Study of *N*-Methylacetamide Solutions

Example of the Behavior of Highly Structured Liquids

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Dielectric constants and freezing points have been measured for solutions of *N*-methylacetamide–dioxane and *N*-methylacetamide–benzene. Both types of data indicate that NMA exists as a more associated liquid in benzene than in dioxane solutions. This is interpreted as confirmation that the structure-breaking effect on NMA is less when solutes solvate by the formation of a charge-transfer complex than when solute-solvent hydrogen bonding occurs.

N-METHYLACETAMIDE (NMA) has been investigated in these laboratories (*2*) as a solvent for freezing-point depression measurements. In the course of these studies, the authors observed that NMA is an unusual solvent in that it is miscible in all proportions with both water and benzene but is essentially immiscible with paraffinic hydrocarbons. Bonner, Bunzl, and Woolsey postulated (*1*) that the solubility behavior is related to the two possible types of solvation which can occur. Solute-solvent hydrogen bonding is the apparent mode in the case of solutions of NMA and alcohols, carbon tetrachloride, etc., while solvation by the formation of a charge-transfer complex is believed to occur in the case of certain aromatic solutes.

NMA is a highly structured liquid in which polymeric chains are formed by hydrogen-bonding. The extremely high dielectric constant is due to this structure. The authors expected that the addition of solutes would result in a solution having a lower dielectric constant and also that the dielectric constant would be lower for solutions in which solvation was accomplished by solute-solvent hydrogen-bonding than in the case of solutions of comparable composition, where solute-solvent charge-transfer complexes occur, since in the former case there is more competition with the solvent-solvent hydrogen-bonding. The results of further dielectric constant and freezing-point measurements are reported as a contribution to the knowledge of the properties of this interesting solvent. Data have also been extracted from the literature for other structured liquids such as alcohols and water, and these are used to substantiate the interpretation of the results of the investigation of NMA. Solvation of alcohols is also possible by two mechanisms, hydrogen-bonding or van der Waals attraction in the case of hydrocarbon solvents, and similarities in the behavior of solutions containing NMA and alcohols should be noted.

EXPERIMENTAL

N-methylacetamide was vacuum distilled and zone refined in the manner reported (*1*, *2*). Reagent grade benzene was distilled and the center fraction was used. Reagent grade dioxane was distilled from sodium and the center fraction was used. Freezing points and dielectric constants were measured using the same apparatus and in the same manner as before (*1*, *2*).

RESULTS AND DISCUSSION

Dielectric Constant Data. The structure of liquids is related to their dielectric constant. Wyman (*7*) and Onsager (*5*) recognized the inverse relationship between the polarization per cubic centimeter and the molar volume for many nonelectrolytes. Scatchard (*6*) used the relationship of Wyman in his treatment of concentrated solutions of electrolytes. Perhaps the most extensive recent investigation of the dielectric properties of solutions of nonelectrolytes is due to Decroocq (*3*). He has derived a simple linear relationship, based upon the Onsager-Kirkwood equations, between the dielectric constants of many binary nonpolar solutions and the volume fraction of the components. A negative deviation from linearity is noted, however, for polar-nonpolar mixtures. This deviation, ΔD, is calculated to be

$$\Delta D = \frac{n^4}{2}\left[\frac{1}{D} - \frac{V_1}{D_1} - \frac{V_2}{D_2}\right]$$

where D is the dielectric constant of the solution, V_1 and V_2 are the volume fractions of the components, D_1 and D_2 are the dielectric constants of the pure components, and n is the average index of refraction at long wave lengths of the two components. The value of n^4 is approximately 4 for many liquids.

Although the equation of Decroocq does not yield values of the dielectric constant of all solutions which agree exactly with those determined experimentally, the agreement is remarkable in many of his examples and seems to lend validity to his theoretical equations. Onsager noted that the linear relationship between dielectric constant and volume fractions did not hold for associated liquids such as alcohols, water, and ammonia; and he commented that the formation of a hydrogen bond increases the electric moment of the group which carries the hydrogen. This type of behavior should furnish a means of examining qualitatively the association of hydrogen-bonded liquids in solutions. Although the primary interests of the authors is in solutions of NMA, it seems desirable to confirm these trends using data for alcohols and water which are available in the literature. The data presented in Figure 1 show that solutions of alcohols in dioxane, where solution is accomplished by solute-solvent hydrogen bonding, have much lower dielectric constants than those of dioxane solutions containing a polar component of approximately the same dielectric constant as the alcohol but which is incapable of hydrogen-bonding. Solutions of methanol and ethanol in benzene are observed to have higher dielectric constants than those of dioxane solutions of comparable composition but not so high as similar solutions of the reference polar compound. This is to be expected, since the average degree of association of the alcohol is less in the dioxane solutions where solute-solvent hydrogen-bonding is possible than in benzene where solution is accomplished by the van der Waal's attraction of the hydrocarbon portion of the alcohol for the other molecule. The data for methanol-benzene solutions give some indication that there is an initial increase

