# Adduction in the Decane-Urea-Ethanol System: Part I. Equilibrium Studies

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**Phase equilibria in the decane–urea–ethanol system were investigated between 15° and 40°C. Solubility limits for urea–decane adduct in ternary liquid solutions and for urea in ethanol were measured over the entire feasible range of compositions, thus defining the phase diagrams. Activity coefficients estimated for the saturated liquid solutions reflected strong positive deviations from ideality. The magnitudes were consistent with the results of independent vapor-liquid equilibrium studies.**

Several novel techniques are enlarging the scope of separation technology. Unfortunately, the costs of many new processes are currently high relative to older processes, thus restricting their use to unusually difficult separations. Greater understanding of the process fundamentals of new separation methods may be expected to improve their future economic attractiveness and to accelerate their commercial acceptance.

One of these unique separation methods is called *adductive crystallization* (*5*). Alkanes and other straight-chain compounds have been isolated by adductive crystallization with urea. Previous studies of urea–alkane adducts dealt with adduct compositions, crystal structures, dissociation constants, and heats of adduction (*2, 7, 8, 15, 18, 19, 21, 22, 25, 27*).

In contrast, adduction kinetics and solvent effects have received little attention. Accordingly, this investigation concentrated on these areas by probing one ternary system in depth. To achieve rapid adduction rates, a polar solvent capable of dissolving both alkanes and urea was required. The decane–urea–ethanol system was selected, mainly on the basis of previous screening (*12*), as qualitatively representative of the systems of interest.

## THEORY

Equilibrium between adduct crystals and an ethanol solution containing dissolved urea and decane can be described by

$$m \text{ urea } (d) + \text{decane } (d) \rightleftharpoons \text{adduct } (s)$$

where $m$ has been reported to be constant for a given urea–alkane system.

However, the analysis of thermodynamic equilibrium in solutions involves some ambiguity when strong specific interactions occur (*9, 14*). Derivation of equilibrium constants by free energy minimization requires postulation of the species involved in the actual equilibrium. Usually a plausible system of components (perhaps including associated or dissociated species) is assumed to be involved in the equilibrium and an equilibrium constant based on this model is derived. This procedure is sound theoretically, but care must be taken in applying the results.

Because of large polarity differences and strong hydrogen bonding in the decane–urea–ethanol system, the possibilities of strong urea autoassociation and urea–ethanol solvation exist. Dissolved adduct has been proposed as a specific interaction (*3, 19, 28*), but this species is neither physically reasonable nor consistent with the results of Ketelaar and Loopstra (*11*). Other specific interactions are possible, including decane aggregations similar to hydrophobic bonding (*1*).

If autoassociation of urea (similar to that often encountered in solutions of organic acids) were assumed, the following dissociation constant would apply:

$$K_{(1)} = \frac{a_{\text{decane }(d)} \prod_{i=1}^{\infty} (a_i)^{p_i}}{a_{\text{adduct }(s)}} \tag{1}$$

where $a_i$ is the activity of a cluster containing $i$ urea molecules, and the $p_i$ are stoichiometric coefficients, which depend upon the cluster size distribution, subject to

$$\sum_{i=1}^{\infty} i\ p_i = m$$

If solvation of urea molecules by integral numbers of solvent molecules were assumed, the dissociation constant would be

$$K_{(2)} = \left(\frac{a_{\text{decane }(d)}}{a_{\text{adduct }(s)}}\right) \prod_{j=0}^{\infty} \frac{(a_j)^{q_j}}{a_{\text{EtOH }(d)}^{\,j\ q_j}} \tag{2}$$

where $a_j$ is the activity of a solvate containing one urea molecule and $j$ ethanol molecules, and the $q_j$ are stoichiometric coefficients subject to

$$\sum_{j=0}^{\infty} q_j = m$$

If no specific interactions are assumed, the dissociation constant is written

$$K_{(3)} = \frac{a_{\text{decane }(d)}\ a_{\text{urea }(d)}^{m}}{a_{\text{adduct }(s)}} \tag{3}$$

Other models are of course possible.

