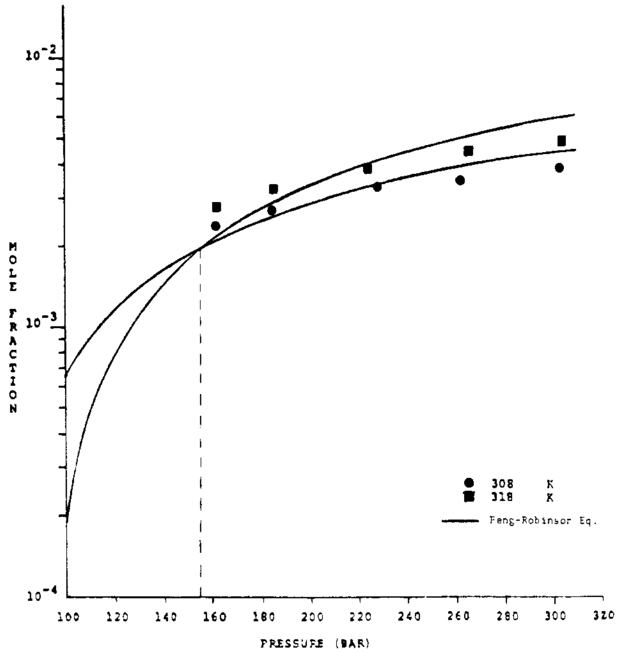

Figure 4. Solubility isotherms of 1,10-decanediol from a solid mixture of benzoic acid and 1,10-decanediol in supercritical carbon dioxide.

an average of 3.8%. In summation, the Peng–Robinson equation of state provides a reasonable correlation of the benzoic acid and 1,10-decanediol solubilities at 308 K. The correlation at 318 K is not as good but is still acceptable.

Glossary

a_i	parameter in equation of state, component i
A	parameter in equation of state
b_i	parameter in equation of state, component i
B	parameter in equation of state
k_{ij}	binary interaction parameter, components, i–j
P	pressure
T	temperature
V_i^s	solid-phase molar volume, component i
y_i	gas-phase mole fraction, component i
Z	compressibility factor

Greek Letters

ϕ	fugacity coefficient, component i

Subscripts

vp	vapor pressure

Registry No. CO_2, 124-38-9; 1,10-decanediol, 112-47-0; benzoic acid, 65-85-0.

Literature Cited

(1) Van Gunst, C. A., Dissertation, Delft, 1950.
(2) Kurnik, R. T.; Reid, R. C. *Fluid Phase Equilib.* **1982**, *8*, 93–105.
(3) Kurnik, R. T.; Holla, S. J.; Reid, R. C. *J. Chem. Eng. Data* **1981**, *26*, 47–51.
(4) Tsekhanskaya, Yu V.; Iometev, M. B.; Mushkina, E. V. *Russ. J. Phys. Chem.* **1964**, *38*, 1173–6.
(5) Pennisi, K. P.; M.S. Thesis, University of Rochester, Rochester, NY, 1985.
(6) Peng, D. Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
(7) Prausnitz, J. M. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969; Chapter 5.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw Hill: New York, 1977; pp 12–19.
(9) Parks, G. S.; Mosher, H. P. *J. Chem. Phys.* **1962**, *37*, 919–20.
(10) Kurnik, R. T. Sc.D. Dissertation, MIT, Cambridge, MA, 1981.

Received for review April 15, 1985. Revised manuscript received August 21, 1985. Accepted January 29, 1986. Autoclave Engineers, Inc., is gratefully acknowledged for supporting this work with an equipment grant.

