

Solvent Effect on the Partition Equilibrium of Normal Aliphatic β -Diketones between Heptane and Water-Dimethyl Sulfoxide Mixed Solvents. The Extended McDevit-Long Approach

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The partition equilibria of 7 normal aliphatic (C_5 – C_9) β -diketones were investigated in the two-phase systems of heptane/water–dimethyl sulfoxide (DMSO) mixed solvents at 25 °C. The partition coefficients, P , of the keto and enol forms of the β -diketones were determined, and the linear correlations between $\log P$ and the number of carbon atoms in the n -alkyl groups were observed. In general, an increase in the mole fraction of DMSO, X_s , in the mixed-solvent phase caused a lowering of the partition coefficient, while with smaller β -diketones, distinct maxima were observed at $X_s \approx 0.2$. The solvent effect of the mixed-solvent phase was interpreted on the basis of the extended McDevit-Long theory previously proposed by the present authors.

The importance of the solvent effect of the aqueous phase on the liquid-liquid partition equilibrium is well recognized by workers engaged in extraction chemistry. For example, an increase in the electrolyte concentration in the aqueous phase improves the extraction of nickel(II) with acetylacetone¹⁾ and the partition of 8-quinolinol²⁾ and β -diketones.³⁾ Recently, it has been reported that the introduction of a water-missible organic solvent, *e.g.*, acetone,⁴⁾ 2-propanol,⁵⁾ or DMSO,⁶⁾ into the aqueous phase also improves the extraction of inorganic substances, *e.g.*, uranium,⁴⁾ protactinium,⁵⁾ or hafnium.⁶⁾ However, no systematic investigation of the role of the aqueous phase has yet been reported.

Previously, we pointed out that the partition coefficient of acetylacetone in the heptane/water–DMSO system shows a distinct maximum at a mole fraction of DMSO of about 0.2.⁷⁾ Recently, we observed that the addition of an organic solvent to the aqueous phase produces an interesting effect like a salting-out on the partition of the nonpolar solute and that the variation in the partition coefficient at a different solvent composition can be interpreted semi-quantitatively by making use of the extended McDevit-Long theory.⁸⁾

In the present study, the partition coefficients of a series of normal aliphatic β -diketones in the two-phase system of heptane/water–DMSO are determined, and the substituent effect and the solvent effect are discussed.

Experimental

Chemicals. The acetylacetone (Nakarai, G. R.) was purified by fractional distillation. The methods of synthesis and purification of the normal aliphatic β -diketones were described previously.⁹⁾ The β -diketones are listed in Table 1. The solvents used in this study were purified by a method described previously.⁷⁾ The mixed aqueous solvents were prepared by weight at desired mole fractions within ± 0.0005 .

Partition Experiment. Five ml of a heptane solution of β -diketone ($< 10^{-2}$ M) and an equal volume of the mixed solvent were stirred by means of a magnetic stirrer in a water-jacketed partition vessel thermostated at 25 ± 0.1 °C for 12 h. After standing for 2 h, the mixed-solvent phase was pipetted out into a quartz cell and the concentration of

β -diketone in the solution was determined photometrically. The partition coefficient was calculated from the initial concentration and the concentration in the mixed-solvent phase. For larger β -diketones, a relatively concentrated solution (0.1 M) in heptane has to be used because of its large partition coefficient, but no concentration effect on the partition coefficient was observed up to 0.54 M. Partition measurements were repeated twice or more, and the relative standard deviation was within 3%.

Estimation of Enol Fraction. β -Diketones are present as enol and keto forms in both phases of the partition system. The NMR method is now considered to be the most reliable one for the determination of the enol fraction of β -diketone in solution.¹⁰⁾ In the present study, however, the NMR method is difficult to apply because of the low solubility of the β -diketones and the large solvent signals of water–DMSO mixed solvent, which make an accurate determination of the enol fraction impossible. Previously, we found, for acetylacetone, a linear relationship between the apparent molar absorptivity at the absorption maximum and the enol fraction as determined by the NMR method.^{7,11)} Therefore, the enol fractions of normal aliphatic β -diketones in the mixed solvents were estimated by making use of the empirical relationship, assuming that the substituent effect of the alkyl group on the molar absorptivity could be neglected. The error in the estimated enol fraction is less than 0.05. The enol fractions in heptane were determined by the NMR method. The enol fraction was calculated from the integrated signal intensities of the keto-methylene protons and the enol-methine proton, or from those of the methyl protons in both tautomers.