Hysteresis is often encountered in measurement of phase equilibria by dynamic methods. This is attributed to the activation energy required to nucleate new phases (*6, 10*). Thus, each stable boundary on a phase diagram can have a metastable counterpart.

## EXPERIMENTAL WORK

Because additional experimental details are reported elsewhere (*24*), only the highlights are reviewed here. Adduct solubility, urea solubility, and vapor–liquid–adduct equilibrium are described in the order indicated.

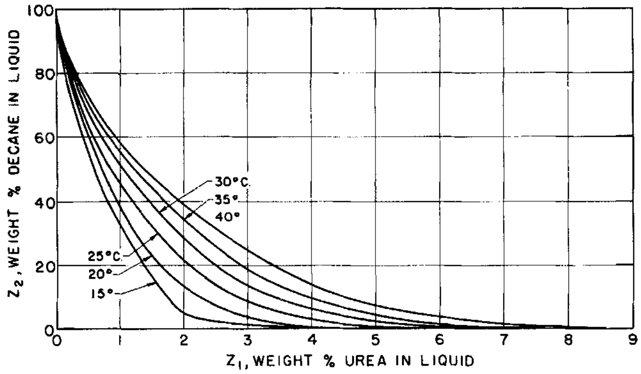

**Fig. 1. Decane–urea–ethanol solution—adduct isotherms.**

### Adduct Solubility

Saturated liquid compositions were determined without using chemical analyses, and water was excluded from the system. Two methods were used—the first involved titrating pure decane or pure ethanol into a ternary mixture of known composition. The adduction vessel was well stirred magnetically so that the relaxation time of overall equilibration was, for practical purposes, definitely less than the allowed time. The solubility limit was reached when only a very small remaining amount of minute adduct crystals could be visually detected when light was passed through the mixture. At this point the temperature and the quantity of titrated liquid were recorded. Liquid composition was taken to be the same as the overall composition, since the amount of adduct present was negligible. Solubility limits were not determined by measurement of the composition at which adduct crystals first appeared.

About 85% of the 165 adduct solubility measurements were made by the second method, which consumed less time and facilitated temperature variation. Mixtures of known composition, which had been chilled in an ice bath until abundant amounts of adduct formed, were slowly heated. Vigorous magnetic stirring ensured adequately small relaxation times. The temperature at which the last visible adduct crystals disappeared was recorded as a saturation point.

Since the solubility data were taken at many different temperatures, each data point was converted to the nearest integral multiple of 5°C. by determining

$$\left(\frac{\partial z_{\text{urea}}}{\partial T}\right)_{z_{\text{decane}}} \text{ and } \left(\frac{\partial z_{\text{decane}}}{\partial T}\right)_{z_{\text{urea}}}$$

over the range of compositions. This procedure did not appreciably degrade the accuracy. Curves were then drawn through the resultant isothermal data points. Some coordinates of the smoothed isotherms are presented in Table 1, and plots are given in Figure 1. Reproducibility of the data was good (*24*).

