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(54) **METHOD FOR GAS SEPARATION BY
PHASE ENHANCED GAS-LIQUID
ABSORPTION**

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(57) **ABSTRACT**

A new method called phase enhanced gas-liquid absorption has been developed. By addition of organic phase into the absorption system of gas aqueous phase, the absorption rate was increased significantly. Absorption rate was enhanced by organic phase.

This invention provides a new technology for improving the efficiency of traditional gas absorption. By reducing mass transfer resistance in absorption process, this technology is able to lead to a more efficient, low cost absorption process and significantly reduce constraints and costs.

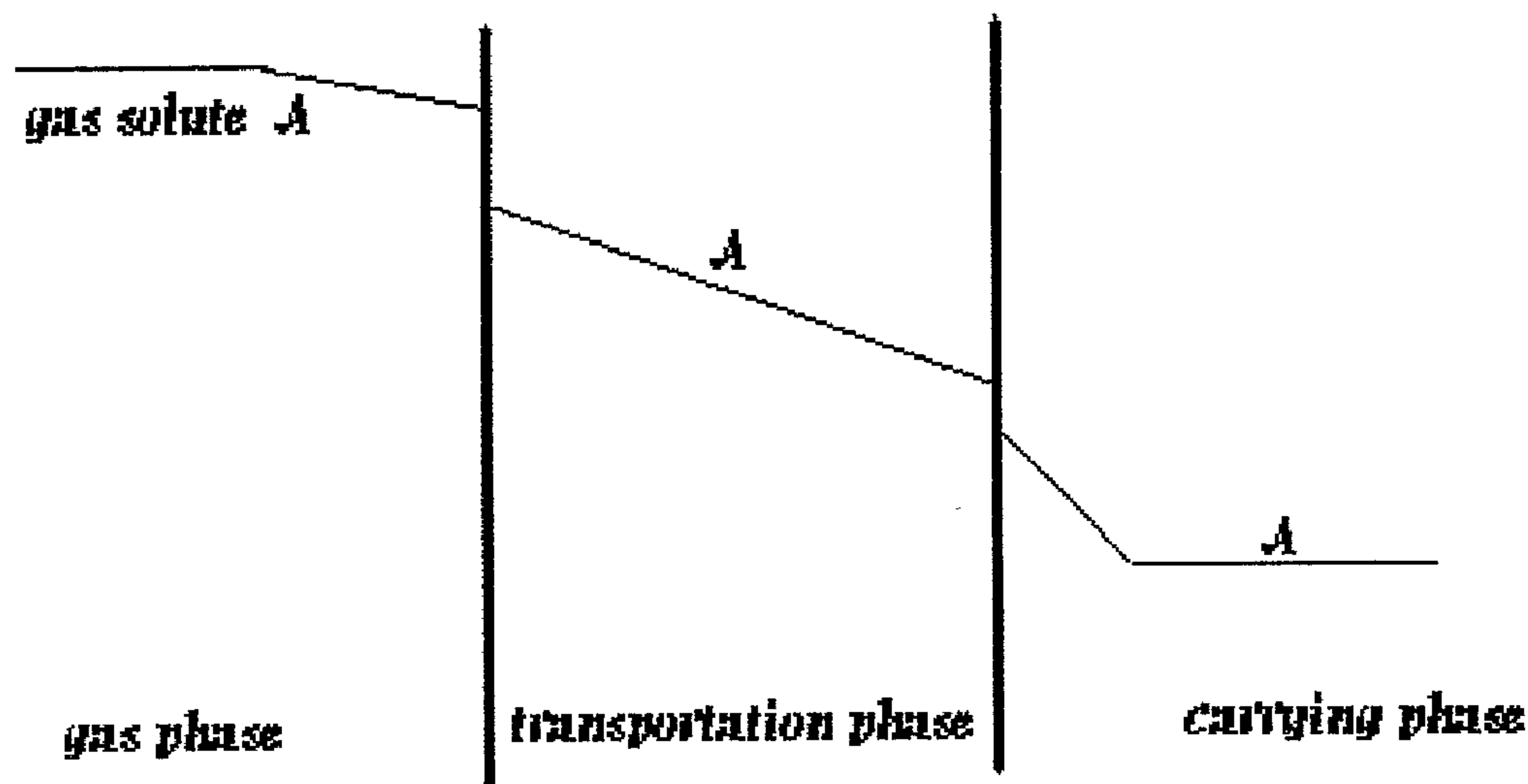


FIGURE 1 Mass transfer model

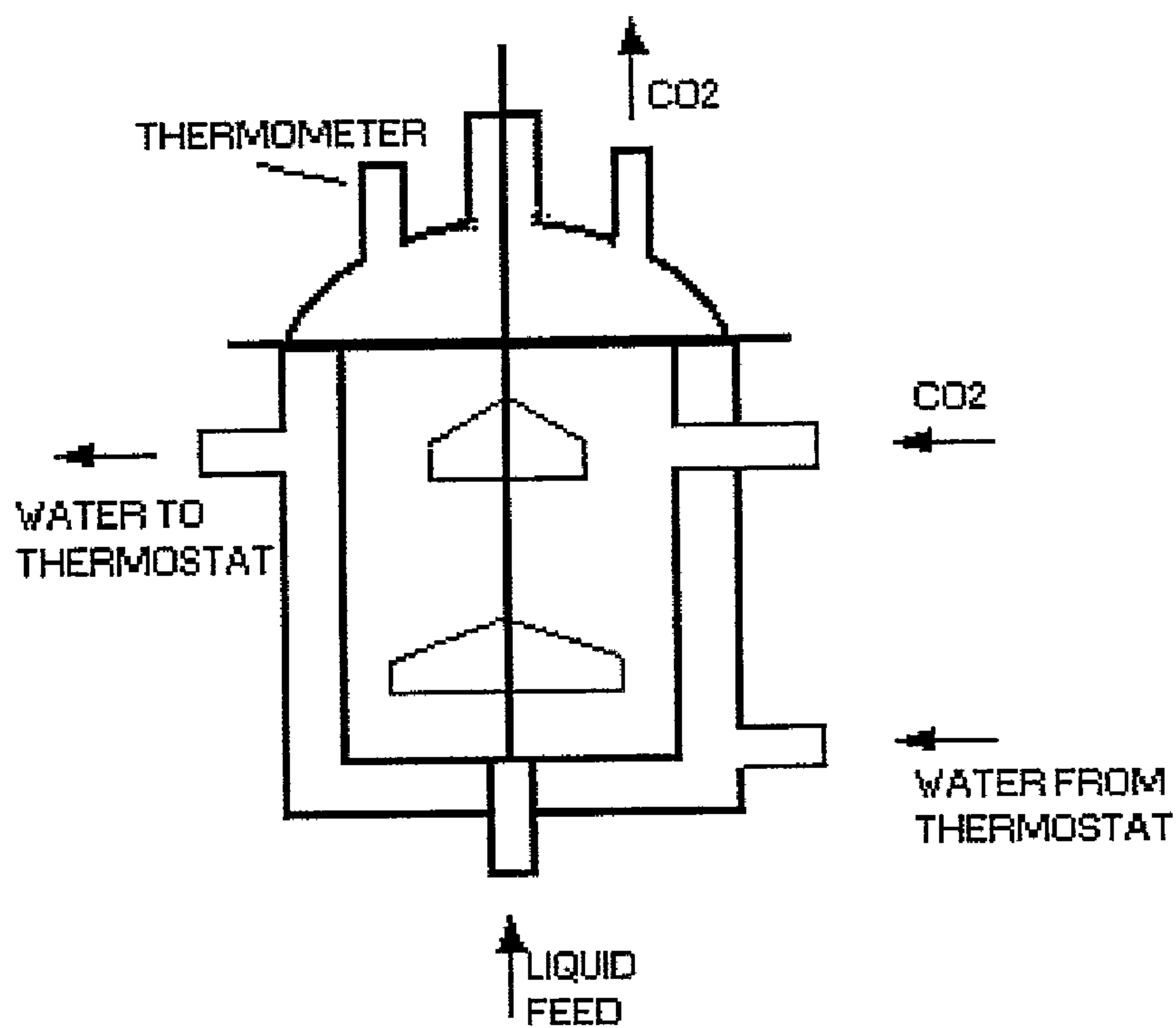


FIGURE 2 STIRRING CELL

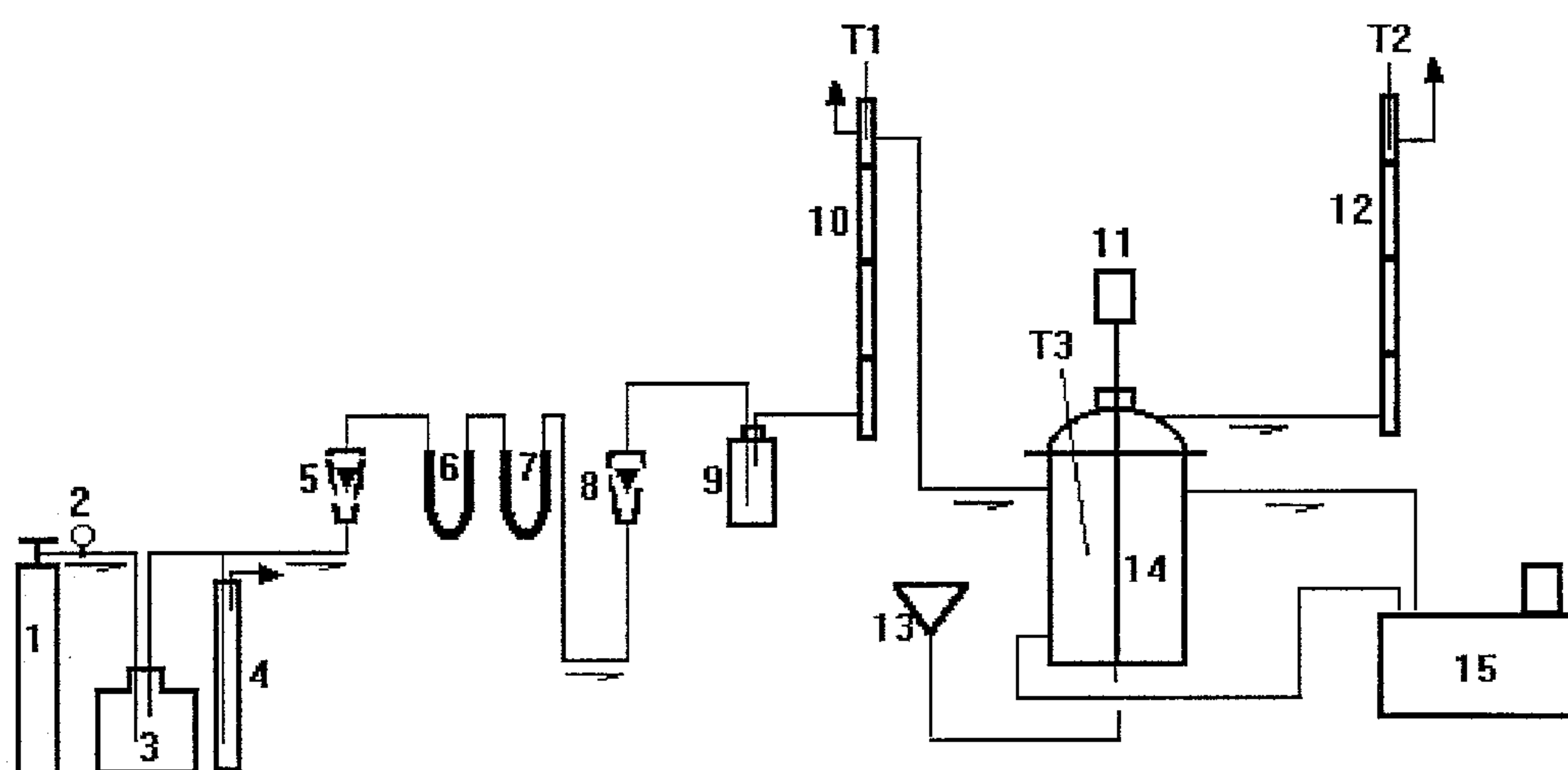


FIGURE 3 EXPERIMENTAL APPARATUS

1 - CO₂ CYLINDER; 2 - REGULATOR; 3 - BUFFEL BOTTLE; 4 - PRESSURE STABLE TUBE;
 5, 8 - ROTATING FLOW METER; 6 - SILICON GEL U TUBE; 7 - ACTIVE CARBON U TUBE;
 9 - SATURATOR; 10, 12 - FOAM FILM FLOW METER; 11 - MOTER; 13 - LIQUID FEED FUNNEL;
 14 - STIRRING CELL; 15 - THERMOSTAT; T1, T2, T3 - THERMOMETER

