

Extension of Flory theory to some pure organic liquids at elevated temperature and pressure

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Flory theory has been extended to evaluate sound velocity in cyclohexane, propane, butane and methane at elevated temperatures and pressures. The agreement between the theoretical and experimental values is good.

SEVERAL attempts¹⁻⁵ have been made to test Flory's^{6,7} statistical theory in the light of excess thermodynamic functions in binary liquid mixtures. It appears from the literature^{8,9} that not much has been done in applying the theory as regards its dependence on temperature and at higher pressure. The present investigation deals with the extension of the theory over a wide range of temperature and pressure to evaluate sound velocity in some complex organic liquids at elevated temperatures and pressures. Cyclohexane, propane, butane and methane have been selected for the present work. The first three liquids have been examined at elevated temperatures whereas the fourth liquid at both elevated temperatures and pressures. The pressure-dependence data on the sound velocity for cyclohexane, propane and butane were not available in the literature. The sound velocity has been experimentally determined very precisely (within 0.2%) in these liquid by various workers¹⁰⁻¹² respectively.

Starting from the equation of state,

$$\frac{\bar{P}\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{(\bar{V}^{1/3}-1)} - \frac{1}{\bar{V}\bar{T}} \quad (1)$$

We have,

$$\bar{V} = \frac{V}{V^*} \quad (2)$$

$$\bar{T} = \frac{T}{T^*} \quad (3)$$

$$\bar{P} = \frac{P}{P^*} \quad (4)$$

$$\text{and } P^* = \gamma TV^2 \quad (5)$$

$$V^{1/2} - 1 = \frac{\alpha T}{3} (1 + \alpha T)^{-1} \quad (6)$$

where α is the thermal expansion coefficient and other symbols have their usual meaning as given by Flory. The values of α at different pressures and temperatures were substituted in eq (6) to obtain the numerical value of reduced volume, \bar{V} , at corresponding pressures and

temperatures. The values of other characteristic and reduced parameters were obtained using eqs. (1) to (6).

Patterson and Rastogi¹³, in their extension of corresponding states theory to deal with the surface tension, used the reduction parameters,

$$\sigma^* = k^{1/2} P^{*2/3} T^{*1/3} \quad (7)$$

called the characteristic surface tension of the liquid. Here k is the Boltzmann constant. Starting from the work of Prigogine and Sarage¹⁴, they obtained the reduced surface tension equation, which in the case of a van der Waals liquid can be written as,

$$\tilde{\sigma}(\bar{V}) = M \bar{V}^{-5/3} = \frac{\bar{V}^{1/3} - 1}{\bar{V}^2} \ln \frac{\bar{V}^{1/3} - 0.5}{\bar{V}^{1/3} - 1}, \quad (8)$$

where M is the fraction of nearest neighbours which a molecule loses on moving from the bulk of the liquid to the surface, and its most suitable value is 0.29. Thus surface tension of a liquid in terms of Flory theory can be described by the expression,

$$\sigma = \sigma^* \tilde{\sigma}(\bar{V}). \quad (9)$$

According to Auerbach relation¹⁹, the velocity of sound U obeys the equation,

$$U = \left(\frac{\sigma}{6.3 \times 10^{-4} \rho} \right)^{2/3} \quad (10)$$

where ρ is the density of the liquid.

In the present paper the validity of Flory theory in cyclohexanes, propane, butane and methane has been tested. The required data were obtained from the literature^{10-12, 15-18}. The values of reduced parameters ($\bar{\rho}$) and \bar{V} were calculated in the light of eqs. (4) to (6) using the values of α at different temperatures. The characteristic parameters P^* , T^* and σ^* for cyclohexane, propane, butane and methane were then computed. These were finally used in eq. (10) to evaluate the sound velocity, and the results obtained are listed in Table 1. For comparison, the observed values¹⁰⁻¹² of sound velocity in these liquids are also given.

Table 1 reveals that the agreement between the calculated and observed velocity values is extremely good in the case of cyclohexane, propane and butane. The sound velocities obtained have little deviation from the observed values. A part of deviation in sound velocity is due to the values of M , which is an adjusting parameter. Different values of M have been used by different workers. Patterson and Rastogi have suggested a range of values from 0.25 to 0.29. Auxillary calculations show that the deviations can be minimized by adopting a value of higher than 0.29.

We can discuss the disagreement in the results obtained from Flory's statistical theory. The discrepancy

Table 1. Calculated and observed sound velocities in cyclohexane, propane and butane at different temperatures.

