

Thermodynamics of Molecular Association of Alcohols and Ketones

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Summary: Studies on the molecular association of some alcohols and ketones, separately, and with each other were performed in the two different solvents diphenyl methane and tetradecane. The investigations were carried out at 25, 35 and 45°C, using a simple vapour pressure technique. The computed thermodynamic functions of these reactions are reported and the solvent effects have been discussed.

Introduction

Molecular interactions between alcohols and ketones are of significance in a number of industrial and medical areas. The pairwise association of solute molecules must be better understood in order to explain the properties of complicated solutions, in which both solute-solute and solute-solvent interactions are important.

The hydrogen bonded complexes between hydroxyl derivatives and oxygen bases have been extensively studied [1-3]. A number of recent publications has been based on the assumption that only binary complexes are important in hydroxylic systems even at high concentrations [4-7]. The exact nature of the molecular species in solution has been discussed by a number of researches [8-10]. The major factors affecting the extent of hydrogen bonding in aliphatic alcohols are the molecular geometry and polarity at the hydroxylic site. In $\text{OH}\dots\text{O}=\text{C}$, the contribution of induced moment to the strength of hydrogen bonding is high [1].

A systematic study of molecular association in binary nonelectrolytic solutions was carried out using various

techniques [11-13]. In the present work, further studies were done, mainly on the molecular complexation of some alcohols and ketones, separately, and with each other using a simple vapour pressure technique [14, 15]. The aim of this study was to obtain more thermodynamic informations related to complex formation in solution. The solvent effect has also been studied using two different solvents. The research included:

1) Studies on the self-association of the aliphatic alcohols: methanol, ethanol, n-propanol, n-butanol, iso-propanol and tert.-butanol and the aliphatic ketones: acetone, methyl ethyl ketone, diethyl ketone, methyl n-propyl ketone and methyl iso-propyl ketone. This has been done in the two non-polar, nonvolatile solvents diphenyl methane (DPM) and tetradecane (TD), which differ greatly in their nature.

2) Studies on the hetero-association of the volatile alcohols: methanol and ethanol each with the nonvolatile ketone acetophenone in DPM solution. Also the interaction of the volatile ketone acetone with each of the nonvo-

lative alcohols: octanol, phenol and 2, 6-dimethyl phenol, again in DPM solution, has been studied.

Self and hetero-associated systems were investigated at the three temperatures 25, 35 and 45°C.

Experimental

Materials

All the chemicals used in this work were either analytical or C.P grade reagents. They were all purified by repeated distillation.

Apparatus and technique

The apparatus used is similar to the one constructed and used previously [14,15]. The experimental procedure is based on measuring the vapour pressure of added increments of the volatile solute (over its solution) either alone (in the self association study) or together with the nonvolatile solute (in hetero-association) both in the nonvolatile, nonpolar solvent. A state of equilibrium is allowed to be attained after each addition before recording the vapour pressure. The concentration ranges of the volatile solute varied from 0.093 M to 0.246 M in case of methyl n-propyl ketone and methanol respectively. The heteroassociation reactions were carried out with 0.05 M solutions of the non-volatile solute.

Calculations

The methods of calculations followed in this work were the same as those adopted previously [15]. The data were fitted by a computer program designed for linear and nonlinear least squares. Enthalpies of formation (H) of the associated species were calculated from the temperature dependence of the corresponding computed formation constants.

It is to be mentioned that the self association of methanol could not be studied in TD because of its high vapour pressure with respect to the range of the employed apparatus.

Results and Discussion

1) Self association reactions

Figure (1-4) show the variation of the total vapour pressure of the investigated alcohols and ketones with their formal concentrations at 25°C in DPM and TD. The same trend is obtained at the other two temperatures 35 and 45°C, which show an apparent high degree of association in the two cases.

