Table IV. Average Expansivities of Hexanol Isomers between 25 and 35 °C

	$10^3\alpha$, °C^{-1}			
	$\bar{\alpha}_{\mathrm{exptl}}$	$\bar{\alpha}_{\mathrm{GD}}$	$\bar{\alpha}_{\mathrm{LL}}$	$\bar{\alpha}_{\mathrm{E}}$
1-hexanol	0.88	1.0	0.9	1.0
2-M-1-P	0.91	1.1	0.9	1.0
2-hexanol	0.97	1.2	1.0	1.1
3-M-2-P	1.01	1.1	1.0	1.1
4-M-2-P	1.03	1.1	1.0	1.1
3-M-3-P	1.08	1.2	1.1	1.2
2-M-2-P	1.08	1.2	1.0	1.1
δ		0.13	0.03	0.09

are given in Table III. To correlate both densities and refractive indices a HP-85 computer was used, the goodness of fit being 1.0 for the densities of all compounds and higher than 0.99 for the refractive indices.

The molar refractions of substances have been evaluated by several empirical formulas of which only the Lorentz–Lorenz (LL) relation has a sound theoretical basis. However, it has been shown that the Gladstone–Dale (GD) and Eykman (E) formulas are as successful as that of Lorentz–Lorenz in giving a temperature-independent molar refraction. If the molar refraction were strictly a function of temperature, then the differential form of Gladstone–Dale, Lorentz–Lorenz, and Eykman formulas would imply a direct relation between coefficient isobaric thermal expansion, α, and the temperature dependence of refractive index. These expressions would be (*10*)

$$\alpha_{\mathrm{GD}} = \frac{-1}{n-1}\left|\frac{dn}{dt}\right| \qquad (3)$$

$$\alpha_{\mathrm{LL}} = \frac{-6n}{(n^2-1)(n^2+2)}\left|\frac{dn}{dt}\right| \qquad (4)$$

$$\alpha_{\mathrm{E}} = \frac{-(n^2+0.8n+1)}{(n^2+1)(n+0.4)}\left|\frac{dn}{dt}\right| \qquad (5)$$

Table IV shows the average expansivities of the alcohols directly obtained from densities between 25 and 35 °C along with those evaluated by means of eq 3–5. These values are in agreement with those found in the literature for 1-hexanol (0.89 (*6*), 0.89 (*7*), 0.87 (*11*)), 2-M-1-P (0.91 (*7*), 0.9 (*11*), 2-hexanol (0.99 (*7*)), 4-M-2-P (1.05 (*7*), 1.01 (*11*)), 3-M-3-P (1.08 (*7*)), and 2-M-2-P (1.05 (*7*)), the largest discrepancy appearing for 3-M-2-P with a difference of 4 × 10^{-5} °C^{-1}.

A survey of Table IV data shows that α_{GD}, α_{LL}, and α_{E} are higher than the experimental values; however, the discrepancy is greater for α_{GD} and α_{E} than α_{LL}.

The mean deviation, $\delta = \sum|\alpha_{\mathrm{calcd}} - \alpha_{\mathrm{exptl}}|/10^{-3}N$, is 0.13, 0.03, and 0.09 for the thermal expansivities calculated from eq 3–5, respectively. The errors of the values calculated through expression 4 oscillate around 2% except for 2-M-2-P, where the error is higher than 7%, which permits one to reproduce sufficiently the data of the isobaric thermal expansion coefficients of these pure substances.

Glossary

A, *B*	parameters of eq 1
a, *b*	parameters of eq 2
N	number of experimental points
n	refractive index
t	temperature, °C

Greek Letters

α	thermal expansivity, °C^{-1}
δ	mean deviation
ρ	density, g·cm^{-3}

Registry No. 2-M-1-P, 105-30-6; 3-M-2-P, 565-60-6; 4-M-2-P, 108-11-2; 3-M-3-P, 77-74-7; 2-M-2-P, 590-36-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7.

