Heat Capacities of Organic Compounds in Solution. I. Low Molecular Weight Alcohols in Water[1]

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Received September 30, 1968

Abstract: The significance of heat capacities of solvation to physicochemical processes in aqueous solution is discussed and the dearth of reliable values is documented. Heat capacities of solution ($\Delta C_{p_2}°$) are reported herein for 21 low molecular weight alcohols from a pure liquid standard state to high dilution in water at 25°. The integral heat method of Cobble and Criss is used wherein the partial molar heat of solution is measured as a function of temperature, each $\Delta C_{p_2}°$ value being based on 40 to 70 heat measurements over a 25° range. $\Delta C_{p_2}°$ values are large, positive, and dependent on the size of the alcohol molecule since within a series they correlate with carbon number or molar volume. Branching, unsaturation, and ring closure reduce $\Delta C_{p_2}°$, but branching has the reverse effect if a gaseous standard state is used. The relatively large magnitude of $\Delta C_{p_2}°$ is even larger when referred to a gaseous standard state, and it is proposed that the principal contribution is the increased order developed in the water adjacent to the hydrocarbon chain. A close correlation of the heat capacity and entropy of transfer from the vapor phase to water supports this hypothesis.

Free-energy changes, as manifested by rates, equilibrium constants, and escaping tendencies, are surely the most practical criteria of chemical reactivity. However, the standard free energies of most processes are very sensitive to temperature and there is precedent,[3] as well as good reason, to believe that the relative reactivity order of closely related compounds may be temperature dependent and does not always correspond to the order of their potential energies. Although, to a first approximation, the temperature coefficients of rates and equilibria can be expressed by equations of the van't Hoff–Arrhenius type, these cannot be applied with rigor to high-precision work or to extrapolations over the wide temperature ranges often used to compare results obtained under different conditions. There is some disagreement about the best equation to use for fitting such data,[4-8] but the failure of purely linear log k (or K) *vs.* $1/T$ treatments may be expected as normal for very precise data and constitutes a breakdown of the useful first-order assumption[9-11] that structural effects on heat capacity changes in chemical processes are negligible.

It is increasingly clear (see below) that enthalpy and entropy (and even heat capacity) changes for important equilibria[3-8,12,13] and kinetic[14-19] processes are sensitive to temperature. Moreover, the important thermodynamic or activation properties (ΔG, ΔH, ΔS) are not always exactly proportional to each other within a series of related compounds,[9] nor is there any *a priori* reason for believing that their temperature coefficients should be. Consequently, there is no experimental justification for the common practice of interpreting small reactivity differences within a series of related compounds in solution at ordinary temperatures strictly in terms of stereoelectronic factors whose theoretical development applies to the gas phase at absolute zero. Unfortunately, it is for small differences that the theoretical basis for linear free-energy relationships holds with greatest rigor.[9,11] The simplifying assumption that heat capacity differences within a series of similar compounds in solution are negligible or constant rests primarily on the paucity of data needed to criticize it rather than any experimental demonstration of its reliability.

In fact, what data may be found for heat capacities of ionization, ΔC_{p_i}[3,5a,6,8,12] for carboxylic acids and ammonium salts or heat capacities of activation, $\Delta C_p^{\ddagger}$[14-19] for solvolysis reactions show clearly that for these processes the heat capacity differences between a neutral state and a charged or highly polar final (or transition) state may be quite large. (Indeed, even covalent hydration of carbonyl functions may involve considerable heat capacity changes.[20]) This is not surprising in view

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(1) This study was aided by a grant from the Office of Saline Water, U. S. Department of the Interior.

(2) On leave from Federal University of Rio de Janiero, 1967–1968.

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," 3rd ed, Reinhold Publishing Corp., New York, N. Y., 1958, p 661 ff.

(4) A typical expression is

$$\ln K = \frac{\Delta H°}{RT} + \frac{\Delta S° - \Delta C_p°}{R} + \frac{\Delta C_p°}{R}\ln T$$

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of what little we know about the partial molal heat capacities at high dilution ($\bar{C}_{p_2}$) for salts[21] as compared with nonelectrolytes.[22-37]

Such a comparison of $\bar{C}_{p_2}$ values indicates that charging a neutral molecule in aqueous solution should lead to a large negative heat capacity change for the process. However, a much more important conclusion, for structure–reactivity comparison, is implied by presently available data for ionization and activation to wit: *there may be large and unsystemmatic irregularities in* $\bar{C}_{p_2}$ *within different series of related compounds in view of the fluctuations in* ΔC_{p_i}, *and* $\Delta C_p^{\ddagger}$ *within such series.* Recent careful determination of ΔC_{p_i} by calorimetry[38] has removed some such irregularities of the older values obtained by the van't Hoff method. There is no such easy approach to improving our knowledge of $\Delta C_p^{\ddagger}$ values.

