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Partition of Tris(acetylacetonato)chromium(III) and Its Temperature Dependence in the Systems of Dodecane/(Water–Organic Solvent Mixture)

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The partition constants $K_t^\ominus$ of tris(acetylacetonato)chromium(III) between dodecane and water-organic solvent mixtures have been measured. The organic solvents used as co-solvents were acetonitrile, *N*,*N*-dimethylformamide, methanol, ethylene glycol, and dimethyl sulfoxide which are all miscible with water but not with dodecane. From the temperature dependence of $K_t^\ominus$ the thermodynamic parameters for the transfer of the complex from dodecane to the mixed solvents have been determined. The dependences of the partition constants on solvent composition of the aqueous phase have been interpreted in terms of changes in the internal pressure and the volume upon mixing of water with the organic co-solvents. The standard transfer enthalpies have been correlated with the excess enthalpies of the mixed solvents.

The solvent extraction of metal chelates is one of the most useful methods for the separation or enrichment of metal ions. The effects of organic phases on the partition behavior of chelating reagents and their metal chelates have been interpreted in terms of the regular solution theory.[1] Quantitative interpretation of the effects of the aqueous phase on the partition behavior is however difficult. This is largely due to strong interactions such as hydrogen bonding or dipole-dipole interactions between solute and solvent molecules in the aqueous phase of the partition system. In spite of the important role of the aqueous phase in solvent extraction, few studies have been made on this subject. Yoshimura and Suzuki[2] examined the effects of some electrolytes on the standard chemical potential of benzoylacetone and benzoyltrifluoroacetone in aqueous solutions, and discussed the changes in the cohesive forces of water and the structure of water.

The present authors reported the partition equilibrium of acetylacetone complexes of chromium(III), cobalt(III), and rhodium(III)[3] in the heptane/(water–dimethyl sulfoxide (DMSO)) system. The dependence of the partition constants on the composition of the mixtures was discussed in terms of the extended McDevit-Long theory.[4] It was found that the partition constant variation with solvent composition was governed by the strong interactions between water and DMSO.

In this study, the partition constants of [Cr(acac)$_3$] have been measured in the partition systems consisting of water–organic solvent mixtures and dodecane, which is less soluble in the polar solvents than heptane. Acetonitrile (AN), *N*,*N*-dimethylformamide (DMF), DMSO, methanol (MeOH), and ethylene glycol (EG) have been used as co-solvents in the aqueous mixtures. The temperature dependence of the partition constants have been examined, and the thermodynamic parameters for the transfer from dodecane to the solvent mixtures estimated. The partition constants and the standard transfer enthalpies are discussed in terms of the solvent-solvent interactions.

Experimental

Reagents. Tris(acetylacetonato)chromium(III) ([Cr(acac)$_3$]) was prepared by the method reported by Fernelius and Blanch.[5] Recrystallization from benzene and petroleum ether was repeated twice and the products sublimed under reduced pressure (*ca.* 10^{-3} mmHg, 100—150 °C). Mp, 214.0—215 °C; lit, 216 °C.[5] Found: C, 51,68; H, 6.02%. Calcd for $C_{15}H_{21}O_6Cr$: C, 51.81; H, 6.06%.

Dodecane (Tokyo Kasei, GR) was washed with a mixture of concd sulfuric acid and fuming sulfuric acid, an aqueous solution of sodium hydroxide, and water. After drying with calcium hydride, the dodecane was distilled under reduced pressure (less than 20 mmHg, 105 °C). Waste dodecane was recovered and purified by the same treatment. Acetonitrile (Wako, GR) was stirred with calcium hydride for 24 h and distilled in the presence of phosphorus pentaoxide under ambient pressure (61 °C). *N*,*N*-Dimethylformamide (Kanto, GR) was dried by stirring with molecular sieve 4A for 24 h, and distilled under reduced pressure under an atmosphere of N_2 (less than 20 mmHg, 62.5 °C). Dimethyl sulfoxide (Wako, GR) was stirred with calcium hydride overnight to dryness and distilled under reduced pressure (17 mmHg, 74 °C). Methanol (Kanto, GR) was distilled under ambient pressure. Ethylene glycol (Kanto, GR) was dried with molecular sieve 4A and distilled under reduced pressure (less than 20 mmHg, 106 °C). These very hygroscopic solvents were preserved in a desiccator over silica gel. Doubly distilled water was used throughout.

