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An Application of the Quasi Chemical Approximation to the NMR Dilution Shift in Some Binary Mixtures

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The theoretical NMR dilution curves for the ethanol - carbon tetrachloride, water-acetone and water-dioxane systems have been derived without the assumption of any particular type of H-bonded complexes in the solution. The expressions so derived contain the interchange energies as variable parameters. The use of the appropriate values of interchange energies (a few kilocalories) gives reasonable quantitative fits of the experimental dilution curves over the entire concentration range of the solutions. These values suggest that the strength of hydrogen bonding in the present systems is in the order of: water-water > water-acetone > water-dioxane > ethanol-ethanol.

A number of papers have reported on the concentration dependence of the proton resonance lines in a variety of binary mixtures, and some quantitative treatments have been made for them. Huggins et al.[1] assumed the simple monomer-dimer equilibrium in order to elucidate the dilution curves of several phenol derivatives in the extremely low concentration range and obtained the association constants by using infrared data. Mavel[2] derived the theoretical dilution curves for various kinds of complex formations over the whole concentration range and compared them with the experimental results.

In most of the papers,[3-9] including those of the above authors, the treatments are based on the assumption that there exists an association equilibrium among the particular hydrogen bonded complexes in a given concentration range of the solution. It is, however, unreasonable to assume only the particular types of H-bonded complexes, since no conclusive evidence has yet been obtained for even the existence of such complexes.

From another point of view, the so-called "hydrogen bond" should be regarded as only a kind of intermolecular interaction which has a comparatively large interaction energy—a few kilocalories. In this connection, it is important to examine whether or not the concentration dependence of the proton chemical shifts in the H-bonded systems can be interpreted in terms of the statistical mechanics without the assumption of any particular H-bonded complex in the solution.

The purpose of this paper is to apply the quasi chemical approximation, developed by Guggenheim,[10] to the ethanol - carbon tetrachloride, water-acetone and water-dioxane systems, and to evaluate the dilution curves by means of information on the number of contacts which can be enumerated by Barker's method.[11] Although several reports[4,5,8,12-14] have already been published on these systems, we have chosen them as model systems for the present discussion.

Theoretical

In general, it can be said that the molecules and their functional groups give rise to molecular contacts with appropriate orientations in conformity with their thermodynamic probability. Thus, the protons of the type i, e. g., the hydroxyl proton of water in the water - organic solvent mixture, can be present as various kinds of pairs or of contacts, such as the proton-proton acceptor group of orgainc molecule, the proton-methylene group contact, and so on. The number of these pairs may then be denoted by N_{ij} $(j=1, 2, \cdots)$, where j indicates the contact points of the molecule.

In H-bonded systems a single sharp line is usually

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11) J. A. Barker, *J. Chem. Phys.*, **20**, 1526 (1952).
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14) E. D. Becker, U. Liddel and J. N. Shoolery, *J. Molec. Spec.*, **2**, 1 (1958).

observed for the protons under consideration because of a rapid exchange among the various types of protons present in the solution. In this case the chemical shift, δ_i, for the protons of the type i is known to be given by the weighted average of each contribution;

$$\delta_i = \sum_j N_{ij}\cdot\delta_{ij}/\sum_j N_{ij} \tag{1}$$

where δ_{ij} denotes the chemical shift for the protons of the type i in the i-j pairs. As may be seen in Eq. 1, the chemical shifts, as well as the proton fraction for each state, must be known in order to obtain the theoretical dilution curve for the H-bonded system.

Consider the mixture consisting of molecules of the types A, B,$\cdots$ arranged on a Z-coordinated lattice. For the numbers of N_{ij}^{AB} pairs, which are formed by the contacts between the i-th class of contact points of the A molecule $\binom{A}{i}$ and the j-th one of the B molecule $\binom{B}{j}$, we have:

$$2N_{ii}^{AA} + \sum_{B,j} N_{ij}^{AB} = Q_i^A\cdot N_A \tag{2}$$

and the quasi chemical equation:

$$(N_{ij}^{AB})^2 = 4\cdot N_{ii}^{AA}\cdot N_{jj}^{BB}\cdot\exp(-U_{ij}^{AB}/\boldsymbol{k}T) \tag{3}$$

where Q_i^A denotes the number of the contact points in the i-th class of the A molecule; N_A, the number of the A molecule, and U_{ij}^{AB}, the interchange energy per pair for the i-j contact.

