Diffusion in Mixed Solvents. 4. Iodine in Polar Nonassociated Solutions

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The diffusion coefficients of iodine diluted in two polar nonassociated solutions, cyclohexane + 1,4-dioxane and cyclohexane + tetrahydrofuran, have been measured at 298.15 K. In contrast to the ethanol + nonpolar liquid systems, the reduced isoviscous diffusion coefficient ($D_{11}{}^\circ\eta_{23}/T$) for iodine in these solutions did not show very large negative deviations from linearity with respect to the molar composition x of the mixed solvent, in spite of the fact that the interaction of iodine with 1,4-dioxane or tetrahydrofuran is comparable with that between iodine and ethanol.

In previous papers of this series (*5–7*), the diffusion coefficients of iodine in various kinds of mixed solvents have been reported. These include aqueous alcohol solutions (*5*), ethanol + nonpolar liquid systems (*6*), and nonpolar solutions (*7*). The purpose of this series of study is to elucidate the effect of complex solute–solvent interaction on diffusivity in mixed solvents. It was found that the difference in the interaction of solute to both solvents leads to a relative decrease in the diffusivity of the solute.

In this study, we intend to collect the data which will supplement lack of information about some of the possible types of mixed solvents. Thus the diffusivity of iodine diluted in two polar nonassociated solutions, cyclohexane + 1,4-dioxane and cyclohexane + tetrahydrofuran (THF), has been measured at 298.15 K. We will compare the present data with those in ethanol + nonpolar liquid systems and discuss the effect of solvent association on the relative decrease in diffusivity mentioned above.

Experimental Section

The source and handling of iodine and organic solvents (cyclohexane, 1,4-dioxane, and THF) were the same as those in previous studies (*5–7*). As before, the diffusion coefficients were determined with the capillary-cell method (*5*). In this method, optimum rate of stirring of solution is important to obtain reliable results. No stirring was applied in the present series of experiments and the justification to do this is only the fact that some of the present results coincide with the literature values (*4*, *10*) obtained by capillary and diaphragm cell methods. The viscosity of mixed solvents was also measured by the same method as that used previously (*6*).

Results and Discussion

Diffusivity in Polar Nonassociated Solutions. In Table I, the experimental results are summarized for the diffusion coefficients of iodine in 1,4-dioxane + cyclohexane and THF + cyclohexane solutions at 298.15 K. In Figure 1, the negative deviation of $D_{11}{}^\circ\eta_{23}/T$ values from linearity with respect to x, which is defined as

$$(D_{11}{}^\circ\eta_{23}/T)^{\mathrm{EX}} = (D_{11}{}^\circ\eta_{23}/T)_{\text{mixed solvent}} - x(D_{11}{}^\circ\eta_{23}/T)_{x=1} - (1-x)(D_{11}{}^\circ\eta_{23}/T)_{x=0}$$

and referred to as the excess quantity of reduced isoviscous diffusion coefficients, is shown as a function of x for four mixed solvents each containing cyclohexane as one component.

Table I. Diffusion Coefficient of Iodine in Two Binary Mixed Solvents at 298.15 K

$x_{\mathrm{c\text{-}C_6H_{12}}}$	$D_{11}{}^\circ$, $10^5\,\mathrm{cm^2\,s^{-1}}$	η_{23}, cP	$D_{11}{}^\circ\eta_{23}/T$, 10^{10} dyn $\mathrm{deg^{-1}}$
	Tetrahydrofuran + Cyclohexane		
0	2.35 ± 0.08	0.480	3.66
0.250	2.25 ± 0.04	0.532	4.02
0.500	2.01 ± 0.02	0.608	4.10
0.750	1.86 ± 0.02	0.720	4.49
1	1.82 ± 0.02	0.894	5.47
	1,4-Dioxane + Cyclohexane		
0	0.96 ± 0.03	1.190	3.83
0.247	1.25 ± 0.03	0.979	3.68
0.500	1.35 ± 0.04	0.871	3.94
0.747	1.57 ± 0.03	0.834	4.39

The diffusivity of iodine in mixtures of ethanol + nonpolar liquid (n-hexane or cyclohexane) has been shown to decrease relatively in such a way as to deviate negatively from the linear relation between $D_{11}{}^\circ\eta_{23}/T$ and x(*2*). Although the $(D_{11}{}^\circ\eta_{23}/T)^{\mathrm{EX}}$ values for the present two mixed solvents show expected negative deviations, they are much smaller than those found in ethanol solutions and only slightly larger than those for cyclohexane + benzene solutions where the difference in interactions of both solvents with iodine is of minor degree.

Interpretation of Diffusivity Data in Mixed Solvents. We have already studied the diffusion of iodine in 16 mixed solvents including the present work. The analysis of these data and of those for other diffusates may lead us to the following general picture of this type of diffusion in dilute solutions. We have so far proposed a four-step mechanism for the diffusion in mixed solvents (*6*). This is based on the assumptions that the magnitude of negative value of $(D_{11}{}^\circ\eta_{23}/T)^{\mathrm{EX}}$ must be proportional to the difference in the interactions of iodine with two solvents and that the rate-determining step is the migration of diffusate from the neighborhood of a more active solvent to that of an inert solvent. Since the enthalpy of formation of the iodine–1,4-dioxane complex is larger than that of the iodine–ethanol complex (*1*, *2*), the results shown in Figure 1 are not consistent with this energy information.