TABLE 1. ADDUCT SOLUBILITY LIMITS FOR THE UREA–DECANE–ETHANOL SYSTEM

| Wt. % Urea | Wt. % Decane at 15°C. | 20°C. | 25°C. | 30°C. | 35°C. | 40°C. |
|---|---|---|---|---|---|---|
| 0.10 | 84.2 | 86.0 | 87.2 | 88.5 | 89.6 | 90.3 |
| 0.30 | 68.0 | 72.4 | 75.0 | 77.2 | 79.3 | 80.7 |
| 0.50 | 55.4 | 60.6 | 64.7 | 67.6 | 71.0 | 72.9 |
| 0.70 | 44.9 | 50.7 | 56.1 | 60.5 | 64.0 | 66.3 |
| 1.00 | 32.7 | 39.6 | 45.8 | 51.3 | 55.5 | 58.3 |
| 1.40 | 19.4 | 26.9 | 34.9 | 41.5 | 46.3 | 50.5 |
| 1.90 | 6.51 | 15.0 | 23.5 | 30.8 | 36.2 | 41.3 |
| 2.40 | 2.78 | 8.00 | 15.3 | 21.9 | 27.3 | 32.9 |
| 3.00 | 1.32 | 5.77 | 8.57 | 13.4 | 18.7 | 24.3 |
| 3.50 | 0.69 | 1.97 | 5.49 | 9.03 | 13.5 | 18.5 |
| 4.00 | 0.37 | 1.03 | 3.02 | 6.32 | 9.55 | 13.8 |
| 4.50 | 0.30 | 0.52 | 1.34 | 4.05 | 6.65 | 9.92 |
| 5.00 | — | 0.31 | 0.64 | 2.24 | 4.44 | 7.28 |
| 5.50 | — | — | 0.35 | 1.08 | 2.88 | 5.50 |
| 6.00 | — | — | — | 0.57 | 1.80 | 4.05 |
| 6.50 | — | — | — | 0.31 | 0.98 | 2.78 |
| 7.00 | — | — | — | — | 0.52 | 1.69 |
| 7.50 | — | — | — | — | 0.32 | 0.95 |
| 8.00 | — | — | — | — | — | 0.52 |
| 8.50 | — | — | — | — | — | 0.33 |

### Urea Solubility

Since published solubility data for urea in ethanol (*4, 13, 16, 17, 23, 26*) were not fully consistent, new measurements were made, taking care to avoid hysteresis. Repeated tests at 22°C. indicated a solubility of 5.45 wt. % urea. At 81.15°C. the solubility was 22.1 wt. %.

It was found that an exponential temperature dependence, as shown in Figure 2, permitted linear interpolation. The solubility could then be represented by the empirical equation

$$S = 3.08 \exp(0.0279\,T)$$

where S has units of g. urea/100 g. EtOH and $T$ is in degrees Centigrade.

### Vapor–Liquid–Adduct Equilibrium

As an order-of-magnitude check on decane activity, dynamic vapor pressure measurements were made. One difficulty with such measurements is that it must be assumed that the relaxation time for phase equilibration is small compared to the time scale of the disturbances which are occurring in the system. Another is that metastability may require a finite displacement from equilibrium before observable changes occur. Nevertheless, useful data can be obtained by dynamic measurements.

Vapor pressures of well-stirred slurries of adduct and saturated solutions near 22°C. were determined by vacuum distillation. After the air was removed from the system, a sample of vapor was distilled off and condensed in a cold trap. The total vapor pressure was read from a mercury manometer. The distillate samples were small enough so that slurry compositions were unaffected by their removal, and their compositions were obtained by measurement of refractive indices.

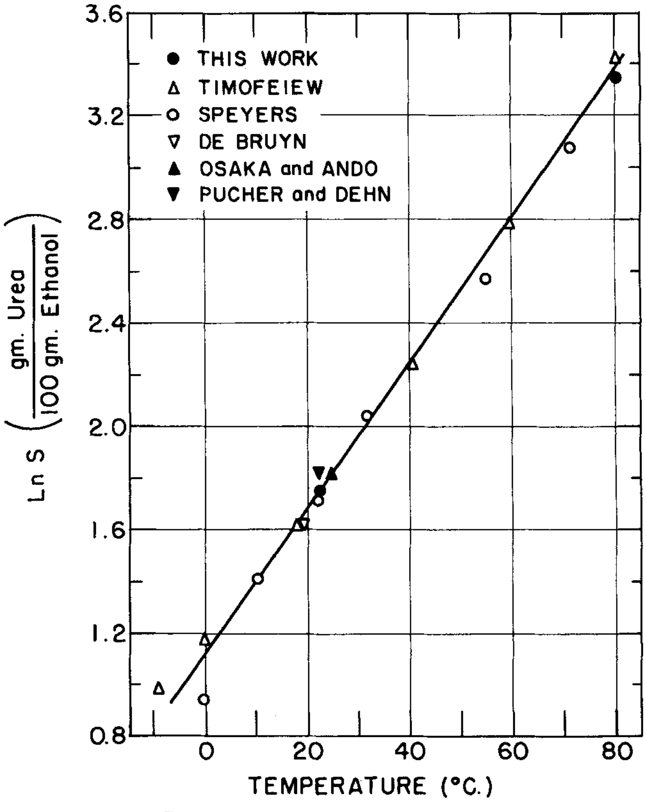

**Fig. 2. Solubility of urea in ethanol.**

## DISCUSSION

The observed solvent effects and phase diagrams are discussed separately.

