Interaction of Potassium and Ammonium ions in Soil

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About K^+ and NH_4^+

A pair of ions with some special and interesting characteristics

Similarity

- Similar crystal ionic radii, 0.133nm and 0.143nm for K^+ and NH_4^+, respectively ;
- Relatively low hydration energies;
- Both ions may be trapped into the hexagonal cavity in the basal oxygen plane of 2:1 phyllosilicates and thought to be fixed by the similar or same mechanism

With these similarities …

- If one of the two ions was added into soil prior to another one , then the amount of the ion added later would be reduced in proportion to the amount of the one previously adsorbed.

- If added together, the amount and rate of adsorption of the 2 ions would be the same.

However, …

- When added simultaneously to an H-saturated Mt, more K^+ than NH_4^+ was fixed at lower concentrations, reversed results found at higher concentrations (Joffe and Levine,1947).
- Other works observed a preference of NH_4^+ to K^+ (Bower, 1950; Nommik, 1957; Nielsen, 1972)

Objective of this study

- To compare the adsorption characteristics of K^+ and NH_4^+ on soil;
- To compare the effect of K^+ and NH_4^+ interaction on the adsorption of these two ions

By some kinetics experiments

Materials and methods

Original soil sample:

Rego Chernozem, from Saskatoon.
Texture: clay (with 20.0% of sand, 36.3% of silt, and 43.7% of clay).

Organic C: 1.102

Materials and methods

Preparation of Ca-saturated clay samples

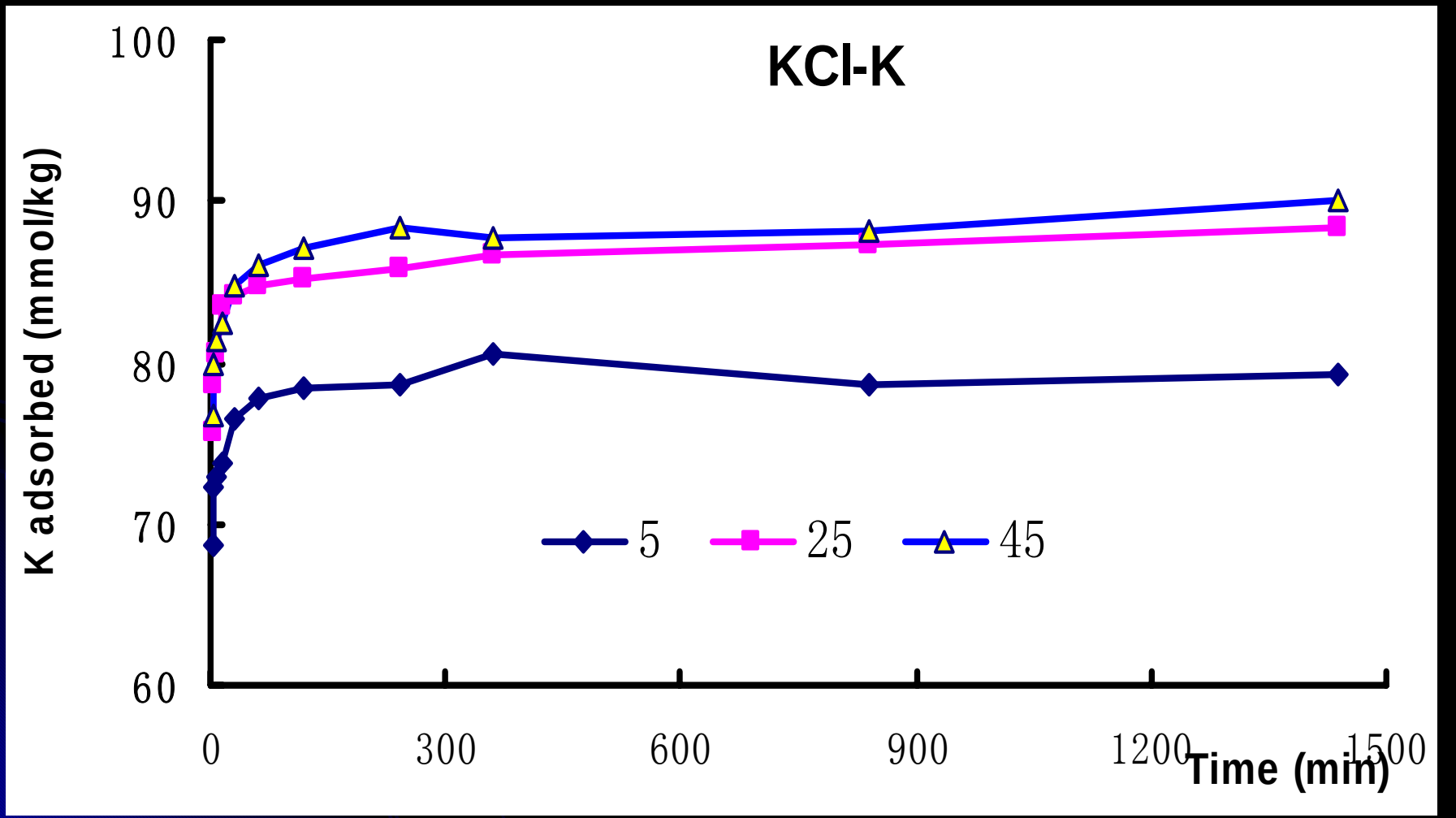
- The sedimentation method was used to obtain the < 2 μ m clay fractions from the soil samples.
- The < 2 μ m clay fractions were then washed with 0.5 M $CaCl_2$ for 5 times to obtain the Ca-saturated clay samples for the purpose of kinetics study.
- The excess Ca^{2+} was removed by the subsequent washing with deionized distilled water until a negative test for Cl^- was obtained by $AgNO_3$.
- The Ca-saturated < 2 μ m clay samples were then dispersed in deionized distilled water by a Sonifier and stored in a 10-L plastic bottle.
- The clay concentration was kept at 0.14 g of clay (DW) in every 10 mL of the well mixed suspension.

