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Solvation of Carboxylic Acids in Nonaqueous Binaries. Solvation Models for Butyric and Trichloroacetic Acids in Nitrobenzene–Toluene Mixtures

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The partitions of trichloroacetic and butyric acids between aqueous solutions and various nitrobenzene-toluene mixtures have been carried out at 25.0 and 30.0 °C, respectively. The observed nonlinearities for both acids of the monomer partition constants and the dimerization constants with the nitrobenzene mole fraction are interpreted in terms of the fractionation factors of effective exchangeable solvation sites of the involved species. Butyric acid monomer is concluded to have three sites for the solvation of the carboxylic hydrogen, carboxylate region, and alkyl chain. Desolvation of the former two sites is necessary for the formation of the dimer for which only two sites corresponding to its two alkyl chain are identified. The solvation sites of trichloroacetic acid monomer and dimer are identical and a singly hydrogen-bonded structure for the dimer is deduced. Dimerization of this acid in the organic phase proceeds by desolvation of what is equivalent to the sites of only one monomer.

Considerable attention has been devoted to solute–solvent interactions in binary solvent mixtures. The larger solute stabilization derived from one of the solvent components compared to that from the other is known to lead to the phenomenon of preferential solvation. This phenomenon is of paramount importance in interpretation of many kinetic data measured in these binaries.[1] Although several studies pertaining to this phenomenon have been reported,[1–3] a refined picture of various solute–solvent interactions has not as yet emerged.

Recently, partition data of acetic acid between aqueous solutions and various nitrobenzene–toluene mixtures have been interpreted in terms of Gross–Butler formalism to deduce various exchangeable sites involved in solvation of the monomer and the dimer in such binaries.[4] Although developed, long time ago, for studying reactions in H_2O–D_2O mixtures,[5–7] this formalism seems to provide a quantitative approach for elucidation of various interactions involved in solute solvation in these extracting binaries. Two assumptions are considered (i) the solvation number of a solute is the same in pure binary components and (ii) solvent exchange processes at various sites take place independently and on the basis of one by one replacement of solvent molecules.

In the present work, the applicability of the above aproach in studying the solvation of butyric and trichloroacetic acids in these binaries are confirmed. The results are compared with those reported for acetic acid in order to examine the effect of solute structural change on the observed solvation behavior.

Experimental

Materials. Nitrobenzene, toluene (Riedel De Haen AG), butyric and trichloroacetic acids (BDH) were used without additional purification.

Procedure. Extracting mixtures of nitrobenzene and toluene as well as aqueous solutions of butyric and trichloroacetic acids were prepared by weight. Appropriate amounts of sodium chloride and hydrochloric acid were added to butyric acid aqueous solution so that their final concentrations were 0.09 and 0.01 mol dm^{-3}, respectively. No sodium chloride was added to trichloroacetic acid solution and the concentration of hydrochloric acid was 0.8 mol dm^{-3}. Partition experiment was made by stirring equal volumes of aqueous and organic phases (20 cm^3 each) in a stoppered conical flask for 1 h with a magnetic stirrer. The contents were transferred into a test tube sealed tightly with a high quality rubber stopper and thermostated at the desired temperature where it is shaked several times before it is allowed to settle overnight for complete phase separation. Carboxylic acid content in the organic phase was determined by titrating a known volume of that phase with NaOH using phenolphthalein indicator. The corresponding concentration in the aqueous phase was determined by difference from initial aqueous phase acid concentration. Blank partition experiments using various extracting mixtures were carried out similarly in the absence of carboxylic acids and no acid (due to HCl) in organic phases was detected. For the determination of association constants of these acids with toluene and nitrobenzene similar partition experiments were carried out using organic phases composed of cyclohexane containing various concentrations of either toluene or nitrobenzene.

