

Dielectric Polarization Measurements on Some β -Diketones & β -Ketoesters in Solution: Part II—Acetylacetone

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The apparent solution moments of acetylacetone in various solvents have been measured. Practically, a linear relation has been observed between the square of the moment at infinite dilution in a given solvent and the corresponding mole percentage of each tautomer. Use has been made of the relation obtained to determine the most probable structures of the keto and enol molecules. From a contribution of the measured Onsager moment of acetylacetone at various concentrations in cyclohexane and carbon tetrachloride, the variation of the Onsager association factor, S , with concentration has been obtained in these solvents.

In part I of this series¹ the method of dielectric polarization measurements has been used to investigate the effects of solvents of different polarities on the keto-enol equilibrium of ethyl acetoacetate. The present paper extends such investigation to acetylacetone. The apparent solution moments of acetylacetone have been determined in four non-polar solvents, namely, cyclohexane, carbon tetrachloride, benzene, and dioxan, at infinite dilution, and at various concentrations over the entire range of concentrations.

Materials and Methods

Experimental procedures and methods of calculation of the dipole moments at infinite dilution and over the whole range of concentration were the same as described¹ in Part I.

Results

The values we obtained for the apparent solution moments of acetylacetone at infinite dilution, μ_{obs} , in the non-polar solvents cyclohexane, carbon tetrachloride, benzene, and dioxan, together with the Onsager² moment, $S^{1/2}\mu_0$, calculated for the pure

liquid diketone at 30 to 50°C, are listed in Table 1. Also included in this table are the enol mole percentages determined by earlier workers³⁻⁶ and those determined in the present work as well as the vapour moment⁷ of acetylacetone. A graphical representation of the relation between the square of the measured dipole moment of acetylacetone in various solvents at infinite dilution, μ_{obs}^2 , at 30°C as well as of that in the vapour and condensed phases, and the corresponding enol mole fraction, N_{enol} , is shown in Fig. 1. Given in Table 2 are the data required for the determination of the apparent solution moments, μ_{obs} , of acetylacetone at infinite dilution in the four non-polar solvents. Fig. 2 shows the variation of the Onsager moment square, μ_2^2 , with the mole fraction of the diketone throughout the whole range of concentrations in these solvents at 38°C.

Discussion

If we accept, as in the case of ethyl acetoacetate¹, that in very dilute solutions of acetylacetone in non-polar solvents, there are no mutual interactions between the different molecules and that in these solutions there are only two tautomers of the unknown

Table 1—Dipole Moments and Enol Mole Per Cent of Acetylacetone in Various Non-polar Solvents

Solvent	μ_{obs}			Mole % Enol (30°C)	Method	Ref.
	30°	40°	50°C			
Cyclohexane	2.92	2.93	2.95	95	UV NMR	present work, (3)
CCl ₄	2.93	2.96	2.98	94	UV NMR	present work, (3)
Benzene	2.94	2.95	2.96	96	NMR	(4)
Dioxan	3.11	3.13	3.14	74	UV	present work
Gas	3.05	(49-204°C)	(17)	86		(5)
Liquid $S^{1/2}\mu_0$	3.88	3.89	3.90	81.4	NMR	(6)

