

Metallization of Alkali Anions in Condensed Phases

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Abstract: The Herzfeld criterion for an insulator-to-metal transition is recast here to predict the critical concentration (n^{cr}) for metallization of a solution having a solute more polarizable than the host solvent. The Clausius–Mossotti relation applied to the pure solvent shows that its polarizability and density affect n^{cr} only through the pure solvent refractive index or high-frequency dielectric constant. The critical concentration is reduced by solvent polarizability but increased by positive solute partial molar volumes. The electric dipole polarizabilities of the alkali metal anions Li^- , Na^- , and K^- in solution are estimated by comparing with the polarizability changes induced on dissolving other ions. The n^{cr} predicted for numerous nonaqueous solutions containing Li^- , Na^- , and K^- coupled with the usual Herzfeld criterion explains why condensed phases containing either Na^- and K^- and cations complexed by crown ethers or cryptand 222 are usually nonmetallic. The critical composition (y^{cr}) for metallization of the liquids $(\text{Li}^+(\text{CH}_3\text{NH}_2)_y)\text{Na}^-$ is predicted to be 5.3 agreeing with the experimental value between 5 and 6. For the condensed phases $(\text{Li}^+(\text{CH}_3\text{CH}_2\text{NH}_2)_y)\text{Na}^-$, a y^{cr} of around 3 is predicted, explaining their nonmetallic nature for $y = 4$ and suggesting that the liquids with compositions close to $y = 3$ should be reexamined experimentally. Although the polarizability of Na^- in the insulating solid $(\text{Li}^+(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2)\text{Na}^-$ is not known, the y^{cr} of 2.35 resulting from using the overestimated anion polarizability taken from $(\text{Na}^+\text{C}_{222})\text{Na}^-$ suggests the possibility of an insulator-to-metal transition induced by applied pressure.

I. Introduction

The singly charged anion of each of the alkali metals is stable in the free state. The ionization potential required to remove one electron from its outermost ns^2 electronic configuration has been measured by photodetachment to be about 0.5 eV.¹ Furthermore, all the alkali anions with the exception of Li^- have been prepared both in solution and in the crystalline solid and have been characterized by using a wide variety of techniques including ultraviolet electronic spectroscopy, liquid-state high-resolution NMR spectroscopy, solid-state NMR, and X-ray diffraction. It was deduced from these experiments that, although the properties of Rb^- and Cs^- are very considerably modified on entering the condensed phase, both K^- and particularly Na^- interact only weakly with such environments especially as gauged from measurements of the NMR nuclear shieldings and relaxation times. The extensive literature describing this work has been reviewed.^{2–4}

Electric dipole polarizabilities both control many optical and dielectric properties⁵ and are crucial in the simple yet highly successful Herzfeld theory⁶ of insulator-to-metal transitions. This viewpoint predicts metallization if the ratio of the molar refractivity (to which the polarizability is proportional) to the

molar volume exceeds unity. It has been applied to systems as diverse as xenon,⁶ TII,⁷ the alkali halides and I_2 ⁸ and Br_2 ⁹ under high pressures, as well as doped semiconductors, electron–hole droplets and expanded metal films,¹⁰ and stress-induced transformations in solids.¹¹ It can also explain the distribution of metals and insulators in the periodic table under ambient conditions^{6,12} as well as suggesting the pressure-induced metallization of the core of the planet Uranus.¹³ Experiments are referenced in the mainly theoretical papers cited. The role of the Herzfeld theory in the field of insulator-to-metal transitions has been recently reviewed.¹⁴

The polarizabilities of free Li^- ,^{15,16} Na^- ,^{16,17} and K^- ¹⁵ ions are computed to be around 1000 au. The polarizability of Na^- , the only alkali anion for which there is condensed phase information, is predicted¹⁷ to be reduced by a factor of 2.7 in solid $(\text{Na}^+\text{C}_{222})\text{Na}^-$ (C_{222} = cryptand 222). All these polarizabilities, even the solid Na^- value, are among the largest known for any ground state, as shown by that of 165.0 au¹⁸ for a neutral

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Na atom and those of 1 to 50 au^{19–23} for most condensed phase ions. The large alkali anion polarizabilities suggest that their condensed phases might be close to an insulator-to-metal transition, a possibility briefly considered²⁴ for Na[−] in methylamine. The object of the present paper is to utilize the Herzfeld theory to understand systematically the insulating or possible metallic behavior of condensed phases containing the three lightest alkali anions. In particular, the solvent and concentration dependence of any metallization in solution is examined by slightly refining the usual application of the Herzfeld theory. The lightest alkalis are studied both because a wide range of systems containing the Na[−] or K[−] ions have been prepared and because they interact sufficiently weakly with their environments that a theory based on individual anion properties is appropriate. In contrast, Rb[−] and Cs[−] interact with their environments sufficiently strongly that an approach based on the properties of individual spherically symmetric anions is questionable.

II. Theory

Each of the solutions considered here is treated by making the one fundamental assumption that it can be considered to consist of a large number of identical domains each of volume V_d , containing a single anion of polarizability α_A , plus a number of solvent molecules each of polarizability α_s . The resulting total polarizability α_d of the domain is taken to be the sum of α_A plus the polarizabilities of all the solvent molecules in that domain. Although the polarizabilities of the cations (each of polarizability α_C) are ignored, these can be included simply by replacing α_A by $\alpha_A + q\alpha_C$, where there are q cations for each anion. The domain polarizability describes only those dipoles arising from the changes in the electronic charge distribution that are induced by an external electric field. This polarizability does not account for any dipoles arising from changes in the positions of nuclei. Since the nuclear positions can respond only negligibly to an electric field alternating rapidly with time, such as that present in electromagnetic radiation, optical properties such as the refractive index are controlled by just the electronic polarizabilities. Both these polarizabilities and the refractive index depend on the wavelength of the applied radiation, the refractive index obtained by extrapolating a series of measurements to infinite wavelength being denoted η_∞ . This refractive index and the high-frequency dielectric constant ($\epsilon_\infty = \eta_\infty^2$) are determined by the zero-frequency (infinite wavelength) extrapolations of the frequency-dependent electronic polarizabilities. Each such extrapolation is the polarizability describing the purely electronic dipole induced by a static external electric field and is thus both readily interpreted physically and amenable to computation using the standard methods of quantum chemistry. All electronic polarizabilities in this paper, such as the domain polarizability α_d , are those appropriate for static fields.