This discrepancy may be interpreted as follows. The $(D_{11}{}^\circ\eta_{23}/T)$ values for iodine in pure 1,4-dioxane and THF are somewhat smaller than those expected if they are regarded as the spherical molecule. This is clearly shown by the Hammond-Stokes diagram (*3*) where the $D_{11}{}^\circ\eta_{23}$ values are plotted against the molar volume of solvents. Figure 2 is a reproduction of a part of this plot for iodine (*9*). Although the $(D_{11}{}^\circ\eta_{23}/T)^{\mathrm{EX}}$ is negative for iodine in cyclohexane + 1,4-dioxane or + THF solutions, the absolute values of $(D_{11}{}^\circ\eta_{23}/T)$ themselves are not smaller than those for pure 1,4-dioxane or THF (cf. Table I). The latter is small enough as compared with those in cyclohexane and ethanol. Accordingly, the negative deviations can be explained almost perfectly by the preferential solvation of iodine to 1,4-dioxane or THF.

On the other hand, large negative values of $(D_{11}{}^\circ\eta_{23}/T)^{\mathrm{EX}}$ for the ethanol + saturated hydrocarbon solutions may be ascribed

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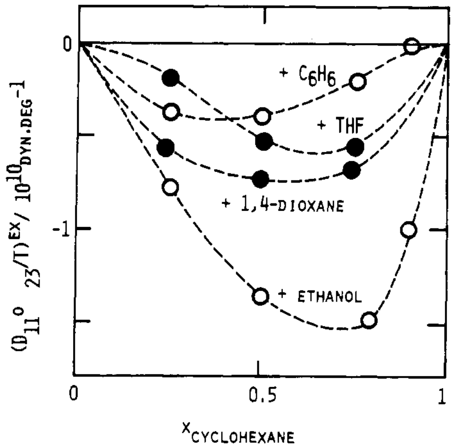

Figure 1. Excess temperature reduced isoviscous diffusion coefficient of iodine in four mixed solvents each containing cyclohexane as one component: ●, this work; O, ref 6 and 7.

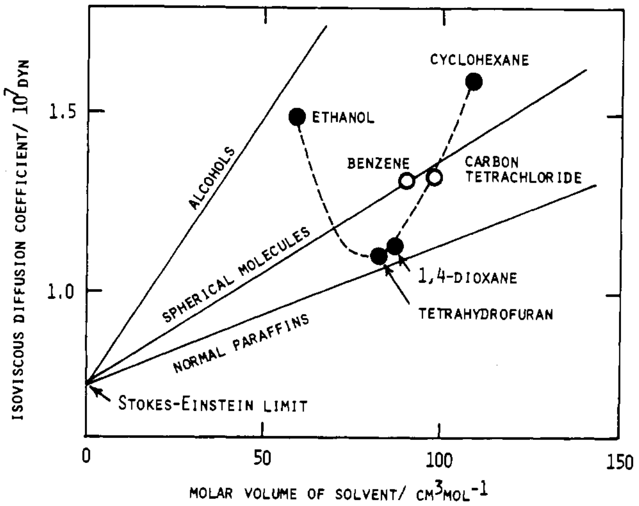

Figure 2. Hammond–Stokes plot for the diffusion of iodine in pure and mixed solvents. For details, see ref 9.

to the degradation of self-association of ethanol in inert solvents. When mixed with nonpolar solvent, ethanol will become more monomeric and the iodine–ethanol complex will be more stable than that in pure ethanol. The solubility measurement has indicated a smaller entropy of solution of iodine in such mixed solvents (*8*). This is also confirmed by the Hammond–Stokes plot as applied to mixed solvents. In Figure 2, the variation of $D_{11}^{\circ}\eta_{23}$ with molar composition in cyclohexane + ethanol solutions is shown as a dashed curve with the assumption that the apparent molar volume of mixed solvents is given by the arithmetic mean of those for the two pure solvents.

It is clear that the $D_{11}^{\circ}\eta_{23}$ value for the mixed solvents decreases rapidly when cyclohexane is added to ethanol and that a minimum of $D_{11}^{\circ}\eta_{23}$ value conforms quite closely to those for 1,4-dioxane or THF. This indicates that the interaction of iodine with ethanol diluted with cyclohexane will play a role comparable with that of 1,4-dioxane or THF, as far as their effects on diffusivity are concerned.

In conclusion, in the cases where the molar volume and viscosity of two solvents do not differ much, the diffusivity of dilute solute can be understood reasonably well by taking the following three important factors into account: (a) preferential solvation due to the difference in the interaction between solute and solvents, (b) changes in the self-association (generally disintegration) of alcohols and other associated liquids, and (c) the structural change in aqueous solutions (*5*).

Glossary

D_{11}°	diffusion coefficient of solute 1 at its infinite dilution in 10^5 cm^2 s^{-1}
T	temperature in K
x	mole fraction of one solvent in mixed solvent
η_{23}	viscosity of mixed solvent

Subscript

1	solute
2,3	solvent

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