FIGURE 4

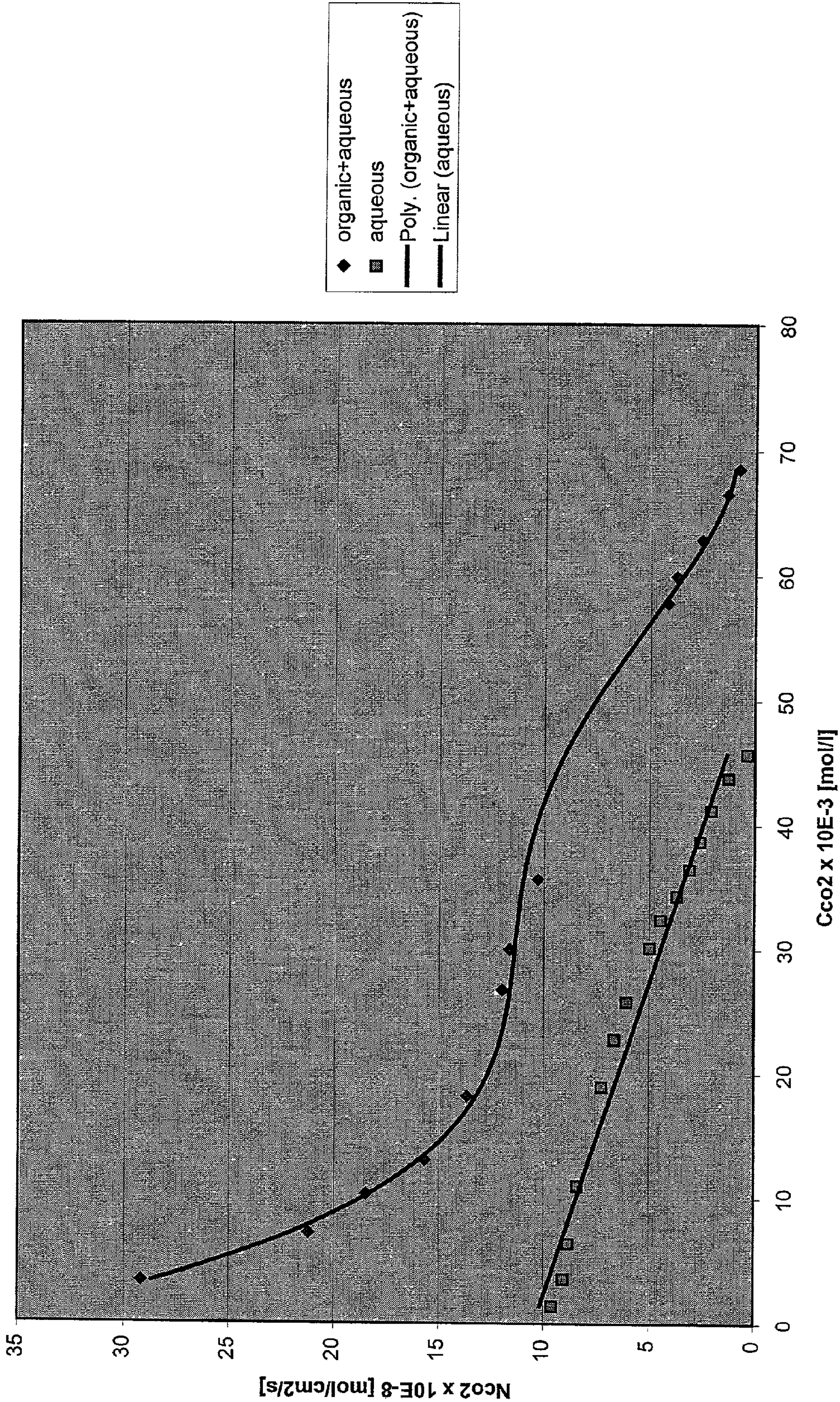


FIGURE 5 A

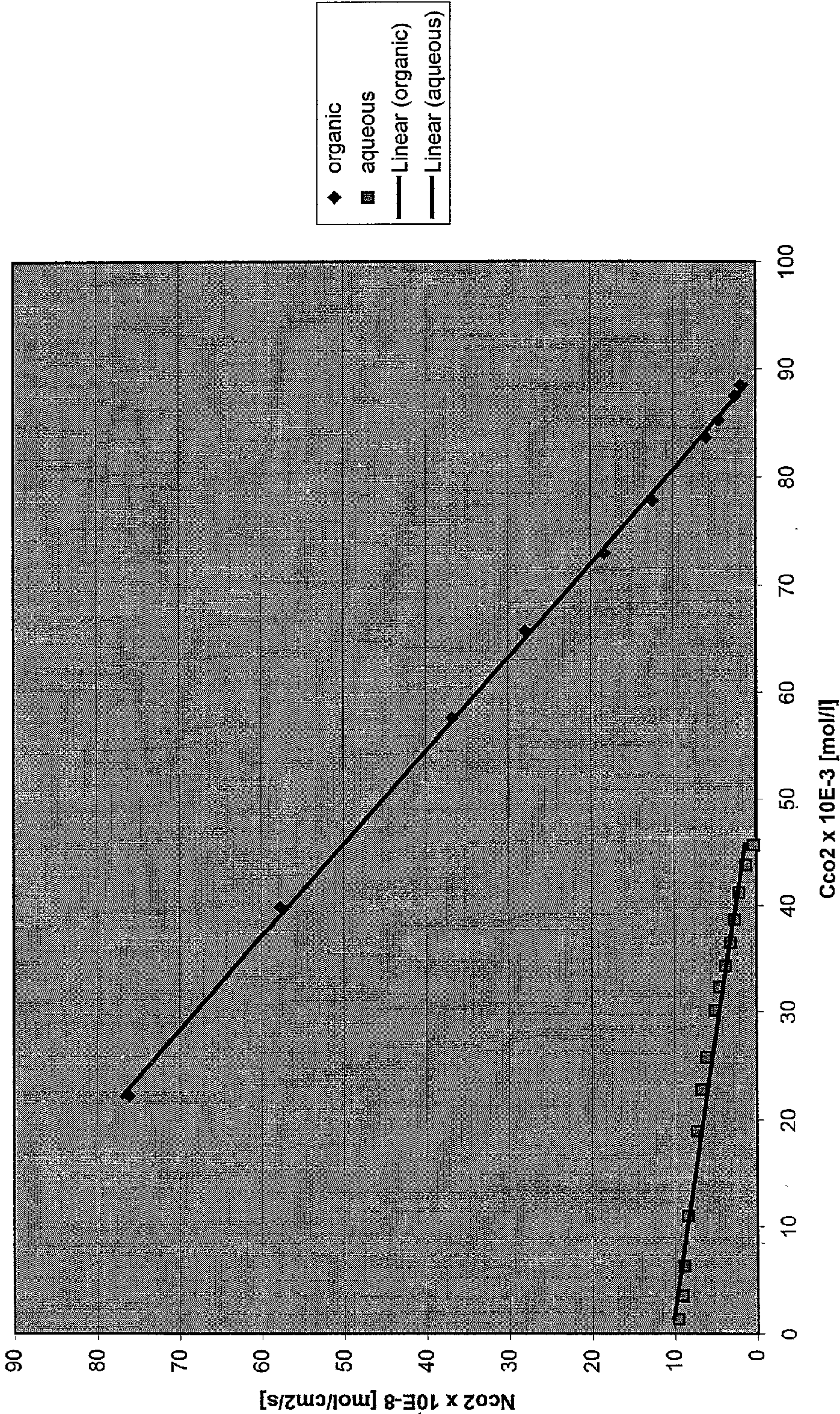


FIGURE 5 B