Results

The observed partition coefficients and the enol fractions in heptane and in mixed solvents are listed in Table 1. The partition coefficients for the keto and enol forms are calculated from the following equations:

$$P_K = \frac{1-f_o}{1-f} P \quad P_E = \frac{f_o}{f} P. \quad (1)$$

In Fig. 1, $\log P_K$ and $\log P_E$ are shown as functions of the mole fraction of DMSO. The results show that the variation in the partition coefficient with X_s is more remarkable for the enol tautomer than for the keto tautomer and that a distinct maximum in the partition coefficient appears at $X_s \approx 0.2$ for smaller β -diketones.

TABLE 1. OBSERVED PARTITION COEFFICIENTS, P , OF NORMAL ALIPHATIC β -DIKETONES IN HEPTANE/WATER-DMSO AND ENOL FRACTIONS IN THE MIXED SOLVENT, f ,^{b)} AND IN HEPTANE, f_o ^{c)}

Solute		Mole fraction of DMSO								
		0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.800	1.000
Acetylacetone	P	0.887	1.06	1.10	0.920	0.675	0.470	0.33	0.21	0.156
	f	0.17 ^{a)}	0.23	0.30	0.38	0.44	0.48	0.51	0.54	0.55 ^{c)}
	f_o	0.97								
2,4-Hexanedione	P	3.28	3.21	3.26	2.31	1.57	1.01	0.644	0.384	0.236
	f	0.12	0.18	0.24	0.30	0.36	0.39	0.42	0.46	0.51 ^{c)}
	f_o	0.96								
3,5-Heptanedione	P	10.4	9.00	7.83	5.59	3.41	2.10	1.21	0.601	0.371
	f	0.10	0.15	0.20	0.26	0.30	0.35	0.37	0.41	0.44 ^{c)}
	f_o	0.95								
2,4-Heptanedione	P	15.0	12.5	10.6	7.18	4.01	2.33	1.49	0.699	0.425
	f	0.16	0.24	0.32	0.39	0.45	0.50	0.52	0.57	0.60
	f_o	0.97								
3,5-Octanedione	P	53.7	38.4	29.7	17.5	9.42	5.03	2.90	1.26	0.644
	f	0.13	0.19	0.26	0.33	0.39	0.43	0.46	0.51	0.52
	f_o	0.96								
2,4-Octanedione	P	54.2	39.4	29.3	17.5	9.36	4.61	2.65	1.16	0.646
	f	0.17	0.24	0.32	0.39	0.46	0.49	0.53	0.57	0.61
	f_o	0.97								
4,6-Nonanedione	P	269	171	113	56.9	26.2	12.3	5.92	2.32	1.18
	f	0.16	0.25	0.34	0.41	0.48	0.52	0.55	0.58	0.64
	f_o	0.97								

a) M. L. Eidinoff, *J. Am. Chem. Soc.*, **67**, 2073 (1945).

c) By the NMR method.

b) Estimated from the relationship between f and ϵ_{\max} .

Discussion

Correlation between $\log P$ and the Carbon Number.

The plots of $\log P_K$ and $\log P_E$ against the number of carbon atoms in the n -alkyl substituent show a linear relationship in every partition system (Fig. 2); i.e.,

$$\log P = An + B, \quad (2)$$

where A corresponds to the logarithm of the partition coefficient of the methylene group, $\log P(-CH_2-)$, and B , to that of the enol or diketone skeleton, $\log P(-COCHCOH-)$ or $\log P(-COCH_2CO-)$. The values of A and B , obtained from the slope and intercept in Fig. 2, respectively, are illustrated in Fig. 3. This decreasing order of the partition coefficients: $P(-CH_2-) > P(-COCHCOH-) > P(-COCH_2CO-)$ was observed in every partition system; it corresponds to the expected order of increase in the dipole moment of the groups. $\log P(-CH_2-)$ decreases monotonously with the increases in X_s and gives an equal value for the two tautomers. Both $\log P(-COCHCOH-)$ and $\log P(-COCH_2CO-)$ show maxima in the water-rich region. From the results shown in Fig. 3, the maxima in $\log P_K$ and $\log P_E$, which become remarkable in smaller β -diketones, as has been noted in Fig. 1, can be ascribed to those in $\log P(-COCH_2CO-)$ and $\log P(-COCHCOH-)$.

