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STUDIES ON THE TELOMERIZATION OF ETHYLENE WITH
CARBON TETRACHLORIDE

II. Properties of Ethylene and Tetrachloro-Alkanes Mixtures

BY KIYOSHI KITAMURA

The phase equilibria and the P - V - T relations of the mixtures of ethylene and tetrachloro-alkanes $\text{C}(\text{CH}_2\text{CH}_2)_n\text{CCl}_3$ under pressures up to 200 kg/cm^2 have been investigated to clarify the nature of the telomerization reaction systems of ethylene with carbon tetrachloride. The tetrachloro-alkanes examined were carbon tetrachloride, 1, 1, 1, 3-tetrachloro-propane, 1, 1, 1, 5-tetrachloro-pentane, 1, 1, 1, 7-tetrachloro-heptane and 1, 1, 1, 9-tetrachloro-nonane.

Ethylene and carbon tetrachloride dissolve each other in all proportions at certain conditions, for example, at a pressure above 100 kg/cm^2 and a temperature below 90°C , to form a homogeneous solution, which has intermediate properties between those of liquid carbon tetrachloride and of compressed ethylene gas. The densities of the solutions with several compositions were measured, and the partial molal volumes of ethylene and carbon tetrachloride, compressibilities and thermal expansion coefficients of the solutions, were calculated. The properties of the mixtures of ethylene and other tetrachloro-alkanes are also similar to the mixture of ethylene and carbon tetrachloride, except that the higher pressures are required to dissolve ethylene. The relations between the properties of the reaction mixtures and the kinetics of the telomerization were discussed.

Introduction

During the course of the preceding kinetic investigation¹⁾ on the telomerization of ethylene with carbon tetrachloride, it became desirable to clarify the phase behaviors, the P - V - T relations and some other physical properties of the reaction mixtures at the reaction conditions. Information of the properties of feed mixtures were also required to prepare and to transmit the feed solutions.

Although there have been some investigations on the phase behaviors of ethylene and carbon tetrachloride binary mixtures by Freidlina et al.²⁾ and by Takagi and Asahara³⁾, the P - V - T relations of homogeneous binary solutions have been scarcely known, except at the gas-liquid equilibrium conditions. There has been no available information about the properties of the reaction mixtures containing the products telomers.

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1) K. Kitamura, *This Journal*, **35**, 83, (1966)

2) R. Kh. Freidlina and Sh. A. Karapetyan, "Telomerization and New Synthetic Materials" Pergamon Press, London, (1961); G. B. Ovakimyan, *Khim. Nauka i Prom.*, **2**, 13 (1959)

3) Y. Takagi and T. Asahara, *J. Chem. Soc. Japan, Industrial Chemistry Section (Kogyo Kagaku Zasshi)*, **65**, 537 (1962)

In the present investigation, the phase behaviors and the P - V - T relations of the feed mixtures and of the reaction mixtures have been studied from these points of view.

Experimentals

Materials

Ethylene with polyethylene grade (with purity over 99.9%), manufactured by Nippon Petrochemicals Co. Ltd. (Kawasaki Factory), was supplied from a commercial bomb. Carbon tetrachloride was of commercial C.P. grade and was used without further purification. The other tetrachloro-alkanes with constants shown in Table 1 were synthesized by the telomerization of ethylene with carbon tetrachloride¹³⁾, and purified by repeated fractional distillations under reduced pressures.

Table 1 Constants for $\text{Cl}(\text{CH}_2\text{CH}_2)_n\text{CCl}_3$

$\text{Cl}(\text{CH}_2\text{CH}_2)_n\text{CCl}_3$	$n=1$	2	3	4
BP., °C/mmHg	54/20	69/2	92/2	101/1
Density, d_4^{20}	1.443	1.351	1.267	1.199
Refractive index, n_d^{20}	1.481	1.488	1.485	1.483

