[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vapor–Adsorbate Equilibrium. III. The Effect of Temperature on the Binary Systems Ethylene–Propane, Ethylene–Propylene over Silica Gel

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Vapor–adsorbate equilibria for gaseous mixtures of ethylene–propane and ethylene–propylene have been determined using silica gel as an adsorbent at barometric pressure and at 0, 25 and 40°. In addition to disclosing the effect of temperature over a narrow range, these systems permit corroborative deductions[1,2] to be made as to the influence of a double bond on adsorption with silica gel. Here it will be noted that a low molecular weight olefin is in competition for the silica gel surface with either a higher molecular weight paraffin or olefin. In the light of the results of the previous work reported[1,2] it is to be expected that the ethylene would be relatively less volatile in the propane system than in the propylene system.

Substantially, the same attack in the collection of data was employed as in the prior work,[1,2] *i. e.*, adsorption–desorption isotherms were determined for each gas at each temperature level, equilibrium concentrations in the two phases were approached from both directions, mixture desorptions were carried out for material balance checks.

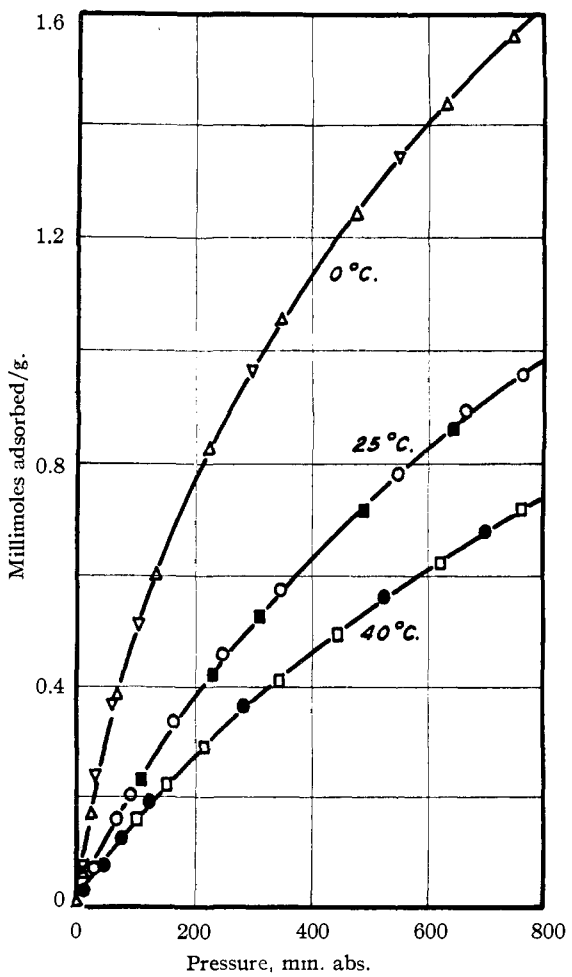

Fig. 1.—Adsorption isotherms of ethylene on silica gel at 0, 25 and 40°: △ ○ □ adsorption; ▽ ■ ● desorption.

