Derived results. Using the heat of formation of water and carbon dioxide reported in the National Bureau of Standards tables *(11)* gives $\Delta Hf^\circ(c) = -121.38 \pm 0.86$ kcal-mol^{-1}. Measurement of the heat of sublimation was made in this laboratory using the Knudsen method which yielded a value of 47.2 ± 1.0 kcal-mol^{-1}. This result is based on five determinations of the rate of effusion at 196.6° and 183.3°C; both sets of experiments were carried out at a pressure of about 10^{-6} torr. The heat of sublimation was calculated from a combined form of the Clausius-Clapeyron equation. Combination of $\Delta Hf^\circ(c)$ and ΔH_{subl} gives $\Delta Hf^\circ(g) = -74.2 \pm 1.3$ kcal-mol^{-1}.

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Viscosity Data of Binary Mixtures in the System Methyl Isobutylketone-*n*-Butanol

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Viscosities and densities were determined for binary mixtures of methyl isobutylketone-*n*-butanol, at temperatures of 30°, 40°, 50°, and 60°C and atmospheric pressure. An empirical relation between viscosity, temperature, and composition of the mixture was obtained. The viscosities of the mixtures predicted through this relation were found to be in fairly good agreement with the experimental data.

One need not overemphasize the importance of the measurement of viscosity of any pure component or a binary mixture at different temperatures, as it is a very important transport property with wide applications. The viscosities and densities of both the pure components and mixtures of methyl isobutylketone-*n*-butanol at different compositions and temperatures were determined. An attempt was made to correlate the viscosity data by a single equation, wherein the effects of temperatures and composition are incorporated, thereby facilitating interpolation of the data.

Materials

Methyl isobutylketone. Laboratory reagent grade methyl isobutylketone (British Drug House Co.) was fractionated; the fraction boiling between 115.9° and 116.0°C was collected and used.

n-Butanol. Analytical Reagent grade material (British Drug House Co.) was used without further purification.

The physical properties of the chemicals used here are compared with those reported in literature (Table I). From Table I, it is evident that the viscosity of *n*-butanol, observed by the authors, differs from that reported and even among the reported data there are differences; while in the case of other physical properties, there is fairly good agreement.

Experimental

Solutions of different compositions of the binary system, methyl isobutylketone-*n*-butanol were prepared by weight in ground glass joint conical flasks using a Mettler balance with an accuracy of 0.00005 gram. The densities were obtained from the specific gravity measurements of the different mixtures at different temperatures. A 5-cc, pyrex pycnometer, calibrated at 20°C, was used to determine specific gravities. The densities obtained thus are reproducible to ±0.0002 gram/cc. Water used in the experiments was doubly distilled.

Viscosities of the pure components and mixtures at various temperatures were measured in a pyrex Ostwald viscometer. Errors resulting from wrong alignment of the viscometer in the constant-temperature bath were avoided. Contamination from moisture and dust were prevented by attaching guard tubes containing calcium chloride and glass wool plugs to the viscometer. Three to four de-

Table I. Physical Properties of the Chemicals

Chemical	Density at 30°C		Refractive index at 30°C		Viscosity at 30°C	
	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
Methyl isobutylketone	0.7919	0.7916 *(4)*	1.4185	1.4181 *(4)*	0.49751	nil
n-Butanol	0.8033	0.80206 *(4)*	1.3958	1.3955 *(4)*	2.2211	2.300 *(1)* 2.268 *(2)* 2.271 *(3, 4)*

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Table II. Viscosity Data of Binary Mixtures at Different Temperatures in the System Methyl isobutylketone–*n*-Butanol

