

VISCOSITY OF POLAR-NONPOLAR GAS MIXTURES

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ABSTRACT. Viscosity of ammonia-nitrogen and sulphur dioxide-hydrogen gas mixtures has been measured over a temperature range from 30° to 200°C and at pressures below 10 cm. Hg. by using a precision oscillating disc viscometer. The results have been utilised to obtain informations on unlike interactions and also to generate inter-diffusion coefficients of these systems.

INTRODUCTION

It has been shown by a number of workers (Weissman *et al.* 1962; Weissman, 1964; Srivastava, 1961 and Hirschfelder *et al.* 1960) that on the basis of the Chapman-Enskog theory it is possible to determine unlike interactions from viscosity of gas mixtures. The combination rules generally used to calculate unlike interactions (Hirschfelder *et al.* 1954) being uncertain, only information obtained from experimental data are reliable. Viscosity, to the first approximation, is not affected significantly by inelastic collisions (Monchick *et al.* 1963). Thus, this property can be used with confidence for obtaining information on the spherical part of the intermolecular potential of polyatomic gases as well.

In this paper we have reported the results of our measurements of the viscosity of the polar-nonpolar gas mixtures, ammonia-nitrogen and sulphur dioxide-hydrogen over a temperature range from 30°–200°C and at pressures below 10 cm. Hg. Attempts have been made to derive information on unlike interactions from these data.

EXPERIMENTAL

The precision all-metal oscillating-disc viscometer together with its accessories used in our measurements has been described in detail in earlier papers (Kestin *et al.* 1959; Kestin *et al.* 1963; Pal *et al.* 1967a and Pal *et al.* 1967b). The working formulae and method of preparation of gas mixtures have also been described (Pal *et al.* 1967a, 1967b).

The gases ammonia and sulphur dioxide were prepared by standard laboratory procedures (Pal *et al.* 1967a). Hydrogen and Nitrogen used for calibration were supplied by the Indian Oxygen Co., Ltd. (purity 99.95%). The overall accuracy of our viscosity data for the mixtures should be within 1%. The viscosity data obtained by us are given in tables I and II. It may be mentioned here that for pure ammonia the viscosity values obtained by us are on the average 2%

lower than those reported earlier (Pal *et al.*, 1967a). Mass spectrometric analysis showed that the previously used ammonia gas contained small percentage of air as impurity which can easily explain the discrepancy. However, the general conclusions drawn (Pal *et al.*, 1967a) regarding ammonia remain unaltered. With the present data for ammonia the agreement with the earlier data (Carmichael *et al.*, 1963 and Iwasaki *et al.*, 1964) become excellent (within 1%) over the whole temperature range.

The only previous data for the systems ammonia-nitrogen and sulphur dioxide-hydrogen are those of Trautz *et al.*, (1931). As the experimental temperatures are different it is not possible to compare our experimental data with the earlier ones. However, in the range where comparison is possible by interpolation the agreement of our data with those of Trautz *et al.*, (1931) is within 2% which should be considered as satisfactory in view of the uncertainties in the earlier experimental methods

COMPARISON WITH THEORY

The viscosity of a binary gas mixture can be expressed as (Hirschfelder *et al.*, 1954),

$$|\eta_{mix}|_1 = \frac{1 + Z_\eta}{X_\eta + Y_\eta} \quad \dots (1)$$

where

$$X_\eta = \frac{x_1^3}{\eta_1} + \frac{2x_1x_2}{\eta_{12}} + \frac{x_2^3}{\eta_2}$$

$$Y_\eta = \frac{3}{5}A^*_{12} \left\{ \frac{x_1^3}{\eta_1} \left(\frac{M_1}{M_2} \right) + \frac{2x_1x_2}{\eta_2} \left(\frac{M_1 + M_2}{4M_1M_2} \right) \left(\frac{\eta_{12}^2}{\eta_1\eta_2} \right) + \frac{x_2^3}{\eta_2} \left(\frac{M_2}{M_1} \right) \right\}$$

$$Z_\eta = \frac{3}{5}A^*_{12} \left\{ x_1^3 \left(\frac{M_1}{M_2} \right) + 2x_1x_2 \left[\left(\frac{M_1 + M_2}{4M_1M_2} \right) \left(\frac{\eta_{12} + \eta_{12}}{\eta_1 + \eta_2} \right) - 1 \right] + x_2^3 \left(\frac{M_2}{M_1} \right) \right\}$$

where x_1 , x_2 are the mole fractions of the components 1 and 2, M_1 , M_2 being the corresponding masses. η_{12} is the viscosity of a hypothetical gas of mass $\frac{2M_1M_2}{M_1 + M_2}$ and A^*_{12} is a ratio of collision integrals which is a very slowly varying function of temperature.