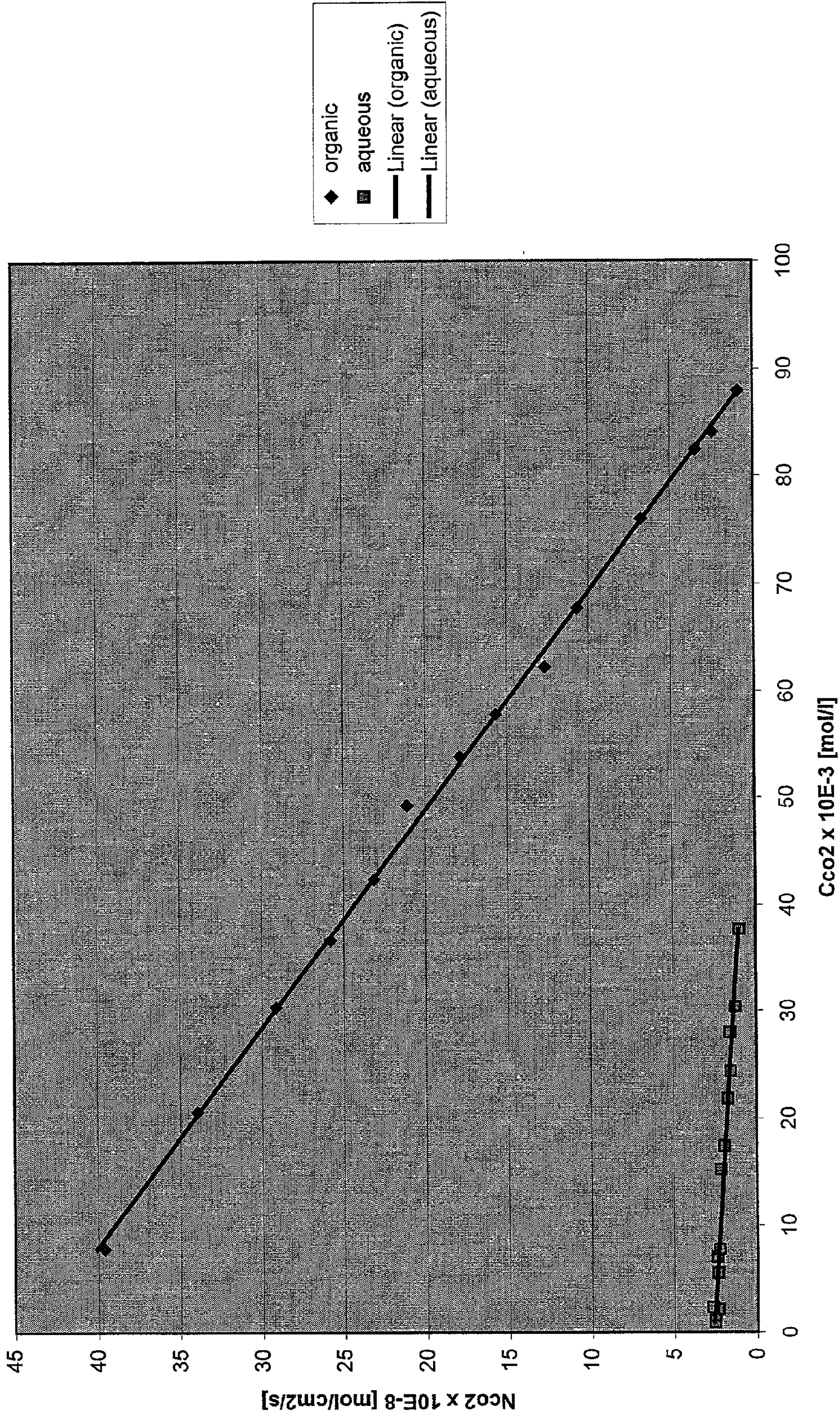


FIGURE 6 A

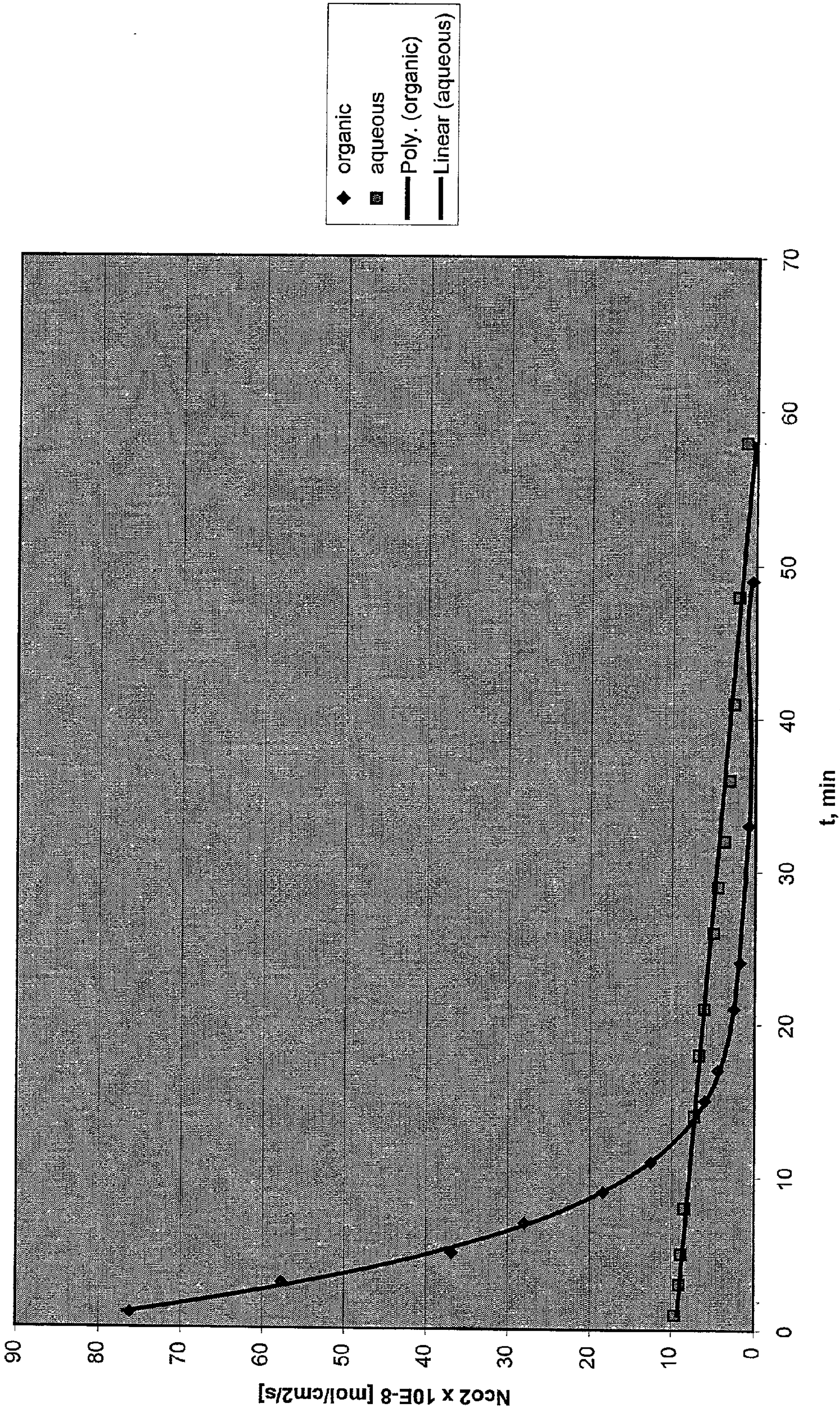
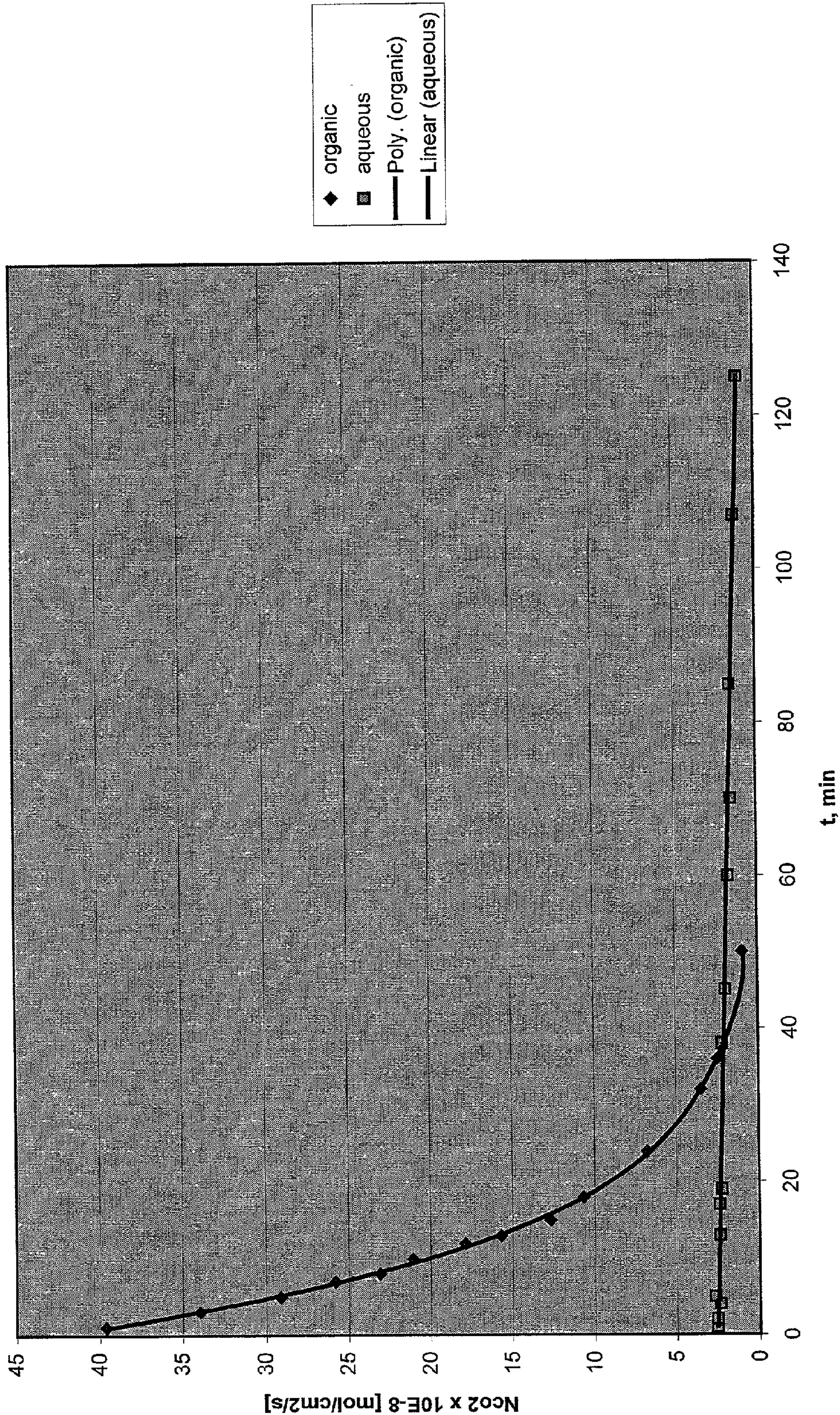


FIGURE 6 B



METHOD FOR GAS SEPARATION BY PHASE ENHANCED GAS-LIQUID ABSORPTION

[0001] No cross-reference to related applications.

