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Excess Molar Volumes & Excess Molecular Polarizations of Acetylacetone in Non-polar Solvents, Cyclohexane, Carbon Tetrachloride, Benzene & Dioxane

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Excess molar volumes ($\bar{V}_2 - V_2^0$) and excess molecular polarizations (P^E) of acetylacetone in four non-polar solvents, namely cyclohexane, carbon tetrachloride, benzene and dioxane, have been determined as a function of composition at 30°, 40° and 50°C. The gradual increase of excess molar volume with dilution in all solvents, indicates dissociation of the dimeric acetylacetone (in pure condensed phase). The solution moment (μ_2) of acetylacetone in pure condensed phase gradually decreases with dilution. All systems studied show positive excess polarization.

Different types of association in acetylacetone (pure liquid) and in solutions have been proposed by Lin and coworkers[1]. The complex species like ketone monomer monohydrate, ketone dimer, and ketone dimer monohydrate, were postulated to explain the available data. The dimer was assumed to be formed by dipole-dipole interaction. The relatively high dipole moment of acetylacetone in the condensed phase was ascribed by Maijes *et al.*[2] to the significant orientation during association. Dielectric constants of dilute solutions of acetylacetone in carbon tetrachloride and tetrachloroethylene were measured by Jain *et al.*[3] to study the presence of specific interactions in these two binary solutions. The large negative excess dielectric constants were attributed[3] to strong specific interactions between solute and solvent. As an extention of such studies, presently we have measured the excess molar volumes ($\bar{V}_2 - V_2^0$) and excess molecular polarizations (P^E) of acetylacetone in four non-polar solvents, such as cyclohexane, carbon tetrachloride, benzene and dioxane, as a function of composition with a view to understanding the nature of such interactions in these solvents.

The molecular polarization (P_{12}) of solution is defined by Eq. (1)

$$P_{12} = \frac{M_1 f_1 + M_2 f_2}{d} \cdot \frac{\varepsilon - 1}{\varepsilon + 2} \qquad \ldots(1)$$

and the modified Onsager[4,5] equation (Eq. 2) is used to estimate the dipole moment (μ_2) associated with solute molecule at each concentration over the entire range of concentration.

$$\mu_2^2 = \frac{9kT}{4\pi N} \cdot V \left[\frac{\frac{\varepsilon - 1}{\varepsilon + 2} - 3\left(\frac{f_1 V_1}{V} \cdot \frac{\varepsilon_1 - 1}{2\varepsilon + \varepsilon_1} + \frac{f_2 V_2}{V} \cdot \frac{v_2^2 - 1}{2\varepsilon + v_2^2} \right)}{f_2 \left(\frac{v_2^2 + 2}{2\varepsilon + 2^2} \right)^2 \cdot (2\varepsilon + 1)} \right] \qquad \ldots(2)$$

In Eqs (1) and (2) the subscripts 1 and 2 denote the solvent and solute, respectively, d, V and ε are the density, molar volume and dielectric constant of solution, respectively and other symbols have their usual meanings.

Materials and Methods

BDH grade acetylacetone, cyclohexane, carbon tetrachloride, benzene and dioxane were purified by standard procedures[6]. Their densities and refractive indices at 30°C agreed within ± 0.0001 with those reported in literature[6,7].

Density, refractive index and dielectric constant were measured as previously described[8,9].

Results

The dielectric constant (ε), refractive index (n_D) and density (d) for the various solvents at 30° to 50°C are given in Table 1. The molecular polarization data (P_{12}) and solution moment (μ_2) for all systems, calculated using Eqs (1) and (2), respectively, are included in Table 2.

From density measurements of acetylacetone in the four non-polar solvents at 30 to 50°C, the partial specific volumes of acetylacetone were first determined at each concentration using the method of intercepts; and when multiplied by the molecular weight, the partial molar volumes ($\bar{V}_2$) were obtained. Also calculated were the excess molar volumes ($\bar{V}_2 - V_2^0$) of the solute and the results obtained are listed in Table 2.

