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SORPTION OF FORMIC ACID FROM AQUEOUS SOLUTIONS ON THE AN-31 ANION EXCHANGE RESIN

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Abstract

The accumulation of heat-stable salts (HSS) in methyldiethanolamine (MDEA) solutions during natural gas sweetening causes corrosion, foaming and a loss of the useful capacity of the amine; such salts are not decomposed under conventional regeneration. One of their principal sources is formic acid produced by the oxidative degradation of MDEA. In this work, the sorption of formic acid on the weakly basic anion exchanger AN-31 was studied in aqueous solutions over the range of 293–313 K. The equilibrium data conformed to the Langmuir model, and the maximum adsorption capacity reached 175.43 mg·g^{-1} at 293 K. The kinetics followed the pseudo-second-order model. The thermodynamic parameters confirmed that the process is spontaneous and exothermic.

Keywords: *AN-31 anion exchange resin, formic acid, adsorption, heat-stable salts, methyldiethanolamine, Langmuir isotherm*

Introduction

Methyldiethanolamine (MDEA) is widely used for the removal of acidic components (H_2S and CO_2) from natural gas because of its high selectivity (Kohl & Nielsen, 1997). As a tertiary amine, MDEA does not form carbamates with CO_2 and reacts with it slowly, whereas its reaction with H_2S is very fast – a considerable technological advantage for the selective separation of hydrogen sulphide from gas mixtures. During prolonged operation, however, heat-stable salts (HSS) accumulate in the solution. These consist mainly of organic acid anions (formate, acetate, oxalate, bicine) generated by oxidation of the amine in the presence of oxygen, together with inorganic ions introduced with the process water (Mertens et al., 2013; Rooney et al., 1996). Degradation of MDEA proceeds along two routes: thermal degradation in

the regenerator under high temperature and CO_2 exposure, and oxidative degradation in the absorber under the action of oxygen and other oxidants. The resulting intermediates include diethanolamine, methylmonoethanolamine and bis-(hydroxyethyl)glycine; being secondary amines, MMEA and DEA react directly with CO_2 and thereby reduce the selectivity of the primary solvent (Islam et al., 2011). The heat-stable salts formed are not decomposed during conventional thermal regeneration. Their accumulation intensifies corrosion in heat exchangers and pipelines, causes severe foaming of the solution and increases the energy demand of regeneration (Pal et al., 2016).

Several approaches to HSS removal are known. Discharging part of the solution and replacing it with fresh MDEA generates large volumes of toxic wastewater and raises the cost of purification. Distillation is energy-intensive, and although neutralisation with strong alkalis minimises amine loss, the soluble sodium salts formed reduce the absorption capacity (Dumée et al., 2012). Electrodialysis has the advantage of being a reagent-free process, but 10–30% of the absorbent is lost through the membranes (Wang et al., 2018). Ion exchange, in contrast, operates at low temperature, minimises absorbent loss and leaves the structure of the sorbent stable, which makes it the most economically viable route (Bayati et al., 2019; Stroganova et al., 2020). The present work aims to study the sorption of formic acid on the weakly basic anion exchange resin AN-31 and to characterise the process in equilibrium, kinetic and thermodynamic terms.

Method

The sorbent was AN-31, a weakly basic anion exchange resin complying with GOST 20301–74. Model solutions were prepared from analytical-grade formic acid (purity not less than 99%) in distilled water at concentrations of 0.025, 0.05, 0.075 and 0.1 M.

Sorption was studied under static conditions: 100 ml of solution was added to 1.0 g of the resin, and the mixture was shaken at 80 rpm. The temperature was maintained at 293, 303 and 313 K. Samples were taken at intervals from 0.5 to 6 hours; sorption equilibrium was attained within 5 hours. The residual concentration of formic acid was determined by potentiometric titration, and each experiment was carried out in triplicate.

The adsorption capacity q_e was calculated from the difference between the initial and equilibrium concentrations, the solution volume and the mass of the resin (1).

