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Viscosities of Solutions of Potassium in Liquid Ammonia and
Deutero-Ammonia.*

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Abstract.

The viscosities of solutions of potassium in liquid ammonia and deuterio-ammonia have been measured with an Ostwald viscosimeter at -33.6°C , 0.0°C , and $+20.0^{\circ}\text{C}$, over a concentration range from zero to approximately $1.5 \text{ mole liter}^{-1}$. The methods of measurement and the experimental results are given. The viscosities, η , of the pure liquids, measured in centipoise, are least squares fitted by the relations,

$$\log_e \eta = \underset{(17)}{-4.677} + \underset{(9)}{1.577/RT} \text{ for ammonia and}$$

$$\log_e \eta = \underset{(32)}{-4.676} + \underset{(17)}{1.670/RT} \text{ for deuterio-ammonia,}$$

in which R is the gas constant and T is the Kelvin temperature. (The standard deviations are given in parentheses.) The viscosities of the solutions have been discussed previously.

Viscosities of Solutions of Potassium in
Liquid Ammonia and Deutero-Ammonia.*

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1. Introduction.

In contrast to the behavior of solutions of inorganic salts in liquid NH_3 ,¹ the coefficients of viscosity of solutions of Na in NH_3 ^{2,3} decrease with increasing concentration of solute. This anomalous behavior is similar to that of the densities of solutions of Na and K in liquid NH_3 and ND_3 .^{4,5} In connection with our previous investigations of the electron paramagnetic resonance spectra of liquid solutions of K in NH_3 and ND_3 ^{6,7} we determined the coefficients of viscosity of such solutions at -33.6°C , 0.0°C , and 20.0°C over a concentration range from 0 to approximately $1.5 \text{ mole } \ell^{-1}$. The viscosities of these solutions are involved in an important way in the theories⁸ of motional narrowing of the magnetic

resonance spectral lines and of the magnetic relaxation times. In view of the importance of information on the viscosities of these solutions in general discussions of their anomalous behaviors on the basis of various models, and because of a lack of data in the literature on viscosities of solutions of K in NH_3 and of any alkali metal in ND_3 , we present here the numerical results of our measurements of the coefficients of viscosity.

An interpretation of the anomalous viscosity behavior of such solutions on the basis of the cavity model has been given previously.⁹

2. Experimental Methods.

The NH_3 and ND_3 which were used for these measurements were prepared in a manner which has been described previously.⁵ The viscosimeter which we used is described in Figure 1. It was constructed of Pyrex glass. The reliability of this viscosimeter and of our techniques for using it were examined by measuring the flow times required for the liquid level to move from the upper fiducial mark, C, to the lower fiducial mark, D, for $(\text{C}_2\text{H}_5)_2\text{O}$ at 0.0 and 5.0°C, for CS_2 at 5.0°C, for $(\text{CH}_3)_2\text{CO}$ at 0.0°C, and for NH_3 at 0.0 and 5.0°C. A comparison of our measured flow times for NH_3 at 0.0°C with our measured flow

times and the viscosity values of Thrope and Rodger¹⁰ for $(C_2H_5)_2O$ at $0.0^\circ C$, for $(CH_3)_2CO$ at $0.0^\circ C$ and for CS_2 at $5.0^\circ C$ gave the values, 0.1705, 0.1697, and 0.1698 centipoise, respectively, for the coefficient of viscosity of NH_3 at $0.0^\circ C$. The average, 0.1700 centipoise, of these values to be compared with the value, 0.1700 centipoise, extrapolated from the measurements of Plank and Hunt¹¹ for NH_3 at $5^\circ C$, $15^\circ C$, and $25^\circ C$. A comparison of our measured flow times for NH_3 at $5.0^\circ C$ with our measured flow times and the viscosity values of Thrope and Rodger¹⁰ for $(C_2H_5)_2O$ at $5.0^\circ C$, for $(CH_3)_2CO$ at $0.0^\circ C$, and for CS_2 at $5.0^\circ C$ gave the values, 0.1619, 0.1616, and 0.1616 centipoise, respectively, for the coefficient of viscosity of NH_3 at $5.0^\circ C$. The average, 0.1617 centipoise, of these values may be compared with the value, 0.1618 centipoise, measured by Plank and Hunt¹¹ at $5^\circ C$.

