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INVESTIGATION OF THE
OCTENE-DECANE-UREA ADDUCT
EQUILIBRIUM SYSTEM

BY

FREDERICK C. GUEST

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

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ABSTRACT

Experimental studies pertaining to urea adduct formed from octene-1 and from mixtures of octene-1 and n decane have been carried out using methanol as a solvent.

Concentrations of equilibrium mixtures formed by adding increments of octene to a solution of urea in methanol to form adduct are reported.

Calorimetric studies indicate that the addition of octene to a urea-methanol solution shows an endothermic heat effect prior to the formation of solid adduct. The heat effect becomes exothermic as solid adduct is formed.

Addition of decane to an equilibrium octene-urea adduct system increased octene concentration in the supernatent liquid, indicating an octene release from the original adduct as decane adduct was formed.

The order in which decane and octene were added to form the decane-octene-urea adduct system was shown to influence the final equilibrium concentration of the adduct and its supernatent liquid.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING
NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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INTRODUCTION

Since the early 1940's it has been known that urea, when mixed with long straight chain organic compounds, forms crystalline addition complexes, or "adducts". The phenomenon does not occur with branched or aromatic compounds. This shape selectivity has found commercial application in removing straight hydrocarbons from hydrocarbon mixtures (1).

Considerable information has appeared in the literature regarding urea adduct formation. X-ray studies of the adducts have revealed that the adducts contain "tunnels" formed by hexagonal prisms of urea, the hydrocarbons being resident in the tunnels (2). It has been postulated that van der Waal's forces hold the hydrocarbon. The hexagonal orientation differs from the tetragonal structure of normal urea crystals. The diameter of the urea "tunnel" has been determined at 5 to 5.25 Angstrom units. It has been found that the limiting cross-sectional diameter of a potential adduct-former must be less than 5.25 A° before urea-adduct

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1. Bailey, W. A. Jr., Bannerot, R. A., Fetterly, L. C., and Smith, A. G., Ind. Eng. Chem., 43, 2125-2129 (1951).

2. Kobe, K. A., and Domask, W. J., Petroleum Refiner, 31, 106-113, (1952)

formation can take place. This requirement is waived, however, when the branching or aromatic radical is formed at the end of a long straight-chain hydrocarbon, in which case the straight end of the molecule enters the urea tunnel. Adduct formation is greatly accelerated in the presence of an activator, eg., methanol, the apparent function of which is to provide a medium for contacting the reactants. Some articles have appeared stressing the physical nature of the adduct, others stressing the chemical. Kobe and Domask (3) point out that, unlike chemical compounds, the partners in urea adducts are not united in whole numbered ratios except in a few instances, by chance. They also point out that the type of molecule which can be entrapped is determined by volume considerations and not by chemical nature, indicating a physical phenomenon rather than a chemical interaction. Redlich, et al (4) have found that the "reaction"

$$\text{complex} = \text{reactant} + \text{m urea}$$

fits the equilibrium constant concept, and have published considerable data giving equilibrium constants as a function of temperature for a variety of adduct reactions. Kobe and

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3. *Ibid*.

4. Redlich, O., Gable, C.M., Beason, L.R., and Millar, R.W., *J. Am. Chem. Soc.*, *72*, 4153-62, (1950)

Domask(5) have used the Clausius-Clapeyron equation to calculate the heat of dissociation for adducts. The calculated heats agree well with experimentally determined values. Thus, the literature suggests that urea adducts constitute a physical entrapment of a hydrocarbon inside a distorted (hexagonal instead of the normal tetragonal) urea lattice, the entrapping forces being van der Waal. The adduct has been found to obey some of the classical laws of chemistry.

When the reaction is carried out in a solvent medium the rate of crystalline adduct formation is accelerated. The possibility of adduct formation in the liquid state prior to precipitation has received some attention in the literature. Zimmerschied, et al,(6) has postulated the following equilibrium system:

$$\text{Urea}_{(\text{solid})} \rightleftharpoons \text{Urea}_{(\text{dissolved})}$$

$$^{n}\text{Paraffin}_{(\text{liquid})} \rightleftharpoons {}^{n}\text{Paraffin}_{(\text{dissolved})}$$

$$\text{Urea}_{(\text{dissolved})} \quad {}^{n}\text{Paraffin}_{(\text{dissolved})} \rightleftharpoons \text{Adduct}_{(\text{dissolved})}$$

$$\text{Adduct}_{(\text{dissolved})} \rightleftharpoons \text{Adduct}_{(\text{solid})}$$

This system clearly recognizes the existance of a dissolved adduct reaction product. Kobe and Domask(7) have shown that water-insoluble adduct formers, such as cetane

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5. Kobe, K.A., op. cit.

6. Zimmerschied, W.J., Higlez, W.S., and Lien, A.P., The Pet. Engr., Ref. Ann., C-44 (1950).

7. Kobe, K.A., op. cit.

and stearic acid, are made soluble by the presence of urea. Moreover, they found that:

$$1 \text{ Urea} + 34 \text{ n-butyric acid} \longrightarrow 1 \text{ Urea in solution} + 95 \text{ cal} \qquad \text{(Equ. 1)}$$

$$1 \text{ Urea} + 34 \text{ isobutyric acid} \longrightarrow 1 \text{ Urea in solution} - 137 \text{ cal} \qquad \text{(Equ. 2)}$$

The solution of urea is normally an endothermic process, as in Equ. 2. Since heat is evolved in Equ. 1, there is evidence of some interaction in the liquid phase.

In light of the above background information, this thesis was undertaken to further explore the behavior of urea adducts. Investigations were along four lines:

(1) Increments of octene were added to a methanol-urea-octene system to determine whether the adduct formation reaction follows an equilibrium relationship. The equilibrium adduct and supernatent liquid concentrations were subsequently determined.

(2) The heat effect of the adduct reaction both prior and subsequent to the formation of crystals was investigated calorimetrically, to gain some insight into the possibility of a dissolved adduct reaction product.

(3) Decane was added to an equilibrium system consisting of dissolved urea, methanol, octene, and solid octene-urea adduct, to determine whether a release of octene from the adduct would take place.

(4) A system consisting of octene, decane, methanol, dissolved urea, and solid adduct was formed by adding decane to the equilibrium octene-methanol-urea system. Identical amounts of the same reactants were used to form a second system, in which the octene was added to the equilibrium decane-methanol-urea system. Analyses of the two final equilibrium systems thus revealed the effect which the order of reactant addition had on final equilibrium composition.

EXPERIMENTAL

Adduct Formation

A solution of urea in methanol was charged to a flask fitted with a variable speed stirrer and immersed in a constant temperature bath held at 25° C.

