion coefficients is that it involves the use of mutual diffusion coefficient data. The problem arises for mutual diffusion in multicomponent systems because a relationship, such as the Hartley–Cranck equation describing the ideal behaviour in binary systems, has not been formulated. One should also note that in evaluating the D^d values from the experimental data *via* equations 7, one has to assume (although it has not been expressed explicitly) that correlation of the motions between 'distinct' molecules must be taken into account as far as mutual diffusion is concerned, but that this phenomenon is neglected in self-diffusion processes. Strong attractions occurring between molecules of the same or of different components resulting in molecular association and in ordering of the structure must affect molecular motions, even if the system is under equilibrium and there is no gradient of chemical concentration. Because of their method of calculation, distinct diffusion coefficients cannot be used to gain insight into molecular interactions in a multicomponent system under thermodynamic equilibrium. Hydrodynamic approaches, however, do offer this opportunity. The most popular hydrodynamic approximation is known as the Stokes–Einstein equation, which interrelates the component self-diffusion coefficient D_i with the viscosity of the solution η and the hydrodynamic radius r_i of the component under study (equation 11):

$$D_i = \frac{k_B T}{\alpha \pi \eta r_i} \tag{11}$$

where k_B and T denote the Boltzmann's constant and temperature, respectively, and α is a parameter resulting from boundary conditions between 'a medium' and 'the diffusing particle'. This parameter ranges from 4 for perfect slipping conditions to 6 for perfect sticking ones.

The applicability of the Stokes–Einstein relationship to self-diffusion in binary mixtures of small molecules was controversial for several years, because the relationship was derived to describe the motions of a large particle in a structureless medium. It has been shown recently[1,12–14] that the relationship can be used to describe the self-diffusion of components of similar sizes, but that the perfect sticking conditions, originally used, should be replaced by perfect slipping ones.

The use of the relation has also been questioned because for several one-component systems the molecular radius evaluated from the molar volume does not fit the self-diffusion data. In recent years it has become obvious that such an agreement should not be expected. First of all the molecular diameter estimated from the density number is not the best approach to the real size of the molecule because a free volume of the liquid is neglected. The difference between the hydrodynamic radius and the value calculated from the density number has been particularly noticeable for hydrogen-bonded systems, such as water or alcohols. The packing density of these liquids is much smaller than for other ones, and confirms that neglecting the free volume causes remarkable inaccuracy.

The hydrodynamic radius obtained from the Stokes–Einstein relationship cannot be considered as the radius of a 'hard sphere'. It reflects the size of the 'diffusion unit', *i.e.* the radius of the molecule under study and its environment, determined by the force-field of the molecule under study.[1] For many years such an interpretation has been applied, without any hesitation, for the self-diffusion of ions. The hydrodynamic radii of ions have been used to calculate ionic solvation numbers. If the hydrodynamic radius is treated as the size of the diffusion unit, it becomes a very informative quantity and it can be used to gain insight into the nearest neighbourhood of the molecule under study. When the 'real' size of a molecule is known, its solvation number can be calculated. The following may serve as good approximations to molecular size: the van der Waals radius, the radius calculated from molar refraction, or the molecular diameter evaluated from intramolecular bonds and valence angles. The meaning of the diffusion unit is, however, not obvious. That unit may be thought of as the molecular aggregate of several molecules, of the same or of different components, diffusing together at the same time and in the same direction, with the same velocity. Such an interpretation does not seem to be very realistic, because the activation energies of self-diffusion for liquids with well-defined structures (as for example water, alcohols, and acids) and for structureless liquids (such as alkanes) are very close to each other. Thus the diffusion unit is best thought of as a quantity indicating a correlation of molecular motions resulting from the liquid structure. It means that the molecule under study and several molecules in its nearest environment must move at the same time, but they can move with different velocities and in different directions.

The hydrodynamic radius is expected to provide information similar to that obtained from distinct diffusion coefficients. To confirm that supposition the hydrodynamic radii of methanol and of carbon tetrachloride have been calculated from the same experimental data of the self-diffusion coefficients as used to evaluate the distinct diffusion coefficients presented in Figures 1b and 1c. To avoid complications connected with the α parameter in equation 11, resulting from the solute–solvent boundary conditions, the relative hydrodynamic radii of both components have been computed, *i.e.* the ratio of the products of the component self-diffusion coefficient and the viscosity in net component and in the binary mixture. Thus the only assumption was that in net components and in the mixture, over the whole range of the composition, the solute–solvent boundary conditions remained unchanged. As seen from Figure 1d the hydrodynamic radius of methanol increases with decreasing methanol concentration. In pure methanol the diffusion unit comprises two molecules, in agreement with its structure consisting of zig-zag chains. The observed increase of the hydrodynamic radius indicates that in methanol-deficit mixtures its self-association plays an important role. On the other hand, small amounts of methanol do not affect the hydrodynamic radius of CCl_4, but in methanol-rich mixtures that hydrodynamic radius decreases noticeably. That decrease may be interpreted as a feature of repulsive interactions between unlike molecules which cause a contraction of the nearest neighbourhood of carbon tetrachloride molecules.

