The Determination of the Apparent Molal Volumes and Viscosities of Some Electrolytes in Anhydrous Ethylenediamine at 25° C.

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Introduction

Much work has been done on the physical chemical properties of solutions of electrolytes. Most of this study has been done on aqueous solutions. Attention is now turning to solutions of electrolytes in non-aqueous solvents of lower dielectric constant than water. In this work, the solvent, ethylenediamine, (D = 12.9) has been used.

All physical properties of solutions of electrolytes are modified by ion association. Through the measurement of viscosities and partial molal volumes of salts dissolved in this amine solvent we hope to gain some knowledge, along with other measured properties, of the extent of formation of ion pairs in the dilute and concentrated regions of solution. Viscosity measurements provide a moderately sensitive indication of the presence of ions other than the simple type. The viscosity of a dilute

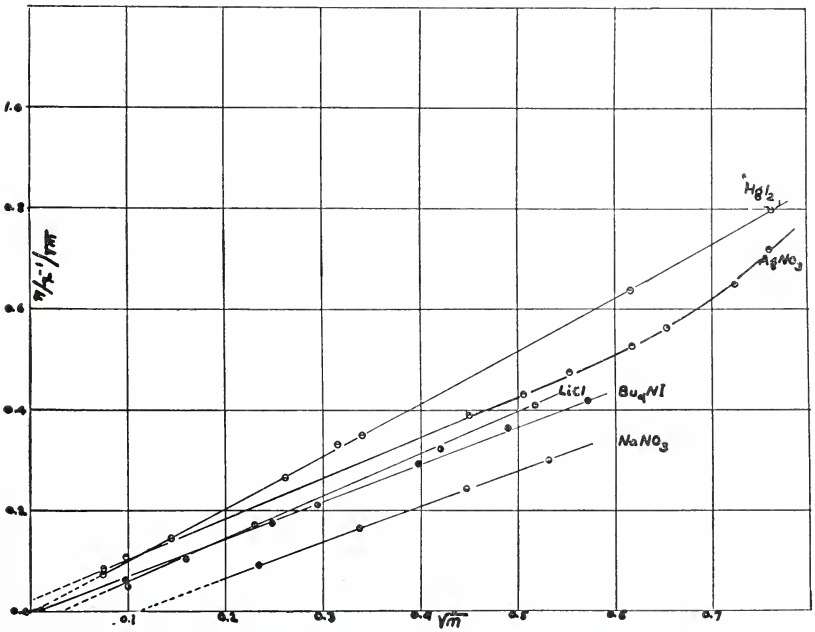

Figure 1. Graph Showing the Experimental Results of the Relationship η/η_0-1 / m½ for Various Electrolytes in Anhydrous En.

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electrolytic solution can be accurately represented in the majority of cases by the equation (1)

$\eta/\eta_o = 1 + A\sqrt{m} + Bm$ in the more dilute regions, ie: less than 0.1m. A and B are constants. The term, $Am^{1/2}$ is due to inter-ionic forces, and can be calculated for a given solute from its charges (valency) and the mobility of its ions, giving the limiting slope. This slope can then be compared with the experimental slope by plotting $[\eta/\eta_o - 1/\sqrt{c}]$ against the $\sqrt{c}$ as shown in Fig. 1. The B coefficient (ax is intercept) may be positive or negative in both aqueous and nonaqueous solution. So apparently besides the positive effect[1] predicted by theory there is another effect (possibly due to the solvent) which can affect the viscosity. A negative B can be regarded in a sense as an ion loosening effect on the solvent.

According to Stokes' law a particle of radius γ cm. moving through a homogenous medium of viscosity η under the influence of a force F will maintain a velocity V, given by $V = F/6\pi\eta\gamma$. When the definition of equivalent ionic conductance is introduced, this becomes

$$\Lambda_i^\circ = \frac{8.20 \times 10^{-9} Z_i}{r_i}$$

transforming:

$$r_i = \frac{8.20 \times 10^{-9} Z_i}{\Lambda^\circ_i}$$

where Z_i is the charge involved on the electrolyte ions. Thus effective ion radii can be calculated from the ion mobilities and viscosities. According to Walden's Rule the conductance—viscosity product is constant (2). It has been shown that the Λ° product varies widely from solvent to solvent. This reflects the solvation numbers and should give the extent of binding of solvent molecules by the ions involved.

Another method of estimating the specie of ions present in solution is the study of the apparent partial molal volumes exhibited by the electrolytes involved. The apparent molal volume can be calculate from the density of the solutions by the following formula.

$$\phi_v = \frac{1000}{mdd_o}(d_o - d)\frac{M}{d}$$

where d_o is the density of the solvent, d, the density of the solution, m the concentration in moles of electrolyte per 1000 grams of solvent and M the moleculer weight of the electrolyte involved. The exactness of the determination ϕ_v is critically dependent upon the density measurements involved. When the $(d_o - d)$ term gets smaller and smaller the accuracy of ϕ_v gets less and less dependent.

Masson (3) found that most aqueous solutions of electrolytes follow the following empirical relationship:

$$\phi_o = a\sqrt{m} + b$$

where a and b are constants characteristic of the electrolytes involved. The constant (a) is related to inter-ionic distances while (b) gives some insight as to the relative size of the ions involved. Redlich (4) finds that, according to the Debye-Hueckel theory, the partial molal volumes of salts in solution should vary linearly with the square-root of the concentration.

TABLE 1

Concentrations, Densities and Viscosities of Solutions of Some Electrolytes in Anhydrous Ethylenediamine at 25.000±0.005° C.