Materials and methods

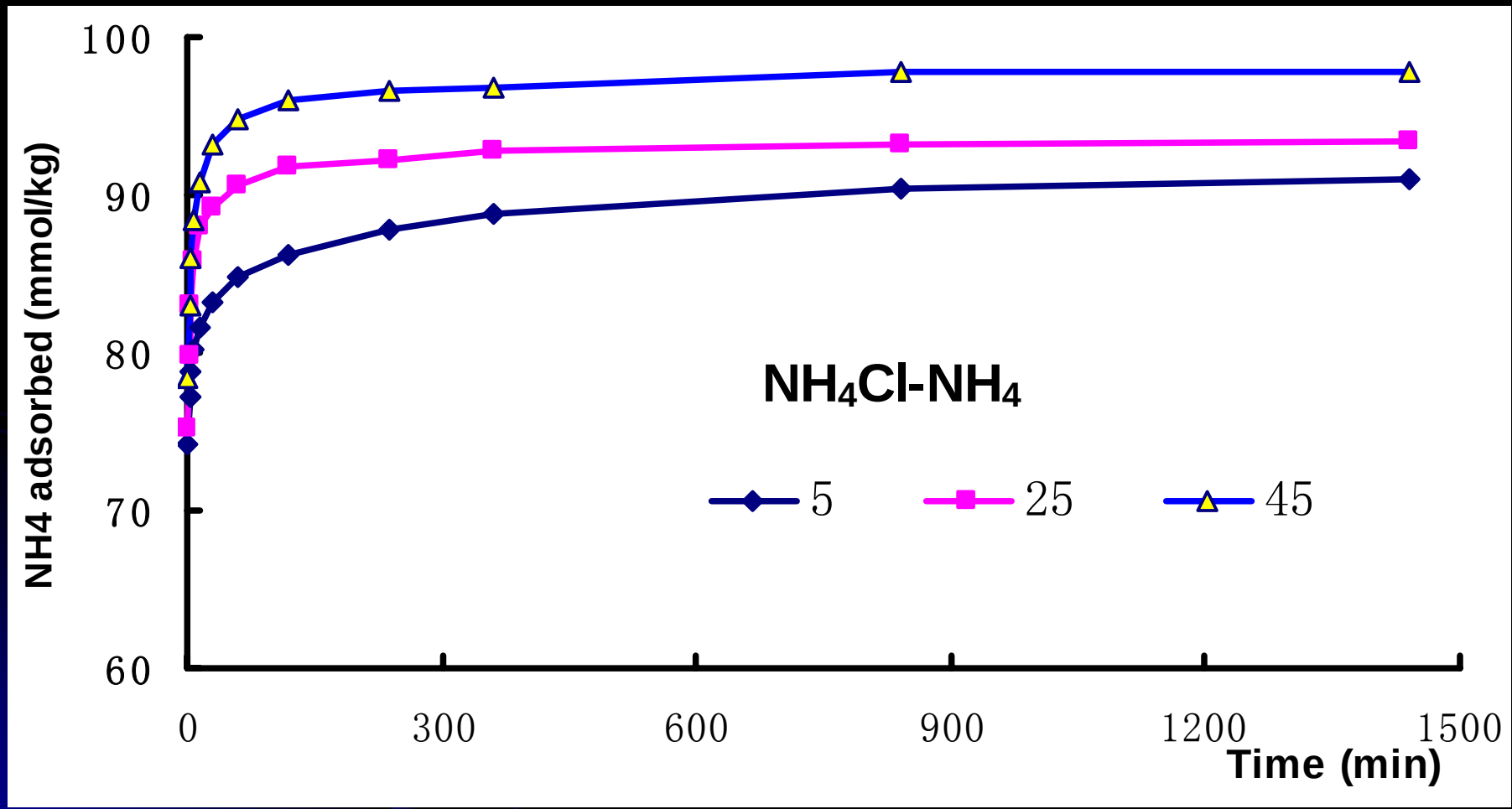
Adsorption kinetics experiment

- The batch technique was used in the kinetics experiments.
- 10 mL of 5.12 mM KCl, NH_4Cl or KCl and NH_4Cl was added into a 125-mL triangular flask with 10 mL of the clay suspension, placed on a shaker bath, and maintained at the temperatures of 5, 25, and 45 ^{o}C.
- Then shake for 2, 4, 8, 16, 30, 60, 120, 240, 360, 840, and 1440 min.
- At the end of each reaction period, the suspension was filtered through a Millipore membrane with 0.25 μ m pore size by a vacuum pump.
- The concentration of K in the filtrate was determined directly by flame emition. And the concentration of NH_4 was determined by the automatic analyzer.
- Each experiment was done in triplicate.

Adsorption of K^+ from KCl solution on soil clay at different temperatures



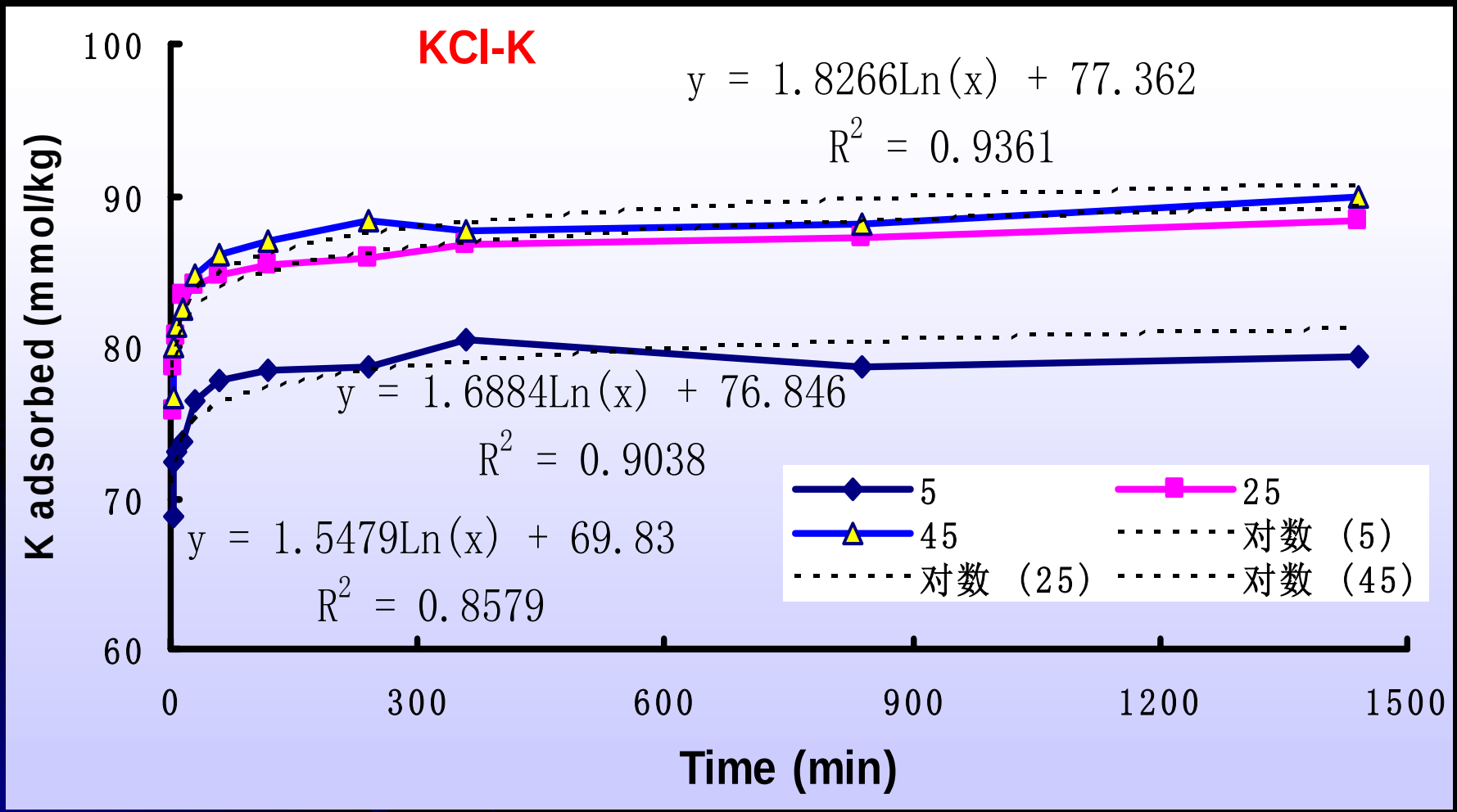
Adsorption of NH_4^+ from NH_4Cl solution on soil clay at different temperatures



