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The System Methyl Ethyl Ketone–Water–*sec*-Butyl Alcohol

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The densities, refractive indices, and viscosities of mixtures of water, methyl ethyl ketone, and *sec*-butyl alcohol have been determined, at 25 °C, over the whole range of composition, for the binary and the ternary systems. Two of the systems, viz., methyl ethyl ketone–water and *sec*-butyl alcohol–water, are known to exhibit miscibility gaps, but it is now found that small additions of the third component to either of these systems produce homogeneity at room temperature. If, however, the temperature is raised above 50 °C, these systems become heterogeneous. On further heating to approximately 100 °C, these systems become homogeneous again. This behavior is compared with that of the system nicotine–methyl ethyl ketone–water, previously studied by us, and shown to be fundamentally the same.

Introduction

The systems methyl ethyl ketone–water and *sec*-butyl alcohol–water are well-known examples of partial miscibility: two equilibrium layers are formed in certain regions of concentration (*1–3*).

The system nicotine–water exhibits a completely closed region of heterogeneity, within an upper and a lower critical solution temperature. In a previous study by us in collaboration with Falconer (*4*) of the ternary system methyl ethyl ketone–nicotine–water, it was shown that the two binary areas of heterogeneity unite in the ternary system in the form of a "tunnel". This is best appreciated in a solid model, such as we have constructed for teaching purposes.

The purpose of the present study was to investigate how far this behavior is repeated in the ternary system methyl ethyl ketone–*sec*-butyl alcohol–water. It may be said at once that the behavior of the present system is fundamentally the same as that of methyl ethyl ketone–nicotine–water, buf differs in detail.

This study consists of an isothermal investigation, at 25 °C, of the system methyl ethyl ketone–*sec*-butyl alcohol–water. In connection with this, density, refractive index, and viscosity were determined for purpose of analysis. It was found that the addition of a small amount of *sec*-butyl alcohol (SBA) (~10%) to the methyl ethyl ketone–water system, or of methyl ethyl ketone (MEK) (~5%) to the *sec*-butyl alcohol–water system produces homogeneity (Figure 4). In the figure it will be seen that the area of homogeneity extends over the largest part of the triangular diagram. Homogeneous systems that lie between the two nodal regions become heterogeneous when the temperature is raised to approximately 50 °C and on further heating become homogeneous again above 100 °C. Hence, a volume $L_1 \rightleftharpoons L_2$ heterogeneity exists in that temperature range. The upper critical solution temperatures of methyl ethyl ketone–water and *sec*-butyl alcohol water lie at 140 and 114 °C, respectively. Between these two temperatures a band of heterogeneity exists. Studies were done to outline the shape of the heterogeneous region.

Experimental Section

As regards a method of analysis, theoretically the determination of any two physical properties, when plotted on a triangular diagram, should determine the composition of a three-component mixture and for this purpose we chose, initially, density and refrative index. It was found, however, that the angle of intersection, in some areas of the diagram, between the density and refractive index curves was so small that the error of interpretation became very large. Viscosity was therefore chosen in place of refractive index, as the second physical property. The work on refractive index, however, was continued to completion because of its intrinsic interest. A knowledge of refractive index permits the calculation of the so-called "incompressible volume", $V' = (n^2 - 1/n^2 + 2)V_{\mathrm{exptl}}$ (*1*). The data for composition, density, and refractive index have been utilized to calculate the apparent molar volume, $V = M/d$ (*2*), and the true or incompressible volume V′, as given above. The change in volume on mixing of the pure components ($\Delta V = V_{\mathrm{exptl}} - V_{\mathrm{ideal}}$) (*3*) has also been obtained.

Densities were determined with a specific gravity bottle and refractive indices with an Abbê refractometer, both with thermostatic control, good to ±0.01 °C. Both density and refractive index are accurate to at least one unit in the third place of decimals and this is sufficient. Viscosities were determined with the Cannon and Fenske modification of the Ostwald viscometer.

In preparing the calibration curves of density, refractive index, and viscosity, the method of experiment adopted was to study pseudobinary systems consisting of a known binary (or ternary) mixture to which progressively increasing amounts of the third component were added. These results were plotted in rectangular coordinates and from these, curves of equal density, refractive index, or viscosity could be obtained and plotted on the large triangular diagram.

Despite the effort expended in obtaining the calibration graph, mixtures of known composition could not be determined with an accuracy greater than ±3% in each component. Therefore, for the 25 °C isotherm recourse was made to the Alexejeff method (*5*) to obtain the consolute curves. The analytical method was used in conjunction with the consolute curve to determine the slope of the tie lines.

