J. Chem. Eng. Data **1984**, *29*, 11–13

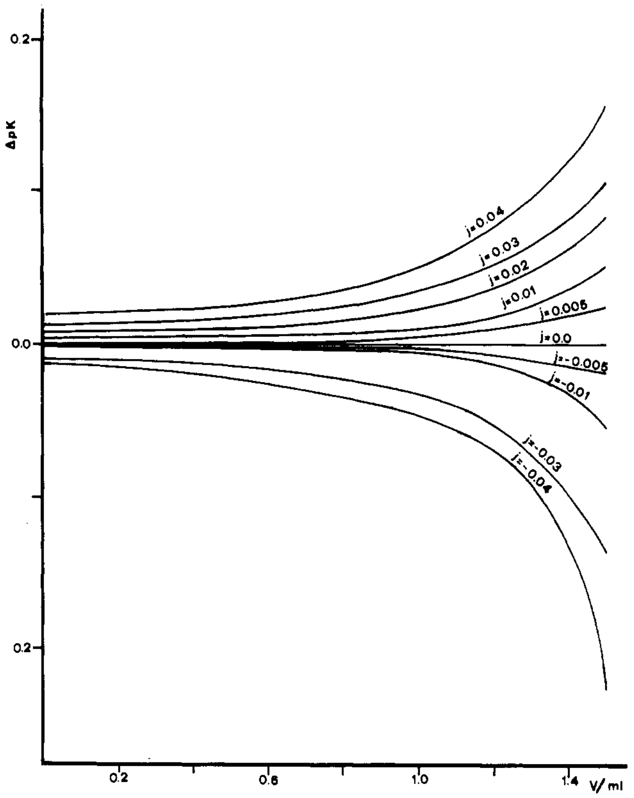

Figure 1. Influence of the error *j* in the initial concentration of TEA upon the value of the ionization p*K* of TEAH$^+$.

Table II. Thermodynamic Ionization Constants of Protonated MEA, DEA, and TEA

	p*K*	
	a	*b*
MEA	9.59 ± 0.01	9.53 ± 0.02
DEA	8.96 ± 0.01	8.96 ± 0.01
TEA	7.84 ± 0.04	7.86 ± 0.01

[a] Extrapolated value. [b] Value calculated as in ref *6*.

where K_{exptl} is a mixed equilibrium constant, V the volume of HCl added, V_0 the initial volume of the solution, c_0 the concentration of the HCl, and B_0 the number of moles of alkanolamine initially present. This equation is deduced as in ref *6* from the conservation of matter together with the conditions of equilibrium and electroneutrality that hold for the aqueous solution. To see how any errors in the determination of the initial concentration of alkanolamine might affect the p*K* value calculated, eq 1 was analyzed by replacing B_0 by $(1 - j)B_0$, j being a hypothetical proportional error which was varied between 1% and 4%. Figure 1 shows the result of this analysis for a typical titration. As can be seen, for $j \neq 0$ the p*K* diverges increasingly from the correct value as the titration proceeds. To reduce this error to a minimum the calculation of pK_{exptl} was based on the least affected period of titration, besides which the value of B_0 itself was optimized by means of the Davies, Swann, and Campey algorithm (*7*), the optimal value being taken as that for which the possible errors in pK_{exptl} would be least. In no case was the error j found to be greater than 2%, which is in accord with the precision of the volumetric apparatus used.

Table I shows the optimized values of the ionization p*K*'s of the protonated alkanolamines for the various inert electrolytes and ionic strengths employed. The basicity of the alkanolamine may be observed to fall as the number of substituent alcohol groups rises. The effect of the nature of the inert electrolyte is minimal. The graphs of p*K* against $I^{1/2}$ are straight lines which allow the extrapolated value of the thermodynamic constant to be obtained. These values are shown in Table II together with those that we have obtained using the experimental procedure described by Albert and Serjeant (*6*). The agreement between the two is quite acceptable.

Registry No. MEA, 141-43-5; DEA, 111-42-2; TEA, 102-71-6.

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Received for review January 17, 1983. Accepted June 6, 1983.

Viscosities, Densities, and Refractive Indexes of Mixtures of Methyl Isobutyl Ketone–Isobutyl Alcohol

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Viscosities, densities, and refractive indexes were determined for methyl isobutyl ketone–isobutyl alcohol mixtures at 20, 25, 30, and 35 °C and at atmospheric pressure. These properties were correlated with the composition and temperature of mixtures through empirical relations. The calculated values were in agreement with the experimental data in the temperature range of the measurements.

Viscosity, density, and refractive index data of binary liquid mixtures are frequently used in chemical engineering work; therefore, an attempt was made to correlate these properties by single equations wherein the effects of temperature and composition are involved, thereby allowing interpolation of the data.

Materials. Methyl isobutyl ketone (AR, Merck) was distilled, refluxed, and fractionated. The fraction boiling between 115 and 116 °C was collected and used in the experiments. Isobutyl alcohol (AR, Merck) was used without further purification and drying (*1*). The physical properties of the substances used are compared with corresponding data reported in the literature in Table I.

