

Prof. L. A. K. Staveley, University of Oxford, England, for permission to record NMR spectra and discussion.

References

1. NIGAM, R. K. & SINGH, P. P., *Trans. Faraday Soc.*, **65** (1969), 950.
2. NIGAM, R. K. & MAHL, B. S., *Indian J. Chem.*, **9** (1971), 1250.
3. NIGAM, R. K. & MAINI, N. N., *Indian J. Chem.*, **10** (1972), 197.
4. NIGAM, R. K. & MAHL, B. S., *J. chem. Thermodynamics*, **4** (1972), 41.
5. NIGAM, R. K. & MAHL, B. S., *J. chem. Soc. Faraday Trans. I*, **68** (1972), 1506.
6. NIGAM, R. K. & MAINI, N. N., *Indian J. Chem.*, **11** (1973), 1288.
7. NIGAM, R. K. & DHILLON, M. S., *J. chem. Thermodynamics*, **3** (1971), 819.
8. NIGAM, R. K. & MAINI, N. N., *Indian J. Chem.*, **9** (1971), 687.
9. NIGAM, R. K. & MAHL, B. S., *Indian J. Chem.*, **10** (1972), 1167.
10. TELANG, M. S., *J. chem. Phys.*, **17** (1949), 556.
11. PALIT, S. R., *J. Indian chem. Soc.*, **40** (1963), 721.
12. PRIGOGINE, I., *Molecular theory of solutions* (North-Holland, Amsterdam), 1957.
13. ENGLERT CHOWLES, A. & PRIGOGINE, I., *Novo Cheminto*, **9** (1950), 347.
14. BELLEMAN, A. & STECKI, J., *J. Molec. Phys.*, **3** (1960), 203.
15. NIGAM, R. K., SINGH, P. P., DHILLON, M. S. & MAINI, N. N., *Indian J. Chem.*, **8** (1970), 658.

Effective Debye Temperature of Liquids on the Basis of Quasi-crystalline Structure

J. D. PANDEY

Department of Chemistry, University of Allahabad
Allahabad 211002

Received 20 February 1975; accepted 8 December 1975

The effective Debye temperature (θ) of liquid argon, oxygen, nitrogen, methane, and neon has been calculated as a function of temperature and pressure using ultrasonic velocity and isothermal compressibility data. The values of θ decrease by increasing temperature while increase by increasing the pressure.

A NUMBER of theoretical and experimental evidences¹⁻¹⁰ are available in support of the quasi-crystalline behaviour of the liquid. By assuming the quasi-crystalline model Joshi¹¹, Mitra *et al.*¹² and Jain *et al.*¹³ evaluated the Debye temperature of water utilizing the data given by Singwi and Sjolander⁵. Recently Kor *et al.*^{14,15} calculated the effective Debye temperature of water, methanol, ethanol, carbon tetrachloride and toluene as a function of temperature and pressure assuming the atomic motions in these liquids as similar to those in solids. These authors utilized the ultrasonic absorption data for their calculations. By applying the quasi-crystalline model to the cryogenic liquids argon, nitrogen, oxygen, neon and methane, the present author has extended the calculation of effective Debye temperature as a function of temperature and pressure.

The following sets of equation^{14,15} have been utilized to evaluate the Debye temperature (θ) of liquids:

$$\theta = \frac{h}{k} \left[\frac{9N}{4\pi v} \left(\frac{2}{c_i^3} + \frac{1}{c_1^3} \right) \right]^{1/3} \quad \dots(1)$$

$$\frac{1}{c_1^3} + \frac{2}{c_i^3} = (\rho\beta_{T,\infty})^{3/2} \left[2 \left\{ \frac{2(1+\sigma)}{3(1-2\sigma)} \right\}^{3/2} + \left\{ \frac{(1+\sigma)}{3(1-\sigma)} \right\}^{3/2} \right] \quad \dots(2)$$

$$\sigma = \frac{3A-2}{6A+2}, A = \left(\frac{K_{T,\infty}}{G_{T,\infty}} \right) = \left(\frac{K_{T,\infty}}{K_{T,r}} \right) \left(\frac{\eta_V}{\eta_S} \right) \left(\frac{\tau_S}{\tau_V} \right) \quad \dots(3)$$

$$\frac{\eta_V}{\eta_S} = \frac{4}{3} \left(\frac{\alpha \text{ expt}}{\alpha \text{ class}} - 1 \right) \quad \dots(4)$$

$$\tau_S = \frac{4}{3} \eta_S \beta_0, K_{T,r} = \frac{1}{\beta_{T,r}} = G_{T,\infty} \frac{\eta_V}{\eta_S}, G_{T,\infty} = \frac{\eta_S}{\tau_S}$$

$$\eta_V = K_{T,r} \tau_V \text{ and } \frac{1}{K_{T,\infty}} = \beta_{T,\infty} = \beta_0 - \beta_{T,r} \quad \dots(5)$$

Here all the symbols have their usual notations¹⁶. Previous workers have evaluated the value of θ using the above relation and have utilized the experimental data for shear viscosity η_S , density ρ ultrasonic absorption α/f^2 and velocity c . In the present case a simplified procedure has been used which avoids the use of absorption and viscosity.