Apparatus and Procedures

Two high pressure vessels were used in the experiments. The one was a commercial autoclave with electromagnetic stirrer. Its inner capacity was 965ml. It was made of stainless-steel, and was equipped with two valves, one at the upper frange and the other at the bottom, a pressure gauge and a safety valve. The temperature of the vessel was controlled by circulation of water from the thermostat through a jacket around the vessel. Measurements by means of the autoclave were carried out as follows; a weighed amount of tetrachloro-alkane and ethylene at a pressure were charged in the vessel, stirred for 20 or 40 minutes at a constant temperature until the pressure in the vessel became constant and the indicated pressure was read. The quantities of the ethylene introduced were measured after the pressure measurement by a gas-meter at room temperature and atmospheric pressure. The composition of the liquid solutions under gas liquid equilibria were determined by analyzing the samples taken from the bottom valve of the vessel. Ethylene in a sample solution was separated from liquid tetrachloro-alkanes at atmospheric pressure and passed through dry-ice methanol cold trap and measured volumetrically.

The liquid component, tetrachloro-alkanes separated from the samples, was also measured volumetrically.

Another high pressure vessel used was a small bomb made of stainless steel with 120ml capacity, equipped with a small valve and a pressure gauge on it. Its total weight was about 1.5 kg and the net content was weighed by mean of a chemical balance. The temperature control of the bomb was carried out by shaking the bomb in a thermostat, and the contents in the bomb were stirred by two or three steel balls of 10mm in diameter charged in the bomb, while the bomb is shaken.

Results and Considerations

Phase equilibria

Fig. 1 shows the relation between the amount of ethylene and the equilibrium pressure, in the presence of a given amount of carbon tetrachloride confined in the constant volume of 965 ml, at 80°C.

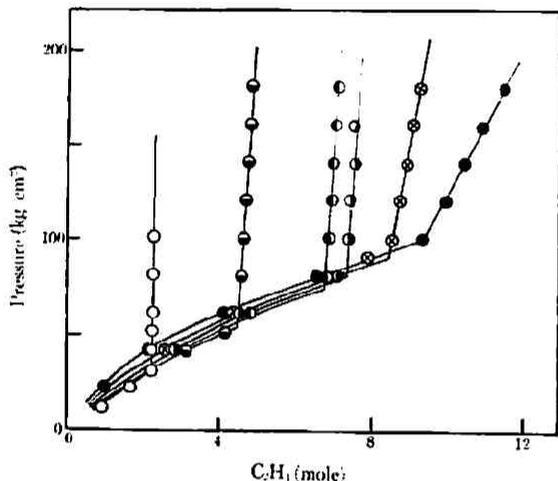


Fig. 1 Relations between amounts of C_2H_4 and pressure for $C_2H_4-CCl_4$ mixtures in constant volume of 965 ml, where \bullet —300 ml, \circ —400 ml, \odot —500 ml, \ominus —600 ml, $\omin�$ —700 ml, and \otimes —800 ml of CCl_4 are charged, respectively

In the course of increasing ethylene charge, there appears a sudden increase in pressure and further introduction of ethylene becomes substantially limited. It is also noted in the figure that the equilibrium pressure with the same amount of ethylene charge below the limit, is reduced by increasing carbon tetrachloride, while, the more carbon tetrachloride is present, the smaller amount of ethylene charge causes the sudden pressure increase.

These phenomena are explained as follows: At a pressure below the point of the sharp change of the slope, two different phases namely a compressed gas phase and a liquid solution phase co-exist in equilibrium. The gas phase consists mainly of ethylene, and the liquid phase is a mixture of ethylene and carbon tetrachloride. Since the solubility of ethylene in carbon tetrachloride is large enough, the ethylene concentration in the liquid phase is always larger than that of the gas phase, so that the increase of carbon tetrachloride always causes pressure decrease at a constant charge of ethylene, or the increase of ethylene at constant pressure. As the pressure is the more increased, the more ethylene in the gas phase is absorbed in the liquid solution and increases the concentration of ethylene and the volume of the solution. Thus, at a pressure above the point of the sharp change of the graph-slope in the figure, the given space is filled with the liquid solution. Since the compressibility of the solution is very small, the inner pressure is increased greatly even by a small amount of additional ethylene further introduced above the pressure; hence, the composition of the solution is mainly decided by the "packing ratio" of the volume of the charged carbon tetrachloride to the given space, and the influence of pressure which dominates the composition at the two-phase-regions becomes almost negligible in this pressure range.