Variations of the hydrodynamic radii with the mixture composition provide information about the local structure of the system, like those resulting from the distinct diffusion coefficients. The most important advantage of the hydrodynamic approach, presented above, is that experimental data of a similar order of magnitude and determined with similar accuracy are compared. It is also very important that one can calculate the hydrodynamic radius of every component in multicomponent systems, without any additional assumptions, having the viscosity and the component self-diffusion coefficients.

4 Self-diffusion in Water–Organic Solvent Mixtures

Much attention has been paid to mixtures of water with organic solvents. The problems of primary interest are changes of water structure caused by the addition of organic components, homogeneity on the molecular level, and solvation of electrolytes. As mentioned above, investigations of the self-diffusion of all components may provide information about local structure and therefore a considerable interest has been shown recently in self-diffusion in binary mixtures, mostly water–alcohol systems.

4.1 Self-diffusion of Water in Water–Organic Solvent Mixtures

Pure water has a well-defined three-dimensional structure built from water pentamer, therefore a correlation of molecular motions is very likely. Indeed the water self-diffusion coefficient is 'too small,' compared with other substances of similar molecular masses. The hydrodynamic radius is noticeably bigger compared with the intramolecular OH distance and it exceeds the radius calculated from molar refraction or even half of the OO distance of the nearest neighbours. A comparison of the hydrodynamic radius with that calculated from molar refraction suggests that the motions of three water molecules are correlated.[15] A similar result has been obtained from the isotope effect[5,6] of water self-diffusion. Thus one may predict that to move a water molecule, three hydrogen bonds must be broken.

Self-diffusion in alcohols is also due to correlated molecular motions, but the comparison of hydrodynamic radii with sizes of molecules evaluated from molar refraction leads to the conclusion that the motions of only two alcohol molecules are correlated.[15] Thus an alcohol molecule can move when two hydrogen bonds are broken. Such a conclusion is in good agreement with the structure of alcohols being built from zig-zag chains.

Mixtures of alcohol with water have a complex structure, resulting from both hydrophilic as well as hydrophobic properties of the alcohol molecules. Although methanol, ethanol, propanols, and *t*-butanol can mix with water at any proportions the question arises whether both components form a common structure of hydrogen bonds.

Self-diffusion coefficients of water in mixtures with methanol (MeOH),[16] *n*-propanol (NPA),[15] and *t*-butanol (TBA)[17,18] were used to calculate hydrodynamic radii. Variations of the relative hydrodynamic radii with the alcohol mole fraction x_{alc} are shown in Figure 2.

As can be seen, the influence of all alcohols on the water structure are similar. Small admixtures of alcohols cause a distortion of the water structure and that effect increases with increase in size of the non-polar group. In solutions of *n*-propanol and of *t*-butanol the smallest water radius is found at about 17 mol% of alcohols. Both these alcohols are believed to form clusters and for that alcohol content (17 mol%) the highest concentration of clusters has been postulated.[19] The reduction of the water radius is significant and the water diffusion units consist, on average, of less than two molecules. This means that in order to move the water molecule, it is enough if two hydrogen bonds are broken.

The observed distortion of the water network is intensified when an electrolyte is added.[15–17,20] In solutions of NaI the water radius is smaller than that in binary mixtures, although the character of the dependence remains unchanged. As shown in Figure 2, an increase in alcohol concentration above 20 mol % causes an increase of the water radius. In water-deficit mixtures it becomes significantly greater than for pure water. Although this effect could be explained as a feature of the self-association of water, such a supposition does not seem to be very likely, for the following reasons.

In all systems studied, when the alcohol concentration reaches about 67 mol%, the self-diffusion coefficients of water and of the alcohol become equal, which suggests the existence of diffusion units consisting of one water and two alcohol molecules. The same result is obtained from the comparison of the hydrodynamic radius with the molecular diameters of water and of alcohol. It means that two alcohol molecules must move simultaneously with one water molecule. The increase in alcohol concentration causes a further increase of the water radius, and in water-deficit solutions, if the alcohol concentration exceeds 90 mol%, motions of one water and of four alcohol molecules are correlated. This suggests that water molecules are incorporated into the alcohol structure and that they must have, at least, four nearest neighbours – in agreement with results from MD simulations[21] indicating that water molecules are able to link two alcohol chains.

The addition of electrolytes affects the structure of the water-deficit mixture significantly. The equality of the self-diffusion coefficients of water and of alcohol disappears, but the water self-diffusion coefficients become equal to those of the cations.[16,20] Such behaviour suggests that strong hydration of cations destroys the common alcohol–water structure. These conclusions are supported by the data for water self-diffusion in mixtures of acetonitrile.

An acetonitrile–water mixture differs noticeably from mixtures of alcohol–water. It belongs to a small group of aqueous solutions having positive values of excess molar Gibbs energy and exhibits a phase separation with an upper critical temperature at approximately 272 K and critical composition of about 38 mol% MeCN. It is thus very likely that even at room temperature the system is inhomogeneous at the molecular level.