The few available $\bar{C}_{p_2}$ data do not indicate that ΔC_{p_i} or $\Delta C_p^{\ddagger}$ should be erratic functions of molecular structure. In fact, they suggest superficially the exact opposite as is evidenced by the frequently cited[30-32,39] increment of 25–30 cal/(mole deg) for each $-CH_2-$ unit in a chain regardless of the adjacent functional unit (hydrocarbon,[22] amino acid,[31] carboxylic acids, and their anions[33]). However, it is clear that if there was no functional group effect on $\bar{C}_{p_2}$, the same increment would be introduced into every carboxylate anion as into its parent acid and into every S_N1 solvolysis transition state and its ground state. This would produce a constant ΔC_{p_i} or $\Delta C_p^{\ddagger}$ in a given series which, as we have seen, is contrary to many of the reported results. Present data for $\bar{C}_{p_2}$ of functionally related molecules are limited so severely it is impossible to separate ΔC_{p_i} or $\Delta C_p^{\ddagger}$ differences into initial state *vs.* final or transition state contributions. If $\bar{C}_{p_2}$ values were available, or could be estimated easily, we would be in a stronger position for understanding the implications of solvent reorganization in solvolysis reactions.[15,16,18] All of the data which are presently available in the references cited above indicate clearly that $\bar{C}_{p_2}$, ΔC_{p_i}, and $\Delta C_p^{\ddagger}$ may be quite sensitive to changes in molecular structure, solute concentration, and medium. The effects of structure and concentration appear to be especially pronounced in aqueous systems where, as bad luck would have it, much of the best physicochemical work has been done. This raises especially serious hazards for temperature extrapolations of free-energy data obtained in aqueous solution. From a more positive viewpoint the same effects might offer an opportunity to employ the unusually large thermal effects in water to manipulate free energy and throw some light on large ΔC_p factors in protein denaturation.[40]

These considerations coupled with the great practical importance of structure–reactivity correlations and the widespread tendency to interpret even small reactivity differences in terms of potential energies have led us to examine the heat capacity behavior of organic solutes as a function of structure, concentration, and medium. This paper and the ones to follow it in this series will report our findings.

The present paper deals specifically with the variation of $\Delta C_{p_2}°$, the heat capacity of solution, for 21 carefully selected alcohols in water at 25°. This homologous series was chosen deliberately because its members are stable and relatively soluble in water and because of the relatively good availability of C_p data for the pure liquids and some previous estimates of $\bar{C}_{p_2}$ obtained by other methods for comparison. Data for the alcohols may also be useful for analyzing the initial-state contribution to $\Delta C_p^{\ddagger}$ of alkyl halide hydrolysis.[15,16] In subsequent papers we shall deal with solute–solute contributions and medium effects on heat capacities of solution.

Methodology. Three approaches have been used in the past for determination of $\bar{C}_{p_2}$ of solutes at high dilution. We have rejected the two most commonly used ones for reasons given below.

For highly insoluble materials,[23,26,27,35] such as hydrocarbons, the only available strategy is to measure the solubility of the solute very precisely at a series of temperatures and then apply a suitably expanded[5-8] form of the van't Hoff equation to the results. The chief problem here is the experimental one of making these difficult measurements with sufficiently high precision to stand the strain of a second-derivative treatment. Secondly, there is a lingering concern over solute–solute interactions at the saturation point for such hydrophobic materials. The choice of a proper function to interpret the temperature coefficients of solubility equilibria[5-8] is unsettled and will, of course, influence the final absolute value although relative values should not be much affected.

Solutes with good water solubility have been studied for many years[20-41] by direct calorimetric determination of the specific heats of a series of increasingly dilute solutions. The apparent molar heat capacity, ΦC_{p_2}, is then plotted against some function of the concentration and extrapolated to infinite dilution. Even the most cursory examination of a few key references on the use of this method for salts[21] or nonelectrolytes[31,32] suffices to show that concentration effects on ΦC_{p_2} are generally large and that the dependence on concentra-

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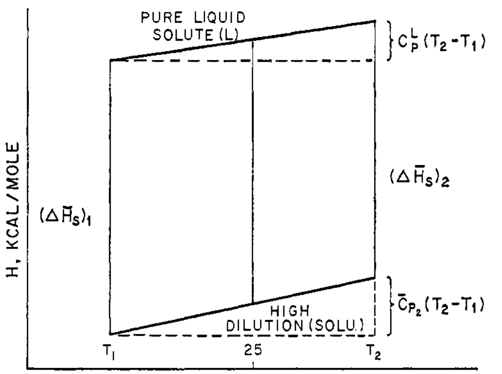

$$\Delta C^{\circ}_{P_2} = \bar{C}^{\circ}_{P_2} - C^{L}_{P} = \frac{(\Delta \bar{H}_S)_2 - (\Delta \bar{H}_S)_1}{(T_2 - T_1)} = \frac{(H_2^{\text{SOLU.}} - H_2^{L}) - (H^{\text{SOLU.}} - H_1^{L})}{(T_2 - T_1)}$$

$$= \frac{(H_2^{\text{SOLU.}} - H_1^{\text{SOLU.}})}{(T_2 - T_1)} - \frac{(H_2^{L} - H_1^{L})}{(T_2 - T_1)}$$

Figure 1. Diagram of the Cobble–Criss integral heat method used to determine $\Delta C_{p_2}°$.

tion is usually quite erratic for all types of solutes. The sudden sharp curvatures and reversals of trend at the crucial low concentration end of such plots undermines our confidence in many such extrapolations to infinite dilution. They suggest that heat capacities of dilution are often very large and may play a commanding role in generating false apparent values of $\bar{C}_{p_2}$ whenever solute–solute interactions can occur. Such a situation obviously applies in the use of the van't Hoff solubility technique described above. Relatively few studies of ΦC_{p_2} have employed concentrations below 0.05 *m* because of the imperceptible effect of small quantities of most solutes on the heat capacity of water. Therefore, many extrapolated values of $\bar{C}_{p_2}$ obtained in this way do not represent pure solvent–solute effects and cannot be applied quantitatively to the analysis of high dilution kinetic or equilibria data.