Volumetric Properties of Molten Hydrated Salts. 7. Mixtures of Ferric Nitrate Nonahydrate with Hydrates of Calcium, Cadmium, Zinc, and Magnesium Nitrates

K. Venkata Ramana, Ramesh C. Sharma,† and Harish C. Gaur*
Centre of Advanced Study, Department of Chemistry, University of Delhi, Delhi 110 007

Volumetric behavior of molten mixtures of ferric nitrate nonahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates has been studied at different temperatures and compositions by using a manometric densimeter. Density and molar volumes varied linearly with composition. Molar volumes were additive except for Mg^{2+} mixtures. Variations of thermal expansion coefficient and molar expansivity have been discussed in terms of changes in hydration of Fe^{3+} ions and the van der Waals volume.

Introduction

In continuation of our studies on the behavior of molten hydrated salts and mixtures (*1–6*), volumetric behavior of mixtures of molten ferric nitrate nonahydrate with hydrates of calcium, cadmium, zinc, and magnesium nitrates are reported.

Experimental Section

Salts were of AnalaR (BDH) grade or equivalent purity. The number of moles of water per mole of the electrolyte (R), determined by volumetric titration using EDTA, was found with a precision of ±0.01 mol/mol of cation. For the samples used, R was 9.08 for ferric nitrate, 4.12 for calcium nitrate, 4.15 for cadmium nitrate, 6.22 for zinc nitrate, and 6.02 for magnesium nitrate. Calibration of densimeter, dilation correction, sample preparation, etc. have been described earlier (*1*). Temperature was controlled and known with a precision of ±0.05 °C.

Results and Discussion

Densities (ρ) of different binary mixtures were measured over a range of composition limited by solubility and at temperatures ranging between 288.2 and 353.2 K at ca. 5-deg intervals (Table I) in both heating and cooling cycles. The data in different sets were reproducible within ±0.0003 g cm^{-3}. Molar volumes were calculated by using mean molecular mass (M) of the mixture. Densities and molar volumes varied linearly with

---

† Present address: Department of Chemistry, Delhi College of Engineering, Delhi 110 006.

0021-9568/86/1731-0288$01.50/0 © 1986 American Chemical Society

Table I. Density and Molar Volume Data of $Fe(NO_3)_3 \cdot 9.08H_2O + M(NO_3)_2 \cdot RH_2O$ Systems