Variations of the water hydrodynamic radius (calculated from the self-diffusion data published in references 22 and 23) with the mixture composition are shown in Figure 2b. In an acetonitrile mixture above 10 mol% An, the water hydrodynamic radius is noticeably greater than that in pure water.[23] This indicates the formation of a water microphase. Its structure is probably more ordered as compared with that of pure water. It has also been found that the addition of electrolyte does not affect the water hydrodynamic radius, but it does the hydrodynamic radius of acetonitrile. Investigations of ionic self-diffusion have confirmed this conclusion,[24] indicating that in water–acetonitrile mixtures ions are preferentially solvated by acetonitrile.

4.2 Self-diffusion of Organic Solvents in Mixtures with Water

Variations of the hydrodynamic radius of alcohols *versus* the mixture composition are summarized in Figure 3. The influence of water on the structure of methanol is unlike that on *n*-propanol and *t*-butanol. Small amounts of water do not affect the structure of *n*-propanol and of *t*-butanol and their hydrodynamic radii remain unchanged, whereas even small admixtures of water to methanol reduce its hydrodynamic radius noticeably. It appears that the addition of water disrupts the structure of methanol, but not that of higher alcohols. As the water concentration increases the difference between mixtures of methanol and of higher alcohols becomes striking.

In a methanol-deficit mixture, if the water content exceeds 70 mol%, the hydrodynamic radius of methanol becomes constant and equal to the value calculated from the molar refraction. It means that methanol self-diffusion results mostly from the motions of single molecules and either the molecules of methanol do not fit the water structure or they occupy external position in the water network.

The behaviour of molecules of *n*-propanol and of *t*-butanol in water-rich mixtures is different. When the water concentration exceeds 80 mol% the hydrodynamic radii of *n*-propanol and of *t*-butanol increase with the dilution and they are noticeably greater than for pure alcohols (Figure 3b). Below a certain concentration of alcohol the hydrodynamic radii of *n*-propanol and of *t*-butanol are independent of concentration and the same as those calculated for infinite dilution.[17] The comparison of these values with the molecular diameters of alcohols and of water leads to the conclusion that a clathrate-like structure is formed around the alcohol molecules. The following clathrate-like aggregates have been proposed: $TBA(H_2O)_{30}$[17] and $NPA(H_2O)_{21}$.[15] The clathrate-like aggregates vanish above the *critical clathrate concentration* (x^{cc}),[17] which is observed as the decrease of the hydrodynamic radii of NPA and of TBA. Above the x^{cc}, variations of the hydrodynamic radii of NPA and of