The approach which we have used is a refinement of that described in a previous communication[42] and is similar to that used by Criss and Cobble[43] for electrolytes. Two groups have recently described a similar method for nonelectrolytes.[20,44] This approach is diagrammed in Figure 1.

Here the partial molal heat of solution at infinite dilution ($\Delta\bar{H}_s$) is measured at a series of temperatures and $\Delta C_{p_2}°$ is derived immediately from the temperature coefficient. The relation between $\Delta C_{p_2}°$ and $\bar{C}_{p_2}$, which would ideally be obtained by extrapolation of directly measured heat capacities as described in the procedure before this, is given by $\Delta C_{p_2}° = \bar{C}_{p_2} - C_p^{\text{pure}}$, where C_p^{pure} is the heat capacity of the pure solute in the particular standard state (vapor, liquid, or solid) from which it is introduced into solution.

$\Delta\bar{H}_s$ is measured easily in a simple dual solution calorimeter using techniques we have described previously.[45] The concentration increment for each injection of solute is *ca.* 4×10^{-3} *m* and the incursion of solute–solute interactions is detected easily (see Experimental Section). Generally, $\Delta C_{p_2}°$ values are derived from about 40 separate $\Delta\bar{H}_s$ measurements covering a range of 10 to 40°. An appropriate curve-fitting of the data leads to $\Delta C_{p_2}°$ and also a refined value of $\Delta\bar{H}_s$ (25°) as the intercept, with much higher precision than our technique afforded previously.

In order to obtain $\bar{C}_{p_2}$ values from our results, C_p^{pure} may be obtained for many gases, liquids, and solids from standard tabulations.[46] In some cases C_p^{pure} may be estimated by additivity[47,48] with much greater reliability than other thermochemical properties.

Our method yields directly a measurement of the excess heat capacity from interaction of the solute with the solvent, the inherent heat capacity of the liquid solute (dissolved in itself in the pure state) being automatically substracted out. All values of $\bar{C}_{p_2}$ obtained by the specific heat extrapolation method require correction for this inherent heat capacity term. We shall consider in the discussion the relative merits of these different terms as a guide to solute–water interactions.

Experimental Section

The method used originally for most of these measurements employed a balanced pair of unthermostated calorimeters, the second one taking the place of the base-line compensator described in our earlier article.[45] They were filled with distilled, deionized water adjusted previously to the desired temperature and then allowed to equilibrate until a straight recorder base line was achieved. During the 15 min required for a group of heat measurements at a given temperature, the calorimeters were essentially at thermal equilibrium compared to the temperature increment between measurements, the greatest drifts being 0.01°/min.

The total range of temperature for a series of 12 to 20 $\Delta\bar{H}_s$ measurements was usually from 18 to 33°, none being more than 10° below ambient or 5° above. Each measurement was based on a series of four heating curves and three injections of 100 μl or less of solute into the 200 ml of water in the calorimeter. The thermal drift during such a series was usually about 0.15° and the total temperature increase from drift, heating curves, and heats of solution was 0.3–0.5°. The temperature was measured to the nearest 0.1° before and after each series of injections, and the thermal drift was averaged over the curve so that the largest heat capacity correction which might be needed for any of our solutes would be less than 10 cal/(mole deg). The averages of these groups of three shots were treated by linear least squares[49] to the equation $\Delta\bar{H}_s = \Delta C_{p_2}°(T - 25) + \Delta\bar{H}_s(25°)$, where $\Delta\bar{H}_s$ is the observed molar heat of solution at temperature T and $\Delta\bar{H}_s(25°)$ is the 25° intercept. In no case was curvature detected for these compounds within our experimental error over this temperature range nor on the basis of prior careful studies of $\bar{C}_{p_2}$[31,41] would it be expected. It was discovered later that serious discrepancies in $\Delta C_{p_2}°$ (but not $\Delta\bar{H}_s(25°)$) arose between values obtained in this way and those using identical calorimeters immersed in a thermostated bath. The results obtained by the two methods were plotted for seven alcohols and produced a smooth calibration curve which was used to correct the rest of the results. The temperature range for the thermostated calorimeters was 10–40°.

Densities of the solutes were estimated by interpolation of literature values cited at different temperatures, the temperature coefficient generally being about 0.2%/deg.

Absence of solute–solute interactions at the low ($<1 \times 10^{-2}$ *M*) concentrations used here was shown in several cases by making 10 to 12 successive injections into a calorimeter maintained at constant temperature. These results indicated an average effect of no more than 1.3 cal per mole per injection.