mole fractn $M(NO_3)_2 \cdot RH_2O$	temp, K	density, g cm^{-3}
$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 4.12H_2O$		
0.0000	293.2	1.6953
	298.7	1.6893
	303.2	1.6848
	313.2	1.6741
	323.2	1.6635
	333.2	1.6526
	343.2	1.6416
	353.2	1.6307
0.0995	288.2	1.7104
	293.7	1.7052
	303.2	1.6959
	313.2	1.6854
	323.2	1.6747
	333.2	1.6641
	343.2	1.6531
	353.2	1.6422
0.1991	293.2	1.7040
	303.2	1.6939
	313.2	1.6843
	323.2	1.6739
	333.2	1.6633
	343.2	1.6525
	353.2	1.6424
0.3988	293.2	1.7164
	303.2	1.7069
	313.2	1.6973
	323.2	1.6874
	333.2	1.6777
	343.2	1.6678
	353.2	1.6575
0.5987	293.2	1.7238
	303.2	1.7152
	313.2	1.7063
	323.2	1.6969
	333.2	1.6878
	343.2	1.6785
	353.2	1.6692
0.7987	293.2	1.7350
	303.2	1.7265
	313.2	1.7180
	323.2	1.7093
	333.2	1.7006
	343.2	1.6919
	353.2	1.6834
0.8988	293.2	1.7370
	303.2	1.7289
	313.2	1.7210
	323.2	1.7128
	333.2	1.7047
	343.2	1.6966
	353.2	1.6885
1.0000	303.2	1.7332
	308.2	1.7294
	313.2	1.7256
	323.2	1.7177
	333.2	1.7094
	343.2	1.7023
	353.2	1.6949
$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.15H_2O$		
0.0995	298.2	1.7379
	303.2	1.7328
	313.2	1.7220
	323.2	1.7112
	333.2	1.7000
	343.2	1.6888
	353.2	1.6775
0.1994	298.2	1.7759
	303.2	1.7707
	313.2	1.7604
	323.2	1.7492
	333.2	1.7380
	343.2	1.7272
	353.2	1.7162
0.3970	298.2	1.8649
	303.2	1.8598
	313.2	1.8485
	323.2	1.8375
	333.2	1.8264
	343.2	1.8156
	353.2	1.8044
0.5962	298.2	1.9723
	303.2	1.9667
	313.2	1.9556
	323.2	1.9448
	333.2	1.9344
	343.2	1.9235
	353.2	1.9124
0.7979	298.2	2.0931
	303.2	2.0876
	313.2	2.0766
	323.2	2.0658
	333.2	2.0549
	343.2	2.0443
	353.2	2.0334
0.8991	298.2	2.1902
	303.2	2.1850
	313.2	2.1741
	323.2	2.1630
	333.2	2.1519
	343.2	2.1412
	353.2	2.1307
1.0000	298.2	2.2898
	303.2	2.2842
	313.2	2.2731
	323.2	2.2622
	333.2	2.2515
	343.2	2.2405
	353.2	2.2300
$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.22H_2O$		
0.0985	303.2	1.7195
	308.2	1.1742
	313.2	1.7090
	323.2	1.6982
	333.2	1.6872
	343.2	1.6761
	353.2	1.6652
0.1994	303.2	1.7278
	308.2	1.7224
	313.2	1.7169
	323.2	1.7056
	333.2	1.6952
	343.2	1.6843
	353.2	1.6732
0.2971	303.2	1.7388
	308.2	1.7336
	313.2	1.7281
	323.2	1.7171
	333.2	1.7060
	343.2	1.6949
	353.2	1.6843
0.4006	303.2	1.7465
	308.2	1.7408
	313.2	1.7353
	323.2	1.7246
	333.2	1.7134
	343.2	1.7026
	353.2	1.6921
0.5949	303.2	1.7666
	308.2	1.7613
	313.2	1.7557
	323.2	1.7450
	333.2	1.7346
	343.2	1.7239
	353.2	1.7132
0.7985	308.2	1.7948
	313.2	1.7894
	318.2	1.7845
	323.2	1.7787
	333.2	1.7680
	343.2	1.7572
	353.2	1.7468
0.8971	303.2	1.8148
	308.2	1.8094
	313.2	1.8038
	323.2	1.7932
	333.2	1.7827
	343.2	1.7723
	353.2	1.7623
1.0000	308.2	1.8273
	313.2	1.8220
	318.2	1.8165
	323.2	1.8110
	333.2	1.8001
	343.2	1.7900
	353.2	1.7792
$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$		
0.1060	298.2	1.6968
	303.2	1.6916
	313.2	1.6813
	323.2	1.6705
	333.2	1.6597
	343.2	1.6488
	353.2	1.6382
0.1964	308.2	1.6798
	313.2	1.6745
	323.2	1.6639
	328.2	1.6590
	333.2	1.6532
	338.2	1.6481
	343.2	1.6429
	353.2	1.6325
0.4015	333.2	1.6371
	338.2	1.6326
	343.2	1.6273
	348.2	1.6229
	343.2	1.6173

temperature. The data were least-squares fitted, using IBM 360/44 data processing system, into an equation of the type

$$\rho,\ V = A \mp B(T - 300) \qquad (1)$$

Parameters A and B, which are characteristic of a given composition, and standard deviations of the fit are given in Table II.