A sharp increase in pressure is also observed in the course of increasing temperature of the system

with a constant volume and constant charge amounts, of which patterns are as shown in Fig. 2. This phenomenon may be also due to the change in the state from a gas-liquid-equilibrium state to a homogeneous solution state, by the thermal expansion of the liquid phase and the volume increase due to the dissolution of ethylene in the course of increasing temperature and pressure.

Fig. 3 shows the relations between amounts of ethylene and pressures for mixtures of ethylene

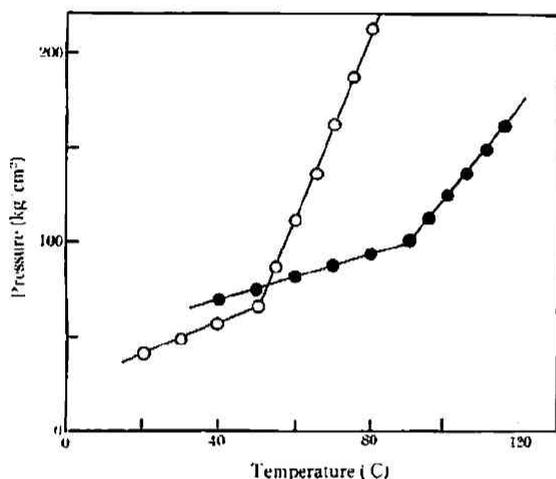


Fig. 2 Relations between temperature and pressure at constant volume 965 ml, for mixtures of C_2H_4 and CCl_4 ;
 ●: 235 g. of C_2H_4 and 474 g. (300 ml) of CCl_4
 ○: 224 g. of C_2H_4 and 790 g. (500 ml) of CCl_4

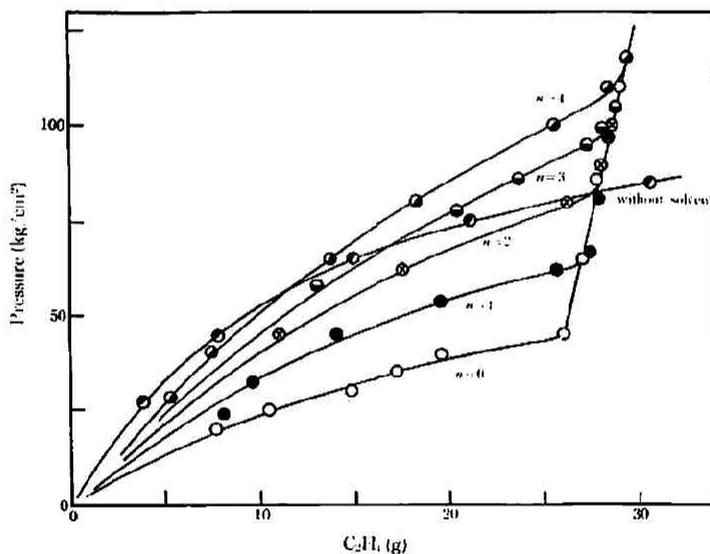


Fig. 3 Relations between amounts of C_2H_4 and pressure for mixtures of C_2H_4 and 60 ml of $Cl(CH_2CH_2)CCl_3$, in constant volume 123 ml, at 30°C

and five kinds of tetrachloro-alkanes in constant volume of 123 ml, at 30°C. In every case, just 60 ml of a tetrachloro-alkane was charged in the vessel. The relations follow the similar patterns, as in the cases of ethylene and carbon tetrachloride mixtures, except that the equilibrium pressure increases with increasing chain length of the tetrachloro-alkane molecule. The phenomena that the vessel is filled

with the homogeneous solutions are commonly observed with these tetrachloro-alkanes, which are caused by nearly the same amount of ethylene, in these conditions. *i. e.*, dissolutions of ethylene in these solvents cause nearly the equal volume increases of the solutions.