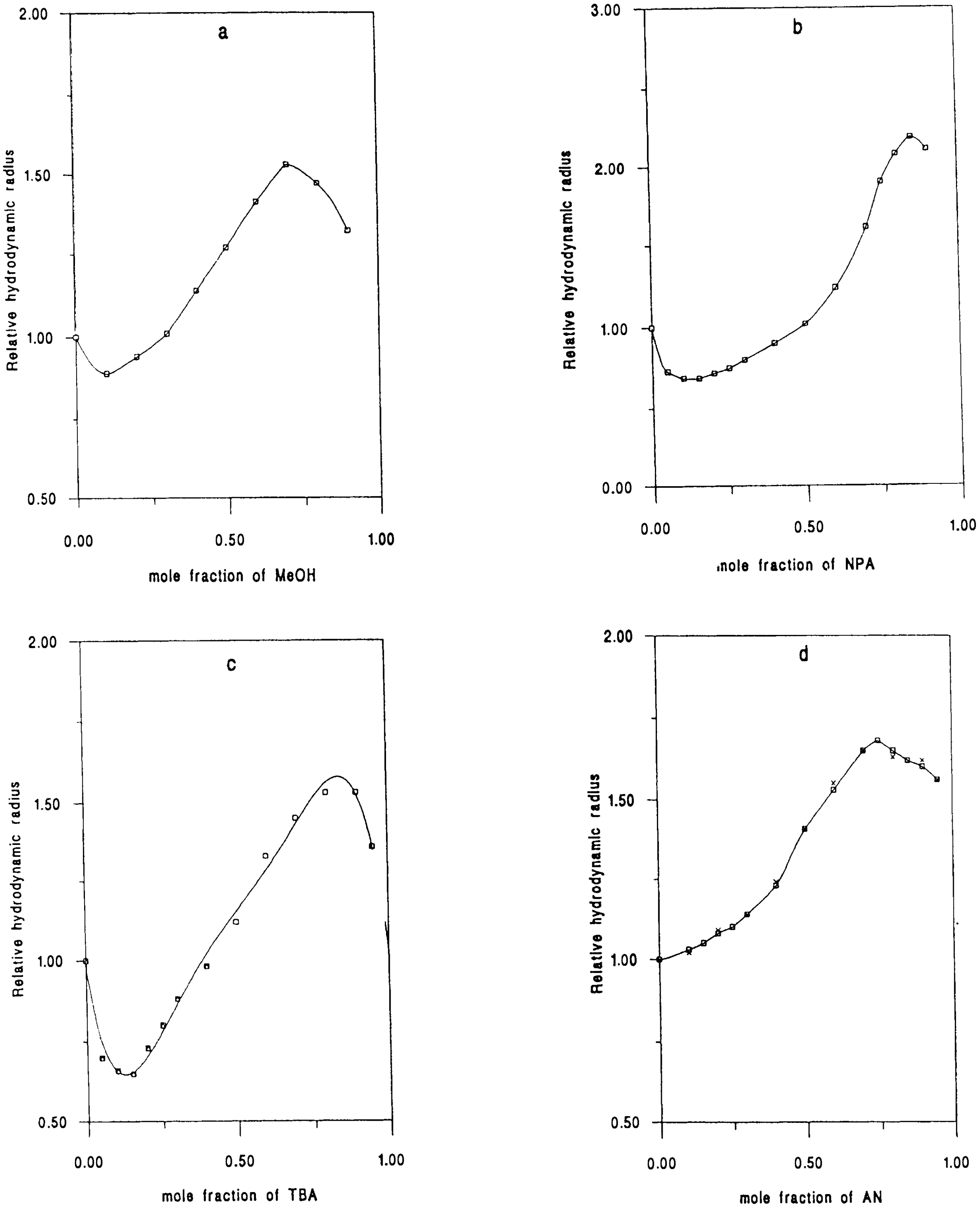

Figure 2 Variations of the relative hydrodynamic radii of water with the mole fraction of the organic component in mixtures with: methanol (*a*), n-propanol (b), *t*-butanol (c), and acetonitrile (d).

TBA are not very likely. In solutions of NPA the hydrodynamic radius decreases smoothly with decreasing water concentration, whereas in TBA solutions the function shows a gap.

Within that range of alcohol concentration the formation of micelle-like alcohol aggregates is expected. Because the hydrodynamic radii of both alcohols decrease noticeably one can suppose that either the micelle-like aggregates are not formed or that their life-time is shorter then 1 ps. The former supposition is likely true for solutions of TBA. In NPA solutions, however, short-lived, micelle-like aggregates are probably formed. The effects of electrolytes and of urea on these mixtures confirm the above supposition.[17] It has been found that the addition of urea shifts the *critical clathrate concentration* to higher values, whereas in electrolyte solutions the values of x^{cc} are smaller. The micelle-like aggregates of NPA are stabilized if urea is added.

Behaviour observed in aqueous solutions of NPA and of TBA is treated as a demonstration of the hydrophobic properties of the alkyl groups. Though molecules of acetonitrile also exhibit hydrophobic properties, the influence of water on the acetonitrile structure is unlike that on the structure of higher alcohols. As seen from Figure 3c, the hydrodynamic radius of acetonitrile decreases monotonously with increasing water content. The comparison of the hydrodynamic radius calculated from pure acetonitrile with that evaluated from the molar fraction suggests a correlation of motions of two acetonitrile molecules, consistent with an anti-parallel ordering of the acetonitrile dipoles.

