THE NUCLEATION OF ICE IN UNDERCOOLED WATER AND AQUEOUS POLYMER SOLUTIONS*

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ABSTRACT

The theory of ice nucleation in undercooled water is reexamined in the light of recent experimental measurements and new specific heat and viscosity data on undercooled water. By the incorporation of these data in the calculation of the ice-nucleation rate, it is found that the nucleation model based on stepwise growth of a cluster fails at temperatures below 230 K.

Results are reported of ice-nucleation rates in concentrated solutions of oxyhaemoglobin; they are compared with data for other aqueous polymer solutions.

INTRODUCTION

An appreciation of the energetics and mechanisms of ice nucleation in supersaturated water vapour and in undercooled liquid water are of fundamental, technological and environmental significance. Ice nucleation is at the basis of precipitation in the form of hail and snow, freeze resistance in living organisms, laboratory preservation of live cells and tissues and technological operations such as the manufacture of food products or the freeze drying of labile materials. In practice, heterogeneous nucleation by particulate matter is much more common than homogeneous nucleation through random density fluctuations, but the latter process is more amenable to theoretical analysis and an unambiguous interpretation of experimental results [1].

The physical properties of water and ice that affect nucleation, density, interfacial tension, heat capacity and self-diffusion, are sensitively dependent on temperature and, until recently, little was known about their magnitudes at subzero temperatures. Mainly through the extensive studies of Rasmussen and MacKenzie [2], and Angell and his co-workers [3], there are now reliable experimental data which indicate that, as the threshold for rapid nucleation is approached, the temperature derivatives of most of the physical properties increase (or decrease) dramatically. Extrapolations from temperatures

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above the equilibrium freezing point therefore give rise to considerable errors in the calculated properties of undercooled water. In order to avoid the catalytic effects of particulate impurities on ice nucleation, undercooled water is conveniently studied in the form of finely dispersed droplets of μm dimensions in an inert carrier fluid [4—6]. The large number of microdroplets in an experimental specimen provides a statistically adequate number of independent nucleation events (one per droplet) for the evaluation of the nucleation rate $J(T)$, especially if the droplet-size distribution is known and kept narrow [5].

Of the experimental studies on record most are limited to determinations of the temperature at which nucleation becomes rapid, e.g., where there is a high probability of nucleation within 1 s [4, 7, 8]. A nucleation-rate value is therefore assumed, and the so-called homogeneous-nucleation temperature T_h is estimated from the measurements. Usually the experimental procedure involves temperature scanning, so that T_h must then be referred to the particular cooling rate employed. From the available techniques, microscopy and thermal methods are favoured. The direct microscopical observation of droplet freezing has certain attractions, mainly because it permits the isothermal estimation of $J(v)$, where v is the droplet volume. On the other hand, observations are of necessity restricted to samples containing a relatively small number of droplets. With thermal methods a typical sample would be polydisperse, but it would contain $> 10^6$ droplets. Furthermore, differential calorimetry can be used in the isothermal or scanning mode, and the instrumental output is the heat capacity, thus permitting the estimation of thermodynamic, as well as kinetic properties of the system under study. Thermal analysis is less useful, because there is no simple relationship between the instrumental output and the heat capacity; only the temperature difference between the sample and the reference standard is monitored.

Both calorimetry and microscopy are based on the assumption that crystal growth is rapid compared to nucleation, so that the nucleation rate is directly proportional to the total frozen mass. The validity of this assumption needs to be checked experimentally [6, 9]. It is valid for pure water but not necessarily for the nucleation of ice in aqueous solutions of high viscosity, where crystallization then becomes the rate-determining process.

The following analysis of the nucleation of ice in undercooled water is based largely on the experimental data of Wood and Walton [5], obtained by temperature-scanning microscopy, and our own results, based on DSC [6]. Several critiques of the experimental techniques have recently been published [9, 10] and will not be repeated here, nor will the development of the detailed theory of homogeneous nucleation. We limit ourselves to an analysis of the quantities that enter into the various equations and the manner in which recent experimental work on undercooled water can provide an improved quantitative evaluation of experimental data.