Fig. 4 shows the pressure-composition phase diagrams at constant temperatures between 10° and

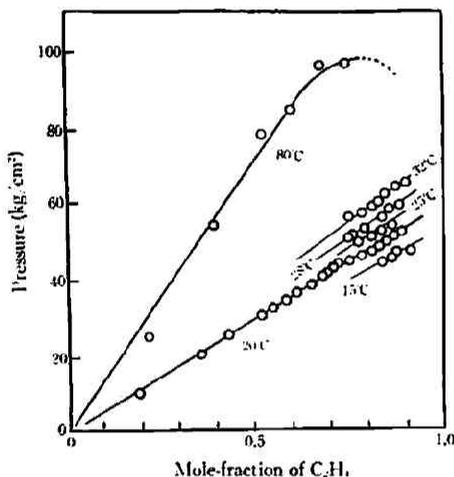


Fig. 4 Pressure-composition diagrams at constant temperature for $C_2H_4-CCl_4$ mixtures

80°C, for ethylene-carbon tetrachloride mixtures. In this figure, the mixtures are in homogeneous state with a single phase at the points above each line, and are heterogeneous ones at the points below each line. At a pressure above the maximum point in the phase diagram, ethylene and carbon tetrachloride dissolve each other in all proportions to form a homogeneous solution.

The phase diagram at 80°C are obtained by plotting the pressure against the composition at each curve point in Fig. 1. The other data are obtained using the 965 ml autoclave, by sampling solutions

Table 2 Densities of $C_2H_4-CCl_4$ solutions

Mole fraction of C_2H_4	Temperature, °C	Pressure, kg/cm ²		
		80	100	120
0.386	20	1.262	1.265	1.268
	40	1.243	1.247	1.281
	60	1.185	1.190	1.195
	80	1.146	1.152	1.158
0.611	20	1.008	1.012	1.017
	40	0.958	0.964	0.970
	60	0.908	0.917	0.926
	80	0.825	0.868	0.880
0.816	20	0.695	0.707	0.717
	40	—	0.648	0.662
	60	—	0.571	0.599
	80	—	—	0.510

from equilibrium mixtures and subsequent analyses.

P-V-T relations

Table 2 and Figs. 5 and 6 show the relations between mole fraction of ethylene and density, of ethylene-carbon tetrachloride solution, at several temperatures between 20° and 80°C and pressures between 80 kg/cm² and 120 kg/cm².

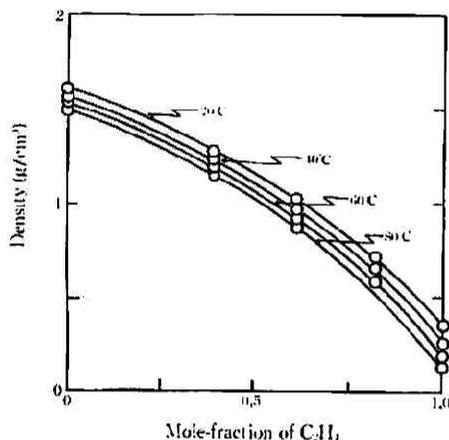


Fig. 5 Densities of $C_2H_4-CCl_4$ solutions at 100 kg/cm²

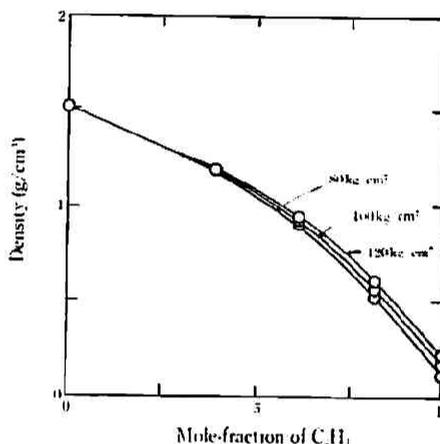


Fig. 6 Densities of $C_2H_4-CCl_4$ solutions at 60°C

As already shown in Fig. 4, ethylene and carbon tetrachloride are miscible in all proportions homogeneously at the conditions. By varying the proportion of the components from that of pure carbon tetrachloride toward that of pure ethylene, the properties of the solution are also varied continuously from those of carbon tetrachloride which is a typical non-polar liquid to those of compressed ethylene gas. Therefore, the distinctions between gas and liquid do not exist with these solutions at the pressures.