Octene was added to the mixture in increments. After several increments were added, solid adduct began to form. The liquid phase of the mixture was sampled after each incremental addition, sufficient time (several days) being allowed for attainment of equilibrium before samples were taken. The samples, containing octene, methanol, dissolved urea, and possibly dissolved adduct, were distilled to separate the octene and methanol from the dissolved urea. The resultant distillates contained all of the methanol and octene in the original samples, including octene contained in whatever dissolved adduct there may have been. The solid urea remaining in the distillation flask was dissolved in water. The solution was inspected for presence of an "oil slick" indicating incomplete removal of octene in the distillation. No slick was observed.

The percentages of octene and of methanol in the distillates were determined from a refractive index correlation developed experimentally for that purpose (see Table 10). This data was then used to calculate the solid and liquid compositions of the equilibrium mixtures. The calculation method is detailed in the appendix.

Results of the adduct formation experiments are shown in Table 1. It was observed that:

> Precipitate that formed at lower octene concentrations dissolved upon stirring. Lasting precipitate did not form until octene and urea concentrations reached about 6 and 14 percent respectively.
>
> Solutions in equilibrium with solid adduct showed lesser amounts of octene than present in the total mixture.
>
> Part of each octene addition remained in solution, while part reacted with urea to form adduct.
>
> The reaction did not progress to "completion". That is, neither the octene nor urea were totally consumed.
>
> The solubility limit of octene was exceeded at a lower concentration than the solubility limit of a binary octene-methanol solution. The available urea was not exhausted at this point.

The significance of the above observations is discussed under "Discussion and Conclusions". For the sake of continuity it will suffice to mention here that the observations suggest "some" intermediate step/steps taking place in the liquid phase prior to solid adduct formation. To investigate this calorimetric investigations were undertaken.

ADDUCT FORMATION - REACTION DATA AND OBSERVATIONS - TABLE 1

	EQUIL.LIQUID		EQUIL.LIQUID		TOT.SOLID&LIQUID		SAMPLE	COMMENTS
	WT.%	MOL.%	GRAMS	MOLES	GRAMS	MOLES	GRAMS	
OCTENE	0.83	0.23	2.2568	0.0201	2.2568	0.0201	0.0703	No ppt.
UREA	15.68	8.03	42.64	0.708	42.64	0.708	1.3280	
METHANOL	83.49	91.74	227.18	7.08	227.18	7.08	7.0760	
			OCTENE ADDED 4.1659 gm.					
OCTENE	2.39	0.74	6.3524	0.0566	6.3524	0.0566	0.2024	PPt.formed locally; dissolved upon stirring
UREA	15.43	9.06	41.31	0.689	41.31	0.689	1.1554	
METHANOL	82.22	90.20	220.10	6.86	220.10	6.86	7.0797	
			OCTENE ADDED 6.8704 gm.					
OCTENE	4.89	1.56	13.0204	0.1160	13.0204	0.1160	0.4091	Ppt.formed locally; dissolved upon stirring
UREA	15.08	9.00	40.15	0.6690	40.15	0.6690	1.2616	
METHANOL	80.03	89.44	213.02	6.64	213.02	6.64	6.6934	
			OCTENE ADDED 4.2601 gm.					
OCTENE	6.30	2.02	16.3510	0.1455	16.8714	0.1500	0.5179	Ppt.deposited at top of flask due to violent stirring. When ppt. was immersed in solution it did not dissolve.
UREA	14.29	8.58	37.12	0.618	38.89	0.648	1.1758	
METHANOL	79.41	89.40	206.33	6.43	206.33	6.43	6.5361	
			OCTENE ADDED 1.4388 gm.					

NOTE: Malfunction of the thermostat on the constant temperature bath resulted in excessive heating of the reaction mixture. A new mixture was made up at this point.

	EQUIL.LIQUID		EQUIL.LIQUID		TOT.SOLID&LIQUID		SAMPLE	COMMENTS
	WT.%	MOL.%	GRAMS	MOLES	GRAMS	MOLES	GRAMS	
OCTENE	7.30	2.37	21.202	0.189	21.7758	0.1941	0.5119	Permanent ppt.
UREA	14.10	8.53	40.96	0.682	42.91	0.715	0.9889	
METHANOL	78.60	89.10	228.14	7.13	228.14	7.11	5.5087	
			OCTENE ADDED 5.7631 gm.					
OCTENE	8.80	2.85	24.8411	0.221	27.0270	0.241	0.5959	Permanent ppt.
UREA	12.22	7.42	34.49	0.575	41.92	0.698	0.8274	
METHANOL	78.98	89.73	222.63	6.95	222.63	6.94	5.3408	
			OCTENE ADDED 5.7925 gm.					

ADDUCT FORMATION - REACTION DATA AND OBSERVATIONS - TABLE 1 (CONT'D.)

	EQUIL.LIQUID		EQUIL.LIQUID		TOT.SOLID&LIQUID		SAMPLE	COMMENTS
	WT.%	MOL.%	GRAMS	MOLES	GRAMS	MOLES	GRAMS	
OCTENE	10.58	3.47	29.5145	0.263	32.2236	0.287	0.8311	Permanent ppt.
UREA	11.43	7.00	31.88	0.532	41.09	0.683	0.8977	
METHANOL	77.99	89.53	217.29	6.79	217.29	6.79	6.1192	

OCTENE ADDED 5.5998 gm.

	EQUIL.LIQUID		EQUIL.LIQUID		TOT.SOLID&LIQUID		SAMPLE	COMMENTS
	WT.%	MOL.%	GRAMS	MOLES	GRAMS	MOLES	GRAMS	
OCTENE	12.35	4.07	33.6689	0.301	36.9923	0.330	0.8566	Permanent ppt.
UREA	10.60	6.50	28.89	0.481	40.19	0.669	0.7350	
METHANOL	77.05	89.43	211.17	6.61	211.17	6.61	5.3728	

OCTENE ADDED 16.1036 gm.

NOTE: Addition of the 16.1036 gm. octene resulted in the formation of two liquid layers. The overall solid-liquid analysis was:

Octene	18.1 wt.%
Urea	13.4 wt.%
Methanol	68.5 wt.%

Binary mixture of methanol and octene soluble at 50% octene.

Calorimetric Investigations

A twin calorimeter consisting of two Dewar flasks suspended inside of a copper submarine box was built. Access to the Dewar flasks was provided by two open stacks fastened to flanges above the Dewars (see Figure 1). Initially, openings for admitting agitators, a heater, and thermocouple to the Dewars were drilled in the flanges. However, leakage problems necessitated sealing these openings. The calorimeter was consequently used as a qualitative rather than quantitative instrument. Thermocouples were introduced via the open stacks. The calorimeter was built in a similar fashion to the one built by Konrad (1).