As can be seen from the 25 °C isotherm (Figure 4), the largest area of the diagram represents ternary mixtures which are homogeneous at that temperature. But systems lying between the two heterogeneous regions become heterogeneous when heated. Rather than pursuing the investigation at higher constant temperatures, it was decided to apply the Alexejeff method to systems of known composition and to determine the temperature at which each mixture became heterogeneous. For this purpose, three binary mixtures of methyl ethyl ketone–*sec*-butyl alcohol were prepared in bulk (30% methyl ethyl ketone/70% *sec*-butyl alcohol; 50% methyl ethyl ketone/50% *sec*-butyl alcohol; and 70% methyl ethyl ketone/30% *sec*-butyl alcohol) and from these known binary mixtures, ternary mixtures were prepared by adding water. Each mixture was heated in a water bath with vigorous stirring and the temperature at which cloudiness was first detected was recorded. These data are given in Table IV and are shown graphically in Figure 9 where an interpolated 52 °C isotherm is also indicated.

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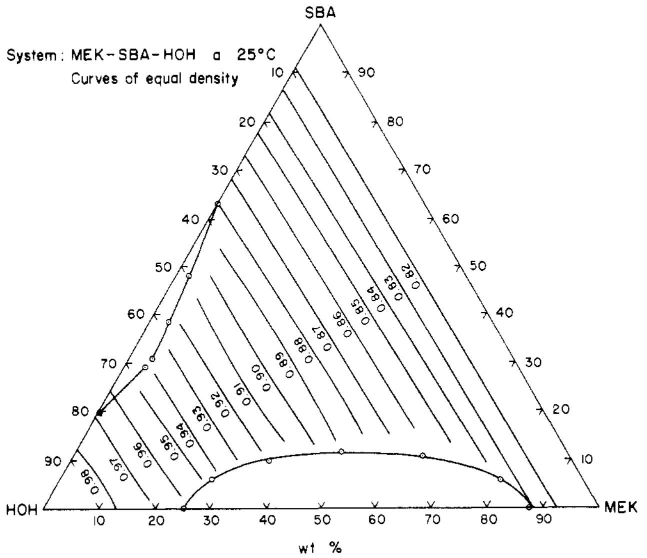

Figure 1. Curves of equal density in the system MEK-SBA-HOH.

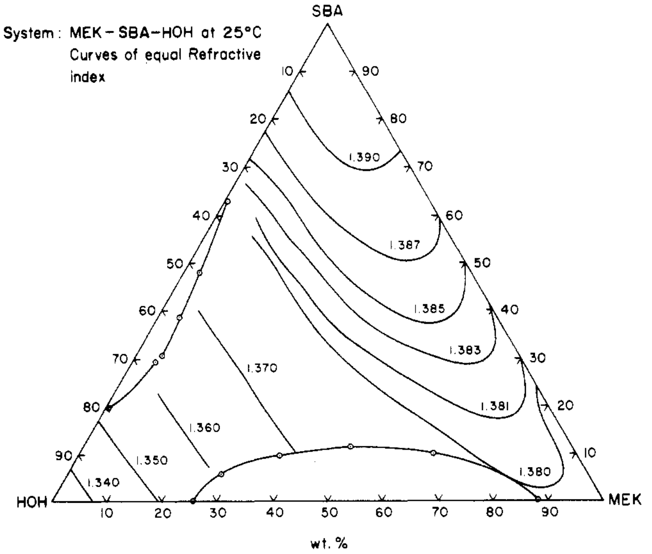

Figure 2. Curves of equal refractive index in the system MEK-SBA-HOH.

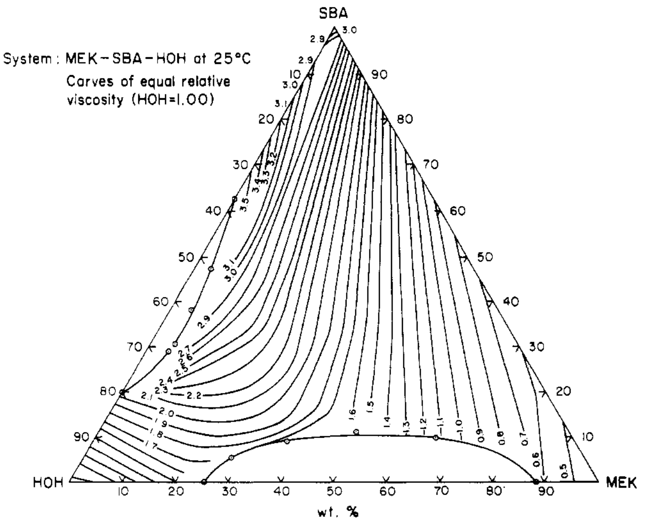

Figure 3. Curves of equal relative viscosity in the system MEK-SBA-HOH.