Mol % *n*-butanol	Density, gram/cc	Viscosity, cP Exptl	Viscosity, cP Calcd	Rel dev, %
		Temp = 30°C		
100.00	0.8033	2.221	2.191	1.3
92.54	0.8026	1.728	1.795	3.7
84.65	0.8018	1.420	1.475	3.8
76.27	0.8012	1.185	1.218	2.4
67.29	0.7992	0.997	1.013	1.6
57.95	0.7981	0.862	0.854	0.9
47.45	0.7970	0.748	0.725	3.1
36.70	0.7958	0.653	0.632	3.3
25.31	0.7944	0.592	0.566	4.7
13.11	0.7931	0.542	0.523	3.6
0.00	0.7919	0.497	0.507	2.0
		Temp = 40°C		
100.00	0.7959	1.720	1.704	1.0
92.36	0.7947	1.430	1.416	1.0
80.44	0.7937	1.177	1.185	0.7
76.04	0.7922	0.980	0.996	1.6
67.04	0.7910	0.844	0.842	0.2
57.54	0.7896	0.733	0.720	1.8
47.45	0.7885	0.647	0.625	3.5
36.77	0.7869	0.578	0.552	4.8
25.33	0.5955	0.526	0.499	5.4
13.11	0.7841	0.482	0.465	3.7
0.00	0.7827	0.443	0.452	1.9
		Temp = 50°C		
100.00	0.7869	1.361	1.347	1.0
93.86	0.7866	1.136	1.143	0.6
84.52	0.7843	0.937	0.970	3.4
75.97	0.7829	0.801	0.828	3.2
67.21	0.7818	0.707	0.714	1.0
57.59	0.7801	0.621	0.618	0.5
47.59	0.7788	0.565	0.544	3.4
36.88	0.7774	0.507	0.486	4.3
25.42	0.7763	0.464	0.444	4.5
13.19	0.7748	0.428	0.416	2.8
0.00	0.7739	0.401	0.405	1.2
		Temp = 60°C		
100.00	0.7787	1.085	1.079	0.6
92.47	0.7769	0.914	0.930	1.7
84.50	0.7758	0.785	0.803	2.2
76.14	0.7739	0.676	0.698	3.1
57.72	0.7721	0.543	0.535	1.5
36.72	0.7692	0.458	0.431	6.3
13.19	0.7657	0.386	0.384	0.7
0.00	0.7645	0.365	0.366	0.4

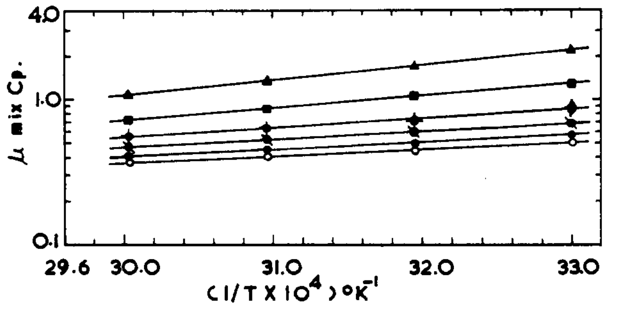

Figure 1. Smoothed viscosity vs. $1/T (K^{-1})$, mol % *n*-butanol
○ 0
● 20
✱ 40
✦ 60
■ 80
▲ 100

terminations of the time of flow of each sample were made at each temperature and composition. The value of 1002 mP was used for the viscosity of water at 20°C. The viscosity measurements reported here are reproducible to within 1%.

Both the density and viscosity measurements were carried out in Fischer's Unitized constant-temperature bath with an accuracy of ±0.03°C. Temperature measurements were made by a mercury-in-glass thermometer of 0.1°C accuracy, which was calibrated against a thermometer tested for its accuracy by the National Physical Laboratory, London.

Results and Discussions

The viscosity data obtained at 30°, 40°, 50°, and 60°C for the system methyl isobutylketone–*n*-butanol was given in Table II. Experimental viscosities of the mixtures were plotted against composition in mole percent for each temperature, and smoothed curves were drawn. Then, smoothed values of viscosities corresponding to 0, 20, 40, 60, 80, and 100 mol % *n*-butanol were obtained at the above temperatures.

The following functional relationship between viscosities of the mixtures and temperatures was assumed.

$$\mu_{\text{mix}} = Ae^{B/T} \tag{1}$$

Smoothed viscosity data of the mixtures are plotted against $1/T$ in Figure 1, keeping mole percent of *n*-butanol as a parameter, which resulted in straight lines for each of the integral values of compositions as stated above. Then A and B values were determined for all the straight lines. From this data, the following relation between B and x is found (Figure 2):