By introducing the parameters[11]:

$$\eta_{ij}^{AB} = \exp(-U_{ij}^{AB}/\boldsymbol{k}T) = \eta_{ji}^{BA} = \eta_{ij} \tag{4}$$

and:

$$X_i^A = (N_{ii}^{AA}/N)^{1/2} \tag{5a}$$

$$X_j^B = (N_{jj}^{BB}/N)^{1/2} \tag{5b}$$

where N denotes the total number of molecules in the system, we have:

$$N_{ij}^{AB} = 2\cdot X_i^A\cdot X_j^B\eta_{ij}\cdot N \quad \text{for } \binom{A}{i} \neq \binom{B}{j} \tag{6a}$$

$$= (X_i^A)^2\cdot N \quad \text{for } \binom{A}{i} = \binom{B}{j} \tag{6b}$$

and;

$$X_i^A\sum_{B,j}\eta_{ij}X_j^B = Q_i^A x_A/2 \tag{7a}$$

$$X_j^B\sum_{A,i}\eta_{ij}X_i^A = Q_j^B x_B/2 \tag{7b}$$

where x_A and x_B denote the mole fraction of the A molecule and that of the B molecule respectively. Assuming appropriate models with reasonable values of Q_i^A's, the values of N_{ij}^{AB} can be estimated according to Eqs. 6a, 6b, 7a and 7b, provided that the values of the η_{ij}'s are known. Then the theoretical dilution curve can be obtained according to Eq. 1, provided that the δ_{ij}'s are known.

1) The Ethanol - Carbon Tetrachloride System.—We will start with the assumptions for the lattice model and molecular geometries; 1) From the approximate ratio of the molecular volume of ethanol to carbon tetrachloride, it is most reasonable to regard the ethanol molecule as a trimer and the carbon tetrachloride molecule as a pentamer. 2) We assume that each lattice point has four nearest neighbors; that is, $Z=4$. Then the number of contact points of ethanol is 8, and that of carbon tetrachloride is 12.

$$\begin{aligned} &C_2H_5OH \quad r_e = 3, \quad Q_H^e = 1, \quad Q_O^e = 2, \quad Q_I^e = 5 \\ &CCl_4 \quad\quad r_s = 5, \quad Q_s = 12 \end{aligned}$$

where the subscripts e and s refer to ethanol and carbon tetrachloride molecules respectively. Q_H^e, Q_O^e and Q_I^e denote the number of contact points of the hydroxyl hydrogen, hydroxyl oxygen and hydrocarbon parts of the ethanol molecule respectively. Further, it is necessary to assign the energy of interaction for each possible contact. The interchange energies among the equivalent contact points are zero by definition. The values of U_{OS}, U_{IS} and U_{HS} are considered to be so small, as compared with U_{HO}, that we may take them to be zero without serious error. The value of U_{HO} was determined so as to give the best fit of the NMR data.

On this simplification, Eqs. 7a and 7b may be written as:

$$\left.\begin{aligned} X_H(X_H+\eta X_O+X_I+X_S) &= x_e/2 \\ X_O(\eta X_H+X_O+X_I+X_S) &= x_e \\ X_I(X_H+X_O+X_I+X_S) &= 5x_e/2 \\ X_S(X_H+X_O+X_I+X_S) &= 6x_s = 6(1-x_e) \end{aligned}\right\} \tag{3}$$

where x_e is the mole fraction of ethanol and where $\eta = \exp(-U_{HO}/\boldsymbol{k}T)$.

The solutions of Eq. 8 can now be obtained by the convenient method described by Barker.[11] By the substitutions of the variables:

$$X_H = CY_1, \quad X_O = CY_2, \quad X_I = CY_3, \quad X_S = CY_4,$$
$$Y_1 = 1, \quad Y_2 = \alpha$$

Eq. 8 may be rewritten as:

$$\left.\begin{aligned} C^2(1+\alpha\eta+Y_3+Y_4) &= x_e/2 \\ C^2\alpha(\eta+\alpha+Y_3+Y_4) &= x_e \\ C^2Y_3(1+\alpha+Y_3+Y_4) &= 5x_e/2 \\ C^2Y_4(1+\alpha+Y_3+Y_4) &= 6x_s \end{aligned}\right\} \tag{9}$$