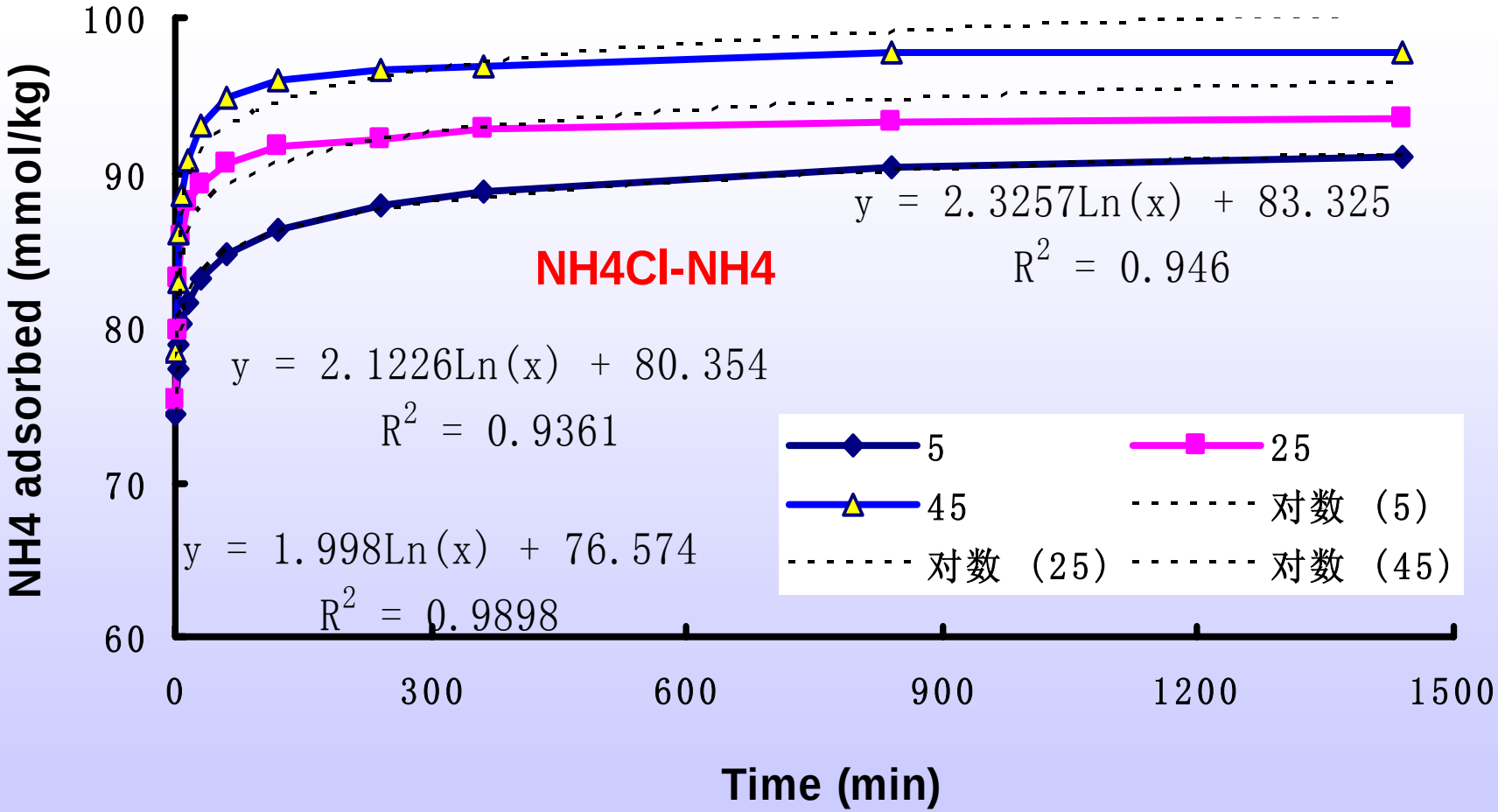
Comparison of K^+ and NH_4^+ adsorption amount from single solution

Temp (°C)	Ion	Amount adsorbed	
		2min	Balanced
5	K	68.71	79.29
	NH_4	77.29	91.00
25	K	75.71	88.26
	NH_4	79.81	93.43
45	K	76.71	90.00
	NH_4	83.00	97.71