Results

The partition coefficient, $D^{(n)}$, of a carboxylic acid between an aqueous solution and a binary mixture of toluene and nitrobenzene (mole fraction n) is related to the partition constant of monomer, $K_d^{(n)}$, and the dimerization constant in the organic phase, $K_{dim}^{(n)}$, by Eq. 1[8]

$$D^{(n)} = (K_d^{(n)} + 2(K_d^{(n)})^2 K_{dim}^{(n)}[HA]_{aq})/(1+K_a/[H^+]), \qquad (1)$$

where $[HA]_{aq}$ is the concentration of undissociated acid in the aqueous phase. The partition data of butyric acid were obtained under conditions where its ionization in the aqueous phase was negligible i.e. $[H^+] \gg K_a$. On the other hand, ionization of tri-

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Table 1. Partition Coefficients of Butyric Acid between Various Binary Mixtures of Toluene and Nitrobenzene (Mole Fraction n) and 0.1 mol dm^{-3} (Na$^+$, H$^+$)Cl$^-$ Aqueous Solutions Containing Various Butyric Acid Concentrations at 30.0 °C

n	10D (10[Butyric Acid]$_{aq}$/mol dm^{-3})
0.000	4.51, 4.74 (0.37); 7.30, 7.09 (0.63); 9.23, 9.17 (0.85); 11.1, 11.1 (1.03); 12.2 (1.22); 13.4 (1.39); 14.9 (1.52).
0.040	5.00 (0.36); 7.55 (0.62), 9.31 (0.84); 9.93 (0.95); 12.2 (1.22).
0.081	5.34 (0.35); 7.48 (0.62); 9.36 (0.83); 10.5 (1.05); 11.7 (1.24).
0.142	5.60 (0.35); 7.62 (0.61); 9.13 (0.84); 10.7 (1.04); 12.3 (1.21).
0.151	7.60 (0.61); 9.34 (0.84); 10.9 (1.03); 13.5 (1.38); 14.5 (1.54).
0.299	5.51 (0.35); 7.51 (0.62); 9.29 (0.84); 10.5 (1.05); 11.7 (1.24).
0.369	7.83 (0.61); 9.41 (0.84), 11.0 (1.03); 12.0 (1.25); 13.1 (1.41); 13.8 (1.59).
0.499	8.18 (0.59); 9.45 (0.83); 11.1 (1.02); 13.2 (1.39); 14.0 (1.57).
0.500	6.06 (0.34); 8.06 (0.60); 9.76 (0.82); 10.2 (1.07); 12.1 (1.22).
0.698	6.81 (0.32); 8.06 (0.60); 9.18 (0.84); 10.3 (1.06); 11.5 (1.25).
0.806	8.42 (0.54); 9.32 (0.84); 11.0 (1.03); 11.9 (1.24); 12.5 (1.44); 13.6 (1.61).
0.900	6.81 (0.32); 8.21 (0.59); 9.00 (0.85); 9.88 (1.08); 11.2 (1.27).
1.00	8.59, 8.27 (0.58); 8.69, 9.07 (0.86); 10.3, 10.6 (1.05); 11.5 (1.20); 11.3 (1.27); 11.5, 11.9 (1.49); 12.4, 12.7 (1.67).

Table 2. Partition Coefficients of Trichloroacetic Acid between Various Binary Mixtures of Toluene and Nitrobenzene (Mole Fraction n) and 0.8 mol dm^{-3} HCl Aqueous Solutions Containing Various Trichloroacetic Acid Concentrations at 25.0 °C

n	10D (10[Trichloroacetic Acid]$_{aq}$/mol dm^{-3})
0.000	1.08 (0.64); 1.12 (1.12); 1.27 (1.59); 1.34 (2.06); 1.41 (2.53); 1.58 (3.13).
0.101	1.97 (0.48); 2.19 (0.95); 2.24 (1.42); 2.43 (1.87); 2.64 (2.31).
0.249	3.43 (0.29); 3.63 (0.70); 3.71 (0.98); 3.95 (1.39); 4.21 (1.63).
0.369	4.73 (0.26); 4.90 (0.64); 5.25 (0.88); 5.50 (1.25); 5.77 (1.47).
0.500	6.59 (0.32); 6.92 (0.941); 7.73 (1.21); 7.94 (1.50).
0.598	7.53 (0.22); 8.01 (0.53); 8.38 (0.73); 8.46 (1.04); 8.99 (1.22).
0.798	10.0 (0.19); 10.6 (0.47); 11.17 (0.64); 11.2 (0.91); 11.8 (1.06).
1.00	13.8 (0.52); 13.6 (0.76); 14.6 (0.94); 15.2 (1.14); 15.7 (1.40).

