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# Liquid-Liquid Extraction

— Extraction of Aromatics —

By

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## Summary

The liquid-equilibria of benzene-diethylene glycol (D.E.G.) and benzene-heptane-D.E.G. system at various temperatures up to 150°C was obtained to know more details about the principle of Udex-Process. A specially designed funnel attached with an agitator was used to obtain the equilibria at elevated temperatures under pressures.

Some binary solvents were searched to find better solvents than D.E.G.; the solubility as well as the selectivity of D.E.G. mixed with methanol or phenol at a room temperature was revealed to be better than those of D.E.G. alone at elevated temperatures.

A batch extraction in a glass vessel with an agitator was carried out for some systems such as benzene-D.E.G., benzene-heptane-D.E.G., and benzene-heptane-binary solvents. The capacity coefficient from these results by the two-film theory was not of constance, but decreased as in an inverse proportion to the passing time, and that obtained by application of Hatta's equation also was not constant. The other obtained by Higbie's equation was not as proportional to the root of the time as expected in that equation.

On the other hand the application of Newman's equation gave relatively good concordances with the experimental data, especially with those of high speed agitations. Some discussions were described on those results.

## Introduction

As the first commercially successful application of extraction of petroleum-refining processes, Edeleanu-Process is of reputation. Another one for the production of benzene, toluene and xylene is Udex-Process, which uses ethylene glycols as the solvent.

The recently increased demand for the aromatics drew the various applica-

tions such as azeotropic-distillation, extractive-distillation, and arosorb-process, besides the liquid extraction.

Among them the process of Udex is known as being proper for the extraction of aromatics from gasoline fractions. For this process some fundamental data as well the commercial operation ones were reported. In spite of the marketable developing of this process, however, fundamental liquid-equilibrium data of three-component systems consisted of the aromatics, non-aromatics and ethylene glycols at elevated temperatures seem to be obtained not so perfectly.

Concerning the kinetics of liquid-extraction, on the other hand, the solution based on two-film theory is well known, which the mass-transfer coefficient is considered as constant in.

As theoretical analyses of unsteady-state conditions, several solutions were derived yet. The differences recognized among these solutions mainly depend upon the opinion given to the flow-pattern in the drop of dispersed liquid.

### I. Liquid Equilibria

In Udex-Process, diethylene-glycol (D.E.G.) with water as the solvent is used at about 10 atm. and 150°C, and an equilibrium datum is given as shown in Fig. 1<sup>1)</sup>. The addition of water as well known decreases the solubility of aromatics to the solvent but increases the selectivity.

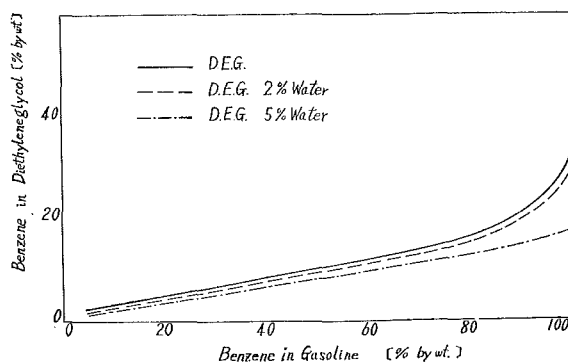


Fig. 1. Equilibrium composition in benzene-gasoline (150~185°F)-diethylene glycol system<sup>1)</sup>.

Some other data of the equilibria of benzene-heptane-D.E.G. system were given by Johnson and Francis as shown in Figs. 2-5<sup>2)</sup>. There might be no other result published yet.

Some fundamental data of D.E.G. as the solvent were thence investigated first of all and then those of some solvents of D.E.G. mixed with another

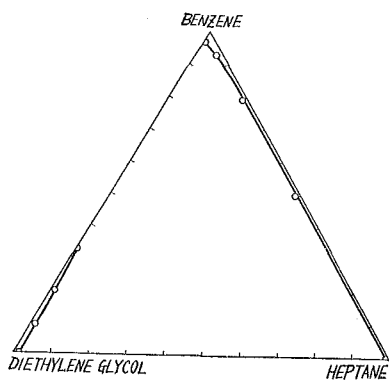


Fig. 2. Equilibrium compositions in benzene-heptane-diethylene glycol system at 25°C.

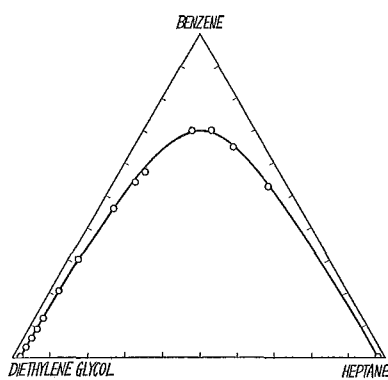


Fig. 3. Equilibrium compositions in benzene-heptane-diethylene glycol system at 125°C.

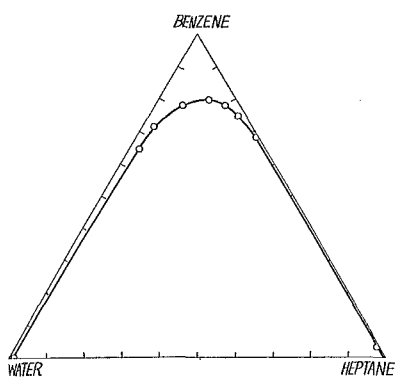


Fig. 4. Equilibrium compositions in benzene-heptane-water system at 25°C.

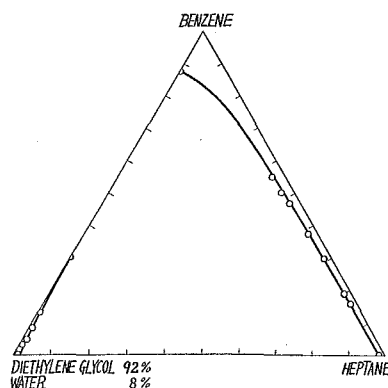


Fig. 5. Equilibrium compositions in benzene-heptane-diethylene glycol + 8% water system at 125°C.

solvent were obtained.

### I.1 Experimental

To obtain the equilibria the analysis method as well as the titration method were applied here.

In the analysis one two sorts of graduated funnel of which the use depends on the solvent ratio, were used (Fig. 6). After the shaking the funnel in which an amount of sample was put, in a thermostat and the following phase settling of two phases, each amount of these phases was measured by reading a boundary surface on the graduation. The raffinate was washed with water in the funnel

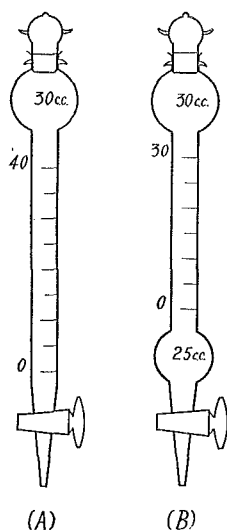


Fig. 6. Funnels used in measuring equilibria.

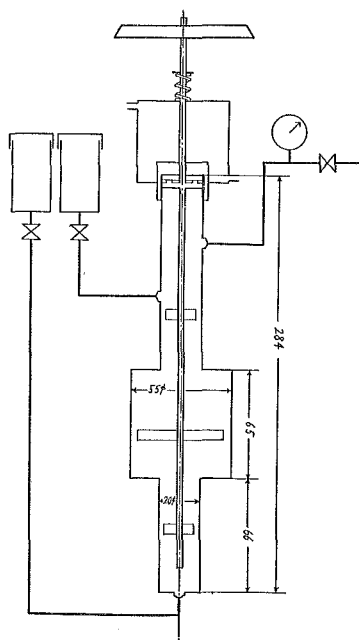


Fig. 7. Pressure-funnel.

from which the extract had been taken out, to determine an amount of the solvent dissolved. The composition of raffinate was determined by measuring its refractive-index; that of extract could be calculated from the total amount of sample and the amount as well the composition of the raffinate. These values obtained were plotted on a ternary diagram by means of the usual way.

A pressure-funnel attached with a mechanical stirrer was made to obtain equilibrium data at elevated temperatures under pressures (Fig. 7 and 8). This is designed to be available up to 30 atm; the vapour pressure of benzene and heptane at 150°C is 6.03 and 3.62 atm, respectively. Nitrogen was charged into the funnel up to 4 atm in order to prevent as possible the vapouring of sample liquid. The funnel was immersed in an oil bath in which soja-bean oil was forced to circulate from another vessel heated by gas burners. The heating time was two hours during which the agitation of 200 r.p.m. was continued. About 10 ml of the extract and raffinate separately were discharged into a receiver of which volume is 20 ml after the phase-settling, at the extractive temperature. The determination of each composition was carried out on these total liquids to avoid the error due to the change of composition accompanied with a fall of the temperature. The heating time of two hours was enough

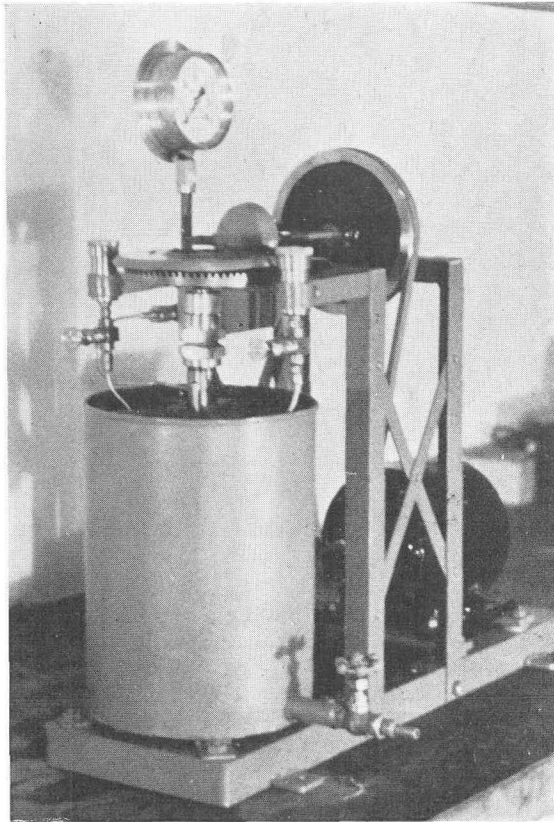


Fig. 8. Pressure-extraction apparatus.