FACTORS WHICH INFLUENCE OBSERVED NUCLEATION RATES

In this section we follow mainly the theoretical treatment of nucleation given by Dufour and Defay [7], because of its lucidity and comprehensiveness. It is based on a combination of the classic treatment by Turnbull and Fisher [11] and the theory of absolute reaction rates, as applied to transport processes in fluids [12]. It must be emphasized at this point that the classic model describes nucleation as a process whereby a cluster of water molecules grows by stepwise addition of molecules until it reaches a critical volume from which it can grow spontaneously into a crystal.

The steady-state rate of nucleation (J) of ice in an undercooled aqueous mother phase at temperature T is given by

$$J(T) = L(\sigma T)^{\frac{1}{2}} \phi_w^2 \exp[-\Delta G^{\ddagger}/RT] \exp[-Q\sigma^3/(\Delta T)^2 T^3] \tag{1}$$

where L and Q are functions of several physical properties of ice and water, as follows:

$$L = (n/4\pi d^2 V_{ice}) (k/h) (2V_{water}/Nk^{\frac{1}{2}}) \tag{2}$$

and

$$Q = (bV_{ice}^2/k) [T_0^4(\Delta H_c)^2] \tag{3}$$

The various symbols have the following significance: ϕ_w is the volume fraction of water, n is the number density of molecules in the liquid phase, σ is the interfacial tension between water and ice, $\Delta G^{\ddagger}$ is the free energy of activation of self-diffusion (or viscosity), $\Delta T = (T_0 - T)$ is the degree of undercooling, d is the density of the liquid phase, V_{ice} and V_{water} are the partial molar volumes of the two phases, ΔH_c is the latent heat of crystallization, N is the Avogadro number and b is a shape factor which depends on the geometry of the critical nucleus; for a spherical nucleus, as used in these calculations, $b = 16\pi/3$.

The subzero temperature values of several of the quantities in Eqn (1), $\Delta G^{\ddagger}$, V_{water}, ΔH_c and σ, were unknown until fairly recently. Fortunately we now possess reliable data, at least down to ≈ 238 K, from which the short extrapolation to T_h (≈ 233 K for droplets of radius 2.5 μm) can be performed with confidence. Recent low-temperature viscosity [13] and self-diffusion [14] data, extending down to 235 K, emphasize the marked curvature in the Arrhenius plot [ln η (1/T)] for water. An extrapolation of the data obtained above 273 K would give rise to errors of more than an order of magnitude. Several previous estimates of nucleation data have used the Arrhenius $\Delta E^{\ddagger}$ in Eqn (1). However, diffusion of water molecules from the undercooled liquid to the cluster surface is governed by the free energy of activation, $\Delta G^{\ddagger}$, given by

$$\Delta G^{\ddagger} = RT \ln \frac{\eta \ V_{water}}{hN} \tag{4}$$

Figure 1 shows a comparison of $\Delta G^{\ddagger}$ (T) based on linearly extrapolated viscosity data [4] and on experimental data. The divergent behaviour leads to differences in $J(T)$ of orders of magnitude. Included in the estimated $\Delta G^{\ddagger}$ is the molar volume of undercooled water. Density measurements on undercooled water extending down to 239 K show that the negative coefficient of expansion, which characterizes water below 277 K, becomes increasingly larger with decreasing temperature. A short extrapolation suggests that close to T_h, $V_W = 19.38 \times 10^{-6}$ m^3 mol^{-1} (cf. 18.06×10^{-6} m^3 mol^{-1} at 273.2 K).
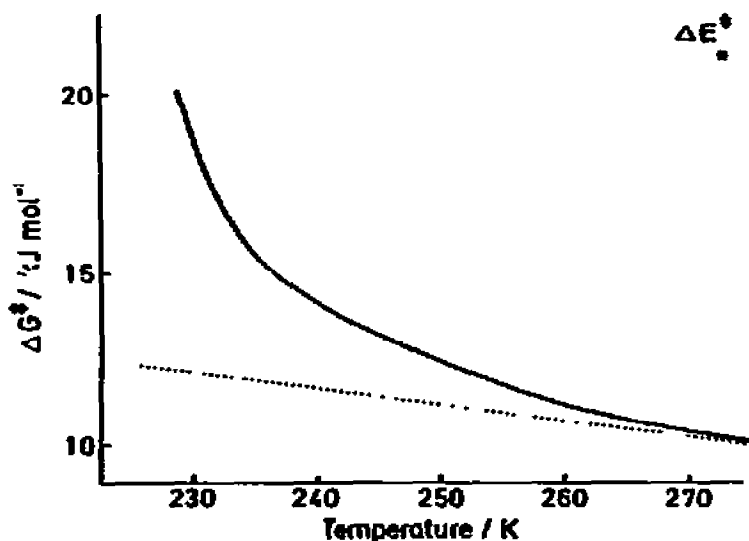

