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Proton Chemical Shifts of Solute Molecules in Binary Solvent Mixtures: Reversal of the Roles of Solute & Perturbing Solvent*

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Values of equilibrium constants for various solute-solvent equilibria have been determined on the basis of NMR chemical shifts of solutes in binary solvent mixtures. The equilibrium constants for the system $S+P \rightleftharpoons SP$ have been determined by studying the variation of chemical shifts of the solute S in mixtures of polar solvent (P) and nonpolar solvent (N) and also by studying the variation of chemical shift of P in binary mixtures of solvents S and N. The K values determined by the reversal of the roles of solute and the perturbing solvent have been found to be different. An attempt has been made to explain this anomaly on the basis of solvation of orders higher than that involved in 1 : 1 interactions.

EARLIER, attempts[1-4] have been made to relate the observed solvent chemical shifts to 1:1 or higher order interactions between the solute and solvent species. Therefore, as in the case of hydrogen-bonded and charge-transfer complexes, existence of various dipole-dipole, dipole-induced dipole and other collision complexes have been proposed[4]. For solutes in binary solvent systems, Eq. (1) (similar to relations used for the calculation of variation in infrared and electronic band shifts and band intensities[5-7]) has been employed[8] for the evaluation of the thermodynamic data of complex formation:

$$\Delta = \frac{K_p \Delta^0 C_p}{1+KC_p} \qquad \ldots(1)$$

where $\Delta = \delta - \delta_0$ and $\Delta_0 = \delta_C - \delta_0$. δ and δ_0 are respectively the chemical shifts of solute protons at infinite dilution in binary solvent mixture containing C_p moles of perturbing solvent and in pure inert solvent. δ_C is the chemical shift for complex in inert solvent. K_p is the equilibrium constant for the solute (S)—solvent (P) interaction of the type $S+P \rightleftharpoons SP$. The following two rearrangements of Eq. (1) have been employed for the evaluation of equilibrium constant:

$$\frac{1}{\Delta} = \frac{1}{\Delta^0 K_p C_p} + \frac{1}{\Delta^0} \qquad \ldots(2)$$

$$\frac{\Delta}{C_p} = -K_p\Delta + K_p\Delta^0 \qquad \ldots(3)$$

Kuntz and Johnston[4] have used Eq. (2) to determine equilibrium constant for various weak interactions including dipole-dipole and dipole-induced dipole types.

In the various studies carried out for the evaluation of equilibrium constant by spectral methods, the variation of spectral parameter of the solute species was only considered. Because of the limitations in the spectral measurements, the variation of spectral parameters of the complexing solvent was seldom followed. In the case of chemical shift studies such limitations do not exist. To determine whether expressions similar to (1) yield true values of equilibrium constant for the system $S+P \rightleftharpoons SP$, in a previous publication[9], we evaluated K values for two systems by studying the variation of chemical shift of the solute (S) in a mixture of polar solvent (P) and the inert solvent (N) and also by studying the variation of chemical shift of (P) in a binary solvent mixture of (S) and (N). The K values were not found to be equal when roles of solute and solvent were changed. It was thought of interest to extend these studies to some more systems and give some reasonable explanation for the anomaly. Studies on various systems exhibiting weak interactions are being reported in this paper.

Materials and Methods

All the chemicals used were of AR or LR grade and were purified by standard methods[10]. All the solvent mixtures were prepared by volume per cent. The NMR spectra were recorded employing a Varian A-60-D spectrometer. As observed by Kuntz and Johnston[4], nearly 1% solute concentration was found to approximately represent the chemical shift of solute at infinite dilution. All the shifts reported are with respect to TMS as the internal reference at 21°. The chemical shifts were reproducible with an accuracy of ±0·2 Hz.