The values of the coefficient of viscosity reported in this paper were obtained by measuring flow times for the solution being studied at $0.0^\circ C$ and for the solution or pure liquid being studied at $-33.6^\circ C$ and $20.0^\circ C$, and comparing these flow times with the flow times for pure NH_3 at $0.0^\circ C$, assuming that the coefficient of viscosity for pure NH_3 at $0.0^\circ C$ is 0.1700 centipoise.¹¹

The standard taper joint shown in Figure 1 was used for the evacuation of the viscosimeter and for the initial introduction of NH_3 or ND_3 . After evacuation the K in side arm, B,

was distilled into bulb, A, and the side arm was then sealed off and removed at point, E. The initial NH_3 (or ND_3) was then added and the standard taper sealed off at F. Then the viscosimeter minus side arm D and the standard taper shown, and containing K and NH_3 (or ND_3), plus a second standard taper joint and a break seal breaker, was weighed. The viscosimeter was then brought to the desired temperature and 3, 4 or 5 times of flow were measured. The 0.8 cm diameter tube returned the solution to the bulb at the top of the capillary when the apparatus was tilted. The standard taper joint was then sealed to one of the break seals, the seal was broken, more NH_3 or ND_3 was added, the standard taper was sealed off at the break seal constriction, and the entire assembly, now containing the additional solvent, was weighed. Then the viscosimeter, minus the second standard taper joint and breaker, plus a third standard taper joint and a new breaker, was weighed in a separate weighing, and the cycle of events was repeated, including the determination of flow times for the more dilute solution which the apparatus now contained. The last break seal was used for the removal of all the NH_3 (or ND_3), leaving only the K in the viscosimeter. A final weighing gave the total weight of solvent in the last solution. The side arm was then opened and the amount of K in the viscosimeter was determined by conversion to hydroxide with moist, CO_2 free,

N_2 gas, with subsequent dissolving in H_2O and titration with a standard solution of HCl . This determination of the weight of K , together with the weighings made during each cycle of measuring operations described above, and the densities of solutions of K in NH_3 and ND_3 measured previously,⁵ gave the information required for knowledge of the concentrations of all of the solutions for which flow times were measured.

The coefficient of viscosity, η , was determined from the relationship,¹²

$$(1) \quad \eta = \frac{(\rho_L - \rho_G)t}{(\rho_L - \rho_{GO})t_0} \left[\eta_0 + \frac{V\rho_{LO}}{16\pi lt_0} \right] - \frac{V\rho_L}{16\pi lt}$$

in which

ρ_L is the density of the solution,

ρ_G is the density of the NH_3 vapor,

t is the average of 3, 4, or 5, flow times for the solution,

ρ_{LO} is the density of pure liquid NH_3 at $0.0^\circ C$, namely, $0.6386 \text{ g. cm}^{-3}$,

ρ_{GO} is the vapor density over pure liquid NH_3 at $0.0^\circ C$, namely, $32 \times 10^{-4} \text{ g cm}^{-3}$,

t_0 is the average flow time for pure liquid NH_3 at 0.0°C , namely 289.6 sec for one capillary and 288.8 sec for the other of the 2 capillaries which were used,

η_0 is the assumed viscosity of pure liquid NH_3 at 0.0°C , namely, 0.1700 centipoise (see discussion above),

V is the volume, $\sim 2.5 \text{ cm}^3$, of liquid which flowed during a flow time measurement,

l is the length of the capillary, $\sim 7 \text{ cm}$.

The measured flow times ranged from 181 to 404 seconds. The standard deviations of the averages of the 3, 4, or 5 flow times measured for each concentration of each solution, ranged from 0.1 to 0.03 per cent. Thus the comparison of flow times for the solutions with those for pure NH_3 at 0.0°C introduced standard deviations of at most 0.15 per cent and typically somewhat less than 0.1 per cent in the measured viscosities. This was the main uncertainty in the measurements at 0.0°C . For the measurements at -33.5 and at 20.0°C , the uncertainty in the constant $1/16\pi$ in the kinetic energy corrections in expression (1) led to larger uncertainties in the viscosities than did the uncertainties in the time measurements. The value of this constant depends upon details of the shape of

the capillary ends. The estimated standard deviations given in Table 1 arise entirely from this source at -33.5 and 20.0°C.

The estimated standard deviation of the measurements of concentration were estimated to be 0.1 per cent and of the measurement of temperature to be 0.05°C.

3. Experimental results.

45 measurements of viscosities of solutions and pure solvents were made. The results are summarized in Table 1. A reduced drawing of an approximately 2m by 1m plot of these results which was used for graphical interpolation is presented in Figure 2. The sizes of the squares and circles in this figure do not give any indication of uncertainties and merely serve to locate the points whose coordinates are given in Table 1. Some results of the graphical interpolations are given in Table 2.

4. Discussion.

The values of the viscosity for the pure solvents were least fitted by the relation,

$$(2) \log_e \eta = \zeta + \frac{\Delta E}{RT},$$

in which η is the viscosity measured in centipoise,

ζ is a constant,

R is the gas constant,

T is the Kelvin temperature,

ΔE is a constant with the dimensions of energy per mole.

The values of ζ and ΔE for least squares best fit are given in Table 3. The 2 best values of ζ are the same to much better than their standard deviations. The 2 ΔE 's are significantly different. A similar situation with respect to the viscosities of isotopic species exists in the cases of H_2O and D_2O , the latter having a larger viscosity.