Variation of the excess molar volumes ($\bar{V}_2 - V_2^0$) and excess molecular polarization (P^E) of the binary mixtures of acetylacetone with the four non-polar solvents, are represented graphically in Figs 1 and 2, respectively.

Table 1—Polarization Data of Non-polar Solvents at Different Temperatures

Temp. °C	ε	n_D	d	P_1
		Cyclohexane		
30	2.0070	1.4200	0.7693	27.493
40	1.9977	1.4149	0.7597	27.647
50	1.9780	1.4094	0.7495	27.606
		Carbon tetrachloride		
30	2.2176	1.4545	1.5748	28.202
40	2.1977	1.4490	1.5557	28.215
50	2.1780	1.4432	1.5361	28.238
		Benzene		
30	2.2672	1.4948	0.8680	26.725
40	2.2475	1.4890	0.8580	26.740
50	2.2273	1.4833	0.8468	26.782
		Dioxane		
30	2.2004	1.4169	1.0224	24.628
40	2.1774	1.4125	1.0115	24.553
50	2.1546	1.4077	1.0003	24.478

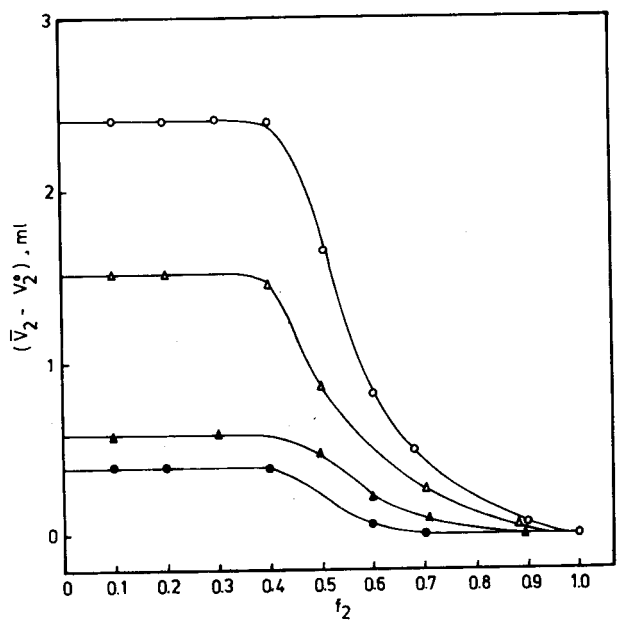

Fig. 1—Variation with composition of excess molar volume ($\bar{V}_2 - V_2^0$) of acetylacetone in cyclohexane (○), carbon tetrachloride (Δ), benzene (▲) and dioxane (●) at 30°C

Discussion

Self association in pure acetylacetone

An estimate of the association factor (S) in pure acetylacetone was first made. Since in the absence of any specific interactions (H-bonding, dipole-dipole type) in pure acetylacetone, the Onsager[4] dipole moment of pure phase of acetylacetone should be equal to its gas phase value determined by Zhan[10]. This in fact, was not the case as the Onsager moment (3.89 D) of liquid acetylacetone at 30°C was greater than the gas moment (3.05 D). This leads to a value of 1.63 for the Onsager association factor (S). This inference indicates the existence of the acetylacetone molecule in an associated form in the pure liquid state.

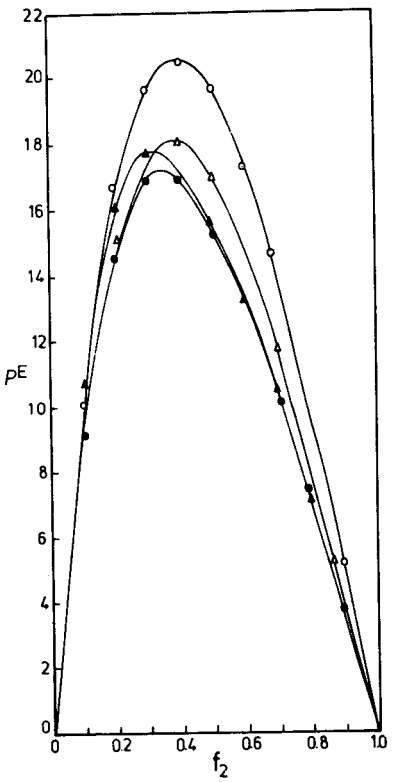

Fig. 2—Variation with composition of excess molecular polarization (P^E) of acetylacetone in cyclohexane (○), carbon tetrachloride (Δ), benzene (▲) and dioxane (●) at 30°C