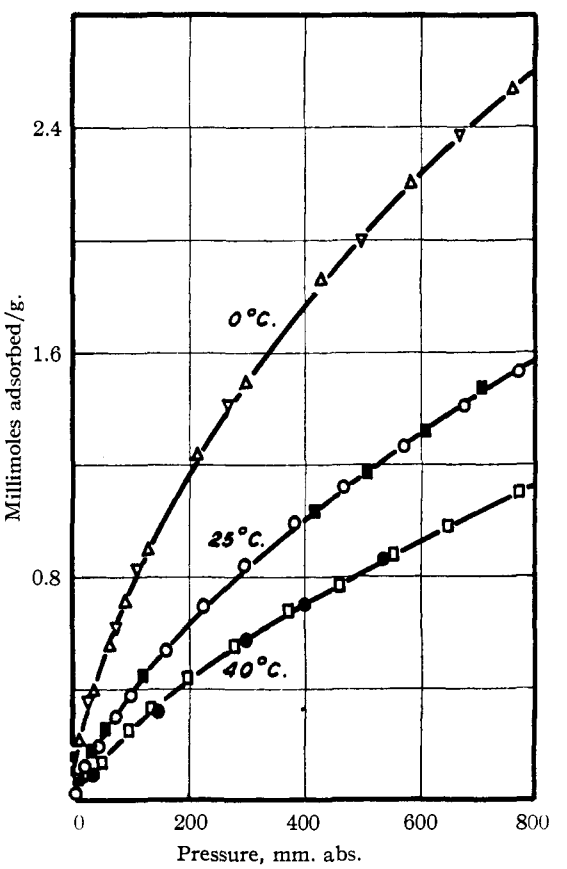

Fig. 2.—Adsorption isotherms of propane on silica gel at 0, 25 and 40°: △ ○ □ adsorption; ▽ ■ ● desorption.

The propane employed contained 0.05% olefin, (see ref. 1) the propylene was 97.0% olefin (necessitating an isotherm determination as described in ref. (2)) and the ethylene was 99.5% pure. Refrigeration grade silica gel, 14/20 mesh was supplied by the Davison Chemical Co. of Baltimore.[1]

(1) W. K. Lewis, *et al.*, THIS JOURNAL, **72**, 1153 (1950).
(2) W. K. Lewis, *et al.*, *ibid.*, **72**, 1157 (1950).

TABLE I

ADSORPTION ISOTHERMS OF ETHYLENE AT 0 AND 40° ON SILICA GEL[a]

n = millimoles adsorbed per g. adsorbent; p = pressure, mm. abs.

0°C.		40°C.	
P	n	P	n
Adsorption		Adsorption	
1.9	0.0120	20.0	0.0386
7.6	.0597	100.9	.1588
23.4	.1710	150.3	.2186
67.9	.3839	214.1	.2894
133.3	.6038	342.5	.4092
226.4	.8338	444.0	.4940
350.4	1.068	620.3	.621
476.1	1.256	763.7	.717
631.6	1.449	Desorption	
745.5	1.576	696.2	0.676
Desorption		524.6	.5638
549.5	1.360	284.6	.3656
295.6	0.993	121.7	.1912
100.1	.516	73.7	.1283
62.4	.3695	37.5	.0738
27.3	.2061	10.6	.0277
8.4	.0826		

[a] Data for 25° will be found in ref. 2.

TABLE II

ADSORPTION ISOTHERMS OF PROPANE AT 0, 40, AND 100° ON SILICA GEL[a]

n = millimoles adsorbed per g. adsorbent; P = pressure, mm. abs.

0°C.		40°C.		100°C.	
P	n	P	n	P	n
Adsorption		Adsorption		Adsorption	
16.6	0.2137	10.1	0.0418	96.4	0.0531
37.7	.3960	27.9	.0900	119.0	.1471
64.4	.5678	46.7	.1407	406.5	.2087
93.2	.7307	96.2	.2580	601.5	.2781
129.3	.9010	136.9	.3352	753.7	.3360
218.4	1.259	204.0	.4470		
298.8	1.520	282.0	.568		
429.4	1.881	373.0	.6871		
587.1	2.241	462.6	.7876		
762.6	2.582	554.9	.904		
Desorption		643.0	.9908		
668.9	2.420	768.9	1.128		
501.1	2.072	Desorption			
264.6	1.443	540.8	0.8840		
109.4	0.9438	400.0	.7068		
73.2	.6306	298.0	.5790		
29.4	.3721	146.6	.3276		
		38.0	.0916		

[a] Data for 25° will be found in ref. 1.

Results.—The results, using the apparatus already described,[1,2] are as follows: isotherms for ethylene at 0, 25 and 40° are in Table I and Fig. 1, propane in Table II and Fig. 2, propylene in Table III and Fig. 3. Ethylene–propane mixture data at 0, 25 and 40° are in Table IV, Figs. 4 and 5, ethylene–propylene data in Table V, Figs. 6 and 7.

TABLE III

ADSORPTION ISOTHERMS OF PROPYLENE AT 0 AND 40° ON SILICA GEL[a]

(Propylene contained 3.08% inerts)

n = millimoles adsorbed per g. adsorbent; P = pressure, mm. abs.

