Importance of Thermal Diffusion in High Subcritical and Supercritical Aqueous Solutions[1]

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ABSTRACT

We have reviewed our experimental and theoretical studies of irreversible thermodynamics of non-isothermal aqueous systems, with particular emphasis on the investigation of thermal diffusion phenomena, via electrochemical methods. By employing Agar's hydrodynamic theory, and by using the experimentally-derived standard entropies of transport, S_2^{*0}, at temperatures from 25 to 125°C, we have calculated high temperature S_2^{*0} values, which exhibit a dramatic rise when the temperature increases above 250°C. Recently reported experimental data for thermal diffusion in $NaNO_3$ aqueous solutions at supercritical temperatures and pressures (Butenhoff et al., 1996) have allowed us to test the validity of our calculations at temperatures up to 450°C. The significance of thermal diffusion in liquid systems with forced convection is discussed, and it is concluded that, as the Lewis number and the Soret coefficient increase, the impact of thermal diffusion on mass transport becomes increasingly important at higher temperatures. We also concluded that the use of an electrochemical cell with forced convection could be a promising experimental technique for determining Soret coefficients for aqueous solutions at elevated temperatures.

KEY WORDS: thermal diffusion; electrolyte aqueous solutions; high temperature; electrochemical cells

1. INTRODUCTION

It is evident that the thermodynamics of aqueous solutions under non-isothermal conditions must be better understood in order to predict mass and heat transport processes in high temperature aqueous environments. There are at least three issues that are directly related to this problem that deserve closer examination. The first one is concerned with the problem of the thermal liquid junction potential [1-4], a knowledge of which is required for accurate potentiometric (including pH) measurements in hydrothermal solutions when an external pressure-balanced reference electrode (EPBRE) is employed. The second issue is related to the phenomena of thermal diffusion in aqueous systems at elevated temperatures [5, 6], which can be of practical relevance in quiescent systems. The third issue lies in the viability of non-isothermal thermodynamic measurements in determining the contributions of individual ions to the properties of electrolyte solutions [7-9].

The main goal of this paper is to review our recent work on the experimental and theoretical development of irreversible thermodynamics of non-isothermal electrolyte solutions in hydrothermal environments, with particular emphasis on the study of thermal diffusion phenomena via electrochemical methods. Although there are several methods of studying the thermodynamics of non-isothermal electrolyte solutions, the measurement of potentials of non-isothermal cells is one of the most promising, in that it has been extended to electrolyte solutions at elevated temperatures [1, 2, 10, 11]. Because of the precision with which the potentials of thermocells can be measured, and because of the relatively well established theoretical base, we expect that this method of investigating thermal diffusion in electrolyte solutions will remain a principal technique in the future.

An additional task of the paper is to use a combination of theory and experiment to show that thermal diffusion effects can be very large for aqueous electrolyte solutions at

high subcritical and supercritical temperatures and that this effect should be of great interest in studying aqueous solutions under these conditions.

In a solution, in which a temperature gradient exists, coupled mass and heat transport is observed. This phenomenon, in the condensed phase, is known as the Soret effect and may be described by applying Onsager's formulation of irreversible thermodynamics [12, 13]. The key parameter in describing the irreversible thermodynamics of a thermal gradient system is the heat of transport of the *i*-th species Q_i^*, which was first introduced by Eastman [14] as the quantity of heat absorbed from the heat reservoir behind and given out ahead of the moving ion. From irreversible thermodynamics, Q_i^* is proportional to the cross Onsager phenomenological coefficients for the coupled flow of matter, L_{ij}, and heat, L_{qj}, and may be given by

$$L_{qj} = \sum_{i=1}^{k} L_{ij} Q_i^* \,. \tag{1}$$

Two other important characteristics of the non-isothermal systems are the electrolyte Soret coefficient σ

$$\sigma = (\nu_+ Q_+^* + \nu_- Q_-^*) / \nu R(1 + \partial \ln \gamma_\pm / \partial \ln m), \tag{2}$$

and the thermal diffusion coefficient of the electrolyte

$$D_T = D\sigma \quad , \tag{3}$$

where $\gamma_\pm$ is the mean ionic activity coefficient, ν_+ and ν_- are, respectively, the number of cations and anions in a salt, $\nu = \nu_+ + \nu_-$, m is the molal concentration, R is the gas constant, and D is the isothermal diffusion coefficient of the electrolyte.