The assembled calorimeter was submerged in a water bath at room temperature. The basic concept of using one of the Dewars as a reactor and one as a blank was followed; that is, all additions of reactants to the "reactor" Dewar were paralleled by additions of water to the "blank" Dewar. By comparing temperature changes in the reactor to temperature changes in the blank, the effect of extraneous temperature changes, such as minor fluctuations in bath temperature could be backed out.

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1. Konrad, F.M., Thesis-Department of Chemical Engineering, Newark College of Engineering, 1955

Three heat effects were investigated:

(1) The heat of mixing for methanol-octene solutions.

(2) The heat of reaction for a methanol-urea-octene system where reactant concentrations were kept below those required for solid adduct formation.

(3) The heat of reaction for a methanol-urea-octene system where solid adduct was formed.

For each of the three systems, a charge of reactant and a corresponding charge of water were initially added to the Dewars. At least 12 hours were allowed for thermal equilibrium to be attained, during which time the water bath was agitated intermittently. Further reactants and the parallel amounts of water were subsequently added via hypodermic syringes which had been charged and positioned inside of the "stacks". The charged syringes were kept inside of the stacks for at least 12 hours prior to injection to eliminate temperature differences between the contents of the Dewars and the contents of the syringes. Temperature of the reactor and blank Dewars were recorded simultaneously at time intervals before and after the syringes were injected.

Results of the calorimeter work are presented on Table 2. It was observed that:

The heat of mixing for octene and methanol in the concentration range of 6.7 to 13.3 wt.% octene is endothermic.

The addition of octene to a methanol-urea system in overall concentrations of 4% octene, 15% urea, 81% methanol results in an endothermic heat effect about 4 times as great as observed from the octene-methanol heat of mixing data. No precipitate was formed at these concentrations.

The addition of octene to a methanol-urea-octene system in sufficient quantity to produce a very small quantity of precipitate results in an almost negligible endothermic heat effect. Addition of a further increment of octene results in a significant exothermic heat effect.

CALORIMETER DATA TABLE 2

I. HEAT OF MIXING - METHANOL AND OCTENE

	TIME	EMF-MV REACTOR	EMF-MV BLANK	CONTENTS OF: REACTOR(BEFORE)	CONTENTS OF: SYRINGE		
	11:30	0.855	0.885				
	11:40	SYRINGES	EMPTIED	272.62 gm.		METHANOL	
	11:45	0.852	0.882		19.17	OCTENE	
RUN	11:55	0.850	0.881				
R-1	12:10	0.848	0.881				
	12:20	0.848	0.881				
	12:35	0.847	0.881				
	12:50	0.847	0.881				
		-0.008	-0.004				
	7:10	0.876	0.875				
	7:15	0.876	0.873				
	7:25	0.876	0.873				
RUN	7:27	SYRINGES	EMPTIED				
R-2	7:32	0.871	0.872	272.62		METHANOL	
	7:40	0.868	0.871	19.17	22.58	OCTENE	
	7:47	0.867	0.872				
	7:57	0.867	0.872				
	8:07	0.867	0.872				
		-0.009	-0.003				

II. METHANOL, UREA AND OCTENE BELOW ADDUCT - FORMING CONCENTRATIONS

	TIME	EMF-MV REACTOR	EMF-MV BLANK	CONTENTS OF: REACTOR(BEFORE)	CONTENTS OF: SYRINGE		COMMENTS
	6:30	0.910	0.876				
	6:40	0.910	0.876	199.61 gm.		METHANOL	No ppt in
RUN	6:50	0.910	0.876	36.93		UREA	Reactor
R-4	6:52	SYRINGES	EMPTIED		10.06		
	6:56	0.902	0.877				
	7:03	0.899	0.877				
	7:12	0.875	0.877				
		-0.035	-0.001				
	6:35	0.875	0.866				
	6:40	0.875	0.866				
	6:46	SYRINGES	EMPTIED				
RUN	6:50	0.873	0.867	200.02		METHANOL	
R-6	7:00	0.870	0.868	37.22		UREA	No ppt in
	7:10	0.840	0.866		10.99	OCTENE	Reactor
	7:20	0.835	0.866				
	7:25	0.834	0.866				
	7:30	0.835	0.866				
		-0.040	-0.000				

CALORIMETER DATA TABLE 2 (CONT'D.)