### Solvent Effects

Some understanding of the liquid phase behavior may be obtained by applying Equation (3) to the adduct saturation data. For example, at 22°C. $K_{(3)} = 0.066$ (*18, 25*) where the standard states are pure liquid and pure crystalline solids at the temperature and pressure of the solution. Combining the activity coefficients into a single parameter Γ, one obtains

$$\Gamma \equiv \gamma_{\text{decane }(d)}\, \gamma^{m}_{\text{urea }(d)} = \frac{0.066}{x_{\text{decane }(d)}\, x^{m}_{\text{urea }(d)}} \qquad (4)$$

From the 22°C. saturation data, Γ was computed at a number of points with the reported value of 8.04 used for $m$ (*18*). Log Γ is plotted against wt. % urea in Figure 3. The smallest value of Γ, $6.86 \times 10^{12}$, occurs at the urea-rich end of the isotherm, and Γ increases rapidly as $x_{\text{urea}}$ approaches 0.

Although it is theoretically impossible to determine $\gamma_{\text{decane}}$ and $\gamma_{\text{urea}}$ separately from Γ alone, an estimate may be made on the basis of the following information. At the urea-rich limit, where solid urea is also present $x_{\text{urea}} = 0.0425$ and $\gamma_{\text{urea}} = (1/0.0425)^{8.04} = 1.03 \times 10^{11}$. Thus

$$\log \gamma_{\text{decane}} = \log \left( \frac{\Gamma}{\gamma^{8.04}_{\text{urea}}} \right) \rightarrow \log \left( \frac{6.86 \times 10^{12}}{1.03 \times 10^{11}} \right) = 1.82$$

$$\text{as } x_{\text{urea}} \rightarrow 0.0425$$

Table 2. Activity Coefficients Estimated from Adduct Solubility Data in the Urea-Decane-Ethanol System

| Wt. % Urea | Decane | Urea |
|---|---|---|
| 0.13 | 320 | 1.10 |
| 0.18 | 246 | 1.15 |
| 0.22 | 209 | 1.20 |
| 0.27 | 181 | 1.25 |
| 0.54 | 111 | 1.5 |
| 0.76 | 97 | 2.0 |
| 0.90 | 79 | 2.2 |
| 1.20 | 66 | 2.5 |
| 1.70 | 53 | 3.7 |
| 2.30 | 44 | 6.3 |
| 2.65 | 40 | 7.7 |
| 3.30 | 34 | 13 |
| 3.60 | 32 | 16 |
| 4.20 | 28 | 25 |
| 4.75 | 26 | 39 |
| 5.47 | 24 | 67 |

As shown in Figure 5, $x_{\text{decane}} = 1.0$ and hence $\gamma_{\text{decane}} = 1.0$ at the decane-rich limit of the adduct solubility curve *AE*. Thus

$$\log \gamma_{\text{decane}} \rightarrow 0 \quad \text{as} \quad x_{\text{urea}} \rightarrow 0$$

On the hypothesis of a linear variation of log $\gamma_{\text{decane}}$ between the limits, estimates of $\gamma_{\text{decane}}$ and $\gamma_{\text{urea}}$ are tabulated in Table 2. $\gamma_{\text{decane}}$ varies from 1.0 to 67.1 and $\gamma_{\text{urea}}$ varies from 23.5 to 320, where it increases sharply.