The dielectric (ϵ_∞) and optical properties (η_∞) of a solution can be related to the domain polarizability and volume through the Clausius–Mossotti equation as applied to each domain, provided that one can make the standard assumptions that the anion and each of the solvent molecules can be treated as a

point polarizable dipole residing in an environment sufficiently symmetrical that all the Lorentz factors equate to $4\pi/3$.²⁵ There is no evidence that any but the most minor errors are introduced through these assumptions which are standard in treatments of the polarizabilities of ions in solution.^{26–32} For the solutions of present interest the Clausius–Mossotti equation therefore takes the form

$$\alpha_d = [3V_d/(4\pi)][(\epsilon_\infty - 1)/(\epsilon_\infty + 2)] = [3V_d/(4\pi)][(\eta_\infty^2 - 1)/(\eta_\infty^2 + 2)] \quad (1)$$

This relation predicts finite values for ϵ_∞ and η_∞ only if the quantity $4\pi\alpha_d/(3V_d)$ is less than unity. As this quantity approaches unity from below, the calculated values of ϵ_∞ and η_∞ increase and tend to infinity as $4\pi\alpha_d/(3V_d)$ tends to one. Such an infinite dielectric constant indicates that the electrons have been set free which is interpreted in the Herzfeld theory as the occurrence of an insulator-to-metal transition.⁶ It follows from (1) that this transition is predicted to occur if the concentration of a solute (more polarizable than the solvent) is sufficiently increased as to cause the domain volume to be lowered to the critical value V_d^{cr} given by

$$4\pi\alpha_d^{\text{cr}} = 3V_d^{\text{cr}} \quad (2)$$

Here α_d^{cr} is the polarizability of a domain at this critical concentration. The criterion (2) for the onset of metallization is the same as that commonly presented¹⁴ as $R_M/V_M = 1$ where the molar refractivity R_M defined in the Appendix is shown by the Clausius–Mossotti equation to equal the quantity $4\pi\alpha_d N/3$ called the molar polarizability where N is Avogadro's number and V_M is the molar volume.

The composition of the solutions of present interest is most usefully defined by the number of moles (n) of anions added to 1 L of pure solvent even though the volume of the resulting solution will not in general be 1 L. The anion molality is thus equal to n/ρ_s where ρ_s is the solvent density expressed in kilograms per liter. One liter of solution of anion concentration n MPLS (MPLS = moles per 1 L of solvent) contains nN anions plus V_1/V_s molecules of solvent where V_s is the volume occupied by one solvent molecule and V_1 is 1 L expressed in the units used for V_s . Since there are $V_1/(V_s nN)$ molecules of solvent for each anion, one domain contains this number of solvent molecules in addition to its single anion. The domain polarizability α_d is given by

$$\alpha_d = \alpha_A + \alpha_s V_1/(V_s nN) \quad (3)$$

The domain volume V_d cannot be exactly calculated without knowing the volume change occurring on introduction of the anions, that is without knowledge of the anion partial molar volume. It is convenient to write

$$V_d = xV_A + V_s[V_1/(V_s nN)] = xV_A + V_1/(nN) \quad (4)$$

where V_A is the volume occupied by one anion and x is a

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Table 1. Phase Dependence of Anion Polarizabilities (au)^a

| | free ion | aqueous solution | in-crystal with the indicated counteraction | | | |
|-------------------------------|----------|------------------|---|-----------------|----------------|-----------------|
| | | | Cs ⁺ | Rb ⁺ | K ⁺ | Na ⁺ |
| F ⁻ | 15.1 | 8.84 (41.5%) | 9.18 (-3.8%) | 8.37 (5.3%) | 8.10 (8.4%) | 6.95 (21.4%) |
| Cl ⁻ | 38.1 | 25.35 (33.5%) | 24.40 (3.7%) | 23.41 (7.7%) | 22.86 (9.8%) | 21.15 (16.6%) |
| Br ⁻ | 51 | 34.22 (32.9%) | 32.30 (5.6%) | 31.51 (7.9%) | 30.63 (10.5%) | 28.83 (15.8%) |
| I ⁻ | | 49.97 | 46.60 (6.7%) | 45.81 (8.3%) | 44.87 (10.2%) | 41.85 (16.2%) |
| NO ₃ ⁻ | | 30.15 | 30.62 (-1.6%) | 29.39 (2.5%) | 29.14 (3.3%) | |
| OH ⁻ | 45.5 | 15.23 (66.5%) | | | 15.82 (-3.9%) | 16.30 (-7.0%) |
| SO ₄ ⁻² | | 42.74 | 43.28 (-1.3%) | 40.82 (4.5%) | 40.31 (5.7%) | 38.13 (10.8%) |
| CO ₃ ⁻² | | 36.44 | | | | 31.25 (14.2%) |

^a See text for sources and definitions of the bracketed percentages

quantity related to its partial molar volume. The determination of suitable values for V_A and x is discussed in the next two sections.

The smallest concentration, to be called the critical concentration n^{cr} , for which the solution becomes metallic is derived by substituting (3) and (4) into (2). This yields n^{cr} (in MPLS) as

$$n^{cr} = \{3V_1/(4\pi\alpha_A N)\} \{1 - [4\pi\alpha_s/(3V_s)]\} / \{1 - [3xV_A/(4\pi\alpha_A)]\} \quad (5)$$

Application of the Clausius–Mossotti relation 1 to the pure solvent allows $4\pi\alpha_s/(3V_s)$ to be expressed in terms of either the solvent high-frequency dielectric constant $\epsilon_{\infty s}$ or the solvent refractive index $\eta_{\infty s}$ extrapolated to infinite wavelength. Use of these two results enables (5) to be recast into the alternative forms

$$n^{cr} = \{3V_1/(4\pi\alpha_A N)\} \{1 - [(\epsilon_{\infty s} - 1)/(\epsilon_{\infty s} + 2)]\} / \{1 - [3xV_A/(4\pi\alpha_A)]\} \quad (6a)$$

$$n^{cr} = \{3V_1/(4\pi\alpha_A N)\} \{1 - [(\eta_{\infty s}^2 - 1)/(\eta_{\infty s}^2 + 2)]\} / \{1 - [3xV_A/(4\pi\alpha_A)]\} \quad (6b)$$