0°C.		40°C.	
P	n	P	n
Adsorption		Adsorption	
51.1	1.052	52.9	0.4586
95.2	1.468	94.0	0.630
213.8	2.065	249.4	1.059
428.4	2.640	503.2	1.499
762.1	3.179	764.9	1.791
Desorption		Desorption	
564.9	2.935	605.4	1.626
354.9	2.548	405.9	1.366
151.7	1.903	184.1	0.926
		74.7	0.5911

[a] Data for 25° will be found in ref. 1.

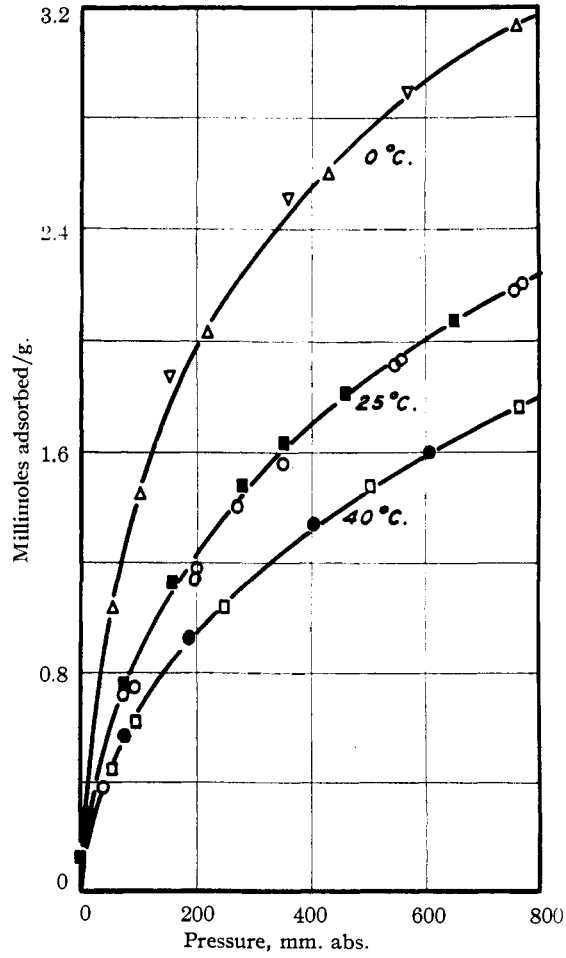

Fig. 3.—Adsorption isotherms of propylene (97% purity) on silica gel at 0, 25 and 40°: △ ○ □ adsorption; ▽ ■ ● desorption.

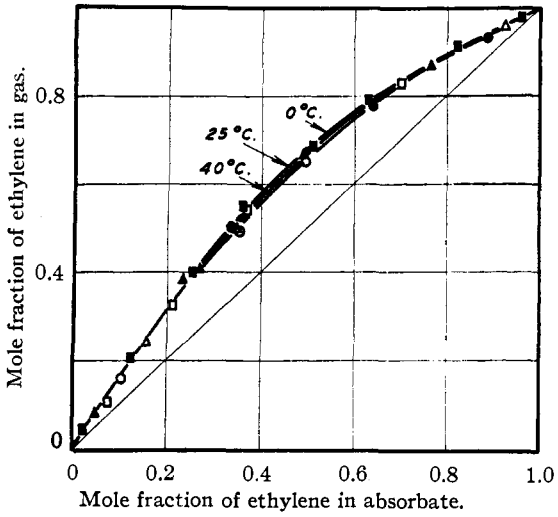

Fig. 4.—Isothermal, isobaric adsorption of ethylene–propane mixtures on silica gel, atmospheric pressure and 0, 25 and 40°: □ ■ 0° ethylene, propane on surface first, resp.; △ ▲ 25° ethylene, propane on surface first, resp.; ○ ● 40° ethylene, propane on surface first, resp.