It is possible to represent polar-nonpolar interaction as interaction between two nonpolar molecules. Consequently, we have used Lennard-Jones (12:6)

potential for our calculations. The combination rules for polar-nonpolar interactions can be written as (Hirschfelder *et al.*, 1954),

$$\sigma_{np} = \frac{1}{2}(\sigma_n + \sigma_p) \xi^{-1/6} \quad \dots (2a)$$

$$\epsilon_{np} = \sqrt{\epsilon_n \epsilon_p} \xi^2 \quad \dots (2b)$$

where the subscript n and p stand for nonpolar and polar component respectively. ξ is given by

$$\xi = \left[1 + \frac{1}{2} \frac{\alpha_n \mu_p^*{}^2}{\sigma_n^3} \sqrt{\epsilon_p / \epsilon_n} \right] \quad \dots (3)$$

where α_n is the polarizability of the nonpolar molecule in cubic angstroms. The force parameters for the nonpolar gases were taken as those determined from viscosity data (Hirschfelder *et al.*, 1954) and for the polar components the values of σ_p and ϵ_p as obtained on the 12-6-3 model (Monchick *et al.*, 1961) were used. The values of η_{mix} at different temperatures as obtained from eqn. (1) are shown in column 4 of Tables I and II. It may be seen that the agreement between the experimental and the calculated values of η_{mix} is excellent (within 1%).

Recently, Chakraborty and Gray (1965) have measured the viscosity of a number of polar-nonpolar gas mixtures over the temperature range from 25°C to 80°C. They found that for those systems generally the agreement between the experimental and the calculated values of η_{mix} to be not quite satisfactory. It is difficult to say whether this discrepancy is due to some particular feature of the systems studied or due to experimental uncertainties.

UNLIKE INTERACTION FROM MIXTURE VISCOSITY DATA

It has been shown by a number of workers (Weissman *et al.*, 1962; Weissman 1964, and Srivastava, 1961) that it is possible to determine unlike interactions from viscosity of gas mixtures. Eqn. (1) can be solved for η_{12} in the following manner (Srivastava, 1961)

$$\eta_{12} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad \dots (4)$$

where

$$a = \frac{6}{5} A^*{}_{12} \left(\frac{x_1 x_2}{\eta_1 \eta_2} \right) \left(\frac{(M_1 + M_2)^2}{4M_1 M_2} \right) (\eta_{mix} - \eta_1 - \eta_2)$$

TABLE I

Viscosity and inter-diffusion coefficient of $\text{NH}_3\text{-N}_2$ gas mixtures at different temperatures

T°C	mole frac- tion of NH_3	$\eta \times 10^7$ ($\text{gcm}^{-1}\text{sec}^{-1}$)	$\eta_{mix} \times 10^7$ ($\text{g.cm}^{-1}\text{sec}^{-1}$)	$({}_pD_{12})$ ($\text{cm}^2\text{sec}^{-1}$)	$({}_p d_{12})$ ($\text{cm}^2\text{sec}^{-1}$)
24	1.0000	102.81	—		
	0.7964	119.44	120.46		
	0.5709	136.17			
	0.5027	141.60	142.21	0.810	0.817
	0.4020	148.61	—		
	0.2007	167.85	165.21		
	0.0000	175.05	—		
54	1.0000	113.72	—		
	0.7700	136.40	134.89		
	0.5876	151.71	—		
	0.5021	158.05	157.61	0.267	0.260
	0.4003	167.03	—		
	0.2007	179.37	179.42		
	0.0000	191.30	—		
100	1.0000	130.75	—		
	0.7700	154.95	154.52		
	0.5876	170.10	—		
	0.5021	177.34	177.25	0.338	0.332
	0.4003	185.08	—		
	0.2007	198.92	198.81		
	0.0000	210.10	—		
150	1.0000	149.28	—		
	0.7603	176.11	175.02		
	0.5920	190.03	—		
	0.4928	179.01	198.21	0.412	0.418
	0.3985	203.75	—		
	0.2252	216.72	217.80		
	0.0000	230.5	—		
200	1.0000	167.98	—		
	0.7603	195.72	197.70		
	0.5920	207.85	—		
	0.4928	215.20	217.91	0.507	0.510
	0.3985	222.11	—		
	0.2252	236.25	238.52		
	0.0000	252.25	—		

TABLE II

Viscosity and inter-diffusion data of SO₂-H₂ gas mixture at different temperatures

