Viscosities of Binary Mixtures of Methyl Ethyl Ketone, 1-Butanol, and Isoamyl Alcohol at 35° C.

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Measurements of viscosity as functions of composition at 35° C. for the binary mixtures, methyl ethyl ketone–isoamyl alcohol, methyl ethyl ketone–1-butanol, and 1-butanol–isoamyl alcohol are reported. The experimental values agree with those obtained from the equations suggested by Katti and Chaudhri and McAllister, within 3% error.

ON the basis of Eyring's theory of viscosities of pure liquids and assuming a regular solution-type model for the activation free energy, Katti and Chaudhri (*1*) and McAllister (*2*) proposed equations which show the dependence of viscosities of mixtures on the composition. In this investigation, the authors determined the viscosities of the binary mixtures of methyl ethyl ketone–isoamyl alcohol, methyl ethyl ketone–1-butanol, and 1-butanol–isoamyl alcohol as a function of composition at 35° C., in order to study the validity of the equations proposed by previous workers (*1*, *2*) for these systems. The size ratios of the systems studied are given in Table I.

EXPERIMENTAL

Materials. Laboratory reagent grade isoamyl alcohol, methyl ethyl ketone, and 1-butanol from British Drug House Co. of India were distilled twice over sodium at atmospheric pressure in a laboratory borosilicate glass Vigreux fractionating column having an effective length of 36 cm. The fractions were collected within about 0.2° C. of their respective boiling points. The observed boiling points were corrected to 760-mm. pressure using Crafts rule, to get the experimental normal boiling point. The refractive index, density, and viscosity values of the pure components were determined experimentally and compared with the literature values in Table II. The refractive index was measured for sodium light with a Carl Zeiss Abbe refractometer which can be used to measure refractive indices, n_D, in the range of 1.3 to 1.7. The upper scale is divided into units of the 3rd decimal of the refractive power; one or two units of the 4th decimal place can be readily estimated by visual observation. The adjustment of this refractometer was tested with double-distilled water. The densities were determined by using a 10-ml. pycnometer. The viscosities were determined in a Ubbelohde viscometer at 35° ± 0.01° C. The standard deviations for the determination of density and viscosity are 0.0001 and 0.0003, respectively.

Table I. Size Ratios of Systems

System	Volumetric Size Ratio	
	Molal	Radii
Methyl ethyl ketone–1-butanol	1/1.016	1/1.006
Methyl ethyl ketone–isoamyl alcohol	1/1.206	1/1.064
1-Butanol–isoamyl alcohol	1/1.187	1/1.059

RESULTS AND DISCUSSION

The experimentally observed values of viscosity for different compositions of the three systems are given in

Table II. Physical Properties of Materials (*3*)

	Normal Boiling Point, ° C.		Density at 35° C., Gram per Ml.		Refractive Index at 35° C.		Viscosity at 35° C., Cp.[a]	
	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.	Exptl.	Lit.
Isoamyl alcohol	132	132	0.8001	0.7990[b]	1.4011	1.4011[b]	2.8153	2.3550[b]
1-Butanol	117.5	117.7	0.7984	0.7983[b]	1.3931	1.3934[b]	1.9867	1.9017[b]
Methyl ethyl ketone	79.5	79.6	0.7891	0.7890[b]	1.3711	1.3713[b]	0.3657	0.3460[b]

[a] Cp = centipoises. [b] Obtained by using temperature correction.

Table III. Viscosities at 35° C.