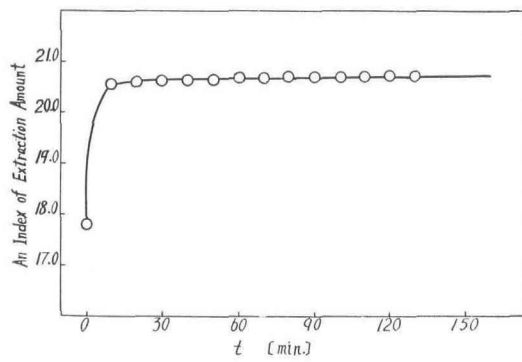


Fig. 9. Effect of time on extraction amount in benzene-heptane-diethylene glycol.

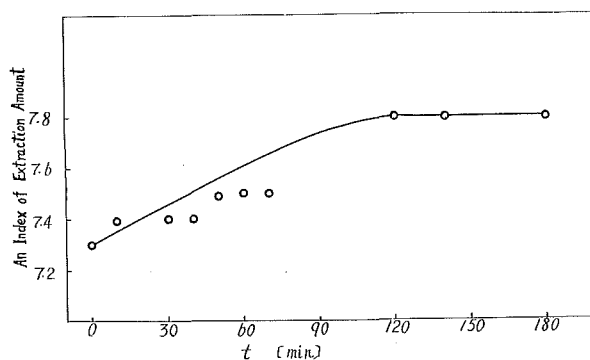


Fig. 10. Effect of time on extraction amount in benzene-hexane-ethylene glycol.

to attain the equilibrium-state condition as shown in Fig. 9 and 10.

The physical properties of chemicals used in this experiment are denoted in Table 1. The refractive index of mixtures of the aromatics and the paraffins is so perfectly proportional to its composition as shown in Table 2 and Fig. 11.

TABLE 1. Physical Properties of Chemicals

	density (at 20°C)	refractive index	boiling point °C
Benzene	0.8781	1.504 (at 15°C)	80.0
Toluene	0.870	1.500 ( " )	110.0
Xylene	0.865	1.499 ( " )	133.9
Hexane	0.660	1.375 ( " )	68.7
Heptane	0.680	1.3870 (at 20°C)	98.0
E.G.	1.1132	1.4310 ( " )	196~198
D.E.G.	1.117	1.4475 ( " )	242~244

TABLE 2. Correlation between Refractive-Index and Composition of Benzene-Heptane Mixture

Benzene % (vol)	$n_D^{15}$	Benzene % (vol)	$n_D^{15}$
0	1.392	60	1.459
10	1.402	70	1.471
20	1.414	80	1.484
30	1.426	90	1.493
40	1.436	100	1.504
50	1.448		

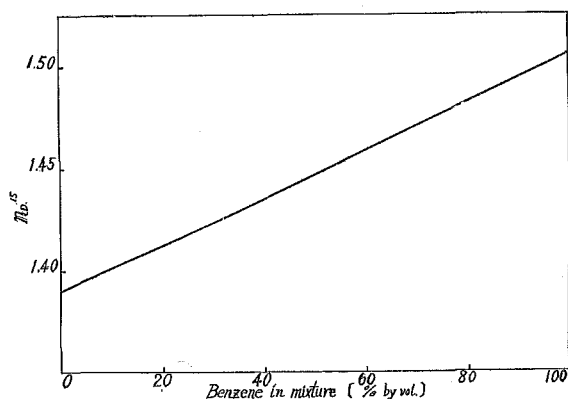


Fig. 11. Correlation between refractive indexes and compositions of benzene-heptane mixtures.

## I. 2 Results

The equilibria of binary systems of benzene-D.E.G. and benzene-ethylene glycol (E.G.) at various temperatures are shown in Table 3 as well Fig. 12 and 13. In Table 4 and Figs. 14-17 there are the results of ternary systems composed of heptane-aromatics (B.T.X.) as the solution and of D.E.G. as the solvent at 50°C, as well as the one at 80°C in which only xylene was used as the aromatic. The equilibria of benzene-heptane-D.E.G. at 125 and 150°C under pressures are denoted in Table 5 as well in Figs. 18-19. The results of E.G. used in stead of D.E.G. as the solvent are shown in Table 6 and Figs. 20-21. To increase the solubility of the aromatics to D.E.G. some substances having-OH group as a secondary solvent had been expected to be tested; some solvents were preferable which have an excellent solubility and selectivity at room temperatures. As one of such substances, methanol was tested. The

TABLE 3. Equilibrium Composition

Solvent	D. E. G.		E. G.
	Benzene % (wt) in Extract	Benzene % (wt) in Raffinate	Benzene % (wt) in Extract
Temp. °C			
20	31.0	97.2	4.8
25	31.3	97.1	5.7
40	32.3	95.5	6.4
50	32.8	93.7	7.0
60	34.5	92.0	7.4



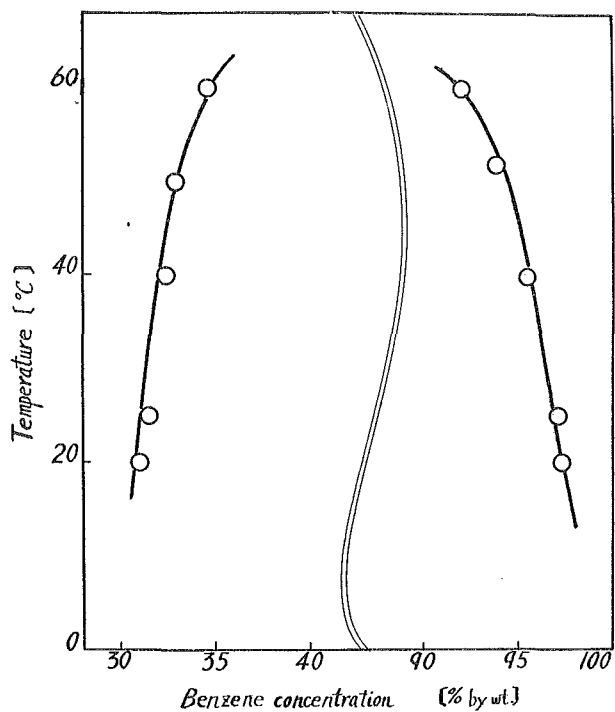


Fig. 12. Equilibrium compositions in benzene-diethylene-glycol system.

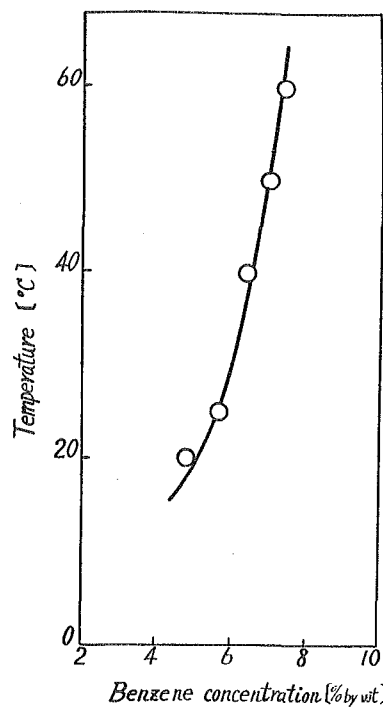


Fig. 13. Equilibrium compositions in benzene-ethylen-glycol system.