Fig. 1. Free energy of activation of viscosity (and self-diffusion) for undercooled water. Drawn-out line: calculated from the viscosity data of Osipov et al. [13]; broken line: linear extrapolation of viscosity data in the temperature range 273—293 K. $\Delta G^{\ddagger}$ has been calculated according to Eqn (4). The asterisk denotes the Arrhenius energy of activation at T_0.

The standard free energy of transferring an H$_2$O molecule from the undercooled liquid to an ice crystal under equilibrium conditions, i.e., the free energy of crystallization, is given by

$$\Delta G_t^0 = -\frac{1}{V} \left[\Delta H_f (\Delta T) + T_0 \int_{T_0}^{T} \left(\int_{T_0}^{T} \frac{\Delta C_p}{T} \, dT \right) dT \right] \tag{5}$$

where ΔH_f is the molar latent heat of fusion and ΔC_p the difference in heat capacity between the crystalline phase and the undercooled liquid. In the case of water, $\Delta C_p < 0$ and increases rapidly in magnitude as the temperature decreases, thus reducing the effective heat of crystallization which appears in Eqn (3). In fact, ΔH_c decreases from -6 kJ mol^{-1} at 273 K to -3.8 kJ mol^{-1} at 233 K. All previously reported calculations of $J(T)$ have

been based on the assumption of a constant, temperature-independent ΔH_c.

The most crucial quantity in the evaluation of $J(T)$ is σ, the interfacial free energy between the cluster and the undercooled mother phase. Like earlier investigators, we must assume that the clusters closely resemble ice in structure and surface energetics. An equilibrium value of σ can be measured only at T_0 by macroscopic methods which usually involve contact-angle determinations. To be absolutely correct, allowance should also be made for the anisotropy of ice. The result of Hardy, 29.1 ± 0.8 mJ m^{-2}, based on the measurement of grain boundary angles, is now considered to be the most reliable estimate [15].

The nucleation of ice in pure water can only be measured in the vicinity of T_h, so that estimates of σ are of necessity confined to T_0 and a narrow temperature range in the neighbourhood of 234 K. The accuracy of σ, as obtained from nucleation measurements, depends among other factors, on a knowledge of the other quantities that make up $J(T)$ in Eqn (1). Since the physical properties of deeply undercooled water were not available to earlier investigators, we believe that published low-temperature estimates of σ and $d\sigma/dT$ are incorrect. Furthermore, previous studies, apart from that by Wood and Walton [5], were confined to measurements of a notional homogeneous nucleation temperature. For instance, Rasmussen and MacKenzie [4] assumed that at T_h, $J = 1 \times 10^{16}$ s^{-1} m^{-3}. They then proceeded to calculate σ from this result.

Our own studies have confirmed previous findings [16] that great care must be taken in ensuring thermal equilibration between the emulsion sample and the measuring cell where temperature-scanning methods are used. Thus, the measured nucleation rates must be shown to be independent of cooling rates. In our experiments [6, 17, 18], aqueous-phase masses never exceeded 1 mg which nevertheless required cooling rates of $\leqslant$ 2.5 K min^{-1} for adequate thermal equilibration. The measurements by Jacobi [8] which were used by Dufour and Defay [7] in their calculation of σ were performed with scanning rates of 18 K min^{-1} which seem to be well outside the allowable rate. Based on these results, Dufour and Defay concluded that $\sigma = 20.24$ mJ m^{-1} at 238.2 K, with $d\sigma/dT = 0.102$ mJ m^{-2} K^{-1} [7]. This latter estimate suggests that $\sigma = 23.8$ mJ m^{-2} at T_0, a value greatly at odds with the most recent equilibrium measurements [15].