The water–organic solvent mixtures were prepared by weight.

Partition Measurements. A specified volume of a dodecane solution of [Cr(acac)$_3$] (1—4×10^{-4} mol dm^{-3}) and a specified volume of mixed solvent were stirred for 30 min in a partition vessel which was equipped with a water jacket and thermostated at the desired temperature within ±0.02 K. The partition constants in the system of dodecane/(water-acetonitrile), dodecane/(water-DMF), dodecane/(water-MeOH), and dodecane/(water-ethylene glycol) were measured at 278.15 K, 288.15 K, and 298.15 K, and those in dodecane/(water-DMSO system) were measured at 288.15 K, 293.15 K, and 298.15 K. The equilibrated dodecane phase was isolated, and the concentration at (298.15 ± 0.2)K determined spectrophotometrically from the absorbance at 336 nm ($\varepsilon=1.715\times10^4$ dm^3 mol^{-1} cm^{-1}). The absorbance was measured by a Hitachi 356 or JASCO Uvidec 2 spectrophotometer. In this study, a partition constant is defined as an equilibrium

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constant for the transfer process from the nonpolar phase to the polar phase. The partition constant was determined from the following relationship:

$$K_t^\ominus = \frac{x_s^p}{x_s^n} = \frac{C_{s,\mathrm{init}}^n - C_s^n}{C_s^n} \frac{V^n}{V^p} \frac{v_p}{v_n}, \qquad (1)$$

where x_s^n and x_s^p are the mole fractions of the solute in the nonpolar (dodecane) and polar (mixed solvent) phase, $C_{s,\mathrm{init}}^n$ and C_s^n are the initial and equilibrium concentrations in the dodecane phase, V^n and V^p are the volumes of the nonpolar and polar phases, and v_n and v_p are the molar volumes of the nonpolar and polar phases, respectively. Literature values[6] for v_n and v_p were used for the calculation $K_t^\ominus$. More than five minutes' stirring made the ratio, $(C_{s,\mathrm{init}}^n - C_s^n)/C_s^n$, independent of the stirring time. The reversed partition experiment (a transfer of the solute from the mixed solvent phase to the dodecane phase) gave an equal value for $K_t^\ominus$ with the normal partition experiment. Stirring for 24 h caused no change in spectra of both phases, and so it has been assumed that the decomposition

TABLE 1. PARTITION CONSTANTS OF TRIS(ACETYLACETONATO)CHROMIUM(III) BETWEEN DODECANE AND WATER–DIMETHYL SULFOXIDE

	$K_t^\ominus$			
	278.15K	288.15K	293.15K	298.15K
x_{AN}				
0.000	2.22	0.937		0.427
0.025	1.50	0.739		0.392
0.050	1.27	0.694		0.407
0.100	1.73	1.08		0.684
0.200	5.49	3.42		2.18
0.300	14.6	9.00		5.88
0.400	27.4	17.0		11.1
0.500	41.8	25.8		18.0
0.600	58.7	37.3		25.1
0.700	78.1	50.0		33.8
0.800	95.8	61.6		41.7
0.900	110	67.7		45.9
0.950	112	68.0		43.6
1.000	105	67.0		40.6
x_{DMF}				
0.000	2.22	0.937		0.427
0.025	2.15	1.06		0.587
0.050	2.15	1.18		0.723
0.100	2.19	1.46		1.03
0.200	3.02	2.32		1.86
0.300	5.48	4.29		3.47
0.400	11.0	8.37		6.59
0.600	39.9	27.9		19.7
0.800	95.2	64.6	52.6	43.2[a]
1.000	167	103	80.0	62.8[a]
x_{DMSO}				
0.000		0.937	0.638	0.427
0.025		0.840	0.593	0.445
0.050		0.723	0.510	0.424
0.100		0.570	0.442	0.388
0.150		0.489	0.409	0.385
0.200		0.514	0.447	0.435
0.300		0.940	0.812	0.810
0.400		2.38	2.03	1.95
0.600		12.8	10.8	9.94
0.800		41.1	34.1	30.8
0.900		64.5	54.0	44.5
1.000		102[a]	78.3	61.0