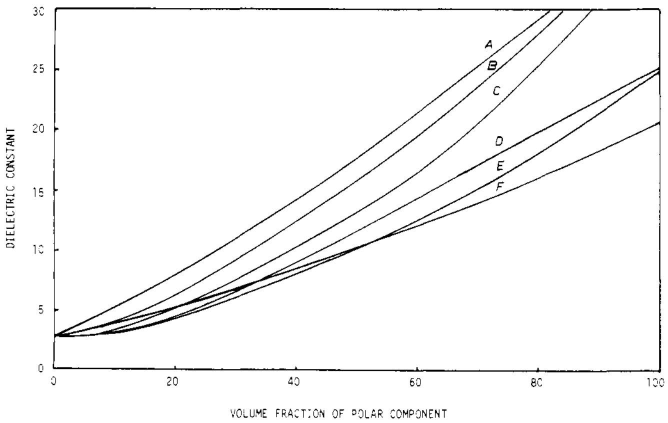

Figure 1. Dielectric constants of solutions

A.	Benzene-acetonitrile	*D.*	Benzene-ethanol
B.	Benzene-methanol	*E.*	Dioxane-ethanol
C.	Dioxane-methanol	*F.*	Benzene-acetone

in the association of methanol when a small amount of diluent is added to the alcohol. This behavior will be substantiated by inspection of the colligative properties of these solutions in the succeeding section. Upon further dilution of the alcohols, the dielectric constant data indicate that dissociation occurs as would be expected.

The dielectric constants of solutions of NMA in benzene and NMA in dioxane are presented in Table I. Although the dielectric constants of benzene and dioxane are quite similar, solutions containing comparable fractions of NMA have widely different dielectric constants. These data indicate that NMA is associated to a much greater extent in benzene than in dioxane. This substantiates the postulate (*1*) that in the case of solutions of aromatic solutes in NMA, where solvation is accomplished by means of the formation of charge-transfer complexes, the structure is not disturbed to as great an extent as is the case where solvation is due to the formation of solute-solvent hydrogen bonds. These data indicate the structure of NMA is apparently disrupted to a greater degree than that of the alcohols by small amounts of both dioxane and benzene. This is confirmed by the observation of the colligative properties of these solutions.

Table I. Dielectric Constants of *N*-Methylacetamide Binary Solutions at 32° C.

NMA, Volume %	Dielectric Constant
NMA-Dioxane	
0	2.09
12.6	10.7
25.0	23.2
50.1	58.3
61.9	75.4
74.9	99.0
87.6	124.7
100.0	190.5
NMA-Benzene	
0	2.13
12.5	16.8
25.0	35.3
50.9	75.1
62.7	95.0
74.8	115.0
87.4	143.5
100.0	190.5

Freezing-Point Data. Freezing-point data for the systems NMA-dioxane and NMA-benzene are tabulated in Table II. The freezing-point diagrams (Figure 2) give a clear picture of the behavior of NMA. Solutions in which NMA is the solid phase exhibit no unusual behavior. The freezing-point depression of NMA by dioxane and benzene is almost identical and follows the theoretical slope

$$\frac{dT}{d \ln N_1} = \frac{RT_0^2}{\Delta H_f}$$

in dilute solutions. The portions of the curves in which either dioxane or benzene is the solid phase show much greater deviations from the theoretical behavior. These systems are quite similar to the water-dioxane system, which was reported by Goates and Sullivan (*4*). In each instance,

Table II. Freezing Points of *N*-Methylacetamide Binary Solutions

Mole Fraction NMA	Freezing Point, °C.
NMA-Dioxane	
0.000	11.78
0.139	7.84
0.273	5.48
0.401	2.25
0.530	−2.63
Eutectic	−3.21
0.646	4.10
0.762	12.09
0.846	18.19
1.000	30.55
NMA-Benzene	
0.000	5.52
0.143	3.23
0.280	1.33
0.413	−2.24
Eutectic	−5.69
0.548	0.01
0.661	5.51
0.776	13.36
0.891	21.34
1.000	30.55