The n^{cr} prediction, denoted n_0^{cr} , of the simplest model in which the solvent is ignored entirely is derived by setting both α_s and x to zero in (5). This yields

$$n_0^{cr} = 3V_1/(4\pi\alpha_A N) \quad (7)$$

It is convenient to express in atomic units all the quantities on the right-hand side of (7) when the results of (5) and (6) reduce to

$$n^{cr} = \{2647.8/\alpha_A(\text{au})\} \{1 - [4\pi\alpha_s/(3V_s)]\} / \{1 - [3xV_A/(4\pi\alpha_A)]\} \quad (8)$$

$$n^{cr} = \{2647.8/\alpha_A(\text{au})\} \{1 - [(\eta_{\infty s}^2 - 1)/(\eta_{\infty s}^2 + 2)]\} / \{1 - [3xV_A/(4\pi\alpha_A)]\} \quad (9)$$

The approach just presented for solutions can also be applied to solids when it reduces to the standard Herzfeld theory.⁶ A solid having a unit cell of volume V_{uc} containing N_{uc} anions has a domain volume V_{uc}/N_{uc} and a domain polarizability α_{uc}/N_{uc} if α_{uc} is the sum of the polarizabilities of all the constituents of the unit cell. The solid is thus predicted to be metallic only if $4\pi\alpha_{uc}/(3V_{uc}) = 4\pi\alpha_{uc}/(3V_{uc})$ is greater than unity which is just the usual Herzfeld criterion.

III. Properties Controlling Metallization

A. Alkali Anion Polarizabilities. The polarizabilities of a variety of anions in their free states, in aqueous solutions at

infinite dilution, and in their alkali metal salts are presented in Table 1. For the polyatomic anions, the isotropic part is reported. The free F⁻, Cl⁻, and OH⁻ polarizabilities are the predictions^{33–35} of accurate ab initio computations taking extensive account of electron correlation. The OH⁻ value is the average²¹ of the results³⁵ obtained using three different basis sets. The free Br⁻ value was derived²¹ by adding an estimate of the electron correlation contribution to the ab initio coupled Hartree–Fock result²⁰ of 42.9 au. Each of the in-solution polarizabilities is the average of those reported in Table 5 of ref 21. The latter were deduced²¹ by combining a wide range of experimental data with the results of a small number of key ab initio computations. The in-crystal F⁻, Cl⁻, and Br⁻ polarizabilities, taken from Table C1 of ref 23, were derived by subtracting from the experimental molar polarizabilities of their alkali salts³⁶ the cation contributions presented in Table 11 of ref 19. The remaining in-crystal polarizabilities in Table 1 were derived by subtracting these cation values from the molar polarizabilities in Table B1 of ref 23 thereby reporting an extra decimal place to the values previously presented.²³

The data in Table 1 show the now well-established results that the anion polarizabilities are reduced not only on entering solution from the free state but also, with the exception of three Cs⁺ salts, on passing from solution to the solid. The difference between each free ion value and that in-solution expressed as a percentage of the free ion polarizability is reported in brackets after the in-solution result. The bracketed figure after each in-crystal polarizability is similarly the difference between the in-solution and in-crystal value expressed as a percentage of the in-solution result with a positive number corresponding to a polarizability reduction on passing from the liquid to the solid. Furthermore, since the polarizability of each anion in-crystal is not a constant but decreases with reduction of the size of the counteraction, the polarizability reduction on passing from solution to crystal decreases with increasing cation size. Each in-solution polarizability is much closer to the corresponding values in-crystal than it is to that of the free anion. The in-solution values are especially close to those in the solid cesium salts where even the largest fraction change, that occurring when I⁻ passes from solution to crystal, is only some 6.7%. This shows that the polarizabilities of the alkali anions in-solution are best estimated from in-crystal values rather than from those of the free ions especially because the fractional polarizability reductions on passing from the free to in-solution ions are not only much greater but are also strongly anion dependent.

The only available estimate for the polarizability of an alkali

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Table 2. Alkali Anion Polarizabilities α_A (au)^{a,b}

| Li ⁻ | | Na ⁻ | | | K ⁻ | |
|-----------------|---------|-----------------|---------|----------------------|----------------|---------|
| free ion | in-soln | free ion | in-soln | in-xtal ^c | free ion | in-soln |
| 798 | 315 | 1090 | 430 | 400 | 1757 | 690 |

^a Sources of accurate ab initio free ion polarizabilities in text.

^b Derivation of in-solution and in-crystal polarizabilities described in text.

^c From ab initio computations¹⁷ for ion in an environment modeling that in solid (Na⁺C₂₂₂)Na⁻.

anion in-crystal is that derived from ab initio electronic structure computations¹⁷ taking account of electron correlation for an Na⁻ ion in the best current models for its environment in solid (Na⁺C₂₂₂)Na⁻. Model environments were considered¹⁷ because the unit cell of even this crystal, one of the simplest solid alkalides, is too large and complex to be introduced into an ab initio computation. The average of the four values computed for the Na⁻ polarizability by using two slightly different calculations (those designated MP2D and MP2E in the last two rows of Table 1 of ref 17) for the two model environments is that of 400 au presented in Table 2 as the Na⁻ in-crystal polarizability. Comparison of the experimentally determined³⁷ crystal structure of (Na⁺C₂₂₂)Na⁻ with that³⁸ of (Na⁺C₂₂₂)I⁻ shows that Na⁻ has the same 2.2 Å radius as the I⁻ ion. The Na⁺C₂₂₂ cation will be closer in size to Cs⁺ than to any of the other cations appearing in Table 1 while the anion polarizability reductions (Table 1) on passing from solution to the solid cesium salt increase with increasing anion size. These observations taken in conjunction with equality of the Na⁻ and I⁻ ionic radii show that the fractional polarizability reduction occurring when Na⁻ passes from solution to crystal will be closest to the 6.7% decrease when I⁻ passes from solution into solid CsI. The best estimate for the polarizability of Na⁻ in-solution is therefore derived by demanding that its diminution by 6.7% yields the 400 au value of the anion polarizability in solid (Na⁺C₂₂₂)Na⁻. This leads to an in-solution Na⁻ polarizability of 430 au