Table 2—Apparent Solution Moments of Acetylacetone in Non-polar Solvents

Cyclohexane										Carbon Tetrachloride										Benzene										Dioxan									
$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$	$w_2 \times 10^3$	$t(^\circ\text{C})$	$\epsilon_{1,2}$	$d_{1,2}$				
0	30	2.0070	0.7698	0	30	2.2176	1.5748	0	30	2.2672	0.8680	0	30	2.2004	1.0224	0	30	2.2004	1.0224	0	30	2.2004	1.0224	0	30	2.1774	1.0115	0	30	2.1774	1.0115	0	30	2.1774	1.0115				
	40	1.9977	0.7597		40	2.1977	1.5561		40	2.2475	0.8580		40	2.1774	1.0115		40	2.1774	1.0115		40	2.1774	1.0115		40	2.1546	1.0003		40	2.1546	1.0003		40	2.1546	1.0003				
	50	1.9780	0.7495		50	2.1780	1.5361		50	2.2273	0.8468		50	2.1546	1.0003		50	2.1546	1.0003		50	2.1546	1.0003		50	2.2286	1.0223		50	2.2286	1.0223		50	2.2286	1.0223				
4.5855	30	2.0399	0.7702		30	2.2645	1.5727		30	2.2847	0.8681		30	2.2847	0.8681		30	2.2847	0.8681		30	2.2847	0.8681		30	2.2042	1.0112		30	2.2042	1.0112		30	2.2042	1.0112				
	40	2.0292	0.7600	2.8274	40	2.2427	1.5534	1.9023	40	2.2643	0.8581	1.9023	40	2.2643	0.8581	2.3590	40	2.2643	0.8581	2.3590	40	2.2643	0.8581	2.3590	40	2.1804	1.0002		40	2.1804	1.0002		40	2.1804	1.0002				
	50	2.0083	0.7499		50	2.2211	1.5336		50	2.2433	0.8470		50	2.2433	0.8470		50	2.2433	0.8470		50	2.2433	0.8470		50	2.2543	1.0221		50	2.2543	1.0221		50	2.2543	1.0221				
6.4277	30	2.0531	0.7703		30	2.2901	1.5716		30	2.2969	0.8683		30	2.2969	0.8683		30	2.2969	0.8683		30	2.2969	0.8683		30	2.2286	1.0111		30	2.2286	1.0111		30	2.2286	1.0111				
	40	2.0419	0.7602	4.3666	40	2.2672	1.5522	3.2332	40	2.2761	0.8583	3.2332	40	2.2761	0.8583	4.5095	40	2.2761	0.8583	4.5095	40	2.2761	0.8583	4.5095	40	2.2038	1.0000		40	2.2038	1.0000		40	2.2038	1.0000				
	50	2.0204	0.7500		50	2.2446	1.5323		50	2.2545	0.8472		50	2.2545	0.8472		50	2.2545	0.8472		50	2.2545	0.8472		50	2.2769	1.0220		50	2.2769	1.0220		50	2.2769	1.0220				
7.8019	30	2.0629	0.7705		30	2.3269	1.5700		30	2.3199	0.8685		30	2.3199	0.8685		30	2.3199	0.8685		30	2.3199	0.8685		30	2.2498	1.0110		30	2.2498	1.0110		30	2.2498	1.0110				
	40	2.0513	0.7603	6.5877	40	2.3026	1.5504	5.7318	40	2.2982	0.8585	5.7318	40	2.2982	0.8585	6.3953	40	2.2982	0.8585	6.3953	40	2.2982	0.8585	6.3953	40	2.2244	0.9999		40	2.2244	0.9999		40	2.2244	0.9999				
	50	2.0295	0.7502		50	2.2785	1.5304		50	2.2754	0.8474		50	2.2754	0.8474		50	2.2754	0.8474		50	2.2754	0.8474		50	2.2912	1.0219		50	2.2912	1.0219		50	2.2912	1.0219				
10.6699	30	2.0834	0.7707		30	2.3645	1.5684		30	2.3587	0.8689		30	2.3587	0.8689		30	2.3587	0.8689		30	2.3587	0.8689		30	2.2633	1.0109		30	2.2633	1.0109		30	2.2633	1.0109				
	40	2.0710	0.7606	8.8541	40	2.3387	1.5486	9.9381	40	2.3353	0.8589	9.9381	40	2.3353	0.8589	7.5854	40	2.3353	0.8589	7.5854	40	2.3353	0.8589	7.5854	40	2.2373	0.9998		40	2.2373	0.9998		40	2.2373	0.9998				
	50	2.0484	0.7504		50	2.3131	1.5284		50	2.3108	0.8479		50	2.3108	0.8479		50	2.3108	0.8479		50	2.3108	0.8479		50	2.3164	1.0218		50	2.3164	1.0218		50	2.3164	1.0218				
14.8502	30	2.1134	0.7710		30	2.3893	1.5673		30	2.3807	0.8691		30	2.3807	0.8691		30	2.3807	0.8691		30	2.3807	0.8691		30	2.2873	1.0107		30	2.2873	1.0107		30	2.2873	1.0107				
	40	2.0997	0.7609	10.3414	40	2.3624	1.5475	12.3305	40	2.3565	0.8591	12.3305	40	2.3565	0.8591	9.6943	40	2.3565	0.8591	9.6943	40	2.3565	0.8591	9.6943	40	2.2605	0.9997		40	2.2605	0.9997		40	2.2605	0.9997				
	50	2.0760	0.7508		50	2.3358	1.5271		50	2.3309	0.8481		50	2.3309	0.8481		50	2.3309	0.8481		50	2.3309	0.8481		50	2.2605	0.9997		50	2.2605	0.9997		50	2.2605	0.9997				
$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}	$t(^\circ\text{C})$	DP_2	$P_{2,1}$	μ_{obs}				
30	29.849	203.41	2.92	30	29.827	204.72	2.93	30	29.732	205.68	2.94	30	29.732	205.68	2.94	30	29.832	226.52	3.11	30	29.832	226.52	3.11	30	29.832	226.52	3.11	30	29.832	226.52	3.11	30	29.832	226.52	3.11				
40	29.828	199.34	2.93	40	29.806	202.28	2.96	40	29.710	201.19	2.95	40	29.710	201.19	2.95	40	29.814	223.52	3.13	40	29.814	223.52	3.13	40	29.814	223.52	3.13	40	29.814	223.52	3.13	40	29.814	223.52	3.13				
50	29.817	196.14	2.95	50	29.743	199.71	2.98	50	29.681	196.99	2.96	50	29.681	196.99	2.96	50	29.790	218.07	3.14	50	29.790	218.07	3.14	50	29.790	218.07	3.14	50	29.790	218.07	3.14	50	29.790	218.07	3.14				