Table 3. $K_d^{(n)}$ and $K_{dim}^{(n)}$ Data for Butyric Acid Transfer between 0.1 mol dm^{-3} (Na$^+$, H$^+$)Cl$^-$ Aqueous Solutions and Various Binary Mixtures of Toluene and Nitrobenzene (Mole Fraction n) at 30.0 °C. A Comparision between the Calculated and Observed $K_{dim}^{(n)}(K_d^{(n)})^2$ Values

n	$K_d^{(n)}$	$K_{dim}^{(n)}$ mol^{-1} dm^3	$10K_{dim}^{(n)}(K_d^{(n)})^2$ mol^{-1} dm^3	$10K_{dim}^{(n)}(K_d^{(n)})^2_{calcd}$ mol^{-1} dm^3
0.000	0.161±0.021	170±32	—	—
0.039	0.225±0.025	81±13	41±9	43
0.081	0.230±0.028	40± 6	36±7	42
0.142	0.288±0.021	47± 5	38±6	40
0.151	0.311±0.018	37± 3	37±4	40
0.299	0.322±0.019	34± 3	35±4	36
0.369	0.431±0.035	17± 2	31±5	34
0.499	0.456±0.031	15± 2	37±5	31
0.500	0.417±0.053	18± 4	31±9	31
0.698	0.511±0.018	9.5±0.6	25±2	26
0.806	0.544±0.034	8.5±0.9	25±4	24
0.900	0.544±0.026	7.3±0.7	22±3	22
1.00	0.604±0.039	5.4±0.6	—	—

Table 4. $K_d^{(n)}$ and $K_{dim}^{(n)}$ Data for Trichloroacetic Acid Transfer between 0.8 mol dm^{-3} Aqueous Solutions and Various Binary Mixtures of Toluene and Nitrobenzene (Mole Fraction n) at 25.0 C°

n	$10^3K_d^{(n)}$	$10^2K_{dim}^{(n)}$ mol^{-1} dm^3	$10^3K_d^{(n)}K_{dim(calcd)}^{(n)}$ a) mol^{-1} dm^3
0.000	119± 4	923±73	—
0.101	235± 6	409±39	1099
0.249	424± 8	201±22	1099
0.369	582± 9	168±14	1098
0.500	798±36	124±27	1099
0.598	955±18	95±12	1096
0.798	1280±24	75±11	1098
1.00	1608±58	61±12	1101
			Av b) 1099±2

a) Calculated on the basis of Eqs. 13 and 14. b) The observed $K_d^{TL}K_{dim}^{TL}$ is 1.10±0.9.

chloroacetic acid (pK_a=0.62)8) was significant at 0.8 mol dm^{-3} HCl used for partition experiments and [HA]$_{aq}$ was accordingly calculated. Salting out effect by such concentration of electrolyte is reported to be insignificantly small.9) The partition coefficients for butyric and trichloroacetic acids by various binary mixtures as a function of the concentration of undissociated acid in the aqueous phase are presented in Tables 1 and 2, respectively. The values of $K_d^{(n)}$ and $K_{dim}^{(n)}$ at