Composition Dependence of Partition Coefficient.

In a previous paper, the McDevit-Long theory has

been extended to the estimation of the activity coefficient in a water-organic solvent mixture.⁸⁾ In this extended treatment, the activity coefficient of a nonelectrolyte infinitely diluted in an aqueous mixed solvent can be expressed by the following equation;

$$\ln f_n = - \frac{v_n^\infty}{RT} \frac{P_1}{\alpha T} \frac{v^E}{v}, \quad (3)$$

where f_n and v_n^∞ refer to the activity coefficient and the partial molar volume of the nonelectrolyte respectively; v and v^E to the mean molar volume of the ideal mixed solvent and the excess molar volume of the real mixed solvent, and P_1 and α , to the internal pressure and the coefficient of the thermal expansion of the mixed solvent respectively. The activity coefficient given by Eq. 3 reflects the difference in the cavity-formation energy or the solvophobic interaction energy of the solute in different solvent systems, the ideal mixed solvent, and the real mixed solvent, because a direct interaction between the solute and the solvent molecules is left out of account in this treatment. When Eq. 3 is applied to an interpretation of the solvent effect, the contribution of the solvation should be eliminated by a reasonable treatment. For this purpose, we adopted the volume-fraction treatment, which is recommended for the calculation of the excess value when the molar volumes of the solute and the solvent differ considerably.¹²⁾

$$\Delta \ln P_x = \ln P_x - (1 - \phi_s) \ln P_{x,0} - \phi_s \ln P_{x,1}, \quad (4)$$

where P_x refers to the partition coefficient in the mole-

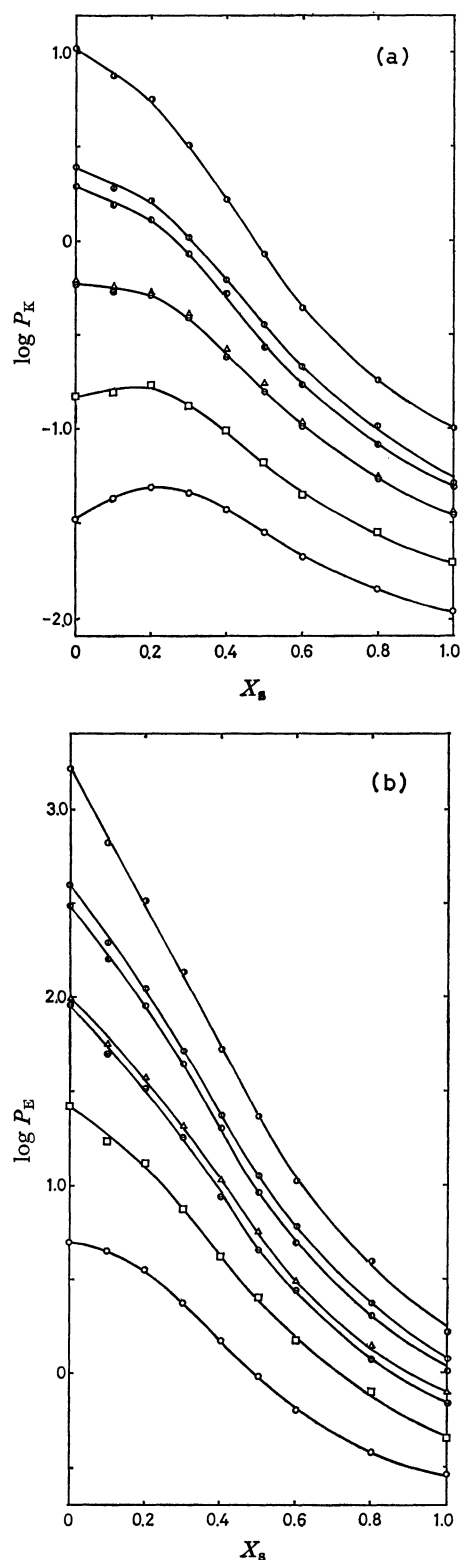


Fig. 1. Variation of partition coefficients of keto form (a) and enol form (b) of β -diketones with mole fraction of DMSO in mixed solvent phase.
 \circ : Acetylacetone, \square : 2,4-hexanedione, \triangle : 3,5-hexanedione, \odot : 2,4-heptanedione, \oplus : 3,5-octanedione, \bullet : 2,4-octanedione, \ominus : 4,6-nonanedione.