Over the nature of the probable polymers of aliphatic alcohols in solution of nonpolar solvents, there has been always a controversy in the literature [8-10]. In the present work, however, the best fitting of the data is obtained on considering the existence of dimers as the most probable associated species, in solution, in equilibrium with monomers at all the investigated temperatures. This is supported by the conclusion of Murty [16] drawn from similar work. It is well known that hydrogen bonding stabilizes the formation of molecules in aliphatic alcohols [17-18]. Tables (I) and (II) summarize the computed values of the dimerization constants (K_2^S), Henry's law constants (K^H) and

the enthalpy changes (ΔH) for the alcohols in DPM and TD respectively. These values indicate, in each case, an increase in the degree and strength of self association on decreasing the molecular weight of the alcohol in the order: methanol > ethanol > n-propanol iso-propanol > n-butanol > tert-butanol. Normally, in studies of base-ROH interactions in condensed phases, one expects inductive effect to predominate (20). The polarizability, the inductive

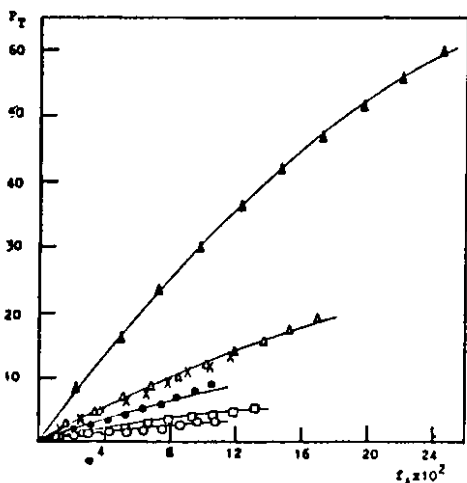


Fig.1: Variation of total pressure with formal concentration of:
 (Δ)methanol
 (Δ)ethanol
 (X)iso-propanol
 (e)tert-butanol
 (O)n-propanol
 and (o)a-butanol, in diphenylmethane at 25°C.

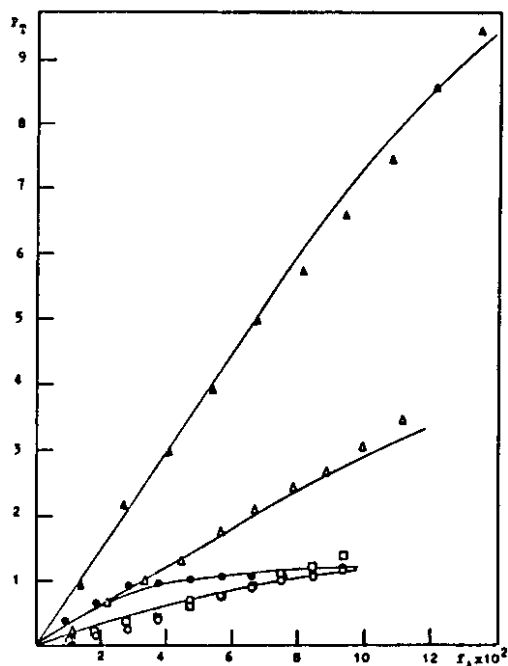


Fig.3: Variation of total pressure with formal concentration of:
 (Δ)acetone, (Δ)methyl ethyl ketone (O) diethyl ketone, (e) methyl is-propyl ketone, and (o) methyl n-propyl ketone, in diphenylmethane at 25°C.

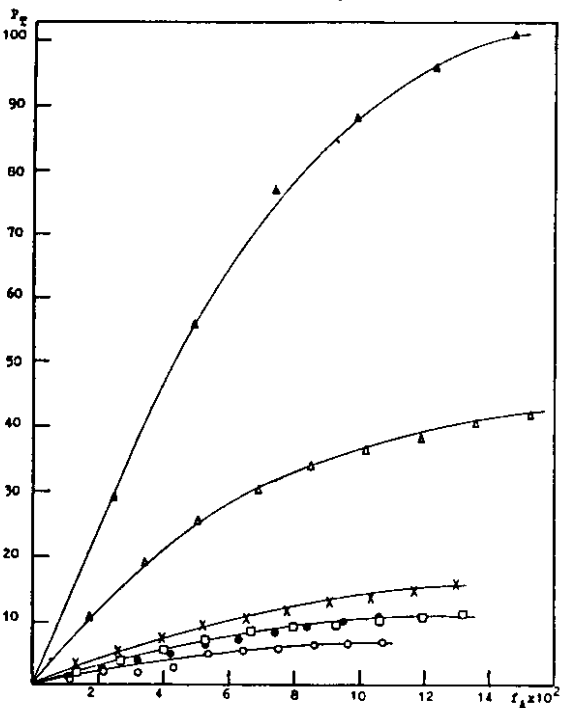


Fig.2: Variation of total pressure with formal concentration of:
 (Δ)methanol
 (Δ)ethanol
 (X)iso-propanol
 (e)tert-butanol
 (O)n-propanol
 and (o)n-butanol, in tetradecane at 25°C.

and steric effects for the investigated alcohols increase as the alkyl group increases in size, thus diminishing the extent and strength of the formed hydrogen bonds according to the above mentioned order.