Materials. Except for the methanol (Baker Reagent) and ethanol (Commercial Solvents, Anhydrous), the alcohols were Eastman Organic Chemicals. They were dried over anhydrous calcium sulfate. All compounds were fractionally distilled through

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Table I. Heat Capacities of Solution for Various Alcohols in Water at 25°

	Alcohol	$\Delta C_{p_2}^\circ$, cal/(mole deg)	C_p^L, cal/(mole deg)	$\bar{C}_{p_2}$,[a] cal/(mole deg)	C_p^V, cal/(mole deg)	$-\Delta\bar{H}_s$ (25°) kcal/mole	$-\Delta\bar{H}_s$ (25°), lit.
	H_2O	0	18	18		0	
1.	CH_3OH	23.1 ± 1.8 18.0 ± 1.8[m] 18.0 ± 0.1[n]	19.50[b]	42.6	10.49[b]	1.754 ± 0.007	1.756[l]
2.	C_2H_5OH	39.2 ± 2.7 33.9 ± 2.7[m] 35.7 ± 0.4[n]	26.62[b]	65.8	17.59[b]	2.433 ± 0.012	2.380[l] 2.415[m] 2.42[o]
3.	n-C_3H_7OH	56.4 ± 3.3 49.9 ± 4.0[m] 51.9 ± 0.5[n]	35.52[b]	91.9	27.73[c]	2.419 ± 0.007	2.43[o] 2.422[m]
4.	i-C_3H_7OH	55.4 ± 3.4 49.2 ± 3.9[m] 52.9 ± 0.9[n]	36.66[b]	92.1	28.46[c]	3.124 ± 0.010	3.102[m] 3.08[o]
5.	$CH_2{=}CHCH_2OH$	46.8 ± 2.9	38.7[j]	85.5	25.79[d]	1.695 ± 0.006	
6.	n-C_4H_9OH	71.6 ± 3.8 62.2 ± 5.0[m] 64.9 ± 0.6[n]	42.78[b]	114.4	35.61[c]	2.249 ± 0.010	2.217[m] 2.20[o]
7.	i-C_4H_9OH	67.8 ± 4.3	43.85[g]	111.6	35.74[c]	2.226 ± 0.009	
8.	sec-C_4H_9OH	68.0 ± 4.7	51.11[f]	119.1	35.84[c]	3.150 ± 0.010	
9.	t-C_4H_9OH	66.2 ± 4.1 63.3 ± 5.1[m] 70.2 ± 6.0[n]	53.74[b,i]	120.0	36.47[c]	4.172 ± 0.015	4.137[m] 4.10[o]
10.	$CH_3CH{=}CHCH_2OH$	57.5 ± 3.8				1.943 ± 0.009	
11.	$CH_2{=}CHCH_2CH_2OH$	57.2 ± 3.3				2.002 ± 0.006	
12.	n-$C_5H_{11}OH$	83.5 ± 5.3	50.0[b,h]	133.5	44.72[c]	1.868 ± 0.011	
13.	t-$C_5H_{11}OH$	74.8 ± 4.6	59.87[e]	134.7		4.435 ± 0.101	4.29[o]
14.	$CH_2{=}CHCH_2CH_2CH_2OH$	57.9 ± 3.8				1.409 ± 0.009	
15.	$CH_3C{\equiv}CCH_2CH_2OH$	48.2 ± 3.2				1.370 ± 0.006	
16.	Cyclopentanol	72.6 ± 4.3	43.98[b]	116.6		2.472 ± 0.007	
17.	Cyclohexanol	74.5 ± 4.5	49.96[b]	124.5		2.154[k]	
18.	2-Cyclohexen-1-ol	67.7 ± 4.0				1.856 ± 0.008	
19.	Cycloheptanol	85.6 ± 5.0				1.736 ± 0.007	
20.	Benzyl alcohol	52.1 ± 3.5				−0.132 ± 0.014	−0.13[o]
21.	F_3CCH_2OH	43.2 ± 2.6				1.491 ± 0.007	

[a] The values in this column represent the partial molal heat capacity of the solvated alcohol at high dilution in water. They are derived from the expression $\bar{C}_{p_2} = \Delta C_{p_2}^\circ + C_p^L$. [b] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Vol. 2, Part 4, Julius Springer, Berlin, 1960. [c] G. C. Linke and T. DeVries, *J. Am. Chem. Soc.*, **75**, 1815 (1953). [d] K. A. Kobe, *et al.*, *Petrochem. Refiner*, **30**, 8, 119 (1951). [e] J. W. Leech, *Proc. Phys. Soc.* (London), **62B**, 390 (1949). [f] *Chem. Abstr.*, **34**, 1514³ (1940). [g] J. W. Leech, *J. Gen. Chem. USSR*, **11** (7), 471 (1941). [h] G. S. Parks, *et al.*, *J. Am. Chem. Soc.*, **55**, 2733 (1933). [i] G. S. Parks and C. T. Anderson, *ibid.*, **48**, 1506 (1926). [j] "International-Critical Tables," Vol. 5, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 108. [k] Calculated from $\Delta\bar{H}_s$ above melting point (25.5°). [l] G. L. Bertrand, F. J. Miller, C. Wu, and L. G. Hepler, *J. Phys. Chem.*, **70**, 699 (1966). [m] D. J. T. Hill, Ph.D. Thesis, University of Queensland, 1965. [n] Calculated from Hill's data (footnote *m*) using our treatment. [o] C. Y. Krishnan and H. L. Friedman, to be submitted for publication.

a 1-m Nestor–Faust spinning-band column and then stored in a dessicator.