TABLE 4. Equilibrium Composition

Benzene-Heptane-D.E.G. System at 50°C						Xylene-Heptane-D.E.G. System at 50°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Benzene	Heptane	D.E.G.	Benzene	Heptane	D.E.G.	Xylene	Heptane	D.E.G.	Xylene	Heptane	D.E.G.
32.5	0.5	67.0	80.6	8.0	11.4	15.0	0.4	84.6	86.3	11.1	2.6
27.5	0.4	72.1	75.3	19.3	5.4	9.7	0.3	90.0	82.0	16.5	1.5
20.4	0.4	79.2	68.5	28.8	2.7	7.2	0.2	91.9	78.3	20.4	1.2
15.4	0.3	84.3	53.7	42.0	4.3	7.2	0.3	91.8	69.4	29.3	1.3
12.2	0.3	87.5	46.8	50.4	3.8	7.2	0.2	91.9	55.2	43.5	1.3
11.0	0.3	88.7	38.2	65.3	1.5	7.0	0.1	92.9	19.8	79.0	1.2
Toluene-Heptane-D.E.G. System at 50°C						Xylene-Heptane-D.E.G. System at 80°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Toluene	Heptane	D.E.G.	Toluene	Heptane	D.E.G.	Xylene	Heptane	D.E.G.	Xylene	Heptane	D.E.G.
22.3	0.2	77.5	83.0	11.9	5.1	16.6	0.9	82.5	93.0	2.8	4.2
15.0	0.2	84.8	81.0	16.6	2.4	15.5	1.3	83.2	88.9	7.8	3.3
12.3	0.2	87.5	79.5	17.6	2.9	12.0	1.3	86.7	86.0	11.6	2.4
10.1	0.1	89.8	76.5	20.7	2.0	10.4	1.8	87.8	74.5	23.0	2.5
7.2	0.1	92.7	31.0	66.3	2.7	8.8	1.8	89.4	62.1	35.8	2.1
7.2	0.1	92.7	24.5	71.5	4.0	6.7	1.1	42.2	29.7	69.5	1.8
						6.0	1.1	93.0	15.0	83.5	1.5

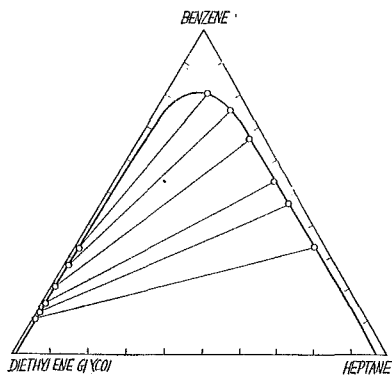


Fig. 14. Equilibrium compositions in benzene-heptane-diethylene glycol system at 50°C.

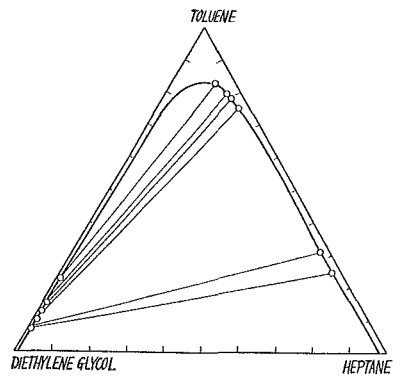


Fig. 15. Equilibrium compositions in toluene-heptane-diethylene glycol system at 50°C.

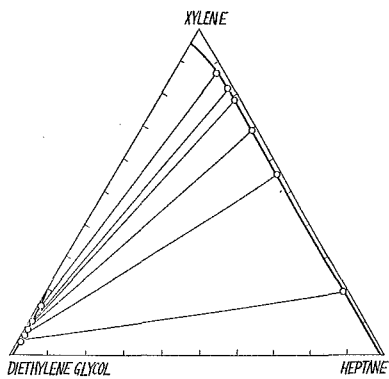


Fig. 16. Equilibrium compositions in xylene-heptane-diethylene glycol system at 50°C.

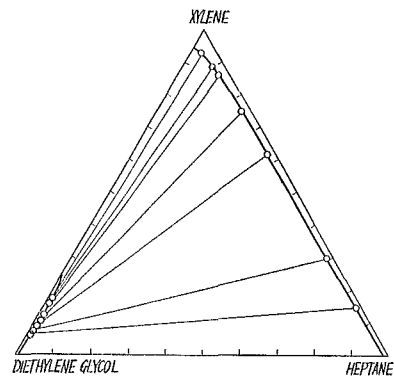


Fig. 17. Equilibrium compositions in xylene-heptane-diethylene glycol system at 80°C.

TABLE 5. Equilibrium Composition

Benzene-Heptane-D.E.G. System at 125°C						Benzene-Heptane-D.E.G. System at 150°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Ben- zene	Hept.	D.E.G.	Ben- zene	Hept.	D.E.G.	Ben- zene	Hept.	D.E.G.	Ben- zene	Hept.	D.E.G.
6.5	2.0	91.5	16.3	81.5	2.2	8.5	2.3	89.2	10.3	87.4	2.3
18.0	2.0	80.0	38.3	59.4	2.3	13.0	2.2	84.8	17.2	78.9	3.9
24.1	2.0	73.9	45.9	50.0	4.1	17.0	2.9	80.1	30.6	64.4	5.0
30.5	1.1	68.4	52.1	43.4	4.5	19.1	2.1	78.8	35.5	59.5	5.0
35.3	2.0	62.7	63.7	30.0	6.3	29.7	2.1	68.2	47.3	46.3	6.4
37.4	1.2	61.4	74.1	13.1	12.8	31.9	2.8	65.3	53.5	40.7	5.8
						34.0	2.1	63.9	56.0	36.5	7.5
						42.4	2.6	55.0	64.0	26.0	10.0
						51.5	4.0	44.5	67.1	16.4	16.4

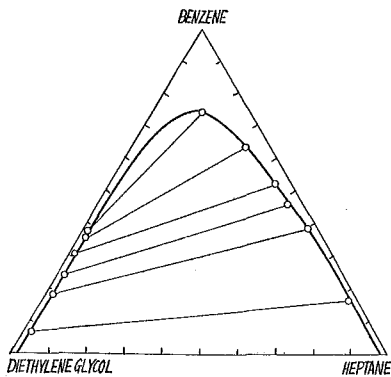


Fig. 18. Equilibrium compositions in benzene-heptane-diethylene glycol system at 125°C.

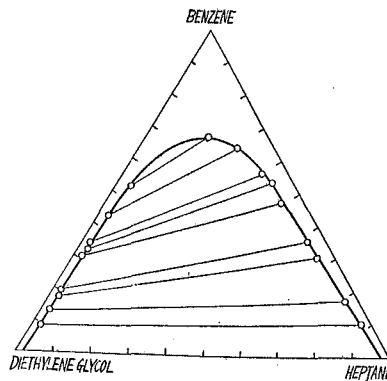


Fig. 19. Equilibrium compositions in benzene-heptane-diethylene glycol system at 150°C.

TABLE 6. Equilibrium Composition

Benzene-Hexane-E.G. System at 30°C						Benzene-Hexane-E.G. System at 50°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Ben- zene	Hexane	E.G.	Ben- zene	Hexane	E.G.	Ben- zene	Hexane	E.G.	Ben- zene	Hexane	E.G.
2.5	0.3	97.2	33.0	64.0	3.0	2.0	2.1	95.9	32.9	63.8	3.3
3.1	0.4	96.5	35.8	61.3	2.9	2.4	1.5	96.1	33.6	62.4	4.0
3.5	1.3	95.2	40.9	56.0	3.1	2.4	1.6	96.0	38.2	59.8	2.0
3.9	1.6	94.5	52.0	45.0	3.0	2.5	1.6	95.9	51.5	46.5	2.0
4.8	1.0	94.2	65.5	31.4	3.1	2.8	2.0	95.2	34.5	62.0	3.5
5.0	0.9	94.1	84.0	12.8	3.2	3.0	2.5	94.5	38.0	52.4	9.6
						4.0	0.7	95.3	50.6	47.1	0.7
						4.5	1.3	64.2	58.6	40.7	2.3
						6.8	1.0	92.2	66.0	33.0	1.0

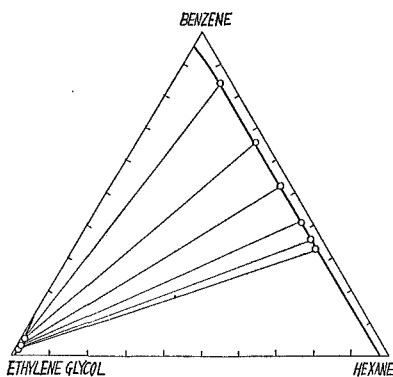


Fig. 20. Equilibrium compositions in benzene-hexane-ethylene glycol system at 30°C.

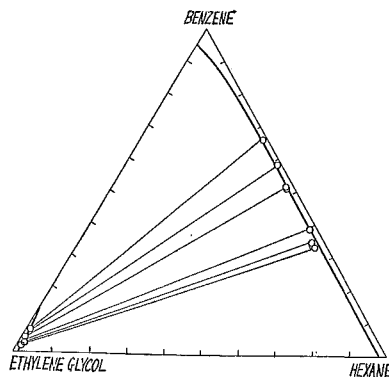


Fig. 21. Equilibrium compositions in benzene-hexane-ethylene glycol system at 50°C.

results on benzene-methanol-D.E.G. system as well on heptane-methanol-D.E.G. system are given in Table 7 and Figs. 22-23. In Table 8 and Figs. 24-28 there are the results in which phenol for the same purpose was used with the aromatics (B.T.X.), and that of xylene-cresol-D.E.G. system. According to the results described yet, some results obtained from the systems composed of D.E.G., and 10, 20 and 27.1% of phenol are denoted in Table 9 and Figs. 29-30

TABLE 7. Equilibrium Composition

Benzene-Methanol-D.E.G. System at 24°C			Heptane-Methanol-D.E.G. System at 22°C		
Benzene	Methanol	D.E.G.	Heptane	Methanol	D.E.G.
31.5	0	68.5	1.9	21.7	76.4
32.0	1.2	66.8	2.9	25.5	71.6
33.5	2.3	64.2	4.9	39.5	55.6
35.5	4.3	60.2	5.2	34.4	60.4
46.8	6.6	46.6	6.9	43.8	49.3
57.6	7.5	35.0	8.3	53.8	37.9
71.1	6.4	22.5	9.9	57.7	32.4
96.5	0	3.5	13.4	67.6	19.0
			17.8	72.1	10.1
			18.1	76.4	5.5
			22.1	75.3	2.6

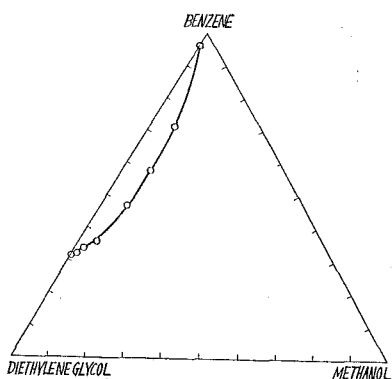


Fig. 22. Equilibrium compositions in benzene-methanol-diethylene glycol system.