	$K_t^\ominus$			
	278.15K	288.15K	293.15K	298.15K
x_{MeOH}				
0.000	2.22	0.937		0.427
0.025	2.07	0.913		0.476
0.050	1.81	0.894		0.509
0.100	1.54	0.924		0.595
0.150	1.62	1.06		0.744
0.200	1.84	1.36		0.966
0.250	2.46	1.83		1.36
0.300	3.36	2.52		1.87
0.400	5.95	4.43		3.33
0.500	9.67	7.17	5.98	4.89[a]
0.600	13.1	9.90	8.12	6.41[a]
0.700	16.4	12.1	10.1	8.22[a]
0.800	16.9	12.6	9.94	7.39[a]
0.900	15.2	12.3	9.28	6.23[a]
1.000	12.2	9.70	7.77	5.82[a]
x_{EG}				
0.000	2.22	0.937		0.427
0.050	1.23	0.636		0.354
0.100	0.836	0.505		0.316
0.150	0.685	0.461		0.317
0.200	0.635	0.441		0.333
0.300	0.699	0.517		0.413
0.400	0.856	0.651		0.527
0.600	1.31	0.984		0.824
0.800	1.82	1.38		1.16
0.900	2.05	1.61		1.32
1.000	2.31	1.79		1.52

a) $K_t^\ominus = x_s^p/x_s^n$. b) Estimated value (see text).

of [Cr(acac)$_3$] is negligible. Thirty minutes' stirring was taken as sufficient to place the system into partition equilibrium. For each system at least three runs were conducted.

Results

Partition Constants. Table 1 illustrates the partition constants $K_t^\ominus$ of [Cr(acac)$_3$] in dodecane/(water–organic solvent mixture) systems observed at several temperatures. All the values have a relative standard deviation within ±5%. Partition constants in the systems of $x_{DMF} \geq 0.8$ and $x_{MeOH} \geq 0.5$ at 298.15 K are the estimated values based on the quadratic regression for the experimental values at the lower temperatures given in the table, because of unsatisfactory phase separation at 298.15 K. For the system of $x_{DMSO}=1.0$ at 288.15 K, this is below the freezing point of DMSO 18.54 °C,[7] and so a hypothetical value was estimated by applying a linear regression for the observed values at 298.15 K and 293.15 K given in the table.

In Figs. 1(a) to 1(e), $-\log K_t^\ominus$ is shown as a function of the mole fraction of the organic co-solvent in the solvent mixture, x_2, in which the subscript 2 denotes the co-solvent. All the curves indicate that the partition constant decreases with increase in temperature and that the partition constant increases with an increase in x_2. In most systems, the curves have maxima in the water-rich regions.

The Thermodynamic Parameters. From the partition constants, the standard transfer chemical potential $\Delta_t\mu^\ominus$ of [Cr(acac)$_3$] from dodecane to the water–organic solvent mixtures at different temperatures were calculated based on the following equation:

$$\Delta_t\mu^\ominus = -RT\ln K_t^\ominus. \tag{2}$$

From the expression for the temperature dependence of $\Delta_t\mu^\ominus$ as a quadratic function of temperature, the standard transfer enthalpy $\Delta_t h^\ominus$ and the standard transfer entropy $\Delta_t s^\ominus$ from dodecane to the solvent mixtures were calculated as follows:

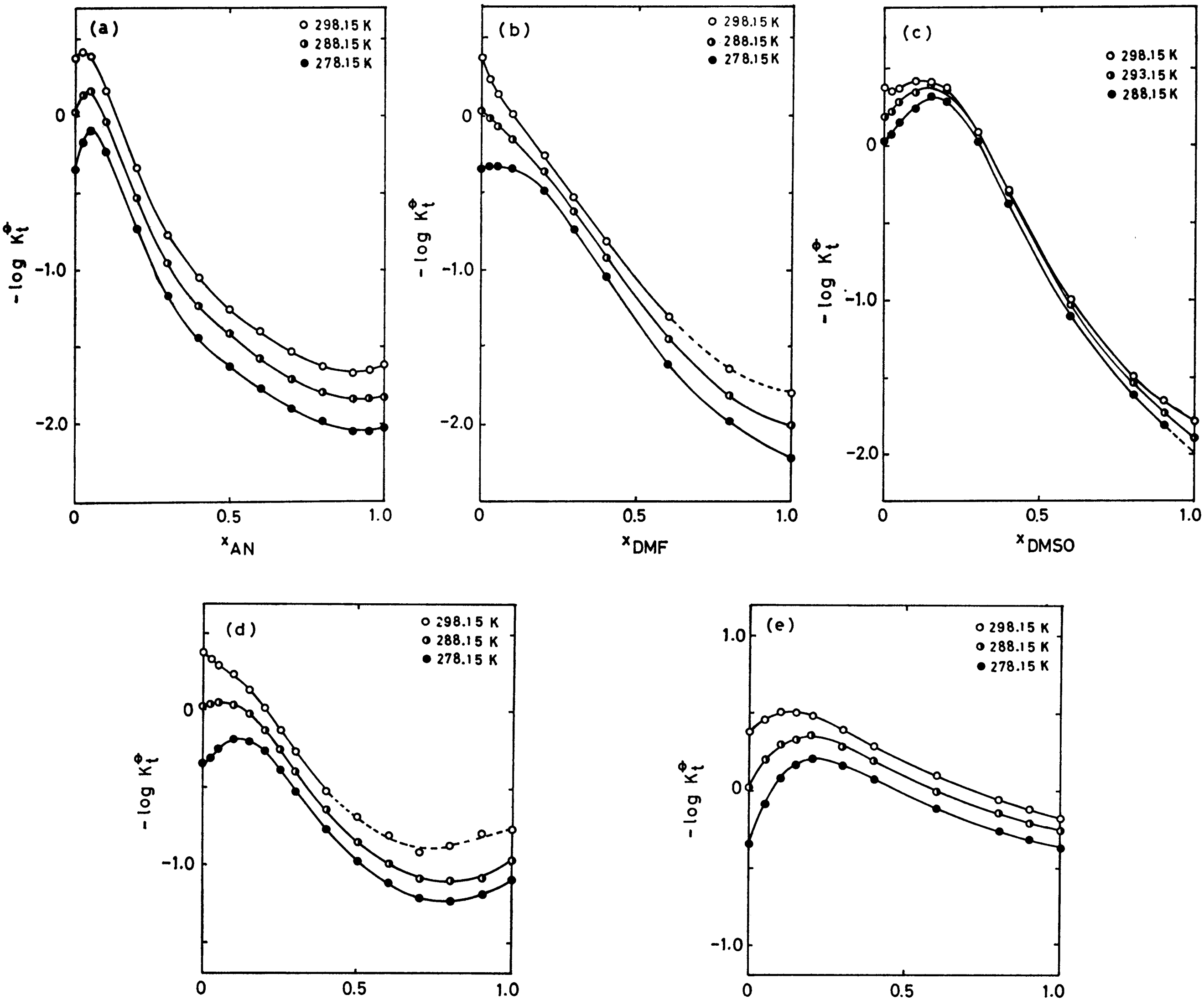

Fig. 1. Variation of the partition constants of [Cr(acac)$_3$] in dodecane/(water-organic solvent mixtures) with mole fraction of the co-solvent; (a) acetonitrile, (b) dimethylformamide, (c) dimethyl sulfoxide, (d) methanol, (e) ethylene glycol.