Statistical mechanical theories of non-isothermal electrolyte solutions have been developed [15 -17]. The electrostatic contribution to the value of Q_i^* has been evaluated

and the Debye-Huckel limiting slope has been found in all approaches. A hydrodynamic model was employed by Helfand and Kirkwood [15] to evaluate the electrophoretic effect in an approximate manner, but the relaxation effect on the heat of transport was ignored. In the papers of Kahana and Lin [16, 17], a molecular statistical theory of the heat of transport of dilute electrolyte solutions was developed based on linear response theory. The effect of the relaxation and electrophoretic forces on the heat of transport was investigated, and the concentration dependence of the heat of transport predicted by the linear response theory was found to be in good agreement with experimental results for several aqueous 1:1 chloride solutions for concentrations up to 0.3 M.

In addition to the statistical molecular theories, Agar [18] derived a theory for calculating Q_i^* based on a macroscopic approach. An evaluation of the original Agar approach has been presented by Agar [9], in which the standard single-ion heat of transport, Q_i^{*0}, in an electrolyte solution was derived based on a hydrodynamic theory. Using Born theory to describe the electrostatic interaction between an ion and a dielectric medium of solvent molecules, the following equation was derived for Q_i^{*0}

$$Q_i^{*0} = -T\frac{K}{R_i}\frac{Ne^2 z_i^2}{2}\frac{1}{\mathrm{e}}\left(\frac{\P \ln \mathrm{e}}{\P T}\right), \tag{4}$$

where R_i is the hydrodynamic radius of the *i*-th ion, e is the solvent dielectric constant, and K is a boundary condition parameter. Note that both K and R_i are not well known values for any real solutions, and hence they should be regarded as empirical parameters to be derived by fitting the theory to experimental data.

2. ELECTROCHEMICAL MEASUREMENTS OF THERMAL DIFFUSION

If a potentiometric method is to be employed in thermal diffusion studies of a metal chloride solution MCl_n(aq), where M is a metal of the cation and n is the

stoichiometric number of chloride ions in the electrolyte, a symmetrical, non-isothermal electrochemical system incorporating Ag/AgCl electrodes may be considered as an appropriate experimental system:

|<———T_1————>|<————T_2————>|<—T_1—
Cu | Pt | Ag | AgCl | MCl$_n$(aq) | AgCl | Ag | Pt | Cu ... Cu (I)
φ_L φ_R
|<——————$E = \varphi_R - \varphi_L$———————>|

where E is the electromotive force (e.m.f.) of Thermocell (I), φ_L and φ_R are the electrostatic potentials of the left and right terminals, respectively, at ambient temperature T_1, and T_2 is an elevated temperature that is higher than T_1. It is already well known that E cannot be regarded as the difference in the reversible potentials of the right and left electrodes, but that it should be treated on the basis of linear irreversible thermodynamics, [4, 5, 13], which yields a general expression for the thermoelectric power, $E_T^{'} = (dE / dT)$ as

$$FE_T^{'} = S_{Ag} - S_{AgCl} - \bar{\bar{S}}_e + \bar{S}_{Cl^-} - \sum_i \frac{t_i S_i{*}}{z_i} + \sum_j (-\mu_{Cl^-,j} - \sum_i \frac{t_i \mu_{ij}}{z_i}) \frac{dm_j}{dT}\,, \tag{5}$$