The polarizabilities of both Li⁻ and K⁻ in-solution have to be estimated from the free ion results reported in Table 2 because in-crystal values are not currently available. These free ion Li⁻ and K⁻ polarizabilities are the predictions¹⁵ of photodetachment calculations taking account of electron correlation and using the dipole-velocity form for the interaction. This Li⁻ result agrees exactly with the best current prediction¹⁶ of 798 ± 5 au from computations using extensive configuration interaction to take account of electron correlation. The value of 1058 au for the free Na⁻ polarizability predicted by the photodetachment calculations¹⁵ differs but little from the currently most accurate result (Table 2), that derived¹⁷ from finite field computations taking account of electron correlation through use of the coupled electron pair approximation. The difference between the free and in-solution polarizability of the Na⁻ ion expressed as a percentage of the free ion value is 60.6% so that the in-solution polarizability of 430 au is 39.4% of the free ion value. The assumption that the free ion polarizabilities of Li⁻ and K⁻ are reduced by the same percentage on entering solution yields the best, albeit rather approximate, in-solution values presented in Table 2. Their likely accuracy can be estimated from the variation of the fractional reductions of halide polarizabilities (Table 1) on passing from the free to the in-solution states.

B. Solvent Properties. The refractive indices (η_s) and densities (ρ_s) of the solvents, methylamine (MA), ethylamine

(EA), ethylenediamine (EDA), *N,N*-dipropylacetamide (DPA), *N,N*-diethylacetamide (DEA), *N,N*-dimethylpropionamide (DMP), 12-crown-4 (12C4), 15-crown-5 (15C5), tetrahydrofuran (THF), and hexamethylphosphoric triamide (HMPA) are assembled in Table 3. The refractive indices enter the relations 6 and 9 which determine the critical concentrations (n^{cr}) for metallization. Although one should use the refractive index extrapolated to infinite wavelength, only small inaccuracies will be introduced by using the only available values, namely those (Table 3) measured for the sodium D light. The densities relate concentrations (n MPLS) to the parameter y , which arises when the composition is expressed²⁴ in the chemical formula form (MS_s)⁺M⁻ with S denoting one formula unit of solvent. Thus one has, with W_s the solvent molecular weight,

$$n \text{ (MPLS)} = 1000\rho_s/(yW_s) \quad (10)$$

The parameter x , which also enters the relations determining n^{cr} , can be determined for the methylamine systems by combining measurements³⁹ of the densities of solutions of LiCl and CH₃NH₃Cl in this solvent with the Hepler theory⁴⁰ of solute molar volumes. This theory expresses the volume \bar{V}_i effectively taken up by a single ion (i) in solution as

$$\bar{V}_i = (4\pi/3)(ar_i)^3 - B/(ar_i) \quad (11)$$

where r_i is the crystal radius of the ion and a and B are constants dependent on the solvent but not on the ion. The first term in (11) represents the volume occupied by the ion itself with the dimensionless parameter (a) accounting for the fact that, in solution, this volume will be slightly greater than that in an ionic crystal. The second term, the electrostriction contribution, arises from the reduction in the volume occupied by those solvent molecules which are significantly interacting with the ion. The volume occupied by 1 mol of ions, the partial molar volume $\bar{V}_i^{(M)}$, is derived by multiplication of (11) by N . This yields

$$\bar{V}_i^{(M)} = (4\pi/3)N(ar_i)^3 - B^{(M)}/(ar_i) \quad (12)$$

with $B^{(M)}$ equal to NB . It was previously reported³⁹ that the parameters in eq 12 (eq 2 in ref 39) were $a = 1.138$ and $B^{(M)} = 42.14 \text{ \AA}^4$. Since, however, the correct units of $B^{(M)}$ and B are $\text{\AA}^4 \text{ mol}^{-1}$ and $\text{\AA}^4 \text{ ion}^{-1}$, respectively, if r_i is measured in \AA , the result and units previously reported³⁹ for $B^{(M)}$ are inconsistent. We therefore recalculated a and $B^{(M)}$ using both the same ionic radii of 0.68, 1.81, and 2.08 Å for Li⁺, Cl⁻, and CH₃NH₃⁺ and the same experimental molar volumes of -21.9 and 32.5 cm³ mol⁻¹ for LiCl and CH₃NH₃Cl as invoked previously.³⁹ After expressing each of these molar volumes as a sum of individual ion contributions taken to have the form of (12), one obtains a pair of simultaneous equations whose solutions are $a = 1.13836$ and $B^{(M)} = 25.39668 \times 10^{-8} \text{ cm}^4 \text{ mol}^{-1}$. The latter corresponds to a B value in (11) of 42.17218 Å⁴ ion⁻¹ equal to 537.80175 au ion⁻¹. It should be pointed out that, despite the inconsistencies and mixing of our eqs 11 and 12, the quantities of primary interest in ref 39, namely the molar volume of a solvated electron and the radius of the cavity it occupies, were evaluated correctly.³⁹

The effective volumes \bar{V}_i of Li⁺, Na⁺, Cl⁻, and Na⁻ ions in methylamine solutions were evaluated from (11) and are reported in Table 4 together with their intrinsic size ($(4\pi/3)$ -

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Table 3. Solvent Refractive Indices (η_s) and Densities (ρ_s)^{a,b}

| | MA | EA | EDA | DPA | DEA | DMP | 12C4 | 15C5 | THF | HMPA |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| η_s^c | 1.4318 | 1.3663 | 1.4565 | 1.4419 | 1.4400 | 1.4400 | 1.4621 | 1.4615 | 1.4070 | 1.4580 |
| ρ_s^d | 0.744 | 0.689 | 0.899 | 0.8992 | 0.925 | 0.920 | 1.089 | 1.109 | 0.886 | 1.030 |

^a Sources of data: MA η_s calculated as $\sqrt{2.05}$, the ϵ_{oss} value from 39 with ρ_s taken from Figure 1 of ref 39 at -50°C ; EA η_s from ref 59 and ρ_s from ref 60; EDA, DEA, DMP, THF, and HMPA from ref 61; 12C4 and 15C5 from ref 60 and DPA from ref 59. ^b See text for definitions of solvents. ^c Measured for sodium D light. ^d In kg dm^{-3} .

