components. A portion of the changes in frequency may be explained simply by the ionization of the carboxylic acid group. This alone does not explain the large broadening actually observed. This inherent broadening of the Raman peaks and the multiplicity of shoulders at 0.4° of neutralization suggest a multiplicity of different structures exists at this degree ionization. When the degree of ionization is either increased or decreased, the number of structures decreases. This multiplicity of structures would normally be characteristic of a randomization of the structure.

Thus the Raman solution data would suggest a locally regular helical conformation, unaffected by neutralization, up to a degree of neutralization of 0.1. In the region $\alpha = 0.1$ to 0.4 an increasing multiplicity of structures is present. As neutralization proceeds in the range $\alpha = 0.4$ to 1.0, the number of structures decreases until an ordered structure characteristic of the polysalt is obtained. This interpretation is consistent with the observations of Liquori and his coworkers that PMAA undergoes a transformation from a tight coil, characterized by hydrophobic interactions, to an extended structure during neutralization. However, our results suggest that this transformation is not cooperative as is postulated for the denaturation of globular proteins, since our data indicate a progressive randomization of structure in this neutralization range.

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Heat Capacity Changes Associated with the Solvolysis of *t*-Butyl Chloride in Binary Alcohol–Water Systems[1]

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Abstract: The heat capacity of activation for the solvolysis of *t*-butyl chloride in the high water range of alcohol–water mixtures shows dramatic changes in value over the alcohol concentration range where quasi-aqueous structure is replaced by other solvent interactions. The corresponding changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were found to be less complex than previously reported. The mechanistic implications of the changes in quasi-thermodynamic terms are discussed. A brief description is given for an automatic, random-access system for rate determination by conductance.

The work reported here is a natural extension of our systematic search for relationships between structure, mechanism, and the accompanying solvent reorganization attending the activation process for hydrolyses in water.[3] The point of departure was the suggestion that evidence of solvent reorganization was more likely to be apparent in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ than in $\Delta F^{\ddagger}$. While this is undoubtedly true, experience soon proved that for solvolyses in water, the temperature dependence of $\Delta H^{\ddagger}$ ($\Delta C_p^{\ddagger}$) was a much more sensitive indicator of solvent reorganization[4] than either $\Delta H^{\ddagger}$ or $\Delta S^{\ddagger}$.[6] That such a correlation exists can be related to the special nature of initial state solvation of nonelectrolytes in aqueous solutions.[7–12]

In water, weakly polar solutes such as the reactive halides may be pictured as surrounded by a hydrogen-bonded solvent shell in which

$$\text{water–water interaction} > \text{water–solute interaction} \qquad (1)$$

There is no implication here as to the "thickness" of the shell; modification of the adjacent water molecules is the major effect. Nor do we imply that water–solute interaction is absent.[13] While admittedly an abstraction, we choose to discuss the temperature effects on this system in terms of the stability of the solvent shell. We neglect any speculation as to the exact nature of the solvent shell where we are dealing with mixed solvents. Our system does not provide an answer to such questions. We do assume that the stability of this solvent shell is temperature dependent, decreasing as the temperature increases. A similar trend is found for the structure of the bulk solvent with which the molecules in the solvent shell are in equilibrium. Granted that the breakdown of the initial state solvation shell determines in part the enthalpy required in the activation process, then this

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(3) R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967).

(4) Note: The initial determination of the heat capacity of activation ($\Delta C_p^{\ddagger}$) for the solvolysis of *t*-butyl chloride in the ethanol–water systems in the high water region was done by Martin.[5]

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term will decrease as the temperature increases. We believe this to be the physical basis for a large part of the observed negative temperature coefficient of $\Delta H^{\ddagger}$ in such reactions.[16] The paths by which the necessary charge development is achieved and the differences in the extent of the accompanying solvent reorganization provide a guide for mechanistic distinction, in terms of relative values of $\Delta C_p^{\ddagger}$, *i.e.*, the heat capacity of activation.

