SCIENTIA
IRANICA

Research Note

Energy of the Crystalline Lattice and Sound Velocity of Lanthanide Chlorides in Aqueous T-Butanol

S.H. Mousavi[1]

The ultrasonic velocity of lanthanide chlorides in aqueous t-butanol has been determined, using a single-crystal interferometer at 25, 30, 35 and 40°C. The velocities are accurate to $\pm\,0.003\%$. The velocity data are correlated with lattice energies of the substances on the basis of Kudriavtsev's theory. The agreement between the calculated and experimental values is good at low concentration ($C \leq 0.03$ mole/liter) of electrolytes containing structure-breaking ions, while it becomes poor with a further increase in concentration. The discrepancy is believed to be due to the invalidity of the theory in the case of higher valance electrolytes, such as rare-earth chlorides. It has been observed that, almost at any concentration, the apparent lowering of velocity is in the order of gadolinium chloride > samarium chloride > neodymium chloride, while lanthanum chloride > neodymium chloride at low concentration and is reversed as the concentration increases. The results are discussed in the light of the structure-breaking property of the ions studied.

INTRODUCTION

A relation between the ultrasonic velocity and lattice energy of dissolved substances was derived by Kudriavtsev [1], assuming the additiveness of the internal energy and making use of the standard thermodynamic formula. The following relation was tested by Kudriavtsev for aqueous solutions of sodium and potassium halides, alkali nitrates and sulphates of cadmium and magnesium at fairly high concentrations:

$$u^2 = (1 \quad W)u_0^2 + W(2.32 \times 10^7 \phi_i), \qquad (1)$$

where u is the sound velocity in the aqueous solution, u_0 is the sound velocity in water, W is the weight fraction of the solute and ϕ_i is the energy of the crystalline lattice in kcal.

In general, there was good agreement between the theory and experiments in most cases [2], except in aqueous solutions of sulfates, where the agreement between experiment and theory was considerably less. Sivakumar and Rajagopal [3] applied Kudriavtsev's theory for the evaluation of lattice energies from elastic

constants data in alkali halides. The agreement between the calculated and literature values was quite good. Single crystal elastic constants from the literature have also been used [4] to evaluate the mean sound velocities in the NH_4Cl and NH_4Br crystals, using Kudriavtsev's theory. The results indicate the utility of sound velocity measurements in evaluating the lattice energies of ionic crystals at any given temperature, making use of Kudriavtsev's equation. Subramanyam and Raghavan [5] applied the theory for aqueous solutions of lithium and rubidium halides, to test the validity of the equation. Good agreement between theory and experiment was found in the case of the rubidium halides, while agreement was found to be poor in the case of the lithium halides. The discrepancy was attributed to the structure promoting nature of the lithium ions, as stated by the authors. Based on single-crystal elastic constant data, Subrahmanyam and Rajagopal [6] applied Kudriavtsev's equation to evaluate the lattice energy of mixed alkali halide crystals. In general, the lattice energies of these mixed crystals have been found to decrease in the concentration of the second component. The lattice energy of fluorite type AB_2 crystals and alkaline earth metal halides, at different temperatures, have been

---

1. *Ahwaz College of Petroleum Engineering, Petroleum University of Technology, Ahwaz, I.R. Iran.*

evaluated by Subrahmanyam and Rajagopal [7,8], by employing Kudriavtsev's equation. The results are explained in terms of the structure interaction of the ions and the discordant effects associated with it as a function of temperature.

Rare-earth, a group of fourteen chemical elements, beginning with cerium (atomic number 58) and ending with lutetium (atomic number 71), exists in dilute solution as trivalent cations. Due to very similar chemical properties and the common trivalency of the lanthanide series, separation of the individual elements was quite difficult before the 1940's and led to their misleading name, rare-earth. As a matter of fact, they are neither rare nor earth. Rare-earth has many important applications in science and industry, the most important of which are, as follows:

The elements exhibit very complex spectra and the mixed oxides, when heated, give off an intense white light, which resembles sunlight. Consequently, mixtures of the oxides are used in the movie industry.

Rare-earth is also used in the petroleum industry as a catalysts. Rare-earth chloride, when mixed with rare-earth oxides, produces petroleum with a higher yield at desired petroleum fractures.