Table 4. Ionic Effective Volumes (\bar{V}_i) and Their Components for Methylamine Solutions (au)^{a,b}

| ion i | Li ⁺ | Na ⁺ | Cl ⁻ | Na ⁻ |
|--------------------|-----------------|-----------------|-----------------|-----------------|
| r_i | 1.285 | 1.890 | 3.420 | 4.157 |
| $(4\pi/3)(ar_i)^3$ | 13.11 | 41.72 | 247.18 | 443.88 |
| $-B/(ar_i)$ | -367.65 | -249.97 | -138.14 | -113.65 |
| \bar{V}_i | -354.54 | -208.25 | 330.23 | 330.23 |

^a Calculated from eq 11. ^b Ionic radii r_i : Li⁺ and Cl⁻ from ref 39; Na⁺ (1.0 Å from ref 53) and Na⁻ (2.2 Å) as described in the text.

$(ar_i)^3$) and electrostriction ($-B/(ar_i)$) components. The volume parameter xV_A (eqs 4–6, 8, and 9) for any solution is the sum of the cation and Na⁻ ion contributions in Table 4. For the solution containing Li⁺ and Na⁻ ions studied experimentally,²⁴ this volume is $-24.31 \text{ au molecule}^{-1}$. This is negative despite the size of Na⁻ because the Li⁺ \bar{V}_i is so large and negative on account of the magnitude of its electrostriction contribution. The use of the 2.2 Å in-crystal Na⁻ radius of (see last section) yields an in-crystal volume V_A of 301 au producing an x value of -0.0808 for solutions²⁴ of Li⁺ and Na⁻ in methylamine. A solution of Na⁺ and Na⁻ ions in this solvent is predicted from the results in Table 4 to have an xV_A value of 121.98 au corresponding to $x = 0.405$.

IV. Predicted Insulating or Metallic Properties of Condensed Alkali Anion Phases

A. Alkali Anions in Solution. The column headed “none” in Table 5 shows the lowest concentrations for which solutions containing Li⁻, Na⁻, or K⁻ ions are predicted to become metallic if the solvent is ignored completely. These are the n_0^{cr} values derived using eq 7 and the in-solution alkali anion polarizabilities in Table 2. These predictions are modified when the role of the solvent is considered by using eq 9 and the refractive indices in Table 3. The remaining columns of Table 5 present the resulting critical metallization concentrations (n^{cr}) of these alkali anions in many of the solvents in which they have been observed. The results for the solutions in DMP are the same as those in DEA because both these solvents have the same refractive index. Predictions using a nonzero value of x were only derived for the Na⁻ solutions because this is the only alkali of the three whose anion radius is currently known. The results in Table 5 show that the n^{cr} values predicted for the same anion in different solvents but using the same x value are very similar because all the solvent refractive indices are roughly the same, being about 1.5. Nevertheless, consideration of the solvent reduces the predicted n^{cr} to about 75% of those (n_0^{cr}) derived considering only the anions. For each anion, use of an x value

Table 5. Predicted Critical Concentrations (n^{cr}) for Metallization in Solution (MPLS)^a

| ion | x | none | MA | EA | EDA | DPA | DEA | 12C4 | 15C5 | THF | HMPA |
|-----------------|-----|------|------|------|------|------|------|------|------|------|------|
| Li ⁻ | 0 | 8.94 | 6.29 | 6.59 | 6.18 | 6.25 | 6.25 | 6.16 | 6.16 | 6.40 | 6.17 |
| Na ⁻ | 0 | 6.22 | 4.61 | 4.83 | 4.53 | 4.57 | 4.58 | 4.51 | 4.51 | 4.69 | 4.52 |
| Na ⁻ | 1 | 6.22 | 5.53 | 5.79 | 5.44 | 5.49 | 5.50 | 5.41 | 5.42 | 5.63 | 5.43 |
| K ⁻ | 0 | 3.88 | 2.87 | 3.01 | 2.82 | 2.85 | 2.85 | 2.81 | 2.81 | 2.92 | 2.82 |

^a Calculated from eq 7 or (eq 9) using the in-solution anion polarizabilities in Table 2.

of one rather than zero increases the predicted n^{cr} which are, however, still only about 88% of the corresponding n_0^{cr} .

The results presented in Table 5 show that only concentrated solutions containing more than about 5.5 mol of Na⁻ or more than 2.8 mol of K⁻ per liter of solvent are predicted to be metallic. This explains why there is presently no evidence for metallization in any of the relatively dilute solutions containing alkali anions which have been studied experimentally using magnetic resonance and other techniques. Thus, the purely nonmetallic and diamagnetic properties of a 0.06 M solution of K⁻ in dimethyl ether containing K⁺(15C5)₂ counterions⁴¹ are readily understandable. Similarly explicable are the nonmetallic nature of solutions containing Na⁻ ions when in 0.1 M THF containing added C₂₂₂,⁴² or when 0.17 M in 12C4^{43,44} or 0.55 M in 15C5.⁴⁵ Although the concentrations were not reported in the NMR studies of either the Na⁻ ion in DEA, DPA, DMP,^{46,47} or HMPA⁴⁸ or of the K⁻ ion in 12C4/THF,⁴⁹ these concentrations were almost certainly much less than the n^{cr} values in Table 5, which again explains the nonmetallic character of these systems.