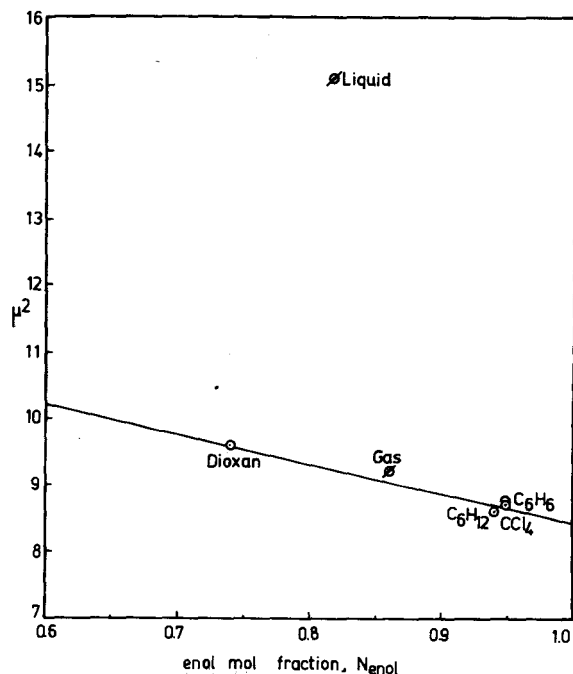


Fig. 1—Relation between the squares of the measured dipole moments of acetylacetonone in various non-polar solvents at infinite dilution at 30°C and the corresponding enol mole fraction

moments μ_{keto} and μ_{enol} , then it follows that a plot of the square of the observed moment, μ_{obs}^2 , against the corresponding enol mole fraction N_{enol} would be linear. This is observed experimentally (Fig. 1). Furthermore, the point representing measurements in the vapour phase of acetylacetonone is obviously in close proximity to the suggested linear relation, thus resembling ethyl acetoacetate¹ in this respect. This is, however, not the case when pure liquid is considered. Thus, while in the case of acetylacetonone, the point representing measurements in the pure liquid phase deviates significantly from the straight-line relation, such a deviation has not been observed¹ in liquid ethyl acetoacetate. Therefore, the points representing measurements in dioxan, cyclohexane, benzene, chloroform and vapour phase, signifying a linear relationship between μ^2 and N_{enol} at 30°C, have been used to draw the best straight line. The equation obtained is,

$$\mu^2 = 13.58 - 5.22 N_{\text{enol}} \quad \dots(1)$$

where μ is expressed in Debye units. Hence, $\mu_{\text{keto}} = 3.62$ D, and $\mu_{\text{enol}} = 2.89$ D.