where F is Faraday's constant, S_{Ag} and S_{AgCl} are the molar entropy of silver and silver chloride, respectively, $\bar{\bar{S}}_e$ is the transported entropy of an electron in the copper wires, and $\bar{S}_{Cl^-}$ is the partial molar entropy of the chloride ion in the MCl$_n$(aq) solution. The symbols t_i, S_i^*, and z_i represent, respectively, the transport number, the entropy of transport, and the charge of the *i*-th ion in the MCl$_n$(aq) solution, and m_j is the molality of the *j*-th component in MCl$_n$(aq) solution. The value $\mu_{Cl^-,j}$ in Eqn. (5) is the derivative $(\partial\mu_{Cl^-} / \partial m_j)_{T,P,i\neq j}$, where μ_{Cl^-} is the chemical potential of the chloride ion.

If we start with a homogeneous solution and instantaneously impose a temperature gradient, then the quantity that is measured is the initial value of the thermoelectric power $(E_T^{'})_{in}$ of Thermocell (I). Over the course of time, a concentration gradient develops due to thermal diffusion in the solution, and after a sufficiently long time a stationary steady state is approached (at time t→∞), in which diffusion and thermal diffusion are balanced. In this case, we measure the steady state value of the thermoelectric power $(E_T^{'})_{st}$. It can be shown that, once the values of $(E_T^{'})_{in}$ and $(E_T^{'})_{st}$ are defined, we may derive experimentally the heat of transport of MCl_n(aq) as

$$Q_2^* = T\frac{Fz_+}{t_+}\left((E_T^{'})_{st} - (E_T^{'})_{in}\right) , \qquad (6)$$

where z_+ and t_+ are, respectively, the charge and the transport number of the cation.

Experimental measurements of the initial $(E_T^{'})_{in}$ and the steady state $(E_T^{'})_{st}$ thermoelectric powers are carried out by employing different approaches. To measure $(E_T^{'})_{in}$, one needs to minimize thermal diffusion, and the distance between the electrodes should be large enough to carry out potential measurements in the first few minutes after installing a thermal gradient and completing the circuit. In contrast, for measuring $(E_T^{'})_{st}$, the thermal diffusion process should be ensured and, as a consequence, the distance between electrodes should be a small and convective flow should be avoided.

Detailed descriptions of the experimental methods and results of thermoelectric power measurements on many aqueous electrolyte solutions over wide ranges of temperature from 25 to 250°C are presented in our previous publications [1, 2, 5, 10, 11, 19-22]. Figure 1 displays an example of our experimental measurements and calculations,

which shows a very pronounced temperature dependence of the entropy of transport, $S_2^{*0} = Q_2^* / T$, for LiCl, NaCl, KCl, and RbCl aqueous solutions.

3. ESTIMATION OF SORET COEFFICIENTS AT HIGH TEMPERATURES

We have found that, at least for electrolyte solutions, it is possible to estimate theoretically the temperature dependence of the Soret coefficient using Eqn. (4). As can be seen from this equation, the ratio of the Soret coefficient, s , at temperature T to the same quantity at a reference temperature T_0 , s_0, can be described by the following function $f_1(T)$

$$\frac{\mathsf{s}}{\mathsf{s}_0} = f_1(T) = \frac{T_0}{T}\frac{\mathsf{e}_0}{\mathsf{e}}\frac{\P \ln \mathsf{e}}{\P T} / \left(\frac{\P \ln \mathsf{e}}{\P T}\right)_{T=T_0}, \tag{7}$$

which is a strong function of temperature. In Eqn. (7), e and e_0 are the static permittivity of water at temperatures T and T_0, respectively. Calculated values of the function $f_1(T)$, which were made by using the dielectric constant of water [23], are presented in Figure 2. This plot demonstrates the dramatic rise in s that occurs when the temperature increases from 200 to 350°C. The reason for this remarkable temperature dependence can be easily understood if we take into account the well known fact that the temperature derivative, $(\P\mathsf{e}/\P T)_p$, goes to infinity when the temperature approaches the critical temperature, T_{crit}, of the solvent. Moreover, the fact that the Soret coefficient $\mathsf{s} \to \pm\infty$ for non-electrolyte solutions, when the system approaches the critical temperature, from higher and lower values, has been previously noted in the literature [13]. Experimental measurements on non-electrolytes [24] directly support this view.

