to yield 4,4-dimethyl-2-pentene and acetic acid.

About 7% rearrangement occurred in this reaction. One of the two rearranged olefins obtained in this reaction was identified as a 2,3-dimethylpentene.

In the case of the principal olefin, 4,4-dimethyl-

2-pentene, little evidence was obtained of the presence of both cis and trans isomers.

2,2-Dimethylpentane, 2,3-dimethylpentane and an unidentified isomer were obtained by the hydrogenation of the heptenes.

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The Ternary Systems Involving Cyclohexene, Water, and Methyl, Ethyl, and Isopropyl Alcohols

By E. Roger Washburn, C. Loren Graham,[1] George B. Arnold and Laurence F. Transue

In continuation of a series of investigations of similar binary and ternary systems the solubility relationships for the systems formed from cyclohexene, water and methyl, ethyl and isopropyl alcohols have been studied at 25.0°. In order to provide an indication of the changes to be expected with changes in temperature the system involving isopropyl alcohol was also studied at 15.0 and 35.0°. The proportions in which the alcohols are distributed between the water-rich and cyclohexene-rich layers have been measured.

Materials.—Good commercial grades of methyl and ethyl alcohol, and isopropyl alcohol from Eastman Kodak Company were dried by refluxing over active lime for many hours. The alcohols were then distilled from the lime into a carefully dried all-glass still. They were then slowly distilled from this still through an efficient fractionating column and preserved in carefully dried glass-stoppered bottles. The specific gravities and refractive indices of the purified materials are listed in Table I.

Several studies carried out in this Laboratory indicate that both the density and the refractive index of cyclohexene change with the passage of time if the material is in contact with oxygen. That this is probably due to the formation of a peroxide is indicated by the fact that while the freshly distilled material fails to liberate iodine from an iodide, the material which has been in contact with oxygen for some time gives positive results when added to an acidified potassium iodide-starch solution. Accordingly our cyclohexene, the better of the two grades sold by Eastman Kodak Company, was repeatedly fractionated through a carefully controlled Snyder column[2] in

an atmosphere of purified nitrogen. It was collected in carefully dried, nitrogen-filled bottles and kept under nitrogen until used. It was our experience that the specific gravity and refractive index were constant at the values indicated in Table I as long as tests with potassium iodide and starch indicated no peroxide.

There is little consistency in the recorded values for the specific gravity, or for the refractive index, of cyclohexene. Therefore, since considerable effort was made in this work to obtain material of a high degree of purity, more than the usual amount of interest may attach to the value which we record. In one distillation these observations were made. Three hundred twenty-five cc. of stock material of d^{25}_4 0.80919 was distilled. The first 50 cc. collected had a value of d^{25}_4 of 0.80558, the second fraction (210 cc.) had a specific gravity of 0.80566, while the 50 cc. of residue showed the high value of 0.82152. The second fraction was then fractionated yielding 35 cc. with d^{25}_4 of 0.80564, 55 cc. of 0.80562 and leaving 50 cc. of residue of 0.80576.

A large number of similar distillations carried out by different investigators in this Laboratory lead us to believe that the specific gravity of cyclohexene d^{25}_4 is 0.8056 ± 0.0001.

Table I

Material	Specific gravity, d^{25}_4	Refractive index n^{25}D
Methyl alcohol	0.7866	1.32659
Ethyl alcohol	.7851	1.35942
Isopropyl alcohol	.7809	1.37487
Cyclohexene	.8056 d^{15}_4 0.8151	1.4434

Procedure and Results.—The ternary solubility curves were determined by a titration method similar to that described elsewhere.[3] The titrations were carried out at the temperatures

(1) Present address: Eastman Kodak Company, Rochester. New York.

(2) Hill and Ferris, *Ind. Eng. Chem.*, **19**, 379 (1927).

(3) This Journal, **62**, 579 (1940).

indicated within ±0.05°. Weighed quantities of the components were used, the titrant being added from a weight pipet. Care was taken to avoid overstepping the end-point and also to avoid confusing the opalescence obtained with certain proportions of the components with the true end-point as indicated by the appearance of a second phase. The angle and intensity of the illumination was varied so as to provide conditions most favorable for the particular titration. To make certain that the end-point had been reached the titration mixture was shaken automatically in the constant-temperature bath for at least fifteen minutes and then reëxamined.

The determinations of the refractive indices of the saturated solutions containing methyl alcohol were particularly difficult with the solutions where the end-point was preceded by an opalescence. In order to overcome this difficulty these solutions were warmed to 30.0° in order to clear up the solutions and the refractive indices were determined at that temperature. These values are indicated in Table I. When solutions in this range of concentrations were encountered in the distribution studies they were, of course, also heated to 30.0° for the refractive index determination.

