P_s	vapor pressure
q	pure-component area parameter
r	pure-component volume parameter
R	gas constant
T	temperature in Kelvin degrees
x	mole fraction in the liquid phase
y	mole fraction in the vapor phase
$\overline{\lvert\Delta y\rvert}$	absolute average deviation of vapor-phase composition
z	coordination number

Greek Letters

γ	activity coefficient
ϕ	segment fraction
Λ	parameter of Wilson equation
σ	mean standard deviation
τ	parameter of UNIQUAC equation
θ	area fraction

Subscripts

1	hydrocarbons
2	nitriles
i	index
exptl	experimental values
calcd	calculated values
W	value calculated with Wilson equation
U	value calculated with UNIQUAC equation

Exponent

∞	infinite dilution

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Density, Viscosity, and Surface Tension of Mixed Molten Hydrates. 2. Mixtures of Zinc Nitrate and Nickel Nitrate Hexahydrates

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Densities, viscosities, and surface tensions of mixtures containing $Zn(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ have been measured as a function of temperature and composition. The equivalent volume-composition and fluidity-composition isotherms were linear but the surface tension-composition isotherms exhibited appreciable negative deviations from the additive values, the deviations being the maximum around equimolar composition. The fluidity data were fitted to the equations $\phi = A_\phi T^{-1/2} \exp[-B_\phi/(T - T_{0,\phi})]$ and $\phi = A_\phi' \exp[-B_\phi'/(V - V_{0,\phi})]$ based upon the free volume model; A_ϕ, B_ϕ, $T_{0,\phi}$, A_ϕ', B_ϕ', and $V_{0,\phi}$ are empirical parameters. Composition dependences of these parameters have been discussed.

Introduction

Recently, quite a few reports concerning the physicochemical studies of hydrated melts in pure and mixed states have been published (*3*, *14*, *16*–*19*). Moynihan et al. (*21*) has shown that the system containing the molten tetrahydrates of calcium and cadmium nitrates behaves nearly ideal above 60 °C but considerable negative deviations in conductance and fluidity isotherms are observed at lower temperatures. A nonideal character of mixing the molten hydrates is also apparent from the studies of the system $Cr(NO_3)_3 \cdot 9H_2O + (Ca,Cd)(NO_3)_2 \cdot 4H_2O$ (*19*).

In order to examine whether such nonideal behavior is related to the polarizability, charge type, and/or the nature of the hydration sphere of the two constituent cations, we selected the present system containing the cations of the same charge to radius ratio and having a similar hydration sphere. The present paper thus presents some of the observations on the system containing the molten hydrates of zinc and nickel nitrate hexahydrate.

Experimental Section

Hexahydrates of nickel nitrate (BDH) and zinc nitrate (S. Merck) were of LR grade purity. The melting temperatures of these salts as determined by the cooling curve method were 56.8 and 36.8 °C for the nickel and zinc salt, respectively, with corresponding literature (*26*) values being 56.7 and 37 °C. An agreement between the measured melting temperatures and the literature melting temperatures leads one to believe that the salts were of the stoichiometry as given by the manufacturers. This was verified for zinc nitrate hexahydrate by an EDTA titration (*24*) and for nickel nitrate hexahydrate by a gravimetric (*24*) method by precipitating Ni^{2+} as dimethylglyoxime. Repeated cross checks gave the water content to be within ±0.02 of the stoichiometric value of six.

Mixtures were prepared by melting the requisite amounts of the salts in Pyrex glass flasks (ca. 100 cm^3) fitted with a airtight ground glass joint at the top and filtered in situ through glass filters (porosity G-3) under a slight positive pressure of dry, CO_2-free air. Filtered melts were then maintained at about 60–70 °C for about 1 h, for maturing.

Densities were measured by measuring the volumes of a certain amount of melt in a precalibrated densitometer capable of reading up to 0.01 cm^3. The details regarding the design and calibration of the densitometer and the measuring technique have been described earlier (*16*, *17*). Estimated accuracy of experimental densities is ±0.1%.