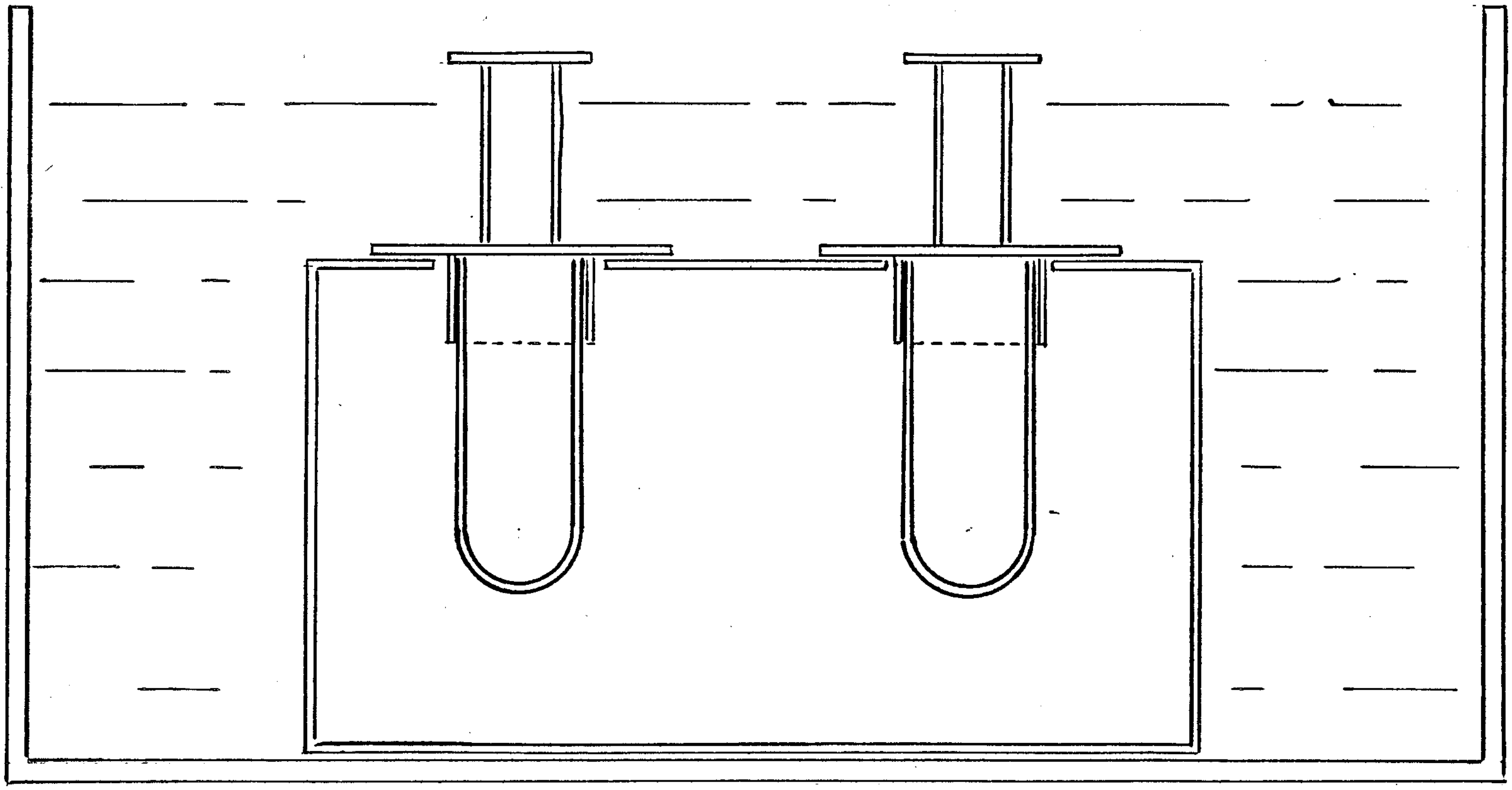
III. METHANOL, UREA AND OCTENE - ABOVE ADDUCT-FORMING CONCENTRATIONS

	TIME	EMF-MV REACTOR	EMF-MV BLANK	CONTENTS OF: REACTOR (BEFORE)	CONTENTS OF: SYRINGE		COMMENTS
	6:30	0.872	0.872				
	6:40	0.869	0.870	199.45 gm.		METHANOL	
	6:45	0.869	0.871	37.17		UREA	Permanent
RUN	6:47	SYRINGES	EMPTIED		15.53	OCTENE	ppt in
R-3	6:50	0.863	0.871				reactor
	7:00	0.869	0.871				
	7:10	0.870	0.871				
	7:20	0.870	0.871				
	7:25	0.870	0.871				
		-0.002	-0.001				
	7:15	0.900	0.894	199.61		METHANOL	
RUN	7:25	0.900	0.894	36.93		UREA	Permanent
R-5	7:45	0.918	0.893	10.06	9.99	OCTENE	ppt in
	7:53	0.919	0.892				reactor
		-0.019	-0.002				

Thermocouples were iron-constantan

Potentiometer - Leeds & Northrup,
Model #8662

TWIN CALORIMETER FIGURE 1



Decane-Octene Replacement Study

The experimental work described in this section examines the effect of adding decane to an equilibrium system consisting of octene, methanol, dissolved urea, solid adduct, and intermediates, if any.

A charge of methanol and urea was added to a stirred flask immersed in a constant temperature bath at 25° C. After the urea dissolved, octene was added in sufficient quantity to produce solid adduct. The equilibrium liquid was sampled, distilled for removal of dissolved urea, and analysed using a chromatograph (sample E-1). Decane was added to the equilibrium mixture, and the resultant equilibrium liquid was sampled, distilled and analysed (sample E-2). The results are shown in Table 3. The calculation method used to determine adduct and equilibrium liquid compositions from the chromatographic analyses is detailed in the appendix.

From the data it was observed that:

The octene/methanol ratio is higher for sample E-2 (decane added) than for sample E-1 indicating that addition of decane resulted in an increase in the amount of octene in solution.

There was free urea available for reaction with decane.

The increase in the amount of octene in solution is greater than if all of the <u>reacted</u> decane replaced octene in octene-urea adduct, based on adduct compositions given in the literature (see Table 5).

DECANE-OCTENE REPLACEMENT TABLE 3

CHROMATOGRAPHIC ANALYSES

SAMPLE E-1

RUN #	METHANOL	OCTENE	OCT/METH
1	93.45	6.55	0.0700/1
2	93.45	6.55	0.0700/1
3	93.38	6.62	0.0713/1
4	93.60	6.40	0.0685/1
AVG.	93.47	6.53	0.0700/1

SAMPLE E-2

RUN #	METHANOL	OCTENE	DECANE	OCT/METH
1	89.10	6.73	4.17	0.0755/1
2	90.94	7.32	1.74	0.0805/1
3	91.38	6.59	2.03	0.0718/1
AVG.	90.50	6.85	2.65	0.0760/1

DECANE-OCTENE REPLACEMENT TABLE 4

INTERMEDIATE RESULTS

COMPONENT	INITIAL CHARGE -GM-	EQUIL.LIQUID UREA-FREE ANALYSIS (Sample E-1) WT.%	TOTAL SAMPLE CONTENT-GMS.	EQUIL.MIXTURE AFTER SAMPLE SOLID & LIQUID	LIQUID	AMT.OCTENE REACTED -GM-
METHANOL	225.70	93.47	6.6941	219.01	219.01	
UREA	43.48	-----	0.6341	42.8459	20.7459	
OCTENE	22.25	6.53	0.4671	21.7829	15.2829	6.50

7.0070 gm DECANE ADDED

COMPONENT	EQUIL.LIQUID UREA-FREE ANALYSIS (Sample E-2) WT.%	EQUIL.MIXTURE BEFORE SAMPLE SOLID & LIQUID-GMS	OCTENE IN EQUIL. LIQ.BEFORE SAMPLE	DECANE IN EQUIL. LIQ.BEFORE SAMPIE
METHANOL	90.50	219.01	$219.01 \times \frac{6.85}{90.50}$	$219.01 \times \frac{2.65}{90.50}$
UREA	-----	42.8459		
OCTENE	6.85	21.7829	$= 16.576$	
DECANE	2.65	7.0070		$= 6.413$

$$\begin{array}{r} 16.576 \\ -\underline{15.283} \\ 1.293 \end{array}$$ gm octene additional in liquid

$$\begin{array}{r} 7.0070 \\ -\underline{6.4130} \\ 0.5940 \end{array}$$ gm decane reacted

DECANE-OCTENE REPLACEMENT STUDY TABLE 5

FINAL EQUILIBRIUM

Final equilibrium liquid composition for octene-decane-urea-methanol system

Octene	16.576 gm
Decane	6.413
Urea	23.466
Methanol	219.01

Moles of octene and urea based on 100 gms. of above solution

Octene	0.0557 moles
Urea	0.1475

Adduct Compositions(2)

Octene-urea	3.4 gm urea per gm octene
Decane-urea	3.4 gm. urea per gm decane

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2. Redlich, O., Gable, C.M., Beason, L.R., and Miller, R.W., *J. Am. Chem. Soc.*, 72, 4154 (1950)

Order of Addition

Work described in this section examines the effect of varying the sequence of addition of octene and decane to methanol-urea solutions in forming two otherwise identical systems.