All compounds gave satisfactory index of refraction readings and boiling points and showed but one component, or less than 0.3% impurity, on a 6-ft SAE 30 column in an Autoprep A-700 gas chromatograph.

Distilled and deionized water was used.

Results

In Table I are presented all of the data on heat capacity terms and heats of solution which we wish to report here, as well as literature values which we believe are relevant to our discussion of the results. Our $\Delta C_{p_2}^\circ$ values are given along with standard deviation estimates of the errors. These can only be combined with or compared with $\bar{C}_{p_2}$ from the literature if C_p^L or C_p^V terms are known. We therefore include those data for this purpose and also for various correlations which will be presented below. There were many sources of widely varying reliability for those numbers so that errors may result in some cases from combining them.

For the most part, our measurements are at least as precise as most of the older ones derived from other sources cited here. Of more importance is the question of their accuracy and there are several external tests of their general reliability.

The first check on our results is obtained by comparing our value of 23.1 ± 1.8 cal/(mole deg) for methyl alcohol with that derivable from the work of Moelwyn-Hughes and Glew,[14] who obtained a $\Delta C_{p_2}^\circ$ of 28.19 cal/(mole deg) for transfer from the gas phase to water. The difference (5.1 cal/(mole deg) between their value and ours agrees within combined experimental error with the heat capacity of condensation ($C_p^L - C_p^V$ = 8.9 cal/(mole deg)) which corresponds to the difference in standard states between their study and ours.

A second check on the method was provided by the work of Dr. James Campion in this laboratory who did a complete repetition using our thermostated calorimeters of the highly precise study of $\Delta C_{p_2}^\circ$ for sodium chloride by Criss and Cobble.[43] The details of this run will be presented in a subsequent paper. The important fact is the heat capacity was reproduced exactly and also its dependence on temperature was over the range from 10 to 60°.

A third check was provided by using the specific heat data obtained by Knight,[50] which included most of the alcohols in our study. The lowest alcohol concentration used by him was generally about 1 *m* so that there

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(50) W. S. Knight, Doctoral Thesis, Princeton University, 1962.

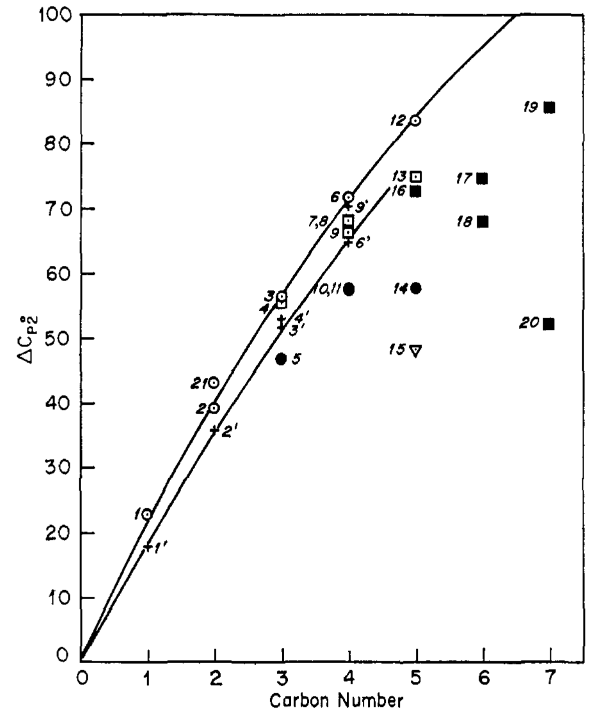

Figure 2. Correlation of $\Delta C_{p_2}°$ values for alcohols in Table I with their carbon numbers: ○, normal alcohols; ●, unsaturated alcohols; □, branched saturated alcohols; ■, cyclic alcohols; Δ, 3-pentyn-1-ol; +, values of Hill.[51]

is the usual problem of a suitable extrapolation to infinite dilution. Nonetheless, we find that the values which we would obtain by such a treatment of his data agree with ours (after correction for $C_p{}^L$) within 5 cal/(mole deg).

Our value for ethyl acetate, $\Delta C_{p_2}° = 68.5 \pm 2.8$ cal/(mole deg), may be compared with that reported recently by Stern and Herman[44] who obtained $\Delta C_{p_2}° = 74$ cal/(mole deg), using the same technique we used but with fewer values at fewer temperatures.

Of greatest relevance to our data are the results of Hill[51] of which we were apprised by Dr. Felix Franks.

Hill used the same general technique as ours, but his measurements on alcohols 1–4, 6, and 9 covered a wider temperature range so that he observed curvature in his plots of $\Delta \bar{H}_s$ *vs.* temperature. In Table I his original values are compared with ours. Also, we have recalculated his $\Delta C_{p_2}°$ for 25° using the same least-squares treatment which we employed. In all cases, our $\Delta C_{p_2}°$ values are somewhat higher than his although agreement is improved by the recalculation described above. For those compounds examined by Hill, his original values are probably more accurate than ours in view both of his calorimeter design and wider temperature range. Until more careful measurements of this type are available, some uncertainty will remain about the absolute accuracy of our values. However, it seems most unlikely that the relative magnitudes through this series are seriously in error. We note in this context the generally excellent agreement between our values of $\Delta \bar{H}_s$ (25°) and those of other workers as shown in Table I.