At a given temperature, the molar volume of the mixture, V, decreases with increase in composition of the hydrated divalent cation (Figure 1). It has been suggested (*7*) that the water of hydration in molten hydrated salts is retained by cations forming weak field hydrated cations of type $M(H_2O)_n{}^{m+}$. Addition of hydrated M^{2+} (where M = Ca, Cd, Zn, and Mg) to $Fe(NO_3)_3 \cdot 9H_2O$ results in preferential orientation of $NO_3{}^-$ ions toward $Fe(H_2O)_n{}^{3+}$, because of its higher cationic potential leading to the formation of solvent-separated ion pairs (SSIP) and displacement of some of the lattice water from hydration sphere of Fe^{3+} ions. This leads to increased packing density and hence a decrease in molar volume with increase in X, as

Table II. Least-Squares Equations of Density and Molar Volume Data of $Fe(NO_3)_3 \bullet 9.08H_2O$ + $M(NO_3)_2 \bullet RH_2O$ Systems

mole fractn $M(NO_3)_2 \cdot RH_2O$		$\rho = A - B(T - 300)$, g cm^{-3}			$V = A' + B'(T - 300)$, cm^3 mol^{-1}			$10^4\alpha$,[a] K^{-1}	$10V_E$, cm^3 deg^{-1}
		A	10^3B	10^3SE	A'	$10B'$	10SE		
$M(NO_3)_2 \cdot RH_2O = Ca(NO_3)_2 \cdot 4.12H_2O$									
0.0000	293–353	1.7169	1.0753	0.22	240.074	1.5747	0.71	6.26	1.575
0.0995	288–353	1.7269	1.0527	0.54	228.801	1.4548	0.05	6.09	1.455
0.1991	293–353	1.7250	1.0307	0.40	219.166	1.3700	0.84	5.97	1.370
0.3988	293–353	1.7363	0.9803	0.26	198.036	1.1678	0.58	5.64	1.168
0.5987	293–353	1.7424	0.9132	0.27	177.682	0.9689	0.46	5.24	0.969
0.7987	293–353	1.7523	0.8621	0.09	157.209	0.8028	0.19	4.91	0.803
0.8988	293–353	1.7532	0.8086	0.06	147.346	0.7035	0.20	4.61	0.704
1.0000	303–353	1.7563	0.7717	0.32	137.252	0.6248	0.28	4.39	0.625
$M(NO_3)_2 \cdot RH_2O = Cd(NO_3)_2 \cdot 4.15\ H_2O$									
0.0995	298–353	1.7658	1.0996	0.31	228.005	1.4919	0.76	6.22	1.492
0.1994	298–353	1.8035	1.0893	0.29	217.837	1.3794	0.59	6.03	1.379
0.3970	298–353	1.8923	1.0972	0.12	197.505	1.1992	0.35	5.79	1.199
0.5962	298–353	1.9992	1.0838	0.21	177.252	1.0033	0.22	5.42	1.003
0.7979	298–353	2.1200	1.0843	0.11	157.937	0.8423	0.08	5.11	0.842
0.8991	298–353	2.2175	1.0880	0.21	146.564	0.7796	0.14	4.90	0.779
1.0000	298–353	2.3167	1.0879	0.19	136.071	0.6622	0.06	4.69	0.662
$M(NO_3)_2 \cdot RH_2O = Zn(NO_3)_2 \cdot 6.22H_2O$									
0.0985	303–353	1.7523	1.0881	0.18	229.211	1.4995	0.50	6.20	1.499
0.1994	303–353	1.7604	1.0901	0.19	222.087	1.4482	0.31	6.19	1.448
0.2971	303–353	1.7718	1.0962	0.15	214.832	1.3993	0.33	6.18	1.399
0.4006	303–353	1.7789	1.0884	0.19	207.786	1.3390	0.16	6.11	1.339
0.5949	303–353	1.7985	1.0664	0.13	194.009	1.2099	0.22	5.92	1.209
0.7985	308–353	1.8323	1.0709	0.20	178.638	1.1016	0.23	5.84	1.102
0.8971	303–353	1.8460	1.0517	0.29	171.622	1.0255	0.14	5.69	1.026
1.0000	308–353	1.8645	1.0685	0.22	164.092	0.9899	0.17	5.73	0.989
$M(NO_3)_2 \cdot RH_2O = Mg(NO_3)_2 \cdot 6.02H_2O$									
0.1060	298–353	1.7237	1.0683	0.20	229.777	1.4947	0.55	6.19	1.495
0.1964	308–353	1.7166	1.0527	0.16	222.695	1.4422	0.24	6.13	1.442
0.4015	333–353	1.6964	0.9860	0.33	206.820	1.2860	0.44	5.81	1.286