Elovich equation fitting curve of K^+ adsorption from KCl solution



Elovich equation fitting curve of NH_4^+ adsorption from NH_4Cl solution



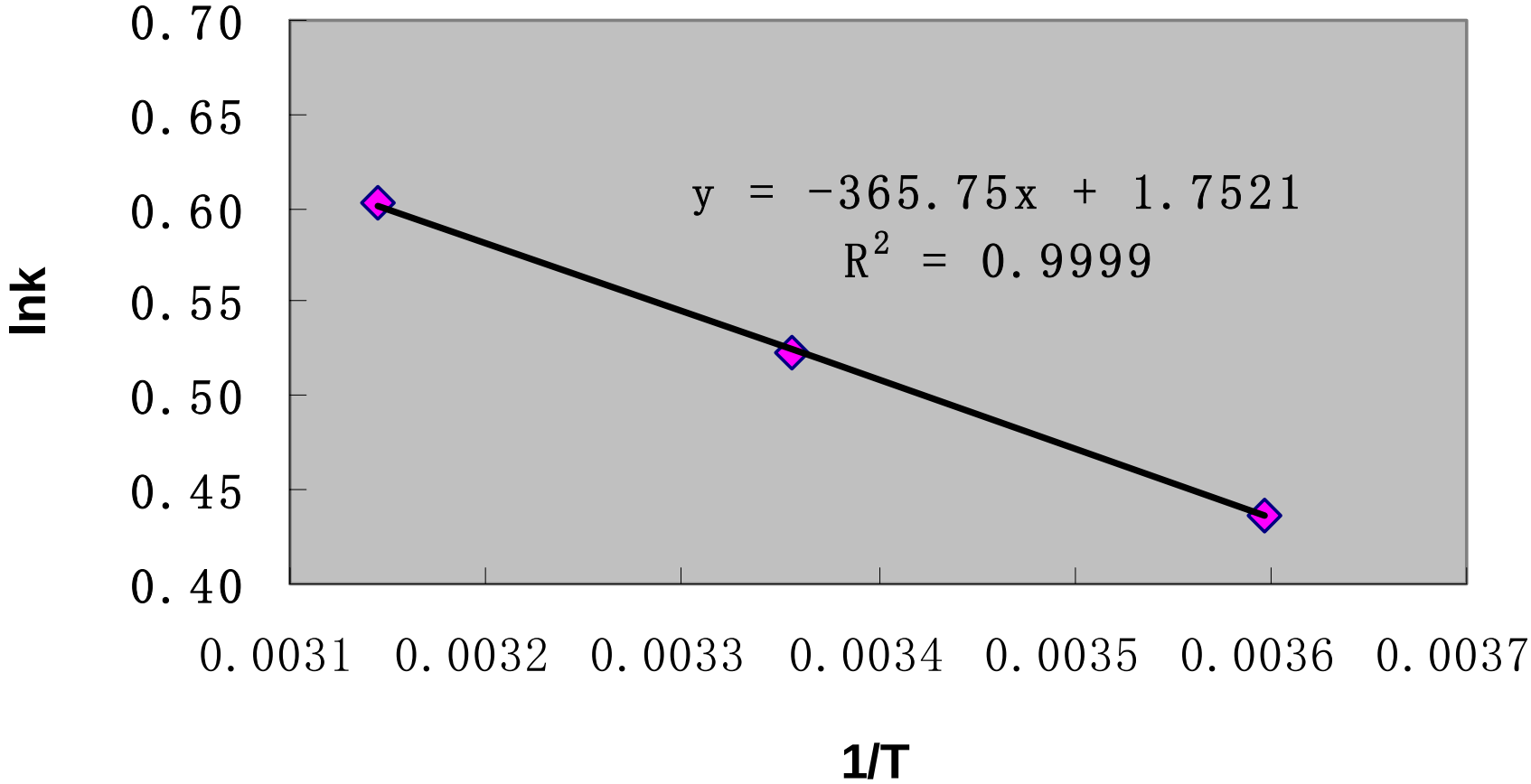
According to

Arrhenius Equation

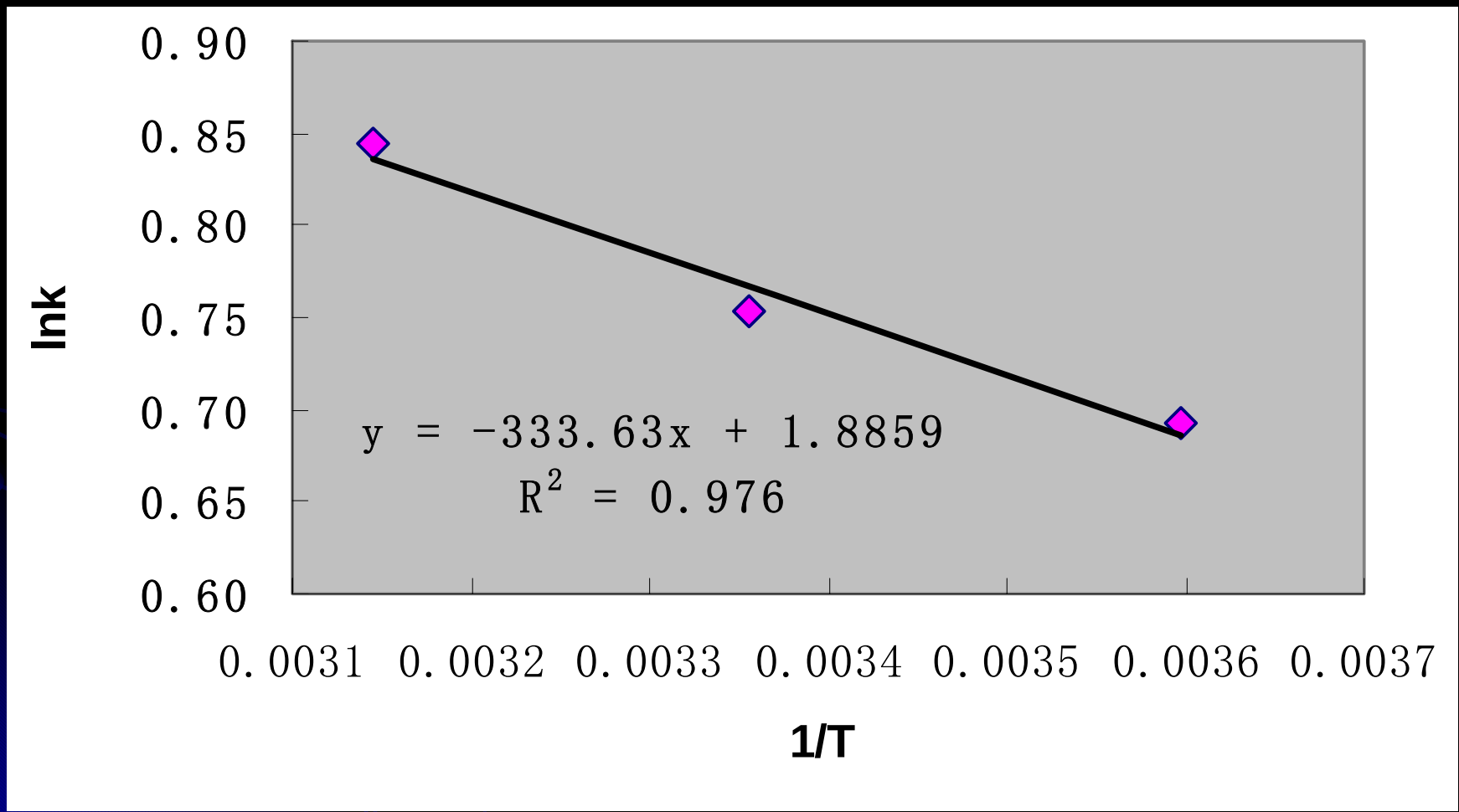
$$\ln k = -\frac{E_a}{RT} + \ln A$$

- **A: pre-exponential factor（frequency factor）;**
- **E_a: *Arrhenius* activation energy**