In order to check the validity of this equation, the value of the difference $\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2$ obtained here has been compared with that calculated from the data of Powling and Bernstein⁵ using the following equation based on the Onsager²-Kirkwood⁸ model,

$$\Delta H_{\text{solution}} = \Delta H_{\text{gas}} - \left(\frac{\epsilon - 1}{2\epsilon + 1} \frac{d}{M} \right)_{\text{solvent}} \times \text{constant} \times (\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2) \quad \dots(2)$$

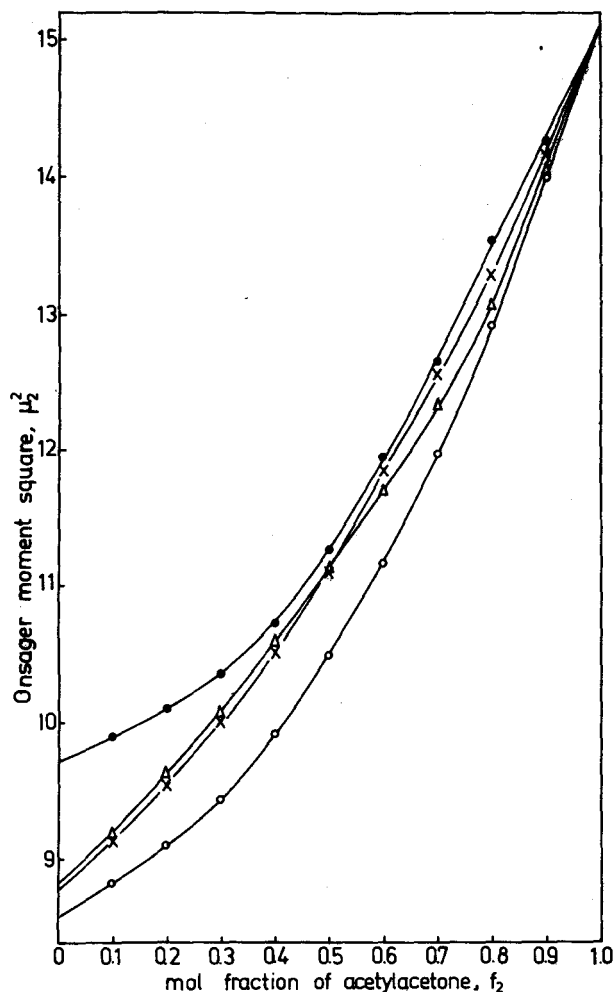


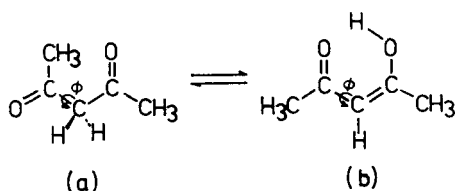
Fig. 2—Variation of the square of dipole moment of acetylacetonone with its mole fraction in different solvents at 38°C, in cyclohexane (O), carbon tetrachloride (x), benzene (Δ), and in dioxan (●)

Thus, if we apply this equation to an infinite dilution of acetylacetonone in cyclohexane using the values -2.8 and -2.4 kcal/mol given by Allen and Dwek³ for $\Delta H_{\text{solution}}$ and by Powling and Bernstein⁵ for ΔH_{gas} , respectively, and the value 1.52×10^{48} (molecule/mol)² for the constant, then difference $\mu_{\text{keto}}^2 - \mu_{\text{enol}}^2$ would be of the order 6.1 D^2 . In like manner, the substitution for $\Delta H_{\text{solution}}$ in carbon tetrachloride by the value³ -2.8 kcal/mol in Eq. (2) would lead to a value of 4.75 D^2 for this difference. Obviously, the average value of the order 5.45 D^2 is in fair agreement with that (5.22 D^2) deduced from dipole moment measurements.

Use has been made of the two dipole moment values μ_{keto} and μ_{enol} to infer the most probable structures of the two tautomers. For this purpose, the structures (a) and (b) shown below were first suggested for the keto and enol molecules, respectively.