Since individual rare-earths are available commercially at reasonable prices, a sizable market has developed for a number of them. This is not surprising, since they represent, as a group, about one-sixth of naturally occurring elements and about one fourth of elemental metals. In fact, these elements form compounds and alloys, many of whose properties change in a predictable manner as one progresses across parts of the series, making them of particular interest to scientists working in various fields of research.

Another very important use of individual rare-earth is in the manufacture of solid-state microwave devices widely used in radar and communication systems. The devices, however, are very small and so the total use of rare-earth is not large.

Still another important use of individual rare-earths is in the construction of lasers.

A number of thermodynamic studies [9-14] have been carried out on rare-earth chlorides and nitrates with the aim of assessing the structure-breaking or structure-making of these high valence electrolytes in water and aqueous organic solutions. In this paper, the status of the relationship between the ultrasonic velocity in 3-1 electrolytic solutions and the lattice energies of dissolved rare-earth is reviewed and the use of Kudriavtsev's theory is verified. In the present study, the authors do not agree with the conclusion drawn by Subramanyam and Sivakumar that the discrepancy is as a result of the structure promoting nature of the ions, but, in fact, must be as a result of low or high valance electrolytes.

EXPERIMENTAL

Rare-earth chemicals (with 99.99% purity) were obtained from M/s. Rare-earth India Ltd. Udyogonandal, India. The ultrasonic velocity in the ternary system (electrolyte + aqueous t-butanol) was determined in the concentration region of 0.004 - 0.1 mole litre $^{-1}$, using a single crystal variable path interferometer working at 1 MHz with an accuracy of $\pm$ 0.003%. The temperature of the interferometer liquid was maintained constant to better than $\pm$ 0.002°C at 25, 30, 35 and 40°C.

Details of the experimental technique and the method of measurement of the velocity were reported somewhere else [12]. Triple distilled and degassed water was used to prepare a stock solution of aqueous t-butanol. The molality of t-butanol in the stock solutions was 0.2742, the concentration at which maximum enhancement of the water structure is supposed to occur, as revealed by TSVM and TACM studies [14]. The experimental velocities were corrected for diffraction effects [15].

RESULTS AND DISCUSSION

The experimental velocities of aqueous t-butanol (U_0) at 25, 30, 35 and 40°C were found to be 1516.07, 1526.78, 1535.32 and 1543.25 m sec $^{-1}$, respectively.

Equation 1 was used to evaluate sound velocities in the ternary solution (electrolyte + t-butanol + water) in a low concentration case, using the lattice energy data available in [16]. The results of such calculation are given in Tables 1 and 2. There is a good agreement between the experimentally determined and calculated amounts of velocities in all the lanthanide salts, namely: Lanthanum, neodymium, samarium and gadolinium chlorides at low concentration, while there is not good agreement at high concentration. In view of the simple nature of the theory, better agreement than that reported here need not be expected. Considerably, a better agreement would be obtained at high concentrations, if the lattice energy evaluated were lower than the literature data by 20%. The indicated discrepancy can be explained, on the one hand, by the unreliability of the data concerning the energy of the crystalline lattices of the rare-earth chlorides (Ld, Nd, Sm and Gd), which are trivalent salts and when dissolved in water are ionized to form trivalent ions. On the other hand, the character of the interaction of the molecules in such a solution is substantially different from the character of the interaction in the solid state.

From TSVM and TACM studies of La, Nd, Sm and Gd chlorides in an aqueous solution of t-butanol, it has been observed that they are structure breaking by nature at low concentrations. This is consistent

Table 1. Experimental and theoretically evaluated sound velocity data in aqueous solutions of lanthanum and neodymium chlorides + tert-butyle alcohol.