[0002] Not Federally sponsored research or development

FIELD OF THE INVENTION

[0003] This invention relates to a method for gas separation. In particular, this invention relates to a new method for gas separation by phase enhanced gas-liquid absorption.

BACKGROUND OF THE INVENTION

[0004] Up to now, absorption is still a powerful tool for the gas separation and purification [Arthur L. Kohl & Fred C. Riesenfeld; Gas Purification. 4th Edition; Gulf Publishing Company; 1985]. However, current processes for the enhancement of gas liquid absorption rate are still limited to the chemical reactions which occurs in the liquid phase between gas component and liquid solution. The drawback is obvious. The reaction will cause difficulty for the release of the gas components from liquid. The chemical reaction brings two benefits for absorption. One is the increase of carrying capacity for gas components. Another is the reduce of mass transfer resistance or increase of mass transfer coefficient. Both factors contribute to the increase of absorption rate. Currently, most popularly used absorbents for carbon dioxide separation include alkanolamines, alkaline salt and their modified form.

[0005] Aqueous solution of alkanolamines has been used widely to separate carbon dioxide from other gas to meet very low treated gas specification. The major commercial interested amines, such as, monoethanolamine (MEA), diethanolamine (DEA) etc. can undergo side reactions with carbon dioxide and form various kinds of degradation compounds. These compounds reduce performance of the solvent and cause more energy consumption and corrosion [R. H. Niswander, D. J. Edwards, M. S. DuPart, and J. P. Tse, Separation science and technology, 28(1-3), pp. 565-578 (1993)].

[0006] Another popular method for carbon dioxide separation is alkaline salt solution. Sodium carbonate and potassium carbonate are the most common used material. The process can be divided into two types based on absorption temperature, ambient temperature (70-100° F.) and elevated temperature (approximating regeneration temperature). At ambient temperature, the absorption is very slow, which causes low efficiency of carbon dioxide recovery and the high steam requirement for regeneration. Absorption at elevated temperature, such as Benfield process, overcome some of the disadvantage of ambient temperature process. By increasing temperature, absorption rate and gas holding capacity are increased. Several modifications have been developed to accelerate the absorption rate of carbon dioxide. In these process, activators or promoters are added into carbonate solution, such as New Activated Benfield Process, The Catacarb Process, The Glammarco-Vetrocoke Process etc. As reported, activated solution is able to reduce the operating costs [The Benfield Corporation. 1971. The way to low cost scrubbing of CO₂ and H₂S from industrial gas].

[0007] Sartori and Savage [Arthur L. Kohl & Fred C. Riesenfeld; Gas Purification. 4th Edition; Gulf Publishing Company; 1985, p 235] compared absorption rates and

vapor-liquid equilibria of CO₂ in unpromoted hot potassium carbonate solutions with solutions promoted with diethanolamine (DEA) and solutions promoted with sterically hindered amines. Both DEA and sterically hindered amines were found to be very effective in increasing the rate of CO₂ absorption. However equilibrium partial pressure of CO₂ is decreased after activator added into the carbonated solution. This means that it is more difficulty to release CO₂ from activated solution than unactivated solution.

[0008] This invention provides a new method for gas liquid absorption process. By introducing another liquid phase into original absorption system to improving mass transfer resistance, the absorption rate is able to be increased significantly. More important, the increase of absorption rate does not cause any difficulty of regeneration.

SUMMARY OF THE INVENTION

[0009] A new method called phase enhanced gas-liquid absorption has been developed. The absorption rate can be enhanced by adding another phase into original absorption system.

[0010] A system with three phase was studied. In the system, gas phase was carbon dioxide. Two liquid phases were used. One was organic phase. Another was aqueous phase. By addition of organic phase into CO₂—aqueous phase absorption system, the absorption rate of CO₂ was increased significantly. CO₂ finally accumulated in aqueous phase. Our experiments proved that

[0011] (1) the absorption rate of carbon dioxide was enhanced by adding organic phase into gas-aqueous phase system;

[0012] (2) organic phase played the role of transportation of gas solute (CO₂). Carbon dioxide finally accumulated into aqueous phase.

[0013] This invention provides a new technology for gas separation by addition of organic phase into CO₂—aqueous phase absorption system. By improving mass transfer resistance in absorption process, this technology is able to lead to a more efficient, low cost absorption process, and significantly reduce design constraints and costs.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is a Schematic diagram of mass transfer model.

[0015] FIG. 2 is a Schematic diagram of the stirring cell in the apparatus of the invention.

[0016] FIG. 3 is a Schematic diagram of the apparatus used for separating gas in accordance with the invention.

[0017] FIG. 4 shows a comparison of the absorption rate of CO₂ by organic phase+aqueous phase with aqueous phase. T=25° C.; P=1 atm; agitation speed =250 rpm.

[0018] FIGS. 5A and 5B show a comparison of the absorption rates of CO₂ by the organic phase and the aqueous phase. T=25° C.; P=1 atm; V=300 ml; agitation speed=250 rpm (5A); 106=rpm (5B)

[0019] FIGS. 6A and 6B show the relationship between the absorption between the absorption rate of CO₂ with

absorption time. $T=25^{\circ}\text{C}$; $P=1\text{ atm}$; $V=300\text{ ml}$; agitation speed $=250\text{ rpm}$ (6A); 106 rpm (6B)

DETAILED DESCRIPTION OF THE INVENTION

[0020] 1. Basic Concept

[0021] The definitions of absorption is a process which transfers one or more components of a gas phase to a liquid phase in which it is soluble. The operation of absorption can be categorized on the basis of the nature of the interaction between absorbent and absorbate into following two types, traditionally[Perry, John H. Chemical Engineering Handbook; McGraw-Hill, Inc. 1963][Danckwerts, P. V. Gas-Liquid Reactions; McGraw-Hill, Inc. 1970]:

[0022] (1) Physical absorption. The component being absorbed in physical absorption is more soluble in the liquid absorbent than are the other gases with which it is mixed but does not react chemically with the absorbent.