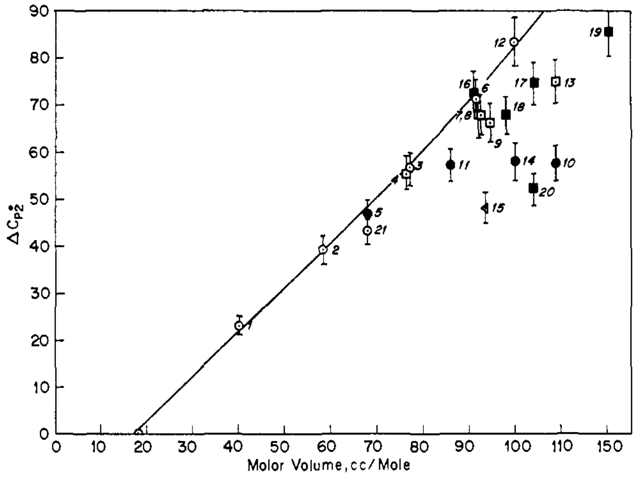

Figure 3. Correlation of $\Delta C_{p_2}°$ for the alcohols in Table I with their molar volumes. See Figure 2 for description of symbols.

Discussion

The Significance of $\Delta C_{p_2}°$. That heat capacities of solution both for nonelectrolytes and electrolytes are large in water is one of the most potent arguments for assigning that liquid a high degree of structure which is sensitive to the presence of solutes. $\Delta C_{p_2}°$, the value which we obtain directly by the temperature coefficients of heats of solution, represents for liquid solutes a heat capacity of transfer for the solute from a concentrated solution in itself to a highly dilute aqueous solution. If the heat capacity of transfer for any liquid alcohol from itself to any other member of the series is small, we may consider, as a rough approximation, that all of the liquid alcohols are essentially in a common standard state. Therefore, their differences in $\Delta C_{p_2}°$ provide directly a crude guide to the peculiar solute–solvent effects which are characteristic of the transfer of each solute to high dilution in water.

It would be more desirable for some purposes to refer all solutes back to a common gaseous standard state. However, $C_p{}^V$ data from the literature are not complete for the entire series considered here and represent quite different degrees of precision, so that an extraneous experimental error would be introduced by this combination of figures. Actually, as we shall see later, correction of $\Delta C_{p_2}°$ back to the vapor phase does not improve correlations with carbon number or molar volume significantly for the straight-chain alcohols since they have identical heat capacities of vaporization ($C_p{}^L - C_p{}^V$). However, it reverses the effect of branching in the butyl series.

If we are specifically interested in the effects of the solute on water structure, it is more realistic in some ways to consider the transfer of a molecule from solution in itself as representative of less structured liquids rather than from the gas phase. This indeed seems to have been the point of view of Gucker and Ayres[32] in their attempt to compare the behavior of nonelectrolytes in water. As we have indicated above, $\bar{C}_{p_2}$, the partial molal heat capacity of the solute at high dilution, contains the heat capacity of the solute along with the solvent–solute interaction term in which we may be interested. $C_p{}^L$ is usually chosen as the model for making this correction. Therefore, our measurement gives directly, without combination of any external numbers,

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(51) D. M. Alexander and D. J. T. Hill, *Aust. J. Chem.*, 22, 347 (1969).

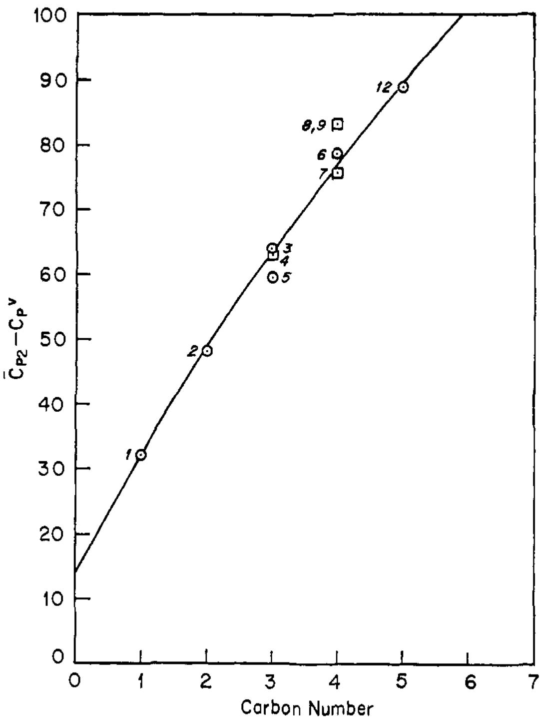

Figure 4. Correlation of heat capacity of transfer from the gaseous standard state to high dilution in water *vs.* carbon number for some alcohols in Table I. See Figure 2 for description of symbols.

the term most likely to exhibit the solvent–solute interactions of a nonelectrolyte peculiar to water compared to nonaqueous hydrogen-bonding liquids. However, it is worth noting that $\bar{C}_{p_2}$ is the property necessary for dissecting heat capacities of activation for the kinetics of solvolysis.[15–19]

Incremental Differences. The data in Table I show clearly that $\Delta C_{p_2}{}^\circ$ values are equal to or greater than the inherent heat capacities of the pure liquid solutes, $C_p{}^L$. Furthermore, $\Delta C_{p_2}{}^\circ$ increases steadily as a function of molecular size and is also sensitive to branching and cyclization. Functions of molecular size with which $\Delta C_{p_2}{}^\circ$ correlates reasonably well are carbon number and molar volume, as shown by Figures 2 and 3.