A methanol-urea solution was added to a stirred flask immersed in a constant temperature bath at 25° C. Octene was added to this solution in sufficient quantity to cause precipitation of solid adduct. After agitating the mixture for more than 24 hours to insure equilibrium, decane was added to the flask. The mixture was then agitated another 24 hours, after which time a liquid sample was withdrawn, distilled for removal of dissolved urea, and analysed using a chromatograph. The entire procedure was then repeated using identical quantities of reactants, octene being added to the decane-urea-methanol system. That is, the first system was formed by adding octene before decane, the second by adding decane before octene. This series of experiments was repeated, giving two sets of data which are summarized in Tables 6 and 7. The accuracy of the sampling, distilling and chromatographic techniques is shown in the Appendix.

From the data it was observed that:

The order of addition affects the final equilibrium distribution of reactants between the equilibrium liquid and the solid adduct.

In both sets of data, when octene was added first more octene was reacted than when octene was added last.

In the set of data represented by samples F-2 and F-3, when decane was added first more decane was reacted than when decane was added last.

In the set of data represented by samples G-0 and G-1, when decane was added first <u>less</u> decane was reacted than when decane was added last.

The confidence level of the data corresponding to samples G-0 and G-1 should be better than for F-2 and F-3 because of the greater number of analyses and shorter sample storage time prior to analysis.

ORDER OF ADDITION TABLE 6

CHROMATOGRAPHIC ANALYSES - DETAIL

Decane added last
SAMPLE G-0

RUN #	METHANOL	OCTENE	DECANE
1	92.59	6.07	1.34
2	91.54	6.72	1.74
3	92.67	5.87	1.46
4	91.72	6.58	1.70
5	92.56	6.07	1.37
6	92.10	6.36	1.54
7	91.37	7.15	1.48
8	92.60	6.12	1.28
9	92.35	6.27	1.38
10	92.40	6.14	1.46

Octene added last
SAMPLE G-1

RUN #	METHANOL	OCTENE	DECANE
1	91.52	6.70	1.78
2	90.90	7.07	2.03
3	91.01	7.15	1.84
4	91.25	6.96	1.79
5	91.39	6.93	1.68
6	91.37	7.00	1.63
7	92.82	5.97	1.21
8	91.26	6.95	1.79
9	91.96	6.43	1.61

SAMPLE F-2

RUN #	METHANOL	OCTENE	DECANE
1	92.59	5.86	1.55
2	93.12	5.56	1.32

SAMPLE F-3

RUN #	METHANOL	OCTENE	DECANE
1	91.79	7.18	1.03
2	92.99	6.15	0.86

Analyses are of liquid phase in equilibrium with solid adduct. Analyses on urea-free basis.

ORDER OF ADDITION TABLE 7

CHROMATOGRAPHIC ANALYSES - SUMMARY

SAMPLE	COMPONENT	AVG. COMP. (WT.%)	MIN	MAX	SPREAD	% OF MAX.	METH.RANGE CONF.LEVEL 95%	NO. OF RUNS IN AVG.	COMMENTS
G-0	Decane	1.47	1.28	1.74	0.19	10.9	91.85 to 92.53	TEN	Decane added last
	Octene	6.34	5.87	7.15	1.28	17.9			
	Methanol	92.19	91.37	92.67	1.30	1.4			
G-1	Decane	1.71	1.21	2.03	0.82	40.4	91.06 to 91.94	NINE	Octene added last
	Octene	6.80	5.97	7.15	1.18	16.5			
	Methanol	91.49	90.90	92.82	1.92	2.1			
F-2	Decane	1.44	1.32	1.55	0.23	14.8		TWO	Decane added last
	Octene	5.71	5.56	5.86	0.30	5.1			
	Methanol	92.85	92.59	93.12	0.53	0.57			
F-3	Decane	0.95	0.86	1.03	0.17	16.5		TWO	Octene added last
	Octene	6.68	6.15	7.18	1.03	14.4			
	Methanol	92.37	91.79	92.99	1.20	1.3			
Blank-X	Decane	1.13	1.11	1.14	0.03	2.63	1.03 (Known Comp.)	TWO	
	Octene	6.35	6.16	6.54	0.38	5.82	5.89 (" ")		
	Methanol	92.52	92.32	92.73	0.31	0.34	93.08(" ")		

Confidence level of 95% established assuming "Bell Curve" distribution.

Analyses are of liquid phase in equilibrium with solid adduct.
Analyses are on urea-free basis.

Analyses of F-2 and F-3 were made after the samples had been stored in ground glass containers all summer.

DISCUSSION AND CONCLUSIONS

The data indicates that the adduct reaction requires certain concentrations of reactants before a lasting precipitate will be formed. Once precipitate forms, the reaction does not progress to completion as might be the case if the formation of a seed crystal were required to initiate the precipitation. As was seen, precipitate forming at areas of high local concentrations dissolved upon stirring. Clearly, then, formation of solid adduct requires attainment of significant concentrations of reactants in solution; the reaction does not progress to completion once initiated by the formation of the first crystal of precipitate.

The fact that succeeding increments of octene are divided between solid adduct and the supernatent solution indicates that an equilibrium exists. Attempts were made (see Appendix) to correlate the equilibrium concentrations of urea and octene to mathematical equilibrium constant expressions assuming various reaction mechanisms. The spread in the results, due partly to accuracy limitations in experimental and analytical technique, to the few data points available and to the simplifying assumptions made in the equilibrium constant expression (eg., using concentrations instead of activities) is too great for mechanism determination. The best results were attained when the mechanism was considered to be

$$\text{octene} + 2\ \text{urea} \rightleftharpoons \text{adduct}_{(\text{SOLID})}.$$

Equilibrium relationships given in the literature(1) were developed for a mechanism

$$\text{complex} = \text{reactant} + m\ \text{urea}$$

It is significant that experimental data best fits a mechanism which does not consider dissolved adduct. In applying the laboratory data shown in Table 1 to the equilibrium expression

$$K = (\text{octene})(\text{urea})^2$$

it was assumed that the observed quantities of octene and urea in the equilibrium solution were present in their free form, and not combined in a dissolved adduct, and that the activity of the solid adduct was equal to one. The validity of this assumption is supported by the fact that results obtained by using this mechanism had greater consistancy than results obtained by including dissolved adduct in the equilibrium calculations. Apparently dissolved adduct, if it exists, exists in very low concentrations.

