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Polarizations and Refractions of Some *N*-Methylacetamide-*n*-Alcohol Systems

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The dependence of polarization on concentration and temperature has been determined for five *N*-methylacetamide-*n*-alcohol systems and the *N*-methylacetamide–water system. Within the homologous alcohol series, departures from Debye behavior in regard to concentration dependence are greatest for the *n*-amyl alcohol system and least for the methyl alcohol system. The departures from Debye temperature dependence however, are greatest for the methyl alcohol system and least for the *n*-amyl alcohol system. The water system displays almost linear concentration dependence, but exhibits a temperature dependence intermediate between those of ethyl and *n*-alcohol. Association by hydrogen bonding is displayed to a high degree by these components and systems. The association in *N*-methylacetamide appears approximately equal to that in methyl alcohol but less than that in water. Within the homologous alcohol series, association characteristics decrease steadily from methyl alcohol to *n*-amyl alcohol.

THE POLARIZATION behavior of alcohol–non-polar solvent systems has been investigated extensively (*3, 4, 12, 13*). Large deviations from Debye behavior have been observed and accredited to association. However, few if any investigations concerned with the polarization behavior of alcohols in extremely polar solvents have been carried out. In 1951, Leader and Gormley (*6*) reported that *N*-methylacetamide was characterized by an exceptionally high dielectric constant which exceeds more than twice that of water at a comparable temperature. With this very polar solvent available, the present investigation concerned with determination of polarization dependence on temperature and concentration for *N*-methylacetamide-*n*-alcohol systems was initiated. Water and the first five normal alcohols (methanol–*n*-amyl alcohol) were chosen for use as the *n*-alcohol components. This selection enables one to make comparisons of polarization behavior within the homologous series and also allows a comparison of effects apparent in polar and non-polar solvents.

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EXPERIMENTAL

Purification of Materials. *N*-Methylacetamide was obtained from a departmental supply and purified by fractional distillation at reduced pressure, followed by fractional freezing (*2*). The physical properties of the final product at 30° C. were as follows: density, 0.9498 gram/ml.; viscosity, 0.03885 poise; dielectric constant, 178.6.

Methanol (Fisher Scientific Co. Reagent grade) was refluxed for several hours in contact with activated alumina and fractionally distilled. The retained middle fraction

Table I. Dielectric Constants, Densities, Indices of Refraction, Molar Polarizations, and Molar Refractions of Solutions of HOH and ROH in NMA at 30° C.