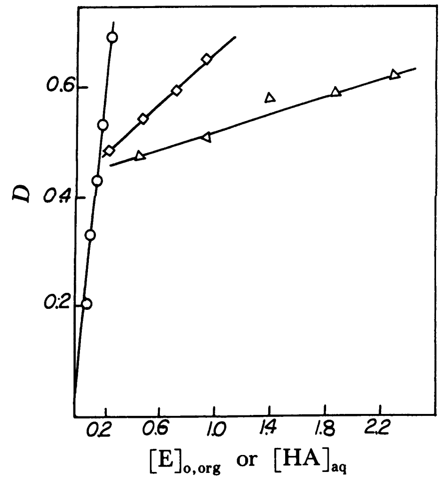

Fig. 1. Partition coefficient of butyric acid at 30 °C between cyclohexane and 0.1 mol dm^{-3} (Na$^+$, H$^+$)Cl$^-$ aqueous solution as a function of the concentration of undissociated acid in the aqueous phase; ○ and as a function of the concentration of free toluene; △ or free nitrobenzene; □ in the cyclohexane phase at a constant butyric acid concentration of 0.2 mol dm^{-3} in the aqueous phase.

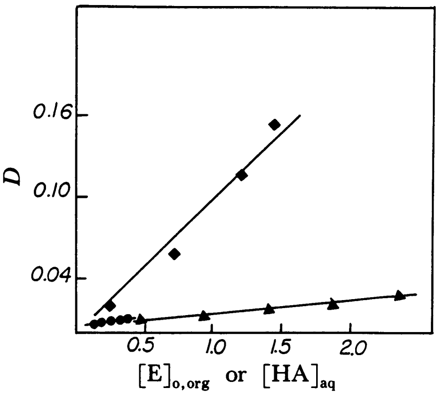

Fig. 2. Partition coefficient of trichloroacetic acid at 25 °C between cyclohexane and 1.0 mol dm^{-3} HCl aqeous solution as a function of the concentration of undissociated acid in the aqueous phase; ● and as a function of the concentration of free toluene; ▲ or free nitrobenzene; ■ in the cyclohexane phase at a constant trichloroacetic acid concentration of 0.24 mol dm^{-3}.

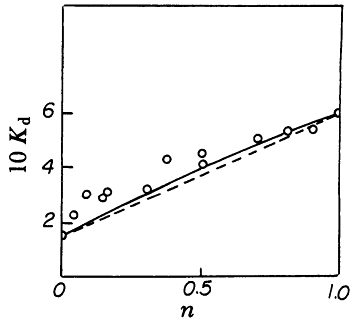

Fig. 3. Dependence of the partition constants of butyric acid monomer on the nitrobenzene mole fraction in the nitrobenzene–toluene mixture at 30 °C. The solid curve is calculated based upon the three sites model represented by Eq. 7.[†]

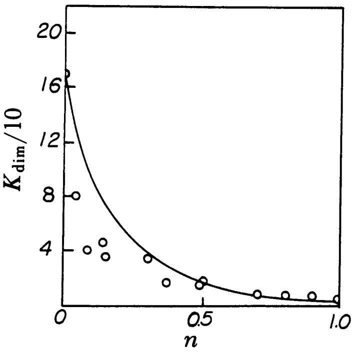

Fig. 4. Plot of the dimerization constant of butyric acid against the nitrobenzene mole fraction in the binary mixture at 30 °C. The solid curve is generated from Eq. 11.

various n were deduced from the intercepts and the slopes of linear least squares D-$[HA]_{aq}$ plots (not shown). These are listed in Tables 3 and 4.

The n dependencies of $K_d^{(n)}$ and $K_{dim}^{(n)}$ for butyric acid are portrayed in Figs. 3 and 4 while those of trichloroacetic acid are presented in Figs. 5 and 6, respectively.