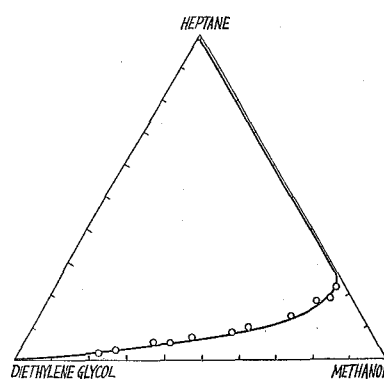


Fig. 23. Equilibrium compositions in heptane-methanol-diethylene glycol system.

TABLE 8. Equilibrium Composition

Benzene-Phenol-D.E.G. System at 19°C			Xylene-Phenol-D.E.G. System at 25°C			Xylene-Cresol-D.E.G. System at 16°C		
Benzene	Phenol	D.E.G.	Xylene	Phenol	D.E.G.	Xylene	Cresol	D.E.G.
31.5	0	68.5	9.0	0	91.0	9.0	0	91.0
32.0	1.0	67.0	11.9	6.6	81.5	13.0	7.5	79.5
33.0	1.5	65.5	17.3	13.5	69.2	18.6	12.7	68.7
34.9	2.8	62.3	23.0	16.0	61.0	24.3	15.9	59.8
46.2	4.3	49.5	26.9	19.5	53.6	35.5	17.4	47.1
72.0	4.9	25.1	34.5	20.5	45.0	42.3	18.9	38.8
97.5	0	2.5	57.2	21.6	21.2	65.2	11.6	23.2
			98.5	0	1.5	73.8	9.4	16.7
						98.5	0	1.5
Toluene-Phenol-D.E.G. System at 22°C			Heptane-Phenol-D.E.G. System at 23°C					
Toluene	Phenol	D.E.G.	Heptane	Phenol	D.E.G.			
17.2	0	82.8	0.5	0	99.5			
17.0	5.0	78.0	0.5	9.0	90.5			
21.0	9.0	70.0	0.9	17.1	82.0			
25.0	12.0	63.0	2.4	13.4	74.2			
34.0	14.5	51.5	5.2	43.0	51.8			
47.3	13.5	39.2	6.2	60.0	33.8			
68.4	9.5	22.1	7.7	72.3	20.0			
98.0	0	2.0						

The same experiments of E.G. in the room of D.E.G. were carried out as shown in Table 10 and Figs. 32-33. Expecting to obtain some commercially fundamental data relating to E.G. mixed with phenol, the mixtures consisted of E.G. and 30 as well as 50% of phenol were tested at 30-70°C as in Table 11 and Figs. 34-38.

As mentioned before, this experiment began to know more details about the equilibria of D.E.G. at elevated temperatures. In Udex-Process, as well known, the operating condition of extraction tower are of about 120°C and 10 atm.; the cost of tower should be higher than that of no pressure-tower.

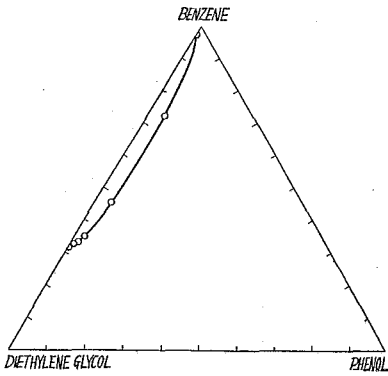


Fig. 24. Equilibrium compositions in benzene-phenol-diethylene glycol system, at 20°C.

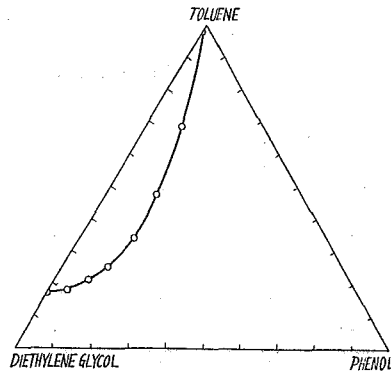


Fig. 25. Equilibrium compositions in toluene-phenol-diethylene glycol system at 22°C.

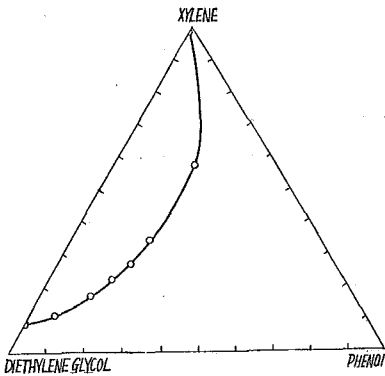


Fig. 26. Equilibrium compositions in xylene-phenol-diethylene glycol system at 25°C.

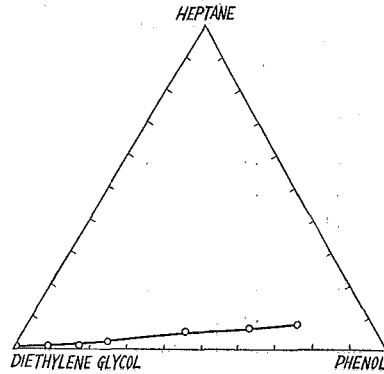


Fig. 27. Equilibrium compositions in heptane-phenol-diethylene glycol system at 20°C.

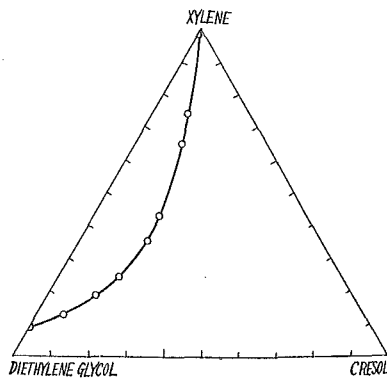


Fig. 28. Equilibrium compositions in xylene-cresol-diethylene glycol system at 16°C.



TABLE 9. Equilibrium Composition

Benzene-Heptane-D.E.G. 10+Phenol 1 System at 20°C						Benzene-Heptane-D.E.G. 10+Phenol 2.71 at 16°C		
Extract % (wt)			Raffinate % (wt)					
Benzene	Heptane	D.E.G. + Ph.	Benzene	Heptane	D.E.G. + Ph.	Benzene	Heptane	D.E.G. + Ph.
9.0	0.5	90.5	15.0	84.0	1.0	0	1.0	99.0
10.0	0.5	89.5	19.8	76.0	4.2	0	99.8	0.2
11.2	0.7	88.1	21.0	75.3	3.7	5.0	1.5	93.5
12.0	1.0	87.0	22.5	74.5	3.0	23.0	75.0	2.0
32.1	1.1	66.8	42.5	54.0	3.5	25.7	4.5	69.8
32.8	1.4	64.8	86.4	8.8	4.8	29.5	4.5	66.0
35.3	1.5	63.2	87.7	7.0	5.3	34.5	6.0	59.5
Benzene-Heptane-D.E.G. 10+Phenol 2 System at 18°C								
Extract % (wt)			Raffinate % (wt)					
Benzene	Heptane	D.E.G. + Ph.	Benzene	Heptane	D.E.G. + Ph.	Benzene	Heptane	D.E.G. + Ph.
10.0	2.0	88.0	15.0	84.0	1.0	42.2	55.5	2.3
11.0	2.0	87.0	21.0	77.0	2.0	43.4	7.1	49.5
11.0	3.5	86.5	23.4	74.0	2.6	52.0	45.0	3.0
11.1	3.9	85.0	30.2	67.5	2.3	62.1	34.8	3.1
31.1	2.3	66.6	42.9	54.5	2.6	71.1	25.8	3.1
32.8	2.0	65.2	73.3	24.0	2.7	80.9	15.6	3.5
36.0	2.0	62.0	91.0	4.0	5.0	82.0	8.0	10.0
						84.0	7.5	8.5
						84.8	11.9	3.3
						85.6	7.9	6.5

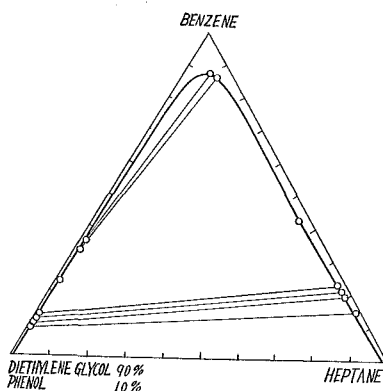


Fig. 29. Equilibrium compositions in benzene-heptane-diethylene glycol 10+phenol 1 system at 18°C.

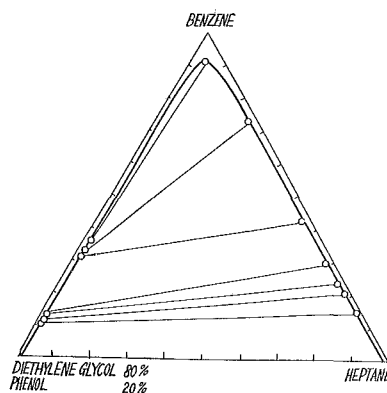


Fig. 30. Equilibrium compositions in benzene-heptane-diethylene glycol 10+phenol 2 system at 18°C.