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Table I. Density/Equivalent Volume-Temperature Equations for $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ Mixtures

mol % $Ni(NO_3)_2 \cdot 6H_2O$	temp range, K	no. of data points	ρ (g cm^{-3}) = $a - b(T - 273.15)$				V_e (cm^3 equiv^{-1}) = $A + B(T - 273.15)$				$10^4\alpha$ (348 K), deg^{-1}
			a	10^3b	10^3SE^b	10^3MD^c	A	10^2B	SE	MD	
0.0[a]	312-353	7	1.8707	1.154	0.15	0.25	79.39	5.29	0.012	−0.015	6.27
9.70	303-349	8	1.8654	1.215	0.25	0.41	79.47	5.56	0.018	−0.026	6.66
22.45	307-347	7	1.8701	1.188	0.33	0.50	79.04	5.40	0.020	+0.028	6.49
27.97	309-349	8	1.8719	1.169	0.12	−0.18	78.86	5.30	0.008	−0.01	6.40
38.92	310-348	7	1.8688	1.153	0.20	0.36	78.80	5.22	0.013	−0.021	6.32
50.53	310-350	8	1.8684	1.087	0.27	−0.39	78.62	4.90	0.013	−0.017	5.95
58.79	320-352	6	1.8721	1.124	0.24	0.34	78.28	5.09	0.014	−0.020	6.19
70.48	312-351	7	1.8727	1.088	0.26	−0.36	78.08	4.87	0.016	+0.022	5.96
79.00	321-349	6	1.8725	1.050	0.07	−0.12	77.93	4.70	0.005	−0.007	5.77
91.19	319-349	6	1.8731	1.020	0.15	0.20	77.69	4.54	0.008	−0.009	5.60
100.00	322-349	6	1.8709	0.963	0.21	−0.22	77.63	4.28	0.011	−0.011	5.29

[a] Adopted from ref 18. [b] SE = standard error. [c] MD = mean deviation.

Table II. Surface Tension (σ) and Related Parameters of $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ Mixtures

mol % $Ni(NO_3)_2 \cdot 6H_2O$	temp range, K	σ (mN m^{-1}) = $a - bT$ (K)			$10^2(H^\sigma/A^\sigma)$, J m^{-2}	$10^4(S^\sigma/A^\sigma)$, J m^{-2} K^{-1}
		a	b	SE[a]		
0.0	312-350	128.83	0.111	0.27	12.88	1.11
9.7	313-347	144.44	0.1576	0.012	14.44	1.58
22.4	313-349	134.73	0.1351	0.046	13.47	1.35
28.0	314-348	135.13	0.1384	0.019	13.51	1.38
38.9	314-350	128.26	0.1235	0.250	12.83	1.23
50.5	315-352	122.30	0.1100	0.129	12.23	1.10
58.8	323-351	124.32	0.1040	0.084	12.43	1.04
70.5	320-349	124.37	0.1017	0.013	12.44	1.02
79.0	331-349	123.38	0.0928	0.087	12.34	0.93
91.2	331-349	125.62	0.0968	0.070	12.56	0.97
100.0	323-350	136.22	0.1260	0.002	13.62	1.26

[a] SE = standard error.

Viscosities were measured with Cannon-Fenske type viscometers, calibrated with aqueous solutions of sucrose and glycerol (*18*); the viscometer constants were 0.2009 and 0.2647 cP s^{-1}. Inherent accuracy of these measurements is estimated to be ±0.5%.

Surface tensions were measured by the differential capillary rise method described in detail earlier (*18*). Under the conditions of thermal equilibrium, the temperature did not vary by more than ±0.1 °C over the region of interest. The difference in the levels of the liquid in the two capillaries was measured with a precision of ±0.001 cm. Measured surface tensions are estimated to be accurate to ±0.3%. In all measurements the temperatures were controlled and measured with a precision of ±0.1 °C.

Results and Discussion

Densities and Equivalent Volumes. The density results for various mixtures of the $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ system were expressed in the form of linear density (ρ)-temperature and equivalent volume (V_e)-temperature equations and are presented in Table I. The maximum departure of any experimental point from the least-squares straight line and the expansivity ($\alpha = (1/V_e)(dV_e/dT)$) for each composition are also included in Table I. A typical equivalent volume-composition (mole percent of nickel nitrate hexahydrate) isotherm at 75 °C is shown in Figure 1. The volumes are found to be additive over the entire composition range. The extrapolated value for the equivalent volume of $Zn(NO_3)_2 \cdot 6H_2O$ at 75 °C, estimated from the present data, is 83.75 cm^3 equiv^{-1}. This can be very favorably compared to the value 83.36 cm^3 equiv^{-1} obtained from the direct measurements (*18*).