[0023] (2) Chemical absorption. Chemical absorption is characterized by the occurrence of a chemical reaction between the gaseous component being absorbed and a component in the liquid phase to form a compound.

[0024] (3) Phase enhanced absorption or Phase enhanced gas-liquid absorption. The new concept we present here is "Phase enhanced gas-liquid absorption". In our study, we found that adding organic phase into the gas-liquid (aqueous phase) absorption system is able to enhance the absorption rate. We call this type of process as phase enhanced gas-liquid absorption. In phase enhanced gas-liquid absorption, more than one liquid phases was involved in the absorption process. One of the liquid phase was called as carrying phase, in which gas solute will be finally accumulated. Other liquid phase is known as transportation phase. The transportation phase only plays the rule for the transportation of the gas solute from gas phase to carrying phase and for the increase of absorption rate. In phase enhanced absorption, the absorption rate is enhanced by the transportation phase.

[0025] (4) Mass Transfer Equation

[0026] Mass transfer equation for physical absorption can be expressed:

$$N_A = k_L(C_A^* - C_A)$$

[0027] where N_A is the rate of absorption per unit area of surface. k_L is the physical mass transfer coefficient. C_A^* is the concentration of dissolved gas corresponding to equilibrium with the partial pressure of the gas at the interface between gas and liquid. C_A is the average concentration of dissolved gas in the bulk of the liquid.

[0028] For chemical absorption, the Mass transfer equation can be expressed:

$$N_A = E_R k_L(C_A^* - C_A)$$

[0029] Here E_R , enhancement factor, can be identified with the ratio of rate of absorption in the presence of reaction to the rate of absorption without reaction.

[0030] Similarly, for the phase enhanced absorption, the Mass transfer equation can be expressed:

$$N_A = E_P k_L(C_A^* - C_A)$$

[0031] Here E_P can be identified with the ratio of rate of absorption in the presence of another phase (transportation phase) to the rate of absorption without transportation phase.

[0032] (5) Mass Transfer Model for Phase Enhanced Absorption

[0033] By above definition, mass transfer of phase enhanced gas-liquid absorption can be described as follows:

[0034] When gas contacts with liquid phases, gas is first absorbed by transportation phase. The absorption is either physical or chemical. The gas solute dissolved in the transportation phase passes through the interface between transportation phase and carrying phase, and then enters into carrying phase. In carrying phase, gas solute may exist in two form, physical solubility or chemical combination. The function of the transportation phase is to deliver gas solute from gas phase to carrying phase and to increase the absorption rate. With film theory, the mass transfer model of phase enhanced gas-liquid absorption can be drawn as FIG. 1.

[0035] The pathway of gas solute from gas phase to carrying phase can be stated as follows:

[0036] (1) gas solute transfer from bulk of gas phase to the interface of gas-transportation phase.

[0037] (2) gas solute transfer from the interface of gas-transportation phase to the interface of transportation-carrying phase. In the transportation phase, gas solute may react with the components in transportation phase or just simply physical solubility.

[0038] (3) gas solute at the interface of transportation-carrying phase transfers into the bulk of carrying phase. Same as above, gas solute has two ways to deal with the components in carrying phase: one is physical solubility, i.e. without reaction between gas solute and the components in carrying phase; another is chemical combination, i.e. there is reaction between gas solute and the components in carrying phase.

[0039] 2. Experimental Apparatus and Method

[0040] The main experimental equipment was a stirring cell. The structure of the cell is shown in FIG. 2. The stirring cell is made of glass with 100 mm inner diameter and 130 mm depth. Two agitating blades, one for liquid, one for gas, was driven by direct current motor. The agitating speed was counted by a laser meter. The experimental apparatus is shown in FIG. 3. Carbon dioxide from cylinder 1 past through buffer bottle 3 and pressure stable tube 4. Gas flow rate was controlled and measured by rotating flow meters 5,8. Gas clean system consists of two U tubes. U tube 6 was filled by silicon gel. U tube 7 was filled by active carbon. Gas was saturated with moisture by bottle 9 which contained the same solution as that in stirring cell 14, and then absorbed in stirring cell 14. Gas was measured by foam film flow meter 10 and 12 before and after reaction cell 14. After measurement, gas was released.

[0041] The absorption rate of carbon dioxide at time t was determined by the difference of two flow rates, in and out of stirring cell, measured by two foam film flow meters 10 and 12. As the results of the measurement, the relationship of absorption rate r and time t would be obtained. Integration

of absorption rate with time, $r \sim t$, the total amount of carbon dioxide absorbed into the liquid phase can be obtained.

[0042] The equilibrium concentration of carbon dioxide in carrying phase can be simply determined by using ideal gas equation after carbon dioxide released from carrying phase by sulfuric acid. The mass balance of carbon dioxide from integration of $r \sim t$ data and the analysis of carrying phase should be matched well. If error higher than 5%, the data discarded.

[0043] The experiments were conducted at room temperature (25° C.) and 1 (atm). Gas solute was carbon dioxide. The purity of carbon dioxide was higher than 99.9% two liquid phases were involved. One was organic phase (transportation phase), which played the role of transportation of gas solute CO₂. Another was aqueous phase, which was carrying phase. The organic phase was made up of Alamine 336, a mixture of C₈-C₁₂ tertiary amine, and 2-ethylhexyl alcohol (1:1 ratio by volume). Aqueous phase was the solution of sodium formate (400 g/l). The absorption was operated at semi-continuous basis. Carbon dioxide run through the absorption apparatus continuously. The liquid was run batchwise. The absorption system was agitated by two blades in agitation cell, one for liquid, one for gas. The agitation speed and phase ratio (transportation phase:carrying phase) is specified in each experiment.

[0044] The method in accordance with the invention is illustrated on the basis of following examples in which gas takes CO₂ for example. Invented method can be applied to the separation and purification of carbon dioxide from gas mixture. However, it is not limited to carbon dioxide absorption process. The invented method also can be applied to other gas absorption processes, such as SO₂, H₂S etc.

EXAMPLE 1

Absorption Rate was Enhanced by Adding Organic Phase Into the Absorption System of CO₂-sodium Formate Aqueous Solution

[0045] Two experiments were designed to compare the rates of carbon dioxide absorption (a) carbon dioxide was absorbed by 280 ml sodium formate solution (400 g/l)+20 ml organic phase (50% Alamine 336 by volume and 50% 2-ethylhexyl alcohol by volume); (b) carbon dioxide was absorbed by 300 ml sodium formate solution (400 g/l) directly.