Literature Cited

(1) Lorentz, H. A. *Wied. Ann.* **1880**, *9*, 641.
(2) Lorenz, L. *Wied. Ann.* **1880**, *11*, 70.
(3) Dale, D.; Gladstone, F. *Philos. Trans. R. Soc. London* **1958**, *148*, 887.
(4) Eykman, J. F. *Recl. Trav. Chim. Pays-Bas* **1895**, *14*, 185.
(5) Weast, R. C. "Handbook of Chemistry and Physics", 55th ed.; Chemical Rubber Publishing Co.: Boca Raton, FL, 1974.
(6) Ortega, J. *J. Chem. Eng. Data*, **1982**, *27*, 312.
(7) TRC Tables. "Selected Values of Properties of Chemical Compounds"; Thermodynamic Research Center Data Project: College Station, TX, 1983.
(8) Bravo, R.; Pintos, M.; Baluja, M. C.; Paz Andrade, M. I. *J. Chem. Thermodyn.* **1984**, *16*, 73.
(9) Kimura, F.; Benson, G. C. *J. Chem. Eng. Data* **1984**, *29*, 72.
(10) Rao, K. J.; Helphay, D. B.; Angell, C. A. *Phys. Chem. Glasses* **1973**, *14*, 26.
(11) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. 2.

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Association of Acridine Orange in Nonaqueous Solutions

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The dimerization constants of acridine orange (AO) in various organic solvents have been measured spectrophotometrically at 20 °C. These constants are 2–3 orders of magnitude lower than in water. The peculiar role of water as a dye solvent has been stressed.

Introduction

The association process of metachromatic dyes in aqueous solution has been the subject of a wide literature (*1*, *2*, and references therein). On the other hand, to our knowledge, the behavior of these dyes in nonaqueous medium has never been particularly studied.

In the concentration range 10^{-5}–10^{-4} mol/L drastic spectral changes are observed in aqueous solution. These changes have been interpreted in terms of multiple association of dye ions that interact through the π-electron orbital system of the aromatic rings, stacking in a sandwichlike mode (*3–6*). Thermodynamic data of association are available in the literature for a variety of dyes (*2*).

On the contrary, in nonaqueous medium very limited changes are shown by the absorption spectra, in the same concentration range, and dye solutions essentially obey Beer's law.

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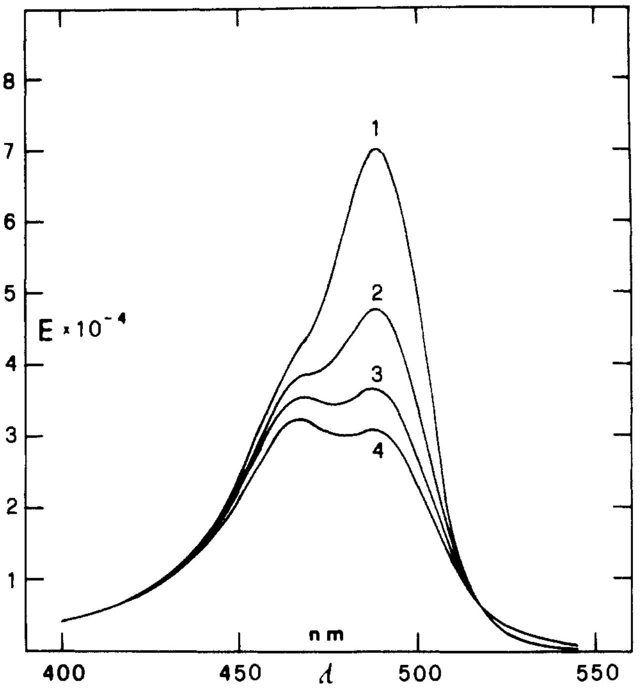

Figure 1. Extinction coefficients of acridine orange hydrochloride in methanol at various molalities: (1) $m < 10^{-4}$, (2) $m = 0.0583$, (3) $m = 0.105$, (4) $m = 0.146$.

