

Table III. Empirical Polynomial for Densities of AlCl₃-LiCl Melts

$$D = a_{00} + a_{01}(t - 200) + a_{10}(X - 0.5) + a_{11}(X - 0.5)(t - 200) + a_{20}(X - 0.5)^2 + a_{21}(X - 0.5)^2(t - 200)$$

where $a_{00} = 1.599737$, $a_{01} = -7.4951 \times 10^{-4}$, $a_{10} = -0.13158$, $a_{11} = -1.584 \times 10^{-4}$, $a_{20} = -0.79577$, and $a_{21} = -5.933 \times 10^{-3}$ and root-mean-square error in $D = 0.06\%$, root-mean-square error in $t = 0.004\%$, and root-mean-square error in $X = 0.2\%$

occupied by the dilatometers. The remaining uncertainty, δD , also was calculated by propagating into D the weighing errors, meniscus location uncertainty, and dilatometer calibration errors. Here, the weighing errors were the most significant.

It was not necessary to make corrections for volatilization of the samples into the vapor space within the dilatometers, for sample masses were chosen such that the capillaries were very nearly filled at the highest temperatures. The vapor pressures of AlCl₃-LiCl mixtures have not been reported but reasonably cannot exceed the saturated vapor pressure of AlCl₃ itself. The largest volatilization correction, assuming this extreme condition (δ), would have been only $0.1\delta X$.

The least-squares fit was iterative. Iterations were continued until

$$\frac{2|\sigma - \sigma_{\text{previous iteration}}|}{\sigma + \sigma_{\text{previous iteration}}} < 10^{-7} \quad (3)$$

where σ , the standard deviation, was calculated from

$$\sigma = \left(\frac{1}{N} \sum_{k=1}^N z_k^2 \right)^{1/2}$$

The values of a_{ij} when the criterion of eq 3 was first satisfied are given in Table III.

Safety

Appropriate precautions should be taken for the containment of liquids above their normal boiling points in glass vessels.

Glossary

a_{ij}	empirical coefficients
D	liquid density, g/cm ³
i	exponent on mole fraction
j	exponent on temperature
k	index for individual experimental points
N	total number of experimental points
t	temperature, °C
X	mole fraction of AlCl ₃
z	perpendicular distance to plane along X , t , D surface; function to be treated by least-squares fitting
δD	estimated uncertainty in density, 0.001 g/cm ³
δt	estimated uncertainty in temperature, 0.05 °C
δX	estimated uncertainty in mole fraction, 0.001
$\Delta \xi$	the difference between the experimentally measured value of the quantity ξ and the value of ξ calculated from eq 1 and the remaining variables ($\xi = D$, t , or X)
σ	standard deviation

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Viscosity of Nonpolar Gases (Quaternary Mixtures)

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Viscosities of quaternary mixtures of N₂-O₂-CO₂-N₂O have been measured in the temperature range 40–140 °C by the capillary flow method. The experimental values of viscosity are compared with theoretical values obtained from the kinetic theory in conjunction with the extended law of corresponding states proposed by Kestin, Ro, and Wakeham. The comparison shows the existence of very good agreement.

A very precise extended principle of corresponding states has been formulated by Kestin, Ro, and Wakeham (3, 5–7). It has made possible the correlation of low-density equilibrium and transport properties of the monatomic gases and their multi-component mixture over the entire experimental temperature range available, with an accuracy comparable to the best measurements.

The Chapman-Enskog theory and its extension to multi-component mixtures (4) predicts that the viscosity of an n -component mixture, using standard symbols, may be written in the form

$$\mu = - \frac{\begin{vmatrix} H_{11} & \dots & H_{1n} & X_1 \\ H_{n1} & \dots & H_{nn} & X_n \\ X_1 & \dots & X_n & 0 \end{vmatrix}}{\begin{vmatrix} H_{11} & \dots & H_{1n} \\ H_{n1} & \dots & H_{nn} \end{vmatrix}} \quad (1)$$

Here

$$H_{ii} = \frac{x_i^2}{\mu_i} + \sum_{\substack{k=1 \\ k \neq i}}^n \frac{2x_i x_k}{\mu_k} \frac{M_i M_k}{(M_i + M_k)} \left(\frac{5}{3A_{ik}^*} + \frac{M_k}{M_i} \right)$$

and

$$H_{ij} = - \frac{2x_i x_j}{\mu_{ij}} \frac{M_i M_j}{(M_i + M_j)^2} \left(\frac{5}{3A_{ij}^*} - 1 \right) \quad i \neq j$$

In this expression X_i and M_i represent the mole fraction and molecular weight of i th component, respectively. The interaction viscosity μ_{ij} is given by

$$\mu_{ij} = \frac{5}{16} \left(\frac{KM_{ij}T}{\pi N} \right)^{1/2} \frac{1}{\sigma_{ij}^2 \Omega_{22}} \quad (2)$$

where $M_{ij} = 2MM_j/(M_i + M_j)$ and where σ_{ij} is a distance scaling parameter.