[0046] In experiment (a), 280 ml sodium formate solution (400 g/L) and 20 ml organic phase were added into agitating cell. The organic phase existed on the top layer. Liquid was agitated gently to avoid breaking the organic layer. Carbon dioxide from gas phase has to pass through the organic phase in order to enter into aqueous phase. In experiment (b), 300 ml sodium formate solution (400 g/L) was placed into agitating cell. Both experiments operated under the same experimental conditions, temperature=25 ° C., pressure=1 atm, agitation speed=250 rpm, the concentration of CO₂ was higher than 99.9%. The results are shown in FIG. 4. From FIG. 4, it can be seen that the absorption rate of carbon dioxide in experiment (a) was higher than that in experiment (b). This means that absorption rate of CO₂ by sodium formate aqueous solution was increased by adding organic phase into the system.

EXAMPLE 2

Organic Phase (Transportation Phase) Plays the Role of Transportation of Carbon Dioxide from Gas Phase to Aqueous Phase

[0047] (1) Comparison of Absorption Rate Both by the Organic Phase and Aqueous Phase

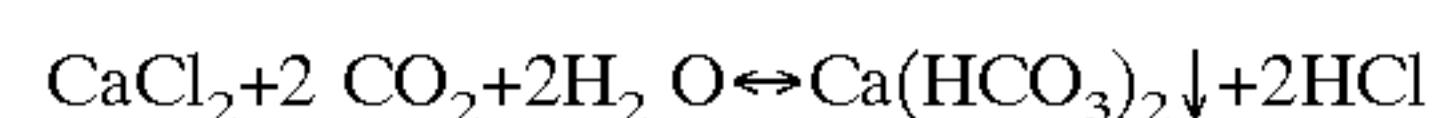
[0048] CO₂ absorption rate by aqueous phase and by organic phase was measured individually at the same experimental condition, i.e., temperature (25 ° C.), pressure (1 atm, 99.9% CO₂ gas used), agitation speed (250 and 106 rpm). The experimental results are shown in FIG. 4. It can be seen from FIG. 4 that the absorption rate of CO₂ by 300 ml organic phase (50% Alamine 336 by volume and 50% 2-ethylhexyl alcohol by volume) much faster than that by 300 ml aqueous phase (the aqueous solution of sodium formate 400 g/L). FIG. 5(a) was the result at the agitation speed of 250 rpm. FIG. 5(b) was the result at the agitation speed of 106 rpm. It can be seen that the absorption rate of carbon dioxide by organic phase was ten times more than that by aqueous phase. When aqueous phase and organic phase existed in the same absorption system, the absorption of carbon dioxide by aqueous phase is able to be neglected as long as the surface area between gas and organic phase is larger than or equal to the surface area between gas and aqueous phase.

[0049] The relationship between the absorption rate of carbon dioxide with absorption time is shown in FIG. 6. From FIG. 6, it is obvious that carbon dioxide reached equilibrium in organic phase much earlier than that in aqueous phase. So, the organic phase was saturated by carbon dioxide much earlier than the aqueous phase when both in the same system at the same time and the same experimental conditions.

[0050] The experimental results also proved that the mass transfer resistance of CO₂ absorption by organic phase was much lower than that by aqueous phase.

[0051] (2) Possibility of Carbon Dioxide to be Transferred from Organic Phase to Aqueous Phase

[0052] To determine whether carbon dioxide absorbed in organic phase was able to be transferred into aqueous phase, the following experiment was designed. The calcium chloride was selected because the similar mechanism of reaction and mass transfer occurs as sodium formate aqueous solution. Furthermore, calcium carbonate and calcium bicarbonate had little solubility in water. The results were easy to be identified by the white deposits if carbon dioxide was able to enter into aqueous phase from organic phase.



[0053] As usual, 300 ml organic phase (50% Alamine 336 by volume and 50% 2-ethylhexyl alcohol by volume) was placed into the agitated cell. Carbon dioxide was absorbed into the organic phase. CO₂ gas was stopped after the organic phase was saturated with carbon dioxide. Then calcium chloride solution with the concentration of 300 g/l was poured into the agitating cell immediately. The liquid was kept agitated at the rate of 300 r/min. The experimental temperature was 25° C. Rest of the experimental conditions were: pressure=1 atm, organic phase volume=300 ml, volume of aqueous phase=80 ml. After about ten minutes of agitation, large amounts of white deposit appeared in the

aqueous phase. This experiment proved that carbon dioxide absorbed into organic phase was able to be transferred into aqueous phase and further reacted with the salt (calcium chloride in this case) in the aqueous phase. was kept agitated at the rate of 300 r/min. The experimental temperature was 25° C. Rest of the experimental conditions were: pressure=1 atm, organic phase volume=300 ml, volume of aqueous phase=80 ml. After about ten minutes of agitation, large amounts of white deposit appeared in the aqueous phase. This experiment proved that carbon dioxide absorbed into organic phase was able to be transferred into aqueous phase and further reacted with the salt (calcium chloride in this case) in the aqueous phase.

1. A method for gas separation by phase enhanced gas-liquid absorption comprising three phase: gas phase, organic phase and aqueous phase, wherein said organic phase is added into gas-aqueous phase absorption system and resulted in an increase of absorption rate, and said organic phase is played the role of transportation of gas solute from gas phase to aqueous phase.

2. The method of claim 1, wherein said gas phase are CO₂, SO₂, H₂S or its mixture.

3. The method of claim 1, wherein said organic phase are alkane, alcohol, ether, ester, amine or organic compounds forming two phases with aqueous phase or their mixture.

4. The method of claim 1, wherein the ratios of said organic phase to said aqueous phase are 1 to 1-1000 by volume.

5. The method of claim 1, wherein the gas solute content in said gas phase is about 0.001% to about 100%.

6. The method of claim 1, wherein said gas separation is carried out at temperature from about 1° C. to about 500° C.

7. The method of claim 1, wherein said gas separation is carried out under a pressure from about 10⁻⁶ atm to about 10⁶ atm.

8. The method of claim 1, wherein said aqueous phase include all types of aqueous solution.

9. Invented method can be applied to the separation and purification of carbon dioxide from gas mixture. However, it is not limited to carbon dioxide absorption process. The invented method also can be applied to other gas absorption processes, such as SO₂, H₂S etc.

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