The solutions of Eq. 9 are given as:

$$\left.\begin{aligned} &Y_1 = 1, \quad Y_2 = \alpha, \quad Y_3 = 5(\alpha-1), \\ &Y_4 = [(2+\alpha\eta-\alpha^2)/(\alpha-2)] - Y_3 \end{aligned}\right\} \tag{10}$$

and:

$$C^2 = 6/[Y_4(1+\alpha+Y_3+Y_4) + 12(1+\alpha\eta+Y_3+Y_4)] \tag{11}$$

Any solution of Eq. 9 then serves to determine the mole fraction, x_e, as the function of α and η.

$$x_e = 12(\alpha-1)(\alpha-2)/[6\alpha^2+\alpha(\eta-21)+16] \quad (12)$$

The variable range of α is $2<\alpha<t$, where:

$$t = [(\eta+15)+\{(\eta+15)^2-192\}^{1/2}]/12 \quad (13)$$

By using Eqs. from 10 to 13, the numerical value of each number of possible contacts occurring in the ethanol - carbon tetrachloride mixture may be easily determined as a function of the concentration, provided the appropriate value of η is taken.

The hydroxyl protons participating in the rapid exchange among ethanol molecules may be classified into two groups from the electronic environmental point of view. To the first group are assigned the protons which participate in the (H-H), (H-I) and (H-S) contacts, and to the second, the H-bonded protons which participate in the (H-O) contacts. The chemical shifts of hydroxyl protons assigned to the first group are different from each other. However, we assign the same value of chemical shift, δ_F, to the protons for the (H-H), (H-I) and (H-S) contacts, since the differences among them may be considered to be fairly small.

The total number of hydroxyl protons in the mixture is $2(X_H^2+X_HX_I+\eta X_HX_O+X_HX_S)$. The number of protons assigned to the first group is $2(X_H^2+X_HX_I+X_HX_S)$, while the number assigned to the second is $2\eta X_HX_O$. If we denote the chemical shift of H-bonded protons as δ_B, the chemical shift of the –OH proton at a given concentration may be written as:

$$\begin{aligned}\delta &= [(X_H^2+X_HX_I+X_HX_S)\delta_F + \eta X_HX_O\delta_B]/\\ &\quad (X_H^2+X_HX_I+\eta X_HX_O+X_HX_S)\\ &= \delta_F + \alpha\eta(\delta_B-\delta_F)/(1+\alpha\eta+Y_3+Y_4) \quad (14)\end{aligned}$$

The substitution of Eq. 10 into Eq. 14 gives the simplified expression for δ; that is;

$$\delta = \delta_F + (\alpha-2)(\delta_B-\delta_F)\eta/(\alpha-1)(\eta-1) \quad (15)$$

Equation 15 gives the chemical shift, δ, of the –OH proton as the function of the parameter α, which is combined with the analytical mole fraction, x_e, through Eq. 12, and the unknown parameters, δ_F, δ_B and η. However, the parameters δ_F and δ_B can be eliminated from Eq. 15 by the use of boundary condition; i. e.,

$$\begin{aligned} x_e &\to 0 \qquad \alpha \to 2 \qquad \delta \to \delta_0\\ x_e &\to 1 \qquad \alpha \to t \qquad \delta \to \delta_1\end{aligned}$$

Here δ_0 is the limiting value of δ which corresponds to the chemical shift of the –OH proton extrapolated to infinite dilution, while δ_1 is the chemical shift of pure ethanol. It follows from Eq. 15 that:

$$\delta_F = \delta_0 \quad (16)$$

and that:

$$\delta_B = \delta_0 + (t-1)(\eta-1)(\delta_1-\delta_0)/\eta(t-2) \quad (17)$$

By the substitution of Eqs. 16 and 17 into Eq. 15, the final expression of the dilution curve is obtained:

$$\delta = \delta_0 + (\alpha-2)(t-1)(\delta_1-\delta_0)/(\alpha-1)(t-2) \quad (18)$$

In Eq. 18, the unknown parameter used to evaluate the value of t is η. The value of η must be determined so as to give the best fit of the observed chemical shifts.