Excess partial molar volumes ($\bar{V}_2 - V_2^0$) of acetylacetone in various solvents

The curves in Fig. 1, which represent the plots of $\bar{V}_2 - V_2^0$ of acetylacetone against its mol fraction (f_2) in the four non-polar solvents, are expected to provide information regarding the extent of dissociation of the dimer acetylacetone[1] in each solvent. Thus, the observed increase of partial molar volume of acetylacetone upon dilution with a non-polar solvent might be attributed to the effective dissociation of the dimer molecules, which play an important role in pure liquid state. The extent of such dissociation in different solvents increases in the order: dioxane < benzene < carbontetrachloride < cyclohexane.

Excess molecular polarization (P^E)

The excess molecular polarization was calculated from the relation:

$$P^E = P_{12} - (P_1 f_1 + P_2 f_2) \qquad \ldots(3)$$

and the results obtained are included in Table 2. The

Table 2—Polarization Data of Acetylacetone in Different Non-polar Solvents

f_2	Temp. °C	ε	n_D	d	$\bar{V}_2$	$\bar{V}_2 - V_2^0$	P_{12}	P^E	μ_2
				Acetylacetone + cyclohexane					
	30	3.0380	1.4209	0.7848	106.290	2.407	44.213	10.074	2.95
0.1012	40	2.9750	1.4156	0.7744	107.539	2.615	43.971	9.643	2.95
	50	2.9115	1.4105	0.7634	108.870	2.876	43.729	9.386	2.97
	30	4.3337	1.4226	0.8007	106.290	2.407	57.441	16.689	3.00
0.2019	40	4.2110	1.4178	0.7897	107.539	2.616	57.206	16.229	3.01
	50	4.0886	1.4121	0.7795	108.870	2.876	56.866	15.820	3.03
	30	5.7936	1.4247	0.8198	106.290	2.407	66.816	19.621	3.06
0.3001	40	5.6016	1.4191	0.8080	107.290	2.615	66.639	19.185	3.07
	50	5.4159	1.4133	0.7977	108.870	2.876	66.397	18.821	3.09
	30	7.6667	1.4267	0.8383	106.290	2.407	74.552	20.475	3.15
0.4048	40	7.3265	1.4218	0.8272	107.539	2.615	74.312	19.940	3.15
	50	7.1170	1.4164	0.8162	108.870	2.876	74.493	19.940	3.17
	30	9.9156	1.4291	0.8583	105.541	1.658	80.408	19.678	3.24
0.5061	40	9.4033	1.4242	0.8468	106.874	1.950	80.268	19.208	3.23
	50	9.0315	1.4289	0.8363	108.098	2.103	80.298	19.002	3.24
	30	12.1749	1.4322	0.8772	104.708	0.826	84.256	17.284	3.32
0.6010	40	11.6110	1.4272	0.8656	105.898	0.974	84.436	17.110	3.33
	50	11.1029	1.4218	0.8551	107.116	1.121	84.535	16.923	3.33
	30	14.5700	1.4354	0.8940	104.388	0.506	87.081	14.727	3.44