The results of these determinations of solubili-

ties and refractive indices are recorded in Tables II to VI. The concentrations of the conjugate solutions are recorded in Tables VII to XI.

TABLE IV
ISOPROPYL ALCOHOL, CYCLOHEXENE AND WATER AT 25.0°

Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index	Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index
94.29	5.25	1.4389	5.94	44.85	1.3679
81.12	17.37	1.4284	5.21	43.87	1.3669
67.49	28.86	1.4182	1.29	33.34	1.3594
54.31	38.58	1.4087	0.48	20.34	1.3501
44.89	44.27	1.4024	.35	14.33	1.3450
30.39	50.39	1.3914	.09	7.10	1.3382
18.76	51.37	1.3816	.06	3.21	1.3348
11.73	49.27	1.3750			

TABLE V
ISOPROPYL ALCOHOL, CYCLOHEXENE AND WATER AT 15.0°

Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index	Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index
97.82	2.02	1.4470	11.38	49.30	1.3779
91.11	8.41	1.4414	7.22	47.52	1.3743
83.16	15.70	1.4348	2.09	39.56	1.3662
77.87	20.34	1.4312	1.28	35.76	1.3634
70.74	26.44	1.4258	0.34	27.44	1.3580
58.60	35.62	1.4171	.11	22.94	1.3541
43.91	44.95	1.4060	.11	17.95	1.3499
31.16	50.67	1.3958	.20	9.72	1.3415
21.63	51.42	1.3884	.08	3.89	1.3361

TABLE VI
ISOPROPYL ALCOHOL, CYCLOHEXENE AND WATER AT 35.0°

Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index	Cyclo-hexene, wt. %	Alcohol, wt. %	Refrac-tive index
94.30	5.13	1.4336	13.76	49.53	1.3726
84.54	14.31	1.4254	7.31	45.01	1.3653
66.88	29.40	1.4119	1.23	31.80	1.3557
51.88	40.47	1.4017	0.46	24.08	1.3507
40.62	46.52	1.3940	.18	14.39	1.3433
31.81	50.10	1.3878	.06	4.79	1.3348
23.62	51.31	1.3814			

TABLE II
METHYL ALCOHOL, CYCLOHEXENE AND WATER AT 25.0°[a]

Cyclo-hexene, wt. %	Methyl alcohol, wt. %	Refrac-tive index	Cyclo-hexene, wt. %	Methyl alcohol, wt. %	Refrac-tive index
89.03	10.86	1.4259[a]	6.57	74.36	1.3416
79.09	20.65	1.4135[a]	3.52	70.79	1.3403
68.09	31.43	1.4000[a]	2.05	64.56	1.3409
56.88	42.35	1.3868[a]	0.87	55.87	1.3410
44.13	54.30	1.3745	.48	47.96	1.3410
30.20	66.31	1.3603	.20	37.12	1.3400
17.87	74.04	1.3490	.10	24.92	1.3380
10.67	76.11	1.3435	.05	15.31	1.3356
	Cyclohexene saturated with water				1.4405[a]
	Water saturated with cyclohexene				1.3320

[a] These refractive indices were measured at 30.0°.

TABLE III
ETHYL ALCOHOL, CYCLOHEXENE AND WATER AT 25.0°

Cyclo-hexene, wt. %	Ethyl alcohol, wt. %	Refrac-tive index	Cyclo-hexene, wt. %	Ethyl alcohol, wt. %	Refrac-tive index
95.48	4.25	1.4387	16.13	64.31	1.3730
85.65	13.86	1.4302	7.39	61.32	1.3659
68.96	28.31	1.4151	3.08	54.54	1.3612
53.61	40.90	1.4018	0.59	41.56	1.3547
39.57	51.92	1.3903	.17	23.94	1.3475
29.46	58.86	1.3832	.12	19.85	1.3453
	Cyclohexene saturated with water				1.4428
	Water saturated with cyclohexene				1.3320

TABLE VII
CONJUGATE SOLUTIONS CONTAINING METHYL ALCOHOL AT 25.0°[a]

	Water layer			Cyclohexene layer	
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Cyclo-hexene, wt. %
1.3341	9.6	90.4	1.4404[a]	0.1	99.9
1.3362	17.8	82.1	1.4403[a]	.2	99.8
1.3384	27.0	72.9	1.4403[a]	.2	99.8
1.3392	31.0	68.9	1.4402[a]	.3	99.7
1.3404	40.0	59.7	1.4401[a]	.4	99.6
1.3406	72.8	22.2	1.4390[a]	1.2	98.8
1.3435	76.0	14.0	1.4378[a]	2.1	97.9

[a] These refractive indices were measured at 30.0° for purposes of analysis.