Surface Tension. For all mixtures, surface tension (σ) varied linearly with temperature. These σ–T equations are presented in Table II. The surface tensions and their temperature coefficients are comparable to that for aqueous solutions of electrolytes. This leads to the belief that the surface tension of these liquids is governed by the electrostricted dipoles of water.

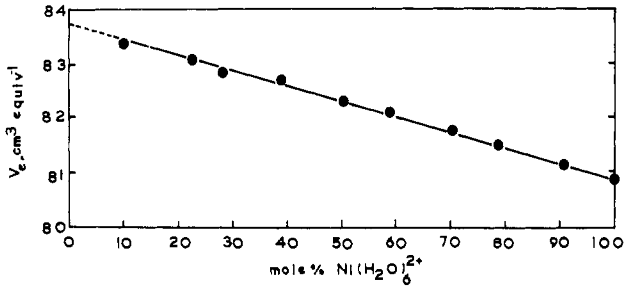

Figure 1. Variation of equivalent volume of $Ni(NO_3)_2 \cdot 6H_2O$ + $Zn(NO_3)_2 \cdot 6H_2O$ mixtures with mole percent of $Ni(NO_3)_2 \cdot 6H_2O$ at 75 °C.

The surface tension of a liquid is defined (*9*) as its surface free energy per unit area, i.e.

$$\sigma = G^\sigma / A^\sigma \qquad (1)$$

where A^σ is the area of the surface. The surface entropy per unit area (S^σ/A^σ) and the surface enthalpy per unit area (H^σ/A^σ) are then described as

$$S^\sigma / A^\sigma = -d\sigma/dT \qquad (2)$$

$$H^\sigma / A^\sigma = \sigma - T(d\sigma/dT) \qquad (3)$$

As the temperature coefficient of surface tension for these mixtures is constant, the H^σ/A^σ is a constant and independent of temperature. Table II lists the values of H^σ/A^σ and S^σ/A^σ for all the mixtures investigated in this study. The magnitude of H^σ/A^σ appears to place these molten hydrates between highly ionized molten salts and the nonpolar liquids; the magnitude for this parameter usually lies around 0.2 J m^{-2} for the former and 0.05 J m^{-2} for the latter class of liquids. The variation of surface tension at 350 K with the mole percent of $Ni(NO_3)_2 \cdot 6H_2O$ is shown in Figure 2. The negative deviations and the occurrence

Table III. Parameters for the Least-Square Fit of the Fluidity-Temperature Data of $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ Mixtures

mol % $Ni(NO_3)_2 \cdot 6H_2O$	temp range, K	no. of data points	ϕ (cP^{-1}) $= A_\phi T^{-1/2} \exp[-B_\phi/(T - T_{0,\phi})]$				ϕ (cP^{-1}) $= A_\phi' T^{-1/2} \exp[-675/(T - T_{0,\phi})]$			
			A_ϕ	B_ϕ	$T_{0,\phi}$	10^3SE[b]	A_ϕ'	$T_{0,\phi}$	10^3SE[b]	T_g,[c] K
0.0[a]	302–353	9	142.58	638.43	183.60	0.44	161.99	179.66	0.54	197
9.7	303–349	8	117.98	593.92	188.98	0.46	157.72	180.16	0.64	
22.4	307–347	7	152.16	682.55	181.43	0.12	148.23	182.22	0.12	
28.0	305–349	8	151.05	689.95	181.00	0.24	143.41	182.56	0.23	
38.9	310–348	7	130.30	659.05	185.97	0.13	137.78	184.27	0.12	
50.5	310–350	8	169.33	782.29	172.82	0.18	118.36	183.78	0.19	
58.8	311–352	8	149.74	746.39	178.97	0.18	117.38	186.28	0.19	
70.5	316–351	8	84.50	607.74	194.32	0.32	107.13	186.94	0.33	
79.0	320–349	6	94.75	675.07	188.34	0.10	94.72	188.34	0.10	
91.2	319–349	6	74.79	639.93	194.58	0.15	84.72	190.85	0.16	
100.0	327–355	5	1957.03	1950.07	91.23	0.31	78.58	193.72	0.53	210

[a] Adopted from ref 18. [b] SE = standard error. [c] Estimated from ref 8.