Results and Discussion

Chemical shift data of various solutes in binary solvent mixtures are given in Tables 1-3. Eq. (4) which is a rearrangement of Eq. (1), was used for the determination of equilibrium constant.

$$C_p/\Delta = 1/(K_p\Delta^0) + C_p/\Delta^0 \qquad \ldots(4)$$

The values of correlation coefficient (r), K, and Δ^0 obtained by the method of least-squares for various systems are summarized in Table 4. It can

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TABLE 1 — CHEMICAL SHIFT DATA (Hz) IN BINARY SOLVENT MIXTURES WITH CYCLOHEXANE AS THE INERT SOLVENT

% of perturber	CH_2Cl_2 in $CHCl_3$		Dioxane in $CHCl_3$		$CHCl_3$ in dioxane	
	C_p	Δ	C_p	Δ	C_p	Δ
5	0·617	1·5	0·617	2·0	0·588	6·5
10	1·233	2·5	1·233	3·5	1·180	14·5
15	1·850	3·0	1·850	4·0	1·763	17·5
30	3·700	6·5	3·700	6·5	3·325	25·0
50	6·167	8·0	6·167	8·5	5·875	30·0
70	8·633	10·0	8·633	10·0	8·225	33·0
90	11·100	11·0	11·100	11·0	10·575	34·5

TABLE 2—CHEMICAL SHIFT DATA (Hz) FOR SOLUTES IN BINARY SOLVENT MIXTURES WITH CYCLOHEXANE AS THE INERT SOLVENT

% of perturber	$CHCl_3$ in $CCl_2 = CHCl$		$CCl_2 = CHCl$ in $CHCl_3$		Acetone in CH_2Cl_2	
	C_p	Δ	C_p	Δ	C_p	Δ
5	—	—	—	—	0·789	1·5
10	1·113	2·0	—	—	1·579	2·5
15	1·670	2·5	1·850	3·0	2·369	3·5
30	3·340	4·0	3·700	4·5	4·738	4·5
50	5·567	5·0	6·167	7·5	7·896	6·5
70	7·794	7·0	8·633	9·0	11·055	7·5
90	10·021	8·5	11·100	11·5	14·214	9·0

TABLE 3— CHEMICAL SHIFT DATA (Hz) FOR SOLUTES IN BINARY SOLVENT MIXTURES WITH CYCLOHEXANE AS THE INERT SOLVENT

% of perturber	$CHCl_3$ in CH_2Cl_2		CH_2Cl_2 in acetone		Acetone in $CCl_2=CHCl$		$CCl_2=CHCl$ in acetone	
	C_p	Δ	C_p	Δ	C_p	Δ	C_p	Δ
5	0·789	2·0	0·683	5·5	0·557	0·5	0·683	8·0
10	1·579	3·0	1·366	11·3	1·113	1·0	1·366	11·0
15	2·369	4·0	2·048	13·5	1·670	1·5	2·048	16·0
30	4·738	6·5	4·097	19·5	3·340	3·0	4·097	25·0
50	7·896	10·0	6·828	23·5	5·567	4·5	6·828	33·0
70	11·055	12·0	9·559	26·5	7·794	6·0	9·559	37·0
90	—	—	12·290	30·5	10·021	7·0	12·290	40·0

be noticed that in no case the equilibrium constant is found to be the same when the roles of solute and perturbing solvent are reversed. For the system $CHCl_3$+acetone, the K_p value is 5·49 when determined by the variation of chemical shifts of $CHCl_3$ and 1·52 when determined by the variation of chemical shifts of acetone protons. Similar differences in the K_p values can be observed in the other cases also. However, different values of correlation coefficient ($r<0·99$) show perfect fit of the chemical shift data to Eq. (1). One concludes, therefore, that the term K_p does not represent the true equilibrium constant. Scott[11] has recently argued that the K_p values found by the methods similar to the ones under discussion for weak interactions are not the real association constants. These are the so-called " sociation constants " which yield the number of complexes formed in excess of those calculated on the basis of random probabilities. Alternatively, on the basis of a plausible quasi-lattice model of the solutions[12-14], random collisions between donor and acceptor molecules lead to the equilibrium constant values $K = z$, where z is the number of the nearest neighbours. However, if the derivation of Eq. (1) is considered[6] on the same line as Langmuir's adsorption isotherm where the changes in spectral parameters of solute molecules in binary solvent mixtures represent the extent of solvation, this anomaly can be well understood.