In this paper we report the temperature coefficient of the enthalpy of activation for the solvolysis of *t*-butyl chloride in a series of alcohol–water mixtures. The study is limited to the high water concentration range where the system changes over from one in which three-dimensional cooperative hydrogen bonding is dominant to the range where quasi-aqueous structure disappears. This study permits an extension of those hypotheses developed to account for similar results in water. It also complements the earlier work of Kohnstam[17] who made an extensive study of temperature effects for solvolyses in solvent systems where the concentration of the organic component effectively cancels out any semblance to water structure.[18]

Evidence bearing on solvolytic effects obtained from rate studies necessarily reveal only solvation differences between the initial and the transition states. This fact should be self-evident. There is no need to restate here the corollary that a knowledge of initial state differences is required for an interpretation of kinetic parameters. In practice initial-state solvation data are frequently lacking and, worse, are frequently unavailable in terms of current technology. This deficiency places limitations on quantitative distinctions but is not an insuperable block to the recognition of general trends. Where substituents in the reactant introduce special initial-state solvation interaction, this fact is usually apparent, and a corresponding effect on $\Delta C_p^{\ddagger}$ can be anticipated in a general way.[1,19]

Solvation in Alcohol–Water Mixtures

A consideration of the magnitude of the excess functions defining the mixing of alcohols (x_2 = mole fraction of alcohol) with water in the concentration range $x_2 = 0\text{–}0.2$ shows a complex behavior in which the dominant features are best understood in terms of a slightly modified aqueous system; *i.e.*, the system tends to preserve what has been figuratively described as a three-dimensional hydrogen-bonded structure, while accommodating the alkyl group of the alcohol. We can visualize the -OH group of the alcohol as fitting into the hydrogen-bonded network of water structure while the water forms a continuous hydrogen-bonded shell about the alkyl group.[20] For the case of ethanol–water binaries, the solution process of the alcohol at low temperatures in the high water range is exothermic but tends to become endothermic as the temperature increases or the concentration of alcohol increases.[22,23] Increasing temperature opposes structure formation; increasing concentration of alcohol taxes further the limited capacity of the aqueous system to accommodate the weakly polar alkyl group while maintaining significant three-dimensional interactions. In both cases, the three-dimensional structure is the dominant characteristic. In the high water range of such systems, it is the entropy change accompanying the process rather than the more easily measured enthalpy change which is the limiting factor to solubility as it is in limiting the solubility of weakly polar molecules in water.[24] The presence of such a solute in water tends to interfere with the librational freedom, resulting in an apparent "freezing" water solvent about the solute.[7] An equivalent statement would be that it lowers the structural temperature of adjacent water molecules.[25] These rationalizations were proposed to account for the fact that the solution of, *e.g.*, methyl bromide is exothermic ($\Delta H_s = 6.3$ kcal mol^{-1})[26] but becomes less exothermic as the temperature increases; *i.e.*, ΔC_p for the solution process is positive. (For the above example, $\Delta C_p = +44.2$ cal deg^{-1} mol^{-1}.[27]) The exothermic nature of the solution process and the temperature sensitivity of ΔH_s are both consistent with the idea that the presence of the alkyl group stabilizes the *adjacent* hydrogen-bonded solvent shell.[28] The apparent enhancement of cooperative structure which occurs about the isolated alkyl halide in water is also found when alcohols are added to water. Over the range $x_2 = 0\text{–}0.15$ this fact is reflected in such physical properties as viscosity,[29] partial molar volume,[30,31] abnormal absorption of ultrasound,[32] and the change in the heat of solution.[22,33]

In the range where quasi-aqueous structure is maintained, the additions of a third component to the alcohol–water system will differ in detail only, from solution in water. In both solvents the effect of solvent structure appears to be dominant, at least at low temperatures. A simple hypothesis would suggest that as structural requirements become successively more stringent, less heat will be given out and the entropy will become successively less favorable. Ben-Naim and Baer[34] found that the solubility of argon in a series of ethanol–water mixtures at first increased ($x_2 = 0\text{–}0.02$) and then decreased ($x_2 = 0.02\text{–}0.15$). The double inflection was most apparent at 6°. Extrema in the solubility *vs.* alcohol concentration curve have been found for other compounds, notably by Mikhailov.[29]

Variation in size and polarizability provide for individual variation, but in all cases the results require a

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[16] This proviso is necessary since it will be apparent from our results as was already shown by Kohnstam[17] that $\Delta C_p^{\ddagger}$ for solvolysis in mixed solvents has a value of about -30 to -40 cal deg^{-1} mol^{-1} over the concentration range of aqueous binaries where all evidence of three-dimensional quasi-aqueous structure has disappeared.

