Thermal Diffusion in Some Non-Aqueous Electrolyte Solutions

JULIUS G. BECSEY, JAMES A. BIERLEIN, and SILAS E. GUSTAFSSON *

Aerospace Research Laboratories, Office of Aerospace Research Wright-Patterson Air Force Base, Ohio

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There is a sizable body of theory and experiment bearing on the thermodiffusional behavior of aqueous solutions of electrolytes, and the kinetic and thermodynamic principles governing these processes are understood in outline if not in detail. In particular, the importance of specific properties of the solvent is now well recognized. From the standpoint of developing a better insight into the nature of the liquid state, thermodiffusional measurements on ionic solutions have a heuristic and diagnostic value which has not been exploited to any serious extent except in the case of water. As a step toward the study of other solvents, we report here some experimental results for the SORET coefficients of potassium halides in formamide (FA), N-methyl formamide (MFA), and N, N-dimethyl formamide (DMFA).

Experimental

The organic solvents were reagent-grade compounds which were dehydrated before use by vacuum distillation over quicklime. To prevent hygroscopic contamination, the salt solutions were prepared in a dry box, and they were not removed from this environment until they had been introduced into the diffusion cell just prior to making an experiment. All diffusion measurements were made at a mean temperature of 25 °C, using the method of wavefront-shearing interferometry which we have described elsewhere [1]. This procedure determines both the SORET coefficient σ and the isothermal diffusivity D; it also affords an estimate of the precision attaching to these quantities.

Table 1 summarizes our experimental results. The range of concentrations covered by the various solutions extends from virtual saturation down to a lower limit set by the sensitivity of our measuring technique. The uncertainty (standard error of estimate) of the values listed is about ± 0.06 for σ and ± 0.03 for D. All entries in the table are the directly measured quantities, except for items enclosed in parentheses. The latter are graphically smoothed coefficients obtained from plots of the raw data; in no case does such an adjusted value differ from the corresponding raw measurement by as much as two standard deviations.

We use the convention that a positive sign for the SORET coefficient denotes migration of the salt toward the colder region of the solution.

* Visiting Research Associate from Department of Physics, Chalmers University of Technology, Gothenburg, Sweden. Supported in part by a grant from Stiftelsen Blanceflor Boncompagni-Ludovisi, född Bildt.

Solvent	Solute	N, mol fraction	$\sigma \times 10^3$, $\deg^{-1}$	$D \times 10^5$, $cm^2\ sec^{-1}$
FA	KCl	0.0086	3.93	0.35
		0.0180	3.30	0.34
		0.0281	2.94	0.33
	KBr	0.0163	4.11	0.33
		0.0388	2.99	0.33
		0.0509	(2.67)	0.32
		0.0660	2.38	0.30
	KI	0.0181	3.02	0.30
		0.0410	2.77	0.30
		0.0666	2.50	0.29
		0.0968	(2.22)	0.28
		0.1251	2.07	0.25
		0.1526	2.07	0.20
MFA	KI	0.0310	2.40	(0.47)
		0.0588	2.33	0.43
		0.0873	2.04	0.38
		0.1179	1.62	0.30
DMFA	KI	0.0351	8.09	0.83
		0.0644	7.05	0.76
		0.0844	6.27	(0.67)
		0.1086	5.45	0.54

Table 1. Experimental Results.

Discussion

According to the picture of ionic solutions first proposed by EASTMAN [2] and later elaborated by FRANK and WEN [3], thermal diffusion is related to structural changes in the solvent induced by the electrostatic field of the moving ion. In this model, the solvated ion is surrounded by a zone of influence within which the solvent molecules are oriented by the electric field but can move relative to the ion. As the ion moves past a solvent molecule, that molecule first experiences a increasing degree of dipolar alignment as it enters this outer zone and then later relaxes to a random orientation as it is left behind. Hence, in a solvent having little or no inherent structure, heat would be liberated ahead of the ion and absorbed behind it; this corresponds to a positive heat (or entropy) of transport, and in such a structureless solvent an ionic species would always migrate down a temperature gradient. But in a highly structured liquid, water being a conspicuous example, the orientation imposed by the ionic field may break up the innate structure of the solvent and produce a net increase in the entropy of the solvent molecules. Both positive and negative SORET coefficients are therefore explicable, and the thermodiffusional properties of ionic solutions can provide information about the degree of molecular organization in the pure solvent.

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Approaching the data of Table 1 from this point of view, we note that all the SORET coefficients are much larger than those for the same solutes in aqueous solutions [4-8]. From this we conclude in a rough way that intermolecular bonding is not so highly developed in our solvents as it is in water, a finding entirely consonant with accepted doctrine concerning the polarities of these liquids. However, it is instructive to consider whether this observation cannot be given a more precise expression. For this purpose, the concepts introduced by WIRTZ [9] are useful. He formulates the diffusional activation energy E as the sum of two parts, E_1 and E_2, required respectively to dislodge the moving particle from its original site and to form a vacancy into which it can jump. The heat of transport associated with such a jump is given by $Q^* = E_1 - E_2$.