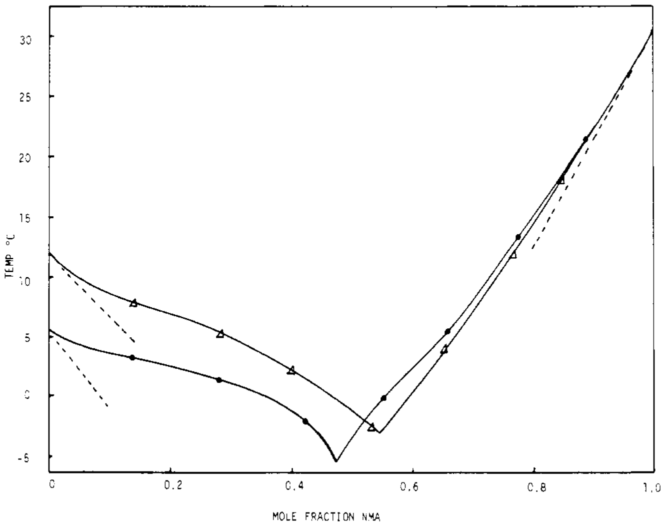

Figure 2. Freezing-point diagrams for *N*-methylacetamide–benzene and *N*-methylacetamide–dioxane solutions

●	NMA-benzene
Δ	NMA-dioxane
---	Theoretical limiting slopes

it is possible to account for these deviations as caused by the association of the NMA or water.

Apparently, the structure of NMA is less affected, and thus has a greater degree of polymerization in benzene than in dioxane. This is in agreement with the postulate made earlier (*1*) and with the dielectric constant data.

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Immiscibility Diagrams of Molten Sodium Bromide–Sodium Polyborates at 800° and 980° C.

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Immiscibility isotherms at 800° and 980° C. were obtained for the boron oxide–sodium metaborate–sodium bromide system. Mixtures of the components were equilibrated in graphite crucibles, which were vacuum-sealed in silica-glass cartridges. The two isotherms differ noticeably in their shapes. In the boron oxide–rich phase, the components appear to form mixed compounds.

IMMISCIBILITY isotherms of molten sodium chloride-sodium polyborate mixtures at 810° and 980° C. have been published (*1*). The study was continued to embrace the corresponding system with sodium bromide at comparable temperatures.

EXPERIMENTAL

The experimental procedures were the same as those employed in studying the immiscibility of sodium chloride-sodium polyborates (*1*). However, in this investigation, the molten sodium bromide phase, denser than the conjugate boron oxide phase, often leaked through the crucible floor owing to the porosity of the graphite. To reduce its porosity, each graphite crucible, prior to use, was lightly dusted on the inside with powdered boron oxide and heated for 1 hour at 980° C. in a capped silica-glass test tube.

The analytical data, expressed in mole per cent B_2O_3, $NaBO_2$, and NaBr, are presented in Table I. The phase diagrams at 800° and 980° C. constructed from these data are depicted in Figure 1. In addition, Figure 2 shows log-log plots of the ratios of $NaBO_2$ to the major components (boron oxide and sodium bromide) in the respective conjugate phases. These plots apply to run numbers 20 to 29 at 800° C. and 7 to 14 at 980° C. The corresponding tie lines in Figure 1 are similarly numbered.

DISCUSSION

Some of the features of the system are outlined below, and, where relevant, are compared with those of sodium chloride-sodium polyborates (*1*):

a. The miscibility gaps for sodium bromide-sodium polyborates are larger than those for sodium chloride-sodium polyborates.

b. The solubility of B_2O_3 in molten sodium bromide (Table I) is much smaller than it is in the molten sodium chloride.

c. Plait-point compositions of the present system are the same at 800° and 980° C. (Table I).

d. At 800° C., a separation is noticeable between the NaBr-$NaBO_2$ composition edge and the binodal curve. For the sodium chloride-sodium polyborate system at 810° C., this separation (disregarding the deformity at the NaCl corner) is barely evident. The difference may be due to a retrograde solubility of B_2O_3, in presence of $NaBO_2$, that is greater in the sodium halide below 810° C. than above it.

e. The quenched boron oxide phases of the mixtures equilibrated both at 800° and 980° C. and having comparable $NaBO_2$-to-B_2O_3 ratios appear alike. But, in contrast to sodium bromide phases, they ostensibly are physically different along the binodal curve. Thus, in the range from the B_2O_3 corner to midway between the 2 to 3 and 1 to 1 $NaBO_2$-to-B_2O_3 ratios, the phases are uniformly glassy and clear. In the subsequent range up to the 2 to 1 $NaBO_2$-to-B_2O_3 ratio, the phases are progressively more opaque and finally are white. From there to the plait point they are increasingly brittle.

f. In Figure 1 (top), a short section on the binary B_2O_3–$NaBO_2$ composition edge, labelled "Solid $Na_2O \cdot 4B_2O_3$ + Liq.", refers to the range within which solid disodium octaborate, m.p. 816° C., separates from the binary melt at 800° C. (Table I). Significantly, only the part of the binodal curve that faces this section is prominently jagged. Although