Since nitrobenzene and toluene are hydrogen-bonding acceptors,[10] it is necessary in the present study to determine the association constants of each of these compounds with each of the individual acids used. These constants, determined in cyclohexane, as an inert solvent, were calculated from Figs. 1 and 2 using Eq. 2[11]

$$D = D_o + K_{ass}K_d[E]_{o,org}/(1+K_a/[H^+]), \tag{2}$$

where D_o is the partition coefficient in the absence of toluene or nitrobenzene and $[E]_{o,org}$ represents the concentration of free toluene or nitrobenzene in cyclohexane phase. The K_d values for both acids in cyclohexane were deduced from the intercepts of the corresponding D-$[HA]_{aq}$ plots shown in Figs. 1 and 2. The association constants for butyric acid with toluene and nitrobenzene are 3.3±0.4 and 9.4±0.1 mol^{-1} dm^3 at 30.0 °C while those of trichloroacetic

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[†] The systematic deviation of the observed K_d values from the fitted ones obtained from Eq. 7 can be attributed to the fact that the fitted values are calculated on the basis of a solvation model for the unhydrated monomer only while the observed value at a given solvent composition represents infact the sum of contributions generated from the solvation of both monomer and its dihydrate. The smaller the extent of hydration the smaller the difference between the observed value and the predicted value will be. The extent of hydration would be expected to decrease as the nitrobenzene mole fraction in the binary increases (I. Kojima, M. Kako, and M. Tanaka, *J. Inorg. Nucl. Chem.*, **32**, 1651 (1970)). Accordingly, the predicted K_d values approach the observed ones at higher nitrobenzene mole fractions, as shown in Fig. 3.

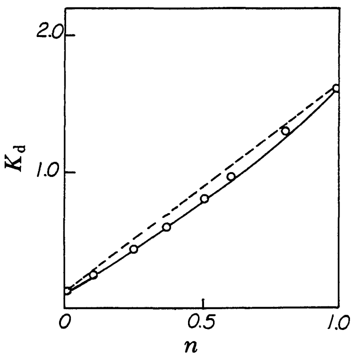

Fig. 5. Dependence of the partition constants of trichloroacetic acid monomer on the nitrobenzene mole fraction in the binary mixture at 25 °C. The solid curve is calculated from Eq. 13 representing the two site model while the dashed line represents the one site model.

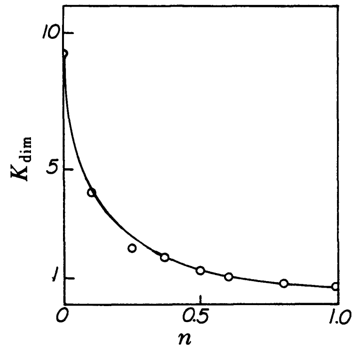

Fig. 6. Plot of the dimerization constant of trichloroacetic acid against the nitrobenzene mole fraction in the binary nitrobenzene–toluene mixture at 25 °C. The drawn curve is generated from Eq. 14.

acid are 1.96±0.09 and 25.1±1.9 $\mathrm{mol^{-1}\,dm^3}$, at 25.0 °C respectively.

Discussion

Consider a single molecular solute partitioned between an aqueous solution and a binary mixture of nitrobenzene (mole fraction n) and toluene (mole fraction $1—n$). The solute partition constant, $K^{(n)}$, according to its additive constituent nature,[12] equals to the product of contributions $A_1^{(n)}$, $A_2^{(n)}$, $A_3^{(n)}$, $\cdots$ $A_m^{(n)}$ generated from stabilization or destabilization of various structural units a_1, a_2, a_3, $\cdots$ a_m of that solute in the organic phase. The contribution from mutual interactions among various structural units is assumed to be negligible,

$$K^{(n)} = A_1^{(n)}\cdot A_2^{(n)}\cdot A_3^{(n)}\cdots A_m^{(n)}, \tag{3}$$

where (n) is just a superscript refering to the binary solvent composition. If each of the solute structural units is assumed to have only one effective exchangeable solvation site, any single contribution $A_i^{(n)}$ will equal to the mole fraction weighted average of contributions of a_i in pure nitrobenzene, A_i^{NB} and in pure toluene, A_i^{TL}:

$$\begin{aligned} A_i^{(n)} &= (1-n)A_i^{\mathrm{TL}} + n\,A_i^{\mathrm{NB}} \\ &= A_i^{\mathrm{TL}}\,(1-n+\Phi_i n), \end{aligned} \tag{4}$$