$$\Delta_t h^\ominus = -T^2\left[\frac{\partial(\Delta_t\mu^\ominus/T)}{\partial T}\right]_p, \tag{3}$$

$$\Delta_t s^\ominus = -\left(\frac{\partial\Delta_t\mu^\ominus}{\partial T}\right)_p. \tag{4}$$

The calculated $\Delta_t h^\ominus$ and $\Delta_t s^\ominus$ at 298.15 K are shown in Figs. 2(a) to 2(e) as function of the mole fraction of the organic co-solvent. The standard transfer entropies are given in the term, $-T\Delta_t s^\ominus$.

The figures show that the transfer of [Cr(acac)$_3$] from dodecane to water is accompanied by a very large decrease in the standard enthalpy (-55.0 kJ mol^{-1}), and that, in most systems variation in the thermodynamic values is remarkable in the water-rich regions. Cancellation of the large negative $\Delta_t h^\ominus$ with the large negative $T\Delta_t s^\ominus$ causes the small $\Delta_t\mu^\ominus$ values.

Discussion

Partition Constants in the Systems of Dodecane/Pure Solvent. The partition constant $K_t^\ominus$ in various systems of dodecane/pure solvent increases in the order: water<ethylene glycol<methanol<acetonitrile<DMSO≃DMF. Less work is needed for solute transfer into solvents with strong solute-solvent interactions and more work is required for solute transfer into solvents with strong solvent-solvent interactions. The dipole moment of solvent molecules is a measure of the electrostatic and polarization interaction between solute and solvent