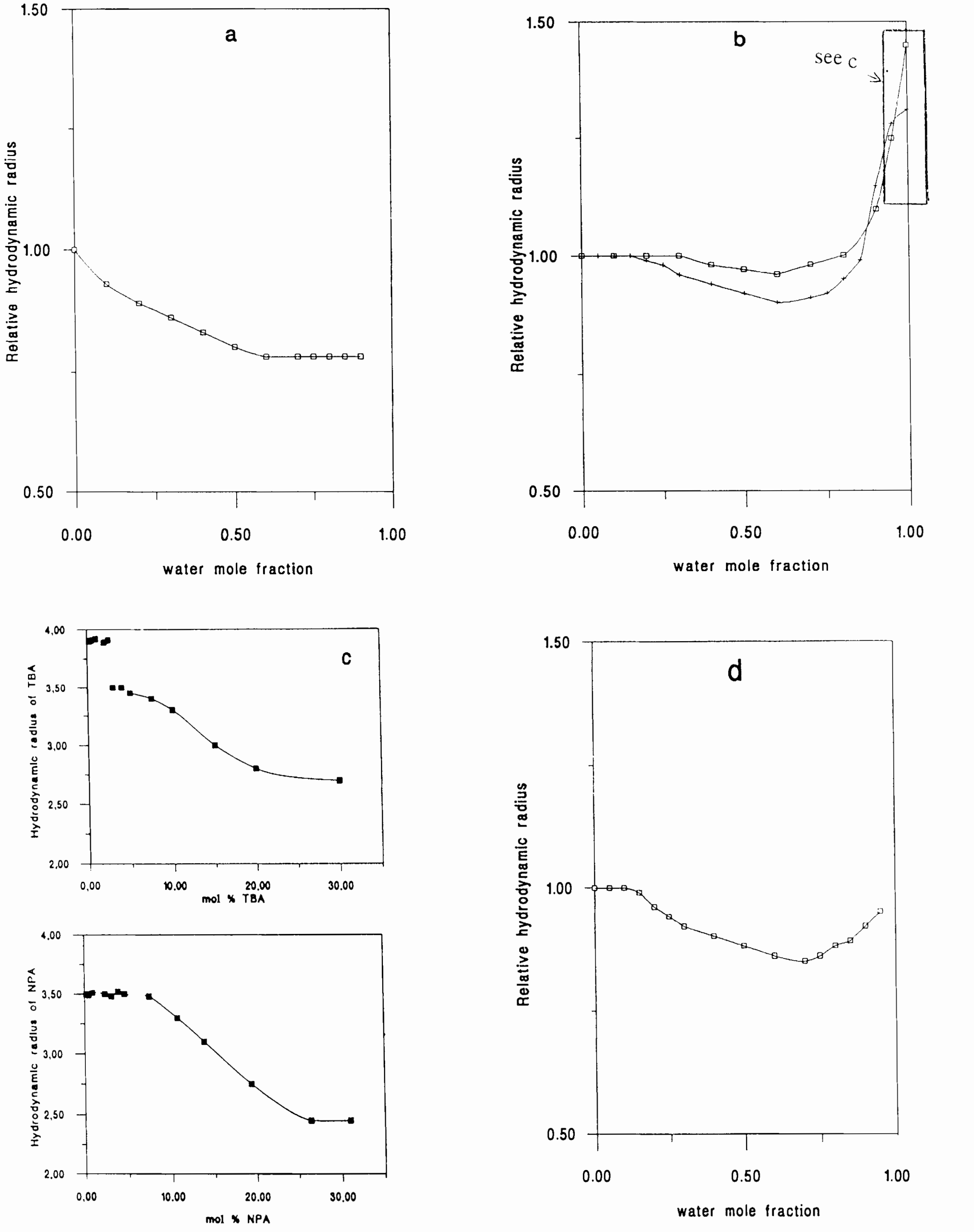

Figure 3 Variations of the relative hydrodynamic radii of organic component with water mole fraction in mixtures with: (a) methanol; (b) *n*-propanol (+) and *t*-butanol (□); (d) acetonitrile. Dependence of the hydrodynamic radii of NPA and of TBA in diluted aqueous solutions are shown in (c) (from reference 17).

Addition of water disrupts the acetonitrile structure and in diluted solution acetonitrile self-diffusion is due to independent motions of single molecules.

5 Self-diffusion of Ions in Binary Solvents

Despite the properties of electrolyte solutions in mixtures of water with organic solvent being of great interest, data on ionic mobilities in such systems are scarce. Ionic mobility can be obtained from the equivalent conductance and transference number or by directly measuring the self-diffusion coefficients. Ionic mobilities are commonly used to gain an insight into the structure of ionic solvation shells. One should, however, remember that the ionic self-diffusion coefficient, like other properties of ions, depends heavily on the ionic strength of the solutions; interpolation to infinitely dilute solutions is therefore necessary. Taking into account the relaxation effect on the self-diffusion processes of ions, Robinson and Stokes[25] proposed the following (equation 13) to express the influence of the salt molarity m on the self-diffusion coefficient D_{ion} for 1:1 electrolyte:

$$D_{\mathrm{ion}} = D^{\infty}_{\mathrm{ion}}\left\{1 - \frac{2.806\times10^{6}}{(\epsilon_{0}T)^{1.5}}[1-\sqrt{d(\mu_{\mathrm{ion}})}]\sqrt{m}\right\} \qquad (13)$$

where T and ϵ_0 denote temperature and the static dielectric constant of the solvent respectively. The term $d(\mu_{\mathrm{ion}})$ denotes a function depending on the mobilities of the ion under study and its counter-ion. That term can be expressed using the limiting self-diffusion coefficients of the ion under study $(D_{\mathrm{ion}})^{\blacklozenge}$ and of its counter-ion $(\mathrm{D}_{\text{co-ion}})^{\blacklozenge}$,[26] yielding equation 14.

$$D_{\mathrm{ion}} = D^{\infty}_{\mathrm{ion}}\left[1 - \frac{2.806\times10^{6}}{(\epsilon_{0}T)^{1.5}}\left(1-\sqrt{\frac{B_{\mathrm{ion}}+3}{4(B_{\mathrm{ion}}+1)}}\right)\sqrt{m}\right] \qquad (14)$$

$$\text{with } B_{\mathrm{ion}} = \frac{D^{\infty}_{\mathrm{ion}}{}^{\blacklozenge}}{D^{\infty}_{\text{co-ion}}}$$

To calculate the limiting self-diffusion coefficients of the ion under study and its counter-ion one must simultaneously minimize the standard deviations for both ions.[25]

To investigate the solvation of ions in binary solvents the hydrodynamic radii of the ions were calculated using the Stokes–Einstein relation (equation 12), assuming perfect slipping boundary conditions. It should, however, be noted that the hydrodynamic radius is not the best approach to the size of the ion and its solvation shell, because dielectric friction forces are neglected. Gill,[27] following Zwanzig's theoretical attempt,[28] has proposed a modification of the Stokes–Einstein equation which leads to the following relationship between the radius of solvated ion r_{ion} and its self-diffusion coefficient:

$$r_{\mathrm{ion}} = \frac{k_{B}T}{4\pi\eta_{0}D^{\infty}_{\mathrm{ion}}} + 0.0103\epsilon_{0} \qquad (15)$$

where the first term represents the hydrodynamic approximation of the ionic self-diffusion and the second describes the dielectric friction forces.

The quantities obtained from equation 15 compared with the crystallographic radius of the ion under study and the diameters of the solvent molecules have been used to investigate the size and composition of solvation shells. Solvation numbers of the ions have been calculated from equation 16.

$$n_{\mathrm{sol}} = \frac{r^{3}_{\mathrm{ion}} - r^{3}_{\mathrm{c}}}{r^{3}_{\mathrm{sol}}} \qquad (16)$$

where r_{c} and r_{sol} denote the crystallographic radius of the ion and the radius of the solvent molecule, respectively.