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(21) F. Franks, *Ann. N. Y. Acad. Sci.*, **125**, 277 (1965).

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(33) G. L. Bertrand, F. J. Millero, C. Wu, and L. S. Hepler, *J. Phys. Chem.*, **70**, 699 (1966).

(34) A. Ben-Naim and S. Baer, *Trans. Faraday Soc.*, **60**, 1736 (1964).

consideration of the structural nature of the solvent, and in this respect, at least, are related to corresponding results in water. This is the ready explanation for the changes in ΔC_p for solvation of argon in a series of alcohol–water mixtures shown in Table I. The initial addition of ethanol ($x_2 = 0.0$–0.1) causes an increase in the sensitivity of ΔH_s to temperature; dependence decreases rapidly with increasing concentration of ethanol. These temperature effects presumably reflect corresponding structural changes in the binary mixture.

Table I. Estimated[a] Values of Heat Capacity for the Gas–Solution Equilibrium of Argon in a Series of Alcohol–Water Mixtures

Ethanol, mole fraction	ΔC_p, cal deg^{-1} mol^{-1}	Ethanol, mole fraction	ΔC_p, cal deg^{-1} mol^{-1}
0	70	0.15	51
0.05	82	0.20	40
0.10	70	0.25	26

[a] Based on graphs in ref 34.

With larger molecules such as the alkyl halides dissolving in these water–ethanol mixtures, other factors appear to be involved although these have not been identified. In contrast to Ben-Naim's results for argon, we found no evidence of a solubility minimum for cyclohexyl bromide at 18° (Table II) but rather a solubility pattern resembling that of argon at 26°.[34] We did find a rapid shift in the solubility characteristics where the quasi-aqueous structure presumably disappeared.[18]

Table II. Solubility of Cyclohexyl Bromide in Ethanol–Water Mixtures at 18°

x_2[a]	Solubility, mol/l. × 10^4	x_2	Solubility, mol/l. × 10^4
0.0	6.40	0.15	31.60
0.02	8.55	0.20	76.71
0.05	10.62	0.25	107.7
0.075	13.11	0.40	113.0
0.11	17.52		

[a] Mole fraction of ethanol.

Arnett and coworkers[22,23] have determined the heat of solution at one temperature for numerous binary systems, both charged and uncharged, and have summarized[35] their observations for ethanol–water systems as follows. (a) All solutes, both ionic and nonpolar, give endothermic maxima (relative to their heats of solution in water) about 0.85 mole fraction of water in aqueous ethanol. (b) In general, the higher the carbon number of the solute, the larger is this endothermic maximum. (c) Careful examination of the data will reveal further that for solutes of the same carbon number, nonelectrolytes produce a larger maximum than salts.

While Arnett and coworkers speak of the solute becoming increasingly "unwelcome" through the series $x_2 = 0.0$–0.15,[22] this description refers to the enthalpy only. The free energy, at least for cyclohexyl bromide, is successively more favorable (Table II); hence the accompanying entropy change must be the controlling factor for solubility of nonelectrolytes in this concentration range even as is true in water.[24]

For the purpose of interpreting kinetic data the above fragmentary evidence would seem to support the postulate that solubility through the high water region is dependent to a significant degree on solvent organization, and this structure is strongly temperature dependent. This does not rule out a contribution from solute–solvent interaction.[14,15] We are unaware of any comparable solubility data for systems at higher temperatures, but this is not an important omission here since the kinetic data reported covered the temperature range 0–30°.

Kinetics Results and Discussion

Prior to determining the temperature coefficients of the rate of solvolysis of *t*-butyl chloride in a series of alcohol–water mixtures, it was important to discover whether a tenfold change in concentration would introduce (1) an anomaly, (2) an indication of micelle formation, or (3) some equilibrium between dimers and monomers[36] in the solvent shell. The rate data for a series of initial concentrations of *t*-butyl chloride in an ethanol–water mixture with the concentration of alcohol, $x_2 = 0.075$, and isopropyl alcohol–water mixture, $x_2 = 0.1$, are summarized in Tables III and IV. No trend with concentration of the halide is apparent; hence in these and other similar systems we assume that the single solvated molecule is reacting. The small rate differences found in these tests were not considered to be indications of any gross kinetic effect and would be eliminated in any case as a consequence of a careful standardization of initial concentrations and other conditions.