M	$\sqrt{M}$	ρ	η^{rl}	η^{sp}	$\eta^{sp}/\sqrt{M}$
I LiCl					
0.0104	0.102	0.89365	1.0056	0.0056	0.005
0.0536	0.232	0.89512	1.0399	0.0399	0.172
0.1782	0.422	0.89906	1.1345	0.1345	0.320
0.2683	0.518	0.90242	1.2141	0.2141	0.413
II $NaNO_3$					
0.0544	0.233	0.89606	1.0227	0.0227	0.097
0.1149	0.339	0.89967	1.0561	0.0561	0.166
0.1977	0.445	0.90315	1.0797	0.0797	0.240
0.2845	0.533	0.90987	1.1655	0.1655	0.311
0.0421	0.205	0.89590	1.0030	0.0030	0.015
0.2220	0.471	0.90490	1.0877	0.0877	0.186
III HgI_2					
0.0202	0.142	0.8992	1.020	0.020	0.140
0.0681	0.261	0.9152	1.070	0.670	0.260
0.1140	0.338	0.9339	1.117	0.117	0.346
0.3771	0.614	1.0231	1.380	0.0380	0.619
0.5652	0.758	1.0868	1.571	0.571	0.760
IV $AgNO_3$					
0.0056	0.075	0.89481	1.0059	0.0059	0.079
0.0100	0.100	0.89561	1.0100	0.0100	0.100
0.0300	0.173	0.89798	1.0289	0.0289	0.167
0.3025	0.550	0.93592	1.2715	0.2715	0.484
0.3799	0.616	0.94638	1.3283	0.3283	0.533
0.4227	0.650	0.95113	1.3580	0.3580	0.551
0.5234	0.723	0.96572	1.4676	0.4676	0.647
0.7237	0.850	0.99168	1.655	0.655	0.771
0.8175	0.904	1.00490	1.7893	0.7893	0.873
0.9855	0.993	1.02648	2.0602	1.0602	1.068
1.0000	1.0000	1.02755	2.0664	1.0664	1.066
V Tetra•n-Butylammonium Iodide					
0.0052	0.072	0.89397			
0.1118	0.334	0.90172	1.0735	0.0735	0.220
0.00016	0.0126	0.89322	1.0000	0.0000	0.0000
0.00998	0.0999	0.80431	1.0062	0.0062	0.062
0.02598	0.161	0.89510	1.0174	0.0174	0.108
0.0503	0.224	0.89656			
0.0563	0.237	0.89742			
0.0625	0.250	0.89784	1.0440	0.0440	0.176
0.08525	0.292	0.90061	1.0631	0.0631	0.216
0.1611	0.401	0.90480	1.1197	0.1197	0.298
0.2422	0.492	0.91076	1.1746	0.1746	0.355
0.3261	0.571	0.91668	1.2383	0.2383	0.417
2.3673	0.606	0.91939	1.2940	0.2940	0.485

TABLE 2

Apparent Molal Volumes (ϕ_v) for Various Concentrations of Several Salts In Anhydrous Ethylenediamine at 25° C.

m	$\sqrt{m}$	ϕ_v(ml/mole)
LiCl		
0.0536	0.232	10.5
0.0713	0.267	9.8
0.1728	0.422	8.0
0.2683	0.518	6.2
		ϕ_v Extrapolated 13.5 ml.
$NaNO_3$		
0.0421	0.205	33.6
0.0544	0.233	33.1
0.1149	0.339	31.4
0.1977	0.445	31.1
0.2220	0.471	30.2
0.2845	0.533	30.4
		ϕ_v Extrapolated 35.5 ml.
HgI_2		
0.0202	0.142	104.8
0.0681	0.261	106.8
0.1140	0.338	92.4
0.5652	0.752	68.2
0.7537	0.869	65.4
		ϕ_v Extrapolated 112.0 ml.
$AgNO_3$		
0.0503	0.224	19.4
0.2507	0.501	18.4
0.3025	0.550	18.3
0.3799	0.616	18.3
0.4227	0.650	17.9
0.5234	0.732	17.6
0.5624	0.750	17.5
0.8175	0.904	17.2
		ϕ_v Extrapolated 20.0 ml.
Bu_4NI		
0.0625	0.250	321.7
0.0853	0.292	319.8
0.0913	0.302	319.5
0.1611	0.401	317.0
0.1785	0.423	316.5
0.3261	0.571	316.2
0.3673	0.606	315.9
		ϕ_v Extrapolated 325 ml.

Work along these lines is to be continued.

This work was carried out by aid from A.E.C. grant (AT-11-1-256).

Experimental

The ethylenediamine used was dried over calcium hydride and fractionated in an atmosphere of nitrogen until constant density (0.8935 g. ml.$^{-1}$) was obtained.

Viscosities were run in a calibrated Ostwald viscometer. Densities were made by use of a 25 milliliter picnometer. Salts were recrystallized reagent grade and dried at 150° C. to constant weight. Constant temperature bath was kept at 25.000±0.005° C.

Summary

Our determinations of the viscosities of solutions of various electrolytes in anhydrous ethylenediamine show that the relationship between $[\eta/\eta_0 - 1/\sqrt{m}]$ and $\sqrt{m}$ is linear for those electrolytes examined over the concentration as shown in Fig. 1 and Table 1. Viscosities measured also will be used to examine the validity of Waldens' Rule for non-aqueous solutions of electrolytes.

The extension of Masson's empirical rule has been extended to non-aqueous solutions and seems to be valid as shown in Table 2.

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