We thought it interesting to study the behavior of a metachromatic dye, acridine orange hydrochloride (AO), in nonaqueous solution, extending the concentration range up to 0.01-0.1 M and using several solvents. We could observe that in this concentration range the dye optical absorption spectra show changes similar to those shown in water in the concentration range 10^{-5}-10^{-4} M (see Figure 1). This is evidence that AO associates also in nonaqueous medium. From the absorption data it has been possibe to compute the dimerization constants of AO in several nonaqueous solvents. The data have been compared with those obtained in water (*6*).

Experimental Section

Materials. Acridine orange hydrochloride (Merck) was purified as described in a previous paper (*7*). The purified AO base was dissolved in methanol and neutralized with the stoichiometric amount of concentrated HCl, and the AO·Cl was precipitated with ethyl ether from the methanol solution.

AO·Cl crystalizes from alcoholic solutions with one water molecule, as found through the X-ray analysis of AO·Cl crystals (*8*) and checked spectrophotometrically on our AO·Cl samples. Accordingly, compositions of all solutions prepared from the purified acridine orange hydrochoride were computed using the molecular weight of the species (AO·HCl)·H_2O.

All solvents were reagent grade. Formamide was vacuum distilled before use. All other solvents were used without further purification.

All solutions were diluted by weighing concentrated stock solutions (compositions are given in molalities).

Absorption spectra were taken with a Perkin-Elmer Model 320 spectrometer using cells of different paths (ranging from 10 to 0.01 mm) and a thermostated cell holder at 20 ± 0.2 °C (extinction coefficients are given in absorbance × cm^{-1} × L × mol^{-1}).

Discussion

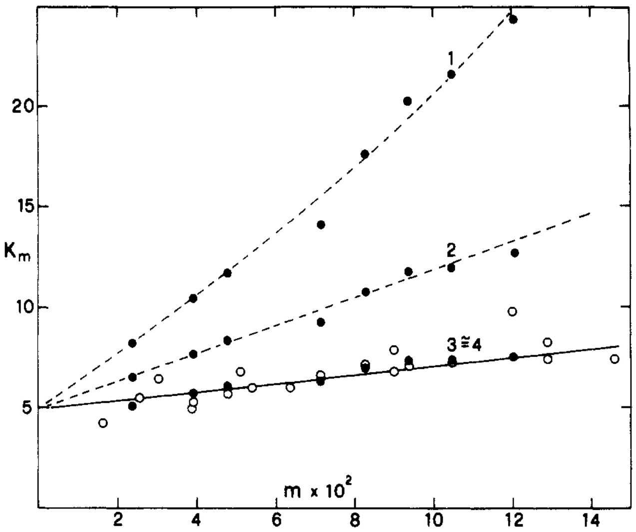

Figure 2. Dimerization constant of acridine orange expressed in terms of molality (eq 4); (●) α_1 computed through eq 5, (1) $E_2 = 16000$ (2) $E_2 = 10000$, (3) $E_2 = 0.0$ (○) α_1 computed by using eq 7 (4).

A recent analysis of the absorption spectra of AO in aqueous solution allowed us to obtain the experimental extinctions of the monomer and those of the highly associated species and to evaluate the spectrum of the dimer (*6*). From these data the constants of the multiple equilibrium

$$D + D = D_2 \qquad K_{12} = [D_2]/[D]^2 \qquad (1)$$

$$D_2 + D = D_3 \qquad K_{23} = [D_3]/([D_2][D]) \qquad (2)$$

$$D_{n-1} + D = D_n \qquad K_{n-1,n} = [D_n]/([D_{n-1}][D]) \qquad (3)$$

were computed according to the model suggested by Robinson et al. (*3*).

This careful analysis of absorption spectra is not possible in nonaqueous medium. In fact, even in the most concentrated solutions the monomer dye species prevails and the only relevant equilibrium is the dimerization (eq 1). The dimerization constant (in terms of molality) assumes the expression

$$K_m = (1 - \alpha_1)/(2\alpha_1^2 m) \qquad (4)$$

where α_1 is the fraction of monomer dye and m the stoichiometric dye molality.

