

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

#### **4.1 Results**

The results of this study are given in Tables 4.1-4.7. The CMC of surfactant with no solubilizates at various temperatures and cloud point temperatures of the binary system are shown in Tables 4.1 and 4.2. Data on coacervate extraction at equilibrium are shown in Tables 4.3-4.5. Data on semi-equilibrium dialysis are shown in Tables 4.6 and 4.7. Figures 4.1-4.6 show the coacervate extraction. Figures 4.7 and 4.8 show the comparison for the chloroethanes in coacervate and for the solubilization of the chloroethanes, respectively.

**Table 4.1** CMC of OP(EO)<sub>7</sub> with no solubilizates at various temperatures

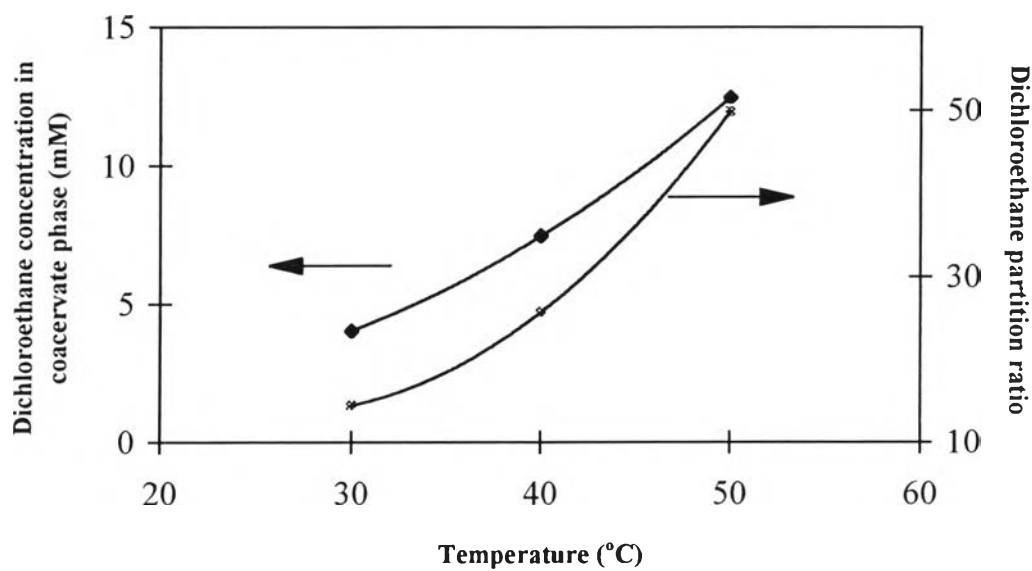
Temperature (°C)	CMC (mM)
30	0.092
40	0.086
50	0.075

**Table 4.2** Cloud point temperatures of 50 mM OP(EO)<sub>7</sub> system

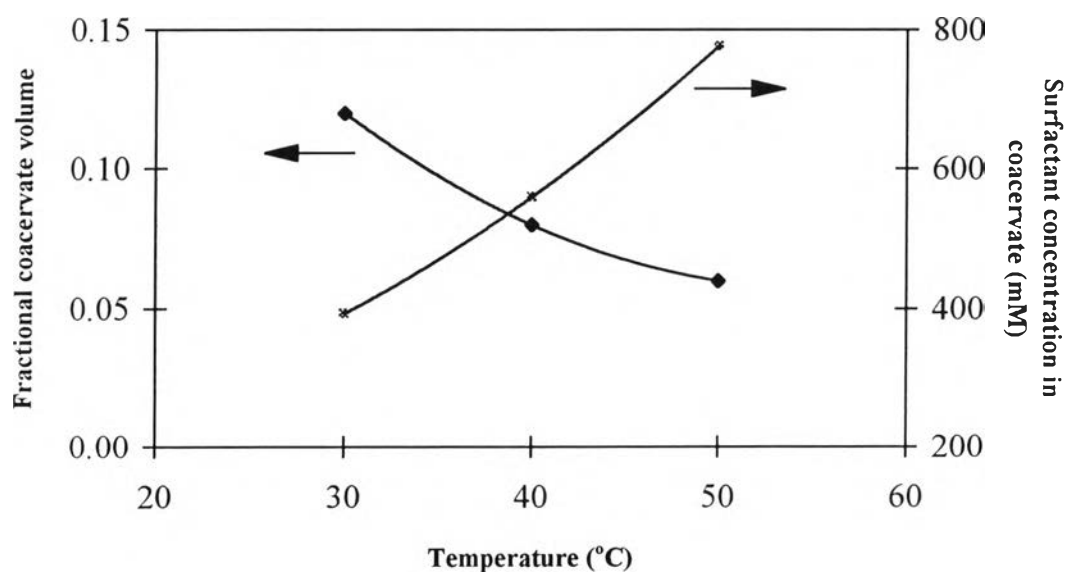
	0 M	1.0 mM
1,2-dichloroethane	22 °C	19 °C
1,1,1-trichloroethane	22 °C	16 °C
1,1,1,2-tetrachloroethane	22 °C	15 °C
Trichloroethylene (TCE)	22 °C	16 °C