Scrutiny of Table I and Figure 2 leads to the following generalizations.

(a) The increment in $\Delta C_{p_2}{}^\circ$ per methylene group decreases steadily from 17 cal/(mole deg) (methyl to ethyl alcohol) to 12 cal/(mole deg) from *n*-butyl to *n*-amyl alcohol. The corresponding increment in $\bar{C}_{p_2}$, the partial molal heat capacity of the solvated species, holds at about 25 cal/(mole deg) per methylene group.

(b) We find that branching causes some reduction in $\Delta C_{p_2}{}^\circ$ (however, see below).

(c) Unsaturation and ring closure cause a sharp decrease in $\Delta C_{p_2}{}^\circ$. In both cases two hydrogen atoms are removed and a new bond is formed. The value for 3-pentyn-1-ol indicates that the effect for a triple bond is about twice that for a double bond. The similarity between the effects of ring closure and unsaturation argues against special interactions of the π-electron system being an important cause of the effect.

The molar volume V_2 is a convenient variable for correlation since within a homologous series it must be nearly proportional to the size of the cavity required to fit the solute molecules. The qualitative interpretation of the linear relationship of Figure 3 is simply that $\Delta C_{p_2}{}^\circ$ measures the increased heat capacity of the layer of water in the neighborhood of the hydrocarbon chain. Nemethy and Scheraga[28] account for this in terms of an enhanced degree of hydrogen bonding between the water molecules. Since this is primarily a function of the size of the cavity in the aqueous solution, it is not surprising that it is related to V_2, all other things being equal. The *failure* of molar volume terms to correlate with molecular size and shape for isomers and isosteres of different families has been clearly demonstrated by Franks and Quickenden[52] so that we draw little theoretical significance from the correlation of heat capacity with molar volume and consider the latter simply as a crude function of the size of the hydrocarbon moiety in the straight-chain series. Although there appears to be some crude relationship between heat capacities of activation for solvolysis[16] and volumes of activation for comparable processes,[53] there appears to be little or no correlation between heat capacities of ionization[12] and volumes of ionization.[53]

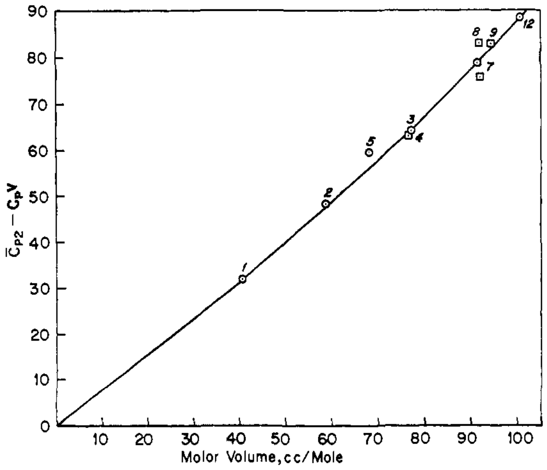

Figure 5. Correlation of molar volume with heat capacity of transfer from gaseous standard state to high dilution in water for some alcohols in Table I. See Figure 2 for description of symbols.

Figures 4 and 5 show the effects of using the gas phase as a standard state instead of each substance in its pure liquid state. A shortage of data excludes the other alcohols from these plots, but it is clear that the correlation has not been damaged seriously by changing the reference state in the available cases.

On closer scrutiny, it is seen that the effect of branching in the butyl series (points 6, 7, 8, 9) is to *increase* ($\bar{C}_{p_2} - C_p{}^V$), the heat capacity of transfer from the gas phase to dilute aqueous solution. This contrasts with the decrease in $\Delta C_{p_2}{}^\circ$ produced by branching noted above. Since $\Delta C_{p_2}{}^\circ = (\bar{C}_{p_2} - C_p{}^L)$, the difference between the two transfer quantities is $(C_p{}^L - C_p{}^V)$, the heat capacity of vaporization. It is easily seen from Table I that this is nearly constant at about 8 cal/(mole deg) for the straight-chain alcohols and increases to 15.3 and 17.2 cal/(mole deg) for *sec*-butyl alcohol and *t*-butyl alcohol, respectively. The effect of branching, therefore, is dependent on the standard state, and the observed decrease in $\Delta C_{p_2}{}^\circ$ in the butyl series is produced by the relatively high heat capacity of the more branched

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(52) F. Franks and M. J. Quickenden, *Chem. Commun.*, 388 (1968).

(53) W. J. LeNoble, *Progr. Phys. Org. Chem.*, 5, 207 (1967).