Thus, the ethylene-carbon tetrachloride solutions exhibit some hybrid properties of the ordinary liquids below critical temperatures and pressures and the ordinary compressed gases above critical temperatures and pressures.

As shown in the figures, the density of the solution decreases and approaches to that of pure ethylene gas, with increasing ethylene mole fraction of the solution, and the apparent molal volume of ethylene in the solution, though nearly constant at lower ethylene concentrations, increases with increasing mole fraction of ethylene and approaches to the volume of ethylene gas at the same temperature and pressure.

The partial molal volume of ethylene and of carbon tetrachloride are as shown in Fig. 10. It seems remarkable that the partial molal volume of ethylene increases monotonously with an increase in the mole-ratio of ethylene to carbon tetrachloride, while the volume of carbon tetrachloride decreases acceleratingly with an increase in the mole-ratio.

With other solvents than carbon tetrachloride, the only available *P-V-T* data are those of Fig. 4, from which the apparent molal volumes of ethylene are calculated to be the same with carbon tetra-

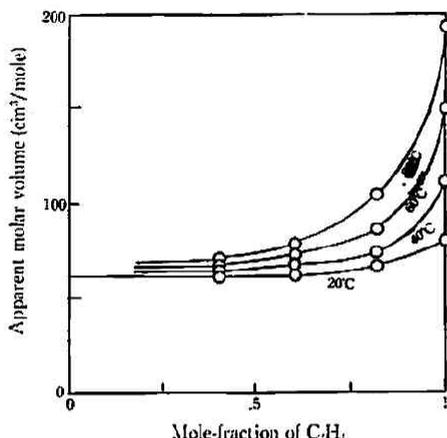


Fig. 7 Apparent molal volumes of C₂H₄ in C₂H₄-CCl₄ solutions at 100 kg/cm²

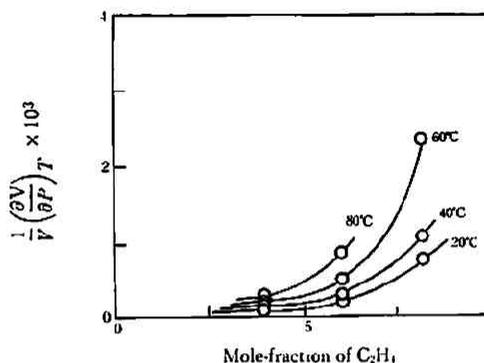


Fig. 8 Compressibilities of C₂H₄-CCl₄ solutions at 100 kg/cm²

chloride and four other tetrachloro-alkanes, 60 cm³/mole, each at 30°C and 120 kg/cm². It seems probable that the dissolutions of ethylene in tetrachloro-alkanes or tetrachloro-alkanes mixtures, cause similar magnitudes of volume increases as in carbon tetrachloride, and also in other conditions, though much more data should be required to conclude it.

Examples that the ethylene-carbon tetrachloride solution has properties with those of ordinary liquids and gases, are also presented in its compressibility and thermal expansion coefficient.

As shown in Figs. 8 and 9, both the compressibility and the thermal expansion coefficient

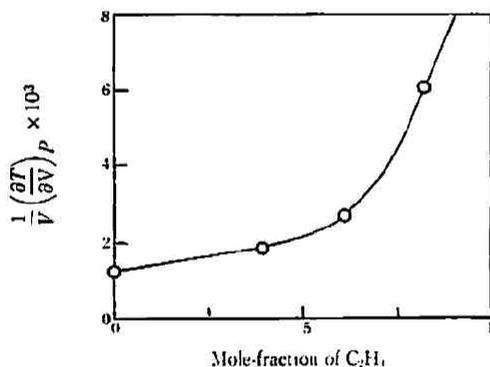


Fig. 9 Thermal expansion coefficient of C₂H₄-CCl₄ solution at 60°C, 100 kg/cm²

increase with increasing ethylene mole-fraction, to approach those of compressed pure ethylene gas, respectively.