The high-temperature transformation (2 liquids → 1 liquid) was investigated by sealing homogeneous systems of known composition in glass vials which were heated in the furnace described in ref *6*. The temperature was raised until complete homogeneity was observed and then the furnace was slowly cooled. The temperature at which mistiness recurred was taken as a point on the upper surface. These data are represented in Figure 9 as *t* °C located in a rectangle covering the composition point. The *t*–*C* values are listed in Table IV.

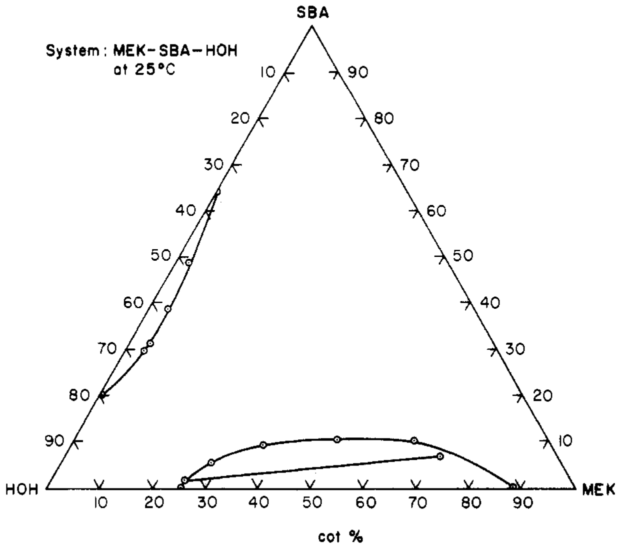

Figure 4. Equilibrium diagram for the system MEK-SBA-HOH at 25 °C.

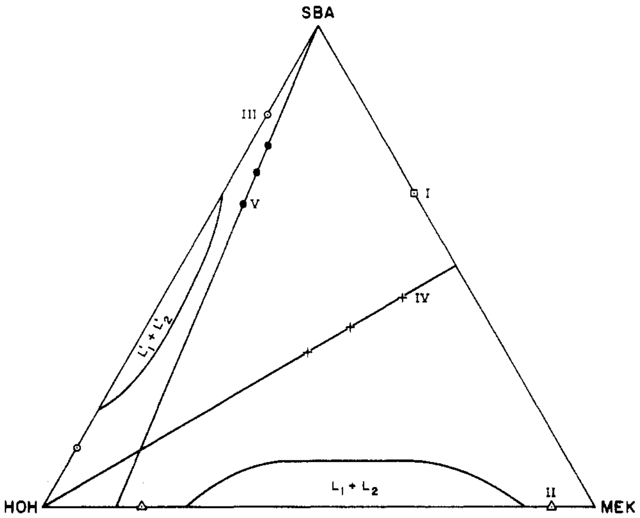

Figure 5. Location of the pseudobinary systems. The positions of the five systems referred to in Figure 6–8: I, MEK–SBA (mole fraction SBA); II, MEK–HOH (mole fraction MEK); III, SBA–HOH (mole fraction SBA); IV, (50.0 MEK–50.0 SBA)–HOH (mole fraction HOH); V, (12.9 MEK–87.1 HOH)–SBA (mole fraction SBA).

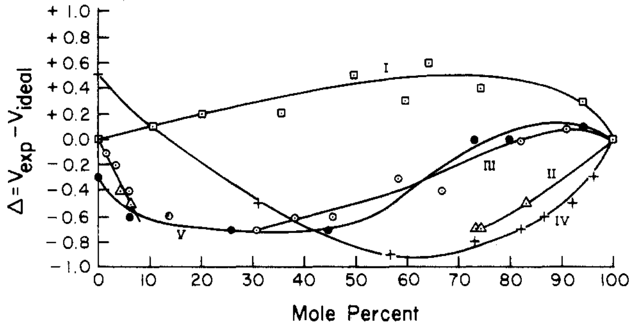

Figure 6. $V = V_{exptl} - V_{ideal}$ vs. mole fraction in the five systems of Figure 5.