Under these conditions any extrapolation to compute the dimer absorption or that of more highly associated species is affected by a large error. We tested two possible ways to obtain reliable K_m values using two different procedures to compute α_1.

(1) The monomer fraction α_1 is related to the extinction coefficient through the expression

$$\alpha_1(m) = \frac{E - E_2}{E_1 - E_2} \qquad \text{(at constant wavelength)} \qquad (5)$$

where E is the extinction coefficient of a solution of molality m at a given wavelength λ_1 (the wavelength of the maximum absorption of monomer dye was used in out computations), and E_1 and E_2 are the limiting extinction coefficients of the monomeric and dimeric dye at the same wavelength.

Since E_2 cannot be obtained with good accuracy, we computed K_m for a set of solutions at different compositions using an arbitrary, although reasonable, value for E_2; the K_m values were extrapolated at infinite dilution. It was found that the limiting K_m value, at infinite dilution, is almost independent of the E_2 choice. This can be seen in the graphs of Figure 2 (black points) where the K_m data for AO in methanol are drawn for three different E_2 values.

(2) An analysis of the AO data in aqueous solution recently published (*6*) has shown that the α_1 value, for $\alpha_1 \gtrsim 0.45$, is almost a linear function of the ratio

$$R = E_M/E_D \qquad (6)$$

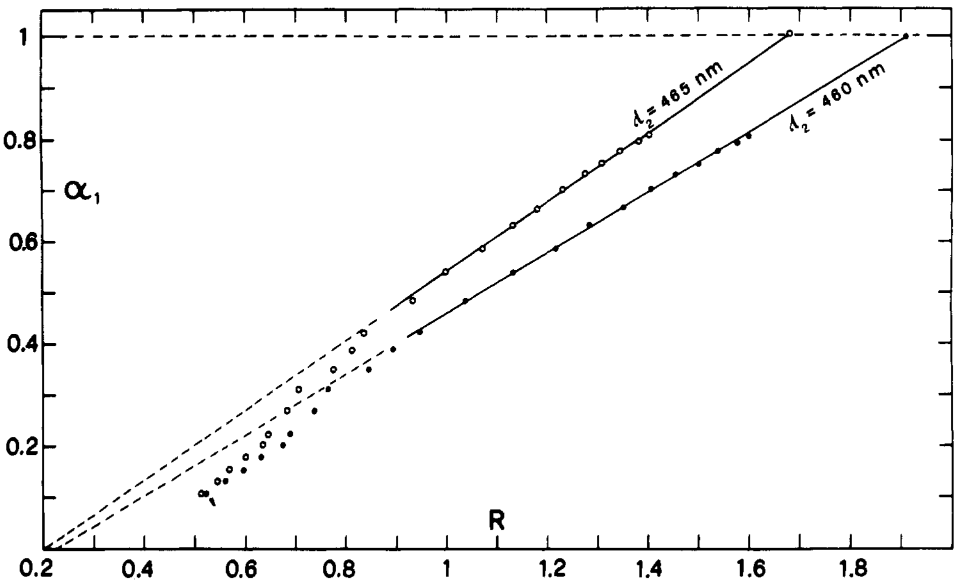

Figure 3. Fraction of monomer acridine orange, in aqueous solution, as a function of the ratio R (eq 6) between the extinction coefficient E_M, measured at λ_1 = 492 nm, and the extinction coefficient E_D measured at two values of λ_2 (experimental data from ref *6*), straight lines from eq 7.