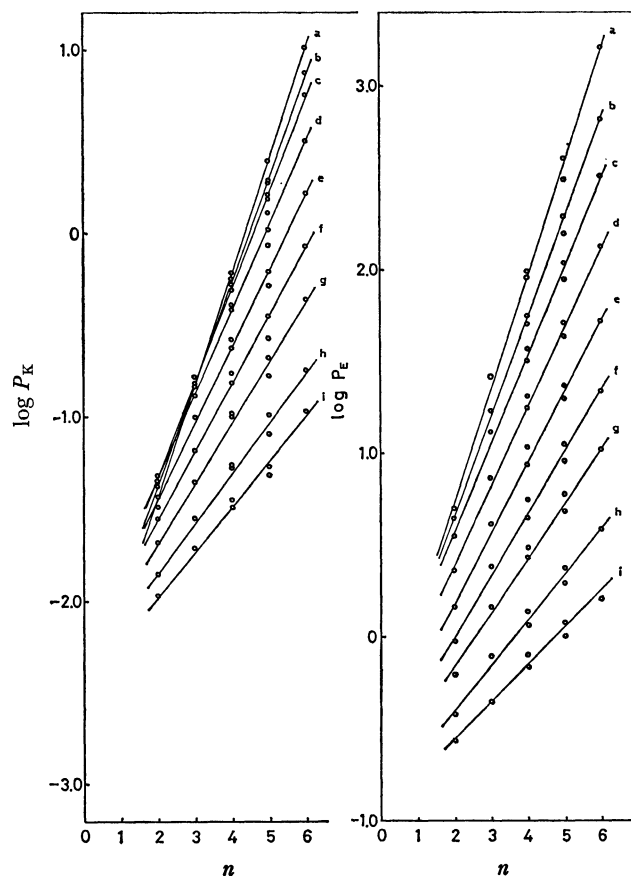


Fig. 2. Correlation between $\log P_K$ or $\log P_E$ and number of carbon atoms in substituent.
 n : Mole fraction of DMSO; a: 0.0, b: 0.1, c: 0.2, d: 0.3, e: 0.4, f: 0.5, g: 0.6, h: 0.8, i: 1.0.

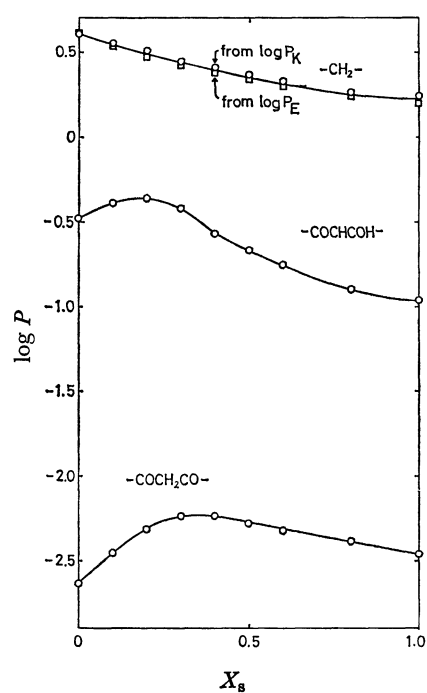


Fig. 3. Variation of group partition coefficients, $\log P(-CH_2-)$, $\log P(-COCHCOH-)$, and $\log P(-COCH_2CO-)$, with X_s .