0.6831	40	13.8316	1.4303	0.8829	105.509	0.585	87.267	14.521	3.43
	50	13.3045	1.4242	0.8720	106.648	0.653	87.646	14.568	3.44
	30	22.2419	1.4418	0.9414	103.945	0.062	91.659	5.258	3.73
0.8970	40	21.3334	1.4362	0.9299	105.007	0.083	92.283	5.415	3.74
	50	20.4001	1.4318	0.9198	106.099	0.104	92.712	5.396	3.75
	30	27.0886	1.4467	0.9638	103.883	0.000	93.165	—	3.89
1.0000	40	25.9638	1.4411	0.9542	104.924	0.000	93.667	—	3.89
	50	24.9065	1.4355	0.9445	105.995	0.000	94.173	—	3.90
				Acetylacetone + carbon tetrachloride					
	30	3.5133	1.4521	1.5073	105.437	1.554	44.843	9.927	3.02
0.1034	40	3.4156	1.4461	1.4893	106.534	1.610	44.411	9.428	3.01
	50	3.2859	1.4401	1.4709	107.662	1.667	43.596	9.541	2.97
	30	5.1512	1.4522	1.4408	105.436	1.553	57.501	15.851	3.10
0.2070	40	4.9705	1.4460	1.4236	106.534	1.610	57.105	15.341	3.10
	50	4.7688	1.4395	1.4064	107.662	1.667	56.502	14.616	3.09
	30	8.7809	1.4517	1.3176	105.437	1.554	72.432	18.101	3.22
0.4022	40	8.4163	1.4458	1.3022	106.534	1.610	72.299	17.769	3.23
	50	8.0677	1.4393	1.2871	107.662	1.667	72.123	17.366	3.23
	30	11.1484	1.4508	1.2563	104.731	0.848	77.913	17.034	3.33
0.5030	40	10.6858	1.4452	1.2421	105.799	0.875	77.954	16.817	3.34
	50	10.2303	1.4388	1.2265	106.898	0.903	78.035	16.632	3.35
	30	16.5185	1.4490	1.1364	104.147	0.264	85.594	11.723	3.54
0.7030	40	15.8188	1.4430	1.1233	105.207	0.284	85.935	11.707	3.55
	50	15.1172	1.4369	1.1098	106.297	0.302	86.259	11.669	3.56
	30	21.7213	1.4478	1.0373	103.928	0.045	90.121	5.307	3.70
0.8715	40	20.7550	1.4419	1.0262	104.977	0.053	90.532	5.283	3.71
	50	19.7683	1.4360	1.0154	106.057	0.062	90.870	5.173	3.71
				Acetylacetone + benzene					
	30	3.6232	1.4887	0.8787	104.464	0.581	42.670	9.122	3.02
0.1027	40	3.5237	1.4824	0.8687	105.455	0.531	42.272	8.659	3.03
	50	3.4397	1.4762	0.8579	106.476	0.481	42.019	8.316	3.06
	30	7.2009	1.4781	0.8980	104.464	0.581	63.566	16.962	3.15
0.2992	40	6.9358	1.4721	0.8881	105.455	0.531	63.352	16.587	3.17
	50	6.7075	1.4662	0.8779	106.476	0.481	63.239	16.293	3.19
	30	11.4726	1.4684	0.9166	104.363	0.481	75.561	15.669	3.32
0.4992	40	10.0752	1.4629	0.9070	105.369	0.445	75.696	15.546	3.34
	50	10.7062	1.4570	0.8969	106.418	0.423	75.886	15.463	3.36
	30	13.9325	1.4637	0.9265	103.986	0.103	80.010	13.395	3.40

Continued

Table 2—Polarization Data of Acetylacetone in Different Non-polar Solvents —*Contd.*