2) The Water-Acetone System.—The elucidation of the dilution curve for water-acetone system is rather complicated, since there are two types of hydrogen bonds in solution. The molecular parameters assumed for this system are:

$$\begin{aligned} &H_2O \qquad r_w = 1 \qquad Q_H^W = 2 \qquad Q_O^W = 2\\ &(CH_3)_2CO \qquad r_a = 3 \qquad Q_H^A = 6 \qquad Q_O^A = 2\end{aligned}$$

and $Z=4$. Further, it is assumed that all of the interchange energies except U_{OH}^{WW} and U_{HO}^{WA} may be ignored. On the basis of these simplifications, two parameters,

$$\eta_1 = \exp(-U_{OH}^{WW}/\boldsymbol{k}T)$$

and

$$\eta_2 = \exp(-U_{HO}^{WA}/\boldsymbol{k}T)$$

are left to be determined. Taking the abbreviations $X_H^W=X_1$, $X_O^W=X_2$, $X_H^A=X_3$ and $X_O^A=X_4$, Eqs. 7a and 7b can be written in this form:

$$\left.\begin{aligned} &X_1(X_1+\eta_1X_2+X_3+\eta_2X_4) = x_w\\ &X_2(\eta_1X_1+X_2+X_3+X_4) = x_w\\ &X_3(X_1+X_2+X_3+X_4) = 3x_a = 3(1-x_w)\\ &X_4(\eta_2X_1+X_2+X_3+X_4) = x_a\end{aligned}\right\} \quad (19)$$

By substitutions of variables similar to those made in Sec. 1, the solutions of Eq. 19 may be easily obtained as follows:

$$Y_1=1, \quad Y_2=\alpha, \quad Y_3=3(\alpha-1)(\eta_2+1)/(\eta_2-4\alpha+3)$$

$$Y_4=2(\alpha-1)(2\alpha-1)/(\eta_2-4\alpha+3)$$

$$C^2=1/[Y_4(\eta_2+\alpha+Y_3+Y_4)+(1+\alpha\eta_1+Y_3+\eta_2Y_4)]$$

where the variable range of α is $1<\alpha<(\eta_2+3)/4$. The mole fraction of water, x_w, can be obtained by any one of the equations in Eq. 19.

Now, the states of the water protons in the solution may be classified into three groups. To the first are assigned the protons which come in contact with the hydroxyl proton of water or the methyl proton of acetone molecules. Their chemical shift is denoted by δ_F. To the second are assigned the protons which participate in the H-bond between the H and O atoms of water molecules. Their chemical shift is δ_W. To the third are assigned the protons which participate in the H-bond between the H atom of water and the O atom of acetone. Their chemical shift is δ_C. The chemical shift of the water proton at a given concentration is given as:

$$\delta = [(1+Y_3)\delta_F+\eta_2 Y_4\delta_C+\alpha\eta_1\delta_W]/(1+\alpha\eta_1+Y_3+\eta_2 Y_4) \quad (20)$$

By the use of boundary conditions, the unknown parameters, δ_W and δ_C, in Eq. 20 may be represented in terms of the chemical shift of pure water, δ_1, and that extrapolated to $x_w=0$, δ_0, i. e.:

$$x_w \to 1 \qquad \alpha \to 1 \qquad \delta \to \delta_1$$
$$x_w \to 0 \qquad \alpha \to (\eta_2+3)/4 \qquad \delta \to \delta_0$$

It follows, therefore, from Eq. 20 that:

$$\eta_1\delta_W = (1+\eta_1)\delta_1 - \delta_F \quad (21)$$

and that:

$$\eta_2\delta_C = (\eta_2+3)\delta_0 - 3\delta_F \quad (22)$$

The substitution of Eqs. 21 and 22 into Eq. 20 gives the final expression of δ for the water-acetone system:

$$\delta = [(1+Y_3-\alpha-3Y_4)\delta_F + \alpha(1+\eta_1)\delta_1 + Y_4(\eta_2+3)\delta_0]/(1+\alpha\eta_1+Y_3+\eta_2 Y_4) \quad (23)$$

Equation 23 contains three unknown parameters, δ_F, η_1 and η_2; the latter two must be estimated so as to give the best fit of the NMR data. If the protons in the first group can be assumed to be equivalent to the gaseous state, the chemical shift of the water vapor may be used in place of δ_F.