TABLE 10. Equilibrium Composition

Benzene-Methanol-E.G. System at 21°C			Heptane-Methanol-E.G. System at 22.5°C		
Benzene	Methanol	E.G.	Heptane	Methanol	E.G.
4.8	0	95.2	0.5	0	99.5
6.9	6.0	87.1	0.6	12.4	87.0
9.0	11.4	79.6	1.0	17.4	81.6
11.6	15.6	72.8	1.9	21.8	76.7
14.6	18.9	66.5	2.1	25.7	72.2
16.2	22.0	61.8	2.3	34.6	63.1
18.8	24.3	56.9	4.9	55.9	39.2
28.8	30.0	41.2	5.8	60.3	33.9
36.2	30.1	33.7	7.2	65.3	27.5
57.0	19.0	24.0	9.5	70.8	19.7
74.4	16.7	8.9	14.3	75.1	10.6

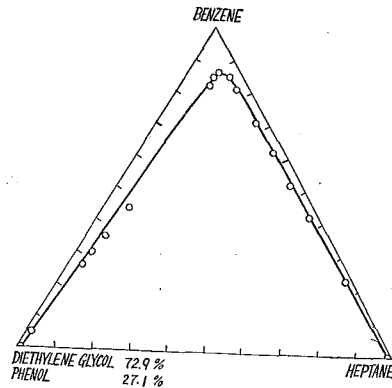


Fig. 31. Equilibrium composition in benzene-heptane-diethylene glycol 10+phenol 2.71 system at 16°C.

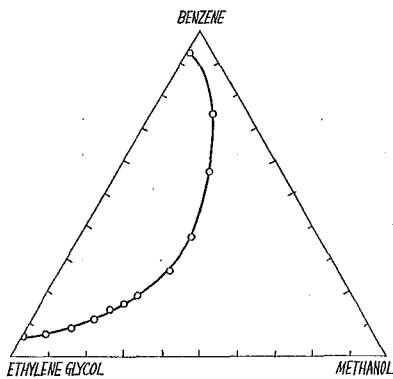


Fig. 32. Equilibrium compositions in benzene-methanol-ethylene glycol system at 20°C.

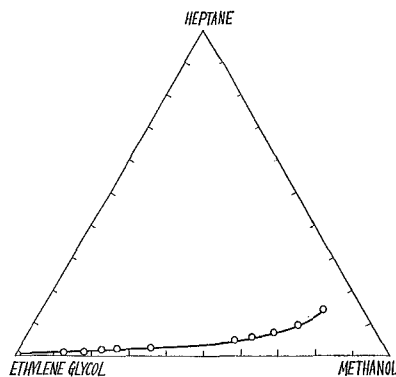


Fig. 33. Equilibrium compositions in heptane-methanol-ethylene glycol system at 22°C.

TABLE 11. Equilibrium Composition

Benzene-Heptane-E.G. 10+Phenol 3 System at 50°C						Benzene-Heptane-E.G. 10+Phenol 5 System at 25°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.
3.3	2.0	94.7	19.2	79.1	1.7	5.7	2.0	92.3	16.1	82.2	1.7
6.0	2.0	92.0	29.2	68.9	1.8	8.8	2.1	89.1	29.6	67.6	2.8
7.1	2.0	90.9	43.0	55.2	1.8	11.6	2.2	86.2	39.2	57.2	3.6
16.1	1.9	82.0	70.0	27.2	2.8	17.9	2.8	79.3	57.2	39.2	3.6
23.0	1.9	75.8	83.0	13.5	3.5	21.2	2.3	86.5	59.2	37.1	3.7
						33.0	2.4	64.6	76.1	16.4	7.5
Benzene-Heptane-E.G. 10+Phenol 3 System at 70°C						Benzene-Heptane-E.G. 10+Phenol 5 System at 50°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.
2.0	1.9	96.1	20.0	78.5	1.5	7.9	2.1	90.0	23.3	74.1	2.6
6.2	1.5	92.3	38.0	60.4	1.6	11.8	3.0	85.2	34.1	63.3	2.6
12.7	1.9	85.3	66.1	31.8	2.1	15.4	3.1	81.5	42.4	53.9	3.8
20.0	2.0	78.0	79.5	17.4	3.1	16.3	4.0	79.7	60.5	34.7	4.8
31.0	2.0	67.0	84.8	8.5	6.7	32.0	4.7	63.3	68.1	27.0	4.9
						42.0	4.5	53.5	77.8	15.0	7.2
						Benzene-Heptane-E.G. 10+Phenol 5 System at 70°C					
Extract % (wt)			Raffinate % (wt)			Extract % (wt)			Raffinate % (wt)		
Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.	Ben- zene	Hept.	E.G.+ Ph.
9.4	2.2	88.4	19.1	78.1	2.7	14.7	2.3	83.0	34.0	62.8	3.2
14.7	2.3	83.0	34.0	62.8	3.2	21.3	1.9	76.8	46.7	50.0	3.3
21.3	1.9	76.8	46.7	50.0	3.3	29.0	2.3	68.7	54.9	42.0	3.1
29.0	2.3	68.7	54.9	42.0	3.1	41.8	3.0	55.2	66.7	26.4	6.9
41.8	3.0	55.2	66.7	26.4	6.9	51.1	3.2	45.7	75.9	14.9	9.2
51.1	3.2	45.7	75.9	14.9	9.2						

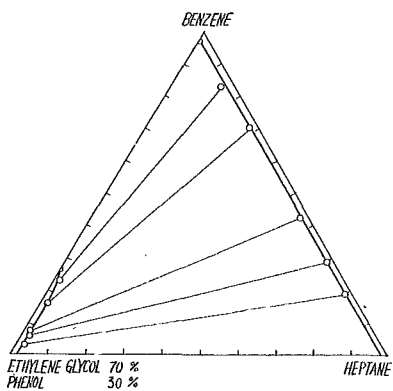


Fig. 34. Equilibrium compositions in benzene-heptane-ethylene glycol 10+phenol 3 system at 50°C.

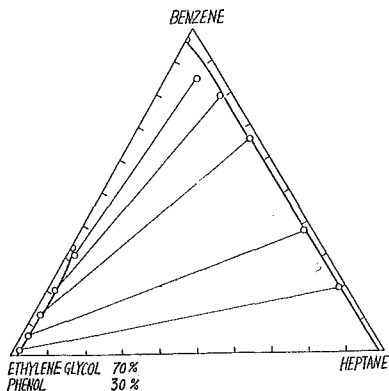


Fig. 35. Equilibrium compositions in benzene-heptane-ethylene glycol 10+phenol 3 system at 70°C.

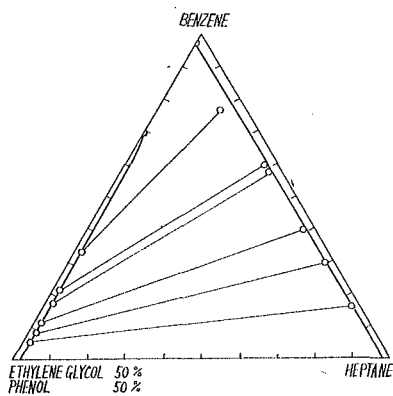


Fig. 36. Equilibrium compositions in benzene-heptane-ethylene glycol 10+phenol 5 system at 25°C.

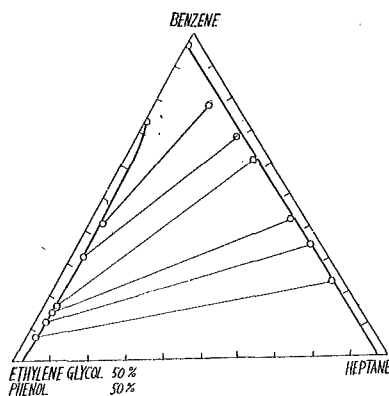


Fig. 37. Equilibrium compositions in benzene-heptane-ethylene glycol 10+phenol 5 system at 25°C.

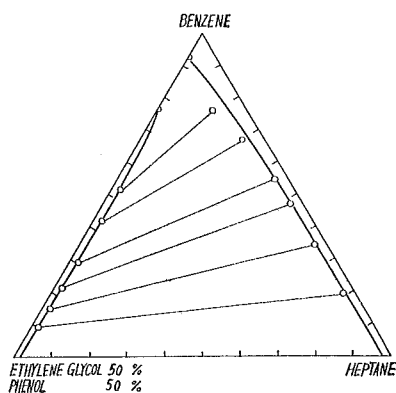


Fig. 38. Equilibrium compositions in benzene-heptane-ethylene glycol 10 + phenol 5 system at 70°C.

When a mixture consisted of D.E.G. or E.G. and methanol would be used at a room temperature, rather better result could be obtained than that of D.E.G. alone at an elevated temperature, as in Fig. 22 and 23. There are some disadvantages in the use of methanol which distills off from the solvent in the stripping process with the aromatics from which methanol has to be washed off with water. The use of phenol has not such disadvantage, and its promoting effect on the solubility of D.E.G. is expected to be better than that of methanol as in Figs. 24–28 as well in Figs. 32–33. As shown in Figs. 3 and 29–31, the selectivity of binary solvent such as D.E.G. and 20% of phenol at a room temperature is better than that of D.E.G. alone at 125°C. Even using E.G. having much less solubility than D.E.G., the result of binary solvent (E.G. + 50% of phenol) is not worse than that of D.E.G. alone at 125°C, as in Figs. 34–38.