Although the nonmetallic nature of both 0.1 M⁴² and 0.2 M⁵⁰ solutions of Na⁻ in ethylamine containing Na⁺C₂₂₂ counterions is again readily explained by the results in Table 5, the more recent investigation⁵¹ of solutions of LiNa alloy in this solvent provides a more stringent test of these predictions. These systems contain, as usual, Na⁻ ions interacting only weakly with their environment plus Li⁺ cations whose strong solvation is responsible for the relatively high solubility. Highly concentrated solutions of Li(CH₃CH₂NH₂)_yNa having compositional parameters y as low as three were prepared. Those with y in the range from 4 to 16 were studied in detail and found to be nonmetallic in complete agreement with the predicted critical metallization concentrations (Table 5) for $x = 0$ and 1 of 4.83MPLS and 5.79MPLS, respectively, corresponding to critical y values (y^{cr}) of 3.17 and 2.64. However, the closeness of these y^{cr} values to 3.0 suggests that the highly concentrated solutions having y in the region of three⁵¹ might be close to an insulator-to-metal transition. Further experimental investigation of these highly concentrated solutions would therefore be valuable provided that

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Table 6. Theoretical and Experimental Critical Metallization Compositions for Na⁻ in Methylamine

| α_A (au) | 430 | 430 | 430 | 1090 | 1090 | 380 |
|------------------------------|---|------|------|-----------------|------|---------|
| x | -0.0808 | 0.0 | 1.0 | ns ^a | ns | -0.0808 |
| n^{cr} (MPLS) ^a | 4.54 | 4.61 | 5.53 | 6.22 | 2.43 | 1.81 |
| y^{cr} | 5.28 | 5.19 | 4.33 | 3.85 | 9.86 | 13.2 |
| expt y^{cr} | between 5 and 6 in solution ²⁴ | | | | | |

^a ns: calculated from eq 7 neglecting the solvent polarizability and solute molar volume.

it could be established that such systems were fully homogeneous.

The results in Table 5 clearly explain why solutions containing Na⁻ ions in methylamine are nonmetallic both when 0.1 M with (Na⁺C₂₂₂) counteranions⁴² or when 0.2 M⁵² or 0.4 M⁴² with (Na⁺18C6) cations. However, the recent study²⁴ of more concentrated solutions of LiNa alloy in methylamine provides an extremely thorough test of the present theory not only because the volume measurements³⁹ enabled a reliable value for x to be deduced as described in section IIIB but also because the most concentrated solutions were found to be metallic.²⁴

B. The Lithium–Sodium–Methylamine System. Magnetic resonance and other techniques have been used²⁴ to study both the liquid and solid phases of the systems Li(CH₃NH₂)_yNa having integer y values ranging from 4 up to 16. These all contain sodium anions plus lithium cations interacting strongly with the methylamine.

The Li(CH₃NH₂)_yNa solutions having a y value of 4 or 5 showed metallic properties while all those of greater y were entirely diamagnetic and nonmetallic.²⁴ This agrees completely with the first column of numerical results in Table 6 which shows that the critical composition (y^{cr}) for metallization is predicted to be 5.28 if one uses both the best in-solution anion polarizability and considers the solvent using the most accurate x value (-0.0808) derived in section IIIB. The predicted value of y^{cr} remains essentially unchanged (Table 6 column 2) if x is taken to be zero. The third column of results in Table 6 shows the importance of using the correct value for x because use of the incorrect x of 1 yields a y^{cr} of 5.19, which erroneously predicts the solution of composition Li(CH₃NH₂)₅Na to be nonmetallic. The necessity for considering the role of the solvent by predicting n^{cr} , and hence y^{cr} , from eq 9 rather than from eq 7 is shown by the fourth column of results in Table 6. Neglect of the solvent yields a y^{cr} value of 3.85 and thus erroneously predicts that all the solutions studied by Dye and co-workers would have been nonmetallic. The necessity for using the correct in-solution Na⁻ polarizability is shown by the fifth and sixth columns in Table 6 which present the y^{cr} predicted using the polarizability of the free anion. This yields a y^{cr} value of 9.86 (column 6) even if the solvent is neglected while introduction (column 7) of the solvent polarization with the correct x value increases y^{cr} to 13.2 which would erroneously predict that all the solutions studied²⁴ would be metallic with the exception of the most dilute having a y value of 16. It should be pointed out that, independently of any experimental results, it would be a priori inconsistent to use the free ion polarizability in eq 7 or 9 because one is concerned with the interaction between ions, which even in-solution at even dilution have a polarizability reduced from the free ion value through their interaction with the solvent.

It was shown²⁴ that all the systems Li(CH₃NH₂)_yNa having y between 4 and 16 could be solidified and, in contrast to the liquids having $y = 4$ or 5, that all the solids were diamagnetic

and insulating. This difference between the liquid and solid phases must arise at least partially if not entirely from the reduction of the Na⁻ polarizability on passing from solution to crystal. The polarizability of Na⁻ in this crystal will certainly be significantly smaller than even that in (Na⁺C₂₂₂)Na⁻ because in-crystal anion polarizabilities are decreased by reduction of the closest cation–anion separation, as shown by the data assembled in Table 1. The reduced Li⁺–Na⁻ distance in Li(CH₃NH₂)₄Na compared with the Na⁺–Na⁻ distance in (Na⁺C₂₂₂)Na⁻ shows that the anion polarizability in the former will certainly be no greater than 380 au, the smallest of the values computed¹⁷ for (Na⁺C₂₂₂)Na⁻. It would not seem reasonable to use for the solid the near zero x value appropriate for the liquid. An x value of 1.029 results from addition of the volumes of spheres having radii equal to 0.68 Å⁵³ and 2.2 Å,³⁷ the respective radii of Li⁺ and ions. The value of 3.70 for y^{cr} predicted (seventh numerical column of results in Table 6) by using this value of x and the overestimated anion polarizability of 380 au accounts for the observed insulating nature of solid Li(CH₃NH₂)₄Na. Naturally this prediction would remain unchanged on using a smaller value for the Na⁻ polarizability.

C. Alkali Anions In-Crystal. The Li/Na ethylamine systems Li(CH₃CH₂NH₂)_yNa having y greater than or equal to four were studied in the solid as well as the liquid phase with all the solids being found to be insulating.⁵¹ This accords with the y^{cr} values predicted (Table 5) from eq 9 using the in-solution Na⁻ polarizability. The results in Table 7 derived using an Na⁻ polarizability of 400 au more appropriate to the anion in-crystal naturally leave unchanged the prediction that solid Li(CH₃CH₂NH₂)₄Na is an insulator.