N_1	D	d	n_D	P	R_D	N_1	D	d	n_D	P	R_D
		HOH						PrOH			
0.0000	76.8	0.9957	1.3325	17.41	3.717	0.0000	19.1	0.7976	1.3830	64.63	17.575
0.0101	77.1	0.9954	1.3370	17.95	3.880	0.0086	19.6	0.7991	1.3836	64.88	17.600
0.0239	78.3	0.9956	1.3430	18.69	4.102	0.0151	19.7	0.7999	1.3840	65.05	17.624
0.0283	78.5	0.9956	1.3449	18.93	4.175	0.0210	20.1	0.8010	1.3843	65.14	17.634
0.0344	78.9	0.9961	1.3470	19.25	4.268	0.0310	20.6	0.8027	1.3853	65.37	17.675
0.0465	79.6	0.9964	1.3518	19.89	4.464	0.0430	21.1	0.8044	1.3858	65.61	17.704
0.1008	82.6	0.9987	1.3699	22.76	5.336	0.1253	25.3	0.8173	1.3899	67.20	17.892
0.2137	88.6	0.9996	1.3945	28.81	7.136	0.1935	29.8	0.8283	1.3927	68.46	18.029
0.3482	96.2	0.9927	1.4106	36.32	9.295	0.3079	39.2	0.8462	1.3987	70.23	18.315
0.4166	101.1	0.9880	1.4152	40.25	10.387	0.3657	44.3	0.8560	1.4012	70.85	18.415
0.4395	102.8	0.9860	1.4170	41.60	10.769	0.5163	64.5	0.8778	1.4080	72.67	18.776
0.5008	108.3	0.9811	1.4198	45.21	11.535	0.5958	76.5	0.8899	1.4116	73.32	18.953
0.5794	115.9	0.9751	1.4229	49.90	13.036	0.7017	96.3	0.9058	1.4165	74.08	19.197
0.6476	123.3	0.9701	1.4246	54.02	14.139	0.8631	134.5	0.9297	1.4235	75.02	19.554
0.8222	146.9	0.9590	1.4275	64.68	16.965	0.9433	158.4	0.9417	1.4270	75.40	19.729
0.9017	159.5	0.9545	1.4286	69.59	18.265	0.9729	168.4	0.9461	1.4279	75.54	19.777
0.9201	162.8	0.9538	1.4288	70.71	18.561	0.9762	169.6	0.9465	1.4286	75.55	19.809
0.9383	166.2	0.9529	1.4289	71.84	18.853	0.9847	172.3	0.9478	1.4287	75.58	19.816
0.9609	170.4	0.9517	1.4292	73.25	19.226	0.9888	174.3	0.9483	1.4289	75.62	19.828
0.9820	175.1	0.9505	1.4292	74.58	19.565	0.9952	175.9	0.9492	1.4291	75.64	19.840
1.0000	178.6	0.9498	1.4291	75.68	19.844	1.0000	178.6	0.9498	1.4291	75.68	19.844
		MeOH						BuOH			
0.0000	31.7	0.7820	1.3252	37.33	8.249	0.0000	16.9	0.8021	1.3958	77.74	22.195
0.0048	32.2	0.7839	1.3271	37.51	8.323	0.0061	17.2	0.8024	1.3959	77.94	22.189
0.0093	32.6	0.7855	1.3279	37.69	8.373	0.0144	17.5	0.8038	1.3960	78.01	22.154
0.0151	32.9	0.7876	1.3283	37.90	8.421	0.0252	17.9	0.8051	1.3962	78.15	22.125
0.0219	33.5	0.7899	1.3298	38.18	8.503	0.0294	18.0	0.8054	1.3963	78.20	22.120
0.0255	33.8	0.7912	1.3308	38.32	8.551	0.0410	18.3	0.8071	1.3970	78.22	22.104
0.0977	40.3	0.8144	1.3444	41.12	9.388	0.1286	22.5	0.8183	1.3995	79.35	21.897
0.1909	49.3	0.8398	1.3623	44.70	10.540	0.1805	25.4	0.8250	1.4011	79.80	21.779
0.3091	61.9	0.8656	1.3759	49.25	11.855	0.3044	34.7	0.8415	1.4050	80.55	21.499
0.4088	73.9	0.8844	1.3880	53.02	13.027	0.4523	49.8	0.8623	1.4096	80.47	21.146
0.5211	89.1	0.9012	1.3981	57.34	14.314	0.5469	62.6	0.8761	1.4129	80.07	20.933
0.5821	97.9	0.9095	1.4037	59.66	15.032	0.6298	75.3	0.8892	1.4158	79.43	20.728
0.6819	114.2	0.9215	1.4111	63.47	16.180	0.7181	94.0	0.9024	1.4188	78.78	20.529
0.7883	133.2	0.9319	1.4181	67.59	17.420	0.7939	110.9	0.9150	1.4217	77.98	20.368
0.9528	167.6	0.9462	1.4271	73.87	19.313	0.9179	144.5	0.9370	1.4262	76.50	20.020
0.9610	168.7	0.9469	1.4277	74.17	19.414	0.9433	156.5	0.9399	1.4272	76.36	19.992
0.9806	173.8	0.9483	1.4285	74.94	19.635	0.9464	157.8	0.9405	1.4273	76.30	19.982
0.9851	175.0	0.9488	1.4289	75.11	19.691	0.9564	161.5	0.9423	1.4277	76.20	19.958
0.9886	175.7	0.9490	1.4290	75.23	19.730	0.9718	167.2	0.9449	1.4281	76.02	10.915
0.9937	177.1	0.9494	1.4291	75.44	19.782	0.9907	174.7	0.9484	1.4290	75.77	19.872
1.0000	178.6	0.9498	1.4291	75.68	19.844	1.0000	178.6	0.9498	1.4291	75.68	19.844
		EtOH						AmOH			
0.0000	23.5	0.7814	1.3580	52.02	12.947	0.0000	14.1	0.8071	1.4063	88.87	26.845
0.0058	24.2	0.7829	1.3585	52.28	12.982	0.0061	14.4	0.8077	1.4069	89.08	26.832
0.0190	25.0	0.7859	1.3598	52.68	13.075	0.0145	14.6	0.8086	1.4070	89.09	26.769
0.0309	25.5	0.7886	1.3612	52.98	13.166	0.0225	14.9	0.8094	1.4071	89.23	26.713
0.0370	25.9	0.7902	1.3623	53.16	13.123	0.0296	15.1	0.8102	1.4071	89.26	26.654
0.0439	26.3	0.7915	1.3626	53.37	13.262	0.0361	15.4	0.8108	1.4072	89.42	26.610
0.1158	30.6	0.8074	1.3691	55.32	13.753	0.0657	16.6	0.8139	1.4078	89.82	26.408
0.1905	36.5	0.8230	1.3758	57.38	14.274	0.2061	23.9	0.8290	1.4100	90.71	25.418
0.2900	45.9	0.8425	1.3842	59.97	14.967	0.2881	29.0	0.8385	1.4113	90.28	24.834
0.3987	57.5	0.8626	1.3938	62.58	15.757	0.4023	39.5	0.8530	1.4136	89.28	24.029
0.5058	70.9	0.8806	1.4008	65.04	16.475	0.5169	53.7	0.8677	1.4160	87.63	23.244
0.6005	85.4	0.8960	1.4069	67.14	17.112	0.6077	67.4	0.8810	1.4179	85.88	22.593
0.7027	103.7	0.9112	1.4132	69.37	17.812	0.7820	104.3	0.9088	1.4225	81.67	21.379
0.7996	123.7	0.9248	1.4190	71.43	18.481	0.8329	117.8	0.9180	1.4240	80.30	21.018
0.9439	161.5	0.9432	1.4266	74.50	19.982	0.8926	136.7	0.9288	1.4258	79.63	20.603
0.9733	169.0	0.9469	1.4281	75.09	19.669	0.9786	168.3	0.9455	1.4283	76.28	19.990
0.9781	171.8	0.9471	1.4285	75.23	19.716	0.9796	169.5	0.9456	1.4284	76.26	19.988
0.9884	174.4	0.9485	1.4288	75.43	19.787	0.9882	173.1	0.9474	1.4289	76.02	10.935
0.9924	175.0	0.9489	1.4290	75.51	19.803	0.9927	175.1	0.9484	1.4289	75.88	19.896
0.9950	176.5	0.9492	1.4291	75.57	19.820	0.9962	176.7	0.9491	1.4290	75.78	19.870
1.0000	178.6	0.9498	1.4291	75.68	19.844	1.0000	178.6	0.9498	1.4291	75.68	19.844