As was seen, no visible reaction took place until the necessary reactant concentrations were reached; moreover, crystal growth or the need for a seed crystal was not required for initiation of a visible reaction. Since it seems unlikely that nothing was happening before the criti-

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1. Redlich, O., Gable, C.M., Beason, L.R., and Miller, R.W., J. Am. Chem. Soc., 72, 4153-4160 (1950).

cal reactant concentrations were reached, it was felt that observation of a measurable change taking place within the system at these concentrations would be meaningful. Hence, calorimeter work to study heat effects above and below the critical reactant concentrations was undertaken.

Calorimetric data indicates that the heat of mixing for a binary methanol-octene system is endothermic in the concentration range investigated. The addition of octene to a methanol-urea solution in approximately the same methanol-octene concentration range as the heat of mixing work has an endothermic effect about four times greater than that observed in the heat of mixing experiments. No precipitate was formed at these concentrations. The addition of octene to a methanol-urea solution in sufficient amounts to form considerable precipitate has an exothermic effect of the same order of magnitude as the endothermic effect noted in the lower concentration ranges. The exothermic heat effect appears to increase with the amounts of precipitate formed.

The endothermic effect noted in the lower octene concentration ranges can have one or both of the following explanations:

(1) An intermediate process is taking place, involving a product in the dissolved state.

(2) The heat of mixing effect has been made several-

fold more endothermic due to dissolved urea.

It may be firmly concluded that the exothermic "heat of reaction" reported in the literature for the formation of solid adduct has within it an endothermic portion attributed to either a heat of mixing or an intermediate liquid phase reaction, or both.

Endothermic heat effects have been reported in the literature. Zimmerschied, et al(2) postulated that an endothermic heat effect is associated with distortion of the urea molecule, a greater exothermic heat effect accompanying the introduction of the hydrocarbon into the distorted molecule. This postulation was used to explain the fact that the "heat of reaction" was not as great as the authors had anticipated. The endothermic heat effect is not reported by the authors as having been observed.

Kobe and Domask(3) postulate that three separate heat effects accompany adduct formation, these being:

(1) The overcoming of molecular adhesion of the reactant molecules in the liquid state to form isolated single molecules.

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2. Zimmerschied, W.J., Dinerstein, R.A., Weitkamp, A.W., and Marschner, R.F., Ind. Eng. Chem., 42, 1306 (July 1950).

3. Kobe, K.A., and Domask, W.G., Petroleum Refiner, 31, 151-157, (May 1952).

(2) The combination of the reactant molecules and the urea molecule.

(3) The transformation of urea from a tetragonal lattice to a hexagonal lattice.

Schlenk(4) reasons that since urea is transformed from hexagonal form to tetragonal form when the adduct is decomposed, the tetragonal form is favored energetically. That is, the transformation from tetragonal to hexagonal form is accompanied by the consumption of heat. Although Kobe and Domask derive the endothermic heat effect mathematically, they do not report having observed it.

The endothermic heat effect documented in Table 2 was directly observed. By mixing adduct-forming reactants in concentrations below those required for solid adduct formation it appears that the endothermic heat effect reported in the literature has been isolated. It is possible that the observed endothermic heat effect is accompanying a conversion of liquid urea aggregate from the tetragonal to the hexagonal configuration.

Attention was given once more to the behavior of the overall reaction. Data taken in the octene-decane replacement study showed that the concentration of octene in a solu-

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4. Schlenk,W., Ann., 565, 204-40 (1949).

tion in equilibrium with solid octene-urea adduct could be increased by the addition of a reactant which would compete with the octene for the urea. Qualitatively, this is what would be predicted for a reversible reaction. That is, if the classical equilibrium concept is followed,

$$(\text{Activity}_{\text{octene}})^{x}\ (\text{Activity}_{\text{urea}})^{y} = K\ (\text{Activity}_{\text{adduct}})^{z}$$

for the reaction

$$x \text{ octene} + y \text{ urea} \rightleftharpoons z \text{ adduct}$$

then decreasing the urea concentration by reacting it with decane should require an increase in the octene concentration.

As was seen, however, the increase in the amount of octene in solution was greater than if all the reacted decane replaced octene in the octene-urea adduct, based on literature for urea-octene and urea-decane adduct compositions. This could be explained by some or all of the following reasons:

(1) Addition of decane could have an appreciable effect on the activities of the reactants and/or products requiring a greater change in the equilibrium concentration of the octene than would normally be expected.

(2) The adduct resulting from reaction of urea with octene and decane may have a different composition than either the octene-urea or decane-urea adducts.

(3) The chromatographic peak for decane is the least reliable of the three because the attenuation is considerably lower for decane at the concentration encountered than for the methanol or octene.

That the activities of the reactants have been affected is somewhat supported by the fact that the product of

$$(\text{octene})\ (\text{urea})^2$$

using the data from Table 1 gives a value of 1.21×10^{-3}, which differs from, but is of the same order of magnitude for the value shown in Appendix (avg. 3.36×10^{-3}) representing an octene-urea-methanol system. The literature(5) states that adducts formed from mixture of adduct-forming reactants consist of a single solid phase containing the various reactants. That is, the resultant adduct is not a mixture of various "binary" adducts, but is rather a unique product containing combinations of the various reactants.

Order of addition experiments were next undertaken. Since, for a truly reversible chemical system the order of addition of the reactants has no effect on the final equilibrium concentrations, it should not matter whether decane or octene is added first to a methanol-urea, octene

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5. Kobe,K.A., op. cit.

decane system. As shown in the order of addition data collected, the sequence did have an effect on the equilbrium concentrations, more total hydrocarbon reacting when decane was added last than when octene was added last. This observation is well within the cumulative limits of accuracy of the sampling, distilling, and analytical procedures as shown by the "Sampling Technique Evaluation" section of the Appendix as well as the 95% confidence range indicated in Table 7.

This observation indicates that some phenomenon other than pure chemical equilibrium is being encountered. One possible reason for this behavior lies with the adduct itself. When one component "replaces" another in a solid adduct it is not known whether the adduct decomposes and reforms with the new hydrocarbon, or whether the structure of the adduct remains intact while the place formerly occupied by one hydrocarbon is taken over by another hydrocarbon, or whether a combination of these takes place. An adduct formed in an octene-decane-urea-methanol system may consist of octene-urea and decane-urea adduct crystals or may be a different adduct in which decane and octene are both present in a single adduct crystal perhaps in different concentrations than the binary decane-urea, octene-urea adducts. Determination of the nature of the adduct is outside of the scope of this thesis. We have, however, established conclusively the fact that the methanol-urea, decane, octene, adduct system is one which deviates from the behavior associated with pure chemical equilibrium, and have provided an incentive for continued investigation into the nature of the adduct itself.

APPENDIX

Mixture Composition - Calculation Method

A mixture of the following composition is initially charged:

Methanol	228.14	gms.
Urea	42.91	gms.
Octene	21.7758	gms.