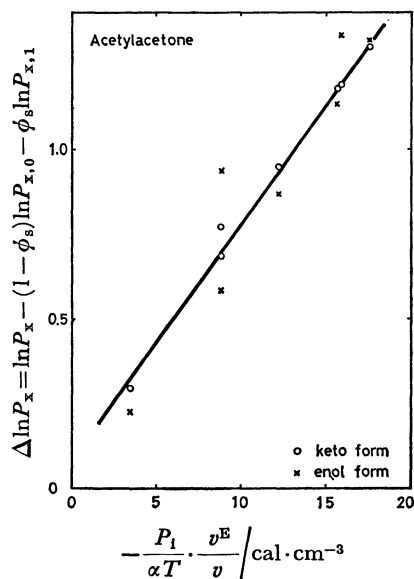


Fig. 4. Correlation between $\Delta \ln P_x$ of keto and enol forms of acetylacetone and the pressure factor.

fraction scale, ϕ_s to the volume fraction of DMSO, and the subscripts 0 and 1 to the heptane/water and heptane/DMSO systems. $\Delta \ln P_x$ in Eq. 4 corresponds to $\ln f_n$ in Eq. 3. From Eqs. 3 and 4, a linear correlation between $\Delta \ln P_x$ and the pressure factor, $-(P_1/\alpha T)(v^E/v)$, can be expected. In practice, for acetylacetone and other β -diketones the plots of $\Delta \ln P_x$ against $-(P_1/\alpha T)(v^E/v)$ show linear correlations both for the keto form and the enol form (Figs. 4 and 5). The slopes in these figures are expected to increase with increases in the molar volume or length of the alkyl chain (*cf.* Eq. 3). The slopes for keto forms were plotted against the molar volumes, v_n , calculated assuming that the molar volume of the acetylacetone-keto form is $110.99 \text{ cm}^3 \text{ mol}^{-1}$ ¹³⁾ and the volume of methylene group is $22.2 \text{ cm}^3 \text{ mol}^{-1}$.¹⁴⁾ Figure 6 shows clearly a proportionality between $\Delta \ln P_x$ and the molar volume. From these results, it may be concluded that the maximum observed in the partition coefficient is correlated to the increase in the pressure factor $-(P_1/\alpha T)(v^E/v)$, which reflects an increase in the solvent-solvent interaction. This situation is quite similar to a salting-out phenomenon induced by a structure-making electrolytes. The composition dependences of the group partition coefficient, $P(-\text{CH}_2-)$, $P(-\text{COCH}_2\text{CO}-)$ and $P(-\text{COCH}-\text{COH}-)$, shown in Fig. 3, can also be understood from the present consideration.

A further discussion will be given to compare the slopes in Figs. 4 and 5 with the one expected from Eq. 3, but the observed slope is one half to one-third of the expected one. This is noted also by McDevit and Long in their original treatment of the salt effect;¹⁵⁾ they ascribed the discrepancy in their results to a disregard of the closest distance between electrolyte and nonelectrolyte and suggested the introduction of the correction term of $a/(a+b)$, where a and b correspond to the distances of the closest approach to the average "solvated" ion and to the nonelectrolyte molecule, respectively. Recently, Cross and McTigue

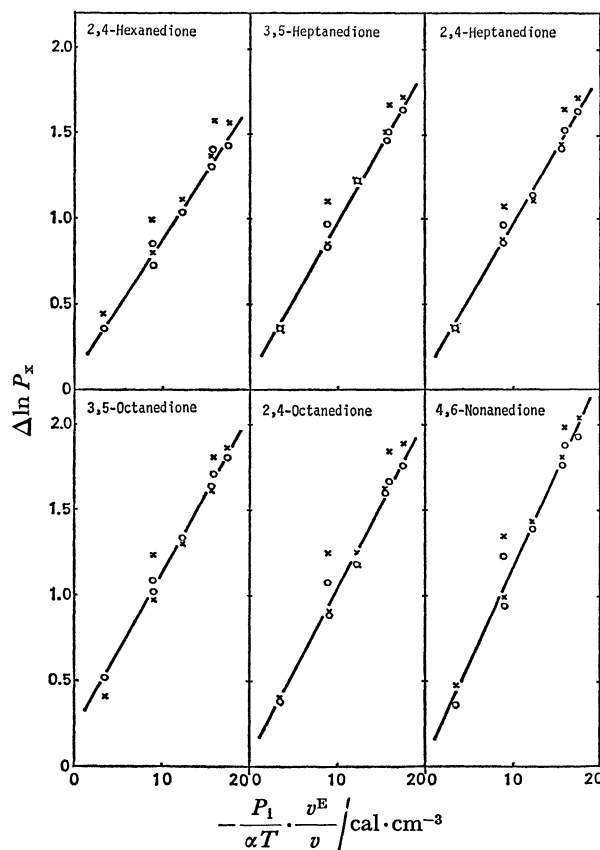


Fig. 5. Correlation between $\Delta \ln P_x$ and the pressure factor for normal aliphatic β -diketones.