3) The Water-Dioxane System.—The molecular parameters assumed for the water-dioxane system are:

Water	$Q_H^W = 2$	$Q_O^W = 2$
Dioxane	$Q_H^D = 10$	$Q_O^D = 4$

and $Z=4$. We also assume that all of the interchange energies except U_{HO}^{WW} and U_{HO}^{WD} are negligibly The parameters to be determined are, then:

$$\eta_1 = \exp(-U_{HO}^{WW}/kT)$$

and:

$$\eta_2 = \exp(-U_{HO}^{WD}/kT)$$

By the same mathematical treatment as in Sec. 2, the theoretical dilution curve for the water-dioxane system may be derived as:

$$\delta = [(1+Y_3-\alpha-5Y_4/2)\delta_F + \alpha(1+\eta_1)\delta_1 + Y_4(\eta_2+5/2)\delta_0]/(1+\alpha\eta_1+Y_3+\eta_2 Y_4) \quad (24)$$

where:

$$Y_3 = 5(\alpha-1)(\eta_2+1)/(2\eta_2-7\alpha+5)$$
$$Y_4 = (7\alpha-3)(\alpha-1)/(2\eta_2-7\alpha+5)$$
$$1<\alpha<(2\eta_2+5)/7$$

Experimental

In the present experiment, the chemical shifts of the water proton in the water-acetone and water - 1, 4-dioxane mixtures were measured as a function of the composition (the concentration in mole fraction) of the mixture. The mixtures were prepared gravimetrically from the purified materials. Acetone was distilled twice with calcium sulfate, and 1, 4-dioxane, with metallic sodium, in order to remove traces of water. Water was distilled twice from the alkaline potassium permanganate solution.

The NMR shifts were obtained by using a Japan Electron Optics High Resolution NMR Spectrometer, JNM-3, operating at 40 Mc. The line separations were measured by the side-band technique, using cyclohexane as an external reference. The shifts were measured to an accuracy of ± 0.4 c. p. s., and each shift was corrected for the difference in the bulk diamagnetic susceptibilities of the reference and the solution.

Results and Discussion

In the present study, we applied Eq. 18 to the dilution curve of ethanol in carbon tetrachloride reported by Becker et al.[14] In Fig. 1, the chemical shift of the OH proton in the ethanol - carbon tetrachloride system determined by them is replotted against the concentration of ethanol. The

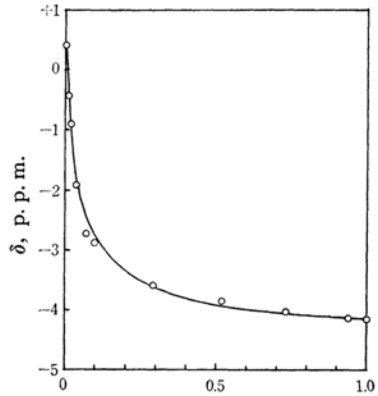

Fig. 1. The dilution curve of OH proton signal in C_2H_5OH—CCl_4 system at 27°C. The chemical shifts are referred to the central peak of the CH_3 triplet in ethanol.
○ Observed[14]
— Calculated from Eq. 18 with $\eta=180$.

most reliable value of η was found to be 180, corresponding to the interchange energy, U_{HO}, of about -3090 cal./mol. bonds at 27°C. The results calculated over the entire concentration range of ethanol is illustrated by the solid line in Fig. 1. Although slight deviations from the experimental values could not be eliminated, the agreement between the calculated and experimental curves is almost entirely satisfactory. Liddel and Becker[15] obtained 3.6 ± 0.8 kcal./mol. for the H-bond energy of this system on the basis of their infrared spectroscopic measurements.

15) U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1957).

The chemical shifts of water protons in water-acetone and water-dioxane mixtures, with reference to cyclohexane, at various concentrations x_w (mole fraction of water), are summarized in Table I.

Table I. Chemical shifts of water in the water-acetone mixture at 25°C and in the water-dioxane mixture at 35°C

Water-Acetone		Water-Dioxane	
x_w	$-\delta$, p.p.m.	x_w	$-\delta$, p.p.m.
0.020	1.415	0.068	1.168
0.050	1.521	0.102	1.314
0.100	1.668	0.145	1.459
0.149	1.823	0.190	1.607
0.197	1.961	0.237	1.747
0.249	2.100	0.295	1.929
0.296	2.198	0.342	2.026
0.315	2.270	0.393	2.129
0.391	2.384	0.493	2.332
0.486	2.607	0.595	2.531
0.605	2.765	0.693	2.729
0.703	2.910	0.795	2.934
0.805	3.090	0.898	3.154
0.904	3.258	1.000	3.360
1.000	3.391		