Considering the solvent effect, it could be noted that the two solvents used affect solvation of the alcohols differently. The extent of self association in TD was found to be larger than that in DPM and also ΔH has more negative values in TD than in DPM. These results are in good agreement with many other reports [16, 21-23] on analogous systems. The DPM ($C_6H_5 \cdot CH_2 \cdot C_6H_5$) belongs to the arene type compounds with prevailing aromatic nature due to the presence of the two phenyl groups, whereas TD ($(CH_3 \cdot (CH_2)_{12} \cdot CH_3)$) belongs to the aliphatic type compounds. The former is expected to have higher solvation

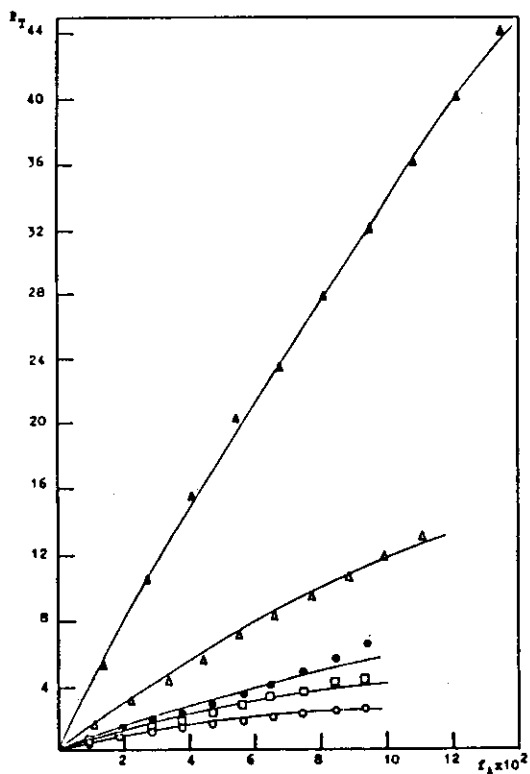


Fig.4: Variation of total pressure with formal concentration of:
 (Δ)acetone,
 (Δ)methyl ethyl ketone,
 (e)methyl iso-propyl ketone,
 (o)methyl n-propyl
 and tetradecane at 25°C.

power than TD, due to the possible interaction between the bonds of the phenyl groups and the solute monomers. This may, then, decrease the extent of dimer formation. Enthalpy changes computed for methanol, ethanol and tert-butanol are comparable with the literature value obtained for ethanol in benzene, 5 kcal/mole (22), possibly indicating the formation of linear dimers. The small size of the lower alcohols and the steric hindrance in tert-butanol may account for this noncyclic dimer formation. However, the cyclic dimers are more probable in case of the other investigated alcohols.

Concerning the self association of ketones, the most probable associated species formed, in the two solvents, are also the dimers. The calculated association constants in DPM (Table III) either have negative values or show very unreasonable inconsistency, which may be due to the increased restriction for dimer formation. Hence, no enthalpy changes were computed. On the other hand, the results obtained in TD shown in Table (IV) indicated, though to a small extent, the self association of the ketones

Table-1: Summary of Constants and Enthalpy Changes for self Association of Alcohols in DPM

Alcohol	T°K	K_2^S (molar ⁻¹)	K^H	ΔH (kcal/mol of dimers)
Methanol	298	1.3294 ± 0.125	370.37 ± 16.3	-5.484
	308	0.9203 ± 0.101	500.86 ± 24.8	
	318	0.7454 ± 0.083	625.43 ± 33.7	± 0.757
Ethanol	298	0.9383 ± 0.112	136.99 ± 7.3	
	308	0.7174 ± 0.079	232.56 ± 11.4	-6.104
	318	0.4902 ± 0.053	291.97 ± 15.1	± 0.914
n-Propanol	298	0.5519 ± 0.059	128.20 ± 6.2	
	308	0.2877 ± 0.031	192.31 ± 10.5	-13.106
	318	0.1063 ± 0.012	256.41 ± 12.2	±1.924
n-Butanol	298	0.4087 ± 0.042	43.10 ± 3.35	
	308	0.2294 ± 0.025	69.44 ± 3.98	-13.101
	318	0.1022 ± 0.011	128.21 ± 6.55	± 2.012
iso-Propanol	298	0.4735 ± 0.048	92.59 ± 4.45	
	308	0.2422 ± 0.028	146.25 ± 7.78	- 13.632
	318	0.1123 ± 0.012	190.09 ± 9.16	±1.962
tert-Butanol	298	0.2440 ± 0.030	33.22 ± 1.82	
	308	0.2005 ± 0.022	54.35 ± 2.92	- 6.097
	318	0.1286 ± 0.014	103.09 ± 5.47	±0.933