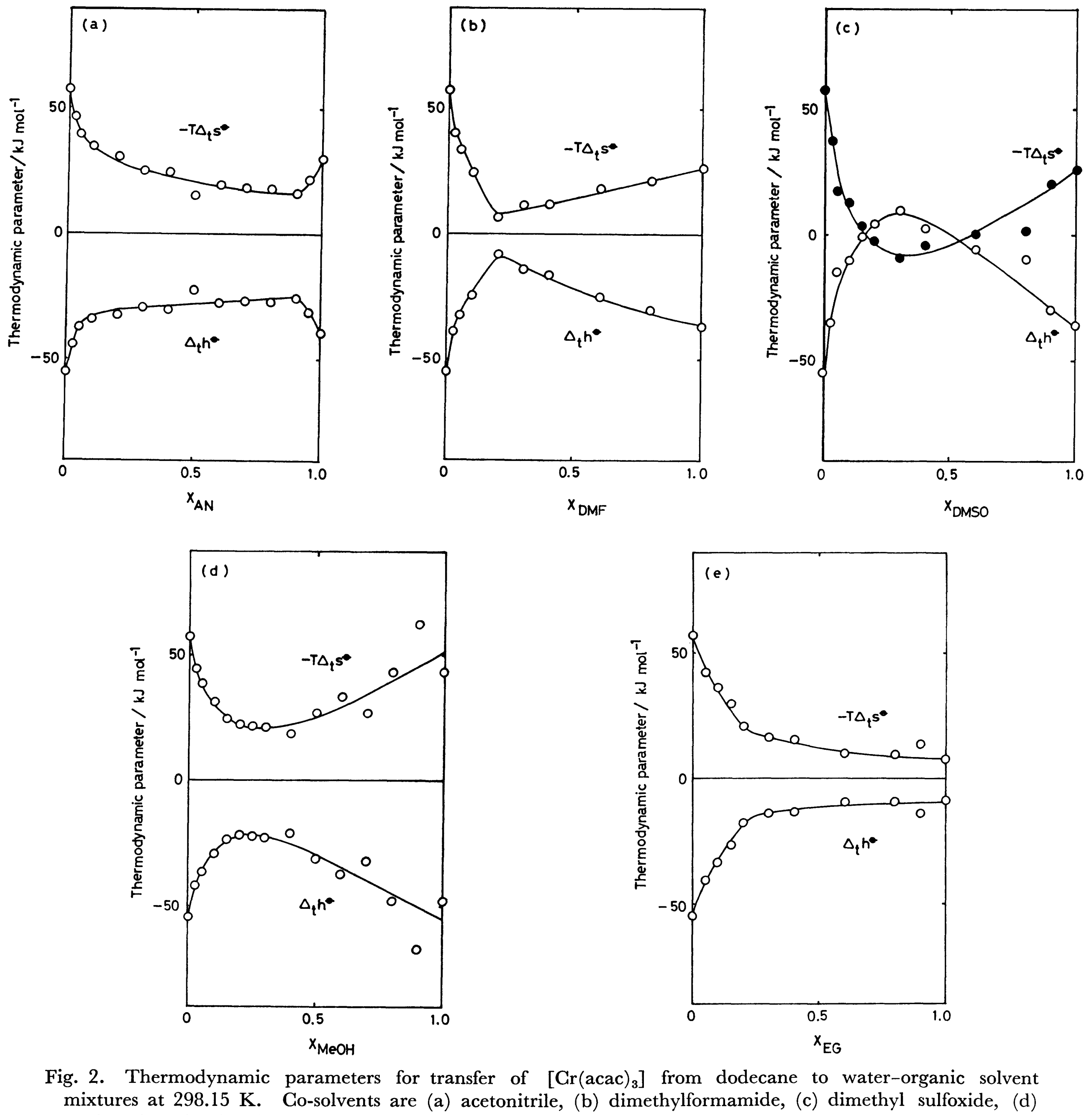

Fig. 2. Thermodynamic parameters for transfer of [Cr(acac)$_3$] from dodecane to water-organic solvent mixtures at 298.15 K. Co-solvents are (a) acetonitrile, (b) dimethylformamide, (c) dimethyl sulfoxide, (d) methanol and (e) ethylene glycol.

TABLE 2. DIPOLE MOMENT AND COHESIVE ENERGY DENSITY OF THE POLAR SOLVENTS STUDIED[a)]

Solvent	Dipole moment	Cohesive energy density
	D[b)]	MPa
Water	1.94	2302
Ethylene glycol	2.28	892
Methanol	2.87	874
Acetonitrile	3.44	582
DMSO	3.9	705
DMF	3.86	582

a) J. A. Riddick and W. B. Bunger, "Organic Solvents," 3rd ed, Wiley, New York (1970). b) 1D=3.333×10^{-30} C m.

and cohesive energy density is a measure of the solvent-solvent interaction. It has been found that the increase in value of $K_t^\ominus$ or the decrease in value of $\Delta_t\mu^\ominus$ corresponds approximately to the increase in dipole moment of the solvent molecules and to the decrease in cohesive energy density of the solvent (see Table 2).

Dependence of the Partition Constant on the Composition of the Solvent Mixture. The pressure-volume approach has been previously proposed in order to interpret the solvent effect of water–organic mixture on the partition constants of acetone, acetylacetone,[4)] and several metal(III) acetylacetonates[3)] in heptane/(water–DMSO) systems. This approach is essentially an extension of the McDevit-Long theory,[7)] introduced to predict the activity coefficients of nonelectrolytes in water–organic solvent mixtures. The pressure-volume approach assumes that the non-ideal change in internal pressure and volume upon mixing two solvents causes a change in chemical potential or activity coefficient of the solute. According to this approach, the following relationship holds for a nonelectrolyte solute in a solvent mixture.[4)]

$$\ln f_s = -k\frac{P_i}{\alpha T}\frac{v^E}{v}, \tag{5}$$

where f_s is the activity coefficient of the solute on the basis of the ideal mixing of the solvent mixture, and α, P_i, v, and v^E are the isobaric thermal expansivity, the internal pressure, the molar volume, and the excess molar volume of the solvent mixture, respectively. k is a proportional constant. In the partition systems studied here, it is acceptable to define the activity coefficient of the solute as