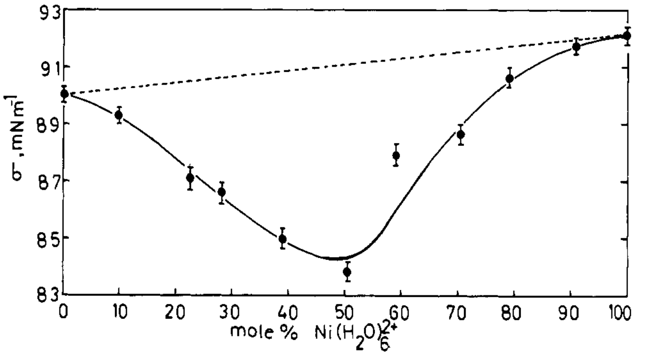

Figure 2. Variation of surface tension (σ) (at 350 K) for $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ mixtures, with mole percent of nickel nitrate hexahydrate.

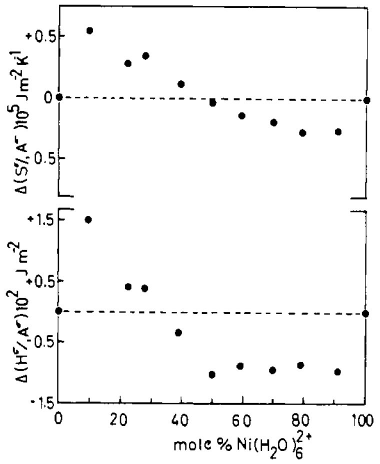

Figure 3. Variation of surface enthalpy and surface entropy of mixing per unit area, with composition (mol % $Ni(NO_3)_2 \cdot 6H_2O$) for $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ mixtures.

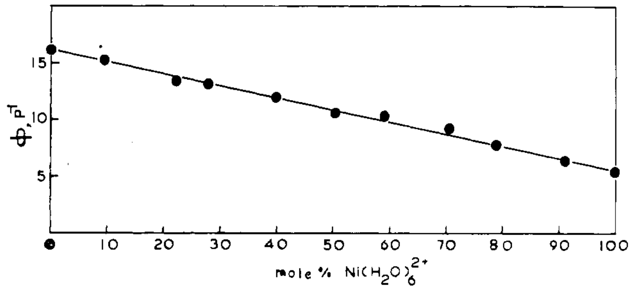

Figure 4. Fluidity (at 75 °C) vs. mole percent of $Ni(NO_3)_2 \cdot 6H_2O$ plot for $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ mixtures.

of minima around 50 mol % of the nickel salt give this plot a considerable significance. Apparently similar isotherms have also been observed (*19*) for $Cr(NO_3)_3 \cdot 9H_2O + (Ca,Cd)(NO_3)_2 \cdot 4H_2O$ systems, where the minima are observed around 30 mol % of divalent ion hydrate. These results when taken together indicate that the position of the minima in σ-composition isotherms may be a reflection of either the nature of the hydration sphere or charge type of the component cations of the system. According to Bloom et al. (*9*), the deviations in surface tension values from ideal behavior values can be explained in terms of surface enthlapy and surface entropy of mixing per unit area, given by

$$\Delta(H^\sigma/A^\sigma) = (H^\sigma/A^\sigma) - \{X_1(H^\sigma/A^\sigma)_1 + X_2(H^\sigma/A^\sigma)_2\} \quad (4)$$

$$\Delta(S^\sigma/A^\sigma) = (S^\sigma/A^\sigma) - \{X_1(S^\sigma/A^\sigma)_1 + X_2(S^\sigma/A^\sigma)_2\} \quad (5)$$

where (H^σ/A^σ) and (S^σ/A^σ) are the surface enthalpy and surface entropy per unit area for the mixture and the quantities with the subscript 1 and 2 refer to those of pure components; these were evaluated through relations 2 and 3. The variation of $\Delta(H^\sigma/A^\sigma)$ and $\Delta(S^\sigma/A^\sigma)$ values with the composition of the mixture is presented in Figure 3. The small positive surface enthalpy and entropy of mixing per unit area for solutions rich in zinc nitrate could be due to a loosening of the cation–water dipole bonding, resulting because of competition between water and NO_3^- for occupying a site next to the cation. Negative values of $\Delta(H^\sigma/A^\sigma)$ and $\Delta(S^\sigma/A^\sigma)$ for melts richer in nickel nitrate hexahydrate can then be considered a reflection of some ordering tendencies resulting from the difference in the strength of ion–dipole interactions for the two cations.

