

Figure 1. Correlation of  $pK_a$ 's with Taft polar substituent constants

titrant was a 0.01M hydrochloric acid solution that was standardized against a standard carbonate free sodium hydroxide solution in the normal way using phenolphthalein indicator. The pH meter and electrodes were standardized and checked for drift with commercial buffers of pH = 4.01 and 7.00.

### Results

Each  $pK_a$  listed in Table I is the average of a minimum of at least 16 individual determinations. A graph of  $pK_a$  vs. Taft steric substituent constants contained too much scatter to indicate any significant relationships. The Taft polar substituent constant ( $\sigma$ ) did show an unambiguous correlation with the  $pK_a$ 's of the ketones as shown in Figure 1.

### Literature Cited

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## Liquid-Liquid Equilibria for System Methanol-2-Propanol-*n*-Hexane

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Ternary liquid-liquid equilibrium data are reported at  $-17.8^\circ$ ,  $5^\circ$ , and  $25^\circ\text{C}$  for the system methanol-2-propanol-*n*-hexane. The tie lines and solubility curves for these Type 1 ternary systems are obtained by gas chromatographic analysis.

Liquid-liquid equilibrium data for a Type 1 ternary system were needed at three different temperatures to establish the temperature dependence of parameters to be used in the prediction of multicomponent equilibria. The system methanol-2-propanol-*n*-hexane was chosen to augment literature data for ternary systems that fit the criteria just established. No tie line data for this system were found in the literature.

### Experimental

**Materials.** Reagent grades of methanol and 2-propanol and pure grade *n*-hexane obtained from Phillips Petroleum Co. were used in this study. An analysis of these solvents is presented in Table I. The manufacturer's stated purity for the solvents was verified by use of gas chromatographic analysis.

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**Procedure.** Clean equilibrium cells were charged with about a 15-ml mixture of approximately 30 wt % methanol and 70 wt % *n*-hexane. To these cells was added a quantity of 2-propanol so that the overall 2-propanol composition of the ternary mixture in the cells would be 0-12 wt % in 1 or

Table I. Analysis of Solvents

Solvent	Purity minimum, %
Methanol	99.5
<i>n</i> -Hexane	99.0
2-Propanol	99.5

Table II. Gas Chromatograph Conditions

Injection port temp	250°C
Detector	TC
Detector temp	250°C
Detector power	165 mA
Oven conditions	140-220°C at 8°C/min
Carrier gas	He
Gas flow rate	30 ml/min

Table III. Liquid-Liquid Equilibrium Data for Ternary System Methanol(1)-2-Propanol(2)-*n*-Hexane(3)

Methanol-rich phase				<i>n</i> -Hexane-rich phase			
Wt fraction		Mole fraction		Wt fraction		Mole fraction	
$W_1$	$W_2$	$X_1$	$X_2$	$W_1$	$W_2$	$X_1$	$X_2$
$t = 25.0^\circ\text{C}$							
0.6004	0.0000	0.8016	0.0000	0.1011	0.0000	0.2322	0.0000
0.5160	0.0183	0.7383	0.0140	0.1428	0.0024	0.3091	0.0028
0.4088	0.0248	0.6462	0.0209	0.1960	0.0097	0.3948	0.0104
Estimated plait point						0.495	0.020
$t = 5.0^\circ\text{C}$							
0.7436	0.0000	0.8864	0.0000	0.0412	0.0000	0.1036	0.0000
0.7203	0.0280	0.8691	0.0180	0.0491	0.0006	0.1219	0.0008
0.6676	0.0414	0.8367	0.0277	0.0578	0.0022	0.1415	0.0029
0.6150	0.0601	0.8010	0.0417	0.0718	0.0048	0.1719	0.0061
0.5603	0.0752	0.7613	0.0545	0.0879	0.0100	0.2051	0.0124
0.4410	0.0906	0.6647	0.0728	0.1258	0.0240	0.2767	0.0281
0.3729	0.1003	0.5993	0.0859	0.1405	0.0379	0.3014	0.0433
Estimated plait point						0.443	0.070
$t = -17.8^\circ\text{C}$							
0.8368	0.0000	0.9324	0.0000	0.0198	0.0000	0.0515	0.0000
0.7775	0.0529	0.8949	0.0325	0.0160	0.0010	0.0419	0.0014
0.6937	0.1002	0.8421	0.0649	0.0302	0.0041	0.0772	0.0056
0.6323	0.1304	0.8003	0.0880	0.0375	0.0081	0.0945	0.0109
0.5648	0.1555	0.7514	0.1103	0.0449	0.0132	0.1117	0.0175
0.4810	0.1627	0.6869	0.1239	0.0661	0.0252	0.1584	0.0322
0.4089	0.1704	0.6231	0.1385	0.0875	0.0380	0.2021	0.0468
Estimated plait point						0.396	0.180