Wood and Walton determined $J(T)$ by direct microscopical observation of droplet freezing and quote $\sigma = 24.22$ mJ m^{-2} for spherical clusters ($d\sigma/dT = 0.211$) and 20.95 mJ m^{-2} ($d\sigma/dT = 0.180$) for hexagonal prisms at 236.1 K [5]. These results produce values at 273.2 K that agree reasonably well with the measured values, but here again the calculations were based or. uncertain viscosities and the assumption that $\Delta C_p = 0$.

RESULTS AND DISCUSSION

We have calculated σ from Eqn (1), using our experimental $J(T)$ values [6] and $\Delta G^{\ddagger}$, V_{water} and ΔC_p, as quoted by Angell [3]. From the limited

TABLE 1

Nucleation rates, $J(T)$, computed from experimental data and from physical properties of undercooled water, provided by Angell [3] For details see text

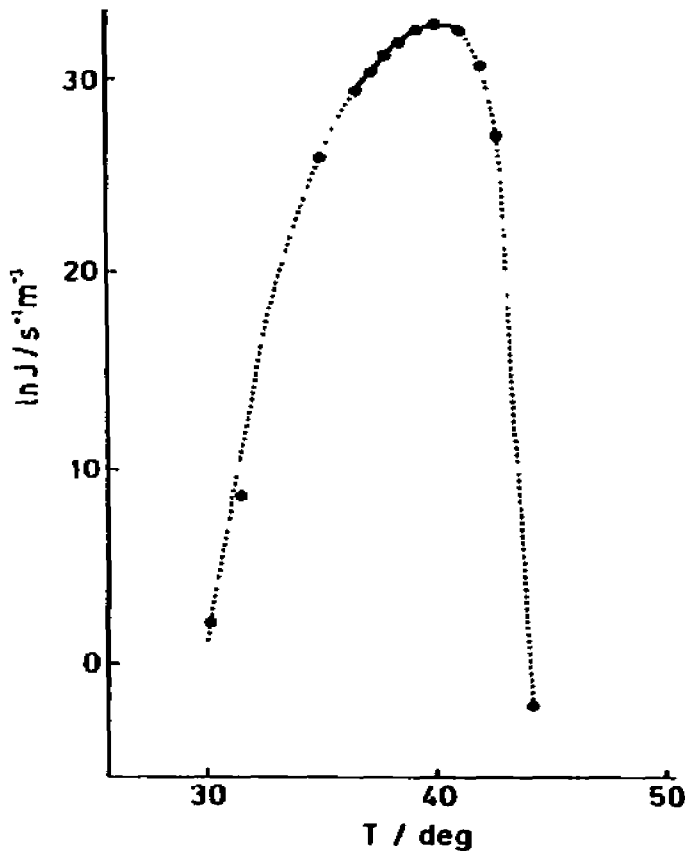| T (K)	ΔT (K)	$\ln(\sigma T)^{\frac{1}{2}}$	σ (mJ m^{-2})	$\Delta G^*/RT$	ΔH_e (J mol^{-1})	$10^{-11} Q$ (m^{4}K^{2}J^{-1})	$Q/(\Delta T)^2 T^4$ (m^{2}J^{-2})	$Q\sigma^3/(\Delta T)^2 T^3$	$\ln J$ (s^{-1} m^{-3})
243 2	30	0.81	20 8	6.14	4600	1 23	9 50 x 10^4	85 50	2 16
241.2	32	0.79	20 2	6.37	4400	1.35	9.40	77.48	9.92
238 2	35	0.74	19.4	6 83	4250	1.40	8.46	61.77	25.12
234 2	39	0.73	18.3	7 54	3900	1.76	8.99	55 10	31 07
233.2	40	0 72	18.0	7 78	3800	1.85	9.12	53 19	32 73
232.2	41	0 71	17.7	8 18	3600	2 01	9 55	52 96	32.36
231.2	42	0 70	17 4	8 32	3350	2.25	10 32	54 37	30.99
230 2	42	0 69	17 1	8 94	3100	2.71	12 00	57.89	26.84
229.2	44	0 67	16 9	9.98	2700	4 16	17.84	86.11	−2.44