**Table 4.3** Liquid-coacervate extraction data : initial [OP(EO)<sub>7</sub>] = 50 mM, initial [solute] = 1.0 mM

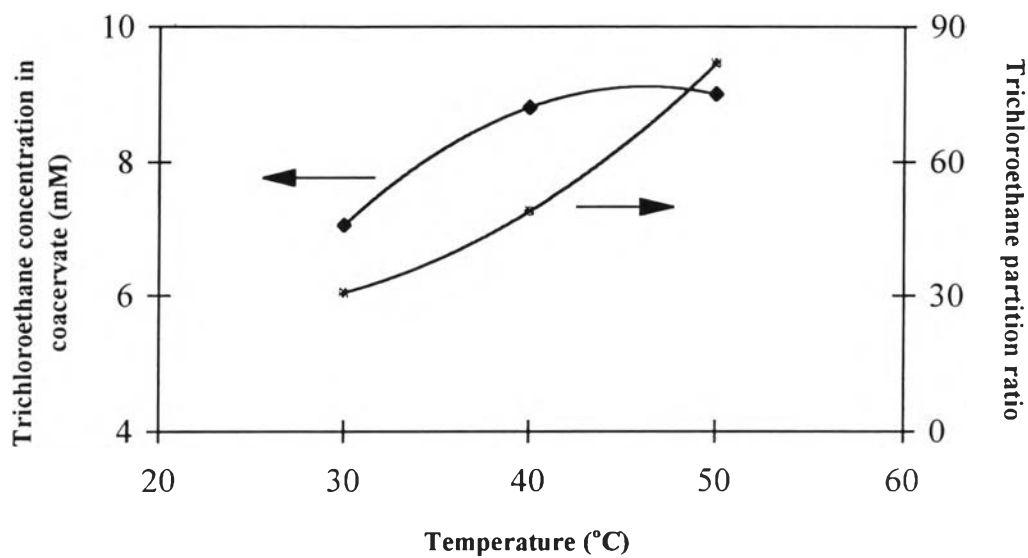
System	Temp. (°C)	Fractional coacervate volume	[OP(EO) <sub>7</sub> ] (mM)		[Solute] (mM)	
			Dilute	Coacervate	Dilute	Coacervate
OP(EO) <sub>7</sub> / dichloroethane	30	0.12	1.13	393	0.28	4.05
	40	0.08	1.05	560	0.29	7.47
	50	0.06	0.74	777	0.25	12.46
OP(EO) <sub>7</sub> / trichloroethane	30	0.12	0.98	409	0.23	7.06
	40	0.08	0.72	603	0.18	8.81
	50	0.06	0.59	816	0.11	9.00
OP(EO) <sub>7</sub> / tetra chloroethane	30	0.13	0.76	422	0.22	7.14
	40	0.08	0.52	633	0.17	9.26
	50	0.07	0.49	846	0.15	12.90