Calculation of the solvation number from the above equation in a binary solvent is difficult if preferential solvation can occur. Even in a one-component system the values obtained from the above relationship can be misleading, because in the derivation of equation 16 the solvent molecules in the solvation shell have been modelled as hard spheres and their closest packing has been assumed, which does not seem to be an appropriate model for the solvation shell. Thus the solvation numbers of the investigated ions are not computed here; only the influence of the solvent composition on solvation shells is discussed below.

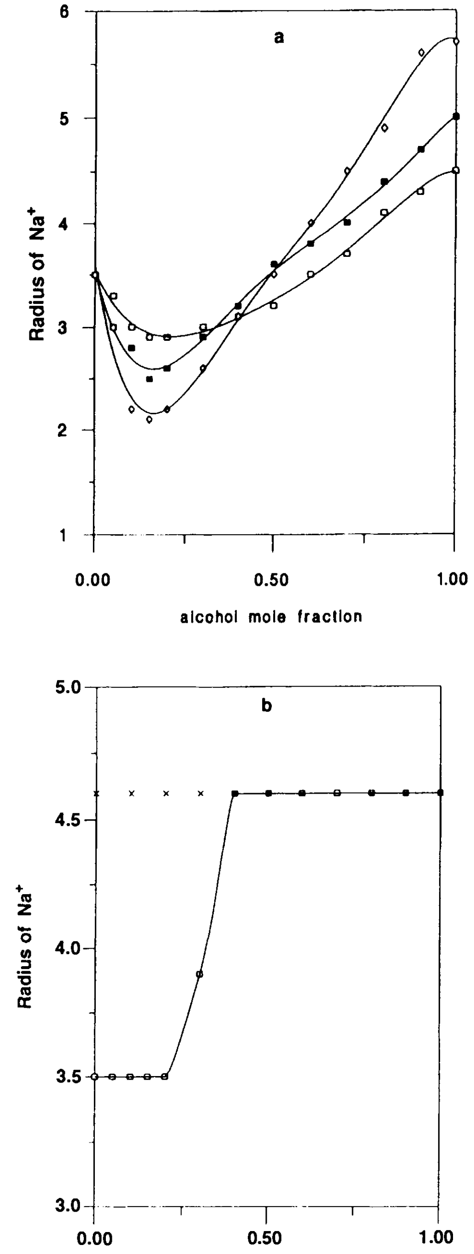

Figure 4 Influence of the solvent composition on the Na^+ radius in mixtures: (a) water with alcohols: methanol (□), *n*-propanol (■) and *t*-butanol (◇); (b) acetonitrile with water (□) and methanol (×).

5.1 Solvation of Sodium Ions in Binary Solvents

Variations of the radius of Na^+ in aqueous solutions of methanol,[26] *n*-propanol,[29] *t*-butanol,[29] and acetonitrile, and in methanol–acetonitrile[30] mixtures are shown in Figure 4. In all mixtures studied the Na^+ radius is noticeably greater than 0.96Å, the crystallographic radius. This means that the motions of the cation and of several solvent molecules are correlated. In aqueous solutions the radius of the solvation shell (3.5 Å) significantly exceeds the average distance between the sodium ion and the oxygens of the six nearest neighbours (2.35 Å) forming the octahedral solvation shell.[31] Thus one may conclude that the motions of the sodium ions and some water molecules from its second hydration shell are also correlated.

As seen from Figure 4, the influence of admixtures of alcohols and of acetonitrile are different. In diluted solutions of acetonitrile the radius of Na^+ is the same as in aqueous solution, whereas in aqueous solutions of alcohols the radius of Na^+ decreases and reaches its smallest value at about 17 mol% of alcohol. For the same concentrations of TBA and of NPA the structure of the water is significantly destroyed (See section 4.1). The effect of alcohols increases in the order MeOH < N-PA < TBA, and in aqueous solutions of TBA and of NPA that radius becomes equal or even less than the average Na^+–O distance. This leads to the conclusion that in the disordered water structure the creation of a second hydration shell is restricted and the first solvation shell is partly destroyed.

In acetonitrile–water mixtures, below 20 mol% AN, the radius of Na^+ remains the same as in aqueous solutions. Over the same range of acetonitrile concentration the water structure is also unchanged, which confirms the supposition that formation of the ionic solvation shells depends not only on the ion–solvent interactions, but also on the structure of the solvent.[26,29,30]

With increasing concentration of the organic components the radius of Na^+ also increases, but the effects of alcohols and of acetonitrile are unlike. As seen from Figure 4, in pure alcohols the radius of the sodium ion is larger than the average distance to the oxygen of the nearest neighbours, which indicates that (as for aqueous solutions) the motions of the cations are correlated not only with the solvent molecules in the first solvation shell, but also with some solvent molecules from the second solvation shell. One should note, however, that over the whole range of the mixture composition the dependence of r_{ion} *verus* alcohol mole fraction shows a negative deviation from the linearity which suggests that solvation shells contain a higher concentration of water molecules than the bulk solution. In water-deficit mixtures the self-diffusion coefficients of water and of sodium ions are equal,[15–17] which also suggests the preferential hydration of Na^+.