Fig. 2. Measured (——) and calculated (· · · ·) nucleation rates of ice in undercooled water as function of the degree of undercooling. For method of calculation see text.

temperature range over which direct nucleation measurements can be made, we found $d\gamma/dT$ = 0.228 mJ m^{-2} K^{-1} which is consistent with Hardy's measured value at 273.2 K [15]. Table 1 provides a summary of the quantities in Eqn (1), and Fig. 2 shows the dependence of $J(T)$ on ΔT, the degree of undercooling. The experimentally-accessible temperature range is indicated by the drawn-out line. For low ΔT values, $J(T)$ shows qualitative agreement with the estimates of Wood and Walton [5], but there are significant quantitative differences.

According to Turnbull [19], $J(T)$ at first rises steeply with increasing ΔT, then levels off to a broad plateau and eventually declines again. The exact shape of the curve depends on T_0, $\Delta G^{\ddagger}$, ΔH_c and σ. Figure 3 shows this dependence of $J(T)$ on the various parameters in Eqn (1), as calculated by Muhr [20] for undercooled water. It should be noted that $\Delta E^{\ddagger}$, rather than $\Delta G^{\ddagger}$, has been used in computing the curves. As shown in Fig. 1, $\Delta E^{\ddagger} \simeq 2 \Delta G^{\ddagger}$ at T_0. The substitution of $\Delta E^{\ddagger}$ by $\Delta G^{\ddagger}$ would therefore result in a slight upward shift of the curves. Such small shifts are insignificant compared to the gross approximations that σ and $\Delta G^{\ddagger}$ are taken to be tempera-
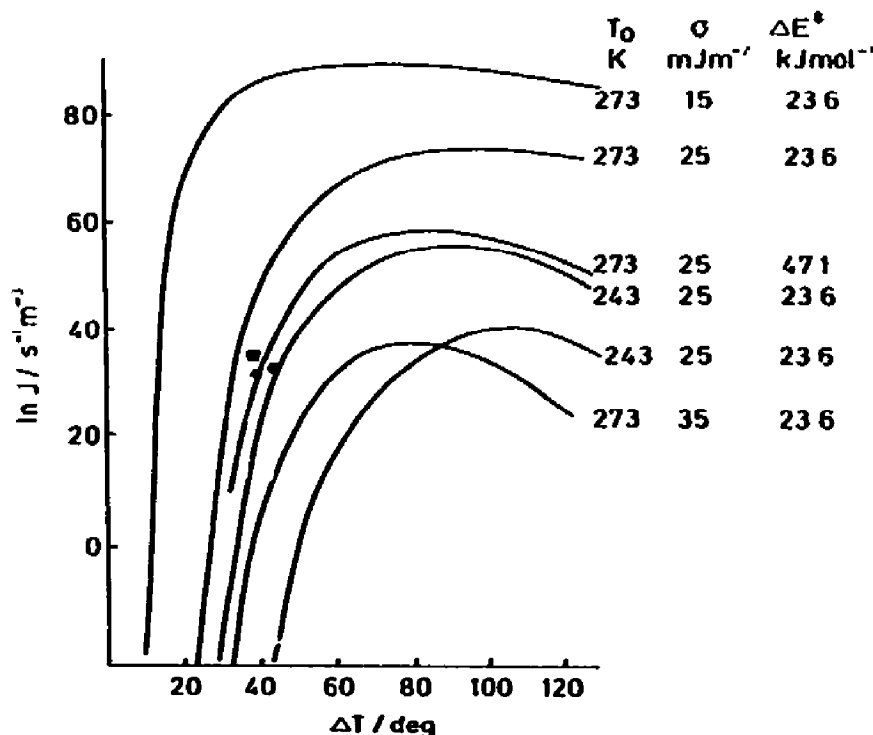