Table I. Composition, Density, Viscosity, and Refractive Index for the System MEK-SBA-HOH at 25 °C

I. System: MEK–SBA

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.00)	n^{25}_{D}
0.0	0.800		1.3760
10.7	0.800		1.3784
20.2	0.799		1.3793
35.9	0.799		1.3818
50.0	0.798	0.732	1.3845
59.8	0.800	0.898	1.3873
64.2	0.798	0.926	1.3888
74.6	0.799	1.179	1.3904
94.7	0.801	2.399	1.3946
100.0	0.804	3.056	1.3956

II. System: MEK–HOH

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.00)	n^{25}_{D}
0.0	0.997	1.000	1.3330
7.90	0.984		1.3398
9.69	0.984		1.3412
10.0	0.984	1.260	1.3418
14.9	0.978		1.3460
20.0	0.971	1.517	1.3500
91.7	0.822		1.3778
92.0	0.821	0.557	
95.2	0.813		1.3775
100.0	0.800	0.424	1.3768

III. System: SBA–HOH

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.00)	n^{25}_{D}
0.0	0.997	1.000	1.3330
5.99	0.988	1.276	1.3391
11.0	0.981	1.563	1.3440
16.5	0.973	1.894	1.3501
18.9	0.969		1.3516
64.6	0.877		1.3823
66.9	0.870	3.533	
71.5	0.863	3.462	
77.3	0.851	3.317	
85.1	0.833	3.075	1.3901
89.2	0.826	2.989	
95.0	0.812	2.835	1.3937
97.5	0.807	2.897	1.3939
98.1	0.807	2.888	
100.0	0.804	3.056	1.3956

IV. System: (50 wt % SBA/50 wt % MEK)–HOH

wt % HOH	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.798	0.732	1.3845
10.0	0.824	1.075	1.3861
24.1	0.856	1.564	1.3833
40.1	0.889	2.040	1.3769
52.6	0.915	2.235	1.3701
61.2	0.932	2.214	1.3656
73.4	0.957	1.957	1.3572
85.6	0.977	1.547	1.3475
100.0	0.997	1.000	1.3330

V. System: (12.9 wt % MEK/87.1 wt % HOH)–SBA

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.983	1.337	1.3432
19.3	0.953	2.201	1.3588
37.1	0.919	2.892	1.3698
56.6	0.884	3.145	1.3796
75.1	0.850	3.061	1.3566
91.0	0.817	2.856	1.3920
93.9	0.812	2.781	1.3928
98.1	0.807	2.888	1.3935
100.0	0.804	3.056	1.3956

VI. System: (74.7 SBA/25.3 MEK)–HOH

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.798	1.215	
10.7	0.824	1.620	
24.0	0.853	2.157	1.3853
34.1	0.873	2.454	1.3810
45.3	0.895	2.664	1.3749
55.2	0.918	2.488	1.3690

VII. System: (68.6 SBA/31.4 MEK)–HOH

wt % HOH	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.798	0.597	1.3818
11.5	0.828	0.876	1.3830
22.8	0.853	1.210	1.3814
34.5	0.879	1.551	1.3772
44.5	0.900	1.815	1.3770
54.5	0.919	1.972	1.3685
72.3	0.956	1.847	1.3573
93.7	0.989	1.220	1.3395

VIII. System: (20.0 SBA/80.0 MEK)–HOH

wt % HOH	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.794	0.560	
6.5	0.816	0.690	
12.4	0.829	0.840	
18.1	0.843	0.973	
23.5	0.857	1.149	

IX. System: (50.0 MEK/50.0 HOH)–SBA

wt % SBA	d, g mL^{-1}	η_{rel}(HOH–1.000)	n^{25}_{D}
0.0			
15.7			1.3713
19.0			1.3741
26.6			1.3767
40.1			1.3820
51.9			1.3850
56.2			1.3872
66.5			1.3874
67.4			1.3889
81.7			1.3912

X. System: (23.0 MEK/77.0 HOH)–SBA

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
8.87	0.952		1.3582
20.6	0.932		1.3642
26.8	0.922		1.3677
45.4	0.891		1.3579
64.0	0.862		1.3840

XI. System: (17.7 MEK/82.3 HOH)–SBA

wt % SBA	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.977	1.457	1.3489
18.2	0.947	2.168	1.3598
34.8	0.918	2.728	1.3695
53.8	0.884	2.993	1.3784

XII. System: (10.0 SBA/90.0 HOH)–MEK

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.983		1.3438
5.70	0.977		1.3475
11.5	0.969		1.3520
16.4	0.962		1.3548
22.6	0.952		1.3580

XIII. System: (17.4 SBA/82.6 HOH)–MEK

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
0.0	0.974		1.3505
8.61	0.963		1.3553
16.8	0.951		1.3598
22.1	0.943		1.3619