A comparison of the solubility curves for these systems indicates that isopropyl alcohol is the

Table VIII

Conjugate Solutions Containing Ethyl Alcohol at 25.0°

Water layer			Cyclohexene layer		
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Cyclohexene, wt. %
1.3405	12.3	87.4	1.4425	0.3	99.7
1.3491	27.8	72.3	1.4422	.6	99.3
1.3539	39.7	60.0	1.4418	1.0	98.8
1.3580	48.7	49.5	1.4410	1.8	98.0
1.3635	58.4	37.0	1.4399	3.1	96.9
1.3690	63.3	25.6	1.4372	5.9	93.7
1.3730	64.3	19.6	1.4360	7.3	92.4

Table IX

Conjugate Solutions Containing Isopropyl Alcohol at 25.0°

Water layer			Cyclohexene layer		
Refractive index	Alcohol, wt. %	Water, wt. %	Refractive index	Alcohol, wt. %	Cyclohexene, wt. %
1.3398	8.8	91.1	1.4428	0.6	99.3
1.3496	19.8	79.9	1.4385	5.7	93.8
1.3569	29.6	69.7	1.4283	17.6	80.9
1.3605	34.9	63.6	1.4181	28.8	68.0
1.3623	37.5	60.2	1.4132	34.2	60.6
1.3643	40.4	55.5	1.4060	41.3	50.0
1.3695	46.0	47.1	1.3920	50.2	31.4
1.3734	48.3	41.5	1.3839	51.6	21.3

most effective in bringing about complete miscibility of the system cyclohexene, water and alcohol, and methyl alcohol is the least effective. In the study of the conjugate solutions very little

Table X

Conjugate Solutions Containing Isopropyl Alcohol at 15.0°

Water layer		Cyclohexene layer	
Refractive index	Alcohol, wt. %	Refractive index	Alcohol, wt. %
1.3439	12.0	1.4480	0.7
1.3521	20.5	1.4457	3.5
1.3600	30.6	1.4366	14.1
1.3636	36.1	1.4284	23.2
1.3685	42.4	1.4159	36.7
1.3740	47.3	1.4021	47.3
1.3770	48.8	1.3970	50.2

Table XI

Conjugate Solutions Containing Isopropyl Alcohol at 35.0°

Water layer		Cyclohexene layer	
Refractive index	Alcohol, wt. %	Refractive index	Alcohol, wt. %
1.3390	9.6	1.4368	1.8
1.3455	17.2	1.4338	4.9
1.3507	23.9	1.4259	14.0
1.3545	29.9	1.4162	24.7
1.3563	32.8	1.4100	31.6
1.3573	34.5	1.4054	36.5

methyl alcohol is found in the cyclohexene layer, even when a considerable portion of the system is alcohol. A slightly larger proportion of ethyl alcohol is found in the hydrocarbon layer especially when the alcohol content is high. As has been found with other systems containing isopropyl alcohol, the proportion of it found in the
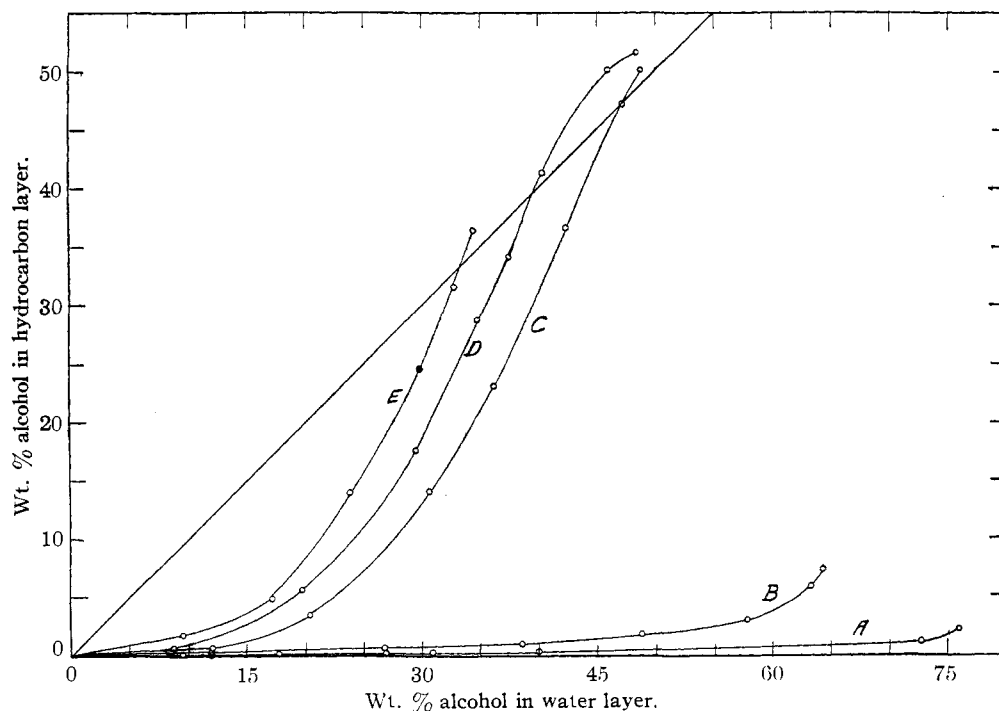

