



SONOCHEMICAL STUDIES OF BENZENE–METHANOL AND ACETONE–METHANOL MIXTURES

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ABSTRACT

Densities [d] and speed of sound [U] have been measured at 298.15, 303.15, 308.15 and 313.15 K for binary mixtures of methanol with benzene and acetone. Isentropic compressibility [K_s] and intermolecular free length [L_f] have been computed. Deviations in isentropic compressibility [ΔK_s], excess intermolecular free lengths [L_fE] have also been calculated. The results have been interpreted in terms of homo and heteromolecular interactions. The sound velocity in these binary mixtures at all temperatures has been evaluated using Nomoto, Van Dael equations, Jacobson's free length and Schaff's collision factor theories. Nomoto equation and collision factor theory predict correctly the value of ultrasonic velocity of these binary mixtures.

Key words : Ultrasonic velocity, Isentropic compressibility, Inter molecular free length.

INTRODUCTION

Accurate knowledge of thermodynamic properties such as ultrasonic velocity [U] along with derived parameters, namely, isentropic compressibility [k_s], intermolecular free length [L_f], acoustic impedance [Z], molar sound velocity [R], relative association [R_A], molecular association [M_A], available volume [V_a], internal pressure [II], and enthalpy [H], along with their deviations for mixtures of protic, aprotic and associated liquids has a great importance in theoretical as well as applied areas of research. Methanol exists as associated, while benzene and acetone are non-associated in liquid state. Thus upon mixing methanol with benzene and acetone, donor–acceptor type of specific interactions are expected between dissimilar molecules, because methanol is a proton donor and benzene and acetone accept it. The present investigation deals with the acoustic and physico–chemical behaviour of methanol + benzene and methanol + acetone mixtures at 298.15, 303.15, 308.15 and 313.15 K. To avoid repetition of interpretation, the relation between K_s , ΔK_s , L_f and L_fE with intermolecular interactions has been discussed.

EXPERIMENTAL

Methanol (S.D., Fine Chemicals, Purity 99 mol %), benzene (Merck purity 99%), acetone (Qualigen Fine Chemical, Purity 99.5 mol %) were used after single distillation. The purity of the liquids after distillation was ascertained by GLC and also by comparing their densities and ultrasonic velocities with the literature values at 298.15 K. They matched well. Binary mixtures were prepared by known masses of each liquid in airtight stoppered glass bottles. The mass measurements were made on a single pan balance (Meter Switzerland, AE-240), to an accuracy of 0.01 mg. The more volatile component (benzene and acetone) was filled directly into the bottle and was weighed. The second component (methanol) was injected into the bottle through the stopper by means of a syringe. This method allowed negligible vapour loss and contamination. The possible error in mole fraction is calculated to be $< \pm 1 \times 10^{-4}$.

The densities of liquids were determined in a double arm pycnometer, which in turn was calibrated with triply distilled water. The speed of sound was determined by using a variable path single crystal interferometer (Mittal Enterprise, New Delhi Model F-81) at frequency of 2 MHz. The accuracy in density and ultrasonic velocity measurements is $5 \times 10^{-5} \text{ g cm}^{-3}$ and 0.03%, respectively. The other experimental details of the measurements of density and ultrasonic velocity are the same as described previously¹⁻¹⁰

RESULTS AND DISCUSSION

From the observed values of d and U , isentropic compressibility [K_s], intermolecular free length [L_f], the deviation in isentropic compressibility [ΔK_s], and excess intermolecular free length [L_f^E] are evaluated from the following expressions.¹⁻¹⁰

$$K_s = \frac{1}{dU^2} \quad \dots(1)$$

$$L_f = K\sqrt{K_s} \quad \dots(2)$$

$$\Delta K_s = K_{s \text{ mix.}} - K_{s1} \Phi_1 - K_{s2} \Phi_2 \quad \dots(3)$$