where $\Phi_i = A_i^{\mathrm{NB}}/A_i^{\mathrm{TL}}$ reflects the preference of structural unit a_i for solvation by nitrobenzene relative to that preference for solvation by toluene. It might be considered as a solvation fractionation factor for structural unit a_i. $K^{(n)}$ can thus be expressed in terms of all possible solvation sites as follows:

$$K^{(n)} = K^{\mathrm{TL}} \prod_i^{v} (1-n+\Phi_i n), \tag{5}$$

where K^{TL} is the solute partition constant when pure toluene is used and v is the number of solvation sites, each contributing a $(1—n+\Phi_i n)$ term to the observed $K^{(n)}$. The magnitude of Φ_i is determined by the electronic and geometric factors involved in both the site under consideration and the exchangeable solvents as well.

In the present study, when Φ_i is greater than unity, the i-th site will be stabilized to a greater extent by nitrobenzene than by toluene and vice versa. As Φ_i approaches one, the site will be equally stable in both solvents and no contribution to $K^{(n)}$ will be seen.

It may be noted that Eq. 5 is a special form of the general Gross-Butler equation originally derived for studying chemical reactions in H_2O–D_2O mixtures and is currently used in the well known proton inventory technique.[5–7] Equation 5 predicts that $K^{(n)}$ will vary linearly with n if the partitioning solute has only one solvation site and nonlinearly if the solute have multisolvation sites.

When a solute dimerizes in such binary mixture, the extent of dimerization is governed by the contributions generated from solvation of various structural units composing the monomer and the dimer. It can be shown, in analogy with the above derivation that the dimerization constant, $K_{\mathrm{dim}}^{(n)}$, in a given nitrobenzene–toluene mixture is related to the dimerization constant in pure toluene, $K_{\mathrm{dim}}^{\mathrm{TL}}$, by a series of correction factors,

$$K_{\mathrm{dim}}^{(n)} = K_{\mathrm{dim}}^{(n)} \prod_i^{v} (1-n+\Phi_j^{D} n)\Big/\prod_i^{v}(1-n+\Phi_i^{M} n), \tag{6}$$

where each correction factor $(1—n+\Phi_i^{D} n)/(1—n+\Phi_i^{M} n)$ represents the contribution of i-th site in the dimer relative to that contribution in the monomer. The total number of sites v in mumerator and denominator is not necessary to be the same since any $(1—n+\Phi_i\,n)$ term may be either contributing if $\Phi_i \neq 1$ or not contributing if $\Phi_i = 1$.

Solvation of Butyric Acid. The nonlinear n dependence of partition constant of butyric acid monomer, $K_{\mathrm{d}}^{(n)}$, portrayed in Fig. 3 suggests the involvement of two or more sites for monomer solvation. It is therefore, necessary to formulate a chemically reason-

Table 5. Comparison of Sum of Squared Residuals after Regressions Representing Various Mathematical Monomer Solvation Models

Proposed model	Values	Sum of squared residual
	Butyric acid[a)]	
Two sites	$\Phi_2=1.30$	6.5×10^{-2}
Three sites A	$\Phi_2=4.32$; $\Phi_3=0.30$	7.5×10^{-2}
Three sites B	$\Phi_2=2.16$; $\Phi_3=0.60$	3.9×10^{-2}
Three sites C	$\Phi_2=1.62$; $\Phi_3=0.80$	5.7×10^{-2}
	Trichloroacetic acid	
One site	$\Phi=13.48$	2.2×10^{-2}
Two sites D	$\Phi_1=14.00$; $\Phi_2=0.96$	3.1×10^{-2}
Two sites E	$\Phi_1=12.85$; $\Phi_2=1.05$	1.2×10^{-2}
Two sites F	$\Phi_1=11.00$; $\Phi_2=1.23$	1.2×10^{-3}
Two sites G	$\Phi_1=9.00$; $\Phi_2=1.50$	1.1×10^{-2}

a) A value of 2.90 is used for Φ_1 in all butyric acid models.