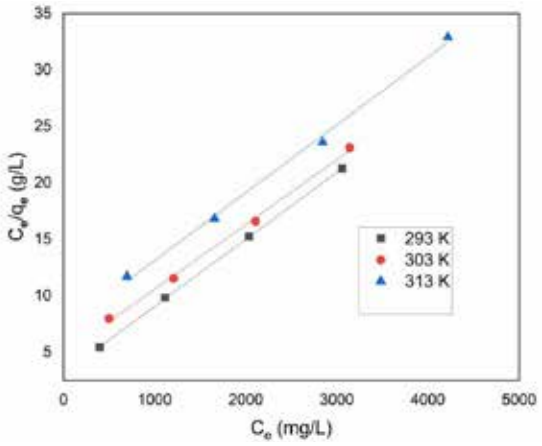
$$q_e = (C_0 - C_e) \cdot \frac{V}{m} \qquad (1)$$

Equilibrium data were described by the linearised Langmuir and Freundlich isotherms, and the kinetics by the pseudo-first-order and pseudo-second-order models. The linearised forms of these equations, the separation factor, and the Arrhenius and Van't Hoff relations used to obtain the activation energy and the thermodynamic parameters were applied in the conventional forms summarised by Ho and McKay (1999) and Foo and Hameed (2010).

Results and discussion

The equilibrium data were processed using both models (Figure 1, Table 1). The Langmuir model gave a higher coefficient of determination than the Freundlich model at all temperatures. This indicates that the surface of AN-31 carries energetically homogeneous active sites and that formic acid is taken up with the formation of a monomolecular layer. At 293 K the maximum capacity was 175.43 mg·g^{-1}. Both q_{max} and K_L decreased as the temperature rose, which points to an exothermic process.

Figure 1. *Linearised Langmuir isotherms for the adsorption of formic acid on AN-31 at 293, 303 and 313 K*



The kinetic data were analysed using two models (Figure 2, Table 2). The pseudo-first-order model gave a calculated equilibrium capacity of 185.7 mg·g^{-1}, which differs considerably from the experimentally measured value of 144 mg·g^{-1}; the model was therefore rejected. The pseudo-second-order model gave a value of 144.7 mg·g^{-1}. This indicates that the rate-determining step involves chemical interaction between the sorbate ions and the functional groups of the sorbent. From the Arrhenius equation, an activation energy of E_a = 9.76 kJ·mol^{-1} was calculated.

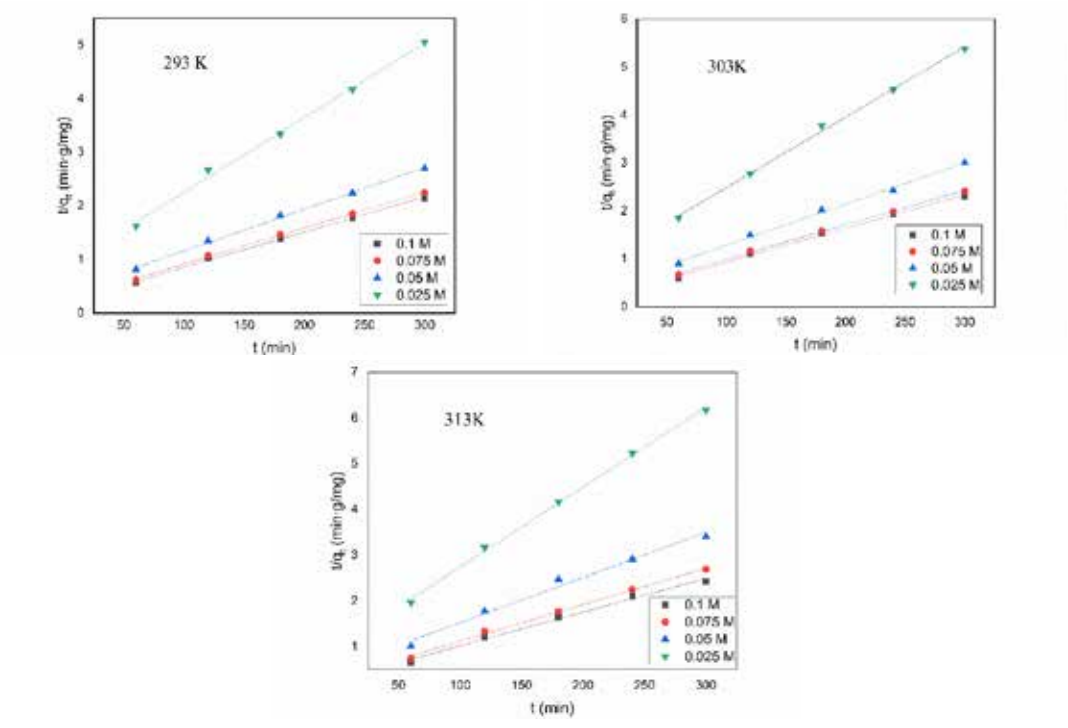
Table 1. *Isotherm parameters for the adsorption of formic acid*