X_A	X_B	$\nu \times 10^2$ Exptl.	Calcd. (1)	Calcd. (2)
Methyl Ethyl Ketone (A)–1-Butanol (B)				
$w_{visc.}$ = 422.485 cal. per gram mole; ν_{AB} = 0.6907; ν_{BA} = 1.1640				
0.0996	0.9004	1.9960	1.9782	...
0.2002	0.7998	1.5570	1.5946	1.6210
0.2999	0.7001	1.3245	1.2999	1.3450
0.4004	0.5996	1.0619	1.0686	1.1110
0.5002	0.4998	0.9029	...	0.9385
0.5998	0.4002	0.8002	0.7689	0.8072
0.6998	0.3002	0.6796	0.6635	0.6996
0.7997	0.2003	0.5966	0.5805	0.6039
0.8998	0.1002	0.5366	0.5149	...
Methyl Ethyl Ketone (A)–Isoamyl Alcohol (B)				
$w_{visc.}$ = 719.715 cal. per gram mole; ν_{AB} = 0.7087; ν_{BA} = 0.9217				
0.0996	0.9004	2.4753	2.5884	...
0.2003	0.7997	1.9362	1.9394	1.8880
0.3000	0.7000	1.4906	1.4924	1.4820
0.4004	0.5996	1.1825	1.1739	1.0910
0.5000	0.5000	0.9474	...	0.9051
0.5997	0.4003	0.8074	0.7831	0.7721
0.6998	0.3002	0.6975	0.6658	0.6704
0.8002	0.1998	0.6050	0.5737	0.6010
0.9001	0.0999	0.5268	0.5092	...
1-Butanol (A)–Isoamyl Alcohol (B)				
$w_{visc.}$ = 14.492 cal. per gram mole; ν_{AB} = 2.8180; ν_{BA} = 3.1490				
0.1001	0.8999	3.3992	3.3888	...
0.2004	0.7996	3.2627	3.2527	3.2880
0.3004	0.6996	3.1809	3.1303	3.1790
0.4001	0.5999	3.0992	3.0158	3.0730
0.4998	0.5002	2.9117	...	2.9690
0.5998	0.4002	2.8764	2.8145	2.8690
0.6998	0.3002	2.7629	2.7228	2.7710
0.8003	0.1997	2.6638	2.6390	2.6760
0.9002	0.0988	2.5826	2.5576	...

column 3 of Table III. In column 4, the viscosity values calculated by the method suggested by Katti and Chaudhri (*1*) are given. The equation can be written as

$$\ln\nu M = X_A \ln\nu_A M_A + X_B \ln\nu_B M_B + X_A X_B \frac{w_{viscous}}{RT}$$

The values of $w_{viscous}$ for the systems are also given. The values calculated by using the McAllister formula (*2*) are given in column 5. The binary constants for each system are also shown in Table III. The experimental values agree with the calculated values (*1, 2*) within about 3% error.

NOMENCLATURE

- X = mole fraction
- ν = kinematic viscosity, cm.^{2} per second
- $w_{viscous}$ = interaction energy for activation of flow, cal. per gram mole
- ν_{AB}, ν_{BA} = binary constants
- M = molecular weight

LITERATURE CITED

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Low-Temperature Heat Capacity and Entropy of Phosphonitrilic Hexaamide Monohydrate

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PHOSPHONITRILIC hexaamide monohydrate, $P_3N_3(NH_2)_6 \cdot H_2O$, is of interest as a potential ultrahigh-analysis phosphorus nitrogen fertilizer compound. It is water-soluble, and preliminary greenhouse tests indicate that the phosphorus and nitrogen contents are readily available to plants. In a continuing program of collection of thermodynamic data on materials involved in fertilizer technology, the low-temperature heat capacity of the compound was measured over the temperature range 10° to 320° K.

MATERIALS AND APPARATUS

The low-temperature calorimeter has been described (*2*). The automatic shield-control system was used for all measurements. Energy was supplied to the calorimeter by a constant-current device (Princeton Applied Research, Model TC-100.2AR) and the voltage was measured by a digital voltmeter (Hewlett-Packard Dymec, Model 2401C). Energy measurements with this system were compared with those made with the previously used battery supply and Hi-Wenner potentiometer. The potentiometer, voltbox, and standard resistors were calibrated by the Redstone Arsenal, Huntsville, Ala., and are traceable to the National Bureau of Standards. Measurements by the two systems agreed within 0.02%.

The defined calorie was taken as 4.1840 absolute joules, the ice point as 273.15° K. The heat capacities were corrected for curvature (*3*). Since small differences were important, temperatures were read to four decimal places, but they were rounded to two decimal places in the final tabulation.

The phosphonitrilic hexaamide monohydrate was prepared by placing in a 2-liter Parr bomb 236 grams (0.68 mole) of distilled and recrystallized phosphonitrilic chloride