T°C	mole frac- tion of SO ₂	$\eta \times 10^7$ (gm.cm ⁻¹ sec ⁻¹)	$\eta_{mix} \times 10^7$ (gm.cm ⁻¹ sec ⁻¹)	(ρD_{12}) (cm ² .sec ⁻¹)	(ρD_{12}) (cm ² .sec ⁻¹)
30	1.0000	133.01	—		
	0.8219	134.45	136.40		
	0.5957	135.01	—		
	0.4919	136.75	140.71	0.600	0.610
	0.4059	137.01	—		
	0.2005	136.41	139.33	—	
	0.0000	90.00	—		
55	1.0000	144.02	—		
	0.7866	145.46	148.42		
	0.5975	147.21	—		
	0.4863	148.46	150.05	0.705	0.701
	0.4000	148.01	—		
	0.2005	147.12	149.76		
	0.0000	95.60	—		
100	1.0000	168.90	—		
	0.7866	168.06	172.62		
	0.5975	167.95	—		
	0.4863	166.91	174.83	0.884	0.876
	0.4000	165.95	—		
	0.2005	162.89	167.31		
	0.0000	104.70	—		
150	1.0000	192.20	—		
	0.8110	192.03	195.24		
	0.6024	192.50	—		
	0.5023	192.52	198.48	1.105	1.086
	0.4018	192.53	—		
	0.2000	177.88	186.00		
	0.0000	115.50	—		
200	1.0000	211.50	—		
	0.8110	214.11	214.23		
	0.6024	214.99	—		
	0.5023	215.40	216.21	1.380	1.306
	0.4018	213.37	—		
	0.2000	194.72	200.30		
	0.0000	122.60	—		

$$b = \frac{3}{5} A^*_{12} \left[2x_1x_2 + x_1^2 \left(\frac{M_1}{M_2} \right) \left(\frac{\eta_{m12}}{\eta_1} \right) + x_2^2 \left(\frac{M_2}{M_1} \right) \left(\frac{\eta_{m12}}{\eta_2} \right) - x_1^3 \left(\frac{M_1}{M_2} \right) - x_2^3 \left(\frac{M_2}{M_1} \right) \right] + \eta_{m12} \left(\frac{x_1^3}{\eta_1} + \frac{x_2^3}{\eta_2} \right) - 1$$

$$c = 2x_1x_2 \eta_{m12}$$

It is possible to determine the unlike interaction parameters, σ_{12} and ϵ_{12} from the temperature dependence of η_{12} . η_{12} can also be used to generate pD_{12} from the relation (Hirschfelder *et al.*, 1954),

$$pD_{12} = \eta_{12} \frac{3}{5} \frac{(M_1 + M_2)}{M_1 M_2} \cdot A^*_{12} RT. \quad (5)$$

p being the pressure in atmosphere. By substituting the values of A^* as obtained by using force parameters calculated from the combination rules pD_{12} values can be obtained. It may be pointed out that this calculation of pD_{12} is equivalent to obtaining unlike interaction parameters. It is possible to measure the viscosity of gas mixtures much more precisely than the diffusion coefficients. Consequently, this method of obtaining D_{12} from the mixture viscosity data should be more reliable than the actual measurements of this property by the existing techniques.

In column 6 of tables I and II are also shown the calculated values of D_{12} on the Chapman-Enskog theory by using the combination rules given in eqns. (2a) and (2b). It may be seen that the agreement between the values of D_{12} thus obtained with those calculated from the mixture viscosity data is excellent. This probably shows the usefulness of the combination rules inspite of their semi-empirical nature.

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REFERENCES

- Carmichael, L. T., Reamer, H. H., and Sage, B. H., 1963, *J. Chem. Eng. Data*, **8**, 400.
 Chakraborty, P. K., and Gray, P., 1965, *Trans. Faraday Soc.*, **61**, 2422.
 Hirschfelder, J. O., Taylor, M. H. and Kihara, T., 1960, *Report WIS-OOR-20*.
 Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., 1954, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York.
 Iwasaki, H., Kestin, J. and Nagashima, A., 1964, *J. Chem. Phys.*, **40**, 2988.
 Kestin, J. and Leidenforst, W., 1959, *Physica*, **25**, 1033.
 Kestin, J. and Mason, E. A., 1961, *J. Chem. Phys.*, **35**, 1676.
 Monchick, L., and Mason, E. A., 1961, *J. Chem. Phys.*, **35**, 1676.
 Monchick, L., Yun, K. S. and Mason, E. A., 1963, *J. Chem. Phys.*, **39**, 654.
 Pal, A. K. and Barua, A. K., 1967a, *Trans. Faraday Soc.*, **63**, 341.
 ———, 1967b, *J. Chem. Phys.*, **47**, 216.
 Srivastava, I. B., 1961, *Indian J. Phys.*, **35**, 86.
 Trautz, M., and Heberlingh, R., 1931, *Ann. Physik*, **10**, 155.
 Weissman, S., 1964, *J. Chem. Phys.*, **40**, 3397.
 Weissman, S. and Mason, E. A., 1962, *J. Chem. Phys.*, **37**, 1289.