$$\ln f_s = -\ln K_t^\ominus + \phi_1 \ln K_{t,1}^\ominus + \phi_2 \ln K_{t,2}^\ominus, \tag{6}$$

where $K_t^\ominus$, $K_{t,1}^\ominus$, and $K_{t,2}^\ominus$ are the partition constants in dodecane/mixed solvent, dodecane/solvent 1, and dodecane/solvent 2, respectively, and ϕ_1 and ϕ_2 are the volume fractions of the components 1 and 2. In this study, solvent 1 and solvent 2 refer to water and the organic co-solvent, respectively.

In dodecane/(water–DMSO) system, a plot of log f_s against the pressure factor $-(P_i/\alpha T)(v^E/v)$ gives reasonably good linearity as shown in Fig. 3. The observed partition behavior of [Cr(acac)$_3$], which is characterized by the minima of the partition constant (Fig. 1), is interpreted from the change in the internal pressure and the volume upon mixing which are caused by a strong interaction between water and DMSO, since the pressure-volume approach takes account of a solvent-solvent interaction as the only factor in the solvent effect.

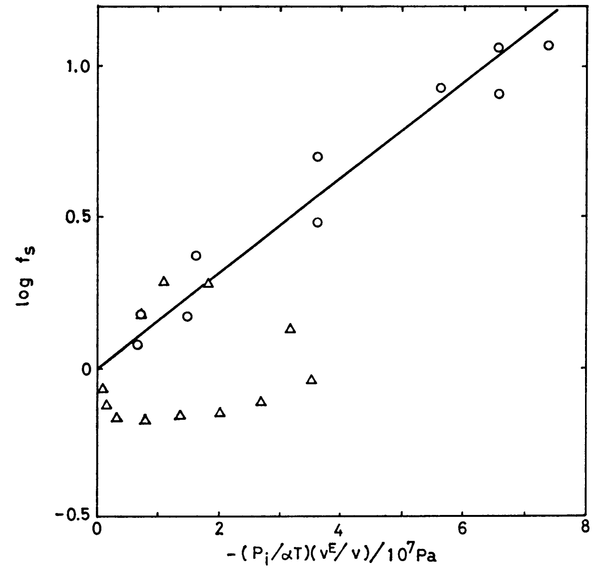

Fig. 3 Plot of logarithms of the activity coefficients of [Cr(acac)$_3$] against the pressure factors of the mixed solvent phase; ○, water-DMSO and △, water-AN.

In dodecane/(water–acetonitrile) system, a plot of log f_s against the pressure factor calculated from the internal pressure and density data reported by Grant-Taylor and Macdonald[8)] does not give a linear plot. In the region of $x_{AN} \leq 0.1$, however the slope of the best line is close to that for the water–DMSO system. A quite large scattering observed in the region $x_{AN} > 0.1$ may be due to the addition of acetonitrile to water causing not only an increase in the internal pressure but also destruction of the solvent structure. The destruction of the solvent structure causes an increase in the activity coefficient of water and acetonitrile. The abrupt increase in $K_t^\ominus$ in the region from $x_{AN} =$ 0.05 to 0.4 or more corresponds to the abrupt structure-breaking of the polar phase upon mixing water and acetonitrile (h^E is positive in this region[9)]). The partition constant has a minimum in the region of $x_{AN} \leq$ 0.05, which may be attributed to structure-making of the solvent upon mixing water and acetonitrile (h^E is negative in this region[9)]).

