VISCOSITY OF POLAR-NONPOLAR GAS MIXTURES EMPIRICAL METHOD

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ABSTRACT. The adequacy of the familiar Sutherland expression for the viscosity of gas mixtures is tested successfully for binary mixtures involving one component as polar. The limited calculations of this paper also reveal that the co-efficients of the Sutherland expression may be treated as approximately temperature independent. This interesting result may find great use in predicting values at high temperatures where no direct measurements are available.

INTRODUCTION

Inspite of the fact that viscosity is the best theoretically understood transport property we still lack enough in our knowledge to be able to predict it with reliance for complicated systems such as polar gas mixtures. This is primarily because of the complicated nature of the interatomic forces of polar gas molecules, in general. Some calculations have recently been reported by Mason and Monchick (1962) for a somewhat over simplified potential model. This is about the best that has been achieved so far, unfortunately. Mathur and Saxena (1964a) have recently examined the Chapman-Enskog expression for the viscosity of a binary gas mixture, η_{mix}, in a fashion analogous to that of Gambhir and Saxena (1964) for nonpolar gas mixtures. This study revealed that most of the simple polar gases are amenable to treatment on the general theory of Chapman-Enskog except the collision cross-sections may require still more sophisticated angular averaging than given by Monchick and Mason (1961). This encouraged us to look into the procedures analogous to the approximate method of Wilke (1950) and semiempirical method of Saxena and Gambhir (1963a, 1963b). All these calculations, which are still to be published, indicated that the over-all accuracy of such calculations is the same as that obtained for nonpolar gases.

The purpose of this article is to look into the possibility of being able to correlate the experimental η_{mix} data on the basis of the following equation, Sutherland (1895) :

$$\eta_{mix} = \sum_{i=1}^{n} \frac{\eta_i}{1+ \sum_{\substack{j=1 \\ j \neq i}}^{n} \phi_{ij} \frac{X_j}{X_i}} , \qquad \ldots \ (1)$$

where η_i and X_i are the coefficient of viscosity and mole fraction respectively of the pure component of molecular weight M_i, and ϕ_{ij} is a constant which as shown by Mathur and Saxena (1964a) is a complicated function of T (temperature), M_i, X_i, and collision integrals. They also showed that the dependence of ϕ_{ij} on temperature and composition is feeble. Here we will treat ϕ_{ij} as disposable parameters to be determined from the knowledge of η_{mix}. This endeavour holds a great promise in predicting the η_{mix} values at high temperatures, as well as values of multicomponent gas mixtures.

CALCULATION OF VISCOSITIES

If the two pure viscosities and the mixture viscosity values be known at two compositions of a binary system, ϕ_{12} and ϕ_{21} can be evaluated directly on the basis of Eq. (1). If the form of Eq. (1) is correct then it should be possible to correlate

TABLE I

Comparison of the calculated and experimental η_{mix} values of H_2–NH_3 system and some other pertinent data

Temp°.K	$\times_{polar}$	$10^7 \times \eta_{mix}$(gm/cm sec) Exptl.	Calc.	%dev.	ϕ_{12}	ϕ_{21}	$\eta_{NH3} \times 10^7$ (gm/cm Sec.)	$\eta_{H2} \times 10^7$ (gm/cm. Sec.)
293.16	0.9005	1004	1005	(+0.1)	0.307	1.659	(a, c, d) 982	(b) 881
	0.7087	1047	1047	(+0.0)				
	0.5177	1080	1080	(+0.0)				
	0.2975	1087	1087	(+0.0)				
	0.2239	1072	1072	(+0.0)				
	0.1082	1011	1012	(+0.1)				
373.16	0.9005	1299	1302	(+0.2)			1279	1035
	0.7087	1333	1341	(+0.6)				
	0.5177	1354	1367	(+1.0)				
	0.2975	1329	1349	(+1.5)				
	0.2239	1299	1320	(+1.6)				
	0.1082	1204	1224	(+1.7)				
473.16	0.9005	1660	1668	(+0.5)			1646	1217
	0.7087	1680	1703	(+1.4)				
	0.5177	1676	1718	(+2.5)				
	0.2975	1610	1669	(+3.7)				
	0.2239	1560	1620	(+3.8)				
	0.1082	1432	1479	(+3.3)				
523.16	0.9005	1825	1836	(+0.6)			1814	1303
	0.7087	1837	1869	(+1.7)				
	0.5177	1823	1879	(+3.1)				
	0.2975	1737	1817	(+4.6)				
	0.2239	1678	1760	(+4.9)				
523.16	0.9005	1825	1826(a)	(+0.1)	0.376	1.605	1814	1303
	0.7087	1837	1837	(+0.0)				
	0.5177	1823	1822	(−0.1)				
	0.2975	1737	1737	(+0.0)				
	0.2239	1678	1678	(+0.0)				