From Eq. (5),

$$\frac{K_{T,\infty}}{K_{T,r}} = \frac{K_{T,\infty}}{K_{T,0}} - 1 = \frac{1}{\gamma} - 1 \quad \dots(6)$$

where $K_{T,\infty}$, $K_{T,0}$ and γ are respectively the isothermal bulk modulus, adiabatic bulk modulus and ratio of the heat capacities. Again,

$$\frac{\tau_S}{\tau_V} = \frac{4}{3} \frac{\eta_S}{\eta_V} \cdot \beta_{T,0} K_{T,r} = \frac{4}{3} \frac{\eta_S}{\eta_V} \cdot \frac{K_{T,\infty}}{K_{T,0} - K_{T,\infty}} \quad \dots(7)$$

Hence,

$$\frac{\tau_S \eta_V}{\tau_V \eta_S} = \frac{4}{3} \left(\frac{1}{1-\gamma} \right) \quad \dots(8)$$

Using Eqs. (6) and (8), one gets,

$$A = \frac{4}{3} \cdot \frac{1}{\gamma} \quad \dots(9)$$

Thus we need only ρ , γ and $\beta_{T,\infty}$ for evaluating the values θ for liquids.

The effective Debye temperatures for liquid argon, liquid oxygen, nitrogen, methane and neon were calculated using Eqs. (1), (2), (3) and (9). The data needed for the calculations were taken from different sources¹⁷⁻²¹. In Table 1, are recorded the calculated values of θ for different liquids at different temperatures and pressures. It is observed that θ decreases by increasing the temperature at constant pressure for argon and neon. For liquid oxygen, nitrogen and methane both the temperature and pressure, have been varied and it has been found that the pressure has marked effect on the effective Debye temperature for liquid oxygen, nitrogen, and methane. The increase of pressure results in an increase in the value of θ , although the increase is not so abrupt. For N₂ at 113.6°K, the effective Debye temperature increases only by 2.5°K for an increase of 21.1 kg/cm² pressure.

The results of the calculation show that the effective Debye temperature has reasonable value for all the liquids investigated. The temperature dependence of effective Debye temperature in the present case is similar to that of other workers¹⁴. The order of θ values and their temperature

TABLE 1 — DEBYE TEMPERATURE OF LIQUID Ar, O₂, N₂, CH₄ AND Ne

T (°K)	P (kg/cm ²)	θ (°K)	T (°K)	P (kg/cm ²)	θ (°K)
LIQUID METHANE			LIQUID NITROGEN		
145.6	8.8	65.4	113.6	87.1	40.4
do	18.6	66.1	113.6	108.2	42.9
do	31.2	69.3	110.2	98.0	45.6
do	51.2	69.9	105.0	45.0	42.1
do	73.5	72.1	90.6	8.8	51.0
145.6	87.5	73.1	85.5	48.5	59.0
125±0.1	3.5	81.2	81.0	120.5	67.6
do	10.4	83.2	81.0	8.5	73.5
do	36.1	85.9	77.6	1.67	61.8
do	60.0	87.7	77.6	63.5	66.2
do	81.0	88.7	80.9	126.0	68.7
do	89.1	91.4	73.6	1.73	65.4
			73.6	124.0	72.9
			75.0	116.3	71.4
LIQUID NEON			LIQUID OXYGEN		
25.0	1.0	62.1			
26.0	do	59.0	86.1	0.60	79.3
27.0	do	56.8	80.1	0.43	79.7
28.0	do	53.5	75.4	0.13	83.1
29.0	do	52.5	70.2	0.06	87.0
30.0	do	50.9	66.3	0.03	88.6
31.0	do	48.0			
32.0	do	46.0	LIQUID ARGON		
33.0	do	43.8			
34.0	do	42.5	84.0	8.0	67.9
35.0	do	39.3	87.0	8.0	66.0
36.0	do	36.7	90.0	8.0	63.9
37.0	do	34.8	112.0	8.0	48.6

and pressure dependences show the validity of the present method of calculation.