Arrhenius plots of K^+ adsorption kinetics from KCl solution



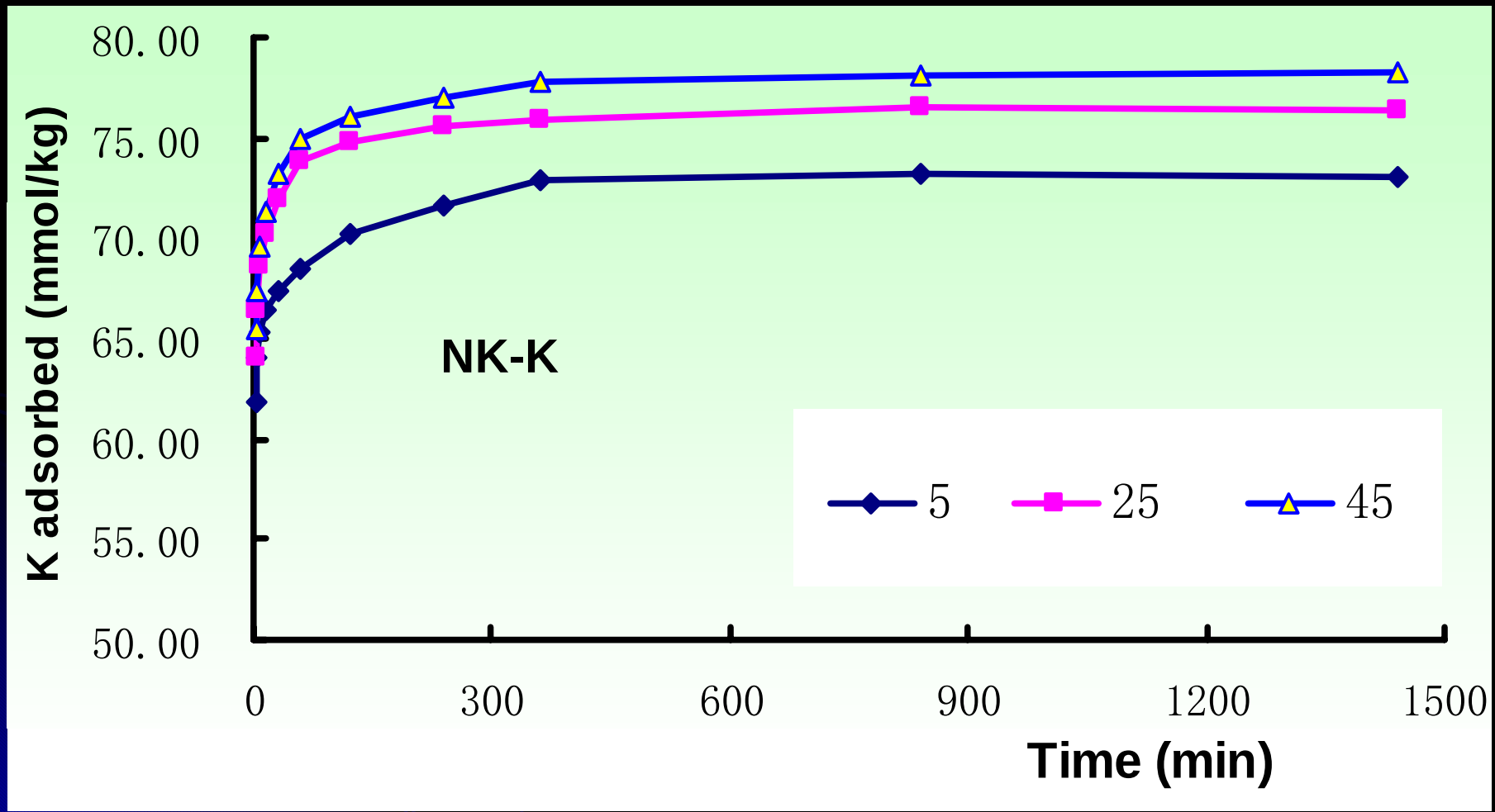
Arrhenius plots of NH_4^+ adsorption kinetics from NH_4Cl solution



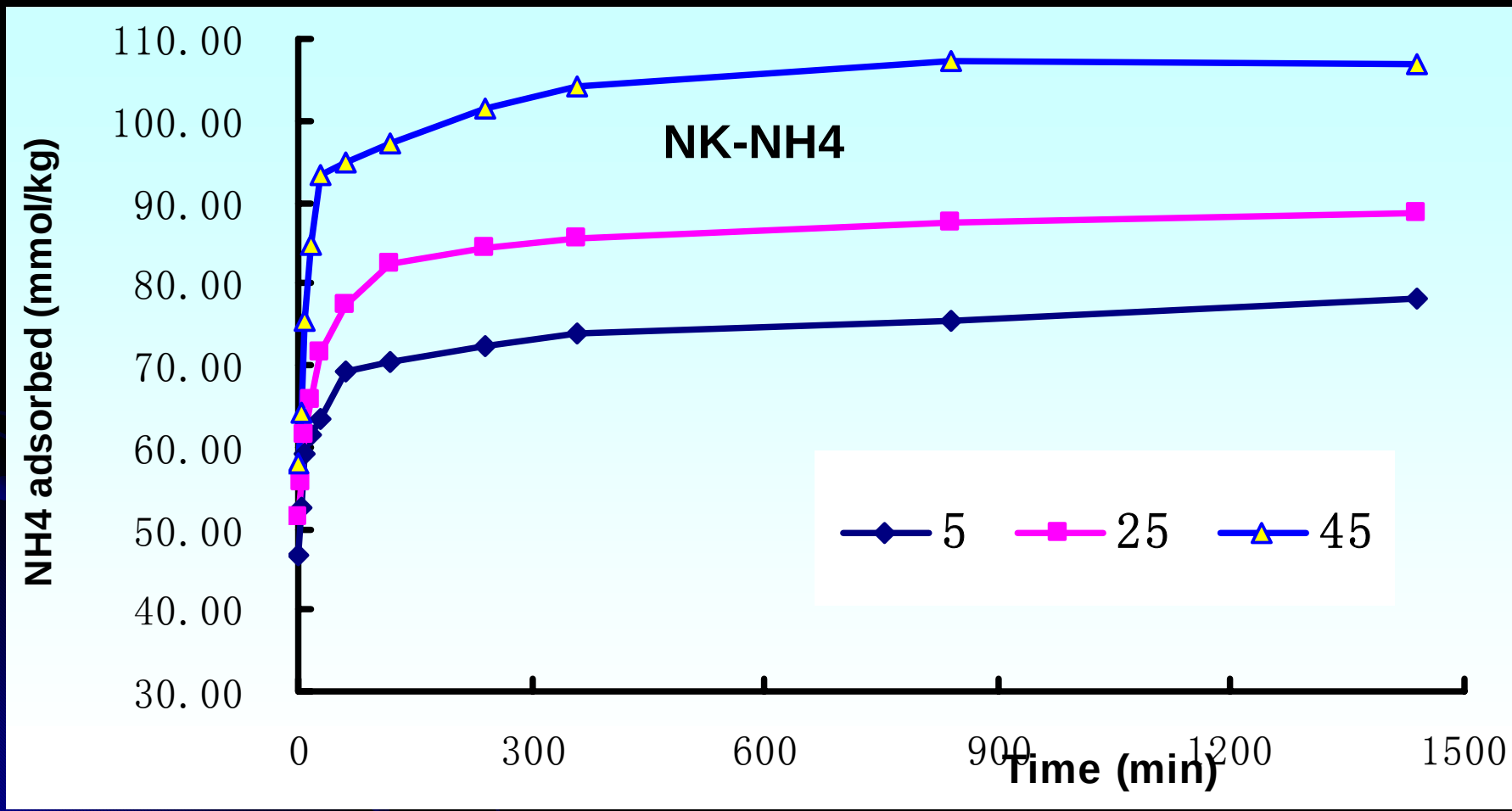
Effect of temperature on K^+ and NH_4^+ adsorption from single solution

Temp (°C)	Rate constant	
	KCl-K	NH_4Cl-NH_4
5	1.548	1.998
25	1.688	2.123
45	1.827	2.326
Ea	3.04	2.77
A	5.77	6.59

Adsorption of K^+ from mixed KCl and NH_4Cl solution on soil clay at different temperatures