The heat of ethylene dissolution in carbon tetrachloride can be estimated from the data of phase equilibria and of the density of the mixture, by the Clapeyron-Clausius, equation:

$$dP/dT = L_s / T(V_g - V_m), \tag{1}$$

where P , the equilibrium pressure, T the equilibrium temperature (absolute), L_s the heat of dissolution, V_g and V_m are the partial molal volumes of ethylene in gas phase and in the mixture, respectively.

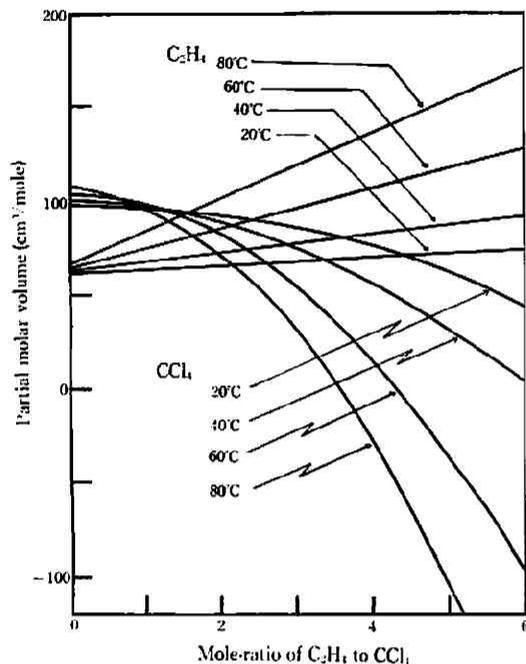


Fig. 10 Partial molar volumes of C_2H_4 and CCl_4 in binary solutions at $100\text{kg}/\text{cm}_2$

Fig. 11 shows approximate values of the heat of ethylene dissolution in carbon tetrachloride at 20°C . In these calculation the molal volume of pure ethylene was used for V_θ , and the partial molal volume of ethylene at $100\text{kg}/\text{cm}^2$ for V_m .

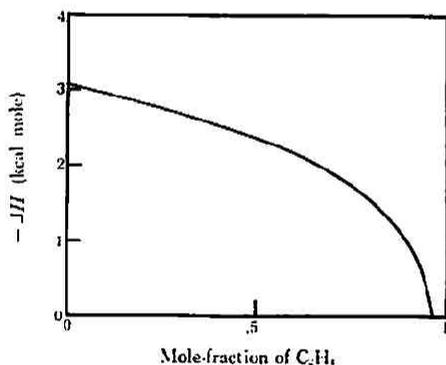


Fig. 11 The dissolution heat of ethylene at 30°C .

The heat of ethylene dissolution in pure carbon tetrachloride is estimated to be about $3\text{kcal}/\text{mole}$ at 30°C . It decreases with an increase in ethylene concentration of the solution, and is assumed to become zero at the pressure and the composition, where the compositions and the densities of the two phases converge together.

Relations between the telomer compositions and phase behaviors of the reaction mixtures

Concerning the telomerization of ethylene with carbon tetrachloride, the relations between the reaction conditions and the compositions of the resulting telomer products have been pursued most

intently^{27,28}. In principle, the molecular weight distributions of telomer products should be decided by the mole-ratio of ethylene to carbon tetrachloride in the reaction mixture. The problem seems to be relatively simple in cases of continuous-line-flow reaction system in which the reaction mixtures are homogeneous as previously discussed¹⁹. However, it is much complicated in batch-systems using autoclaves as batch-reactors, mainly, due to the heterogeneous nature of the reaction mixtures at the batch conditions. The complications seem to be explained by the informations obtained, as follows.