possessed the following physical properties at 30° C.: density, 0.7820 gram/ml.; dielectric constant, 31.7; index of refraction, 1.3253.

Each of the materials, ethanol (Commercial Solvents Co. Reagent grade), *n*-propanol (Eimer and Amend Chemical Co. Reagent grade), *n*-butanol (Baker Analyzed Reagent grade), and *n*-amyl alcohol (Fisher Certified Reagent grade) were refluxed several hours in contact with preheated calcium oxide, followed by fractional distillation. Physical properties of the middle fractions for ethyl, *n*-propyl, *n*-butyl, and *n*-amyl alcohols respectively, were at 30° C.: density, 0.7814, 0.7978, 0.8021, 0.8071 gram/ml.; dielectric constant, 23.8, 19.1, 16.9, 14.1; index of refraction, 1.3580, 1.3830, 1.3958, 1.4063.

Pure water was obtained by fractional distillation from alkaline permanganate.

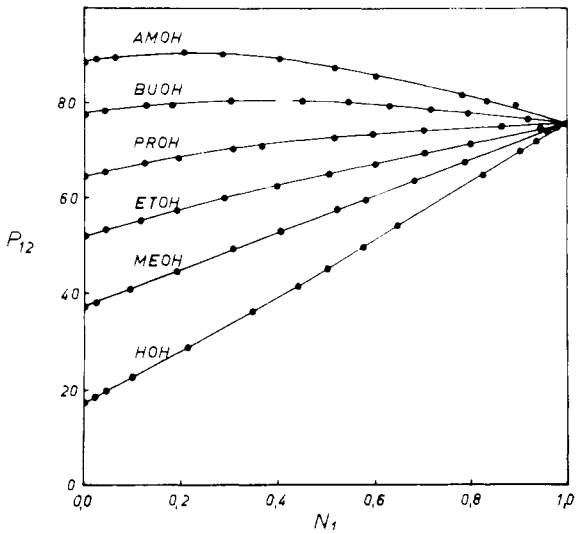

Figure 1. The polarization of NMA–ROH systems as a function of concentrations of NMA at 30° C.