Table III. Rates of Solvolysis for a Series of Concentrations of *t*-Butyl Chloride in 0.925 Mole Fraction of Water–Ethanol ($T = 12.026°$)

Series	A	B	C	D	E
Mean $k_1 \times 10^{-3}$	1.886	1.893	1.872	1.886	1.896
n_{obsd}	4	3	3	4	3
Std dev	±0.009	±0.003$_4$	±0.002	±0.011	±0.003
% deviation	0.48	0.18	0.10	0.58	0.16
Temp, °C	12.026	12.026	12.023	12.026	12.027
t-Butyl chloride, 10^{-5} *M*	3.24	3.24	16.2	32.4	48.6

A series of rate determinations for the solvolysis of *t*-butyl chloride (initial concentration = 3–4 × 10^{-5} *M*) in each of the alcohol–water mixtures as determined over a range of temperatures. The details of this work are given in the Experimental Section. The temperature dependence of these rate data could be expressed by means of a least-mean-squares fit to an equation of the form

$$\log k_1 = (A/T) + (B \log T) + C \qquad (2)$$

using the method of Clarke and Glew[38] to avoid mathematical uncertainties. The value of the constants so derived for each series together with the density of the

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(36) Arnett and McKelvey[35] suggest that the kinetics results of Winstein and Fainberg may have been influenced by micelle formation.[37]

(37) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5937 (1957).

(38) E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, **62**, 539 (1966).

Table IV. Rates of Solvolysis for a Series of Concentrations of *t*-Butyl Chloride in 0.90 Mole Fraction of Water–Isopropyl Alcohol (T = 18.047°)

Series	A	B	C	D	E	F	G	H	I
Mean $k_1 \times 10^{-3}$	1.047	1.047	1.046	1.044	1.044	1.042	1.041	1.044	1.041
n_{obsd}	3	4	4	4	4	4	4	4	4
Std dev	±0.002	±0.005	±0.001	±0.003	±0.001	±0.0016	±0.0013	±0.0025	±0.0014
% deviation	0.19	0.47	0.10	0.29	0.10	0.15	0.12	0.24	0.13
t-Butyl chloride, $10^{-5}M$	3.24	3.24	6.48	9.72	12.96	16.2	19.44	22.68	32.4

Table V. Empirical Constants for a Least-Mean-Squares Fit to Eq 2 of Solvolysis Data for *t*-Butyl Chloride

H_2O, mole fraction	Exptl density,[d] g cm^{-3}	$-A$	$-B$	C
		(a) Ethanol–Water Mixtures		
1.0[a]		10340.7211	40.7885	134.0848
0.925	0.9704	13222.2473	67.3338	208.9545
0.89[b]	0.9629	11853.4741	57.6907	180.3265
0.85[b]	0.9475	7411.9969	23.5630	80.4960
0.75[c]	0.9185	6790.4175	15.9116	58.7490
		(b) Isopropyl Alcohol–Water Mixtures		
1.0[a]		10340.7211	40.7885	134.0848
0.98	0.9867	12606.5276	60.2868	189.7619
0.95	0.9747	13155.6866	66.9823	207.9542
0.925	0.9648	11579.6648	58.4207	181.1712
0.90	0.9549	5425.3652	9.6418	39.4141
0.80	0.9133	8163.5443	25.0351	85.5905
		(c) *t*-Butyl Alcohol–Water Mixtures		
1.0[a]		10340.7211	40.7885	134.0848
0.98	0.9855	11721.0542	53.2710	169.4304
0.95	0.9714	16216.6837	96.4622	290.9624
0.90	0.9441	5447.7272	7.0702	32.6155
0.80	0.9987	7707.5499	20.9795	73.6797

[a] E. A. Moelwyn-Hughes, R. E. Robertson, and S. E. Sugamori, *J. Chem. Soc.*, 1965 (1965). [b] Reference 5. [c] L. Hakka, A. Queen, and R. E. Robertson, *J. Amer. Chem. Soc.*, **87**, 161 (1965). [d] At 25°.

alcohol–water mixture at 25° and the corresponding mole fraction of water are given in Table V.