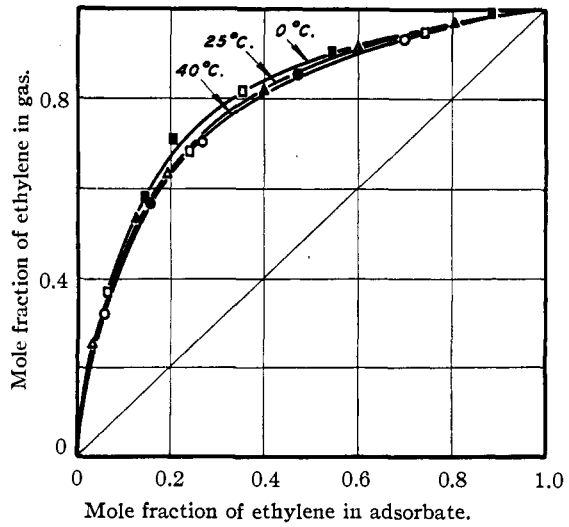

Fig. 6.—Isothermal, isobaric adsorption of ethylene–propylene mixtures on silica gel: □ ■, 0° ethylene, propylene on surface first, resp.; △ ▲ 25° ethylene, propylene on surface first, resp.; ○ ● 40° ethylene, propylene on surface first, resp.

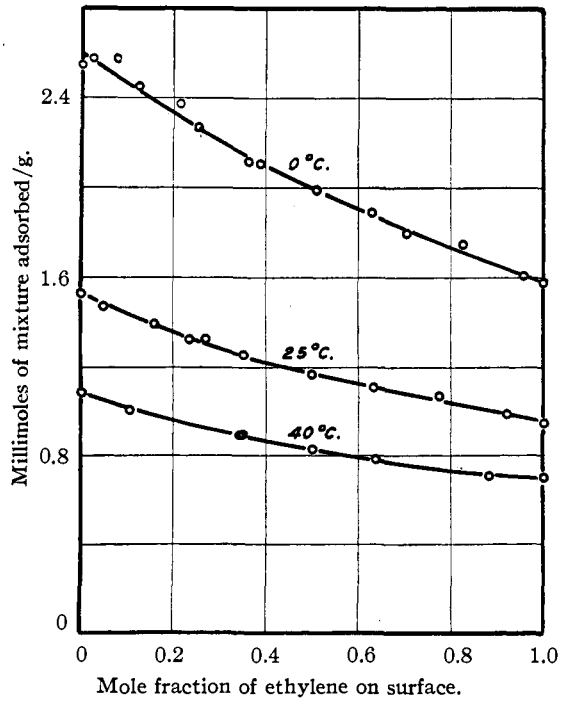

Fig. 5.—Total quantity adsorbed from ethylene–propane mixtures, silica gel, atmospheric pressure.

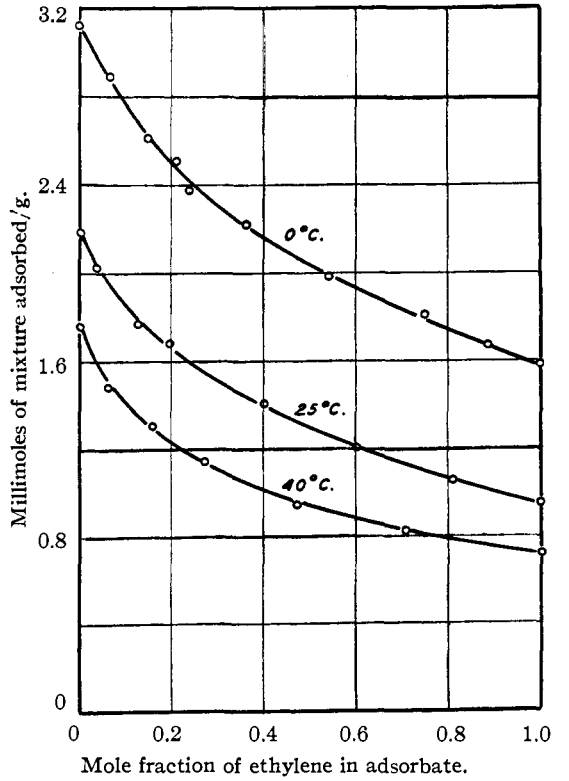

Fig. 7.—Total quantity adsorbed from ethylene–propylene mixtures, silica gel, atmospheric pressure.

Discussion.—The ethylene and propane isotherms obey the Langmuir isotherm equation fairly satisfactorily, with propylene the agreement was unsatisfactory. The mixtures studied show slightly decreasing relative volatilities in the vapor–adsorbate equilibrium with increasing temperature despite the substantial decrease in the total moles adsorbed per gram as the temperature is increased. This would seem to indicate that portions of the surface which are doing the adsorbing are relatively fairly homogeneous.