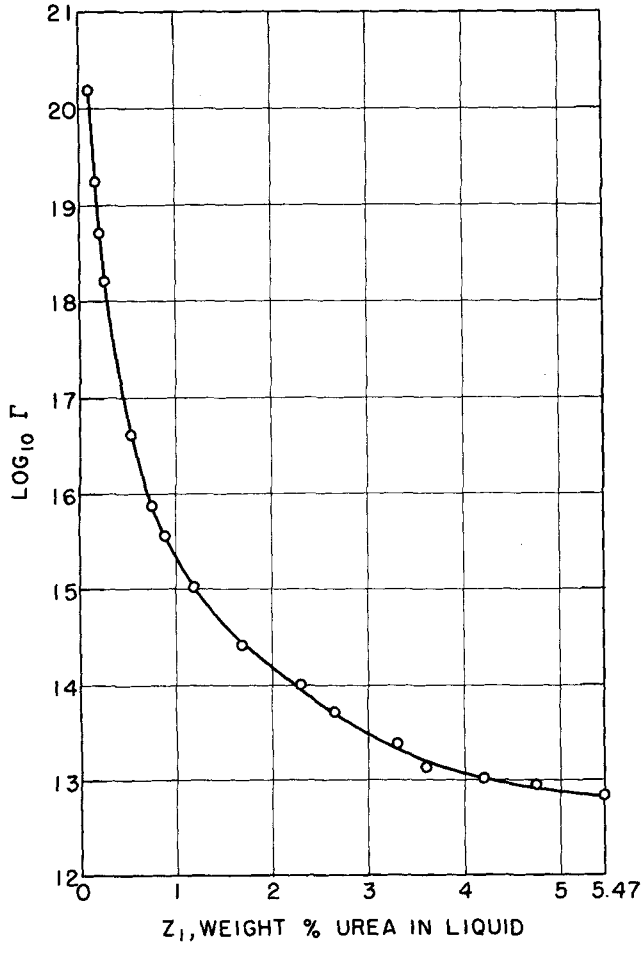

Fig. 3. Activity coefficient parameter determined from 22°C. solution—adduct isotherm.

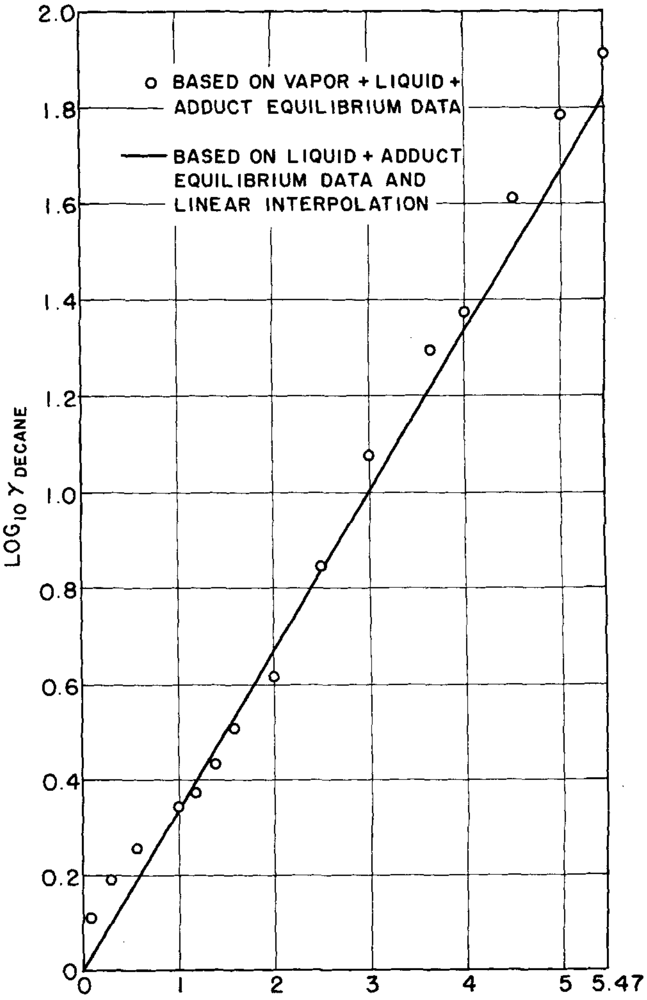

Fig. 4. Comparison of activity coefficients at 22°C.