Experimental Section

Solutions of different compositon of the methyl isobutyl ketone–isobutyl alcohol system were prepared by weight in a

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Table I. Physical Properties of Components in the Present Work and in the Literature

	ρ		n_D		η	
temp, °C	exptl	lit.	exptl	lit.	exptl	lit.
			Methyl Isobutyl Ketone			
20	0.8010	0.8008 (*1*)	1.395 76	1.3962 (*3*)	0.575	
25	0.7963	0.7961 (*1*)	1.393 62	1.3933 (*1*)	0.543	0.542 (*1*)
30	0.7920		1.391 45		0.518	
35	0.7868		1.389 29		0.494	
			Isobutyl Alcohol			
20	0.8017	0.8017 (*1*)	1.395 91	1.3959 (*1*)	4.02	4.028 (*3*)
25	0.7980	0.7978 (*1*)	1.393 89	1.3939 (*1*)	3.40	
30	0.7942	0.7943 (*2*)	1.392 01		2.89	
35	0.7901		1.390 42		2.47	

Table II. Experimental Viscosity and Density Data for the Mixture at 20, 25, 30, and 35 °C

	η				ρ			
X_{B_3}	20 °C	25 °C	30 °C	35 °C	20 °C	25 °C	30 °C	35 °C
1.0000	4.02	3.38	2.89	2.47	0.8017	0.7980	0.7942	0.7901
0.8988	2.52	2.18	1.90	1.67	0.8016	0.7978	0.7940	0.7897
0.7987	1.78	1.58	1.41	1.26	0.8016	0.7976	0.7937	0.7894
0.7000	1.37	1.23	1.126	1.013	0.8015	0.7975	0.7935	0.7891
0.5964	1.101	1.002	0.922	0.841	0.8014	0.7973	0.7933	0.7887
0.4937	0.929	0.851	0.786	0.730	0.8013	0.7971	0.7931	0.7884
0.3997	0.819	0.756	0.703	0.656	0.8013	0.7970	0.7929	0.7881
0.3024	0.732	0.680	0.637	0.591	0.8012	0.7968	0.7927	0.7878
0.1971	0.662	0.619	0.585	0.550	0.8011	0.7966	0.7924	0.7874
0.0992	0.615	0.576	0.546	0.512	0.8011	0.7964	0.7922	0.7871
0.0000	0.575	0.543	0.518	0.494	0.8010	0.7963	0.7920	0.7868

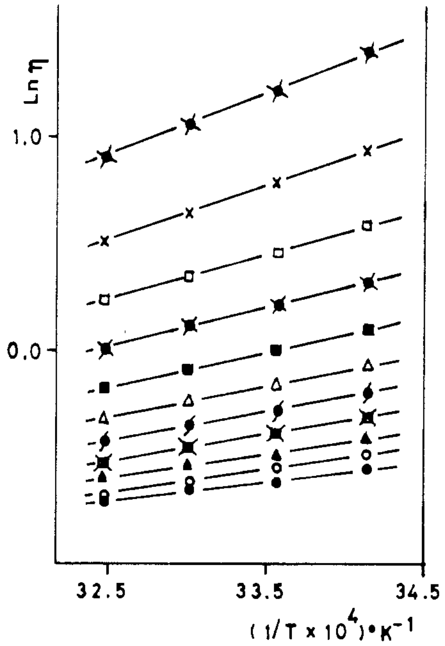

Figure 1. Viscosities of the mixture vs. temperature.

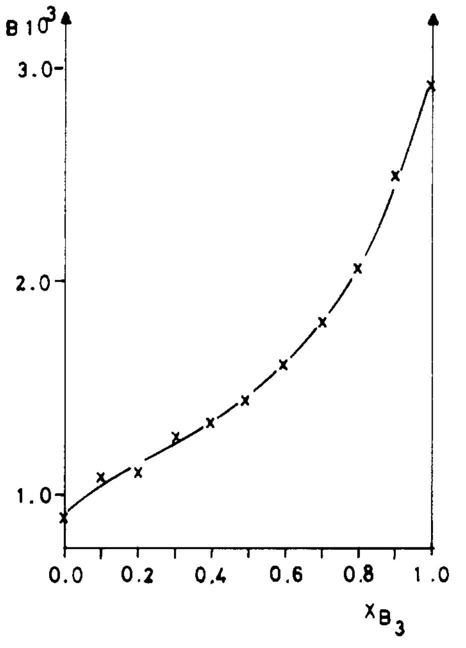

Figure 2. B constant in eq 1 vs. mole fraction of isobutyl alcohol.

ground-glass-joint conical flask by using a Mettler H-311 balance with an accuracy of ±0.0005 g. The viscosities of the pure components and mixtures at various temperatures were measured with a Cannon-Fenske viscosimeter, calibrated with doubly distilled water, benzene, and sucrose solution (*4*), with an accuracy of ±0.5%. Densities were obtained with a Robertson specific gravity bottle (*5*) with an accuracy of ±0.0001 g cm^{-3}. Refractive indexes for the sodium D line of the pure components and mixtures were measured with a Jena dipping refractometer with an accuracy of ±0.000 02. In all cases, a thermostatically controlled bath, constant to 0.01 °C, was used.