(a) Utilising φ_{ij} calculated at this very temperature. a, b, c, and d stand for the same references as given in the foot-note of Table 2.

TABLE II

Comparison of the calculated and experimental η_{mix} values of N_2-NH_3 system and some other pertinent data

Temp. °K	×polar	$\eta_{mix} \times 10^7$ (gm./cm-sec) Exptl.	Calc.	%dev	φ_{12}	φ_{21}	$\eta_{N_2} \times 10^7$ (gm/cm-sec)	$\eta_{NH_3} \times 10^7$ (gm/cm-sec)
							(b)	(a,c,d)
293.16	0.8883	1092	1093	(+0.1)	0.954	0.839	1758	982
	0.7147	1254	1254	(+0.0)				
	0.5638	1383	1383	(+0.0)				
	0.2920	1585	1585	(+0.0)				
	0.1111	1690	1698	(+0.5)				
373.16	0.8883	1398	1407	(+0.6)			2145	1279
	0.7147	1569	1591	(+1.4)				
	0.5638	1710	1736	(+1.5)				
	0.2920	1920	1961	(+2.1)				
	0.1111	2031	2082	(+2.5)				
473.16	0.8883	1768	1787	(+1.1)			2560	1646
	0.7147	1946	1988	(+2.1)				
	0.5638	2085	2145	(+2.9)				
	0.2920	2296	2380	(+3.7)				
	0.1111	2408	2501	(+3.9)				
523.16	0.8883	1939	1960	(+1.1)			2740	1814
	0.7147	2112	2167	(+2.6)				
	0.5638	2250	2327	(+3.4)				
	0.2920	2460	2564	(+4.2)				
	0.1111	2572	2683	(+4.3)				
							(b)	(a,c,d)
293.16	0.8883	1092	1090	(-0.2)	0.533	2.401	1758	982
	0.7147	1254	1254	(+0.0)				
	0.5638	1383	1385	(+0.1)				
	0.2920	1585	1585	(+0.0)				
	0.1111	1690	1697	(+0.4)				
373.16	0.8883	1398	1392	(−0.4)			2145	1279
	0.7147	1569	1572	(+0.2)				
	0.5638	1710	1718	(+0.5)				
	0.2920	1920	1946	(+1.4)				
	0.1111	2031	2074	(+2.1)				
473.16	0.8883	1768	1753	(−0.8)			2560	1646
	0.7147	1946	1937	(−0.5)				
	0.5638	2085	2092	(+0.3)				
	0.2920	2296	2340	(+1.9)				
	0.1111	2408	2482	(+3.1)				
523.16	0.8883	1939	1916	(−1.2)			2740	1814
	0.7147	2112	2100	(−0.6)				
	0.5638	2250	2257	(−0.3)				
	0.2920	2460	2512	(+2.1)				
	0.1111	2572	2659	(+3.4)				

(a) Braune. H. and Linke, R., 1930, *Z. Phys. Chem.*, **A148**, 195.

(b) Hirschfelder, J. O., Bird, R. B., and Spotz. E. L., 1948, *J. Chem. Phys.*, **16**, 968.