Here the angle ϕ was considered as the angle of rotation of the CH_3CO -group around the C-C axis taken for simplicity as the Y axis, the Z-axis being

perpendicular to the plane of the paper. By assuming for ϕ values varying between 0 and 180°, the dipole moment of the resultant conformation have been calculated by the usual vector summation method of bond moments⁹. It has been found that for a dihedral angle (ϕ) of 48.6°, which was previously suggested by Lowrey¹⁰ in the case of the keto molecule, the calculated value of dipole moment is 3.39 D. Therefore, structure (a) with $\phi = 48.6^\circ$ might be taken as the most probable structure for the keto molecule since this value is in fair agreement with the value 3.62 D deduced above from Eq. (1). Similarly in the case of enol structure, when we assigned for ϕ the value 0°, the calculated dipole moment (2.94 D) was in fair agreement with the value (2.89 D) deduced above; structure (b) can, therefore, be taken as the most probable for the enol tautomer.



In pure liquid form of acetylacetone, had there been no specific interactions of the type keto-keto, enol-enol, or keto-enol through hydrogen-bonding action or dipole-dipole forces, leading in turn to association, the Onsager dipole moment, $S^{1/2}\mu_0$, of the pure liquid phase should have been equal to the moment calculated from Eq. (1). This, in fact, is not the case; the Onsager moment of liquid acetylacetone at 30°C is 3.89 D (see Table 1) whereas the moment calculated from simple-mixture law is 3.05 D, corresponding to an enol mole fraction of 0.816 as reported by Reeves⁶. Hence, a rough estimate of the association factor S in pure liquid acetylacetone can be made by dividing the squares of the above two values, the value obtained at 30°C being 1.63. As has been realized before¹, this situation does not hold for pure liquid ethyl acetoacetate; calculation of S factor in a like manner gave a value practically equal to unity.

Expectedly, association in liquid acetylacetone decreases with dissolution in the non-polar, inert solvents cyclohexane, carbon tetrachloride, benzene, and dioxan, and nullifies at infinite dilution in these solvents, and in the gas phase of the β -diketone, as obtained by Eq. (1) based on the simple mixture law. Consequently, Eq. (1) can be utilized to estimate, in an

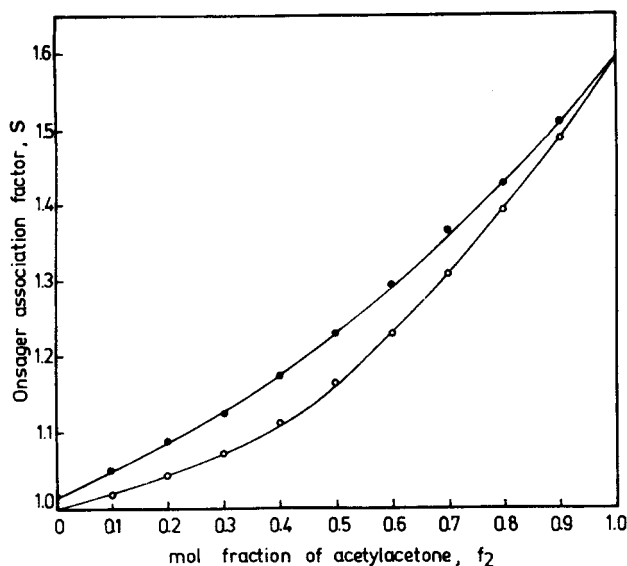


Fig. 3—Variation of the Onsager association factor of acetylacetone with its mole fraction in cyclohexane (O), and carbon tetrachloride (●) at 38°C

approximate way, the variation of the association factor S of acetylacetone with its concentration in these solvents, provided, of course, that the relative proportions of the two tautomers at each concentration, together with the corresponding Onsager moment, μ_2 , are known. Thus, from a knowledge of N_{enol} at various concentrations of acetylacetone in cyclohexane and carbon tetrachloride as given by Allen and Dwek³, the association factor S of acetylacetone at various concentrations in these two solvents has been estimated by dividing the square of the measured Onsager moment, μ_2^2 , at each concentration (see Fig. 2) by that calculated from Eq. (1) assuming no association. The results obtained are represented graphically in Fig. 3.

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