From these rate constants following the normal assumptions of the transition state theory, the assumption of well-behaved differentiability of log k with respect to T and the attenuating *approximation* that $d\Delta C_p^{\ddagger}/dT = 0$, the pseudothermodynamic constants for the solvolysis of *t*-butyl chloride for the specified alcohol–water mixtures were calculated and are collected in Table VIa–c.

The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ found for solvolysis in ethanol–water mixtures (Table VIa) follow the general trend previously reported by Winstein and Fainberg[37] with some variation in detail. A plot of the values of $\Delta H^{\ddagger}$ (Figure 1) and $\Delta S^{\ddagger}$ for varying solvent compositions is no more complicated than might be expected to result from the change from a solvent system in which three-dimensional structure is dominant to one where other forms of solvent organization prevail. Corresponding values in isopropyl alcohol–H_2O and *t*-butyl alcohol–H_2O binaries show corresponding trends with individual differences, the source of which is probably related to specific structural changes in the solvent, though this has not been proven. Evidence from other processes[22,39–41] in these binary mixtures support the conclusion that the relative amount of alcohol compatible with a three-dimensional quasi-aqueous structure is directly dependent on the volume of the alkyl group, extrema being observed at successively lower concentrations of alcohol as the hydrophobic alkyl group increased in volume. Our kinetic results point to the same conclusion.

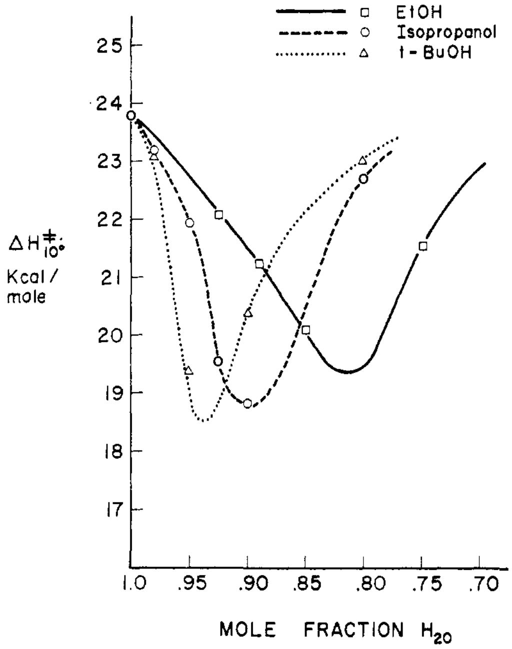

Figure 1. Correlation of $\Delta H^{\ddagger}$ with alcohol–water concentration for the solvolysis of *t*-butyl chloride.

The correlation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ may be significant in that values from these studies appear to conform to two linear plots of different slopes (Figure 2). Those values determined in solvent mixtures, where quasi-aqueous structure persists, fall along one line, while those points corresponding to determinations in binary mixtures, where three-dimensional structure is no longer significant, fall along a plot of lesser slope. The determining factor apparently is related to the volume of the alkyl group present and hence to the capacity of the system to preserve quasi-aqueous structure. Thus corresponding values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ appear at successively lower concentrations of ethanol, isopropyl alcohol, and *t*-butyl alcohol in water.

If we accept the hypothesis that the trend in ΔH_s in the alcohol–water range x_2 = 0.0–0.15 mole fraction is related in some way to the capacity of the system to preserve a quasi-aqueous structure, it is not surprising that these characteristics are reflected in the activation process which requires a reorganization of that initial-state adaptation. There is an evident logic in recognizing that the solvent shell in the aqueous solutions of reactive halides (which is characterized by a large positive heat

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(40) C. J. Burton, *J. Acoust. Soc. Amer.*, **20**, 186 (1948).
(41) V. Sarojini, *Trans. Faraday Soc.*, **57**, 1534 (1961).