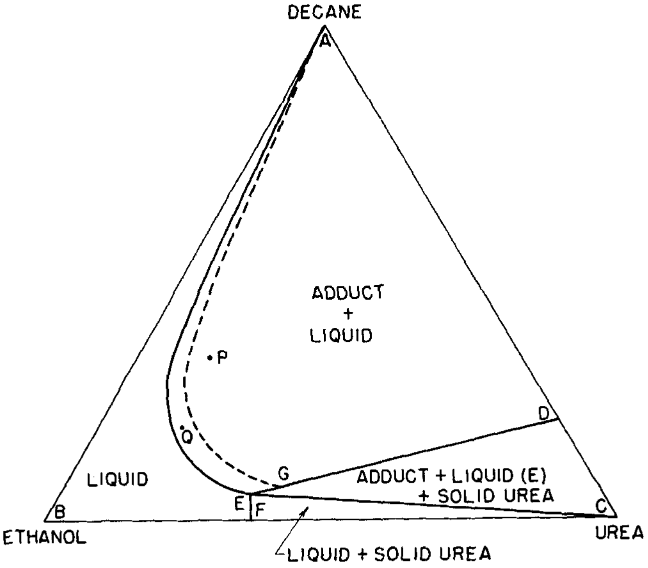

**Fig. 5. Schematic isothermal phase diagram for the urea–decane–ethanol system.**

These values are reasonable compared with the activity coefficients computed from the vapor pressure data by using

$$\gamma_{\text{decane}} = \frac{y_{\text{decane}} P_T}{x_{\text{decane}} P^*_{\text{decane}}}$$

In addition to assuming an ideal vapor phase, this expression includes the same assumptions concerning the liquid phase as are inherent in Equation (3). Figure 4 shows that the activity coefficients determined by the two methods are consistent within the accuracy of the vapor-liquid measurements.

Application of Equations (1) and (2) to the adduct solubility data produced interesting results when only one cluster size and one solvate coordination number, respectively, were considered. This is equivalent to letting all $p_i$ except one, $p_\delta$, and all $q_j$ except one, $q_\epsilon$, be zero. Reasonable integer values such as $\delta = 3$ and $\epsilon = 5$ could be chosen so that when lumped activity parameters (similar to $\Gamma$) were calculated for the association model in the decane-rich region and for solvation in the urea-rich region, the parameters exhibited smaller composition dependence than did $\Gamma$. Although these results are not conclusive they suggest that specific interactions are quite strong in the saturated ternary solutions.

### Phase Diagrams

Figure 5 is a distorted-scale schematic of the phase diagrams proposed for decane–urea–ethanol at 1 atm. within the temperature range studied. On a true-scale diagram, line *BF* would be only 4 to 9% of line *BC* (depending on temperature) and line *EF* would be only about 0.3% of line *AB*.

Point *D* represents adduct, which contains 20.5 wt. % decane. Point *F* was determined from the urea solubility studies discussed earlier. Boundary *AE* was obtained from the adduct solubility experiments. The metastability curve *GA* was not measured. The existence of the region *CDEC* was supported by the observation that the refractive index of the liquid phase of an equilibrium mixture within that region did not depend upon the overall composition.

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## NOTATION

$a$ = activity
$d$ = dissolved state
$K$ = equilibrium constant
$m$ = stoichiometric ratio of urea molecules to decane molecules in adduct
$p$ = cluster size
$P_T$ = total pressure
$P^*$ = vapor pressure of pure liquid
$q$ = solvate coordination number
$S$ = solubility, g. solute/100 g. solvent
$s$ = solid state
$T$ = temperature
$x$ = mole fraction in liquid at equilibrium
$z$ = weight fraction in liquid at equilibrium
$\gamma$ = activity coefficient
$\Gamma$ = activity parameter, as defined by Equation (4)

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