able solvation model capable of reproducing the experimental data. Possible models may include a site for the carboxylic hydrogen and one or two sites for the remainder of the molecule. A reasonable estimate for the fractionation factor of carboxylic hydrogen site, Φ_1, is obtained from the ratio of the association constants of butyric acid with nitrobenzene and toluene in the inert solvent cyclohexane. This ratio (2.9) is used for this site in all proposed models, listed in Table 5. The other fractionation factors Φ_2 and Φ_3 corresponding to the other sites are derived so that the product of all fractionation factors for any single model is equal to $K_{\text{d}}^{\text{NB}}/K_{\text{d}}^{\text{TL}}$ ratio. In order to arrive at the most probable solvation model, the sums of squared residuals after various regressions were computed and compared. The minimum sum of squared residuals is exhibited by model B. Substitution of various values of n in Eq. 7 duplicates reasonably the experimental data, as illustrated in Fig. 3.

$$K_{\text{d}}^{(n)} = K_{\text{d}}^{\text{TL}}(1-n+2.90n)(1-n+2.16n)(1-n+0.6n) \tag{7}$$

It is of interest to compare this equation with that reported earlier for solvation of acetic acid monomer in the same binaries,[4)] Eq. 8.

$$K_{\text{d}}^{(n)} = K_{\text{d}}^{\text{TL}}(1-n+2.85n)(1-n+1.91n) \tag{8}$$

The additional term in Eq. 7 with a fractionation factor of 0.6 must reflect the contribution generated from the solvation site of alkyl chain in butyric acid. A reasonable estimate for the fractionation factor of this site can be independently produced from the ratio of contributions of this alkyl chain to K_{d}'s in nitrobenzene and toluene. These contributions can be obtained from the K_{d}'s of acetic and butyric acids in both solvents using Hansch equation;[12)]

$$\Phi_3^{\text{calcd}} = \frac{\text{Antilog}(\log K_{\text{d.But}}^{\text{NB}} - \log K_{\text{d.Acet}}^{\text{NB}})}{\text{Antilog}(\log K_{\text{d.But}}^{\text{TL}} - \log K_{\text{d.Acet}}^{\text{TL}})}. \tag{9}$$

The excellent agreement between the calculated value of 0.7±0.1 and the one obtained from model B, 0.6±0.1, offers a support for the proposed solvation model of butyric acid monomer in these binaries.

The similarity in the second terms of Eqs. 7 and 8 implies their contributing sites are nearly identical. These terms are more likely to arise from interactions of carboxylate region of the monomer with the exchangeable solvent molecules.

In order to deduce a suitable solvation model for butyric acid dimer, it is necessary to determine the various fractionation factors involved. The product of these factors obtained from Eq. 6 (n=1) equals 0.45±0.13. Because of the known cyclic and the nearly symmetrical nature of this dimer,[13)] an even number of solvation sites might be anticipated. The value of 0.45 is more likely, therefore, to represent the product of at least two similar fractionation factors (0.67±0.14 each) corresponding to two identical sites. This predicted value for each site is very close to the fractionation factor for alkyl chain solvation site in the monomer obtained from both Eq. 9 and the above $K_{\text{d}}^{(n)}$–n analysis. It is not unreasonable, therefore, to assign this obtained fractionation factor product to solvation sites of the two alkyl groups present in the dimer. According to this picture, no contribution is seen from the other two sites involved in monomer solvation. This seems to be consistent with the conclusion drawn earlier for the dimerization of acetic acid in such binaries that desolvation of its two monomer sites is necessary for the formation of the dimer.[4)] The n dependence of $K_{\text{dim}}^{(n)}$ may thus be represented by:

$$K_{\text{dim}}^{(n)} = K_{\text{dim}}^{\text{TL}}(1-n+0.67n)^2/((1-n+2.90n)(1-n+2.16n)(1-n+0.6n))^2, \tag{10}$$