In acetonitrile–water mixtures, above 20 mol% AN, the radius of Na^+ increases rapidly and reaches a constant value – the same as in pure acetonitrile at about 40 mol% AN. As already mentioned, the mixture is heterogeneous at the molecular level and consists of an ordered water microphase and acetonitrile molecules. The observed behaviour of the Na^+ radius may be explained by assuming that either the cations are incorporated into the water globules or that they are preferentially solvated by acetonitrile molecules, inducing the formation of an acetonitrile microphase. Although preferential hydration of Na^+ was expected, this has turned out not to be the case. It has been found that the addition of electrolytes does not affect the hydrodynamic radius of water, but that it does affect the hydrodynamic radius of acetonitrile.[23] The hydrodynamic radius of acetonitrile increases by about 50%.

Variations of the Na^+ radius in methanol–acetonitrile mixtures are unlike those in other binary solvents. In pure methanol or acetonitrile the radii of Na^+ are equal, within experimental error, and over the whole range of the mixture composition that value is constant. It means that the solvent composition in the vicinity of cations is the same as in bulk solution.

5.2 Solvation of Iodide Ions in Binary Mixtures

Self-diffusion coefficients of iodide ions have been measured in the same binary mixtures used in the investigations on sodium ions. The radii of the anions, calculated from equation 15, are presented in Figure 5. In aqueous solutions the radius of I^- (2.2 Å) is almost the same as that in the crystal (2.16 Å) *i.e.* the motions of iodide ions and of water molecules are uncorrelated. Such behaviour is to be expected, since iodide ions destroy water structure and accelerate the motion of water molecules in their vicinity.[31] In pure alcohols and acetonitrile the radius of I^- is noticeably larger than the crystallographic radius, suggesting that iodide ions are able to bind molecules of these components to form the first solvation shells and to affect the motion of some molecules in the second shells.

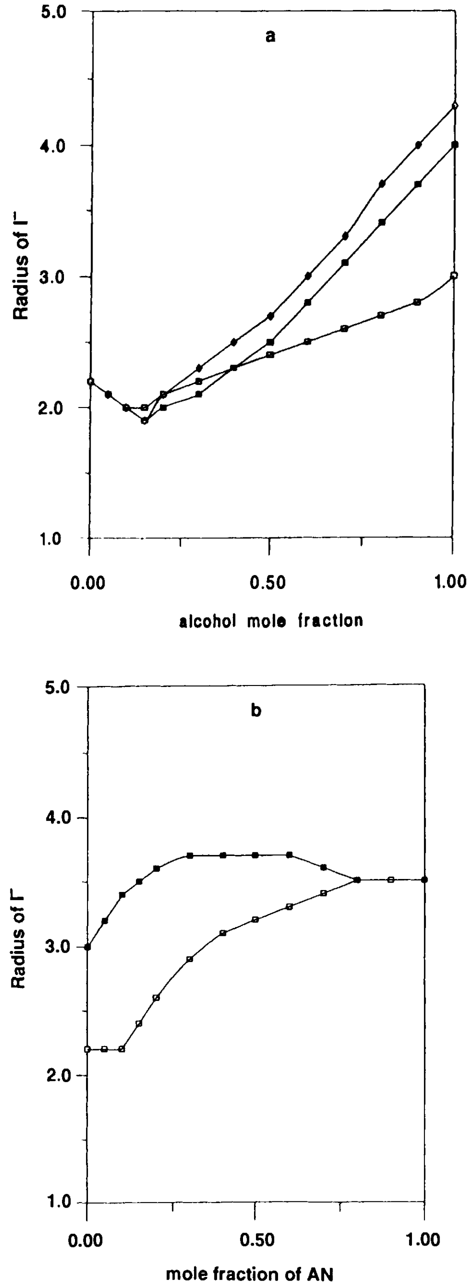

Figure 5 Influence of the solvent composition on the I^- radius in mixtures: (a) water with alcohols: methanol (□), *n*-propanol (■), and *t*-butanol (◇); (b) acetonitrile with water (□) and methanol (■).

As seen from Figure 5, variations of the I^- radius with the solvent composition for all alcohol–water mixtures studied are similar. Small admixtures of alcohols cause a decrease of the I^- radius, which reaches its lowest value at about 17 mol% of alcohol (the same composition as for minimium Na^- radius). In aqueous solutions of alcohols the radius of the iodide ion becomes even smaller than its crystallographic value. Such a feature can be understood if the ionic radius is considered as the dimension of a spherical force field and not as the radius of a hard sphere. As seen earlier in the case of sodium ions, the effect of alcohol increases in order MeOH < NPA ~ TBA, confirming that creation of the solvation shell depends not only on ion–solvent interactions, but also on solvent structure.