XIV. System: (40.0 SBA/60.0 HOH)–MEK

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.000)	n^{25}_{D}
11.7	0.914		1.3702
25.4	0.903		1.3728
51.1	0.870		1.3780
70.4	0.846		1.3793
82.1			1.3808
91.4			1.3798

Table I (Continued)

XV. System: (60.0 SBA/40.0 HOH)–MEK

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.000)	$n^{25}{}_D$
10.6	0.879		1.3799
33.4	0.863		1.3817
51.4	0.848		1.3820
68.9	0.833		1.3812

XVI. System: (90.0 SBA/10.0 HOH)–MEK

wt % MEK	d, g mL^{-1}	η_{rel}(HOH = 1.000)	$n^{25}{}_D$
0.0	0.825		1.3930
13.8	0.822		1.3908
25.6	0.819		1.3896
49.0			1.3858
57.4			1.3840
67.4	0.809		1.3824
79.0			1.3803
85.1			1.3788

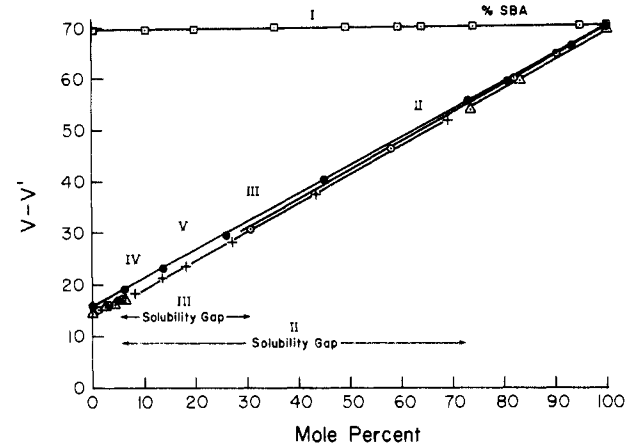

Figure 7. $V' = V_{exptl} - V'$ vs. mole fraction in the five systems of Figure 5.

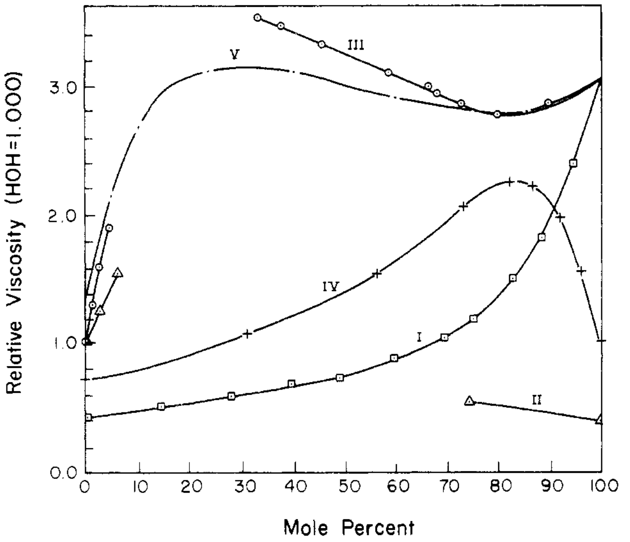

Figure 8. Relative viscosity vs. mole fraction in the five systems of Figure 5.

Results

The density, refractive index, and viscosity data are to be found in Table I. In Figures 1, 2, and 3, curves of equal density, refractive index, and viscosity in the ternary system are shown.

The equilibrium data for the system methyl ethyl ketone–*sec*-butyl alcohol–water at 25 °C are given in Table II and the equilibrium diagram is shown in Figure 4.

Discussion of Results. The curves of equal density approximate to straight lines parallel to the methyl ethyl ketone–*sec*-butyl alcohol side of the diagram. On the other hand curves of equal viscosity which are approximately linear in some regions show marked curvature in the area between the two heterogeneous regions. Refrative index curves show extreme curvature in the region having less than 50% water.

Table II. Equilibrium Data for the System MEK–SBA–HOH at 25 °C (Alexejeff Method)[a]

% MEK	% SBA	% HOH	% MEK	% SBA	% HOH
	20.1	79.9	25.5		74.5
3.80	31.0	65.2	28.1	5.40	66.5
3.30	29.7	67.0	36.7	9.10	54.2
3.20	38.8	58.0	48.6	11.7	39.7
2.20	48.1	49.7	64.1	10.2	25.6
	64.1	35.9	88.4		11.6

[a] Tie line: bottom layer, 25 MEK; 1 SBA; 74 HOH. Top layer, 71 MEK; 7 SBA; 22 HOH.