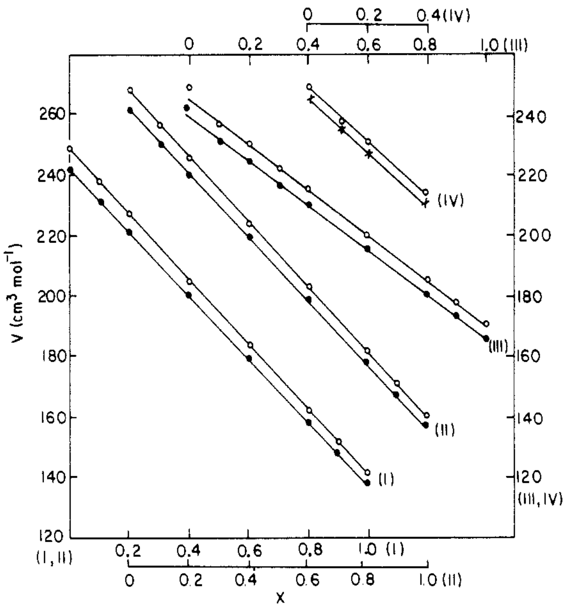

Figure 1. Isotherms of molar volumes (V) vs. mole fraction of divalent cation (X) for $Fe(NO_3)_3 \cdot 9.08\ H_2O + M(NO_3)_2 \cdot RH_2O$ systems at (●) 303, (×) 313, (○) 353 K. Scales on the axes are (I) for Ca, (II) for Cd, (III) for Zn, and (IV) for Mg.

observed. V–X isotherms were linear, indicating applicability of the principle of additivity of volumes, at least to a first approximation. Variation in molar volume with changes in temperature and composition may be represented by the equation

$$V = \int \Delta V_T \, dT + \int \Delta V_X \, dX \qquad (2)$$

where ΔV_T, the change in volume with temperature has been shown (*1*) to be equal to the product of thermal expansion coefficient (α) and the van der Waals volume (V_0). For a volumetrically ideal system, ΔV_X, the change in volume with composition, would be equal to ($\bar{V}_2 - \bar{V}_1$), where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of the components. Partial molar volumes were evaluated by extrapolating the V–X plots and also by least-squares fitting the V–X data into the linear equation, $V = E + FX$ (Table III). Partial molar volumes of divalent nitrates were found to be within ±1% of the literature values except for Mg^{2+}-containing mixtures. $\bar{V}(Mg(NO_3)_2 \cdot 6H_2O)$ were about 4–6% lower than the literature values (*10*). It has been shown (*11*) that Mg^{2+}–H_2O interactions are strong in consistence with the high charge-to-radius ratio of Mg^{2+} ion. In $Mg(NO_3)_2 \cdot 6H_2O$ the NO_3^- ions are oriented toward H atoms of water resulting in a decrease in Mg^{2+}–H_2O interactions. In mixtures, the preferential orientation of NO_3^- ions toward Fe^{3+} ions (vide supra) would decrease their interactions with H atoms of water. This would lead water molecules to be strongly held

Table III. Partial Molar Volumes of $Fe(NO_3)_3 \bullet 9.08H_2O$ + $M(NO_3)_2 \bullet RH_2O$ Systems