Fluidity. The variation of fluidity of the system $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ with the composition at 75 °C is shown in Figure 4. The system behaves ideally with respect to flow characteristics. The ln ϕ vs. T^{-1} plots (not given) showed slight curvature in a direction corresponding to an increase in the apparent activation energy with decreasing temperatures. Such non-Arrhenius behavior exhibited by concentrated electrolyte solutions in the fluidity range of 10^{-1}–10 P^{-1} has frequently been interpreted in terms of the Vogel-Tammann-Fulcher (*12*, *23*, *25*) equation

$$\phi = A_\phi T^{-1/2} \exp[-B_\phi/(T - T_{0,\phi})] \quad (6)$$

where, A_ϕ, B_ϕ, and $T_{0,\phi}$ are constants. The parameter $T_{0,\phi}$ has been interpreted as the zero mobility temperature at which free volume (*10*) or the configurational entropy (*1*) becomes zero. The fluidity data obtained in this study were processed on a IBM 360/44 data processing system to fit into eq 6 by an iterative method. Refinement in the values of the parameters A_ϕ, B_ϕ, and $T_{0,\phi}$ were carried out till the two successive values of these parameters did not differ by more than ±0.01. In Table III are recorded the parameters A_ϕ, B_ϕ, and $T_{0,\phi}$ obtained from the least-squares fit of the fluidity data. Inspection of the best fit parameters does not reveal any systematic trends in A_ϕ, B_ϕ,

Table IV. Least-Square Fits of the Fluidity-Molar Volume Data for $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ Mixtures

		ϕ (P^{-1}) = $A_\phi' \exp[-B_\phi'/(V - V_{0,\phi})]$					
mol % $Ni(NO_3)_2 \cdot 6H_2O$	temp range, K	A_ϕ', P^{-1}	B_ϕ', $cm^3\ mol^{-1}$	$V_{0,\phi}$, $cm^3\ mol^{-1}$	10^2SE^a	$V_{0,extrap}$, $cm^3\ mol^{-1}$	γ
0.0	302-353	540.70	59.56	149.85	0.37	148.93	0.397
9.7	303-349	454.35	58.30	150.14	0.44	148.62	0.389
22.4	307-347	571.38	65.11	148.75	0.17	148.28	0.438
28.0	305-349	567.58	64.69	148.52	0.22	148.14	0.436
38.9	310-348	491.78	60.91	149.03	0.16	148.34	0.408
50.5	310-350	620.33	67.83	147.95	0.37	148.50	0.459
58.8	311-352	553.13	67.36	147.53	0.31	147.74	0.456
70.5	316-351	320.92	52.20	148.93	0.66	147.78	0.352
79.0	320-349	353.92	56.15	148.37	0.19	147.90	0.378
91.2	319-349	284.22	51.60	148.69	0.29	147.92	0.347
100.0	327-355	5608.34	188.67	136.39	0.61	148.48	

[a] SE = standard error.

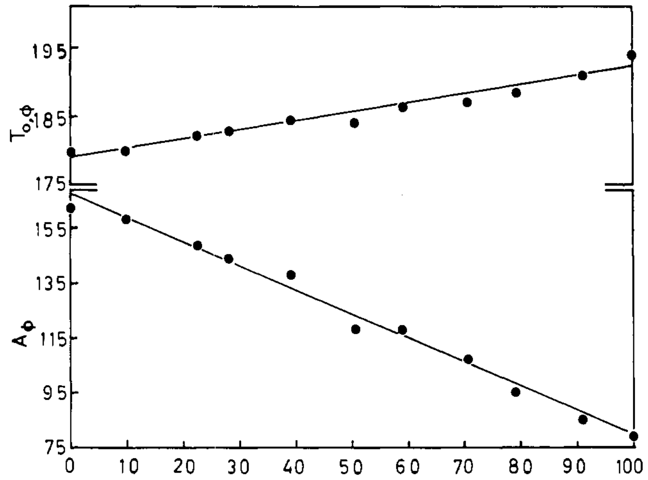

Figure 5. Variations of parameters A_ϕ and $T_{0,\phi}$ (eq 6) with mol % of $Ni(NO_3)_2 \cdot 6H_2O$ for $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ mixtures.