The density and fractive index data were used to calculate molar volumes

$$V_{exptl} = \sum MX/d \tag{2}$$

$$V_{ideal} = \sum (MX/d^0) \tag{4}$$

$$V' = V_{exptl}\frac{n^2 - 1}{n^2 + 2} \tag{1}$$

and the change in molar volume

$$\Delta V = V_{exptl} - V_{ideal} \tag{3}$$

$$\Delta V' = V_{exptl} - V' \tag{5}$$

ΔV is the difference between observed molar volume of solution and the sum of the molar volumes of its constituents while $\Delta V'$ is the difference between the observed molar volume and the so-called "incompressible" or true volume of the molecules. The molar volumes calculated were confined to the three binary systems and to two pseudobinary systems whose positions in the ternary system are designated as I, II, III, IV, and V in Figure 5. The calculated molar volumes are given in Table III. $\Delta V = V_{exptl} - V_{ideal}$ (*3*) is plotted vs. mole fraction in Figure 6 for the five systems. The homogeneous binary system methyl ethyl ketone–*sec*-butyl alcohol forms solutions with small expansion at all compositions. All other binary or pseudobinary systems studied show contraction on mixing. Two of these (II, III) exhibit a solubility gap and three (I, IV, V) are completely miscible. The feature common to all of the systems that exhibit contraction is the presence of water. Experiment and calculation (from the b values of van der Waals equation) show that the expression $(n^2 - 1/n^2 + 2)M/d$ gives a good approximation to the true or incompressible volume of the molecules. When this expression is plotted against composition in mole per cent (Figure 7) straight line graphs are obtained. This seems to indicate that, despite the formation of two liquid layers under certain circumstances, the components of mixtures of methyl ethyl ketone, *sec*-butyl alcohol, and water are without chemical effect on one another.

The viscosity data are plotted in Figure 8 for the five systems. The addition of 5.0 mol % of *sec*-butyl alcohol to water (III) doubles the viscosity. At this concentration, water is saturated with *sec*-butyl alcohol (a second layer forms). The layer rich

Table III. Composition and Molar Volumes (V_{exptl}, V_{ideal}, V') for the Constituent Binary Systems and for Two Pseudobinary Systems in Figure 5[a]

I. System: MEK-SBA

wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$	wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$
0.0	0.0	90.1	90.1	0	20.7	69.4	59.8	59.1	91.6	91.3	0.3	21.6	70.0
10.7	10.4	90.4	90.3	0.1	20.9	69.5	64.2	63.6	92.0	91.4	0.6	21.7	70.3
20.2	19.8	90.7	90.5	0.2	21.0	69.7	74.6	74.1	92.1	91.7	0.4	21.9	70.2
35.9	35.3	91.1	90.9	0.2	21.2	69.9	94.7	94.6	92.4	92.1	0.3	22.1	70.3
50.0	49.3	91.6	91.1	0.5	21.4	70.2	100.0	100.0	92.2	92.2	0	22.1	70.1

II. System: MEK-HOH

wt % MEK	mol % MEK, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$	wt % MEK	mol % MEK, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$
0.0	0.0	18.05	18.05	0	3.71	14.3	20.0	5.9	21.8	22.3	−0.5	4.69	17.1
7.90	2.1	19.5	19.6	−0.1	4.09	15.4	91.7	73.4	70.2	70.9	−0.7	16.2	54.0
9.69	2.6	19.7	19.9	−0.2	4.14	15.6	92.0	74.2	70.8	71.5	−0.7		
10.0	2.7	19.8	20.0	−0.2	4.17	15.6	95.2	83.2	77.5	78.0	−0.5	17.8	59.7
14.9	4.2	20.7	21.1	−0.4	4.40	16.3	100.0	100.0	90.1	90.1	0	20.7	69.4

III. System: SBA-HOH

wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$	wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$
0.0	0.0	18.05	18.05	0	3.71	14.3	77.3	45.3	51.0	51.6	−0.6		
5.99	1.5	19.1	19.2	−0.1	3.99	15.1	85.1	58.1	60.8	61.1	−0.3	14.4	46.4
11.0	2.91	20.0	20.2	−0.2	4.24	15.8	89.2	66.7	67.1	67.5	−0.4		
16.5	4.58	21.1	21.5	−0.4	4.54	16.6	95.0	82.1	79.0	79.0	0	18.9	60.1
18.9	5.35	21.7	22.1	−0.4	4.69	17.0	97.5	90.4	85.2	85.1	+0.1	20.4	64.8
64.6	30.7	40.2	40.8	−0.6	9.36	30.8	98.1	92.6	86.7	86.7	0		
71.5	37.9	45.5	46.1	−0.6			100.0	100.0	92.2	92.2	0	22.1	70.1