Hence it might be possible to say that the use of D.E.G. at an elevated temperature could be replaced with the process using E.G. mixed with phenol.

## II. Extraction by Batch Method

### II.1 Experimental apparatus and procedure

150 ml of a sample composed of the solution and the solvent were put in a glass vessel of which inner diameter and height are 6.0 and 9.0 cm, respectively. The agitation was carried out by an impeller of which diameter was 3.8 cm and width was 0.7 cm, and the height of position in the liquid was two-thirds of the total liquid height from the liquid-surface. The revolving number of impeller was measured with a trochometer connected to the revolving

shaft by a string. After the mixing and the phase-settling, the extract and raffinate were separated to determine their each volume as well composition. The analysis was carried out by the same way as mentioned in Chap. 1.

## II.2 Results

Results obtained by the extraction of benzene with D.E.G. are given in Table 12 where the revolving number of impeller was 210–392 r.p.m. and the solvent-ratio was 1.90.

In Table 13 are there results of the experiments in which the solution of benzene and heptane was extracted with D.E.G. at various solvent-ratios as

TABLE 12. Extraction of Benzene by Diethylene Glycol

No.	1	2	3	4	5	6	7	8	Unit	
D.E.G.	100	100	100	100	100	100	100	100	g.	
Benzene	52.8	61.6	52.8	52.8	52.8	52.8	52.8	51.6 (toluene)	g.	
Solvent Ratio	1.90	1.62	1.90	1.90	1.90	1.90	1.90	1.94	—	
Revolving Number	210	222	240	288	320	344	392	210	r.p.m.	
<i>C</i>	5 min	0.410	0.416	0.413	0.427	0.423	0.439	0.445	0.183	—
	10 "	0.413	0.420	0.414	0.428	0.427	0.442	0.396	0.157	
	30 "	0.416	0.453	0.456	0.459	0.432	0.459	0.417	0.163	
	60 "	0.422	0.459	0.477	0.468	0.436	0.420	0.428	0.165	
	120 "	0.452	0.469	—	—	—	—	—	0.171	
<i>C/C<sub>0</sub></i>	5 min	0.770	0.668	0.782	0.809	0.800	0.830	0.842	0.355	—
	10 "	0.780	0.685	0.785	0.810	0.809	0.837	0.748	0.304	
	30 "	0.789	0.739	0.860	0.868	0.817	0.868	0.788	0.316	
	60 "	0.800	0.746	0.892	0.883	0.825	0.795	0.806	0.320	
	120 "	0.855	0.760	—	—	—	—	—	0.332	
<i>K<sub>ext</sub></i>	5 min	0.4080	0.4170	0.4140	0.4760	0.5200	0.5360	0.5800	0.2440	$\frac{1}{\text{min}}$
	10 "	0.2090	0.2262	0.2110	0.2400	0.2480	0.2790	0.1840	0.1445	
	30 "	0.0715	0.1070	0.1137	0.1223	0.0790	0.1223	0.0720	0.0531	
	60 "	0.0380	0.0626	0.0912	0.0842	0.0353	0.0360	0.0400	0.0290	
	120 "	0.0340	0.0456	—	—	—	—	—	0.0151	

TABLE 13. Extraction of Benzene-Heptane Solution by Diethylene Glycol

No.		11	12	13	14	15	22	24	32	34	42	44	Unit
D.E.G.		100	100	100	100	100	100	100	100	100	100	100	g.
Benzene		44.0	35.2	26.4	17.6	8.8	35.2	17.8	35.2	17.8	35.2	17.8	g.
Heptane		6.8	13.6	20.4	27.2	34.0	13.6	27.2	13.6	27.2	13.6	27.2	g.
Solvent Ratio		2.27	2.84	3.78	5.68	11.35	2.84	5.62	2.84	5.62	2.84	5.62	—
Revolving Number		210	210	210	210	210	240	240	320	320	400	400	r.p.m
<i>C</i>	5 min	0.227	0.161	0.111	0.070	0.026	0.164	0.075	0.166	0.076	0.169	0.076	—
	10 "	0.228	0.164	0.113	0.072	0.033	0.165	0.075	0.169	0.077	0.172	0.082	
	30 "	0.239	0.166	0.114	0.076	0.034	0.169	0.077	0.170	0.080	0.173	0.083	
	60 "	0.244	0.168	0.116	0.082	0.036	0.171	0.082	0.170	0.085	0.174	0.087	
	120 "	0.253	0.173	0.125	0.083	0.036	0.171	0.087	0.171	0.088	0.179	0.089	
	∞	0.258	0.180	0.134	0.089	0.039	0.180	0.089	0.180	0.089	0.180	0.089	
<i>C/C<sub>0</sub></i>	5 min	0.516	0.458	0.420	0.395	0.375	0.468	0.425	0.473	0.438	0.480	0.435	—
	10 "	0.518	0.465	0.427	0.410	0.380	0.470	0.425	0.480	0.440	0.488	0.468	
	30 "	0.544	0.470	0.430	0.430	0.390	0.480	0.435	0.483	0.455	0.490	0.470	
	60 "	0.554	0.478	0.440	0.465	0.410	0.485	0.465	0.483	0.480	0.495	0.490	
	120 "	0.578	0.490	0.473	0.470	0.410	0.485	0.490	0.485	0.500	0.508	0.505	
	∞	0.585	0.510	0.508	0.505	0.440	0.510	0.505	0.510	0.505	0.510	0.505	
<i>K<sub>e</sub>a</i>	5 min	0.0385	0.1520	0.1010	0.1340	0.1730	0.1166	0.1788	0.1200	0.1620	0.1290	0.1620	$\frac{1}{\text{min}}$
	10 "	0.0191	0.0532	0.0520	0.0693	0.0865	0.0588	0.0894	0.0602	0.0810	0.0673	0.1026	
	30 "	0.0069	0.0189	0.0175	0.0270	0.0314	0.0201	0.0279	0.0214	0.0346	0.0228	0.0352	
	60 "	0.0036	0.0127	0.0094	0.0171	0.0188	0.0108	0.0171	0.0107	0.0197	0.0117	0.0220	
	120 "	0.0021	0.0057	0.0055	0.0088	0.0094	0.0050	0.0118	0.0054	0.0115	0.0081	0.0210	
	∞												
<i>C/C<sub>0</sub></i>	5 min	0.875	0.897	0.826	0.783	0.852	0.918	0.841	0.927	0.867	0.941	0.860	—
	10 "	0.878	0.911	0.840	0.812	0.864	0.920	0.841	0.940	0.871	0.956	0.927	
	30 "	0.922	0.921	0.846	0.847	0.886	0.941	0.861	0.946	0.900	0.960	0.930	
	60 "	0.940	0.937	0.866	0.915	0.930	0.950	0.920	0.946	0.950	0.970	0.970	
	120 "	0.980	0.960	0.931	0.925	0.930	0.950	0.970	0.951	0.990	0.994	1.000	
	∞												
<i>b</i> × 10 <sup>3</sup>		1.53	1.52	1.14	1.10	1.31	1.62	1.17	1.79	1.31	1.87	1.38	1/sec
$1 - e^{-bt}$	5 min	0.368	0.368	0.285	0.280	0.338	0.383	0.296	0.415	0.330	0.424	0.338	—
	10 "	0.601	0.601	0.494	0.483	0.546	0.621	0.500	0.656	0.546	0.675	0.564	
	30 "	0.936	0.936	0.871	0.864	0.903	0.940	0.878	0.960	0.903	0.965	0.914	
	60 "	0.995	0.995	0.984	0.982	0.980	0.997	0.985	0.998	0.980	0.998	0.992	
	120 "	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	
	∞												

well as numbers of the agitation. Table 14 gives results when the binary solvents such as D.E.G., and 20 and 28.8% of phenol were used. Connecting to the results in Table 13 some short-time experiments by 120 seconds were carried out as Table 15 shows. From the result described yet, the capacity coefficient was calculated basing upon the two-film theory by the usual way as follows :

1) Extraction of benzene by D.E.G.

$$\frac{dc}{dt} = K_e a (C_0 - C) \quad (1)$$

$$K_e a = \frac{1}{t} \ln \frac{C_0}{C_0 - C} \quad (2)$$

TABLE 14. Extraction of Benzene-Heptane Solution by Diethylene Glycol mixed with Phenol

No.	51	52	Unit
D.E.G.+Phenol	112	112	g.
Phenol Ratio	0.20	0.288	—
Benzene	22.0	26.4	g.
Heptane	17.0	13.6	g.
Solvent Ratio	4.23	5.10	—
Revolving Number	210	210	r.p.m.
<i>C</i>	5 min	0.169	0.256
	10 "	0.171	0.257
	30 "	0.172	0.260
	60 "	0.173	0.263
	120 "	0.175	0.268
<i>C/C<sub>0</sub></i>	5 min	0.689	0.770
	10 "	0.692	0.773
	30 "	0.700	0.790
	60 "	0.706	0.797
	120 "	0.715	0.807
<i>K<sub>e</sub>a</i>	5 min	0.1430	0.2520
	10 "	0.0776	0.1030
	30 "	0.0265	0.0493
	60 "	0.0135	0.0253
	120 "	0.0071	0.0152



TABLE 15. Result of Extraction of Benzene-Heptane Solution with Diethylene Glycol by 120 Seconds

No.	11 S	12 S	13 S	14 S	15 S	Unit
D.E.G.	100	100	100	100	100	g.
Benzene	44.0	35.2	26.4	17.6	8.8	g.
Heptane	6.8	13.6	20.4	27.2	34.0	g.
Solvent Ratio	2.27	2.84	3.79	5.68	11.35	—
Revolving Number	210	210	210	210	210	r.p.m.
<i>C</i>	10 sec	0.186	0.087	0.044	0.018	0.004
	30 "	0.211	0.115	0.079	0.045	0.012
	60 "	0.225	0.148	0.092	0.058	0.016
	120 "	0.229	0.157	0.101	0.060	0.027
<i>C/C<sub>0</sub></i>	10 sec	0.424	0.247	0.167	0.104	0.046
	30 "	0.482	0.328	0.299	0.255	0.135
	60 "	0.514	0.422	0.349	0.332	0.204
	120 "	0.521	0.448	0.383	0.396	0.305

The equilibrium value  $C_0$  was determined as 0.471. As an example a few series of  $K_a a$  were calculated as shown in Table 12 and in Fig. 39; the value of capacity coefficient is not of constance but evidently decreases as the time passes, where the slope seems almost of unit.