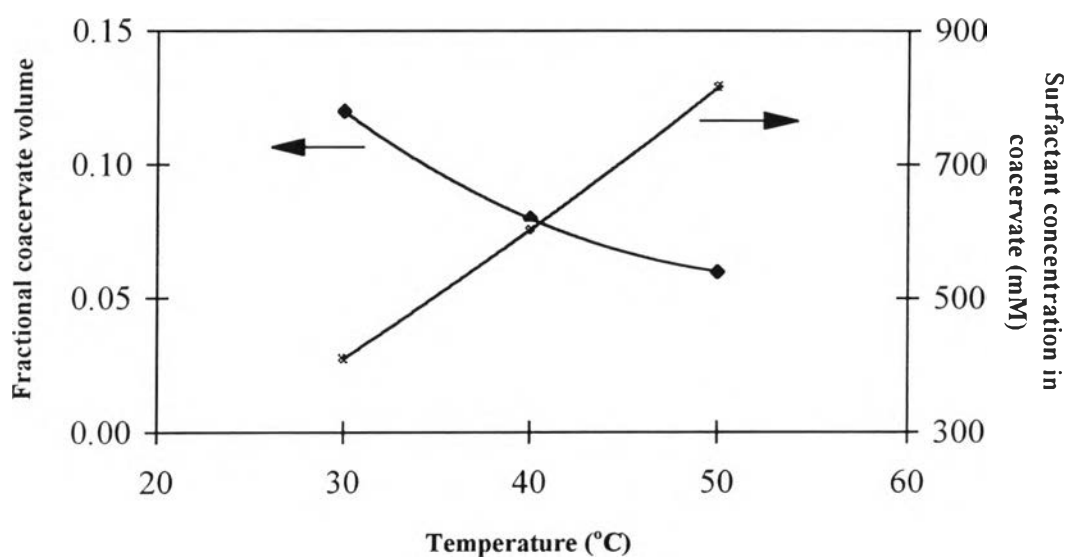
**Figure 4.1** Dichloroethane concentration and partition ratio in coacervate as a function of temperature.



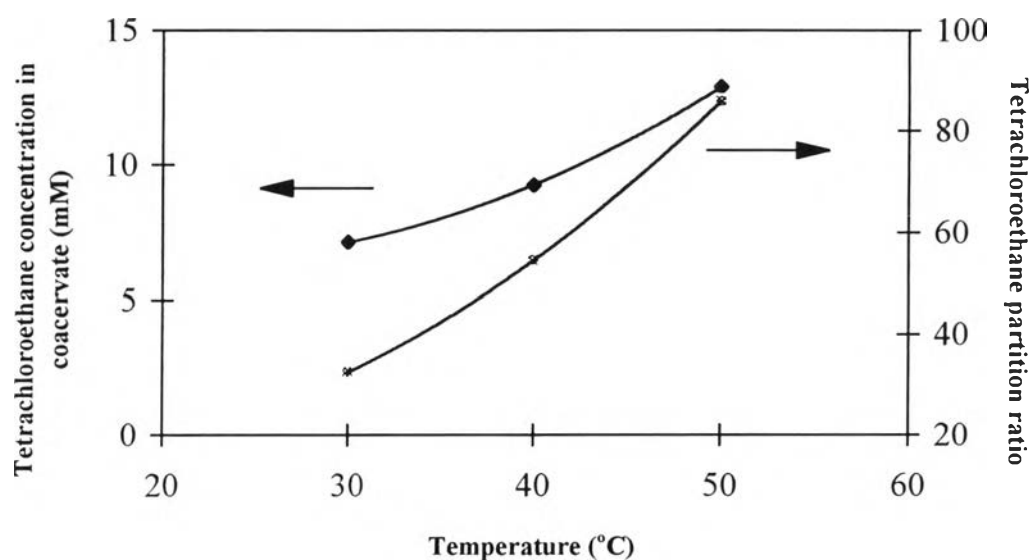
**Figure 4.2** Surfactant concentration in coacervate and fractional volume of coacervate phase in system with dichloroethane.