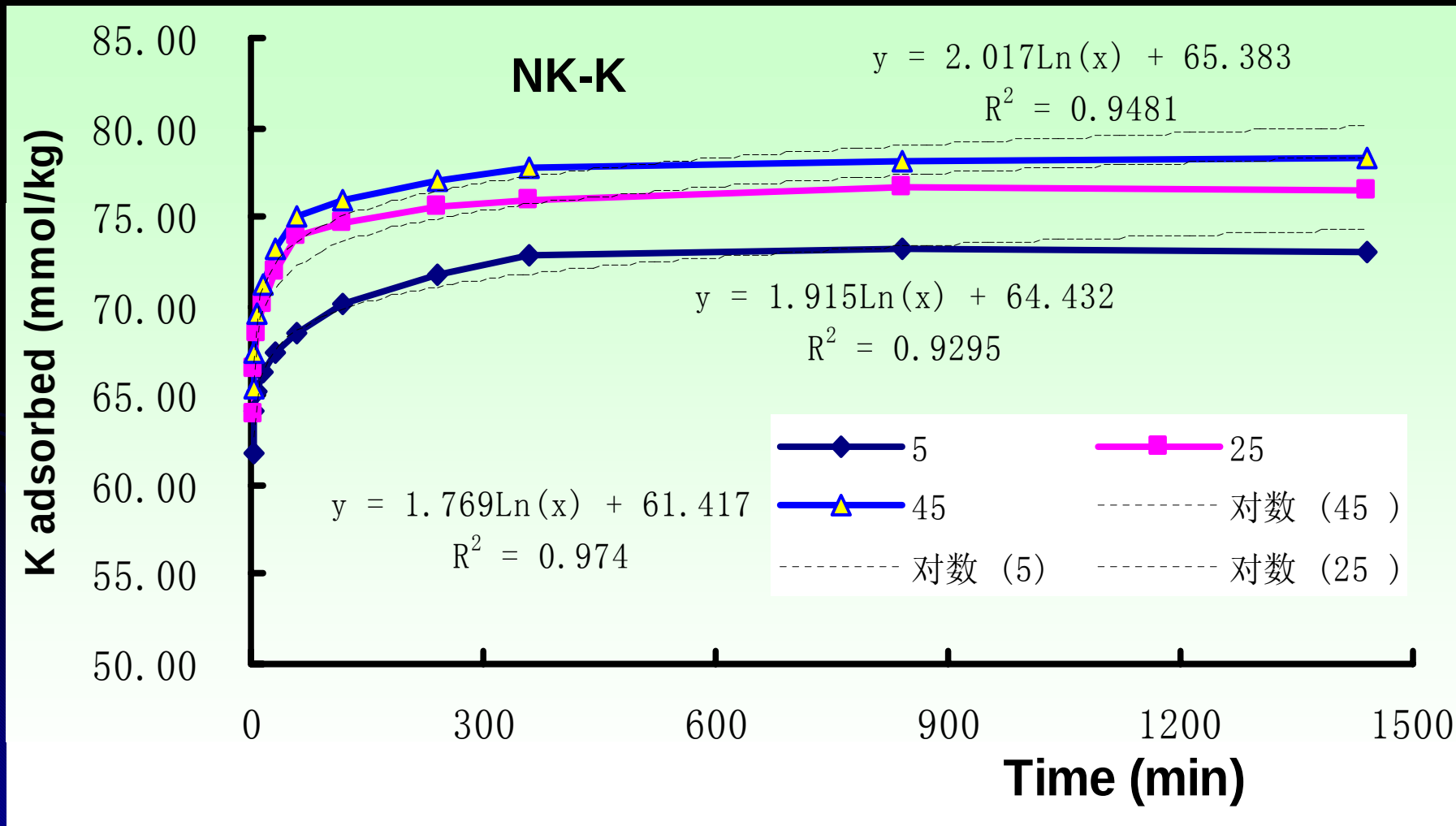
Adsorption of NH_4^+ from mixed KCl and NH_4Cl solution on soil clay at different temperatures



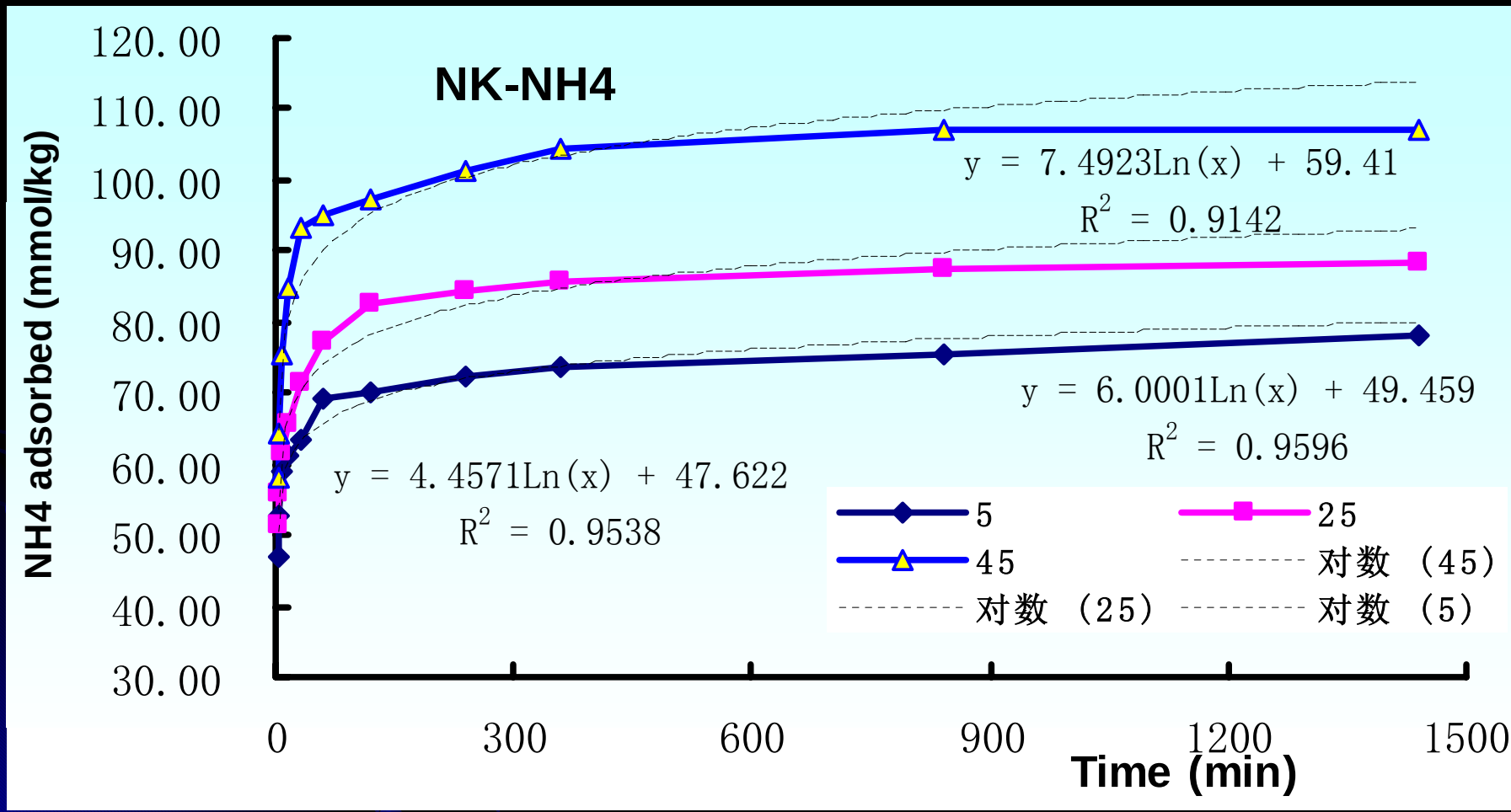
Comparison of K^+ and NH_4^+ adsorption from mixed solution