and $T_{0,\phi}$ values. This might be a reflection of a strong interdependence of these parameters, so that if the data do not cover a reasonably extensive range in the magnitude of fluidity values, the system can be described equally well by a number of different A_ϕ-B_ϕ-$T_{0,\phi}$ sets. To investigate if there existed any significant composition dependence of A_ϕ and $T_{0,\phi}$, we assumed that the value of B_ϕ, the exponential coefficient in eq 6, is independent of composition as observed for a large variety of fused nitrates and chlorides (*2-6*, *20*). The fluidity data were processed to fit eq 6 at a constant value of 675 K for B_ϕ (cf. Moynihan et al. (*21*) and Jain (*19*)) without much loss of precision of the fit. The computed parameters are presented in Table III. The estimated $T_{0,\phi}$ values for pure salts lie about 16-17 °C below the experimentally determined glass transition temperatures (*8*). Lower T_0 (or T_g) values for $Zn(NO_3)_2 \cdot 6H_2O$ relative to $Ni(NO_3)_2 \cdot 6H_2O$ and a systematic variation of $T_{0,\phi}$ with the composition of the melt (Figure 5) across the composition range could be rationalized (*7*) in terms of $m^{-1/2}$ dependence of T_g (hence T_0) on the effective masses of the component particles of the amorphous phase and also r^{-1} dependence of T_0 (hence T_g) on cation radii. Rao et al. (*22*), however, ascribed this lowering in T_0 values to the presence of more covalent character in metal-nitrate ion bonding in the case of more polarizable cations, it being Zn^{2+} in this case.

The values of the preexponential coefficient, A_ϕ, systematically decrease (Figure 5) in going from zinc nitrate to nickel nitrate hexahydrate, indicating a direct dependence of A_ϕ's on the cationic mass, a trend in the reverse direction to that predicted by the theory (*10*). Similar observations, have also been made by Moynihan et al. (*21*) and Jain (*19*). The interesting observation at this stage is that the preexponential factor, A_ϕ, goes almost parallel to the thermal expansivity (α) of the medium, thereby indicating that the parameter A_ϕ is related to the rigidity of the medium.

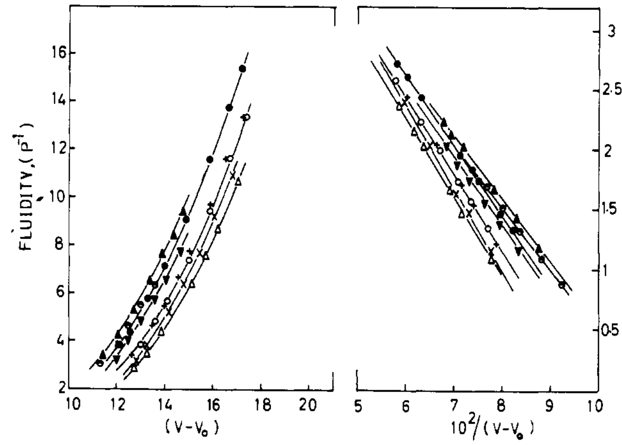

Figure 6. Fluidity vs. ($V - V_{0,\phi}$) and log (fluidity) vs. $(V - V_{0,\phi})^{-1}$ plots for $Zn(NO_3)_2 \cdot 6H_2O$ + $Ni(NO_3)_2 \cdot 6H_2O$ mixtures: (●) 9.7, (○) 22.4, (+) 28.0, (×) 50.5, (△) 58.8, (▲) 70.5, (▼) 79.0, and (◒) 91.2 mol % of $Ni(NO_3)_2 \cdot 6H_2O$.

The discrepancy between theory and the experiment has also been explained (*21*) by postulating that the composition dependence of A_ϕ's may be related to the differences in the lability of the water or nitrate ion in the coordination shell of the cations.