Temp. (K)	U_{cal} (m sec ⁻¹)	U_{expt} (m sec ⁻¹)	$\Delta\%$
Cyclohexane			
293	1263	1274	0.86
303	1241	1226	-1.22
313	1217	1177	-3.39
328	1193	1129	-5.67
333	1166	1081	-7.86
Propane			
143	1270	1510	15.89
153	1247	1452	14.12
163	1226	1395	12.11
173	1201	1337	10.17
183	1171	1272	7.94
193	1140	1210	5.78
203	1107	1150	3.74
213	1084	1091	0.64
223	1053	1034	-1.83
228	1037	1003	-3.38
Butane			
148	1456	1772	17.83
153	1448	1743	16.92
158	1441	1715	15.97
173	1400	1630	14.11
183	1386	1573	11.89
193	1370	1515	7.57
203	1339	1454	7.90
213	1311	1400	6.35
223	1284	1343	4.39
233	1239	1286	3.65
243	1229	1230	-0.08
253	1198	1173	-2.13
263	1169	1115	-4.84
268	1150	1085	-5.99

and hence may be applied at elevated pressure also. The present calculated values are obtained by using $M=0.28$.

Table 2 consists of the calculated and experimental¹⁷ values of sound velocity for liquid methane at different temperatures and pressures. It appears from this table that the agreement between the theoretical and experimental sound velocities in liquid methane at elevated pressures is not very good but not far from the expectations. At all temperatures (120 K, 140 K, 160 K and 180 K), the theory underestimates the values of sound velocity. Theoretical sound velocities in liquid methane are found to increase by increasing the pressure at all temperatures, which is in agreement with the observed trend.

Thus the basic advantage of Flory theory over other theories in computing sound velocity is that all essential parameters, density, thermal expansion coefficient and isothermal compressibility, required for the calculation, can be determined experimentally in very precise manner. Moreover, this theory is simpler to elaborate. Thus there is no probability of serious error in the prediction of sound velocity from Flory's statistical theory.

Table 2. Calculated and observed sound velocities in methane at different temperatures and pressures.

Pressure (kg cm ⁻²)	U_{cal} (m sec ⁻¹)	U_{expt} (m sec ⁻¹)	$\Delta\%$
T=120 K			
20	856	1037	17.45
50	918	1132	18.90
100	997	1286	22.47
150	1077	1424	24.36
200	1078	1446	25.45
250	1089	1421	23.36
T=140 K			
20	871	1164	25.17
50	907	1156	21.54
100	972	1196	18.73
150	1006	1243	19.06
200	1049	1272	17.53
250	1090	1282	14.97
T=160 K			
20	610	835	26.94
50	762	886	13.99
100	855	993	13.89
150	938	1071	12.42
200	996	1106	9.94
250	1047	1161	9.82
T=180 K			
50	541	790	31.65
100	768	869	11.62
150	900	985	8.63
200	964	950	-1.47
250	1131	1257	10.02

in the results may be due to two factors: the limitations of the Flory theory and the empirical nature of the equations used. Equations (1)–(6) are rigorously derived in the Flory theory. Equations (7) and (8) are suggested by Patterson and Rastogi¹³ on theoretical ground. Different values of M between 0.25 and 0.29 have been used by various workers^{8,9,19–23}. A part of the deviation in the results may be due to the choice of M . The uncertainties in the experimental values of α and β used for estimating the characteristic and reduced parameters are not more than 2%. The only empirical relation used in the present case is eq. (10) between surface tension and ultrasonic velocity. This equation has been rigorously tested by a number of workers, during recent past, for pure organic and inorganic liquids^{8,9,19–21} (at elevated pressures and temperatures), binary^{8,9,22} and ternary liquid mixtures^{20–23}. In all the cases the agreement was found to be within 5%. Hence larger fraction of deviation in results is due to the adjustable parameter M of eq. (8).

The success of Flory theory in predicting the velocity of sound at elevated pressure, as in the case of methane, can be used by adopting the higher values than 0.29

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A new species of *Pseudolimea* Arkell (Bivalvia) from Dhosa Oolite (Oxfordian: upper Jurassic), Jhura Hill, Kachchh, West India

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A new bivalve species, (*Pseudolimea rajnathi* n. sp.) has been described and illustrated from the Oxfordian (early Late Jurassic) rocks of the northwestern part of the Jhura Hill, Kachchh, Gujarat, in West India.

THE present note records a new bivalve species of the genus *Pseudolimea* Arkell from northwestern part of the Jhura Hill, District Kachchh, Gujarat. The genus hitherto represented in Kachchh by *P. duplicata* (J. de

C. Sowerby), is a wide ranging taxon (Bathonian to Kimmeridgian). The significance of this fossil is the presence of another form in Kachchh showing the extent of the Limids in Kachchh. The present specimen is preserved in the Department of Geology, Banaras Hindu University, Varanasi.

One left valve specimen was collected. The specimen occurs at the horizon top of Dhosa Oolite (=Mebha Oolite), bed no. 1, Upper Oxfordian comprising Oolitic limestone. The specimen was collected by O. P. Upadhyay on 22 December 1986, from point A (Figure 1), which is approximately 3 km south-east of Orira Village (latitude, 23°26'28" and longitude, 69°34'.