Table-2: Summary of Constants and Enthalpy Changes for Self Association of Alcohols in TD

Alcohol	T ⁰ _K	K ₂ ^S (molar ⁻¹)	K ^H	H (kcal/mole of dimers)
Ethanol	298	99.48 ± 10.20	1250.8 ± 37.8	
	308	21.80 ± 2.60	1763.6 ± 52.2	- 27.861
	318	5.37 ± 0.49	2503.2 ± 75.6	± 3.393
n-Propanol	298	49.90 ± 5.10	1113.6 ± 33.3	
	308	12.76 ± 1.30	1410.2 ± 41.9	-26.646
	318	2.98 ± 0.28	1992.8 ± 59.9	± 3.123
n-Butanol	298	29.59 ± 2.20	850.1 ± 22.1	
	308	7.07 ± 0.58	1062.8 ± 29.2	-25.593
	318	1.98 ± 0.17	1412.1 ± 39.8	± 2.987
iso-Propanol	298	41.32 ± 4.30	907.4 ± 26.4	
	308	10.73 ± 1.10	1137.3 ± 35.5	- 26.121
	318	2.63 ± 0.27	1615.8 ± 42.7	± 3.067
tert-Butanol	298	16.47 ± 1.20	652.7 ± 18.8	
	308	4.19 ± 0.42	710.3 ± 22.5	-23.699
	318	1.35 ± 0.11	930.3 ± 26.8	± 2.545

Table-3: Summary of Constants for Self Association of Ketones in DPM

Ketone	T ⁰ _K	K ₂ ^S (molar ⁻¹)	K ^H
Acetone	298	0.9600	80.0000
	308	0.6606	114.9425
	318	0.5089	153.8462
Methyl ethyl ketone	298	-1.1127	23.2975
	308	-0.5890	38.0900
	318	0.4163	61.1023
Diethyl ketone	298	-1.8190	8.4918
	308	-0.8813	16.7291
	318	-1.0293	25.4621
Methyl iso-propyl ketone	298	94.1827	49.8504
	308	0.4622	18.5925
	318	3.4317	46.9021
Methyl n-propyl ketone	298	-1.7710	6.9056
	308	3.1811	27.3411
	318	0.2985	28.3447

investigated follows the order: methyl iso-propyl ketone > methyl n-propyl ketone > diethyl ketone > methyl ethyl

ketone > acetone. This may show that the inductive and steric effects discussed in case of alcohols are operating in this case in an opposite direction. The dimers formed are expected to be a mixture of cyclic and non-cyclic dipole-dipole interacting species. Accordingly, the computed ΔH can be considered as an average value per mole of dimers. These values, which are in accordance with literature results [24], show that these dipole-dipole interactions are relatively weak.

Obviously, the undergo studied alcohols self associate to a much greater extent than the considered ketones.

2) *Hetero-association reactions between alcohols and ketones*

These studies were carried out using DPM as a solvent, as it permits a good chance for hetero-interaction. The OH...O association occurs usually through hydrogen bonding (1).

a) Association of volatile alcohols with a nonvolatile ketone

The systems studied, in this section, were methanol and ethanol with acetophenone in DPM. The results achieved indicate, most probably, the presence of 1:1 and 2:1 alcohol-ketone complexes at the three temperatures. Similar findings were reported [25]. The values determined for the heteroassociation constants and enthalpy changes (Table V) show that the degree of association of ethanol with acetophe-

none is larger than that of methanol. This is, presumably due to the higher tendency of methanol to self-association, thus competing with the hetero-interaction.

b) Association of a volatile ketone with nonvolatile alcohols:

The association of acetone was studied with each of n-octanol, phenol and 2,6-dimethyl phenol. The alcohols chosen were such to compare, first, an aliphatic alcohol with an aromatic

Table-4: Summary of Constants and Enthalpy Changes for Self Association of Ketones in TD

Ketone	T ^o K	K ₂ ^S (molar ⁻¹)	K ^H	H (kcal/mole of dimers)
Acetone	298	0.9795 ± 0.052	75.82 ± 2.5	- 3.486
	308	0.7989 ± 0.044	92.61 ± 2.7	± 0.682
	318	0.6622 ± 0.035	131.33 ± 4.1	
Methyl ethyl ketone	298	1.0345 ± 0.057	98.15 ± 3.1	- 2.531
	308	0.8331 ± 0.041	115.31 ± 3.5	± 0.550
	318	0.6785 ± 0.037	207.90 ± 8.9	
Diethyl ketone	298	1.1838 ± 0.055	192.60 ± 6.2	- 4.237
	308	0.9123 ± 0.047	301.84 ± 10.2	± 0.807
	318	0.7588 ± 0.040	395.32 ± 12.6	
Methyl n-propyl ketone	298	1.2451 ± 0.063	240.37 ± 7.5	- 4.203
	308	0.9728 ± 0.053	386.53 ± 11.0	± 0.843
	318	0.7979 ± 0.043	493.42 ± 15.4	
Methyl iso-propyl ketone	298	1.5867 ± 0.081	404.04 ± 12.4	-4.566
	308	1.2320 ± 0.062	565.29 ± 17.9	± 0.924
	318	0.9823 ± 0.055	713.27 ± 22.2	

Table-5: Summary of Constants and Enthalpy Changes for Hetero-association of Alcohols with Acetophenone in DPM

Acetophenone with	T ^o K	K ₁₁ ^S (molar ⁻¹)	K ₂₁ ^S (molar ⁻²)	ΔH ₁	ΔH ₂ (kcal/mole of complex)
Methanol	298	13.33 ± 1.25	28.87 ± 3.11	3.923	7.877
	308	10.45 ± 1.03	17.75 ± 1.81	±0.472	± 0.862
	318	8.81 ± 0.90	12.61 ± 1.33		
Ethanol	298	18.96 ± 1.72	58.42 ± 3.91	3.616	7.189
	308	15.19 ± 1.53	37.50 ± 2.02	± 0.383	± 0.791
	318	12.97 ± 1.18	27.34 ± 1.43		

Table-6: Summary of constants and Enthalpy Changes for Hetero-association of Acetone with Nonvolatile Alcohols, in DPM

Acetone with	T ^o K	K ₁₁ ^S (molar ⁻¹)	K ₂₁ ^S (molar ⁻²)	Δ H ₁	Δ H ₂
				(kcal/mole of complex)	
Phenol	298	7.279 ± 0.371	12.982 ± 0.655	5.706	11.455
	308	5.233 ± 0.272	6.711 ± 0.411	± 0.731	± 1.336
	318	3.986 ± 0.202	3.872 ± 0.197		
2,6-Dimethyl phenol	298	2.934 ± 0.154	insignificant		
	308	1.440 ± 0.075	results, not taken		
	318	0.738 ± 0.042	in consideration		
n-Octanol	298	4.935 ± 0.253	4.262 ± 0.223	8.604	18.720
	308	3.350 ± 0.176	1.684 ± 0.087	± 1.013	± 2.434
	318	1.984 ± 0.107	0.590 ± 0.033		

one, and second, a substituted with a nonsubstituted alcohol. In this case, the 1:1 and 2:1 alcohol-ketone complexes seem to be the most probable ones only with n-octanol and phenol. While with 2,6-dimethyl phenol, the formation of the 2:1 complex is insignificant. The respective thermodynamic functions presented in Table (VI) substantiate that phenol is a stronger hydrogen bonding agent than n-octanol, being more acidic and having a stronger potency for hydrogen bond formation. Comparing between phenol and 2,6-dimethyl phenol it is apparent that the presence of the two methyl groups causes a steric hindrance around the OH group to hydrogen bonding and also lowers the acidity of phenol by the double acting +I effect of the methyl groups. Accordingly, the tendency for hetero-complexing with acetone may be in the order: phenol > n-octanol > 2,6-dimethyl phenol.

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