T_0 K	σ mJm^{-2}	$\Delta E^{\ddagger}$ kJmol^{-1}
273	15	236
273	25	236
273	25	471
243	25	236
243	25	236
273	35	236

Fig. 3. Estimated ln $J(\Delta T)$ curves for different values of T_0, σ and $\Delta E^{\ddagger}$. In these calculations σ, $\Delta E^{\ddagger}$ and ΔH_c are taken to be constant, independent of temperature. Three experimentally determined points are included: (●) this study and Ref. [6]; (■) Rasmussen and MacKenzie, Ref. [4]; (▲) Dufour and Defay, Ref. [7].

ture independent and that $\Delta C_p = 0$, i.e., $|\Delta H_c| = |\Delta H_f|$. However, the sensitivity of $J(T)$ on the numerical values of the parameters is well demonstrated.

Beyond a certain limiting ΔT, it becomes impossible to measure J, at least for droplet dimensions that can be achieved by normal emulsification methods, so that the exact shape of the curve in Fig. 2 cannot be verified for pure water. However, by inserting the experimental or extrapolated values for ΔC_p, V_{water}, $\Delta G^{\ddagger}$ and $\sigma(T)$ into Eqn (1), we find that after reaching the maximum, $J(T)$ rapidly falls off as ΔT exceeds 42 K. This is due to the fact that $d(\Delta C_p)/dT$ and dV/dT appear to diverge at 228 K. Oguni and Angell have drawn attention to this anomalous behaviour which appears to be confined to liquid water and can be suppressed by the addition of solutes, e.g., 18% H_2O_2 [21].

Angell has investigated these rather startling divergences of physical properties. It appears that the effect of pressure on T_h is closely paralleled by its effect on T_s, the temperature at which heat capacity, compressibility and coefficient of expansion appear to diverge, such that $(T_h - T_s) \simeq 5$ K [3]. There is as yet no convincing interpretation for this behaviour which resembles a critical type phenomenon or a spinodal instability [22, 23]. Whatever its origin, at temperatures $< T_s$ there would be no barrier to cluster growth, so that $\Delta G_t^0 \rightarrow 0$ and the classical theory of stepwise cluster growth can no longer be applicable. We conclude that for pure water, as distinct from concentrated aqueous solutions, the homogeneous nucleation of ice is adequately described by Eqn (1), but only within the limits $0 < \Delta T$ K < 45. An alternative, but less likely explanation is that the short extrapolation of the various physical properties down to T_s is unreliable, but this would call into question the existence of the spinodal instability which seems well established.

Since water does indeed freeze at temperatures below T_s, it is necessary to search for another mechanism of nucleation, possibly involving large-scale fluctuations of the type first described by Frenkel (heterophase fluctuations) [24]. The existence of long-range correlations in undercooled water has been established by small-angle neutron-scattering measurements [25].

AQUEOUS SOLUTIONS

The presence of a solute, especially one with a high molecular weight and a low diffusion coefficient, will markedly affect the nucleation of ice. We here report results on ice nucleation in 25% aqueous oxyhaemoglobin (HbO_2) solutions which are of particular interest because they correspond to the HbO_2 concentration in red blood cells, the low-temperature behaviour of which we are currently studying in some detail. The experimental details have already been described [17, 26]. Figure 4 shows the measured nucleation rates as a function of $[(\Delta T)^2 T^3]^{-1}$, see Eqn (1). Also shown are some corresponding results for polyethylene glycol 400 (PEG) [6], hydroxyethyl starch (HES) [18] and a 9.7 mol per cent solution of LiCl [27].