Fig. 1.—A, methyl alcohol; B, ethyl alcohol; C, D, E, isopropyl alcohol at 15, 25, 35°, respectively.

hydrocarbon layer increases rapidly with increasing total amount of alcohol until the tie lines change the sign of their slope. These facts are clearly indicated in Fig. 1 in which the % of alcohol in the cyclohexene layer is plotted against the % of alcohol in the water layer.

Increasing the temperature from 15 to 35° causes very little change in the area in which conjugate solutions are found; the area is slightly larger at the lower temperature. The slopes of the tie lines change by a large amount. The plait point at 15° is not far from the highest point of the solubility curve, while at 25° it is farther

down on the water-rich side of the curve. It was experimentally difficult to approach very closely to the plait point at 35° but the indications are that at this temperature it is still farther down on the water side of the curve.

Summary

The solubility relationships for the ternary systems containing water and cyclohexene and methyl, ethyl or isopropyl alcohol have been determined at 25°. The system containing isopropyl alcohol has been investigated at 15 and 35°.

Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations[1]

BY S. B. HENDRICKS,[2a] R. A. NELSON[2b] AND L. T. ALEXANDER[2b]

Introduction

The hydrous magnesium aluminum silicate mineral montmorillonite, because of its unusual properties and widespread occurrence in clays and soils, has attracted the attention of workers in many fields. It is extremely plastic when moist and can be dispersed in water, readily forming thixotropic gels at moderate concentrations. The dispersed material upon drying reorganizes, forming a crystalline material one lattice constant of which depends upon the humidity. Montmorillonite is a salt of a moderately strong acid, from which other salts and the free acid can be prepared by cation replacement, that is, base exchange. It strongly absorbs organic bases with formation of the corresponding salts and also shows marked adsorption for neutral organic compounds, which is the basis for its use as a clarifying agent. Many reactions are catalyzed by montmorillonite.

Study of montmorillonite as a base exchange complex has come about largely because it is a component of many soils showing high base exchange capacity. Replacement of one cation by another has been investigated to a considerable extent and several series have been set up showing ease of replacement. The one generally accepted shows[3,4]:

$H^+ > Ba^{++} > Sr^{++} > Ca^{++} > Mg^{++} > Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$; thus, for example, a greater fraction of the K^+ ions is displaced at equivalent concentrations by Ca^{++} than by Li^+. These differences usually have been attributed to "ionic hydration."[5] A successful correlation has been found with zeta potentials[6] derived from migration velocities of clay micelles in suspensions. No attempt has been made, however, to determine the environment of the ion in the clay, which is fundamental to understanding the nature of the replacements.

For a number of years the authors have been interested in the identification and structures of minerals present in clays. During the course of this work it became evident that a study of water sorption by the various salts of montmorillonite probably would go far toward determining the environment of the replaceable cation. The material is one of the few in which sorption can be followed by means of lattice changes.

Methods and Materials

Since montmorillonite might be expected to differ in behavior depending upon its origin, samples were obtained from several localities. All of these were bentonites, that is, they were formed by devitrification of volcanic ash. One was a commercial material from Wyoming, sold under the trade name "Volclay," which is known to contain finely divided quartz and appreciable silica that can be dissolved in weak bases. This particular sample has not been ana-

(1) Not copyrighted.

(2a) Bureau of Agricultural Chemistry and Engineering.

(2b) Bureau of Plant Industry.

(3) G. W. Robinson, "Soils, Their Origin, Constitution, and Classification." D. Van Nostrand Co., New York, N. Y., 1936, Chapter V.

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