Recent experimental data for thermal diffusion coefficients, $D_T = \mathsf{s}D$, in $NaNO_3$ aqueous solutions at supercritical temperatures [25], allow us to test the validity of Eqn.

(7) at temperatures up to 450°C, for which Eqn. (7) yields σ / σ_0 = 24.05. The diffusion coefficient for $NaNO_3$ in infinitely dilute solution at this temperature and pressure can be derived from a linear extrapolation of $D = f(\sqrt{m})$ to m = 0 using the experimental data given in Ref. [24]. The value of *D* was found to be $15.8 \times 10^{-9}\,\mathrm{m}^2/\mathrm{s}$ at 450°C and 450 bar. The diffusion coefficient at 25°C and 1 bar was taken from Ref. [26], and is 1.57×10^{-9} m^2s^{-1}. Performing these calculations we obtain $D_T / D_{T_0} = (\sigma / \sigma_0)(D / D_0) = 242$, which is in good agreement with the experimental value of 250 reported by Butenhoff et al. [25] for T = 450°C and P = 450 bar.

For comparison, the temperature dependence of the diffusion coefficient, calculated from Walden's rule,

$$D / D_0 = f_2(T) = (T / T_0)(\eta_0 / \eta) \tag{8}$$

is also represented in Figure 2, where η and η_0 are the viscosity of water at temperatures *T* and T_0, respectively, calculated using the NIST software package [23]. It is evident that as $T \to T_{crit}$, $f_1(T)$ changes more rapidly with temperature than does $f_2(T)$. Thus, Figure 2 clearly demonstrates the increasingly greater importance of thermal diffusion compared with ordinary diffusion, as the temperature approaches the critical value.

3. DISCUSSION AND CONCLUSIONS

We have found that when the state parameters of an aqueous solution approach the critical point, the entropy of transport of an electrolyte becomes very large. This finding is in contrast to the general opinion that thermal diffusion is not usually important in industrial systems [27]. For example, in our recent paper [6] we have calculated the

thermal diffusion fluxes in the case of a first order chemical or electrochemical reaction on the surface of an electrode in the entry region of channels at elevated temperature. In that paper, we showed that, as the result of increasing Lewis number, and especially increasing Soret coefficient, with increasing temperature thermal diffusion can become a significant mechanism of mass transport in aqueous systems containing thermal gradients. In the general case, the quantitative description of mass transfer near the critical point must include thermal diffusion, even when the temperature drop is low. This finding challenges the general belief that thermal diffusion is not important in non-isothermal systems. Explicit expressions for the mass fluxes have been derived for the cases of very rapid and very slow reactions in the entry regions of channels [6], and these expressions can be applied when the thermal diffusion effect is not very strong. This approach can be used for the experimental determination of Soret coefficients in the entry regions of channels at high temperatures, if the temperature drop in the solution does not exceed 10 degrees. We also conclude that, due to the relatively large thermal diffusion effect at elevated temperatures, the use of an electrochemical cell with forced convection might be a promising experimental technique for determining Soret coefficients.