IV. System: (50 SBA/50 MEK)-HOH

wt % HOH	mol % HOH, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$	wt % HOH	mol % HOH, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$
0.0	0.0	91.6	91.1	+0.5	21.4	70.2	61.2	86.5	27.3	27.9	−0.6	6.11	21.2
10.0	31.1	67.9	68.4	−0.5	16.0	51.9	73.4	91.8	23.5	24.0	−0.5	5.15	18.4
24.1	56.6	49.1	50.0	−0.9	11.5	37.6	85.6	96.0	20.7	21.0	−0.3	4.45	16.3
40.1	73.1	36.9	37.7	−0.8	8.49	28.4	100.0	100.0	18.05	18.05	0	3.71	14.3
52.6	81.8	30.6	31.3	−0.7	6.92	23.7							

V. System: (12.9 MEK/87.1 HOH)-SBA

wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$	wt % SBA	mol % SBA, 100(X)	V_{exptl}	V_{ideal}	ΔV	V'	$\Delta V'$
0.0	0.0	20.3	20.6	−0.3	4.29	16.0	91.0	73.1	72.9	72.9	0	17.4	55.5
19.3	6.05	24.3	24.9	−0.6	5.35	19.0	93.9	80.5	78.3	78.3	0	18.7	59.6
37.1	13.7	29.8	30.4	−0.6	6.74	23.1	98.1	93.3	87.3	87.4	+0.1	21.0	66.3
56.6	25.9	38.5	39.2	−0.7	8.91	29.6	100.0	100.0	92.2	92.2	0	22.1	70.1
75.1	44.8	52.0	52.7	−0.7	11.4	40.6							

[a] ($V_{\mathrm{exptl}} = \sum MX/d$ (2); $V_{\mathrm{ideal}} = \sum (MX/d^0)$ (4); $V' = V_{\mathrm{exptl}}(n^2 - 1/n^2 + 2)$ (1); $\Delta V = V_{\mathrm{exptl}} - V_{\mathrm{ideal}}$ (3); $\Delta V' = V_{\mathrm{exptl}} - V'$ (5). V_{exptl}, V', V_{ideal} in mL mol^{-1}.

in *sec*-butyl alcohol has a relative viscosity of 3.5. The gap can be eliminated if a constant amount of methyl ethyl ketone is present: the system (V) is now completely miscible and the viscosity exhibits large positive deviation from the mixture rule. Negative deviation is exhibited by the system methyl ethyl ketone–*sec*-butyl alcohol (I). Again, in the system methyl ethyl ketone–water (II) the viscosity of water increases abruptly to a value of 1.5 at the saturation point, while the layer rich in methyl ethyl ketone has a viscosity of 0.56, as compared to that of pure methyl ethyl ketone (0.424). Curve IV shows the variation in viscosity caused by addition of water to a 50/50 wt % mixture of MEK–SBA: the viscosity passes through a sharp maximum at 85 mol % water.

Range of Heterogeneity in the System MEK–SBA–HOH. If the system MEK–HOH, in such concentration that two layers are formed at room temperature, is cooled below room temperature, ice forms at some constant temperature, −11.4 °C, corresponding to the existence of three phases. During this process, the transformation $L_1 \rightarrow L_2$ + ice is going on, until finally the phase L_1 (aqueous phase) is exhausted. The tem-

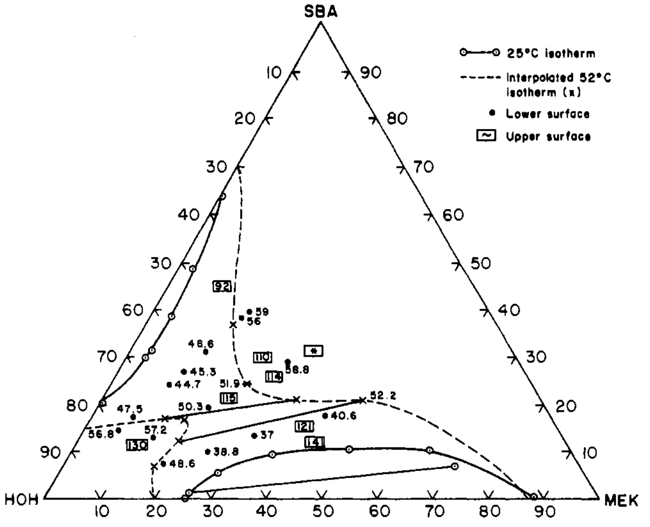

Figure 9. Range of heterogeneity in system MEK–SBA–HOH.