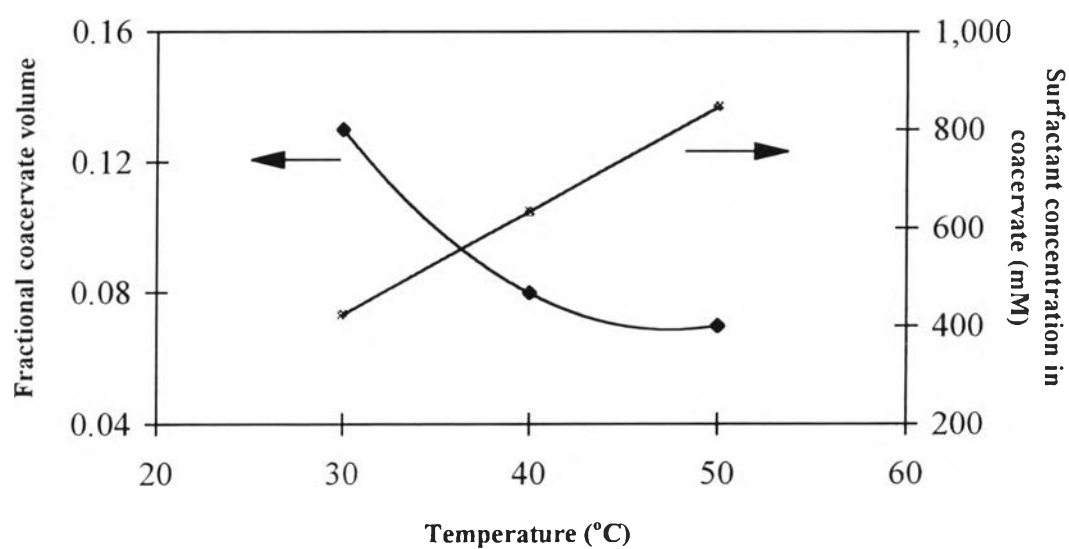
**Figure 4.3** Trichloroethane concentration and partition ratio in coacervate as a function of temperature.



**Figure 4.4** Surfactant concentration in coacervate and fractional volume of coacervate phase in system with trichloroethane.



**Figure 4.5** Tetrachloroethane concentration and partition ratio in coacervate as a function of temperature.



**Figure 4.6** Surfactant concentration in coacervate and fractional volume of coacervate phase in system with tetrachloroethane.

**Table 4.4** Fractional distribution of components between coacervate and dilute phases

System	Temperature (°C)	Fraction of surfactant in coacervate	Fraction of solute in coacervate
OP(EO) <sub>7</sub> / dichloroethane	30	0.98	0.66
	40	0.98	0.69
	50	0.99	0.79
OP(EO) <sub>7</sub> / trichloroethane	30	0.98	0.81
	40	0.99	0.81
	50	0.99	0.84
OP(EO) <sub>7</sub> / tetra- chloroethane	30	0.99	0.83
	40	0.99	0.83
	50	0.99	0.87

**Table 4.5** Partition ratios of components between coacervate (C) and dilute (D) phases

System	Temperature (°C)	$\frac{[\text{Surfactant}]_C}{[\text{Surfactant}]_D}$	$\frac{[\text{Solute}]_C}{[\text{Solute}]_D}$
OP(EO) <sub>7</sub> / dichloroethane	30	347.8	14.5
	40	533.3	25.8
	50	1050.0	49.8
OP(EO) <sub>7</sub> / trichloroethane	30	417.3	30.7
	40	837.5	48.9
	50	1383.1	81.8
OP(EO) <sub>7</sub> / tetra- chloroethane	30	555.3	32.5
	40	1217.3	54.5
	50	1726.5	86.0



**Table 4.6** Semi-equilibrium dialysis data for micellar solubilization of 50 mM OP(EO)<sub>9</sub> and 1.0 mM organic solute initial retentate concentrations