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REFERENCES

1. D.D. Macdonald and A.C. Scott, *J. Electrochem. Soc.*, **126**: 1618 (1979).
2. S.N. Lvov, A. Marcomini, and M.M. Suprun, 1993. in: *Proc. of 4-th International Symposium on Hydrothermal Reactions*, M. Cuney and M.Cathelineau, ed., (GREGU, Nancy, 1993) pp. 135-138.
3. S.N. Lvov S.N., Perboni G., M. Broglia, in "High Temperature pH Measurements in Dilute Aqueous Ammonia Solutions." *Proc. of 12-th International Conference on the Properties of Water and Steam*, J. V. Sengers, (Begell House, NY, 1995), pp. 441-448.
4. S.N. Lvov and D.D. Macdonald, *J. Electroan. Chem.*, **403**: 25 (1996).
5. S.N. Lvov and D.D. Macdonald, in: *Proc.of the 1995 ASME International Mechanical Engineering Congress & Exposition*, (San Francisco, California, 1995), pp.1-13.
6. G.R. Engelhardt, S. N. Lvov, and D.D. Macdonald, *J. Electroan. Chem.*, (1997), (in press).
7. K.S. Pitzer and L. Brewer, *Thermodynamics.* 2nd ed., New York, McGraw-Hill, 1961.
8. P.R. Tremaine, N.H. Sagert, and G.L. Wallace, *J. Phys. Chem.*, **85**: 1977 (1981).
9. J.N. Agar, C.Y. Mou and L. Jeon-long, *J. Phys. Chem.*, **93**: 2079 (1989).
10. J.S. Hwang, A. Boateng, and D.D. Macdonald, in: *Proc. of the Symposia on Corrosion in Batteries and Fuel Cells and Corrosion in Solar Energy System*. (Denver, Colorado, 1983) pp. 492-501.
11. S.N. Lvov., Y.D. Rakhmilevich, and I.A. Dibrov, *Russ. J. Phys. Chem.*, **60**: 2896 (1986).

12. S.R. DeGroot, *Thermodynamics of Irreversible Processes.* Amsterdam: North-Holland, 1951.

13. R. Haase, *Thermodynamics of Irreversible Processes.* Massachusetts: Addison-Wesley, 1969.

14. J. Eastman, *J. Am. Chem. Soc.*, **50:** 292 (1928).

15. E. Helfand and J.G. Kirkwood, *J. Chem. Phys.*, **32**: 857 (1960).

16. P.Y. Kahana and J. Lin , *J. Chem. Phys.*, **74**: 2993 (1981).

17. P.Y. Kahana and J. Lin , *J. Chem. Phys.*, **75**: 5043 (1981).

18. J.N. Agar. in: *Advances in Electrochemistry and Electrochemical Engineering*., (v.3, New York, Interscience Publishers 1963), pp. 31-121.

19. Y.D. Rakhmilevich, S.N. Lvov, and I.A. Dibrov, *Russ. J. Phys. Chem.*, **58**: 2019 (1984).

20. Y.D. Rakhmilevich, S.N. Lvov, and I.A. Dibrov, *Russ. J. Phys. Chem.*, **61**: 554 (1987).

21. Y.D. Rakhmilevich, S.N. Lvov, and I.A. Dibrov, *Russ. J. Phys. Chem.*, **61**: 2391 (1987).

22. M.M. Suprun, I.A. Dibrov, and S.N. Lvov, *Russ. J. Phys. Chem.*, **64**: 1232 (1990).

23. S. A. Klein and A.H. Harvey, Formulation for General and Scientific Use. PC Software Package. Department of Commerce, 1996.

24. G. Thomaes , *J. Phys. Chem.*, **25**, 32 (1965).

25. T. Butenhoff, M. Goemans, and S.J. Buelow, *J. Phys. Chem*, **100**: 5982 (1996).

26. R. A. Robinson, and R. H. Stokes, *Electrolyte Solution*, Butterworths, London,

1959.

27. J.S. Newman, *Electrochemical Systems*. 2nd ed., New Jersey, Prentice-Hall, 1991.

FIGURE CAPTIONS

Figure 1. The temperature dependence of the standard entropies of transport $S_2{}^{*0}$ for aqueous LiCl, NaCl, KCl, and RbCl solutions.

Figure 2. Temperature dependence of the relative diffusion and Soret coefficients calculated from Walden's and Agar's relations.