Model	Parameter	293 K	303 K	313 K
Langmuir	q_{max} (mg·g^{-1})	175.43	169.50	166.66
	K_L(L·mol^{-1})	84.28	52.98	37.93
	R^2	0.9948	0.9988	0.9935
Freundlich	K_F	9.92	4.51	3.53
	n	2.95	2.32	2.28
	R^2	0.975	0.959	0.959

Table 2. *Kinetic parameters for the sorption of formic acid (0.1 M, 293 K)*

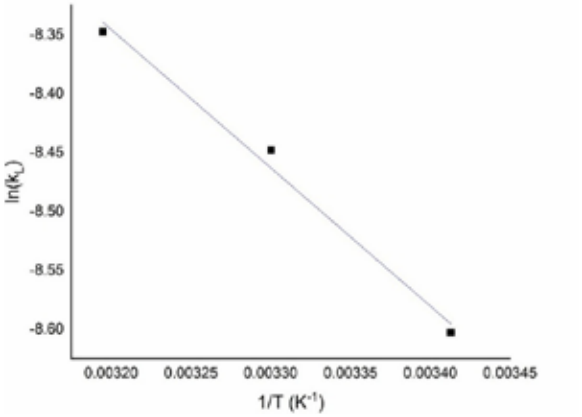
Model	Parameter	Value
PFO	$q_{e,\,exp}$ (mg·g^{-1})	144.0
	$q_{e,\,cal}$ (mg·g^{-1})	185.7
	R^2	0.9762
PSO	$q_{e,\,exp}$ (mg·g^{-1})	144.0
	$q_{e,\,cal}$ (mg·g^{-1})	144.7
	k_2 (g·mg^{-1}·min^{-1})	1.836·10^{-4}
	h (mg·g^{-1}·min^{-1})	3.84
	R^2	0.998

Figure 2. *Pseudo-second-order kinetic plots for the sorption of formic acid on AN-31 at (a) 293 K, (b) 303 K and (c) 313 K*



The Van't Hoff plot was highly linear (Figure 3), and the values derived from it are given in Table 3.

Figure 3. *Van't Hoff plot for the sorption of formic acid on AN-31*



The negative ΔG at every temperature shows that the process is spontaneous, while the decrease in its magnitude with rising temperature indicates that sorption is more favourable at lower temperatures. The value ΔH = –30.481 kJ·mol^{-1} lies above the range typical of purely physical adsorption and below that of covalent bonding, which is characteristic of chemisorption involving acid–base interaction with the amino groups of the resin. The negative ΔS reflects an increase in order at the solid–solution interface: freely moving formic acid molecules become fixed at specific active sites of the sorbent. Thus, a rise in temperature accelerates the process but lowers the equilibrium capacity, from which it follows that purification should be carried out at lower temperatures.

Table 3. *Thermodynamic parameters for the sorption of formic acid*

T (K)	K_L (L·mol^{-1})	ln K_L	ΔG (kJ·mol^{-1})	ΔH (kJ·mol^{-1})	ΔS (J·mol^{-1}·K^{-1})
293	84.28	4.4341	–10.802	–30.481	–67.305
303	52.98	3.9699	–10.001		
313	37.93	3.6357	–9.461		

Conclusion

The weakly basic anion exchange resin AN-31 takes up formic acid efficiently from aqueous solutions, with a maximum adsorption capacity of 175.43 mg·g^{-1} at 293 K. The equilibrium data follow the Langmuir model, and the kinetics conform to the pseudo-second-order model, the deviation between the calculated and measured equilibrium capacities being 0.49%. The activation energy of 9.76 kJ·mol^{-1} shows that the rate is limited by a diffusion step. The thermodynamic parameters indicate a spontaneous and exothermic process in which uptake proceeds through acid–base interaction with the amino groups of the resin. The results obtained allow AN-31 to be recommended as an efficient sorbent for the purification of MDEA solutions from heat-stable salts.

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