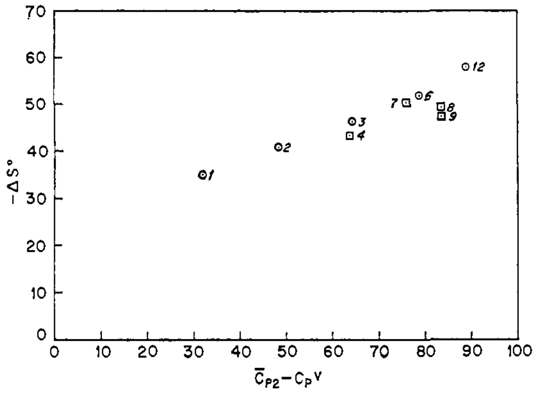

Figure 6. Correlation of heat capacity ($\bar{C}_{p_2} - C_p{}^V$) and entropy (ΔS°) of transfer for some alcohols in Table I from the vapor phase to high dilution in water. See Figure 2 for description of symbols.

alcohols (8, 9) as liquids rather than by a special solvation effect.

We note that at 25° Hill's data show a slight increase of $\Delta C_{p_2}{}^\circ$ with branching in the butyl alcohols, but this trend seems to be temperature dependent.

By means of ($\bar{C}_{p_2} - C_p{}^V$), the heat capacity of solution for alcohols from the vapor phase to water may be compared to the entropies (ΔS°) for the same process. Figure 6 shows some correlation between these properties for those cases where comparable data are available. It was this ΔS° which originally led Frank and Evans[54] to postulate the water structure-enforcing character of hydrocarbon chains. The correlation shown here gives strong added support to their hypothesis.

Implications for Structure–Reactivity Correlations. The over-all success of linear free-energy relationships for comparing structural changes with reactivity is unassailable. Such correlations provide invaluable means for the storage and prediction of rate and equilibrium data. However, beyond this, they have frequently been applied as primary sources of information for potential energy terms such as resonance, inductive, and steric effects. This assumes that free-energy measurements obtained in solution near room temperature are a good guide to *relative* potential energies at absolute zero in the gas phase. Considerable experience and also some theoretical justification support this extraordinary conclusion for large changes in ΔG. Although it is not uncommon to find even small rate or equilibrium constant differences interpreted in quite considerable detail in terms of potential energy differences, the large heat capacity terms described in this paper serve as a warning that in water or highly aqueous solution there may be an incursion of heat capacity effects from several sources not commonly recognized. Firstly, ΔC_p for a reaction or process affects the free-energy change at temperatures above absolute zero through the following equation

$$\Delta G^\circ = \Delta H_0 + \int_0^T \Delta C_p \, dT - T \int_0^T \Delta C_p \, d \ln T$$

in which ΔH_0 is the enthalpy at absolute zero and the two integral terms are equal, respectively, to the excess enthalpy and entropy at temperature T. Therefore, small but erratic changes in heat capacity of solution within a series of similar compounds in aqueous solution could produce an erroneous estimate of their relative potential energies referred back to absolute zero. Since there is no necessary or observed correlation between heat capacities or heat capacities of solution and enthalpies, free energies, or entropies, this factor could easily intrude without detection and may vary from one head group to another.

A second problem with heat capacity terms can arise whenever rate or equilibrium data are extrapolated from one temperature to another in order to make free energy comparisons under comparable conditions. If the extrapolation is a long one and heat capacity of ionization of activation is large, appreciable errors can result (*e.g.*, a heat capacity term of 100 cal/(mole deg) obviously introduces 1 kcal for every 10° extrapolation).

Thirdly, in view of the large effects of concentration on heat capacity terms in aqueous solution, it is especially important to use results obtained at high dilution, *i.e.*, less than 10^{-3} *M* for analysis of rates and equilibria.

An important conclusion from the present study is that it is hazardous to draw conclusions from small differences in enthalpies obtained at a single temperature in water. In accordance with this belief, we have made no attempt to interpret the effect of molecular structure on the $\Delta \bar{H}_s$ values in Table I. These represent the heats of transfer for each alcohol from its pure liquid state to high dilution in water at 25°. In view of the large differences in heats of vaporization of the pure liquid alcohols and the large effects of temperature on $\Delta \bar{H}_s$, we see little profit in attempting to interpret $\Delta \bar{H}_s$ values in this solvent at a single temperature.

We expect that heat capacity problems will be much smaller in other solvents, but as Ives and Marsden[5b] have warned us: "When water is the solvent, the complexities are such as to exclude as yet the possibility of detailed interpretation. The task is rather to use the measured functions to find what is happening and to identify the effects which require interpretation."

Acknowledgment. We are glad to acknowledge the contributions of Dr. James Campion, Mr. C. Fisher, Miss Margaret Ho, Mr. Charles Thompson, Mr. Timothy Drury, and Mrs. M. J. Pugh who made many of the enthalpy measurements recorded here. Helpful comments from Professor Loren Hepler and Dr. Felix Franks are appreciated.

Appendix

Glossary of Special Terms

$\Delta C_{p_2}{}^\circ$	heat capacity of solution of the solute (2) from a pure, liquid standard state to high dilution in water
$\bar{C}_{p_2}$	partial molal heat capacity of solute (2)
ΔC_{p_i}	heat capacity of ionization
$\Delta C_p{}^\ddagger$	heat capacity of activation
ΦC_{p_2}	apparent molar heat capacity
$C_p{}^{\text{pure}}$	heat capacity of pure solute
$C_p{}^L$	heat capacity of pure liquid
$C_p{}^V$	heat capacity of pure vapor
$\Delta \bar{H}_s$	partial molar heat of solution at infinite dilution

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[54] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 13, 507 (1945).