Temp (°C)	Ion	Amount adsorbed	
		2min	Balanced
5	K	61.82	73.00
	NH_4	46.71	78.14
25	K	64.00	76.43
	NH_4	51.43	88.57
45	K	65.43	78.29
	NH_4	57.86	107.00

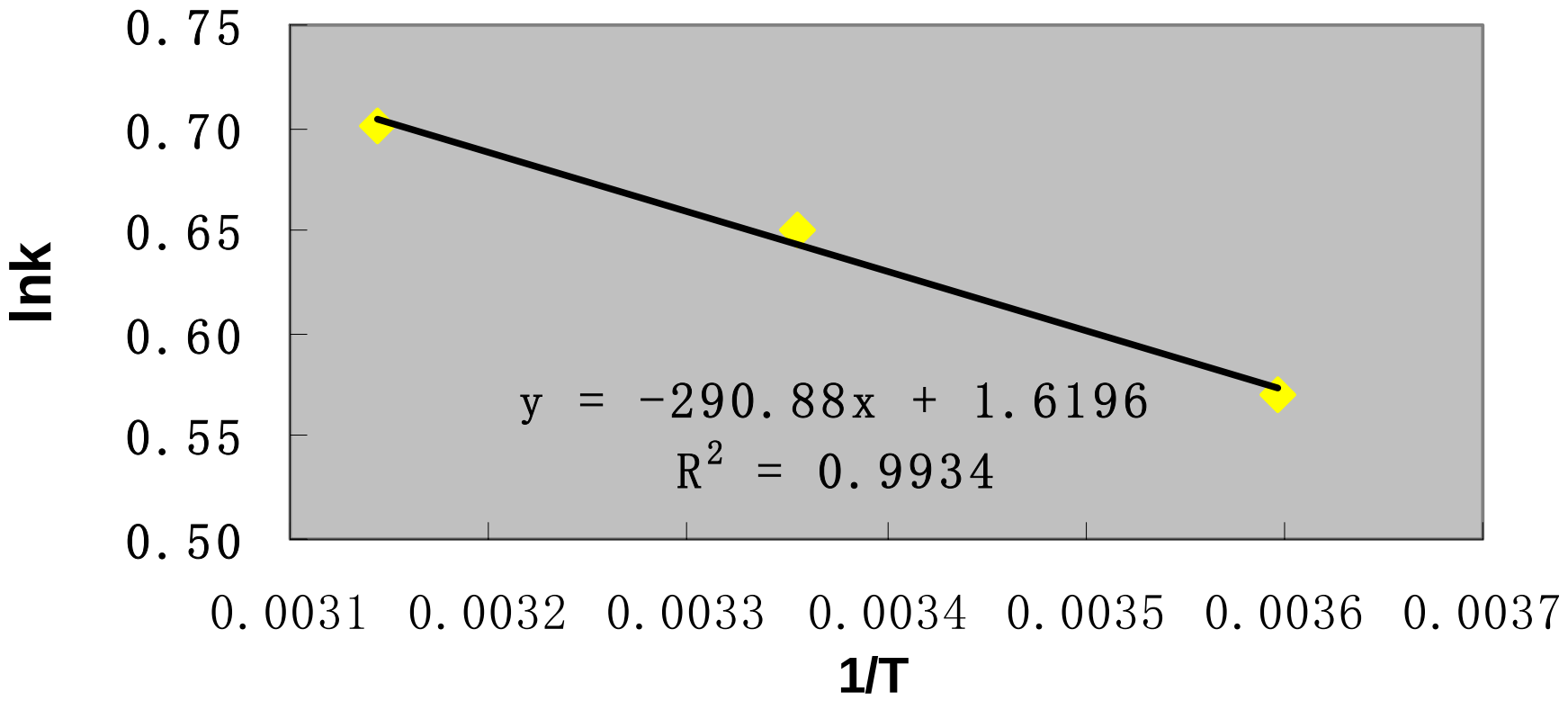
Elovich equation fitting curve of K+ adsorption from mixed KCl and NH_4Cl solution



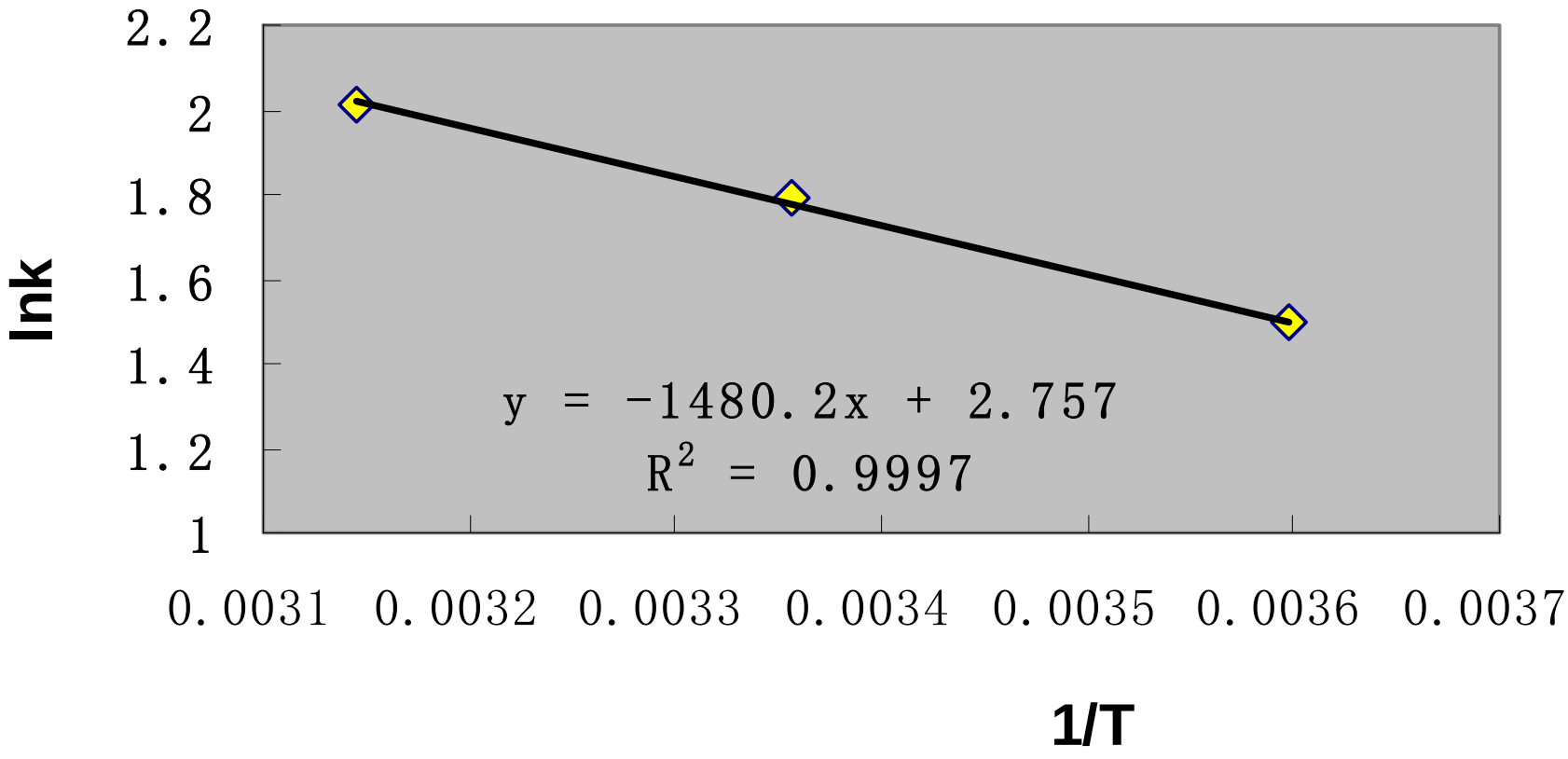
Elovich equation fitting curve of NH_4^+ adsorption from mixed KCl and NH_4Cl solution