A solid precipitate is formed and settles to the bottom of the reaction flask. A sample of the liquid is weighed and then distilled. Refractive index of the distillate is 1.3337. Using the equation shown in Table 10:

$$1.3337 = (7.8097 \times 10^{-4})\ (\text{wt.\% octene}) + 1.32706$$
$$\text{or wt. \% octene} = 8.502$$
$$\text{wt. \% methanol} = 91.498\ \text{(by difference)}$$

Amount of octene in solution (liquid) before sample is taken:

$$228.14\ \frac{(8.502)}{(91.498)} = 21.202\ \text{gm. octene}$$

Amount of octene in adduct:

$$\begin{array}{rl} 21.7758 & \text{gm. octene charged} \\ -\underline{21.2020} & \text{gm. octene in solution} \\ 0.5738 & \text{gm. octene reacted} \end{array}$$

Adduct contains 3.4 gm. urea per gm. octene
1.5738 (3.4) = 1.9509 gm. urea reacted

Amount of urea in solution before sample is taken:

$$\begin{array}{rl} 42.91 & \\ -\underline{1.95} & \\ 40.96 & \text{gm. urea in solution before sample} \end{array}$$

Solution before sample:	228.14	gm. methanol
	21.202	gm. octene
	40.96	gm. urea

Weight of sample = 7.0097 gms.

Let x = grams methanol in sample

$$\frac{21.202}{228.14}\,x = \text{grams octene in sample}$$

$$\frac{40.96}{228.14}\,x = \text{grams urea in sample}$$

$$x + \frac{21.202}{228.14}\,x + \frac{40.96}{228.14}\,x = 7.0097$$

$$x = 5.5087 \text{ gm. methanol}$$

$$\frac{21.202}{228.14}\,x = 0.5119 \text{ gm. octene}$$

$$\frac{40.96}{228.14}\,x = 0.9889 \text{ gm. urea}$$

$$\overline{7.0095 \text{ gm.}}$$

Summary:

	Charge	Solution	Sample	
Octene	21.7758 gm.	21.202 gm.	0.5119 gm.	7.30 wt%
Urea	42.91	40.96	0.9889	14.10
Methanol	228.14	228.14	5.5087	78.60

The 4.1 figure exceeds the literature figure of 3.4 gm urea per gm octene. This is most likely due to incomplete separation of dissolved urea from the adduct sample by the benzene wash. In addition, some octene was lost due to adherence to the sides of the separatory funnel. This entire technique was simple, but crude.

Adduct composition via liquid analyses. A known amount of methanol, urea and octene were charged to a stirred flask to form solid adduct. A sample of the equilibrium liquid was weighed and distilled. The residue and distillate were both weighed. The composition of the distillate was determined both from the index of refraction correlation and from chromatographic analysis. Using the weights of initial charge, sample, distillate and residue, and the composition of the distillate, the composition of the equilibrium adduct was calculated. Calculated adduct composition ranged from 4.22 to 0.966 gm urea/gm octene, the range being due to discrepancies in the analysis of the distillate.

The accuracy of the refractive index analysis was damaged by the distillation step. In effecting complete distillation of the liquid sample, a small amount of urea was apparently carried over with the "last few cc's" of distillate. This is apparent from the wide spread in refractive indices taken of the distillate when the distillation was 99.5% complete and when it was fully complete.

Adduct Composition Determination

Calculations used to determine the amounts of octene and urea reacted required use of the adduct composition given in the literature:

3.4 grams of urea per gram of octene.

It was decided to check the adduct composition experimentally. This was done by two separate methods:

(1) Analysis of the solid liquid

(2) Analysis of the liquid in equilibrium with an adduct.

Adduct composition via adduct analysis. A sample of solid adduct was taken from a methanol, urea, octene system at equilibrium. The sample was washed with benzene, air dryed, and dissolved in a weighed amount of water. The octene layer from the resultant two-phase system was separated and weighed. The water layer was weighed, and the weight of urea was determined by the difference between the weight of the water layer and the weight of the water charged.

Weight of water used to dissolve adduct	67.8	gm
Weight of octene layer	0.8078	gm
Weight of water and dissolved urea	71.15	gm
Weight of dissolved urea	3.3	gm

Ratio of urea/octene $= \frac{3.3}{0.8078} =$ 4.1 gm urea per gm octene

In addition, the refractive index correlation relies heavily on the fourth decimal of the refractive index, which is gotten by interpolation.

The urea carry-over problem mentioned above did not affect the chromatographic analysis of sample F-1, consequently the chromatographic results are more reliable than results from the refractive index correlation. This ratio of 3.62 gm urea per gm octene gotten from this data is within reasonable experimental error of the literature value.

INITIAL CHARGE	108.31 gm methanol 21.00 gm urea 16.8224 gm octene	
SAMPLE OF EQUILIBRIUM LIQUOR	63.73 gm sample	
DISTILLATION	99.5% Complete	100% Complete
WT. OF DISTILLATE	51.91 gm	53.23 gm
I/R OF DISTILLATE @25° C	1.3373	1.3361
RESIDUE		8.34

Calculation of Adduct Composition:

$$\begin{array}{rl} 63.73 & \text{Sample Wt.} \\ -\underline{8.34} & \text{Wt. of residue (urea)} \\ 55.39 & \text{gm octene and methanol in sample} \end{array}$$

Urea-free composition of distillate using I/R of 1.3373

13.11 Wt. % octene
86.89 Wt. % methanol

$$13.11 \times \frac{108.31}{86.89} = 16.3 \text{ gm octene in solution}$$

16.8224 gm octene charged
-16.3000 gm octene
0.5224 gm octene reacted

55.39 x 0.8689 = 48.12 gm methanol in sample

$8.34 \times \frac{108.31}{48.12}$ = 18.8 gm urea in liquid

21.00 gm urea charged
-18.80 gm urea in liquid
2.20 gm urea reacted

$\frac{2.20}{0.5224}$ = 4.22 gm urea/gm octene adduct composition

Urea-free composition of distillate using I/R of 1.3361

11.58 Wt. % octene
88.42 Wt. % methanol

Using same calculation methods as above:

Amount of octene reacted = 2.64 gm
Amount of urea reacted = 2.55 gm

$\frac{2.55}{2.64}$ = 0.966 gm urea/gm octene adduct composition

Urea-free composition of distillate using chromatograph

13.0% octene
87.0% methanol

Using same calculation methods as above:

Amount of octene reacted = 0.6224
Amount of urea reacted = 2.25

$\frac{2.25}{0.6224}$ = 3.62 gm urea/gm octene

Adduct Formation - Mechanism Determination

Equilibrium data for the octene-urea-methanol system given in Table 1 was reduced to a constant weight basis and used in equilibrium equations derived from four assumed reaction mechanisms.