$$B = 1097 + 1286\, \chi^{1.89} \tag{2}$$

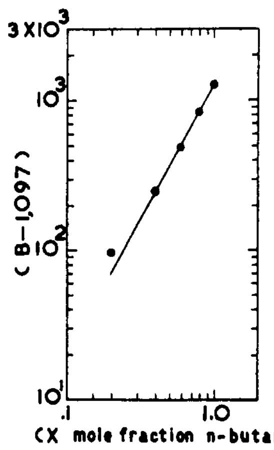

Figure 2. B vs. x

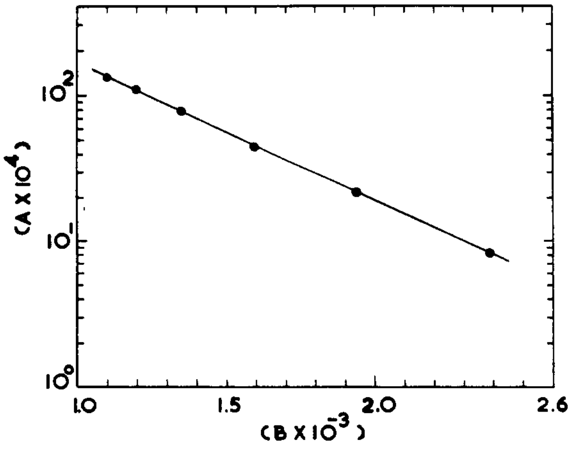

Figure 3. A vs. B

Further, another relationship between A and B (Figure 3) is given by

$$A = 0.1456\, e^{-21.62 \times 10^{-4} B} \qquad (3)$$

The following equation is obtained by substituting Equations 2 and 3 in Equation 1:

$$\mu_{\mathrm{mix}} = 0.1456\, e^{[(1/T) - 21.62 \times 10^{-4}]\,(1097 + 1286\,\chi^{1.89})} \qquad (4)$$

For associated liquids, the relationship between log μ_l and $1/T$ becomes slightly curved; in the present case this relationship resulted in straight lines. This may be due to negligible effect of association of *n*-butanol in the range of temperatures studied.

By means of Equation 4, viscosity data at any given temperature and composition of the binary mixture can be predicted. Viscosity data predicted through Equation 4 compare well with experimental data (Table II), and the average percent deviation is 2.3.

Nomenclature

A, B = constants in Equation 1
T = absolute temperature, °K
χ = composition, mole fraction *n*-butanol
μ_{mix} = viscosity of mixture, cP

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Total Pressure Method: Binary Systems Cyclohexane–*n*-Pentanol, –*n*-Heptanol, and –*n*-Octanol

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Vapor-liquid equilibria for the binary systems cyclohexane–*n*-pentanol, –*n*-heptanol, and –*n*-octanol were obtained by the total pressure measurement method. Isothermal and isobaric vapor-liquid equilibria were calculated by numerical methods. For the isothermal conditions the calculations were performed at 10°C intervals between 70° and 130°C while for the isobaric conditions, they were performed at 400, 600, 760, and 900 mm Hg. The excess free energy was also calculated under all these conditions.

The total pressure measurement method consists of measuring the total pressures as a function of the composition of only one of the phases (usually the liquid phase) at constant temperature. The composition of the other phase is calculated with the help of the Gibbs-Duhem equation. The main advantage of this method is the great reduction of the experimental work involved.

In previous papers by the same authors *(2, 3)*, the Ramalho and Delmas method *(5)* has been improved and also extended to calculate numerically isobaric data. This modified method has been used in performing the necessary calculations in this work. A brief description of the method used to calculate vapor-liquid equilibrium data has been filed with the ACS Depository Service.

The method of calculation was fully described in previous articles *(2, 3)*. The average deviation of the results obtained by calculation when compared to reliable experimental data was well within 1% and the maximum local error never exceeded 1.5%.

Experimental

Apparatus. The apparatus used in this investigation is, with some modifications, essentially the same as the one used elsewhere *(4, 6)*. The overall experimental setup is illustrated in Figure 1. Four ebulliometers of the Swietoslawski type were operated in parallel at the same pressure to speed the collection of data. With a vacuum pump, the ebulliometers could be operated below atmospheric pressure and operation above was accomplished by using a high-pressure nitrogen cylinder to create the desired pressure. Pressure is finely controlled by a Cartesian manostat. Quartz thermometers were used to measure temperature with a precision of ±0.02°C. Pressure was read with a manometer coupled with a cathetometer. The precision in the measurement of pressure was ±0.5 mm Hg. A quieting reservoir was incorporated before the manometer to eliminate the fluctuations in the manometer owing to the boiling of the solution. The liquid mixtures were prepared by weighing appropriate amounts of the components. The precision in the composition was ±0.001.

Full descriptions of the apparatus with detailed descriptions and precisions of the equipment used can be found elsewhere *(1)*.

Materials. All the materials used were of the chromo quality standard 99+ mol %. The density and index of refraction of these materials were measured and are given in Table I. They were used as received without further purification.

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