Doolittle (*11*) and Williams, Landel, and Ferry (*27*) have empirically shown that the viscosity can be related to the free volume in a liquid, by the relation

$$\eta = A \exp(BV_0/V_f) \tag{7}$$

where V_f is the free volume and V_0 the closed packed molecular volume and A and B are the constants. Cohen and Turnbull (*10*) placed this expression on a solid theoretical basis by deriving eq 7 under the considerations of "hard-sphere" model for liquids. Recently, Doolittle's equation in the form

$$\phi = A_\phi' \exp[-B_\phi'/(V - V_{0,\phi})] \tag{8}$$

was found to hold good for describing the temperature dependence of transport properties of certain glass-forming anhydrous (*15*) and hydrated melts (*14*, *19*), the terms A_ϕ' and B_ϕ' being empirical parameters, V the volume per mole of the salt at any temperature, and $V_{0,\phi}$ the intrinsic volume, i.e., the molar volume at $T_{0,\phi}$. Hildebrand (*13*) proposed the equation

$$\phi = B(V - V_0)/V_0 \tag{9}$$

to describe the dependence of fluidity on the free volume in the liquid. Plots of fluidity vs. ($V - V_0$) tend to be nonlinear (Figure 6) indicating the inadequacy of the Hildebrand equation for de-

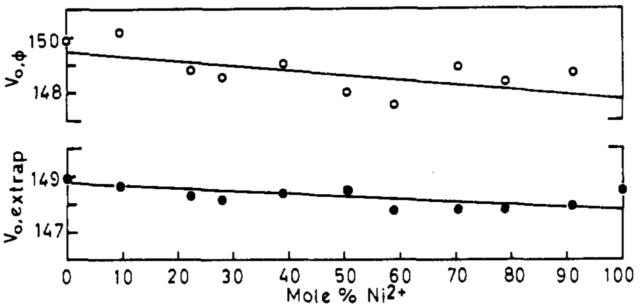

Figure 7. The variation of intrinsic volume, $V_{0,\phi}$ (○), and the molar volume at T_0 (K), $V_{0,\mathrm{extrap}}$ (●), for $Zn(NO_3)_2 \cdot 6H_2O + Ni(NO_3)_2 \cdot 6H_2O$ mixtures, with the mole percent of nickel nitrate hexahydrate.

scribing the dependence of fluidity on the free volume for the system investigated in this study. To test the relevance of the Doolittle equation, we fitted the present fluidity data into eq 8 by an *iterative* method as described above. The "best fit" parameters are listed in Table IV. Linear plots obtained when ln ϕ is plotted against $(V - V_{0,\phi})^{-1}$ (Figure 6) demonstrate the success of eq 8 in describing the free volume dependence of fluidity in the systems investigated presently. $V_{0,\phi}$ is shown as a function of composition in Figure 7. It is interesting to note that the V_0's obtained by extrapolating the equations

$$V = \alpha + \beta(T - 273.15) \qquad (10)$$

to $T_{0,\phi}$ (K) are nearly equal to those obtained from the least-squares fit of the fluidity-molar volume data. This recognizes the view that free volume becomes zero at $T_{0,\phi}$ (K) and not 0 K. A poorer agreement between $V_{0,\phi}$ and $V_{0,\mathrm{extrap}}$ for $Ni(NO_3)_2 \cdot 6H_2O$ may be due to the smaller temperature range of investigation for this salt. The parameters $V_{0,\phi}$ and $V_{0,\mathrm{extrap}}$ may be considered to vary linearly (±1%) with composition. The interesting fact which emerges out from this analysis is that V_0's for the two salts are nearly equal, despite a sizable difference in their isothermal molar volumes. This appears to be a direct reflection of the differences in the α values and the temperature range ($= T - T_{0,\phi}$) over which the extrapolation is made.

The exponential coefficient (B_{ϕ}'), according to the "hard sphere" model (*10*) equals the product $\gamma V_{0,\phi}$, γ being a geometric factor to correct for the overlap of free volume in the calculation of probability of occurrence of a critical void. The computed values of γ(0.34–0.46) are considerably lower than the value 0.5–1 required by theory (*10*). This indicates that a random distribution of free volume is apparently not obtained in these systems.

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