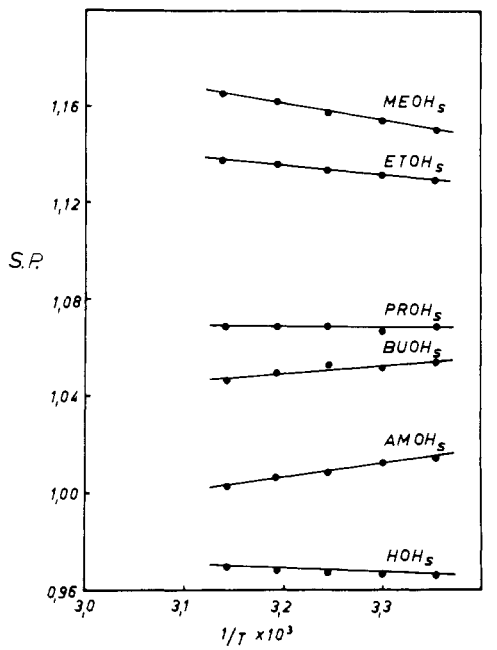

Figure 2. The polarization of dilute NMA in ROH systems as a function of temperature.

Apparatus and Procedure. For measurements of the dielectric constants of the various systems, a General Radio Company Twin-T Impedance Measuring Circuit was used. A General Radio Co. Type 1001-A Standard Signal Generator supplied radio frequency current and a Hallicrafters Model S-40A multiband receiver was used as a null detector.

The sample cell used for capacitance measurements was similar in design to that described by Leader (*5*). The inner electrode was made of electroplated stainless steel; the remaining inside metallic surface was heavily plated with silver.

The procedure involved in making measurements has been described previously (*5*, *6*). The standard media which were used to calibrate the dielectric constant cell were air and water. All measurements were made at a frequency of ten megacycles. The estimated uncertainty associated with any experimental dielectric value did not exceed 0.2 of a dielectric unit.

Densities were determined in the usual manner using 25ml. Reischauer pycnometers.

Measurements of the refractive indices were made with a Spencer Abbe refractometer equipped with a prism jacket through which water of the proper temperature was pumped rapidly from a nearby thermostat.

All temperatures were measured with thermometers graduated to 0.1° C. which were compared against a standard thermometer calibrated by the National Bureau of Standards.

Solutions were prepared on a weight basis with all transfers being made in a dry box under a positive pressure of dry nitrogen. Weights which were used were compared against a set calibrated by the National Bureau of Standards. Necessary buoyancy corrections were applied.

RESULTS AND DISCUSSION

Densities, dielectric constants, and indices of refraction were determined over the entire concentration range at 30° C. for solutions of *N*-methylacetamide in water (HOH) and each of the alcohols; methyl (MeOH), ethyl EtoH), *n*-propyl (PrOH), *n*-butyl (BuOH), and *n*-amyl (AmOH). These data as well as molar polarizations and refractions are presented in Table I. Molar polarizations (P_{12}) were plotted *vs.* mole fractions NMA (Fig. 1) as suggested by the Debye equation in the form:

$$P_{12} = \frac{D_{12} - 1}{D_{12} + 2} \frac{(M_1N_1 + M_2N_2)}{d_{12}}$$

$$= \frac{D_1 - 1}{D_1 + 2} \frac{M_1N_1}{d_1} + \frac{D_2 - 1}{D_2 + 2} \frac{M_2(1 - N_1)}{d_2} \quad (1)$$

where D,d, N, and M refer to dielectric constant, density, mole fraction, and molecular weight respectively, and subscripts 12, 1, and 2 refer to solution, pure NMA, and pure ROH (water or alcohol) respectively. Although the Debye equation is of dubious significance for polar compounds, it is entirely sufficient for comparisons attempted here.

Linear dependence is displayed by all six major systems over the approximate range $N_1 = 0.4$ to $N_1 = 1.0$. Within the range $N_1 = 0.0$ to $N_1 = 0.4$, a slight negative deviation is seen to develop in the NMA–HOH system, linearity persists in the NMA–MeOH system, and a slight positive deviation, appearing in the NMA–EtOH system, increases gradually in magnitude through the successively higher alcohol systems. Positive departures from linearity for these NMA–ROH solutions may be summarized by the series:

$$\text{AmOH} > \text{BuOH} > \text{PrOH} > \text{EtOH} > \text{MeOH} (=0) > \text{HOH}$$

In their work concerned with the polarization of heptane solutions of EtOH, BuOH and *n*-octyl alcohol (OcOH), Smyth and Stoops (*12*) found a reverse trend.