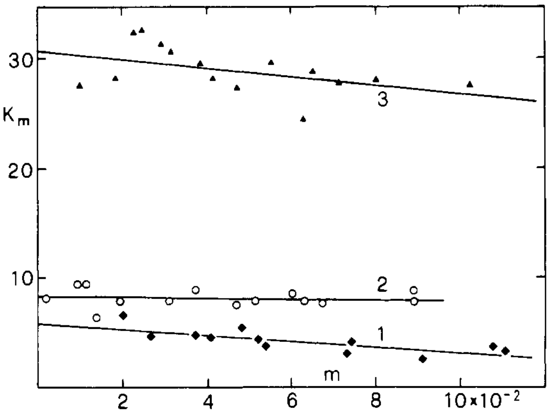

Figure 4. Dimerization constant of acridine orange in dimethylformamide (1), *N*-methylformamide (2), and formamide (3) (α_1 computed through eq 7).

where E_M is the extinction coefficient at the wavelength of the monomer maximum (λ_1 = 492 nm) and E_D is the extinction coefficient at a wavelength near to the dimer maximum (λ_2 = 465 nm). For different λ_2 values, in the range 460–465 nm, the following general expression holds for α_1:

$$\alpha_1 = \frac{1.095}{R_0 - 0.070}R - \frac{0.0766}{R_0 - 0.70} - 0.095 \qquad (7)$$

where R_0 is the limiting value of R at α_1 = 1. In Figure 3 the experimental α_1 vs. R and eq 7 are compared for two λ_2 values: at λ_2 = 460 nm, R_0 = 1.91; at λ_2 = 465 nm, R_0 = 1.68.

The wavelengths of maximum absorption and the corresponding extinction coefficients are different in different solvents (see Table I); on the contrary, the ratios R_0 are reasonably constant and all included in the range 1.60–1.90.

Under these conditions we thought it reasonable to assume the same relationship between R and α_1 in nonaqueous solutions as the one found in water (eq 7). The R_0 constants in nonaqueous solutions, used in eq 7, are given in Table I.

The dimerization constants (eq 4) computed by using α_1 from eq 7 were found almost constant with concentration (see Figure 4). Furthermore, in the cases where both procedures 1 and 2 were used to compute K_m, the same extrapolated value was obtained (see Figure 2, circlets).

Table I

solvent	K_m[a]	Δ[b]	λ_1[c]	E_M[d]	λ_2[e]	R_0[f]	ϵ[g]
formamide	31.0	0.9	495	61100	468	1.82	111
N-methylformamide	8.1	0.3	492	56800	468	1.76	177
dimethylformamide	5.7	0.4	492	58600	465	1.85	38
methyl alcohol	5.0	0.4	488	69900	465	1.75	33
ethyl alcohol	6.2	0.4	490	67900	468	1.80	25
n-propyl alcohol	9.3	0.4	489	65700	468	1.73	20
n-butyl alcohol	15.1	0.5	490	67300	468	1.81	17
acetic acid	~25		493	61700	465	1.92	6.2
dimethyl sulfoxide	~1.4		495	58300	470	1.77	47
methyl alcohol (51%)–water (49%)	30	2	490	68200	465	1.83	
dimethylformamide (36%)–water (64%)	11.0	0.7	492	59000	470	1.72	
water (ref *6*)	1.4×10^4		492	63800	465	1.68	89

[a] Dimerization constant of AO in 1000 g of solvent mol^{-1}, as defined by eq 4. [b] Mean square error on the intercept of $K = f(m)$, from least-squares. [c] Wavelength of maximum absorption of monomer dye. [d] Extinction coefficient of monomer dye at λ_1. [e] Wavelength of maximum absorption of dimer dye. [f] Limiting ratio E_M/E_D (eq 6) in very dilute solution. [g] Dielectric constant of solvent. The K_m data for acetic acid and dimethyl sulfoxide are only indicative.

We preferred to choose procedure 2 for all solvents as it is simpler, is independent of the optical path, and minimized the errors connected with small concentration errors. The results are collected in Table I.