2) Extraction of benzene-heptane solution by D.E.G.

Assuming that heptane does not dissolve in to D.E.G., the calculation was carried out by Eq. (3) considering the distribution coefficient.

$$K_a a = \frac{-1}{(m\phi + 1)t} \ln \left\{ \frac{mC_0 - (m\phi + 1)C}{mC_0} \right\} \quad (3)$$

The distribution coefficient was determined as 0.294, and the value of capacity coefficient is denoted in Table 13. An example of the same number of agitation is illustrated in Fig. 40, where the same inclination of  $K_a a$  is recognized as in case of benzene alone: the value decreases in an inverse proportion to the time. These results are not of concord with those given by Yates and Watson.<sup>3)</sup>

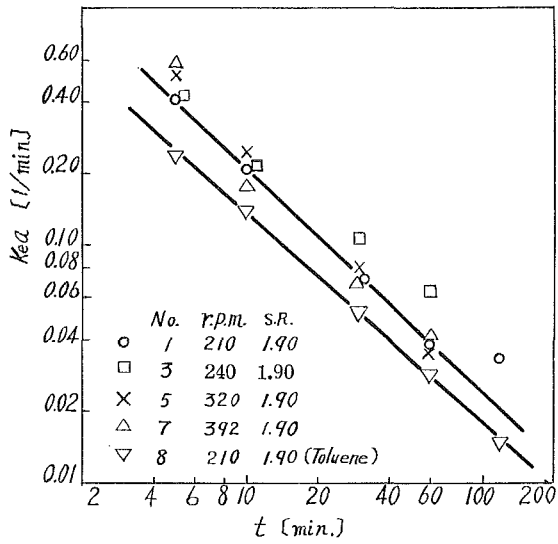


Fig. 39. Capacity coefficients in benzene-diethylene glycol system.

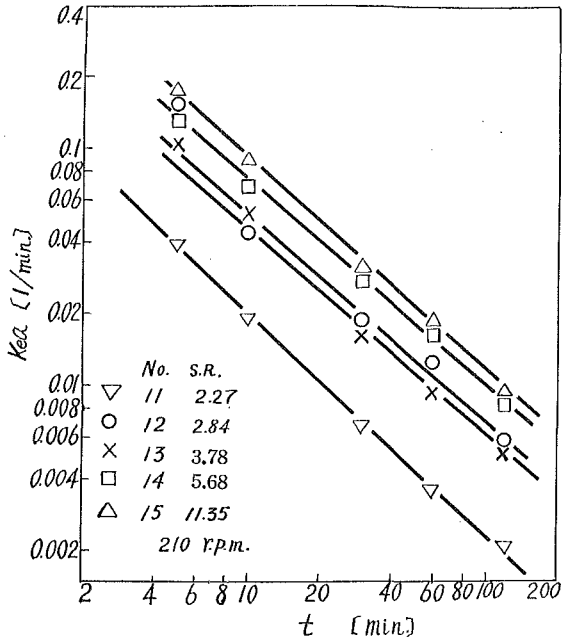


Fig. 40. Capacity coefficients in benzene-heptane-diethylene glycol system.

3) Extraction of benzene-heptane solution by D.E.G. mixed with phenol.

The calculation was carried out on the same way by Eq. (3). The distribution coefficient of benzene between heptane and D.E.G. mixed with 20 and 28.8% of phenol was 0.396 and 0.472, respectively. The value calculated is given in Table 14 and Fig. 41 where the same inclination is observed, and it is considerably higher than that obtained by D.E.G. alone as in Fig. 40.

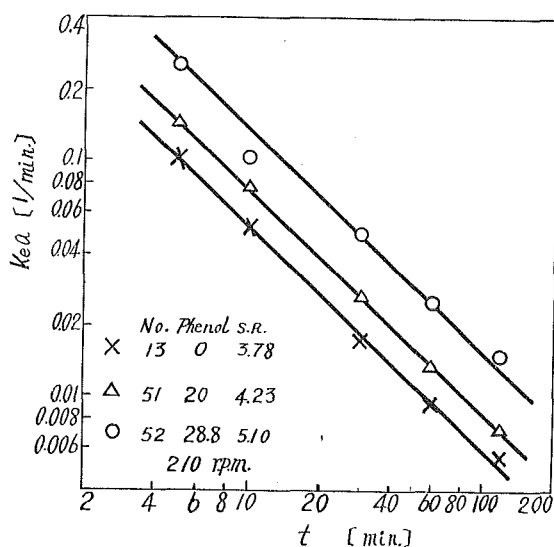


Fig. 41. Capacity coefficients in benzene-heptane-diethylene glycol+phenol system.

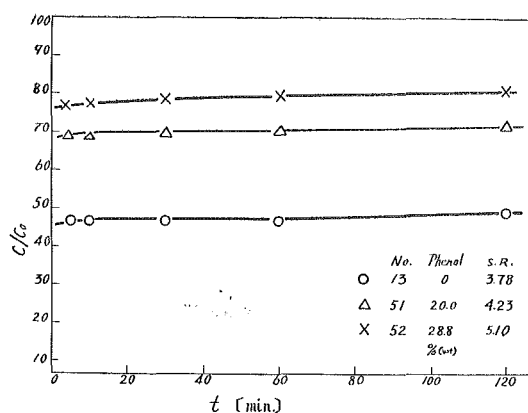


Fig. 42. Rate of extraction in benzene-heptane-diethylene glycol+phenol system.

It means that the extractive power of binary solvent is remarkably superior to that of D.E.G. alone as shown in Fig. 42.

### II.3 Kinetics of Extraction

The amount extracted from the solution increases rapidly during about two minutes passing from the beginning, and then becomes gradually slow as approaching asymptotically a constant value which is of equilibrium; the effect of extractive time upon the amount immensely appears on the initial term as in Fig. 43. The same inclination was observed on the result where the

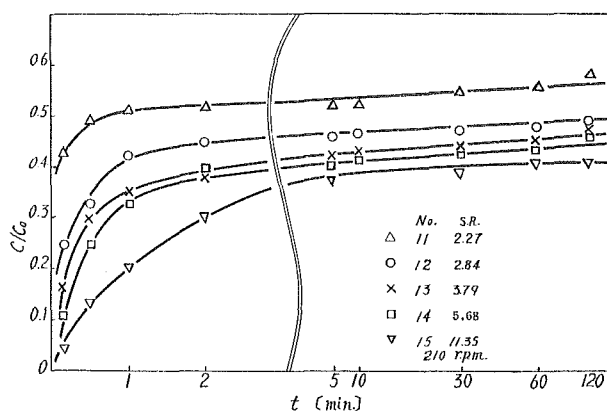


Fig. 43. Rate of extraction in benzene-heptane-diethylene glycol system.

benzene-D.E.G. system was researched. In that case as shown in Fig. 39, the capacity coefficient based upon the film theory is considerably higher than that of benzene-heptane-D.E.G. system, but not immense. It would be possible therefore that an existence of a film enveloping the drop such as one in the film theory is to be assumed. There is, however, still a problem concerning that the capacity coefficient is not constant, but inversely proportional to the time. Even when Hatta's Eq.  $(C/C_0 = 1 - e^{-\frac{3K_e t}{a}})^{4)}$  was applied to the results, it was impossible to find a constancy of  $K_e a$ . Besides that  $K_e a$  calculated by Higbie's Eq.  $(N_m = 2\sqrt{D/\pi t} \cdot C_i)^{5)}$  was not in an inverse proportion to the root of time, as expected from Fig. 37. It is well known that the diffusion coefficient depends upon concentrations of solutions, especially of concentrated solutions. Consequently the capacity coefficient would be changed with a variation of the diffusion coefficient which is to be caused by a concentrating of the extract accompanied with a progress of the procedure. In Table 13 it is of evidence that  $K_e a$  increases with the increase of solvent ratio where the

ratio of solvent to the solution was constant. This fact may be an example of what  $K_e$  was relatively high because of the higher value of the diffusion coefficient due to the smaller quantity of solute in the solvent. In the application of Higbie's equation it is also imagined that the capacity coefficient decreased with a decrease of the diffusion coefficient owing to the enrichment of solute in the solvent. The diffusion coefficient of benzene in D.E.G. is not exactly known yet. Therefore the dependence on the concentration also is not of evidence. To know roughly an order of that dependence, some ratios of the diffusion coefficient of the saturated solution to that of some diluent ones were calculated by Van Laar's method<sup>9)</sup>; the value of saturated solution was estimated as about 70% of that of a dilute solution.