where the denominator represents the contribution from solvation of two butyric acid monomers. Since the contribution of alkyl chain in both the dimer and monomer is nearly the same, the alkyl chain terms in Eq. 10 could be cancelled out and the n dependence of $K_{\text{d}}^{(n)}$ can be expressed by Eq. 11

$$K_{\text{dim}}^{(n)} = K_{\text{dim}}^{\text{TL}}/((1-n+2.90n)(1-n+2.16n))^2, \tag{11}$$

which duplicates reasonably the experimentally determined $K_{\text{dim}}^{(n)}$ data by substitution of various values of n, as shown in Fig. 4. The excellent agreement between $K_{\text{dim}}^{(n)}(K_{\text{d}}^{(n)})^2$ values, calculated from Eq. 12,

$$K_{\text{dim}}^{(n)}(K_{\text{d}}^{(n)})^2_{\text{calcd}} = K_{\text{dim}}^{\text{TL}}(K_{\text{d}}^{\text{TL}})^2(1-n+0.67n)^2, \tag{12}$$

and the corresponding experimental ones, displayed in Table 3 lend another support to the proposed solvation model of butyric acid dimer in these binaries.

Solvation of Trichloroacetic Acid. The curved $K_d^{(n)}$-n relationship, depicted in Fig. 5 implies the presence of more than one solvation sites for the monomer. It is therefore necessary to formulate a solvation model that is both statistically and chemically acceptable. The fractionation factors of carboxylic hydrogen solvation site for various two sites models, listed in Table 5, are derived either from the ratio of association constants of this acid with nitrobenzene and toluene or from other assumed value in the neighborhood of that ratio. It transpires form Table 5 that regression F represents the most probable model. The experimentally determined $K_d^{(n)}$ values fit nicely the curve generated from

$$K_d^{(n)} = K_d^{TL}(1-n+11.0n)(1-n+1.23n). \qquad (13)$$

The product of fractionation factors for the dimer sites is predicted from Eq. 6 (n=1) to be ca. 12, a value very close to that obtained for the monomer sites. This speaks for the similarity in the solvation sites of both species and is consistent with a singly hydrogen-bonded structure for the dimer in nitrobenzene–toluene binaries. Formation of the two hydrogen bonds linking the two monomers is known to be favorable when the dimer has an eight membered cyclic structure.[14] The presence of nitrobenzene in such solvent binaries would tend, however, to form with the acid monomer a stronger hydrogen bond than those formed between the two monomeric entities. This occurs because of the higher hydrogen bonding acceptor basicity of nitrobenzene compared to that of trichloroacetic acid monomer itself.[10] Two effects are thus generated i) a dramatic decrease in the extent of dimerization as the nitrobenzene mole fraction increases in the binary and ii) formation of an open singly hydrogen-bonded dimer. According to this view dimerization proceeds by desolvation of what is equivalent to the sites of one monomer. The n dependence of $K_{dim}^{(n)}$ could thus be represented by:

$$K_{dim}^{(n)} = K_{dim}^{TL}/((1-n+11.0n)(1-n+1.23n)). \qquad (14)$$

Substitution of n values in Eq. 14 duplicates reasonably the experimentally determined $K_{dim}^{(n)}$ values, as shown in Fig. 6. Equation 14 predicts that:

$$(K_{dim}^{(n)} K_d^{(n)})_{calcd} = K_{dim}^{TL} K_d^{TL} = \text{constant}.$$

This is born out to be true as illustrated in Table 4.

In summary, the present work offers an approach towards elucidation of various solute–solvent interactions involved in binary nonaqueous mixtures. The nonlinear n dependence of both $K_d^{(n)}$ and $K_{dim}^{(n)}$ for butyric and trichloroacetic acids has been quantitatively rationalized in terms of fractionation factors of various solvation sites of involved species using Gross–Butler formalism. The interactions of the studied species with nitrobenzene are certainly different from those with toluene and require reorientation of solvent molecules upon exchanges. This factor does not seem to materially affect the results reported here.

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