The values of y^{cr} predicted for solutions of Na⁻ in ethylenediamine using the in-solution polarizability are presented in Table 7. Although such solutions have not yet been prepared, the solid Li(NH₂CH₂CH₂NH₂)₂Na has been synthesized, shown to contain Na⁻ ions, and found to be entirely insulating⁵⁴ despite its ethylenediamine stoichiometric coefficient of two being smaller than the y^{cr} in Table 7. Although the in-solution anion polarizability will be larger than that in-crystal, use of even the smallest of the values computed¹⁷ for Na⁻ in-crystal coupled with the 1.029 x value more appropriate for the solid still yields an y^{cr} of 2.35. However, this cannot be taken as a failure of the present approach because the Na⁻ polarizability in Li(NH₂CH₂CH₂NH₂)₂Na will be significantly less than that of 380 au computed¹⁷ for a model of (Na⁺C₂₂₂)Na⁻. Nevertheless, the predicted 2.35 value of y^{cr} indicates that solid Li(NH₂CH₂CH₂NH₂)₂Na might be close to the insulator to metal transition which suggests that experiments seeking its metallization at high pressure might be fruitful.

Table 7. Predicted Critical Metallization Compositions for Selected Na⁻ Systems

| solvent | EA | EA | EDA | EDA | EDA |
|-----------------|------|------|------|------|-------|
| α_A (au) | 400 | 400 | 430 | 430 | 380 |
| x | 0.0 | 1.0 | 0.0 | 1.0 | 1.029 |
| n^{cr} (MPLS) | 5.19 | 6.32 | 4.53 | 5.44 | 6.36 |
| y^{cr} | 2.94 | 2.42 | 3.30 | 2.75 | 2.35 |

Numerous crystalline solids containing either the Na⁻ or the K⁻ ion have been prepared and characterized by a variety of techniques including high-resolution solid-state NMR spectroscopy. These salts, (Na⁺C₂₂₂)Na⁻, (K⁺C₂₂₂)Na⁻, (Rb⁺C₂₂₂)Na⁻, (K⁺(15C5)₂)Na⁻, (Rb⁺(15C5)₂)Na⁻, and (K⁺18C6)Na⁻,⁵⁵ as

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Table 8. Domain Polarizabilities, Volumes, and R_d/V_d for Crystals Containing Na^- Ions (au)

| crystal | R_e^a | α_d | V_d | R_d/V_d |
|---|---------|--------------------|--------|-----------|
| $(\text{Na}^+\text{C}_{222})\text{Na}^-$ | 13.34 | 666.6 | 4747.9 | 0.59 |
| $(\text{Na}^+(12\text{C}4)_2)\text{Na}^-$ | 13.34 | 639.0 | 4747.9 | 0.56 |
| $(\text{K}^+(12\text{C}4)_2)\text{K}^-$ | 14.72 | 933.3 ^b | 6379.0 | 0.61 |

^a Derivation of R_e described in the text. ^b The in-solution K^- polarizability used will be greater than that in the crystal.

well as $(\text{K}^+(15\text{C}5)_2)\text{K}^-$, $(\text{Rb}^+(15\text{C}5)_2)\text{K}^-$, and $(\text{Cs}^+(15\text{C}5)_2)\text{K}^-$,⁴¹ were all found to be entirely diamagnetic and nonmetallic in character. Their insulating nature is best understood by applying the usual Herzfeld criterion (2) rather than by using relations (8) or (9) developed for solutions. Although not many of their crystal structures have yet been determined, it would be inconsistent to apply (2) to any other than cubic materials because only these have the Lorentz factor of $4\pi/3$ used to derive the Herzfeld criterion. All the salts were therefore assumed to have the rock salt structure, experiment both showing³⁷ this to be a good approximation for $(\text{Na}^+\text{C}_{222})\text{Na}^-$ and providing its closest cation–anion separation (R_e) presented in Table 8. The domain volume is therefore $1/4$ of the that of the unit cell with the domain polarizability being that of one formula unit. The solids $(\text{Na}^+\text{C}_{222})\text{Na}^-$, $(\text{Na}^+(12\text{C}4)_2)\text{Na}^-$, and $(\text{K}^+(12\text{C}4)_2)\text{K}^-$ were chosen for detailed study because those containing the Rb^+ or Cs^+ cations or two 15C5 rather than two 12C4 cation complexing agents will be further from the insulator to metal transition. The polarizabilities of the cations Na^+ and K^+ are known to be 1.0 and 5.3 au, respectively,⁵⁶ while that of a 12C4 molecule was deduced for its experimental refractive index and density as described in the Appendix. The polarizability of C_{222} was derived as the sum of atomic and group polarizabilities as described in the Appendix. The R_e value used for $(\text{Na}^+(12\text{C}4)_2)\text{Na}^-$ was taken to be the sum of the 2.2 Å ionic radius³⁷ of Na^- plus the 4.86 Å radius estimated⁴³ for $(\text{Na}^+(12\text{C}4)_2)$ using normal bond lengths and angles. The domain volumes predicted for the systems containing cations complexed by one 18C6 molecule rather than by two 12C4 molecules will be very similar to the 12C4 case because an $(\text{Na}^+18\text{C}6)$ complex ion has been estimated⁴³ to have a radius of 4.9 Å essentially identical with that of $(\text{Na}^+(12\text{C}4)_2)$. Since the polarizability of one 18C6 molecule will be less than that of two 12C4 molecules, the systems containing the 18C6 complexed cations will be further from the insulator to metal transition than those containing the same cation complexed by two 12C4 molecules. Since the radius of the K^- ion is not known, this was estimated by adding 1.6 Å to the K^+ radius of 1.33 Å⁵³ on the grounds that the 2.5, 3.2, and 3.5 Å radii reported⁵⁷ for Na^- , Rb^- , and Cs^- , respectively, are 1.5, 1.73, and 1.82 Å greater than the cation radii⁵³ of 1.0, 1.47, and 1.68 Å. The resulting domain polarizabilities and volumes in Table 8 yield the ratios $4\pi\alpha_d/(3V_d)$, which are much less than unity for all three salts thus explaining their insulating character. This then accounts for the insulating nature of all the salts considered in this paragraph.