Results and Discussion

Experimental viscosity and density data at 20, 25, 30, and 35 °C for the methyl isobutyl ketone-isobutyl alcohol system are shown in Table II. The following functional relationship between viscosity of the mixtures and temperature was assumed:

$$\eta = Ae^{B/T} \quad (1)$$

Smoothed viscosity data of the mixtures are plotted against $1/T$ in Figure 1. The mole fraction of isobutyl alcohol was kept as a constant parameter. Straight lines were obtained for each composition, as stated above.

Based on these data, the following relation between B and X was found (Figure 2):

$$B = 918.81 + 1544.07X - 2363.99X^2 + 2840.34X^3 \quad (2)$$

$$\sigma_B = 33.48$$

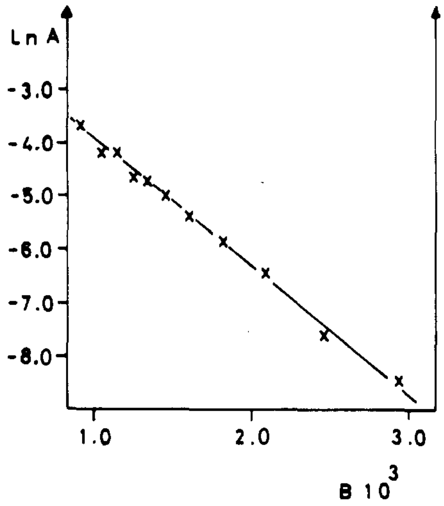

Figure 3. *A* vs. *B* constant in eq 1.

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

$$A = 0.2187e^{(-24.17 \times 10^{-4})B} \tag{3}$$

$$\sigma_A = 1.05 \times 10^{-1}$$

Then, the following equation was obtained:

$$\eta = 0.2187 \exp\{(1/T - 24.17 \times 10^{-4}) \times (918.81 + 1544.07X - 2363.99X^2 + 2840.34X^3)\} \tag{4}$$

For density data, an equation proposed by us in a previous work (*6*) was used:

$$\rho = A'e^{B't} \tag{5}$$

A similar form of calculation, as described before, was applied. The following results were obtained:

$$B' = -11.82 \times 10^{-4} + (2.10 \times 10^{-4})X \tag{6}$$

$$\sigma_{B'} = 2.62 \times 10^{-6}$$

$$A' = 0.804993 - 12.875B' \tag{7}$$

$$\sigma_{A'} = 3.8 \times 10^{-5}$$

Consequently, the relation of density with composition and temperature is

$$\rho = [0.8202 - (27.04 \times 10^{-4})X] \exp\{(-11.82 + 2.10X)t \times 10^{-4}\} \tag{8}$$

For the refractive indexes, the same relation assumed previously (*6*) was used:

$$n_D = A''e^{B''t} \tag{9}$$

By means of the same kind of calculation, we achieved the following results:

$$B'' = -3.10 \times 10^{-4} + (0.47 \times 10^{-4})X \tag{10}$$

$$\sigma_{B''} = 8.89 \times 10^{-7}$$

$$A'' = 1.39599 - 27.22B'' \tag{11}$$

$$\sigma_{A''} = 1.11 \times 10^{-5}$$

Then

$$n_D = [1.40443 - (12.79 \times 10^{-4})X] \exp\{[-3.10 \times 10^{-4} + (0.47 \times 10^{-4})X]t\} \tag{12}$$

The plots of η against $1/T$ become slightly curved for associated liquids, but in the present case straight lines were obtained. This may be due to the negligible effect of association of isobutyl alcohol in the range of temperatures studied. Viscosity, density, and refractive index data predicted through eq 4, 8, and 12 compare well with experimental data and the average percent deviatons are 2.3, 1.6×10^{-2}, and 4.3×10^{-3}, respectively.

Acknowledgment

We express our thanks to Mariana Hernandez Ubeda for experimental assistance.

Glossary

A, B	constants in eq 1
A', B'	constants in eq 5
A'', B''	constants in eq 9
η	viscosity of the mixture, cP
ρ	density of the mixture, g cm^{-3}
n_D	refractive index
X_{B_3}, X	mole fraction of isobutyl alcohol
T	temperature, K
t	temperature, °C
σ_B, σ_A, $\sigma_{B'}$, $\sigma_{A'}$, $\sigma_{B''}$, $\sigma_{A''}$	standard deviations for eq 2, 3, 6, 7, 10, and 11, respectively

Registry No. Methyl isobutyl ketone, 108-10-1; isobutyl alcohol, 78-83-1.

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Received for review August 2, 1982. Accepted May 17, 1983. This work was supported by the INENCO of the Universidad Nacional de Salta, República Argentina.