1) If a batch space is filled with a homogeneous reaction mixture, the telomer compositions are decided by the composition of the feed mixture, namely, the mole charge ratio of the reactants. The situation is quite the same with those of continuous-flow-systems.

2) If a batch space is heterogeneous and occupied by two phases, namely, a gas phase and a liquid phase, then the reaction occurs only in the liquid phase and the composition of the liquid, accordingly, the telomer composition is mainly governed by its equilibrium pressures.

3) Discriminations between 1) and 2) are capable by the phase data and the P - V - T data presented already. Thus, it becomes possible to predict the composition of the products, if the temperature, the pressure, the charged carbon tetrachloride and the batch volume of the system are known.

4) Above statements 1), 2) and 3) are only applicable for cases of relatively lower conversions. If the consumptions of ethylene and of carbon tetrachloride are large and a considerable amount of telomer products is accumulated in the reaction mixture, then, the phase conditions which govern the composition of the mixture are accordingly changed. In such a case, a change in the solubility of ethylene should be taken in account besides other variants such as the pressure and the quantities of the remaining reactants. The tendencies that the solubilities of ethylene in the reaction mixtures are lowered by the accumulation of the telomer products, are indicated from the data in Fig. 3. However, more detailed informations about the mixtures containing the telomer products, will be required to afford the quantitative explanations and predictions with the cases of higher conversions.

Influences of the contraction of the reaction mixture

In the preceding paper, the rate equations concerning the telomerization of ethylene with carbon tetrachloride have been expressed in terms of molar concentration assuming that the volume of the reaction mixture is constant throughout the reaction. As discussed above, there occurs a considerable amount of contraction of the reaction volume during the course of ethylene consumption and accumulation of telomer products, so that the constant volume approximation should be regarded as somewhat a bold one, except with the cases of relatively lower ethylene conversions. In spite of the boldness of the approximation the derived rate equations explains the experimental results rather well. However, there should be some deviations in calculated rate constants k' and k'' .

Considering the contraction of the reaction mixture, the rate of ethylene consumption expressed with constant-volume-approximation by

$$\left. \begin{aligned} -dC_e/dt &= k' C_e C_{t_1}^{\frac{1}{2}} \\ -dC_{t_1}/dt &= k_1 C_e \end{aligned} \right) \quad (2)$$

should be written more strictly as

$$\left. \begin{aligned} -dX_e/dt &= k' \rho^{\frac{1}{2}} X_e X_t^{\frac{1}{2}} \\ -dX_t/dt &= k_i X_t \end{aligned} \right) \quad (3)$$

where C_e and C_t are the molar concentrations of ethylene and AIBN, while X_e and X_t signify the mole-contents of ethylene and AIBN in unit mass of the reaction mixture with density ρ , respectively.

On the other hand, the molar volume of the telomer $\text{Cl}(\text{CH}_2\text{CH}_2)_n\text{CCl}_3$ increases by a constant increment, *e. g.* about 32 cm^3 at 20°C per one ethylene linkage $-\text{CH}_2\text{CH}_2-$, and the apparent molal volume of ethylene in solution may be assumed constant, *e. g.* about $80\text{ cm}^3/\text{mole}$ at 80°C , $100\text{ kg}/\text{cm}^2$ and 1.7 mole-ratio (about 63 mole % of ethylene), hence, the amount of contraction may be nearly proportional to the amount of consumed ethylene in the solution. Thus, the density of the reaction mixture is expressed in a term of ethylene conversion x as,

$$\left. \begin{aligned} x &= 1 - X_e/X_{e0}, \\ \rho &= \rho_0/(1 - \alpha x), \\ \alpha &= X_{e0}(V_e - V_t), \end{aligned} \right) \quad (4)$$

where X_{e0} is the initial value of X_e , V_e is the apparent molal volume of ethylene and V_t is the increment of telomer volume per ethylene unit.