As shown in Fig. 1, a maximum in the $-\log K_t^\ominus$ *vs.* x_2 curve becomes remarkable as the temperature is lowered. As the temperature is lowered the interaction between water and the co-solvent becomes stronger, so that transfer of the solute from dodecane to the water-rich mixture becomes more unfavorable. It is expected that the interaction between water and the co-solvent affects the partition behavior of [Cr(acac)$_3$] in a similar fashion in every system except dodecane/(water–acetonitrile), because the h^E's of the mixed solvent have negative values in order of H_2O–EG> H_2O–MeOH>H_2O–DMF>H_2O–DMSO except for the water–acetonitrile system. The lack of data of internal pressure and/or isobaric thermal expansivity, prohibits application of the pressure-volume approach to the other systems.

Dependence of the Standard Transfer Enthalpy of the Composition of the Solvent Mixture. It has been noted that a mixed solvent with a large negative value of h^E shows a large value of $\Delta_t h^\ominus$. A semi-quantitative formulation to represent this observation is developed by assuming that if 1 mol of the solute molecule is transferred from dodecane to the water–organic solvent mixture, then the interactions among the mixed solvent molecules included in volume V_s would be broken. The "excess" transfer enthalpy $\Delta_t h^{\ominus E}$ which is defined as

$$\Delta_t h^{\ominus E} = \Delta_t h^\ominus - x_1 \Delta_t h^\ominus(1) - x_2 \Delta_t h^\ominus(2), \tag{7}$$

where $\Delta_t h^\ominus(1)$ and $\Delta_t h^\ominus(2)$ are the standard transfer enthalpies from dodecane to solvent 1 and solvent 2, respectively will be proportional to the excess cohesive energy density, $-h^E/v$, *i.e.*,

$$\Delta_t h^{\ominus E} = V_s\left(-\frac{h^E}{v}\right), \tag{8}$$

where v refers to the mean molar volume of the solvent mixture. A plot of the calculated $\Delta_t h^{\ominus E}$ values against $(-h^E/v)$ gives a linear correlation, as shown in Fig. 4. From the slope the parameter V_s has been estimated as 616 cm^3 mol^{-1}. This value is about 2.2 times larger than the molar volume of [Cr(acac)$_3$] in the crystalline state, 275.3 cm^3 mol^{-1}.[10] This observation may reflect the distance of closest approach of the solvent molecule to the complex molecule is larger than the radius of the complex molecule.

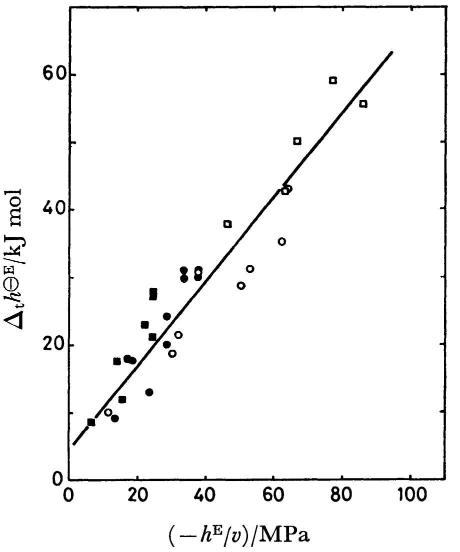

Fig. 4 Plot of the "excess" transfer enthalpy of [Cr(acac)$_3$] against the excess cohesive energy density of water-organic solvent mixture; ○, water-DMF,[11) □, water-DMSO,[6,d)] ●, water-methanol,[12)] ■, water-ethylene glycol.[13)]

Conclusion

In this study, it has been found that the activity coefficient derived from the partition coefficient may be correlated linearly with the pressure factor of the solvent mixture in Eq. 5 in the water–DMSO system, but not in the water–AN. This apparent discrepancy may be result from differences in the types of interactions, that is, the aqueous mixture is structure-making ($h^E<0$) or structure-breaking ($h^E>0$). It has been found that, in dodecane/aqueous mixtures with DMF, DMSO, MeOH, and EG, which are structure-making, the "excess" transfer enthalpy defined in Eq. 7 can be correlated linearly with the excess cohesive energy density. These findings show the importance of the solvophobic interaction between [Cr(acac)$_3$] and polar solvent molecules in the aqueous mixed solvent phase.

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