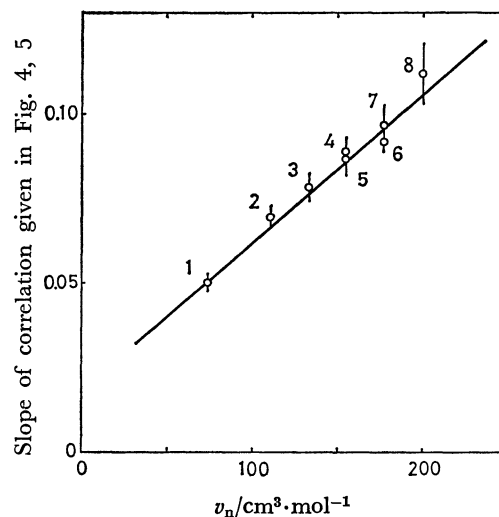


Fig. 6. Correlation between the slopes shown in Figs. 4 and 5 and the estimated molar volumes of the solutes. 1: Acetone (Ref. 8), 2: acetylacetone, 3: 2,4-hexanedione, 4: 3,5-heptanedione, 5: 2,4-heptanedione, 6: 3,5-octanedione, 7: 2,4-octanedione, 8: 4,6-nonanedione.

have reported a successful interpretation of the salting effect in a concentrated electrolyte solution by taking into account the correction term.¹⁶⁾ In the present study also, we introduce the term of $a'/(a'+b')$, where a' and b' correspond to the van der Waals radius of the mixed solvent and radius of the nonelectrolyte.

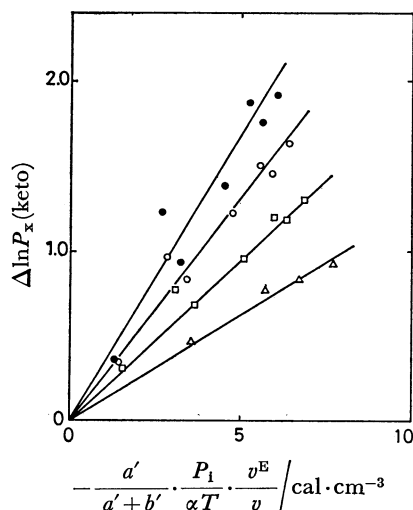


Fig. 7. Correlation between $\Delta \ln P_x$ of keto forms and $-\{a'/(a'+b')\}(P_1/\alpha T)(v^E/v)$.

The slopes of the solid lines are the expected one of v_n/RT ; \triangle : Acetone (Ref. 8), \square : acetylacetone, \circ : 3,5-heptanedione, \bullet : 4,6-nonanedione.

The values of a' and b' were calculated by

$$a' = \left(\frac{v - 593/P_1}{4.189} \right)^{1/3} \quad (5)$$

$$b' = \left(\frac{v_n}{4.189} \right)^{1/3} \quad (6)$$

Equation 5 is based on the same idea as that proposed by Bagley et al. in which the occupied volume in a liquid is estimated from the internal pressure.¹⁷⁾ The slopes obtained from the plot of $\Delta \ln P_x$ against $-a'/(a'+b')(P_1/\alpha T)(v^E/v)$ were very close to the expected one of v_n/RT , as is shown in Fig. 7.

In conclusion, it is noteworthy that the solvent effect of a highly associated mixed solvent such as water-DMSO, could be interpreted by means of a new solvent parameter, i.e., the pressure factor, which can be calculated from the available solvent parameters. The usefulness of the pressure factor as a measure of

the solvent effect due to the solvent-solvent interaction was demonstrated. We believe that the solvophobic contribution to the solvent effect should be investigated in detail for a quantitative elucidation of the role of an aqueous solvent in solvent extraction and in reversed-phase chromatography.

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