From equations (3) and (4) we obtain

$$\begin{aligned} -\frac{d(1-x)}{dt} &= k' \rho_0^{\frac{1}{2}} X_{e0}^{\frac{1}{2}} (1-x)(1-\alpha x)^{-\frac{1}{2}} \exp[-k_t t/2] \\ &= k' C_{e0}^{\frac{1}{2}} (1-x)(1-\alpha x)^{-\frac{1}{2}} \exp[-k_t t/2]. \end{aligned} \quad (5)$$

while equations (2) can be rewritten at a constant temperature as

$$-\frac{d(1-x)}{dt} = k' C_{e0}^{\frac{1}{2}} \exp[-k_t t/2] \cdot (1-x). \quad (6)$$

Thus, the rate parameters calculated by the approximate equations (2) will be deviated by a factor of $(1-\alpha x)^{-\frac{1}{2}}$, due to the contraction effect, from the theoretically defined values. In continuous flow experiments as in the preceding studies, the volume changes also affect the flow rate of the reaction mixtures and the reaction times, hold-up times in these cases, so that there should be an additional error in the estimation of k' by a factor of $(1-\alpha x)^{-1}$, if the hold-up time is calculated from the initial feed rate and the reactor volume using the equation (6). Then, k' should be over-estimated totally by a factor of $(1-\alpha x)^{-\frac{3}{2}}$. For instance, with a case of mole feed ratio of ethylene to carbon tetrachloride: 1.7, the reaction temperature: 80°C , the pressure: $100\text{ kg}/\text{cm}^2$, and the ethylene conversion: 50%, the effect of the volume change can be roughly estimated from the data previously shown as follows: $X_{e0} = 8.4\text{ mole}/\text{kg}$, $V_e = 82\text{ cm}^3/\text{mole}$, $V_t = 32\text{ cm}^3/\text{mole}$, $\alpha = 0.37$, $\alpha x = 0.185$, $(1-\alpha x)^{-\frac{1}{2}} = 1.11$ and $(1-\alpha x)^{-\frac{3}{2}} = 1.36$, respectively.

Phase behavior and explosion of batch reactor

The explosions which may out-break in the batchwise telomerization of ethylene with carbon tetrachloride have been ascribed to the induced decomposition of the peroxide initiators²⁾³⁾. However

4) R. O. Bolt and R. M. Joyce, *Chem. Eng. News* 25, 1966 (1947)

an uncontrollable sudden rises of temperature and pressure of which the extreme becomes explosion, may take place occasionally for batches of more than 1 l where AIBN are used for the initiator and the induced decomposition may not occur. Hence, the explosions seem to be attributed not only to the induced decompositions but to other specific conditions of the reaction, such as the unusual *P-V-T* relations of the reaction mixtures as are shown in Fig. 2, the highly exothermic and temperature-sensitive natures of the reaction and so on.

These explosions are assumed as a kind of thermal chain explosion, which may take place if a part or the whole of the reaction mixture is overheated by the reaction heat so that the temperature difference between the part and its environment exceeds a critical magnitude ΔT_c defined by

$$\Delta T_c = RT^2/E \quad (7)$$

where R is the gas constant, T the absolute temperature of the overheated area and E the apparent activation energy of the process. In the case of the AIBN induced telomerization of ethylene with carbon tetrachloride, E is about 20 kcal/mole,¹⁾ hence T_c is estimated to be about 13° at 100°C. Since the reaction is highly exothermic, this limiting condition is rather severe for larger scale batch systems such as autoclaves. Once the reaction temperature exceeds such a limiting condition, an uncontrollable temperature rise together with an endless acceleration of the reaction may break out. Especially, in the cases of higher packing ratios of carbon tetrachloride to reactor volumes, $(dP/dT)_p$ becomes suddenly very large, as are shown in Fig. 2, and the pressure rises within a very short period to an enormous magnitude and causes the destruction of the reactors or the explosions.

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*Technical Research Laboratory of
Asahi Chemical Industry Co., Ltd.,
Itabashi-ku, Tokyo, Japan*