f_2	Temp. °C	ε	n_D	d	$\bar{V}_2$	$\bar{V}_2 - V_2^0$	P_{12}	P^E	μ_2
0.6004	40	13.4306	1.4585	0.9170	105.021	0.097	80.229	13.306	3.42
	50	12.9664	1.4522	0.9074	106.085	0.090	80.471	13.228	3.44
	30	16.9220	1.4587	0.9377	103.968	0.085	84.134	10.176	3.51
0.7109	40	16.3044	1.4532	0.9280	105.008	0.084	84.473	10.154	3.53
	50	15.6355	1.4473	0.9179	106.077	0.082	84.767	10.078	3.54
	30	22.5276	1.4510	0.9542	103.883	0.000	89.943	3.827	3.69
0.8939	40	21.7312	1.4460	0.9447	104.924	0.000	90.423	3.856	3.72
	50	20.8894	1.4395	0.9350	105.995	0.000	90.875	3.852	3.73
				Acetylacetone + dioxane					
	30	3.7908	1.4206	1.0149	104.272	0.390	42.425	10.752	3.13
0.1028	40	3.6932	1.4161	1.0040	105.304	0.380	42.095	10.437	3.14
	50	3.6093	1.4113	1.0003	106.366	0.370	41.547	9.904	3.16
	30	5.6514	1.4243	1.0013	104.273	0.391	55.002	16.187	3.16
0.2070	40	5.4902	1.4196	0.9967	105.304	0.380	54.489	15.629	3.18
	50	5.3271	1.4147	0.9932	106.366	0.370	53.867	14.926	3.20
	30	9.5590	1.4309	0.9944	104.273	0.391	69.222	16.898	3.25
0.4041	40	9.2396	1.4259	0.9838	105.304	0.380	69.271	16.788	3.27
	50	8.9414	1.4211	0.9804	106.366	0.370	68.821	16.179	3.29
	30	14.3576	1.4366	0.9837	103.945	0.062	79.120	13.390	3.44
0.5997	40	13.8683	1.4315	0.9737	104.984	0.060	79.379	13.378	3.46
	50	13.3744	1.4263	0.9686	106.054	0.059	79.199	12.925	3.48
	30	17.1336	1.4393	0.9784	103.883	0.000	83.184	10.546	3.53
0.7005	40	16.5067	1.4340	0.9684	104.924	0.000	83.514	10.546	3.55
	50	15.8957	1.4287	0.9638	105.995	0.000	83.358	10.059	3.57
	30	23.1972	1.4442	0.9686	103.883	0.000	89.944	3.763	3.74
0.8981	40	22.2489	1.4388	0.9587	104.924	0.000	90.393	3.768	3.75
	50	21.3827	1.4332	0.9538	105.995	0.000	90.382	3.311	3.77

Table 3—Coefficients of Relation (4), Determined by the Method of Least Squares

Temp. °C	A_1	A_2	A_3	σ(*)
		Solvent: Cyclohexane		
30	78.759	33.895	9.398	0.09
40	77.113	31.191	10.107	0.10
50	76.609	29.530	8.186	0.10
		Carbon tetrachloride		
30	68.171	37.709	15.426	0.10
40	67.381	34.898	12.625	0.10
50	66.754	30.924	6.052	0.10
		Benzene		
30	62.913	37.904	13.073	0.11
40	62.450	36.050	11.144	0.12
50	61.893	34.630	10.020	0.13
		Dioxane		
30	62.265	44.072	27.997	0.13
40	61.812	41.271	24.788	0.12
50	59.810	40.250	19.933	0.14

(*)σ = Standard deviation in P^E

composition dependence of P^E was correlated by the polynomial:

$$P^E = f_2(1-f_2)\sum_{i=0}^{k} A_i(1-2f_2)^i \quad \ldots(4)$$

The coefficients of relation (4), A_i, and the standard deviation, σ, at temperature 30° to 50°C, of the best fit, determined by the method of least squares, are given in Table 3.

The P^E values are positive over the entire range of concentration. The deviation from the additivity law, and the magnitude of the constants A_1, with respect to the solvents used, increase in the same order as that observed in the case of partial volume data. Hence, one may conclude that more inert the solvent is, the greater is the extent of dissociation of the solute acetylacetone in that solvent.

Variation of solute moment with concentration

The dipole moments (μ_2) of the solute acetylacetone in four non-polar solvents at various concentrations covering the entire composition range, are recorded in Table 2. The gradual decrease of dipole moment from the values obtained in the pure liquid state to that determined at infinite dilution, provides further evidence for the possible dissociation of the dimer molecules, predominating in the pure condensed phase, to the monomer.

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