TABLE 4 — RESULTS OF LEAST-SQUARE ANALYSIS FOR EQ. 4 FOR THE CHEMICAL SHIFT DATA IN BINARY SOLVENT MIXTURES

Systems*	r	K (litre/mole)	Δ°
$CHCl_3$ in acetone†	0·99	0·485	61·0
Acetone in $CHCl_3$†	0·95	0·075	22·5
Acetone in C_6H_6†	0·98	0·307	30·0
C_6H_6 in acetone†	0·94	0·170	16·0
CH_3NO_2 in dioxane†	0·99	0·776	10·7
$CHCl_3$ in CH_2Cl_2	0·96	0·103	21·9
CH_2Cl_2 in $CHCl_3$	0·97	0·121	19·3
Dioxane in $CHCl_3$	0·99	0·217	15·3
$CHCl_3$ in dioxane	1·00	0·416	42·3
$CHCl_3$ in $CCl_2=CHCl$	0·94	0·123	14·4
$CCl_2=CHCl_3$ in $CHCl_3$	0·91	0·057	28·7
Acetone in CH_2Cl_2	0·98	0·152	12·4
CH_2Cl_2 in acetone	0·99	0·258	38·6
Acetone in $CCl_2=CHCl$	0·96	0·032	29·9
$CCl_2=CHCl$ in acetone	0·99	0·203	56·0

*Cyclohexane is taken as the inert solvent.
†Data from ref. (13).

The concept of incomplete solvation can be assumed in the derivation of such an expression similar to the derivation of adsorption isotherm. Let the amount of polar solvent needed to solvate all the solute molecules to the maximum extent possible be x_0. If the amount of polar solvent involved in solvation at a concentration C_p is x, then for the equilibrium,

$$S+P \underset{k'}{\overset{k}{\rightleftharpoons}} (S)P$$

the ratio $x/x^0 = \theta$ is given by

$$kC_p(1-\theta) = k'\theta$$

giving

$$x = \frac{x^0KC_p}{1+KC_p} \qquad \ldots(5)$$

where solvation constant, $K = k/k'$ (k and k' are respectively the specific rate constants for solvation and desolvation of S by P). On increasing the number of perturbing molecules P, around the solute molecules, the electric field capable of polarizing the solute molecules will increase. Hence the change in spectral parameter ξ of S will increase with increasing x. Taking $\Delta\xi$ as a direct measure of the amount of P involved in solvation, the above expression can be written as

$$\Delta\xi = \frac{K\Delta\xi^0C_p}{1+KC_p} \qquad \ldots(6)$$

The expression (6) is similar to Eq. (1) except that 1:1 interaction constant K_p is replaced by the 1:n solvation constant, K. Thus, K_p values determined above are identical with the K values. Eq. (1) derived on the basis of 1:1 interaction only cannot explain the variation of K_p with the change of roles of solute and solvent. But on the basis of Eq. (6) the K values can be different when the role of solute and perturbing solvent is reversed. This is because of the fact that the value of K is governed by specific values of rates of solvation and desolvation ($K = k/k'$) and the solvation number which determines the value of x and hence $\Delta\xi$. If the validity of the above-mentioned assumptions is justified — though the exact implications of these assumptions in the derivation of the solvation equations are not too clear — and if proportionality constant for the expression $\Delta\xi \propto x$ is worked out, the $\Delta\xi$ and $\Delta\xi^0$ values can be employed to evaluate the solvation numbers. More work in this direction is in progress and will be communicated shortly.

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