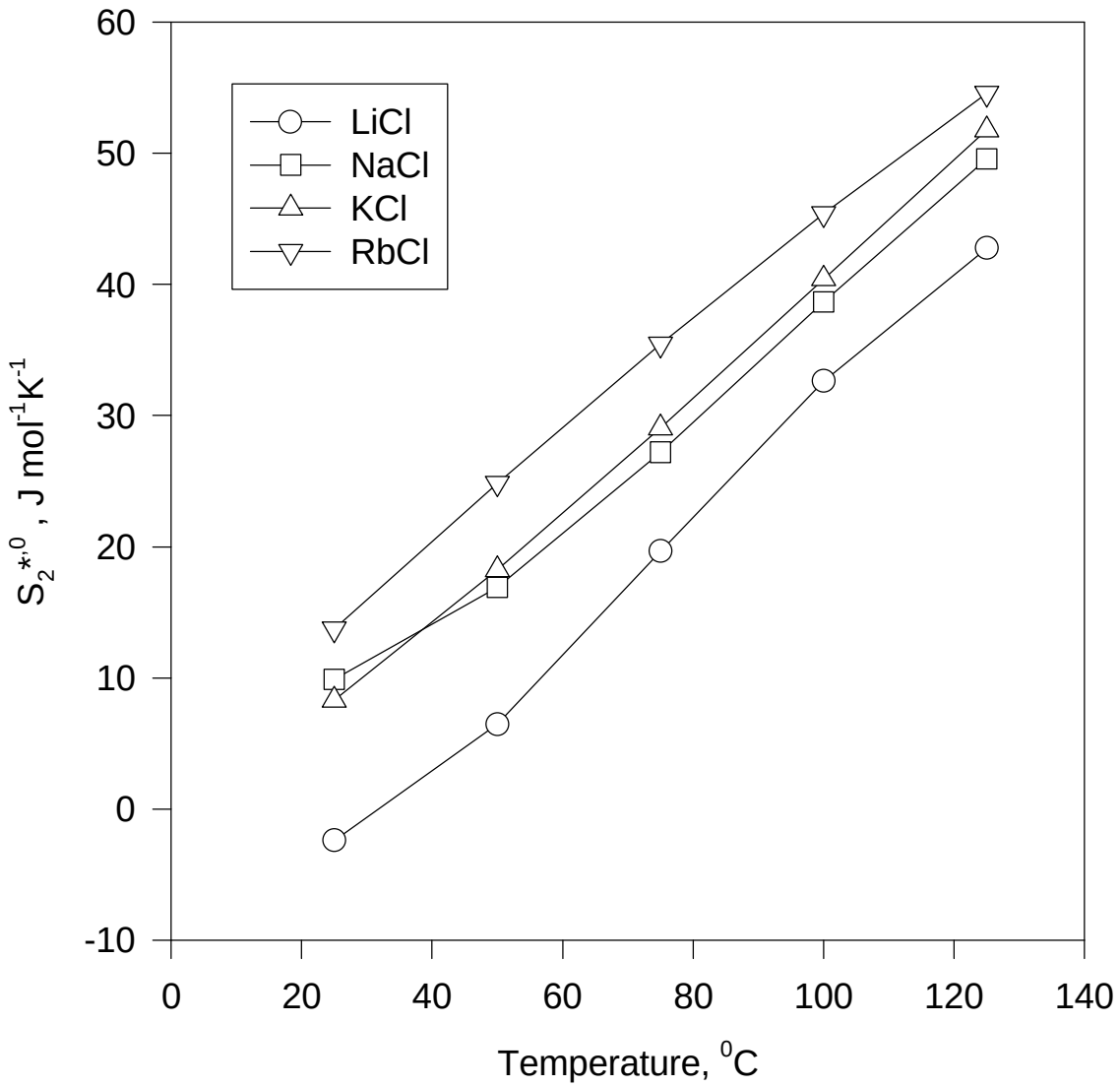
60
50
40
30
20
10
0
-10
0
20
40
60
80
100
120
140
LiCl
NaCl
KCl
RbCl
$S_2^{*,0}$, J mol^{-1}K^{-1}
Temperature, ^{0}C