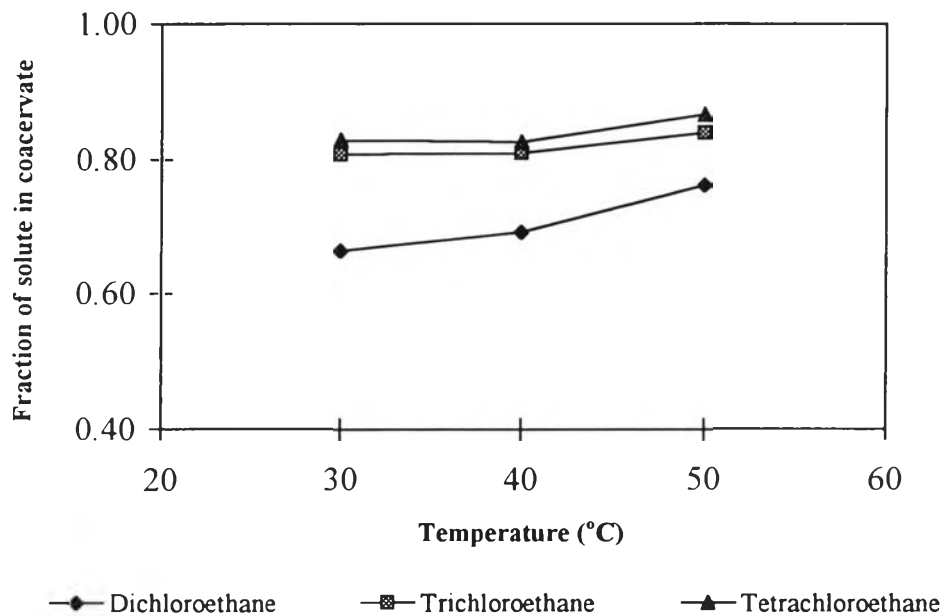
	Initial		Permeate		Retentate		K <sub>m</sub> (L/mol)
	[S] <sup>†</sup>	[Solute]	[S] <sup>†</sup>	[Solute]	[S] <sup>†</sup>	[Solute]	
	(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	
30 °C	50	1.0 <sup>*</sup>	1.13	0.28	48.9	0.72	35.3
40 °C	50	1.0 <sup>*</sup>	1.05	0.25	49.0	0.75	42.0
50 °C	50	1.0 <sup>*</sup>	0.74	0.20	49.3	0.80	63.4
30 °C	50	1.0 <sup>**</sup>	1.98	0.19	48.0	0.81	80.2
40 °C	50	1.0 <sup>**</sup>	0.72	0.17	49.3	0.83	88.1
50 °C	50	1.0 <sup>**</sup>	0.59	0.14	49.4	0.86	107.7
30 °C	50	1.0 <sup>***</sup>	0.76	0.17	49.2	0.83	82.5
40 °C	50	1.0 <sup>***</sup>	0.52	0.16	49.5	0.84	89.4
50 °C	50	1.0 <sup>***</sup>	0.49	0.15	49.5	0.86	105.0

<sup>†</sup> [OP(EO)<sub>9</sub>]

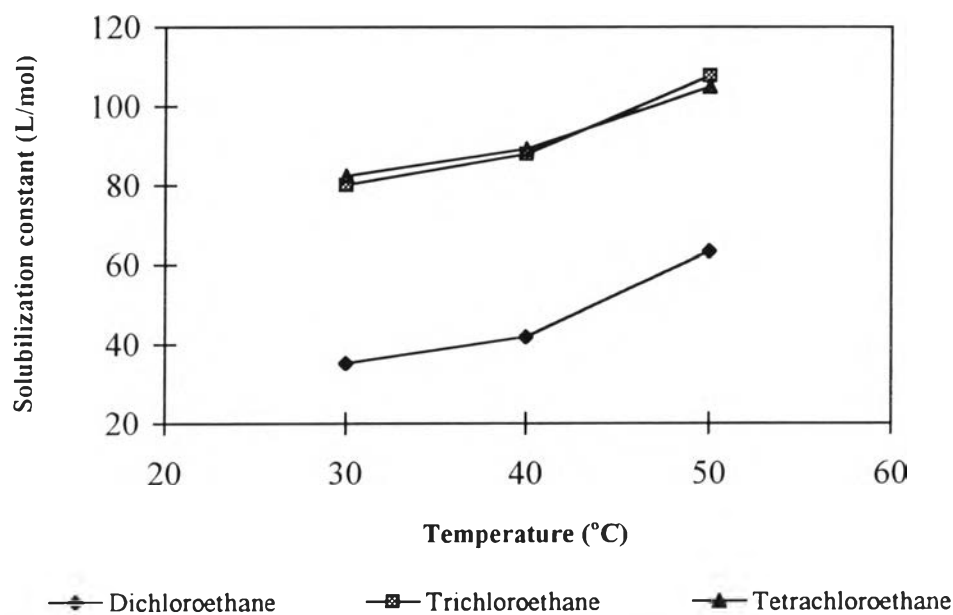
<sup>\*</sup> Dichloroethane

<sup>\*\*</sup> Trichloroethane

<sup>\*\*\*</sup> Tetrachloroethane



**Figure 4.7** Comparison for the fraction of the chloroethanes in coacervate.



**Figure 4.8** Comparison for the solubilization of the chloroethanes.

**Table 4.7** Comparison of  $K_m$  and  $K_c$ 

System	Temperature (°C)	$K_m$ (L/mol)	$K_c$ (L/mol)
OP(EO) <sub>n</sub> / dichloroethane	30	35.3	34.9
	40	42.0	41.5
	50	63.4	62.4
OP(EO) <sub>n</sub> / trichloroethane	30	80.2	78.8
	40	88.1	86.9
	50	107.7	106.5
OP(EO) <sub>n</sub> / tetra- chloroethane	30	82.5	81.1
	40	89.4	88.1
	50	105.0	103.5