$M(NO_3)_2 \cdot RH_2O$	temp, K	$\bar{V}(Fe(NO_3)_3 \cdot 9.08H_2O)$, cm^3 mol^{-1}	$\bar{V}(M(NO_3)_2 \cdot RH_2O)$, cm^3 mol^{-1}	lit.
$Ca(NO_3)_2 \cdot 4.12H_2O$	313.2	241.37	137.59	(135.80)[a]
	333.2	244.50	138.84	
	353.2	247.80	140.04	
$Cd(NO_3)_2 \cdot 4.15H_2O$	313.2	240.82	137.10	(136.71)[a]
	333.2	243.97	138.39	
	353.2	247.24	139.68	
$Zn(NO_3)_2 \cdot 6.22H_2O$	313.2	239.70	165.10	(161.37)[b]
	333.2	242.82	167.05	
	353.2	246.06	168.98	
$Mg(NO_3)_2 \cdot 6.02H_2O$	313.2	241.82	152.56	(166.88)[c]
	333.2	244.42	160.43	
	353.2	247.69	161.91	

[a] Reference *8*. [b] Reference *9*. [c] Reference *10*.

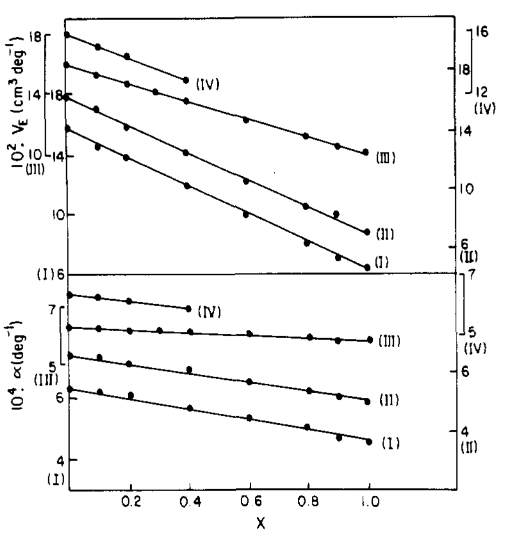

Figure 2. Composition variation of thermal expansion coefficient (α) and molar expansivity (V_E) of $Fe(NO_3)_3 \cdot 9.08H_2O + M(NO_3)_2 \cdot RH_2O$ systems at 300 K. Scales on the Y axis are (I) for Ca, (II) for Cd, (III) for Zn, and (IV) for Mg.

with Mg^{2+} ions resulting in a decrease of $\bar{V}(Mg(NO_3)_2 \cdot 6H_2O)$ as observed.

Both the expansion coefficient ($\alpha = -(1/\rho)(d\rho/dT)$) and the molar thermal expansivity ($V_E = dV/dT$) of the mixtures show a decrease (Figure 2) on addition of hydrated M^{2+} to $Fe(NO_3)_3 \cdot 9H_2O$. Sharma et al. (*8*) have shown that V_E could be approximated to the product of α and V_0. The addition of hydrated M^{2+} decreases the number of moles of NO_3^- ions from 3 to 2 per mole of the mixture. Also, the moles of water associated with the cations decrease from 9 to 4 or 6 per mole of the mixture. Both these factors would lead to a decrease in V_0 and hence in V_E, as observed.

Variation in α is opposite to that expected from the Born model of ion-water interactions. Inove et al. have shown (*12*) that a decrease in water content changes the hydration number of Fe^{3+} ion from 6 to 4 and results in ion-pair formation displacing coordinate water into lattice water which has high configurational contribution to α (*13*). It may be concluded that the addition of divalent cations results in a greater electrostriction to lattice water and a decrease in α, as observed.

Registry No. $Fe(NO_3)_3 \cdot 9H_2O$, 7782-61-8; $Ca(NO_3)_2 \cdot 4H_2O$, 13477-34-4; $Cd(NO_3)_2 \cdot 4H_2O$, 10022-68-1; $Zn(NO_3)_2 \cdot 6H_2O$, 10196-18-6; $Mg(NO_3)_2 \cdot 6H_2O$, 13446-18-9.