References

1. MOELWYN-HUGHES, E. A., *Physical chemistry* (Pergamon Press, London), 1965.
2. TABOR, D., *Gases, liquids & solids* (Penguin) 1969.
3. FRENKEL, J., *Kinetic theory of liquids* (Dover Publication), 1946.
4. HUGHES, D. J., PABEVERKY, H., KLEY, W. & TVNKATO, E., *Phys. Rev.*, **119** (1960), 872.
5. SINGWI, K. S. & ALF SJOLANDER, *Phys. Rev.*, **119** (1960), 863.
6. EGELSTAFF, P. A., *Thermal neutron scattering* (Academic Press, New York), 1965.
7. BERNAL, J. D. & FOWLER, R. H., *J. chem. Phys.*, **1** (1933), 515.
8. POPLE, J. A., *Proc. roy. Soc.*, **A 205** (1951), 163.
9. EYRING, H. & JOHN, M. S., *Significant liquid structure* (John Wiley, New York), 1969.
10. PANDEY, J. D., *J. acoust. Soc., India*, accepted for publication.
11. JOSHI, S. K., *J. chem. Phys.*, **35** (1961), 1141.
12. MITRA, S. K. & DASS, N.: *Proc. nucl. Phys. & Solid state Phys. symposium, Madurai (India)*, III, 1970, 337.
13. JAIN, S. C. & BHANDARI, R. C., *J. phys. Soc. Japan*, **23** (1967), 476.
14. KOR, S. K. & TRIPATHI, N. D., *J. phys. Soc. Japan*, **36** (1974), 552.
15. KOR, S. K., PRASAD, R. & AGARWAL, A., *Acoustica*, **29** (1973), 239.
16. LITOVITZ, T. A. & DAVIS, C. M., *Physical acoustics*, Vol. IIA, edited by W. P. Mason (Academic Press, New York), 1965.
17. NAUGLE, D. G., *J. chem. Phys.*, **44** (1966), 741.
18. VICTOR, A. E. & BEYER, R. T., *J. chem. Phys.*, **52** (1970), 1573.
19. SINGER, J. R. & LUNSFORD, J. H., *J. chem. Phys.*, **47** (1967), 811.
20. SINGER, J. R., *J. chem. Phys.*, **51** (1969), 4729.
21. NAUGLE, D. G., *J. chem. Phys.*, **56** (1972), 5730.

Limiting Apparent Molal Volume of KCl, NaCl, KBr & NaBr in Dioxane-Water Mixtures at Different Temperatures

P. P. MISRA, N. C. DAS & P. B. DAS*

Department of Chemistry, S. C. S. College, Puri

Received 16 August 1975; accepted 4 December 1975

The limiting apparent molal volumes (ϕ°) of KCl, NaCl, KBr and NaBr have been determined in 10, 20 and 30% dioxane-water mixtures at 30°, 35°, 40° and 45°. The ' ϕ° ' increases with increase in temperature for all the salts studied but $d\phi^\circ/dt$ decreases with increase in dioxane content. The anomalies observed in the present case have been explained on the basis of electrostatic solvation, electrostriction, hydrogen bonding and dielectric constant effect.

THE variation of limiting apparent molal volume, ϕ° , of electrolytes with temperatures in aqueous and non-aqueous solutions have been employed to study ion-solvent interaction by many workers¹⁻⁵. In this note the apparent molal volume of KCl, NaCl, KBr and NaBr in aqueous-dioxane mixtures at 30°, 35°, 40° and 45°C have been determined. The effect of the dielectric constant of the medium, temperature and hydrogen bonding on limiting apparent molal volume have also been examined.

All the salts used were of E. Merck grade (extra pure). The methods of measurements of density were the same as reported earlier⁶. The density measurements have been made with a pycnometer with buoyancy correction and are accurate up to 4 in 10⁶.

The ϕ° values of KCl, NaCl, KBr and NaBr determined in the usual manner⁶ in 10, 20 and 30% of dioxane-water mixtures at different temperatures are given in Table 1. The limiting apparent molal volume, ϕ° , increases with increasing temperature for all the salts studied at all the solvent compositions but $d\phi^\circ/dt$ decreases with increase in dioxane content. The decrease in $d\phi^\circ/dt$ is sharp for KCl and NaCl as compared to that of KBr and NaBr indicating ion-solvent interaction to be stronger in KCl and NaCl than that of KBr and NaBr.

The variation of ϕ° with temperature can be explained on the basis of ion-solvent interactions and solvation as follows: As dioxane is somewhat non-hydrogen bonded solvent, the ion-dipole interaction energy would be appreciable and the attachment of the solvent molecules to ions may not be loose and at the same time no structure formation would occur around the ion⁷. The net result will be stronger solvation. The expansion of solution on heating thus would be appreciably less than that of pure solvent. The reason may be ascribed due to high surface charged density, which would lead to strong ion-solvent interaction together with primary and secondary solvation depending on the ionic radius.

It is interesting to note that while for KBr and NaBr the apparent molal volume increases with

*To whom correspondence should be made.