In the absence of any knowledge of the relevant physical properties of such solutions at subfreezing temperatures, the experimental results can only be discussed in qualitative terms. In general, $J(T)$ is reduced by solutes because (1) the volume fraction of water has been reduced. Such effect is likely to be small, because even when $\phi_w = 0.5$, ln ϕ_w^2 is only -1.4; (2) the radius of the critical nucleus is increased and this may possibly be accompanied by a change in σ; (3) the value of $\Delta G^{\ddagger}$ to be employed relates to the slowest-diffusing species in the mixture. The diffusion coefficient of HbO_2 (at 293 K) in an infinitely-dilute solution is 7×10^{11} m^2 s^{-1}, smaller by a factor of 300 than that of water; (4) as a cluster grows, it becomes surrounded by a region impoverished in water, i.e., the chemical potential of water increases so that, quite apart from the potential barrier associated with a phase change, the crossing of a diffusion layer is an additional factor that retards nucleation. On the other hand, the anomalous divergence of the physical properties of water is suppressed by high solute concentrations, and much larger degrees of undercooling can be achieved than are possible in pure water.
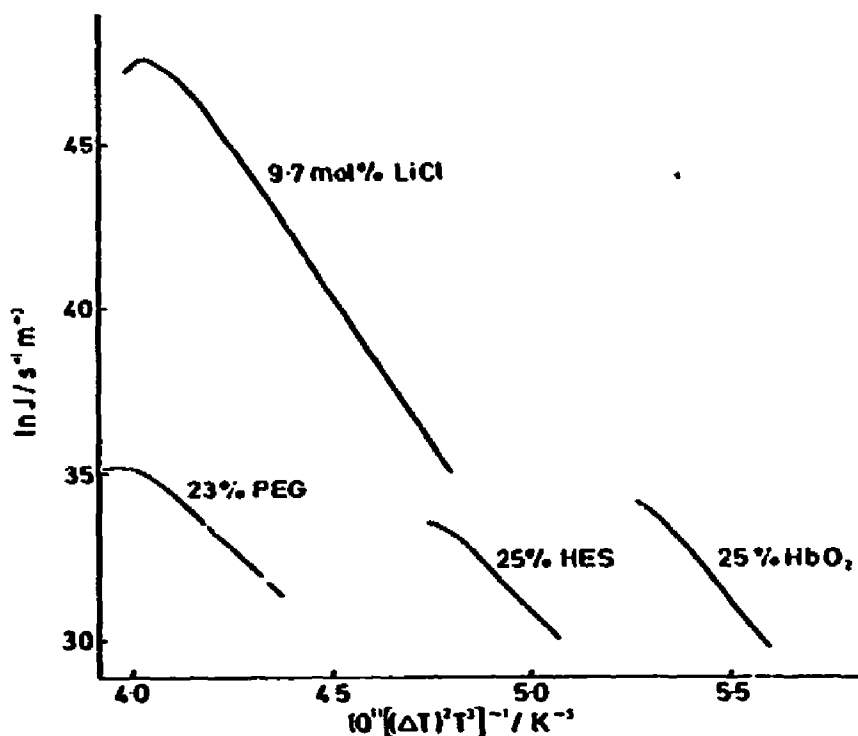

Fig. 4. Nucleation rate ln $J(T)$ plotted according to Eqn (1) for aqueous solutions of PEG [6], HES, HbO_2 (this study) and LiCl. In all cases J was determined by DSC. Note that for the solutions of the three polymers the relative degree of undercooling $\Delta T/T_0 \simeq 0.15$, whereas for the LiCl solution $\Delta T/T_0 \simeq 0.4$.

Michelmore and Franks were unable to observe any freezing during the cooling of a 37.5% solution of PEG [6]. This can be interpreted in terms of a very large $\Delta G^{\ddagger}$ which would depress the $J(T)$ curve below the minimum level at which freezing could be detected. When the sample was rewarmed, crystallization of PEG was observed, followed by a eutectic melting and a recrystallization and melting of ice, suggesting that nucleation of ice had indeed occurred during cooling. A quantitative evaluation of calorimetric data obtained at very low temperatures and with viscous solutions must be uncertain, because the basic assumption that crystal growth is rapid compared to nucleation is no longer valid. However, Kadiyala and Angell have demonstrated that such slowly freezing systems can provide valuable information about undercooling, nucleation and crystallization [27].

It is to be hoped that experimental data on aqueous solutions at subzero temperatures will become available which will make possible a better description of undercooled states and ice nucleation.

ACKNOWLEDGEMENTS

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