The value of σ_{ij} turns out to be nearly, but not quite, equal to the value σ_0 such that $V(\sigma_0) = 0$; the precise value is $\sigma_0/\sigma_{ij} = 1.016$ (7).

The quantities Ω_{22} and A_{ij}^* depend on the temperature T and the intermolecular potential. The viscosities of the noble gases are correlated in the extended principle of corresponding states by the formula (3, 5-7)

$$\ln \Omega_{22} = \ln \frac{\Omega^{(2,2)^*}}{f_{\mu}} = 0.45677 - 0.53955(\ln T^*) + 0.18265(\ln T^*)^2 - 0.03629(\ln T^*)^3 + 0.00241(\ln T^*)^4 \quad (3)$$

$1 < T^* < 90$

where f_{μ} is higher-order correction to the viscosity. The collision integral Ω_{11} obtained by a corresponding-state correlation of diffusion data is given by (3, 5-7)

$$\ln \Omega_{11} = \ln \Omega^{(1,1)^*} = 0.347 - 0.444(\ln T^*) + 0.093(\ln T^*)^2 - 0.010(\ln T^*)^3 \quad (4)$$

$0.5 < T^* < 25$

where $A^* = \Omega^{(2,2)^*}/\Omega^{(1,1)^*} = \Omega_{22}/\Omega_{11}$. The reduced temperature T^* is defined by the relation $T^* = k_B T/\epsilon$ where ϵ is (say) the depth of the potential well. As a result, more accurate calculations are possible for viscosities of mixtures.

In this paper we attempt to determine the validity of the extended law of corresponding states using the kinetic-theory expression for multicomponent gas mixtures (4), with special emphasis on the viscosity. All measurements are performed in the range of temperature 40-140 °C with the capillary flow method. The measurements are evaluated on a relative basis and the experimental details and procedure are much like those used by Burch (2) which were based on the apparatus first developed by Graham with later refinements by McCoubrey (9). We assume the reader is familiar with ref 2, and confine ourselves here to a presentation of the experimental results.

Experimental Section

The determinations reported here were made with a constant-volume gas viscometer similar to that of Burch (2). The viscometer bulb and capillary were thermostated by means of an oil bath (up to 140 °C). The bath temperature was controlled to within ± 0.1 °C. In all cases, the temperature was obtained using a copper-constantan thermocouple and a Leeds & Northrup potentiometer ($\pm 1 \mu V$). Times were measured with a precision stopwatch (calibrated in tenths of a second). Pressure measurements were made with a traveling microscope reading to 0.05 mm. At each temperature the gas viscosity coefficients were determined from the well-known Poiseuille equation modified for the slip correction. The apparatus constant was determined at each temperature using nitrogen and checked with oxygen. The pressure range of these measurements was 22-11 cm of mercury.

Table I. Viscosity of Quaternary Mixtures

compn (mole fraction)				temp, °C	viscosity, μP		
N ₂	O ₂	CO ₂	N ₂ O		exptl	calcd	dev, ^a %
0.50	0.25	0.10	0.15	40	187.0	187.2	-0.11
				60	196.5	196.9	-0.20
				80	205.3	206.3	-0.48
				100	216.9	215.6	+0.60
				120	227.1	224.6	+1.11
0.25	0.25	0.25	0.25	140	234.8	233.4	+0.60
				40	178.0	179.8	-1.00
				60	187.1	189.8	-1.42
				80	196.7	199.4	-1.35
				100	205.2	208.9	-1.77
				120	215.6	218.1	-1.15
				140	225.0	227.1	+0.92

^a Standard deviation = 0.99%.

Nitrous oxide was supplied by the Fluka Co. (99.9% purity). Nitrogen and oxygen were obtained from Bahar Oxygen and Acetylene Co. Carbon dioxide was supplied by the Chemical Co., Shiraz, Iran. The minimum purities of N₂, O₂, and CO₂ were 99.9, 99, and 99%, respectively. In every determination of a viscosity coefficient at least three runs were made, and the average time was used in the calculation of the experimental results.

Results and Discussion

The experimental results for N₂-O₂-CO₂-N₂O are given in Table I. The viscosity of the two quaternary mixtures can be calculated with the aid of eq 1-3 and the scaling parameters, for the gases N₂, O₂, and CO₂, are taken from ref 8. The nitrous oxide molecule has the same mass as that of the carbon dioxide molecule and many other similar features. Thus the scaling parameters for the N₂O molecule are assumed to be equal to those for the CO₂ molecule. In our case, evaluation of the viscosity is made by using the computer program developed by Kestin and co-workers. In this temperature range the agreement is on the order of 1%.

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