V. Conclusion

The Herzfeld criterion⁶ for the occurrence of an insulator-to-metal transition has been recast into a form suitable for predicting the critical concentration for metallization of a

solution containing a solute more polarizable than the solvent. The resulting criterion, eq 6, is the product of two factors which are both enclosed in curly brackets in (6). The first factor is that which would yield the concentration of solute required for metallization in the absence of both volume changes on dissolution and solvent dielectric properties and it therefore depends only on the solute polarizability. The second factor consists of a denominator which accounts for any volume changes occurring on solution and a numerator taking account of the solvent dielectric properties through the occurrence of the refractive index or alternatively the high frequency dielectric constant of the pure solvent. The latter factor, derived by applying the Clausius–Mossotti relation to the pure solvent, takes full account of both the solvent polarizability and density. The form of the second factor in curly brackets in eq 6 shows that the solvent polarizability entering its numerator always acts to lower the concentration of solute required for metallization whereas positive solute molar volumes, expressed by values of the x parameter greater than zero in the denominator, act to increase this critical concentration.

The polarizabilities of the alkali metal anions Li^- , Na^- , and K^- in-solution have been estimated from the values known for both the free^{15–17} and in-crystal¹⁷ ions. This was achieved by comparing with the changes induced in the polarizabilities of other ions when these enter solution from either the gaseous or solid states.

Relations 6, which take the form of 9 when expressed in atomic units, have been used to predict the critical concentrations (n^{ct}) required for metallization of solutions containing the alkali anions Li^- , Na^- , or K^- in a wide variety of solvents in which the latter two have been prepared. Consideration of the solvent polarizability reduces each of the n^{ct} predicted to about 75% of that derived by neglecting the solvent and taking the solute partial molar volume to be zero. These calculations explain why there has been no evidence for metallization in either relatively dilute solutions in crown ethers^{43–45} or in those containing either these ethers⁴¹ or the C_{222} cryptand⁴² required to form the strong complexes with countercations responsible for the formation of such metal solutions. Application of the usual Herzfeld criterion, eq 2, to the corresponding solids explains why these are also entirely nonmetallic.^{41,55}

For methylamine solutions, the Hepler theory⁴⁰ of solute partial molar volumes taken in conjunction with those measured³⁹ for LiCl and $\text{CH}_3\text{NH}_3\text{Cl}$ enabled the partial molar volume and hence the x parameter in eqs 6 and 9 to be derived for solutions containing Li^+ and Na^- ions. The prediction that the solutions $\text{Li}(\text{CH}_3\text{NH}_2)_y\text{Na}$ will be metallic for y less than 5.28 is in excellent agreement with the experimental result that such solutions are metallic for y values of 4 and 5 but are entirely diamagnetic and nonmetallic for y values of 6 or greater.²⁴ This excellent agreement with experiment requires that one uses correct values for both the x parameter and the in-solution Na^- polarizability. The observed insulating character of the corresponding solids²⁴ is explained by a reduction of the Na^- polarizability on passing from solution to the solid state.

The prediction of a critical composition of about three for solutions of Li^+ and Na^- ions in ethylamine explains the experimental observations⁵¹ that the systems $\text{Li}(\text{CH}_3\text{CH}_2\text{NH}_2)_y\text{Na}$ having y greater than or equal to four are not metallic in either the liquid or solid states. This prediction also suggests that it might be fruitful to reexamine experimentally for evidence of metallic properties the previously prepared⁵¹ solutions having $y = 3$. The critical composition for metallization of the solids $\text{Li}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_y\text{Na}$ could not be reliably predicted because

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the polarizability of the Na^- ion in this system is not known. However, the prediction of a y^{cr} value of about 2.5 on using an overestimate of this polarizability indicates that $\text{Li}(\text{NH}_2\text{CH}_2\text{-CH}_2\text{NH}_2)_2\text{Na}$ might be close to an insulator-to-metal transition even though it is a diamagnetic insulator.⁵⁴ This suggests that it might be fruitful to attempt to induce this electronic phase transition through the application of external pressure.

Appendix: Derivation of the Polarizabilities of Individual Solvent Molecules

The polarizabilities (α_s) of an individual molecule of those solvents of known refractive index can be derived from the experimental data presented in Table 3 by using the Clausius–Mossotti relation. For 12C4 and 15C5, this yields α_s values of 119.1 and 145.9 au, respectively. The lack of refractive index data meant that the polarizability of C₂₂₂ had to be derived as the sum of group refractivities.⁵⁸ The molar refractivity or molar refraction (R_M) is defined, as discussed in any standard textbook

of physical chemistry, by

$$R_M = [(\eta_\infty^2 - 1)/(\eta_\infty^2 + 2)](W_s/\rho_s) \quad (\text{A1})$$

where W_s and ρ_s are defined after eq 10. This definition is given in eq 1 of ref 58 with the misprint that the density factor appears in the numerator while it should enter a denominator as given in (A1). Since the factor W_s/ρ_s equals the molar volume V_M , it follows from the Clausius–Mossotti relation that R_M is numerically equal to the quantity $4\pi\alpha_s N/3$ which is often called the molar polarizability. The extensive experimental work reviewed in ref 58 has shown that the molar refractivity of most commonly occurring nonconjugated organic molecules can be derived to a high degree of accuracy as the sum of group refractivities. A tertiary nitrogen atom in an aliphatic amine, an oxygen atom in an ether, a CH_2 group, and an NH_2 group contribute 2.744, 1.764, 4.624, and 4.438 cm^3 , respectively,⁵⁸ to R_M . The molar refractivity of C₂₂₂, numerically equal to $4\pi\alpha_s N/3$, is predicted from these values to be 99.304 cm^3 from which an α_s value of 265.6 au is derived. A check on the accuracy of α_s values derived from such group refractivities is provided by the α_s predictions of 117.82, 147.27, and 39.42 au for 12C4, 15C5, and ethylamine, respectively. These compare well with both the two experimentally deduced values for the crowns and the α_s value of 39.24 au for ethylamine derived from the Clausius–Mossotti relation using the data of Table 3.

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