Literature Cited

(1) Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1977**, *22*, 41.
(2) Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1978**, *23*, 228.
(3) Sharma, R. C.; Bhatia, K.; Gaur, H. C. *J. Chem. Eng. Data* **1979**, *24*, 183.
(4) Sharma, R. C.; Jain, R. K.; Gaur, H. C. *J. Chem. Eng. Data* **1979**, *24*, 185.
(5) Gupta, S.; Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1981**, *26*, 187.
(6) Venkata Ramana, K.; Sharma, R. C.; Gaur, H. C. *J. Chem. Eng. Data* **1985**, *30*, 449.
(7) Angell, C. A. *J. Electrochem. Soc.* **1965**, *112*, 1224.
(8) Sharma, R. C.; Jain, S. K.; Gaur, H. C. *J. Chem. Eng. Data* **1978**, *23*, 72.
(9) Jain, S. K.; Tamamushi, R. *Can. J. Chem.* **1980**, *58*, 1897.
(10) Jain, S. K.; Jindal, H. L.; Kulshreshta, N. P. *J. Chem. Eng. Data* **1978**, *23*, 38.
(11) Chang, T. G.; Irish, D. E. *J. Phys. Chem.* **1973**, *77*, 57.
(12) Inove, Y.; Deki, S.; Yokoyama, M.; Massie, N.; Kamaji, K. *Nippon Kagaku Kaishi*, **1974**, *12*, 2297.
(13) Gildseth, W. M.; Habenschuss, A.; Spedding, F. H. *J. Chem. Eng. Data* **1975**, *20*, 292.

Received for review May 3, 1985. Accepted January 27, 1986. We thank the Centre of Advanced Study, Department of Chemistry, University of Delhi, for continued financial assistance. K. V. Ramana is grateful to the Department of Atomic Energy, Government of India, for the award of a Research Fellowship.

Ultrasonic Speed in Liquid Phase of Bromotrifluoromethane (R13B1) under High Pressures

Toshiharu Takagi* and Hiroshi Teranishi

Department of Chemistry, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyoku, Kyoto 606, Japan

The ultrasonic speeds in the liquid phase of bromotrifluoromethane (R13B1) were measured at temperatures from 283.15 to 323.15 K and pressures from near saturated vapor pressure to about 50 MPa by using a sing-around technique operated at a frequency of 2 MHz. The ultrasonic speeds show a large pressure effect in the lower pressure region as the temperature comes close to critical. The smoothing curve for the experimental values fits well to the observed values in high-pressure range. However, in the vicinity of vapor pressure, acoustic absorption in the liquid phase was observed which induced distortion in speed; so the present results in this region have large deviations from the fitting curve.

Introduction

Experimental work on ultrasonic speed for refrigerants are rare, especially at high pressure. In our recent work (*1*), a new apparatus was constructed using a sing-around technique employing a fixed-path ultrasonic interferometer of 2 MHz, which was used to observe the precise ultrasonic speed in liquid under high pressure. The speed in the liquid phase of dichlorotetrafluoroethane (R114) was measured at various conditions of temperature and pressure. Kokernak and Feldman (*2*) measured the ultrasonic speed in liquid of dichlorodifluoromethane (R12) under its saturated vapor pressure, and estimated the values of some refrigerants including R114 by a theoretical rule. This report is the only one concerning study of the speed in the liquid phase of refrigerant R114. However, the value of R114 reported in their paper was ascertained to differ about 15% from that obtained by extrapolation of our experimental results (*1*) to the saturation vapor pressure. In this paper, the ultrasonic speed in the liquid phase of bromotrifluoromethane (R13B1) was measured at temperatures from 283.15 to 323.15 K, at pressures from near saturation to about 50 MPa. Temperature and pressure effects on sound speed are discussed and compared with those for refrigerant R114 reported previously.

0021-9568/86/1731-0291$01.50/0