Following this model, we now define a ratio

$$\Phi = E_1/E = (E + Q^*)/2E .$$

It is clear that Q^*/E must lie within the range ± 1, and Φ is similarly restricted to values between 0 and 1. We proceed to consider the significance of different values of Φ. In the particular limiting case $\Phi = 1$, $E_2 = 0$ and all the activation energy is consumed in detaching the ion from the local structure which it has created by its presence at the initial site; no cooperative phenomena are required ahead of the particle to insure a jump, which is eventually terminated by the action of the ion itself in building anew an immobilizing cage of solvent. The condition $\Phi = 1$ therefore defines an altogether structureless fluid. Values of Φ decreasing from unity reflect finite values of E_2, indicating an increasing degree of innate solvent structure. At $\Phi = \frac{1}{2}$, where σ vanishes, the structural stability of the free solvent just matches that of the oriented fluid near an ion. Below this neutral point, σ is negative and $E_2 > E_1$, corresponding to a net structure-breaking effect of the solute. The lower limit $\Phi = 0$, representing a condition in which E_2/E_1 is infinite, is probably never approached very closely in a real liquid, save perhaps near the freezing point of some which melt at a sufficiently low temperature.

Insofar as the foregoing arguments are valid, the parameter Φ should serve as a useful guide for interpreting thermal diffusion experiments; it normalizes the specific effects of different solutes and it furnishes a rational scale for ranking different solvents in order of structural energy. To test this line of thought against our data, it was necessary to evaluate the activation energy for diffusion. This was done through an auxiliary series of measurements in which we first determined the viscosities of our solutions at the lower concentrations as a function of temperature [10]; the diffusional activation energy was then estimated from the relation $E = A + RT$, where A is the experimental activation energy for viscosity at 25 °C. Lacking any information on the activity coefficients in our solutions, we computed the heat of transport simply as $Q^* = 2RT^2\sigma$; this approximation implies that

$$B \equiv 1 + \partial \ln \gamma / \partial \ln N = 1 ,$$

a condition which is fulfilled at infinite dilution but which is not necessarily true at any other concentration. Therefore our values of Φ, shown in Fig. 1, are "apparent" values, but this is not an important limitation so long as we focus attention only on the intercepts at $N = 0$, where the true and apparent quantities

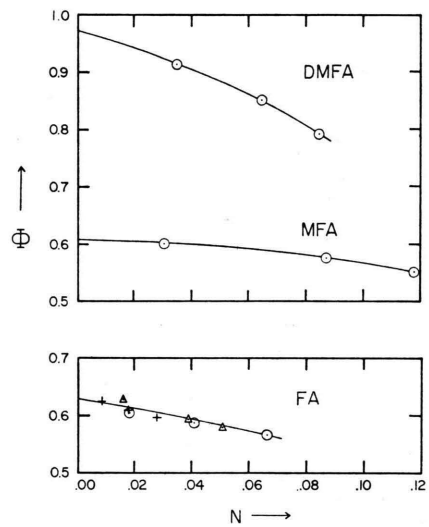

Fig. 1. Correlation of experimental data by the parameter Φ. Plotted symbols identify different solutes: circles = KI, triangles = KBr, crosses = KCl.

coincide. These intercepts, viewed as measures of molecular randomness in the respective pure solvents, classify DMFA as a highly unstructured liquid, approaching the upper bound of unity. FA and MFA are seen by this criterion to be much more highly ordered, MFA perhaps the more so of the two; it is difficult to be positive on this question, considering the uncertainties in extrapolation and the fact that the individual plotted points are susceptible to error. In the

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[10] The viscosity measurements on the KI solutions were used in conjunction with the isothermal diffusivities to compute the WALDEN product ηD; it was found to be a strong function of concentration in each solvent. However, at equal concentrations below a mol fraction of about 0.07, the ηD for all three solutions maintained a fixed ratio to one another: DMFA/MFA/FA = 1.29/1.13/1.00. This result defines the relative STOKES–EINSTEIN radii of the solvated ions in the three liquids.

case of FA, it is interesting to note how well the points for the different solutes are marshaled onto a single curve; the three separate curves of σ against N diverge widely (see Table 1).