$$\text{EtOH} > \text{BuOH} > \text{OcOH}$$

Before attempting to explain and correlate these results, a discussion of the temperature dependence of P_{12} for these NMA–ROH systems is in order. Fig. 2 depicts plots of specific polarization (S.P.) *vs.* $1/T$ for dilute ROH solutions of NMA, (ROH_s), according to the Debye relationship:

$$P_{12} = \frac{4\pi A}{3} (\alpha_1N_1 + \alpha_2N_2) + \frac{4\pi A}{9kT} (N_1\mu_1^2 + N_2\mu_2^2) \quad (2)$$

Table II. Temperature Dependence of Specific Polarization for NMA–ROH Solutions as Indicated by the Slopes of Debye Plots

System	Slope	System	Slope
NMA	−72.5	HOH_s	−19.5
$MeOH_s$	−70.0	$PrOH_s$	00.0
MeOH	−69.0	$BuOH_s$	30.0
$EtOH_s$	−42.0	$AmOH_s$	55.0

where α, μ, A, k, and T are polarizability, dipole moment, Avogadro's number, Boltzmann's constant and absolute temperature respectively. Similar plots for pure NMA (*14*) and pure MeOH (*10*) were constructed from the data of other workers.

Linear dependence on reciprocal temperature is shown in every case. However, with the exception of $BuOH_s$ and $AmOH_s$ abnormal behavior is observed. That is, the polarization increases with an increase in temperature. The order of decreasing abnormality may be summarized by the series:

$$NMA > MeOH_s > MeOH > EtOH_s > HOH_s > PrOH_s > BuOH_s > AmOH_s$$

The temperature dependence found by Smyth and Stoops was similar:

$$EtOH > BuOH > OcOH$$

Alcohols, water and *N*-methylacetamide are known to exist in the liquid state as hydrogen bond polymers (*11*). Due to reversible polymerization, a liquid composed of these polymers will display a lesser temperature dependence of dielectric constant and polarization than one composed of monomer units. When temperature dependence measurements for alcohols are carried out at elevated temperatures (*12*) or at high dilutions (*8*) (*i.e.*, conditions under which few, if any, polymers exist), normal behavior is observed. Therefore, it seems reasonable to postulate that these series of abnormality merely reflect the strength or extent of association.

However, the position of water in this series is puzzling. Because of its small size, considerable dipole moment and possession of two hydrogens for bonding, one would expect this compound to be associated to a greater extent than NMA or the alcohols. Instead, it lies between EtOH and PrOH in order of abnormality. Possibly, the strong three dimensional hydrogen bonding in water produces the abnormally small density temperature coefficient which opposes the abnormal temperature coefficient of the dielectric constant.

The polarization temperature dependences for NMA, $MeOH_s$, and MeOH are nearly equal (Table II), thus indicating that the strength or extent of hydrogen bonding is similar for NMA and MeOH. The other ROH compounds display an orderly increasing temperature dependence (Table II), indicating, with the possible exception of HOH, an orderly decreasing strength or extent of hydrogen bonding.

Since hydrogen bonding characteristics are indicated to be similar for NMA and MeOH, the linear additivity of polarization for these substances, as shown in Fig. 1, is not too surprising. Similarly, deviations from linearity depicted by the other NMA–ROH systems reflect differences in hydrogen bonding characteristics. Then our series of departures from linearity as well as that of Smyth and Stoops indicate that the polarization of liquids of similar association properties tend more toward additivity than those of dissimilar association properties. This concept is similar to that put forward by Schallamach (*9*), Bauer (*1*) and Magot (*7*) to explain the number of dielectric dispersion regions and loss maxima.

It may be noted that, in the series of departures from linearity, HOH occupies the expected position, that is the association characteristics for HOH appear stronger than for NMA or the alcohols. Thus more weight is lent to the assumption that HOH is out of place in the temperature dependence series when considered on the basis of dielectric constant temperature dependence alone.

From Fig. 1, it appears that polarization dependence on concentration of systems composed of NMA plus a liquid of stronger, similar or weaker association characteristics exhibits a negative linear or a positive deviation, respectively.

In summary, polarization behavior data for NMA–ROH systems indicate that association in *N*-methylacetamide is approximately equal to that in methyl alcohol but less than that in water. Further, within the homologous alcohol series, association characteristics decrease steadily from methyl alcohol to *n*-amyl alcohol.

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