The general behavior of metachromatic dye absorption spectra as a function of concentration shown by AO in nonaqueous solvents confirms that the spectral shifts connected with dye stacking are due to the direct dye–dye interaction through the π-orbital system without solvent interference (*6*). Further support for this evidence comes from the spectra of AO salts in the solid state. These spectra correspond to those of a stacked species and the crystal structure shows the presence of the π-electron interaction (*8*).

Table I data show that the medium dielectric constant does not affect the dye stacking tendency, although the dye ions associate against the electrostatic repulsion between charges

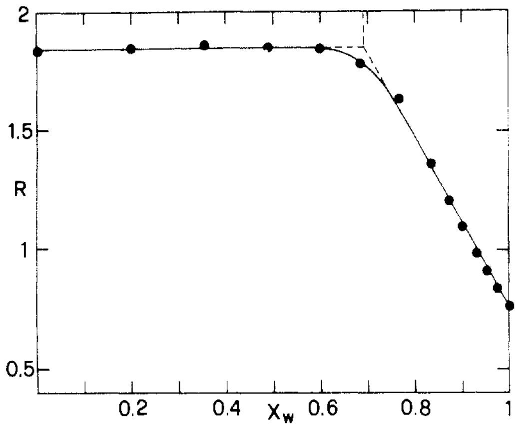

Figure 5. Ratio R (eq 7) for acridine orange in methanol-water solutions X_w = mole fraction of water; dye molality ~ 10^{-4} mol/1000 g.

of equal sign. We may compare K_m in acetic acid (~25, ϵ = 6.2), K_m in *N*-methylformamide (6.5, ϵ = 177), and K_m in water (1.4×10^4, ϵ = 89). On the other hand, the K_m constants of Table I seem to show a possible correlation between the dye stacking tendency and the self-association tendency of the solvent. Particularly interesting is to observe the K_m change along the formamide series (see Figure 4): it increases with the increasing possibility of the solvent molecules associating through hydrogen bonding. No H bonds are expected in dimethylformamide; linear sequences of H bonds are possible in *N*-methylformamide (as in the alcohol series), while the presence of the NH_2 group in formamide allows for the possible formation of a two-dimensional network of H bonds (*9*, *10*); the same possibility is present in acetic acid.

On the other hand, the peculiar role of water as a dye solvent must be stressed. The AO dimerization constant in water is 2-3 orders of magnitude higher than in other solvents. In this case several authors suggested that hydrophobic interactions give a dominant contribution to the stacking process (*4*, *6*, *11-18*). The evidence that the increasing possibility of H bonding seems to increase the dye stacking tendency suggests that the dye association in nonaqueous medium may be favored by some process similar to the hydrophobic interactions in water.

It is also interesting to observe that the addition of water to methanol and to dimethylformamide increases the K_m value. In the light of our previous suggestion this depends on the possibility of H_2O molecules increasing the net of solvent H bonds and favoring the possibility even of a two- or three-dimensional network. Actually it must be stressed that even in mixed solvents we are always in a "nonaqueous" medium. Water in mixed solvents is in fact far from being "common water". In the water-methanol system it has been observed that the AO stacking increases slightly up to a water-to-methanol ratio ~2:1 (see Figure 5). At higher water concentration the dye association increases drastically. So we may assume that the clusterlike structure of water, responsible for the very high stacking tendency of dyes, starts to organize itself for water-to-methanol ratios higher than 2:1.

Registry No. AO, 65-61-2; formamide, 75-12-7; *N*-methylformamide, 123-39-7; dimethylformamide, 68-12-2; ethyl alcohol, 64-17-5; *n*-propyl alcohol, 71-23-8; *n*-butyl alcohol, 71-36-3; acetic acid, 64-19-7; dimethyl sulfoxide, 67-68-5; water, 7732-18-5; methyl alcohol, 67-56-1.