Fig. 1

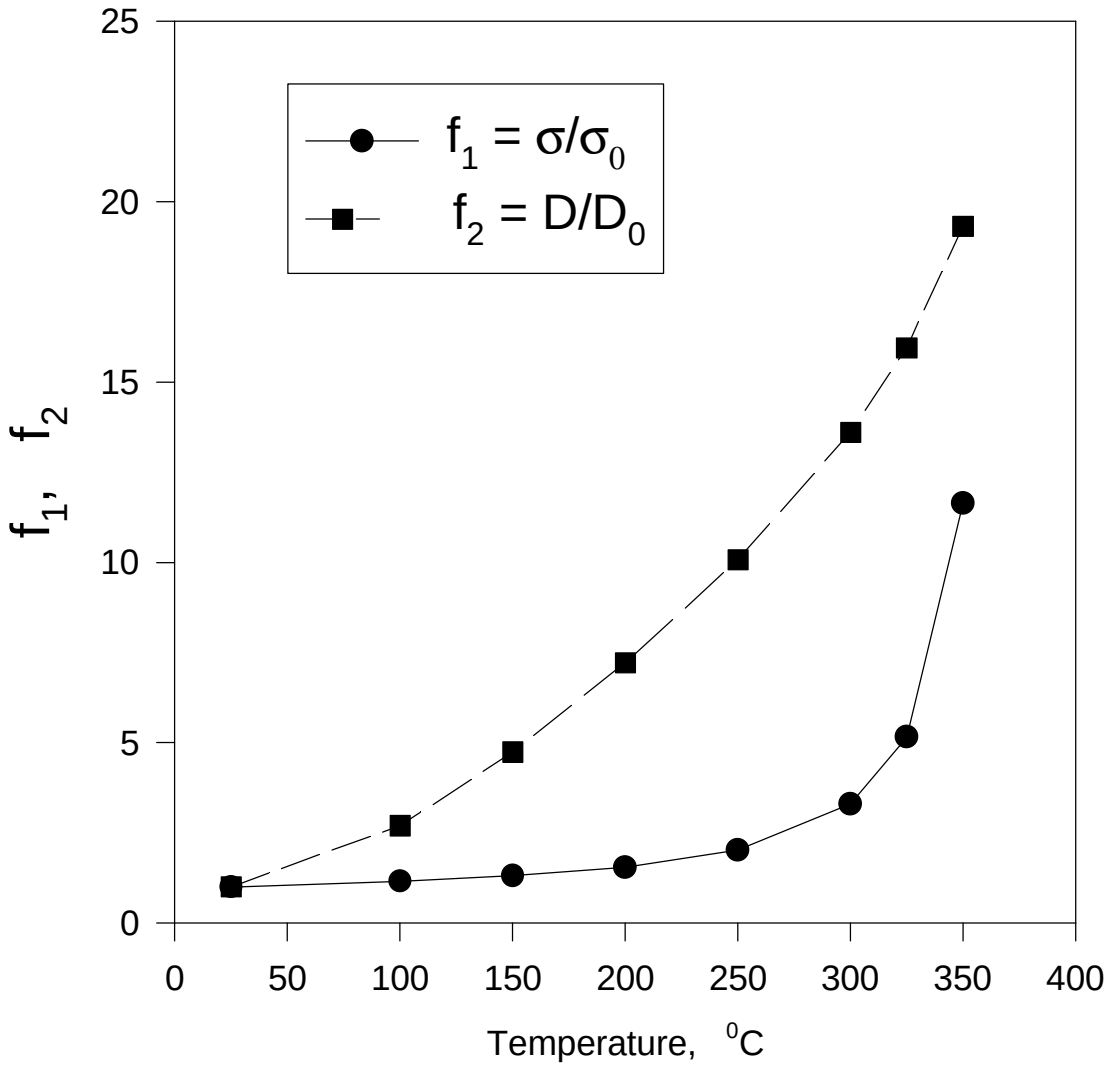
25
20
15
10
5
0
0
50
100
150
200
250
300
350
400
f1 = σ/σ0
f2 = D/D0
f1, f2
Temperature, 0C

Fig. 2