Equilibrium data.

Moles octene per 100 gm solution	Moles urea per 100 gm solution
0.0559	0.238
0.0650	0.235
0.0785	0.203
0.0942	0.1905
0.1095	0.1760

Mechanism 1. Assume mechanism is

$$\text{octene} + \text{urea} \rightleftharpoons \text{adduct}_{\text{solid}}$$

then

$$(\text{Activity}_{\text{octene}})(\text{Activity}_{\text{urea}}) = K$$

Using the concentrations shown above instead of activities, the calculated values of K are:

0.0133
0.0153
0.0159
0.0180
0.0193

Mechanism 2. Assume mechanism is

$$\text{octene} + 2\ \text{urea} \rightleftharpoons \text{adduct}_{\text{solid}}$$

then

$$(\text{Activity}_{\text{octene}})(\text{Activity}_{\text{urea}})^2 = K$$

Using the above concentrations the calculated values of K are:

3.17×10^{-3}
3.59×10^{-3}
3.24×10^{-3}
3.42×10^{-3}
3.40×10^{-3}

Mechanism 3. Assume mechanism is

$$\text{octene} + \text{urea} \rightleftharpoons \text{adduct}_{\text{liquid}}$$

then

$$\frac{\text{Activity}_{\text{adduct}}}{(\text{Activity}_{\text{octene}})(\text{Activity}_{\text{urea}})} = K$$

Assuming the concentration of liquid adduct is constant due to its limited solubility:

$$(\text{Activity}_{\text{octene}})(\text{Activity}_{\text{urea}}) = K'$$

Let ϕ = conc. of octene, both in solution and as liquid adduct
U = conc. of urea, both in solution and as liquid adduct
x = moles of octene present in liquid adduct
$6.8x$ = moles of urea present in liquid adduct (1)

$$(\phi - x)(U - 6.8x) = K'$$

Using this equation with various pairs of equilibrium data, the following values of x were calculated.

0.0220
0.0217
0.0213
0.1815
0.0208 average

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1. Redlich, O., Gable, C.M., Dunlop, A.K, and Miller, R.W., J. Am. Chem. Soc., 72, 4154 (1950).

Using the average x, the following values of K' were calculated:

3.39×10^{-3}
4.13×10^{-3}
3.55×10^{-3}
3.60×10^{-3}
3.06×10^{-3}

<u>Mechanism 4.</u> Assume mechanism is

$$\text{octene} + 2\ \text{urea} \rightleftharpoons \text{adduct}_{\text{liquid}}$$

Then

$$\frac{\text{Activity}_{\text{adduct}}}{(\text{Activity}_{\text{octene}})(\text{Activity}_{\text{urea}})^2} = K$$

Making the same assumptions and using the same symbols as above:

$$(\phi - x)(U - 6.8x)^2 = K'$$

The following values of x were calculated using various pairs of equilibrium data:

0.0331 0.0298
0.0317 0.0284
0.0308 average

Using the average x the following values of K' were calculated:

2.11×10^{-5}
2.31×10^{-5}
0.17×10^{-5}
21.7×10^{-5}
85.8×10^{-5}

Order of Addition - Sampling Technique Evaluation

Analyses of samples G-0 and G-1 shown in Table 7 indicate that order of addition influences the equilibrium composition of a decane, octene, methanol-urea mixture. To determine the degree to which the sampling and sample processing technique contributed to the difference in equilibrium concentrations, the following work was undertaken.

The reactants itemized below were charged to a reactor flask.

Methanol	55.00 gm.
Urea	12.81 gm.
Octene	4.24 gm.
Decane	1.39 gm.

After equilibrium was attained, two samples, G-2 and G-3 were taken of the equilibrium liquid. The two samples were distilled separately, and chromatographically analysed.

The results, shown in Tables 8 and 9, indicate that the sampling and distilling technique account for only 23% (approx.) of the difference between the equilibrium concentrations of samples G-0 and G-1.

Inaccuracies in the chromatographic analyses resulted in approximately the same spread in analyses of samples G-2 and G-3 as for G-0 and G-1. For samples G-0 and G-1 there is very little "overlap" in the range of equilibrium methanol concentration. Consequently, the conclusion that order of addition influences the equilibrium concentration of a decane, octene, methanol-urea mixture, may be made within the confidence limit of the data.

SAMPLING TECHNIQUE EVALUATION TABLE 8

CHROMATOGRAPHIC ANALYSES - DETAIL

SAMPLE G-2

RUN #	METHANOL	OCTENE	DECANE
1	91.63	6.78	1.59
2	91.01	7.15	1.84
3	91.58	6.78	1.64
4	91.47	6.82	1.71
5	92.04	6.55	1.41

SAMPLE G-3

RUN #	METHANOL	OCTENE	DECANE
1	90.85	7.32	1.83
2	91.29	7.13	1.58
3	91.61	6.75	1.64
4	91.62	6.82	1.56
5	91.50	6.97	1.53

SAMPLING TECHNIQUE EVALUATION TABLE 9

CHROMATOGRAPHIC ANALYSES - SUMMARY

SAMPLE	COMPONENT	AVG.COMP. (WT.%)	MIN	MAX	SPREAD	% OF MAX.	METH.RANGE CONF.LEVEL 95%	NO. OF RUNS IN AVG.
G-2	Decane	1.64	1.41	1.84	0.43	23.3	91.11 to 91.95	FIVE
	Octene	6.82	6.55	7.15	0.60	8.4		
	Methanol	91.54	91.01	92.04	1.03	1.1		
G-3	Decane	1.63	1.53	1.83	0.30	1.6	90.97 to 91.77	FIVE
	Octene	7.00	6.75	7.32	0.57	7.8		
	Methanol	91.37	90.85	91.62	0.77	0.8		

Confidence level of 95% established assuming "Bell Curve" distribution.

INDEX OF REFRACTION MEASUREMENTS TABLE 10

METHANOL-OCTENE SOLUTION

WT. % OCTENE	INDEX OF REFRACTION (25° C)
0.00	1.3270
1.45	1.3284
2.44	1.3290
3.23	1.3294
3.80	1.3303
4.59	1.3308
5.62	1.3316
6.12	1.3321
6.29	1.3318
6.85	1.3323
7.06	1.3323
7.58	1.3328
7.62	1.3332
7.74	1.3327
11.78	1.3363
14.68	1.3387

"Best straight line" using method of least squares:(2)

$$(\text{Index of Refraction}) = (0.78097 \times 10^{-3})(\text{Wt.\% Octene}) + 1.32706$$

Fourth decimal place in refractive index by interpolation.

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2. Thomas, G.B., Calculus and Analytic Geometry, Addison-Wesley Publishing Company, Inc., Cambridge, Mass., 1954 pp. 512-515.

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