The concentration dependences of the water signals are also represented in Figs. 2 and 3. On applying Eqs. 23 and 24 to the water-acetone and water-dioxane systems respectively, we have used the value of +0.603 p.p.m. for δ_F, which has been determined by Schneider et al.[16] We have used the values, of −1.31 p. p. m. for δ_0 in Eq. 23 and −0.76 p. p. m. for that in Eq. 24, which have been determined by the extrapolation of the experimental dilution curves. The value of δ_0 for the water-acetone system agrees well with that (−1.308 p. p. m.) determined by Holmes et al.[5] The theoretical dilution curve calculated from Eq. 23 is given by the solid line in Fig. 2, and that calculated from Eq. 24, in Fig. 3. For the water-acetone system, the most reliable set of η_1 and η_2 vaules are found to be 1200 for η_1 and 500 for η_2; these values correspond to the interchange energies of −4200 and −3680 cal./mol. bonds respectively at 25°C. For the water-dioxane system, we find that $\eta_1=1300$ and $\eta_2=200$, corresponding to the interchange energies of −4400 and −3200 cal./mol. bonds respectively at 35°C.

Although the present treatment is an approximate one in nature, the agreement between calculated and experimental dilution curves seems almost entirely satisfactory over nearly all the concentration range. The slight deviations observed may be ascribed to the assumptions included in these treatments. The thermodynamic properties of hydrogen bonds have been determined by a number of authors, and the results have been summarized by Pimentel and McClellan.[17] However, the

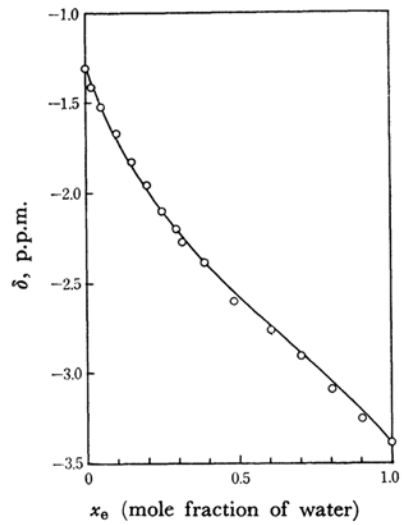

Fig. 2. The dilution curve of H_2O proton signal in H_2O—$(CH_3)_2CO$ system at 25°C. The chemical shifts are referred to the cyclohexane.
○ Observed
— Calculated from Eq. 23 with a set of $\eta_1=1200$ and $\eta_2=500$.

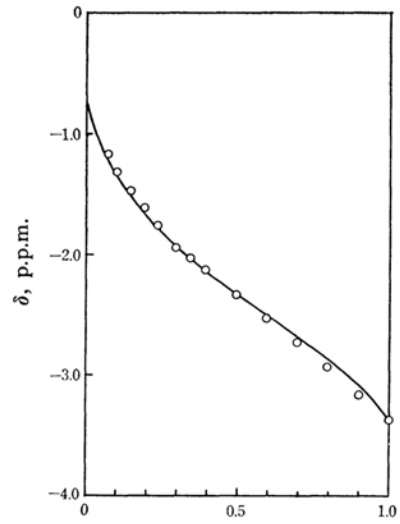

Fig. 3. The dilution curve of H_2O proton signal in H_2O-$C_4H_8O_2$ system at 35°C. The chemical shifts are referred to the cyclohexane.
○ Observed
— Calculated from Eq. 24 with a set of $\eta_1=1300$ and $\eta_2=200$.

16) W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

17) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco and London (1960).

interchange energies obtained above are not directly comparable with them because of the considerable scattering of ΔH values. The values of the interchange energies obtained from the present discussion are in the order of H_2O-H_2O > H_2O-$(CH_3)_2CO$ > H_2O-$C_4H_8O_2$ > C_2H_5OH-C_2H_5OH, indicating that the strength of hydrogen bonding is in this order.

Summary

The generalized quasi-chemical approximation has been applied to the ethanol - carbon tetrachloride, water-acetone and water-dioxane systems for the elucidation of NMR dilution curves. The theoretical dilution curves can be derived as the function of the interchange energies and the proton fraction by assuming appropriate molecular models. The values of the interchange energies were determined so as to give the best fit of NMR data. The most reliable set of interchange energies so determined were −3090 cal./mol. bonds at 27°C for the ethanol - carbon tetrachloride system, −4200 and −3680 cal./mol. bonds at 25°C for the water-acetone system and −4400 and −3200 cal./mol. bonds at 35°C for the water-dioxane system. The agreements between the calculated and experimental dilution curves were almost entirely satisfactory over the entire concentration range. On the basis of the values of the interchange energies obtained in the present study, the strength of hydrogen bonding was found to be in the order of water-water > water-acetone > water-dioxane > ethanol-ethanol.