Table VI. Quasi-Thermodynamic Parameters for the Activation Process in the Solvolysis of *t*-Butyl Chloride in Solvent Mixtures

Solvent, v/v_{H_2O}	H_2O, mole fraction	$\Delta C_p^{\ddagger}$, cal deg^{-1} mol^{-1}	$\Delta H^{\ddagger}$, cal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
		(a) Values for Ethanol-Water Mixtures at 10°		
Water[a]	1.0	−83 ± 4.5	23,830	14.4
20.8:79.2	0.925	−136 ± 8	22,051 ± 23	6.4 ± 0.01
27:73[b]	0.89	−116	21,213	2.8
37:63[b]	0.85	−49	20,093	−3.2
50:50[c]	0.75	−34	21,550	−2.9 (20°)
		(b) Values for Isopropyl Alcohol-Water Mixtures at 10°		
Water[a]	1.0	−83 ± 4.5	23,830	14.4
8:92	0.98	−122 ± 4	23,190 ± 13	11.7 ± 0.05
18:82	0.95	−135 ± 4	21,936 ± 14	6.5 ± 0.05
25.7:74.3	0.925	−118 ± 6	19,550 ± 23	−3.1 ± 0.08
32:68	0.90	−21 ± 9	18,830 ± 31	−7.4 ± 0.10
51.5:48.5	0.80	−52 ± 2	22,696 ± 38	0.6 ± 0.10
		(c) Values for *t*-Butyl Alcohol-Water Mixtures at 10°		
Water[a]	1.0	−83 ± 4.5	23,830	14.4
9.6:90.4	0.98	−108 ± 6	23,086 ± 18	11.3 ± 0.06
21.6:78.4	0.95	−194 ± 8	19,356 ± 25	−3.0 ± 0.09
35.7:63.3	0.90	−16 ± 2	20,386 ± 33	−4.5 ± 0.10
56.6:43.4	0.80	−44 ± 3	23,002 ± 5	−0.36 ± 0.28

[a] See footnote *a*, Table V. [b] Reference 5. [c] See footnote *c*, Table V.

capacity and a large negative entropy[26] for gas-solution equilibrium) must be broken down in the activation process. It is less easy to visualize a similar rationalization when the solvation process is accompanied by a positive shift in entropy and is endothermic. Arnett has shown[22,23] that the ΔH_s's for nonelectrolytes dissolved in alcohol-water mixtures in the high water region are successively more endothermic as the capacity for maintaining three-dimensional structure is reduced. Since ΔF_s is probably reduced through this region for alkyl halides (Table II), ΔS_s must be even more favorable for the initial state. By the same token, $\Delta H^{\ddagger}$ in the activation process decreases over the same range, but $\Delta F^{\ddagger}$ increases and again $\Delta S^{\ddagger}$ is dominant and unfavorable with respect to the same reaction occurring in water. If the complementary relation between ΔH_s and $\Delta H^{\ddagger}$ to which Arnett has drawn attention is real, as seems likely, then even more dramatic changes must occur in ΔS_s and $\Delta S^{\ddagger}$. These terms suggest strongly that reorganization of solvent structure is involved, and that the involvement in the activation process is in opposition to that in the initial state solvation process. It seems unlikely that the initial-state solvation process for nonelectrolytes in water and quasi-aqueous systems should be characterized by both structure-making and structure-breaking tendencies for relatively small changes in the concentration of alcohol, or in temperature. Hence we regard the initial-state solvation for *t*-butyl chloride in alcohol-water mixtures, where the structural characteristics of water exist,[18] to require the extension of structural relationships, whatever else may be involved.