The viscosities of the solutions of K in NH_3 and ND_3 have been discussed in detail previously by O'Reilly.⁹

5. Acknowledgements.

We thank Edward Bartal for construction of apparatus used in this work.

Table 1. Experimental Results. Viscosities of Solutions of K in Liquid NH_3 and ND_3

Estimated Standard Deviation of Concentrations: 0.1 per cent

Estimated Standard Deviation of Temperature: 0.05°C

NH_3				ND_3			
Temp- erature	Concen- tration	Viscosity	Estimated Stan- dard deviation of coefficient of viscosity	Temp- erature	Concen- tration	Viscosity	Estimated Stan- dard deviation of coefficient of viscosity
$^\circ\text{C}$	Mole ℓ^{-1}	Centipoise	Centipoise	$^\circ\text{C}$	Mole ℓ^{-1}	Centipoise	Centipoise
-33.6	0.000	0.2551	0.0010	-33.5	0.000	0.3102	0.0013
	0.0968	0.2535	0.0010		0.263	0.3004	0.0013
	0.299	0.2480	0.0010		0.515	0.2901	0.0012
	0.475	0.2422	0.0010		1.074	0.2674	0.0010
	0.664	0.2346	0.0009		1.489	0.2484	0.0008
	0.981	0.2207	0.0008				
	1.426	0.2012	0.0006				
0.0	0.000	0.1700	0.0002	0.0	0.000	0.2028	0.0003
	0.167	0.1672	0.0002		0.482	0.1957	0.0003
	0.209	0.1668	0.0002		0.522	0.1946	0.0003
	0.248	0.1664	0.0002		0.605	0.1936	0.0003
	0.251	0.1665	0.0002		0.690	0.1908	0.0003
	0.405	0.1638	0.0002		0.832	0.1883	0.0003
	0.473	0.1631	0.0002		1.016	0.1815	0.0003
	0.943	0.1593	0.0002		1.159	0.1777	0.0003
	0.988	0.1593	0.0002				
	1.130	0.1570	0.0002				
	1.367	0.1539	0.0002				

Table 1. (cont.)

NH ₃				ND ₃			
Temp- erature	Concen- tration	Viscosity	Estimated Stan- dard deviation of coefficient of viscosity	Temp- erature	Concen- tration	Viscosity	Estimated Stan- dard deviation of coefficient of viscosity
°C	Mole l ⁻¹	Centipoise	Centipoise	°C	Mole l ⁻¹	Centipoise	Centipoise
20.0	0.000	0.1392	0.0006	20.0	0.000	0.1634	0.0007
	0.0904	0.1387	0.0006		0.240	0.1606	0.0007
	0.269	0.1376	0.0006		0.487	0.1574	0.0007
	0.443	0.1358	0.0006		0.755	0.1540	0.0007
	0.610	0.1341	0.0006		0.995	0.1504	0.0008
	0.908	0.1303	0.0007		0.1405	0.1456	0.0008
	1.347	0.1240	0.0008				

Table 2. Viscosities of Solutions of K in Liquid NH_3 and ND_3 .
(Interpolated from Table 1.)

NH_3			ND_3	
Concen- tration	Temp- erature	Viscosity	Temp- erature	Viscosity
Mole ℓ^{-1}	$^{\circ}\text{C}$	Centipoise	$^{\circ}\text{C}$	Centipoise
0.000	-33.6	0.2551	-33.5	0.3102
0.150		0.2520		0.3047
0.300		0.2491		0.2989
0.600		0.2374		0.2868
0.900		0.2241		0.2743
1.200		0.2110		0.2616
0.000	0.0	0.1700	0.0	0.2028
0.150		0.1679		0.2004
0.300		0.1656		0.1983
0.600		0.1620		0.1933
0.900		0.1597		0.1857
1.200		0.1562		0.1764
0.000	+20.0	0.1391	+20.0	0.1634
0.150		0.1383		0.1619
0.300		0.1372		0.1597
0.600		0.1342		0.1560
0.900		0.1305		0.1518
1.200		0.1263		0.1478

Table 3. Values of Constants in Equation (2) for Least Squares Best Fit of Viscosity Data for Pure NH_3 and ND_3 . (Viscosity Measured in Centipoise. σ Denotes Standard Deviation.)

Liquid	ζ	$\sigma(\zeta)$	ΔE kcal mole ⁻¹	$\sigma(\Delta E)$ kcal mole ⁻¹
NH_3	-4.677	0.017	1.577	0.009
ND_3	-4.676	0.032	1.670	0.017

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Figure 1. Viscosimeter.

Figure 2. Coefficient of Viscosity
vs Concentration of K in
Liquid NH_3 and ND_3 .