Arrhenius plots of K^+ adsorption kinetics from mixed KCl and NH_4Cl solution



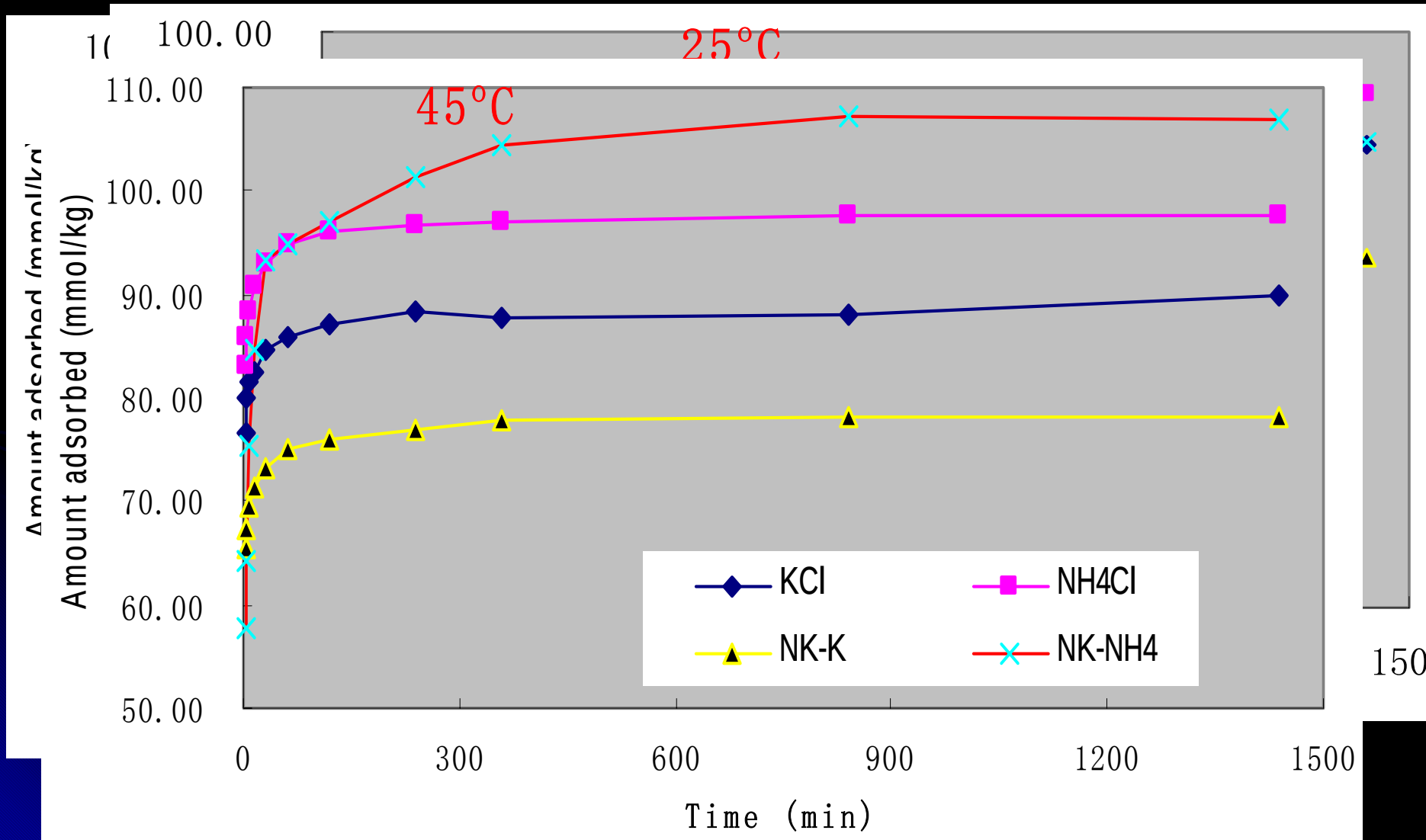
Arrhenius plots of NH_4^+ adsorption kinetics from mixed KCl and NH_4Cl solution



Effect of temperature on K^+ and NH_4^+ adsorption from mixed KCl and NH_4Cl solution

Temp (°C)	Rate constant	
	KCl-K	NH_4Cl-NH_4
5	1.769	4.457
25	1.915	6.000
45	2.017	7.492
Ea	2.42	9.56
A	5.05	13.97

Comparison of K^+ and NH_4^+ adsorption amount from single and mixed solution



Amount ratio of K^+ to NH_4^+ adsorbed from KCl and NH_4Cl mixed solution

Time (min)	Temperture (°C)		
	5	25	45
2	1.32	1.24	1.13
4	1.22	1.19	1.05
8	1.10	1.12	0.92
16	1.08	1.07	0.84
30	1.06	1.01	0.78
60	0.99	0.95	0.79
120	1.00	0.91	0.78
240	0.99	0.90	0.76
360	0.99	0.89	0.75
840	0.97	0.88	0.73
1440	0.93	0.86	0.73

Conclusion

- The adsorption amount of both K and NH_4 enlarged with the increase of temperature
- The amount of NH_4 was higher than that of K adsorbed at the same temperature
- The adsorption of K was greatly retarded by NH_4 co-application; the adsorption of NH_4 was also reduced by K at low temperature, but facilitated at high temperature
- Arrhenius activation energy (Ea) and pre-exponential factor (A) could bring a clue to explore the mechanism of effect of K and NH_4 interaction on the adsorption of these two special ions


THANKS

活化能 E_a 的求算

作图法：

$$\ln k = (-\frac{E_a}{R}) \cdot \frac{1}{T} + \ln A$$

由实验测得不同温度 T 时的速率常数 k，作图 $\ln k \sim 1/T$，曲线的在某一温度的斜率为：

$-\frac{E_a}{R}$ $\Rightarrow$ 该温度的活化能：E_a