As a reason for the decrease of capacity coefficient with the extractive time, it should be kept in mind that the total contact-surface of two phases diminishes as a diameter of the drop become smaller with a decrease of the solute in the drop. The two factors which have some affects on the decrease of capacity coefficient seem not be the one as giving a fundamental solution on that decrease.

Newman<sup>7)</sup> presented a solution concerning the extraction of unsteady state conditions. In this solution the drop of dispersed liquid was considered as a rigid sphere in which there are not any flows.

For the basic equation

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} \right) \quad (4)$$

following boundary conditions are given.

$$\text{at } t = 0 \quad C = 0$$

$$\text{at } x = a \quad C = C_g$$

The solution is obtained as follows :

$$\frac{C}{C_g} = 1 + \frac{2a}{\pi x} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} e^{-\frac{n^2 \pi^2 D t}{a^2}} \sin \frac{n \pi x}{a} \quad (5)$$

When an average concentration of solute in drops is applied to Eq. (5), a following equation is derived.

$$E = \frac{C_g - C}{C_g - C_0} = 1 - \frac{C}{C_g} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\frac{n^2 \pi^2 D t}{a^2}} \quad (6)$$

The value of  $C/C_g$  obtained by this experiment is denoted in Table 12. According to Newman's principle a following equation was made; this is of an approximate one neglecting the terms of Eq (6) in which  $n$  is more than two.

$$\frac{C}{C_0} = 1 - e^{-bt} \quad (7)$$

This is also of the same form as Hatta's equation, but  $b$  as an exponential number has different contents from those in Hatta's equation.

The values of  $b$  obtained approximately from the results are given in the lowest line of Table 12, and the curves drawn from this equation are shown in Figs. 44-47. The concordance between the experimental values and calculated ones becomes better with the increase of agitation speed, but generally is not good during the initial term. The neglect of terms such as  $n$  is more than two which affect the result the more, the less is the passing time, might be a reason of such worse concords. Besides it is also considered as the reason that the concentration of outer zone of the drop was not as zero as assumed in Newman's equation.

As being evident in comparing Eq. (6) with Eq. (7), the value of  $b$  is to be proportional to  $D/a^2$ . Langlois<sup>9)</sup> suggested that the drop diameter of dispersed phase is in an inverse proportion to  $N^{1.2}$  which is r.p.m. of an impeller.

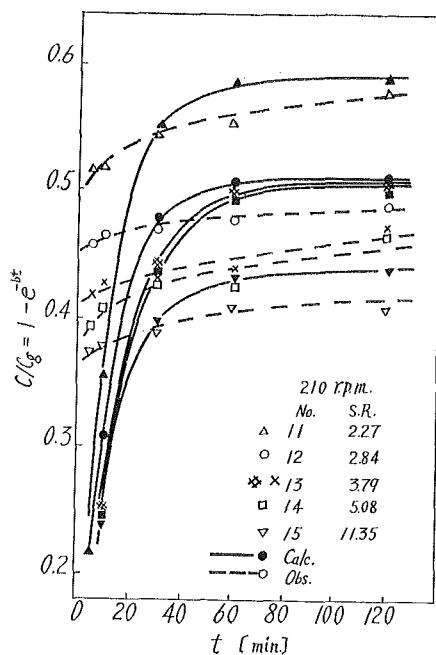


Fig. 44. Extraction coefficients in benzene-heptane-diethylene glycol system. (1)

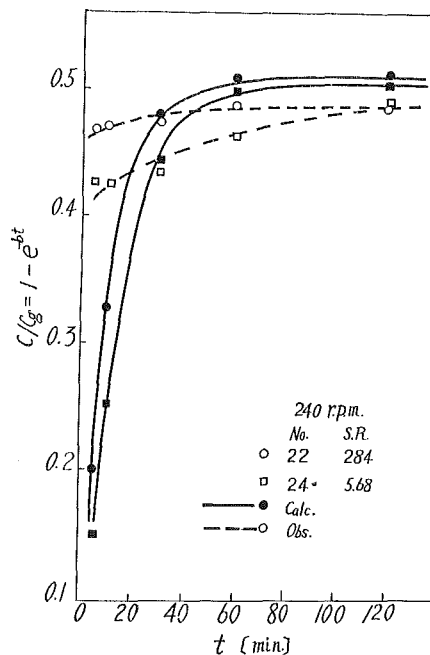


Fig. 45. Extraction coefficients in benzene-heptane-diethylene glycol system. (2)

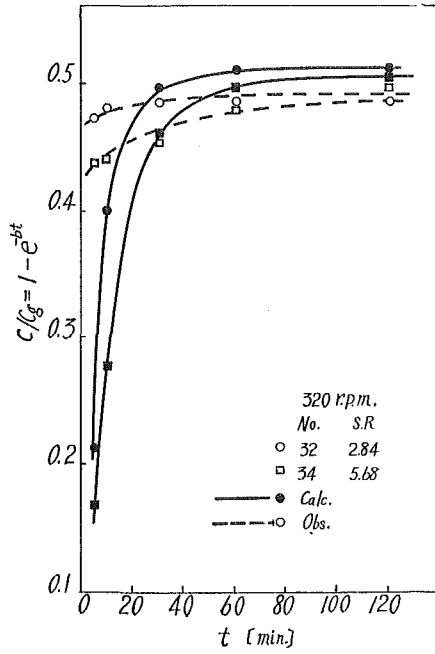


Fig. 46. Extraction coefficients in benzene-heptane-diethylene glycol system. (3)

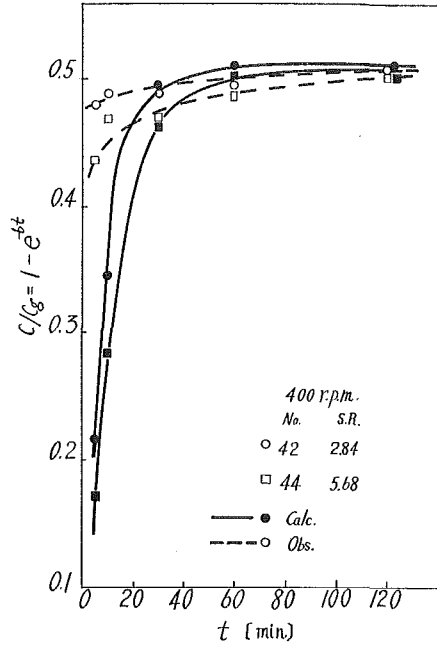


Fig. 47. Extraction coefficients in benzene-heptane-diethylene glycol system. (4)

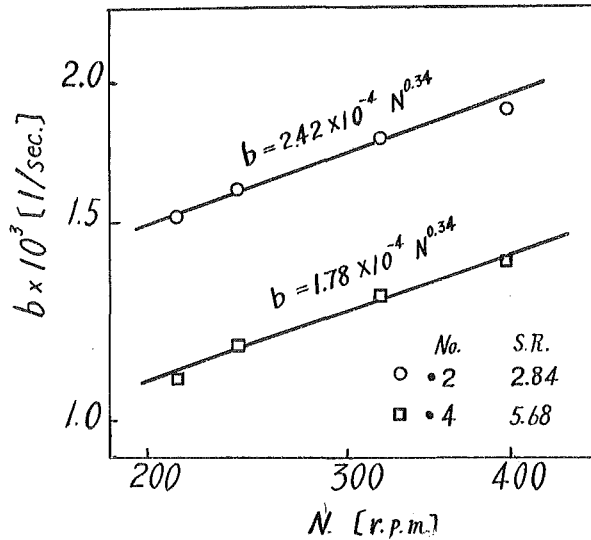


Fig. 48. Effect of revolving number of agitator on exponential coefficient  $b$ .

Therefore  $b$  is to be proportional to  $N^{2.4}$ . The relation of  $b$  to  $N$  is illustrated in Fig. 48 where the solvent ratios are 2.84 and 5.63, respectively. In these results  $b$  is determined as being proportional to  $N^{0.34}$  of which the exponential value is approximately one seventh of that expected from Langlois equation. This difference also might show that Newman's equation does not perfectly solve the mechanism of liquid-liquid extraction, and some resistances in an outside of the drop for the transfer of solute have to be put in the consideration to solve this problem.

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#### Symbols Used

- $a$  = drop radius (cm).
- $b$  = coefficient used in Eq. (7).
- $C$  = concentration of solute in solvent at time  $t$  (g/g).
- $C_o$  = equilibrium concentration of solute in solvent.
- $C_x$  = concentration of solute at equilibrium with solution at  $x=0$ .
- $C_0$  = concentration of solute in solvent at  $t=0$ .
- $D$  = diffusion coefficient of solute in solvent (cm<sup>2</sup>/sec).
- $E$  = extraction coefficient.
- $K_e a$  = capacity coefficient (l/min).
- $K_e$  = mass transfer coefficient (cm/min).
- $m$  = distribution coefficient of solute between solvent and solution.
- $N$  = revolving number of impeller (r.p.m.).
- $n$  = integral number.
- $t$  = time (min).
- $x$  = distance from drop-surface.
- $\Phi$  = ratio of solvent to diluent in solution.

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