There appears to be a significant connection between the intercepts and the general rate of droop (negative slope) of the curves: the higher the intercept, the greater the droop rate. This is a reasonable expectation. As one increases the amount of ionic solute in a structureless solvent, more energy is required on the average to open up a terminal site for a jumping ion, simply because the liquid has been everywhere structured above its normal level by the ionic population distributed throughout; hence E_2 rises, and Φ falls, as N increases. In a liquid having a considerable structure of its own, this effect would be less pronounced; indeed, in solutions where $\Phi < \frac{1}{2}$, one would anticipate a reversal of behavior, that is, the curves should approach the Φ-axis with a positive slope. To the extent that Φ is adequate as a single correlating parameter, a unique terminal slope might also be expected for each possible intercept value. The experimental test of this hypothesis would of course require measurements of true Q^* values (i. e., including the B-factor) in solutions more dilute than those we have dealt with thus far.

In future, we hope to extend this preliminary work both to a wider variety of systems and to lower regimes of concentration, in order to assess these speculative ideas more fully.

Änderungen der Schmelzentemperatur und Wachstumsrate bei tiegelgezogenen Kristallen

A. Mühlbauer

Institut für Elektrowärme der Technischen Hochschule Hannover

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Annähernd periodische Schwankungen der Störstellenkonzentration längs der Ziehachse des Kristalls, die als schmale Wachstumsstreifen in Erscheinung treten, sind in tiegelgezogenen Silicium-, Germanium- und Indiumantimonidkristallen beobachtet und untersucht worden [1]. Sie werden auf periodische Schwankungen der Wachstumsgeschwindigkeit der Kristalle zurückgeführt, die sehr wahrscheinlich durch periodische Schwankungen der Schmelzentemperatur verursacht werden.

An einer Reihe tiegelgezogener Siliciumeinkristalle, welche unter gleichen Bedingungen gezüchtet worden sind (Ziehgeschwindigkeit 2,3 mm/min; Keimdrehzahl 9 U/min; Tiegeldrehzahl 5,6 U/min, Drehrichtung entgegen der Keimdrehrichtung), sind die Breite und der spezifische Widerstand der Wachstumsstreifen bestimmt, und dabei eine unsystematische Schwankung der Streifenbreite und des spezifischen Widerstandes mit einer Periodizität von $10-50\ \mu$m festgestellt worden [1]. Die experimentell gefundene Abhängigkeit der Widerstandsschwankungen $\varrho_{\max}/\varrho_{\min}$, also des Verhältnisses der innerhalb einer Meßreihe auftretenden Widerstandsextrema von der Störstellenart, konnte mittels der Theorie von Burton et al. [2] erklärt werden [3].

Für diese in [1, 3] mitgeteilten Ergebnisse läßt sich eine befriedigende Übereinstimmung von Rechnung und Messung erreichen, wenn eine periodische Schwankung der Wachstumsgeschwindigkeit von $\hat{\Delta v} = \pm 4{,}2 \cdot 10^{-3}$ cm s^{-1} um deren Mittelwert [4] von $\bar{v} = 4{,}5 \cdot 10^{-3}$ cm s^{-1} angenommen wird.

In der vorliegenden Arbeit soll nun, unter Außerachtlassung jeglicher Unterkühlungseffekte an der Phasengrenze flüssig – fest, der Zusammenhang zwischen den Änderungen der Wachstumsrate des Kristalls und der Schmelzentemperatur bestimmt und am Beispiel der erwähnten Siliciumkristalle ausgewertet werden.

Schmelzentemperatur und Wachstumsrate

Wird ein Kristall mit konstantem Querschnitt aus der Schmelze gezogen, so gilt an der Erstarrungsfront die Wärmebilanz

$$q = -\lambda_l (\mathrm{grad}_l\, \vartheta)_M + L\, v = \mathrm{const} \qquad (1)$$

mit q = Wärmestromdichte im Kristall, λ = Wärmeleitfähigkeit, ϑ = Temperatur, L = Erstarrungswärme, v = auf die Phasengrenze bezogene Wachstumsgeschwindigkeit des Kristalls, M = Phasengrenze, l = liquid.

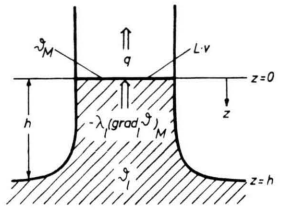

Abb. 1. Wärmestromdichten in der Umgebung der ebenen Erstarrungsfront.

Aus Gl. (1) wird für Kristalle mit ebener Erstarrungsfront und damit eindimensionaler Wärmeströmung unter Einführung von Mittelwerten der Temperatur $\bar{\vartheta}_l$ und Wachstumsgeschwindigkeit $\bar{v}$ sowie deren Abweichungen $\Delta\vartheta_l$ und Δv

$$q = -\lambda_l [(\mathrm{d}/\mathrm{d}z)(\bar{\vartheta} + \Delta\vartheta)_l]_M + L(\bar{v} + \Delta v) = \mathrm{const}. \qquad (1a)$$

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