## 4.2 Discussion

The CMC of OP(EO)<sub>7</sub> at 25 °C with no solubilizates is 0.184 mM. As the temperature increases, the CMC of nonionic surfactants appear first to decrease to some minimum value around 50 °C and then to increase with further increase in temperature. The temperature reduces the CMC of surfactants as shown in Table 4.1. The dilute phase surfactant concentration of all systems shown in Table 4.3 are at least 3 to 10 times the CMC. Discussion of the results follows.

### 4.2.1 Effect of Temperature on Coacervate Extraction

The cloud point of the 50 mM OP(EO)<sub>7</sub> system (same concentration as used in coacervate extraction experiments) is shown in Table 4.2 at several solute concentrations. The cloud point is only mildly dependent on the presence of the solute at the low solute concentrations used. The cloud point depression is greater as the degree of chlorination of the solute increases. Tables 4.3-4.5 show the concentrations in coacervate and dilute phases, fractional distributions of components in phases, and partition ratio of solute and surfactant. As shown in Table 4.4, up to 98 % of OP(EO)<sub>7</sub>, 66 % of 1,2-dichloroethane, 81 % of 1,1,1-trichloroethane, and 83 % of 1,1,1,2-tetrachloroethane are removed in the coacervate phase. From a previous study (Kimchuwanit, 1994) under the same conditions, 81 % of trichloroethylene was removed in the coacervate. As the temperature increases, the separation improves; the fractional volume of the coacervate decreases, partition ratio increases, and fraction of solute in coacervate increases. The reason is when the temperature of the system increases, the system is further from the low consolution solution temperature (cloud point), resulting in increasing dissimilarity between the coacervate phase and dilute phase, causing a

decrease in the coacervate phase volume. The concentration of the surfactant and the chloroethanes in the coacervate phase increases with increasing temperature while these concentrations in the dilute phase are not much affected.

#### 4.2.2 Effect of Organic Solute Structure on Coacervate Extraction

The 1,1,1-trichloroethane and 1,1,1,2-tetrachloroethane partition more effectively into the coacervate phase than 1,2-dichloroethane as seen in Table 4.5. The large increase in the distribution coefficient with an increase in solute hydrophobicity was chiefly due to the decrease in the water solubility of the aromatic hydrocarbon compounds (Nawakowska, White and Guillet, 1989). The exact structure of the surfactant in coacervate is not known. However, the aggregate structure probably consists of the surfactant hydrocarbon chains intertwining, removing themselves from aqueous solution, and covering the surface of this hydrophobic region with hydrophilic groups.

#### 4.2.3 Comparison of Solute Solubilization between Coacervate and Micelles

In order to compare solubilization in coacervate and micelles, a surfactant with a higher cloud point was used for micelle studies (7 vs 9 ethylene oxides in hydrophilic group). The solubilization of the chlorinated hydrocarbons is predominant in the core of the micelle and the change of the hydrophilic group length is slightly as expected to have very little effect on  $K_m$  (Lee, Christian, Tucker and Scamehorn, 1990). Table 4.6 shows the SED data and calculated values of  $K_m$ . Table 4.7 shows the comparison between  $K_m$  and  $K_c$ . The solute distribution coefficient for coacervate extraction is nearly the same as the micellar solubilization for the octylphenol

polyethoxylate surfactants studied. This supports the view that the surfactant aggregates in coacervate are micelle-like in structure.

It is interesting to note that the partition ratio increases much more rapidly with temperature than the value of  $K_c$  or than the coacervate solute concentration. For example, the ratio of partition ratios at 50 °C to 30 °C are 3.43, 2.66, and 2.65 for the di, tri, and tetrachloroethanes, respectively and equivalent ratios of  $K_c$  are 1.79, 1.35, and 1.28 for these same compounds. This is primarily due to the reduced dilute phase solute concentration which is due to a reduced surfactant concentration (much lower concentration of micelles) with increasing temperature. A very important conclusion is that micellar solubilization in the dilute phase substantially reduces the coacervate extraction separation efficiency, particularly at low temperature.