(c) Trautz, M. and Heberling, R., 1931, *Ann. Physik.*, **10**, 155.

(d) Van Cleave, A. B. and Maass, O., 1935, *Canadian J. Res.*, **13**, 140.

the entire composition range in this way. As this approach has proved very successful for the binary combinations of nonpolar gases it will be interesting to see how far this procedure holds when polar gases are involved. To check this we consider the specific systems H_2–NH_3 and N_2–NH_3 for which elaborate data are available as a function of composition at various temperatures. It may be pointed out that the procedure for ϕ_{ij} determination suggested above will, in general, lead to two sets of coupled ϕ_{ij} values. In certain cases it may be possible to discard one in favour of the other but sometimes it may not be. In Table I, we list the calculated values for H_2–NH_3 while in Table II for N_2–NH_3. Only one set of appropriate ϕ_{ij} values were found in the case of H_2–NH_3 system but in the case of N_2–NH_3 system two sets were found. It may be possible to decide about their relative appropriateness by the degree of agreement between the calculated and experimental values. Thus, for the N_2–NH_3 system the first set of ϕ_{ij} values, reproduce the η_{mix} values within the average absolute deviation of 2.5%, while for the latter set this number drops to 1.3% only. However, the other relatively rigorous procedures of evaluating ϕ_{ij} lead to values closer to the first set (Mathur and Saxena, 1964a, 1964b) and therefore this particular set should be preferred over the second set. A little enhanced discrepancy found in the values using this set when compared with the experimental values should not matter much for ϕ_{ij} are also dependent on M_i and to some extent on the temperature, composition and nature of molecular interactions. The other set owes its origin to the fact that a large number of coupled ϕ_{ij}'s are possible which will reproduce the data almost equally well (Gray and Wright, 1961). Here, of course, we are looking for such values of ϕ_{ij}, which are independent of temperature, composition and nature of potential energy functions.

Cowling (1961) gave a simple but approximate interpretation of the physical significance of ϕ_{ij}. According to him ϕ_{ij} is the ratio of the efficiencies with which molecules j and molecules i separately impede the transport of momentum by molecules i. Thus, on this picture one should get only one set of ϕ_{ij} values. The fact that we get here two sets is not necessarily a contradiction. The reason for this anomaly lies in the assumptions made in arriving at this simple definition for ϕ_{ij}. As pointed out by Cowling (1961) Eq. (1) with this meaning for ϕ_{ij} assumes the interaction between molecules of different gases purely as opposition to transport of momentum and neglects other interactions, for example, the one most important arises from the transfer of momentum transport from one gas to another at collisions. This has been discussed by Cowling, Gray and Wright (1963) and when this effect is also included much more complicated expressions result for ϕ_{ij} and its simple definition is found to be no more valid. Therefore, the only criterion of choosing one set of ϕ_{ij} values amongst many should be the concordance of their actual values with those obtained on the basis of rigorous theory (Mathur and Saxena, 1964a).

To investigate the adequacy of the temperature independent ϕ_{ij} for purposes of prediction at high temperatures we also compute η_{mix} at high temperatures where direct measured values are available. The ϕ_{ij} were always evaluated at the lowest temperature and it is interesting that the reproduction even at the highest temperature is not bad. A somewhat better correlation is possible if ϕ_{ij} are calculated at the same temperature. Thus for H_2–NH_3, where calculations were repeated at $T = 523.16°K$, it was found that the values get reproduced within the maximum deviation of 0.1%

CONCLUSIONS

As for nonpolar binary and higher order mixtures, the Sutherland form seems adequate to correlate the data even when polar gases are involved. Numerical calculations performed here for the two systems indicate that Sutherland's expression holds the promise of being extended to high temperatures with ϕ_{ij} values determined at a lower temperature. By this analogy one may expect the generalised Sutherland formula to be adequate also for multicomponent mixtures involving polar gases though no checks could be made because of the lack of experimental data.

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