TABLE IV

VAPOR–ADSORBATE EQUILIBRIUM DATA FOR MIXTURES OF ETHYLENE–PROPANE AT 0, 25 AND 40° OVER SILICA GEL

X = mole fraction of ethylene in adsorbate; Y = mole fraction of ethylene in gas phase; N = millimoles of mixture adsorbed per g. adsorbent; π = total pressure mm. abs.

0°C.				25°C.				40°C.			
Y	X	N	π	Y	X	N	π	Y	X	N	π
0.0429	0.0270	2.572[a]	762.4	0.081	0.047	1.466	768.1	0.159	0.103	1.013[e]	769.5
.0990	.0760	2.575[a]	763.7	.237	.158	1.392	763.8	.494	.340	0.900[c,e]	772.6
.204	.123	2.452[a]	762.7	.381	.233	1.323	767.8	.492	.346	.900[d,e]	771.2
.322	.214	2.375[a]	763.7	.401	.265	1.329	773.6	.648	.494	.838[a]	775.4
.401	.251	2.273[a]	761.4	.488	.348	1.262	762.3	.775	.635	.785[a]	775.7
.545	.361	2.116[b]	766.7	.661	.491	1.171	773.2	.931	.884	.716[a]	776
.542	.386	2.108[b]	767.5	.762	.626	1.112	762.3				
.684	.505	1.990[a]	766.5	.868	.769	1.078	773.6				
.790	.625	1.888[a]	766.6	.953	.919	0.990	764.4				
.825	.699	1.804[a]	759.1								
.917	.821	1.747	761.4								
.978	.955	1.620[a]	766.6								

[a] Sample B, premixed gas, 10 passes. [b] Sample A. [c] Propane on surface first, ethylene added, 20 passes at 0°, 10 at 40°. [d] Ethylene on surface first, propane added, 20 passes at 0°, 10 at 40°. [e] Sample C, premixed gases, 10 passes.

TABLE V

VAPOR–ADSORBATE EQUILIBRIUM DATA FOR MIXTURES OF ETHYLENE–PROPYLENE AT 0, 25 AND 40° OVER SILICA GEL

X = mole fraction ethylene in adsorbate; Y = mole fraction ethylene in gas phase; N = millimoles of mixture adsorbed per g. adsorbent; π = total pressure, mm. abs.

0°C.				25°C.				40°C.			
Y	X	N	π	Y	X	N	π	Y	X	N	π
0.364	0.0662[a]	2.890	771.8	0.248	0.0369	2.025	768.1	0.321	0.0602[a]	1.481	769.6
.579	.145[b]	2.611	771.0	.526	.123	1.763	767.1	.563	.109[b]	1.305	768.2
.711	.207[b]	2.504[b]	770.4	.628	.195	1.680	767.4	.703	.270[a]	1.143	766.9
.682	.238[a]	2.372[c]	759.5	.817	.397	1.405	773.3	.852	.471[b]	0.942	765.1
.814	.362[a]	2.228	775.4	.908	.597	1.208	772.3	.935	.705[a]	0.824	765.7
.903	.541[b]	1.981	774.5	.968	.807	1.049	771.2				
.948	.745[a]	1.807	769.2								
.989	.885[b]	1.662	769.1								

[a] Ethylene on surface first, 10 passes. [b] Propylene on surface first, 10 passes.

It will be observed, for the mixture data, that for each binary system the higher molecular weight compound is the less volatile over the adsorbent, but that there is more competition for the silica gel surface between ethylene and propane than between the two olefin mixtures.

Summary

1. Adsorption–desorption isotherms at 0, 25 and 40° have been determined for ethylene, propane and propylene on silica gel.

2. Vapor–adsorbate equilibrium curves at one atmosphere have been obtained for the binary systems ethylene–propane and ethylene–propylene at 0, 25 and 40°.

3. Ethylene is relatively more volatile than propane or propylene in the isobaric, isothermal binary systems.

4. Ethylene exhibits a much greater relative volatility in the propylene system than in the propane system demonstrating the influence of the double bond.

5. The adsorption phenomena reported herein are reversible.

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