Literature Cited

(1) Vitagliano, V. In "Chemical and Biological Applications of Relaxation Spectrometry"; Wyn-Jones, E., Ed.; Reidel: Dordrecht, Holland, 1975; pp 437-66.
(2) Vitagliano, V. In "Aggregation Processes in Solution"; Wyn-Jones, E., Gormally, J.; Eds.; Elsevier: Amsterdam, 1983; pp 271-308.
(3) Robinson, B. H.; Löffler, A.; Schwarz, G. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 56-69.
(4) Vitagliano, V.; Costantino, L.; Staiano, N.; Ortona, O.; Wurzburger, S. *Adv. Mol. Relaxation Interact. Pocesses* **1976**, *12*, 251-63.
(5) Costantino, L.; Ortona, O.; Sartorio, S.; Silvestri, L.; Vitagliano, V. *Adv. Mol. Relaxation Interact. Processes* **1981**, *20*, 191-8.
(6) Costantino, L.; Guarino, G.; Ortona, O.; Vitagliano, V. *J. Chem. Eng. Data* **1984**, *29*, 62-6.
(7) Vitagliano, V.; Costantino, L.; Zagari, A. *J. Phys. Chem.* **1973**, *77*, 204-10.
(8) Mattia, C. A.; Mazzarella, L.; Puliti, R.; Vitagliano, V. *J. Cryst. Spectr. Res.* **1984**, *14*, 71-87.
(9) Blake, I. O.; Rubio, M. *Theor. Chim. Acta* **1975**, *36*, 221-5.
(10) Lemley, A. T. In "Solution Phenomena and Aprotic Solvents IV"; Lagowski, J. J.; Ed.; Academic Press: New York, 1976; pp 19-73.
(11) Nemethy, G.; Sheraga, H. *J. Chem. Phys.* **1962**, *36*, 3401-17.
(12) Uedaira, Ha.; Huedaira, Hi. *Kolloid.-Z.* **1964**, *194*, 148-50.
(13) Haugen, G. R.; Hardwich, E. R. *J. Phys. Chem.* **1963**, *67*, 725-31.
(14) Blandamer, H. J.; Brivati, J. A.; Fox, M. F.; Symons, M. C. R.; Verna, G. S. P. *Trans. Faraday Soc.* **1967**, *63*, 1850-7.
(15) Mukerjie, P.; Gosh, K. *J. Am. Chem. Soc.* **1970**, *92*, 6419-24.
(16) Rohatgi, K. K.; Mukhopadhyay, A. K. *Chem. Phys. Lett.* **1971**, *12*, 259-60.
(17) Clark, A. H.; Franks, F.; Pedley, M. D.; Reid, D. S. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 290-305.
(18) Ben Naim, A. "Water and Aqueous Solutions"; Plenum Press: New York, 1974; Chapter 8.
(19) Part of this research has been presented to the IUPAC Conference on Chemical Thermodynamics held in London, Sept 6-10, 1982.

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Viscosity of Gaseous Chlorotrifluoromethane (R 13) under Pressure

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The viscosity of gaseous chlorotrifluoromethane (R 13) was measured by using an oscillating disk viscometer of Maxwell type at 273.15-373.15 K in the pressure range up to 10.4 MPa. Two empirical equations were obtained for the viscosity as a function of temperature and pressure below 2 MPa and as a function of temperature and density in the whole range of pressure. Also an empirical equation was obtained for the atmospheric viscosity as a function of temperature. The intermolecular force parameters of the Lennard-Jones 12-6 model were determined from the temperature dependence of the atmospheric viscosity as follows: ϵ/k = 204.0 K, σ = 0.4971 nm.

Viscosity data of fluids are needed for the analysis of heat and mass transfer and for the design of related equipment. Also those are important information in determining the intermolecular force parameters available for the prediction of various physicochemical properties.

Many halogenated hydrocarbons are commonly used as refrigerants and expected to be used as working fluids of turbines. However, the experimental data for gas viscosity under pressure are scarce and the reliability of the literature data is uncertain because of the large discrepancies among them. Therefore, the measurement of the gas viscosity of halogenated hydrocarbons under pressure is being continued by us, and the viscosities of chlorodifluoromethane (R 22) and dichlorodi-