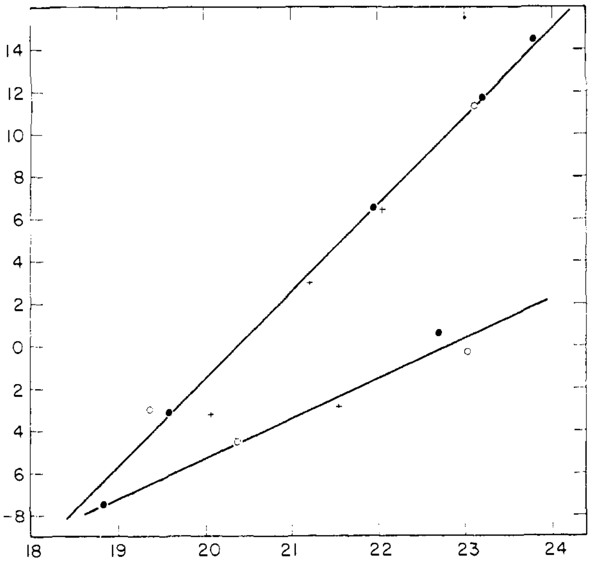

Figure 2. Compensation diagram relating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the solvolysis of *t*-butyl chloride in a series of alcohol-water mixtures: abscissa, $\Delta H^{\ddagger}$ (kcal mol^{-1}); ordinate, $\Delta S^{\ddagger}$ (cal mol^{-1} deg^{-1}).

The temperature coefficient of the $\Delta H^{\ddagger}$ ($\Delta C_p^{\ddagger}$) has proven of considerable value in probing the details of the activation process for solvolysis in water,[3] and it seemed reasonable to extend interpretations, deduced from such studies to systems where quasi-aqueous characteristics exist.

From Table VI we note that the addition of each alcohol results in a more negative value of $\Delta C_p^{\ddagger}$ up to the concentration where presumably the structural capacity of water is exceeded. This is an assumption based on our results with cyclohexyl bromide and will require further initial state data to be firmly established. However, there seem no reason to doubt that the qualitative conclusion is correct. For mixtures in which the alcohol content is in excess of the above critical region, important structural changes occur; this is reflected in the rapid decrease in the value of $-\Delta C_p^{\ddagger}$ to the -30 to -40 cal deg^{-1} mol^{-1}. Kohnstam[17] found values in this range where other evidence suggests that three-dimensional structure has been dissipated.

Where quasi-aqueous structures exist, the indications from many physical measurements suggest that the system possesses a more extensive structural organization than water (see above). The properties of this structure are apparently dependent on the size and shape of the alkyl group of the alcohol.[18] As yet the nature of this dependency has not been defined, but sufficient evidence is known to suggest that the extent of the structural adaptation required is successively greater through the series ethanol, isopropyl alcohol, and *t*-butyl alcohol. Our values of $\Delta C_p^\ddagger$ are consistent with the idea that this structure about the reactive solute must be disorganized in some fashion in the activation process. Whether the initial-state solvation process is exothermic or endothermic is of less consequence than how ΔH_s changes as temperature increases. If we accept Ben-Naim's data for argon[34] as a reasonable model for a weakly polar solute, then $\Delta C_{p,s}$ will become more positive through the range $x_2 = 0\text{–}0.15$ and then rapidly become less positive as structure disappears. In the activation process this is just the trend observed in $\Delta C_p^\ddagger$. In water where inequality 1 was reasonable, logic required that charge development in the activation process would pass through some charge level where first the developing anion, then the cation, satisfied the relation[3]

$$\text{water–water interaction} = \text{water–quasi-ion interaction} \quad (3)$$

The second point of balance, involving cation–solvent interaction corresponds to the transition state for the SN1 mechanism.[42] While the nature of the solution process in the alcohol–water series where structure is maintained differs in detail from that in water, it is reasonable to assume that the same inequality 1 obtains in some respect in the initial state. Further, the same kind of an argument will account for the large negative temperature coefficients of $\Delta H^\ddagger$ which we find. A similar shift to more negative values of $\Delta C_p^\ddagger$ is found in each binary system. While too few values of $\Delta C_p^\ddagger$ were determined to define exactly the change in this coefficient with alcohol concentration, Figure 3 probably gives a fair indication of the trend. It also gives some indication of the complexity of the terms. Thus $-\Delta C_p^\ddagger$(max) for isopropyl alcohol–H_2O is just about the same as for ethanol–H_2O, but this point is reached at a lower concentration of the isopropyl alcohol. The former goes through a minimum along with the corresponding curve for *t*-butyl alcohol. The latter system shows a very high maximum value for $-\Delta C_p^\ddagger = 200$ cal deg^{-1} mol^{-1}. The values of $\Delta H^\ddagger$ (Figure 1) over the same range, in so far as we can judge from our data, show a systematic progression of values.