Systematic description

Class	: Bivalvia Linne', 1758
Subclass	: Pteriomorphia Beurlen, 1944
Order	: Pterioida Newell, 1965
Suborder	: Pteriina Newell, 1965
Superfamily	: Limacea Rafinesque, 1815
Family	: Limidae Rafinesque, 1815
Genus	: <i>Pseudolimea</i> Arkell, 1932
Type species	: <i>Plagiostoma duplicata</i> J. de C. Sowerby, 1827, Middle Jurassic; England.

The present species, *Pseudolimea rajnathi* n. sp. (Figure 2, a and b), is named in honour of late Prof. Rajnath, of this university, a pioneer worker who started investigations of the Jurassic Fauna of Kachchh.

Dimensions: Sp. no. M 86/1537; length, 29.2 mm; height, 29.5 mm (101); inflation, 6 mm (20.5). The figures in parentheses denote its percentage with respect to the length.

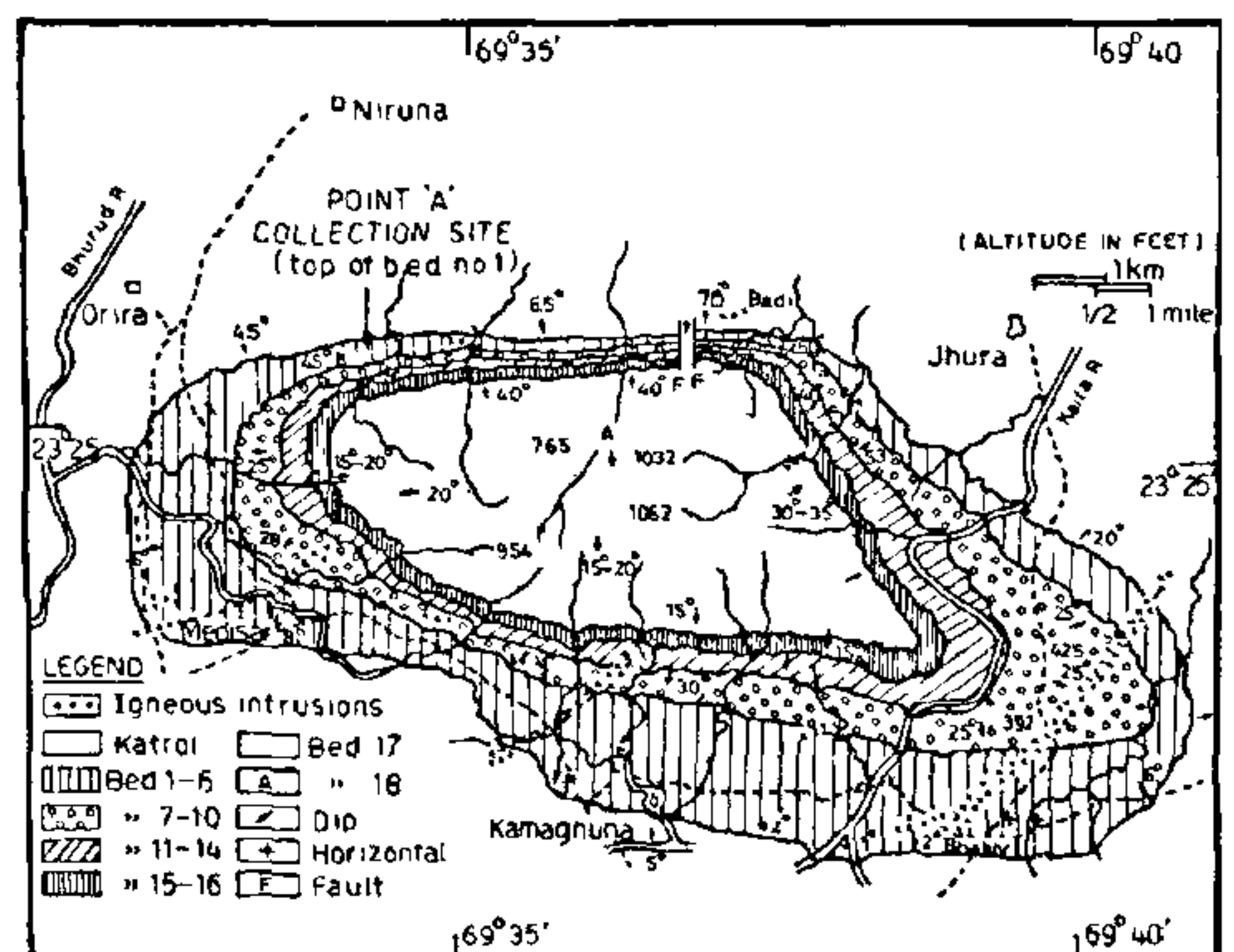


Figure 1. Modified geological map of the Jhura Dome (after Agrawal³).