Concentration g.mol/lt $\times 10^3$	Weight Fraction $W \times 10^3$	Velocity (m/s) 25°C		Velocity (m/s) 30°C		Velocity (m/s) 35°C		Velocity (m/s) 40°C		Apparent Velocity of Water U_0''	Lowering of Velocity ΔU_0
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.		
Lanthanum Chlorides + Tert-Butyle Alcohol+ Water. $\phi_i = 1019$ kcal/mole											
4.31	1.6004	1515.30	1515.94	1525.93	1526.08	1533.66	1534.85	1542.78	1542.76	1541.20	0.06
5.65	2.0974	1515.90	1516.83	1526.40	1526.92	1534.87	1535.72	1543.54	1543.63	1541.16	0.10
14.43	5.3587	1518.60	1519.46	1528.37	1529.68	1537.90	1538.24	1546.88	1546.92	1540.88	0.40
19.64	7.2963	1521.48	1521.48	1531.58	1532.76	1539.84	1540.65	1548.28	1548.55	1540.47	0.80
32.23	11.9688	1527.37	1527.47	1536.70	1537.42	1545.50	1546.34	1552.84	1553.81	1539.31	1.90
49.50	18.3840	1532.66	1533.70	1541.98	1543.54	1550.96	1552.04	1558.05	1559.72	1537.23	4.00
63.61	23.6257	1537.50	1539.98	1547.02	1549.78	1556.97	1558.15	1563.72	1565.78	1537.05	4.20
79.36	29.4737	1543.35	1547.83	1554.13	1557.03	1562.67	1565.75	1569.38	1572.79	1536.09	5.20
Neodymium Chlorides + Tert-Butyle Alcohol+ Water. $\phi_i = 1038$ kcal/mole											
4.37	1.5677	1515.96	1516.66	1527.26	1527.79	1536.30	1536.70	1543.04	1544.67	1514.00	0.40
5.86	2.1024	1517.24	1517.84	1527.38	1527.56	1536.22	1536.29	1544.10	1544.20	1514.12	0.20
7.52	2.7005	1517.82	1518.22	1528.43	1528.44	1537.82	1538.11	1544.34	1545.19	1513.88	0.05
19.87	7.1288	1523.26	1527.65	1533.18	1534.68	1542.66	1543.35	1550.84	1551.18	1512.87	1.50
33.41	11.9873	1529.40	1531.72	1539.66	1541.65	1548.95	1550.24	1556.60	1558.00	1511.96	2.40
52.21	18.7307	1540.24	1541.38	1548.34	1551.19	1557.56	1559.66	1564.90	1567.33	1511.06	3.30
67.91	24.3609	1548.24	1549.49	1557.46	1559.18	1564.32	1567.54	1572.34	1557.12	1511.06	3.30
81.80	29.3463	1552.84	1556.08	1561.24	1565.68	1570.34	1573.98	1578.58	1581.49	1510.43	3.90
106.25	38.1179	1569.00	1569.18	1573.98	1578.62	1581.08	1586.78	1589.62	1594.15	1510.13	4.20

with the results obtained by verification from Kudri-avtsev's theory for the same solutions. However, as the concentration increases, the open-packed structure of aqueous t-butanol becomes more stable, in other words, the behavior is such that they promote the open-packed structure of water. In fact, in water rich regions, aqueous t-butanol behaves as pure water, in respect of the velocity temperature profile.

The structure making ions promote an open-packed structure of water. Since the ultrasonic velocity in a loosely packed arrangement of molecules will be lower than that of a close-packed arrangement of the same molecules, aqueous t-butanol, in the presence of these structure making ions, at any particular temperature, behaves as if it has a velocity lower than its original value at that temperature, i.e., the velocity in aqueous t-butanol is apparently lowered. The apparent velocity, U_0', in aqueous t-butanol at various concentrations for lanthanum, neodymium, samarium and gadolinium chlorides at 25, 30, 35 and 40°C, respectively, was calculated by substituting lattice energy data, ϕ_i, and the observed velocity of solution (U) in Equation 1.