An increase in alcohol concentration causes a significant increase in the I^- radius. As in the case of sodium ions, the function r_{I} *versus* alcohol mole fraction shows negative deviation from linearity, interpreted as a feature of preferential hydration. This means that the concentration of water in the vicinity of anions exceeds that in the bulk solution even though the anions are unable to bind the water molecules and their motions are uncorrelated. Variations of the I^- radius in solvents containing acetonitrile are different. In aqueous solutions the I^- is not affected by acetonitrile when its concentration is less than 10 mol%. Further increase in the acetonitrile concentration causes a monotonous increase of the anionic radius. The highest value, the same as in pure acetonitrile, is reached above 75 mol% of AN. Since the addition of NaI does not affect the hydrodynamic radius of water, but does affect the radius of acetonitrile, the observed dependence can be interpreted as due to a slight preferential solvation of iodide ions by acetonitrile. One may suppose that anions (like cations) are either able to bind acetonitrile and to create acetonitrile aggregates, or that they are attracted by the acetonitrile aggregates surrounding the cations. Studies of ionic association[33] suggest that the latter explanation is more likely.

In methanol–acetonitrile mixtures[34] the I^- radii exhibit significant, unexpected deviations from the linear dependence (see Figure 5). Although in pure components of the mixture the solvation numbers of iodide ions are similar, in mixtures their solvation shells are enriched with acetonitrile – in agreement with the data on the self-diffusion of methanol and of acetonitrile.[34] It has been found that the addition of NaI does not affect the hydrodynamic radius of methanol, but that it noticeably increases the hydrodynamic radius of acetonitrile.

5.3 Solvation of Tetraethylammonium Ions in Alcohol–Water Mixtures

Self-diffusion coefficients of tetraethylammonium ions have been measured in mixtures of water with acetonitrile[30] and *n*-propanol.[29] The cation radii obtained from equation 15 are presented in Figure 6. In aqueous solutions the hydration of tetralkylammonium ions is not like that of other cations, but it is similar to the hydration of hydrophobic solutes.[35] In water the Et_4N^+ radius (5.2 Å) is larger than the crystallographic radius (4.1 Å). Unfortunately, *X*-ray scattering data have not been reported for the Et_4N^+ ions. In aqueous solutions of Me_4NCl the average N–O distance has been found to be 4.5 Å and the hydration shell of the cation consists of 20 water molecules.[36] The Et_4N^+ ion is bigger with longer hydrophobic chains, thus its radius (5.2 Å) and hydration number (31 ± 3) seem to be reasonable.

The addition of alcohol causes a rapid decrease of the Et_4N^+ radius and for alcohol concentrations higher than 25 mol%, it becomes independent of the mixture composition, having the same value as the crystallographic radius. There is, however, a remarkable difference between aqueous solutions of AN and of NPA. In NPA solutions the Et_4N^+ radius becomes even smaller than its crystallographic value. Such behaviour has been found at about 17 mol% NPA, *i.e.* in a solvent of disordered structure.

In acetonitrile–methanol mixtures,[34] as is to be expected, the Et_4N^+ radius is independent of the solvent composition, having the same value as the crystallographic radius. This means that the motions of the Et_4N^+ ions and of solvent molecules are uncorrelated and the cations remain unsolvated.

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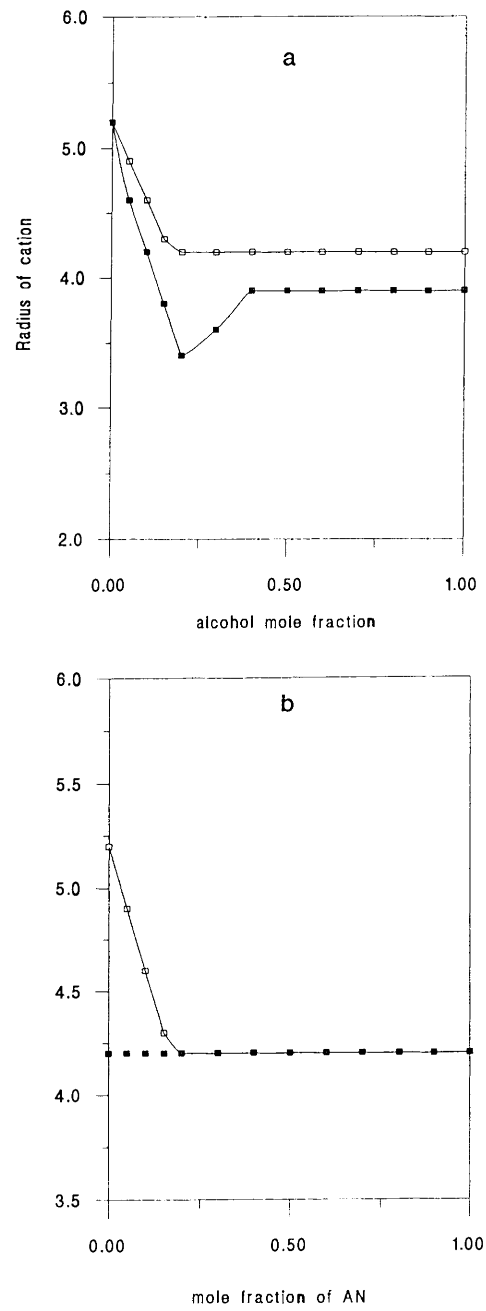

Figure 6 Influence of the solvent composition on the Et_4N^+ radius in mixtures: (a) water with alcohols: methanol (□), *n*-propanol (■); (b) acetonitrile with: water (□) and methanol (■).

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