Table IV. Temperature–Composition Data for the Upper and Lower Surfaces of Heterogeneity

Lower

70 MEK/30 SBA		50 MEK/50 SBA		30 MEK/70 SBA	
% HOH	*t*, °C	% HOH	*t*, °C	% HOH	*t*, °C
22.0	*a*	22.7	*a*	34.8	*a*
31.8	52.2	30.7	*a*	41.6	*a*
40.4	40.6	41.9	58.5	43.8	59.0
55.2	37.0	51.1	51.9	45.2	56.0
65.6	88.8	61.2	50.3	55.9	46.6
75.0	48.6	74.7	57.2	61.9	45.3
80.3	*a*			65.5	44.7
				75.6	47.5
				79.5	55.8

Upper: Constant % HOH = 45.0

% MEK	*t*, °C
10.1	92
28.8	114
39.3	121
44.3	141

cst[b]	SBA–HOH	113.8 °C (*1*)
cst	MEK–HOH	142.0 °C (2)

Tie Lines at 51.5 °C

	MEK	SBA	HOH
(1)			
bottom	14	16	70
top	35	22	43
(2)			
bottom	18	12	70
top	47	33	20

[a] Homogeneous to boiling at 1 atm. [b] Critical solution temperature.

perature now drops until, in theory, the eutectic is reached. In practice, the eutectic is not reached because methyl ethyl ketone refuses to crystallize; a glassy mass is obtained. This investigation was completed previously (*2*).

Similar predictions apply to system *sec*-butyl alcohol–HOH, even to the impossibility of realizing the eutectic, and for the same reason. The $L_1 \rightarrow L_2$ + ice transformation occurs at −5.2 °C. Mixtures of *sec*-butyl alcohol and water were cooled in liquid nitrogen and thermal analysis conducted, using a recording potentiometer.

The data of Table IV, shown in Figure 9, were plotted temperature vs. % HOH for three pseudobinary systems. In each there occurs a minimum in temperature between 50 and 60% HOH. Alternatively when temperature is plotted vs. % MEK for fixed water content a set of curves each with a maximum at 50% MEK results. Hence the lower surface of the heterogeneous volume may be roughly described as saddle-shaped.

The upper surface drops from 114 °C on the SBA–HOH side to a minimum (at constant water content = 45%) around 10% MEK (see Figure 9) and then rises to 142 °C on the MEK–HOH side. Along the 50 MEK/50 SBA–HOH line it falls from 130 °C to below 114 °C. The system • is outside the heterogeneous region at all temperature studied (up to 200 °C).

Also shown in Figure 9 are two tie lines at 52 °C. The remainder of the isotherm was interpolated from the temperature–composition data of Table IV.

Registry No. MEK, 78-93-3; SBA, 78-92-2.

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Thermal Conductivity Measurement of Heavy Water over a Wide Range of Temperature and Pressure

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New measurements of thermal conductivity coefficients of heavy water have been performed in the temperature range from 210 to 510 °C and in the pressure range from 1 to 100 MPa corresponding to a density range from 3 to 700 kg/m^3. Most of the measurements were performed in the supercritical region where the typical enhancement of the thermal conductivity is observed. The experimental values are compared with a recommended correlation.

Introduction

Previously, we have used the classical method of coaxial cylinders to determine the thermal conductivity of some polar fluids, in particular light water (*1*) and ammonia (*2*, *3*), in their supercritical ranges. This stationary method allows one to carry out accurate measurements in large temperature and pressure ranges including the critical region if one takes care to ensure that the convection remains small compared to the heat transfer by conduction.

In this paper, we present a new set of measurements of the thermal conductivity coefficients of heavy water in the temperature range from 210 to 510 °C and the pressure range from 1 to 100 MPa. They complete our first measurements obtained in the liquid range (*4*) and vapor phase (*5*).

Several measurements of the thermal conductivity of heavy water have been previously performed and an extensive list of references has been reported by Matsunaga and Nagashima (*6*). However, there were almost no measurements in the supercritical region and correlations of the thermal conductivity surface in this range are made with difficulty.

Experimental Method

The principle of the coaxial cylinder cell was described previously in several reports (*7*–*9*). The temperature rise in the internal cylinder generates a temperature difference between the cylinders. The thermal conductivity λ is calculated by Fourier's law with a number of corrections to take into account the heat losses by solid interfaces (centering pins, electrical

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