The values of the apparent velocity (U_0') and the amount of velocity reduction (ΔU_0), i.e., $(U - U_0')$, are presented in Tables 1 and 2 respectively. The variation of ΔU_0 with composition, is represented in Figure 1. In all cases, ΔU_0 is lowered by an amount approx-
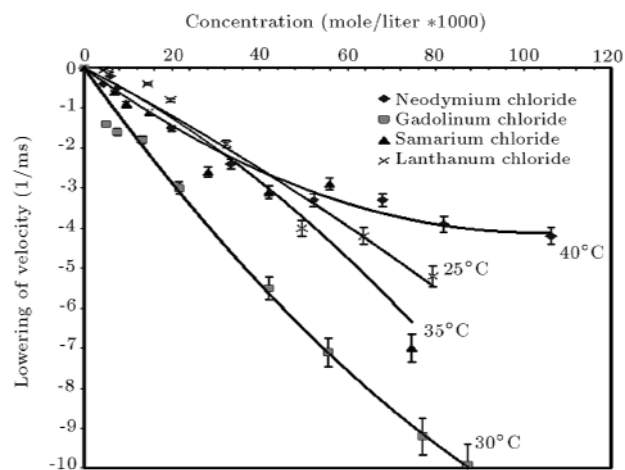

Figure 1. Variation of lowering velocity as a function of concentration at different temperatures.

agreement [2] between the calculated and observed values.

REFERENCES

1. Kudriavtsev, B.B. "A relation connecting between the ultrasonic velocity in an electrolytic solution and the lattice energy", *Sov., Phys., Acoust.*, **2**, pp 36-45 (1956).

2. Kudriavtsev, B.B. "Ultrasonic studies in aqueous solution of sodium and potassium halides, alkali nitrates and sulphates of cadmium and magnesium", *Sov, phys., Acoust.*, **2**, pp 172-177 (1956).

3. Sivakumar, K.V. and Rajagopal, E. "Evaluation of lattice energy from elastic constant data in alkali halides", *Acoust., Lett.*, **7**, pp 87-91 (1983).

4. Subrahamanyam, M. et al. "To evaluate the mean sound velocities in the ammonium of chloride and bromide crystals using the Kudriavtsev's theory", *J. of Acoustical Society of India*, **17**, pp 128-134 (1989).

5. Subrahanyam, S.V. and Raghavan, C.V. "Application of Kudriavtsev theory for aqueous solution of lithium and rubidium halides", *J.A.P.A. Cad., Sci.*, **6**, pp 21-27 (1971).

6. Subrahamanyam, M. et al. "To evaluate the lattice energy of mixed alkali halid crystals", *Indian Journal of Pure and Applied Physics*, **38**, pp 495-498 (2000).

7. Subrahamanyam, M. et al. "Temperature dependence of lattice energy of fluorite type AB$_2$ crystals", *Indian. J. of Pure and Applied Physics*, **43**, pp 660-663 (2005).

8. Subrahamanyam, M., Rajagopal, E. et al. "Temperature dependence of lattice energies of alkali chlorides, bromides and iodides", *Indian. J. of Physics and Proceedings of the Indian Association for the Cultivation of Science*, **79**, pp 1169-1172 (2005).

9. Mousavi, S.H. and Rama Murthy, L. "Structural interaction view of ultrasonic studies in aqueous solution of rare-earth nitrates", *Acoust., Lett.*, **11**, pp 167-173 (1988).

10. Mousavi, S.H. and Rama Murthy, L. "TSVM and TACM studies in aqueous solution of rare-earth nitrates", *Acastica*, **69**, pp 31-34 (1989).

11. Mousavi, S.H., Venkat Ramana, K. et al. "Effect of rare-earth chlorides on the structure of water", *Phys., Chem., Liq.*, **20**, pp 71-79 (1989).

12. Mousavi, S.H., Rama Murthy, S. et al. "Ultrasonic studies in praseodymium nitrates and acetate in aqueous methanol", *Acoust., Lett.*, **18**, pp 151-155(1989).

13. Silber, H. "Ultrasonic studies in rare-earth solutions", *J. Less-Common Metals*, **112**, pp 207-211 (1985).

14. Mousavi, S.H. and Rama Murthy, L. "Effect of t-Butanol on the structural propensities of lanthanide salts in water", *Acaustica*, **73**, pp 162-167 (1991).

15. Subrahmanyam, S.V. et al. "Effect of diffraction on the experimental studies", *J. Acoust., Soc., Am.*, **46**, pp 141-146 (1969).

16. Ladd, M.F.C. and Lee, W.H., *Solid State Chemistry*, (Ed. Reiss)**1**, New York, USA, pp 57-58 (1969).