Since the determination of $\Delta C_p^\ddagger$ values requires that the reaction be studied over a range of temperature, it should be clear that in the alcohol concentration range approaching that where three-dimensional structure breaks down, increasing temperature will introduce effects corresponding to two solvent systems. For this reason it seems unlikely that a more detailed analysis is possible for the region where quasi-aqueous characteristics are maintained, even though the solvation process may be characterized by positive ΔS_s and ΔH_s.

Experimental Section

For all the rate determinations, AR *t*-butyl chloride was purified by passage through Al_2O_3 for absorption, and was shown to be kinetically pure. This sample was shielded from light and placed in a desiccator which was opened only for removal of samples.

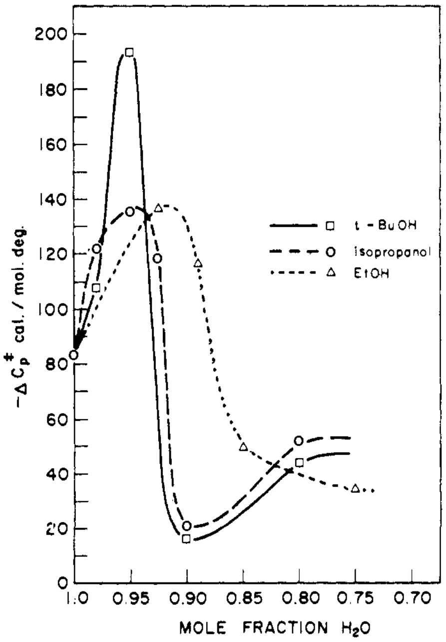

Figure 3. Correlation of $\Delta C_p^\ddagger$ with alcohol–water concentration for the solvolysis of *t*-butyl chloride.

Solvolyzing Media. Distilled H_2O was passed through an ion-exchange column (Rexyn R208-1-300 H-OH) and used without further purification. Anhydrous ethanol was a very pure grade obtained from Commercial Alcohol Ltd., and used without further purification. Isopropyl alcohol, reagent grade, was distilled (bp 82.6°) and the middle fraction used. *t*-Butyl alcohol, reagent grade, was used without further purification.

All concentrations used throughout this investigation were mixed by volume and then checked by density measurements.[42] Densities of the mixtures were done prior to and at the end of each series. Enough of each solvent mixture was made to complete the series of studies. Incremental amounts were siphoned from a stock bottle provided with a double vapor trap.

Kinetic Studies. Rates of reaction were determined by a conductance method using Queen-type stirred cells. Considerable difficulty was experienced in obtaining reproducibility of rates in 27:73 v/v ethanol–water mixtures for reasons which we have been unable to discover.[5] It follows that the errors in $\Delta C_p^\ddagger$ for the latter series are somewhat higher than normal, but are not sufficient to alter the general picture. Rate data were collected by means of our automatic rate acquisition machine (Auto-RAM).[43] This system incorporates a General Radio 1680-A automatic capacitance bridge assembly together with a crystal clock, logic control with random access. The system outputs data in printed and punched tape form on a Teletype ASR 35. A switching center provides a means for obtaining identified balance requests at regular time intervals from 10 sec to 100 Ksec for ten groups of four cells each. When balance is completed, the conductance, time of balance completion as registered on the internal crystal clock, and the identification of group and cell are simultaneously printed and punched. The resulting primitive data can then be processed by computer. Such a system not only makes possible obtaining data overnight but also frees the experimentalist from much of the drudgery concealed in normal kinetic studies of this type. For well-behaved systems, *i.e.*, those where supersaturation, isomerization, impurities, and other sources of errors are absent or small, reproducibility to a few tenths per cent are normal, and in many instances the actual errors are much less than this limit.

A detailed description has not been given since it seems probable that the same end could be achieved by combining the bridge and crystal clock with one of the small computers which are commercially available.

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(42) G. R. Robertson, *Ind. Eng. Chem., Anal. Ed.*, **11**, 464 (1939).

(43) The final design changes were due to Mr. L. Itiniant, Technical Services, Univac, Toronto, Canada.