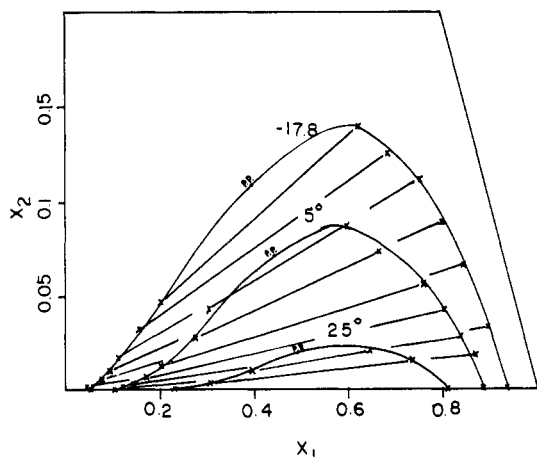


Figure 1. Ternary diagram for system methanol(1)-2-propanol(2)-*n*-hexane(3) at  $-17.8^\circ\text{C}$ ,  $5^\circ\text{C}$ , and  $25^\circ\text{C}$

2% increments. Each of these mixtures could be in the two-phase region if the temperature of the cell were lowered sufficiently.

The cells were tightly capped, shaken, and placed in a temperature-controlled environment, i.e., constant temperature water bath for the  $5^\circ\text{C}$  and  $25^\circ\text{C}$  runs or refrigerator-freezer for the  $-17.8^\circ\text{C}$  run. The temperature was maintained at  $\pm 1/4^\circ\text{C}$  for the water bath and  $\pm 1/2^\circ\text{C}$  for the  $-17.8^\circ\text{C}$  run. The cells were periodically shaken to ensure complete mixing so that equilibrium was encouraged. They were allowed a minimum of 3 hr to attain equilibrium.

After equilibrium was assumed to be attained, 2-ml samples of each layer of all cells that exhibited two-phase mixtures were quickly and carefully taken with a hypodermic syringe. Each of these samples was transferred to smaller cells for analysis. The mixtures in each of these smaller cells were always a one-phase mixture at any temperature above the run temperature.

Each mixture was analyzed with a Hewlett-Packard 5700 gas chromatograph. An approximate analysis was obtained using the ratio of the areas under the curves associated with each component. Preliminary investigation revealed that an approximate weight percent analysis could be obtained for this system by using correction factors applied to the areas (7).

Since the correction factors were not constant throughout the entire composition range, a method of successive approximations was used to accurately determine the composition of each mixture. A known mixture closely approximating the initial weight percent analysis was prepared by accurately weighing each component. Area correction factors were then computed and applied to the areas associated with the unknown. A new estimate was thus established, and the procedure was continued until the correction was negligible. Since the correction factors did not vary drastically with composition, only two or three corrections needed to be applied so that the computed composition varied less than 0.01%. Liquid-liquid tie lines were thus established for each of three temperatures at intervals of 1-2% 2-propanol.

The operating conditions of the gas chromatograph are listed in Table II.

## Results

The liquid-liquid equilibrium data for the ternary system methanol-2-propanol-*n*-hexane are presented in Table III. The methanol-rich phase was observed as the lower phase, and the *n*-hexane-rich phase was observed as the upper phase. The mole fraction values reported were calculated from the observed weight fraction.

The data from Table III are presented graphically in Figure 1.

## Literature Cited

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