$$L_f^E = L_{f \text{ mix.}} - L_{f1} \Phi_1 - L_{f2} \Phi_2 \quad \dots(4)$$

where K_{s1} , Φ_1 and K_{s2} , Φ_2 are isentropic compressibility, and volume fraction of components 1 and 2, respectively of binary mixtures. $K_{s \text{ mix.}}$ and $L_{f \text{ mix.}}$ are isentropic compressibility and intermolecular free length of mixtures, respectively. K is Jacobson's temperature dependent constant and other symbols have their usual meanings. Φ_1 is the volume fraction of 1th component of mixture and defined as,

$$\Phi_i = \frac{X_i V_i}{\sum X_i v_i} \quad \dots(5)$$

where X_i and V_i are mole fraction and molar volume of i^{th} component in the mixture. Tables 1 and 2 include d , U , K_s and L_f values of binary mixtures of benzene – methanol, acetone – methanol at 298.15, 303.15, 308.15 and 313.15 K. Table 3 lists ΔK_s and $L_f E$ values for both systems at all temperatures. Fig. 1 and 2 illustrate variation of ΔK_s and $L_f E$ with Φ_1 (benzene or acetone) at 298.15 K, respectively. Similar plots are obtained at other temperatures.

Table 1. Density [d], ultrasonic velocity [U], isentropic compressibility [Ks], intermolecular free length [L_f], for benzene [1] – methanol [2] mixtures at 298.15, 303.15, 308.15 and 313.15 K.

X_1	d g cm ⁻³	U m sec ⁻¹	$K_s \times 10^{11}$ cm ² dyne ⁻¹	$L_f \times 10^9$ cm
T = 298.15 K				
0.0000	0.7864	1108.00	10.358	6.36
0.0422	0.7968	1121.40	9.980	6.24
0.0904	0.8068	1142.80	9.491	6.09
0.1474	0.8165	1165.40	9.018	5.94
0.2149	0.8262	1168.40	8.866	5.79
0.2893	0.8350	1209.40	8.188	5.66
0.3836	0.8440	1231.40	7.814	5.52
0.4897	0.8518	1250.80	7.504	5.41
0.6103	0.8584	1267.00	7.257	5.32
0.7878	0.8658	1282.80	7.019	5.24
1.0000	0.8736	1300.00	6.773	5.14
T = 303.15 K				
0.0000	0.7698	1100.00	10.736	6.54
0.0422	0.7809	1111.20	10.371	6.43
0.0904	0.7917	1130.00	9.892	6.28
0.1474	0.8022	1149.80	9.429	6.13
0.2149	0.8130	1170.20	8.982	5.98
0.2893	0.8229	1189.60	8.587	5.85
0.3836	0.8332	1209.60	8.203	5.72
0.4897	0.8421	1227.60	7.880	5.60

X_1	d $g\ cm^{-3}$	U $m\ sec^{-1}$	$K_s \times 10^{11}$ $cm^2\ dyne^{-1}$	$L_f \times 10^9$ cm
0.6103	0.8499	1243.30	7.612	5.51
0.7878	0.8588	1259.00	7.346	5.41
1.0000	0.8682	1276.00	7.074	5.31
T = 308.15 K				
0.0000	0.7652	1088.00	11.040	6.68
0.0422	0.7761	1097.00	10.707	6.58
0.0904	0.7867	1113.40	10.254	6.44
0.1474	0.7973	1131.40	9.798	6.30
0.2149	0.8080	1149.80	9.361	6.15
0.2893	0.8179	1167.40	8.971	6.02
0.3836	0.8281	1186.00	8.585	5.89
0.4897	0.8370	1203.20	8.253	5.78
0.6103	0.8484	1218.90	7.933	5.68
0.7878	0.8536	1235.00	7.681	5.57
1.0000	0.863	1252.00	7.392	5.54
T = 313.15 K				
0.0000	0.7607	1080.00	11.270	6.82
0.0422	0.7713	1086.40	10.985	6.73
0.0904	0.7819	1100.20	10.566	7.60
0.1474	0.7924	1115.00	10.151	6.47
0.2149	0.8031	1131.00	9.734	6.33
0.2893	0.8129	1146.40	9.360	3.21
0.3836	0.8231	1163.00	8.982	6.08
0.4897	0.8319	1179.00	8.648	5.97
0.6103	0.8396	1194.60	8.346	5.87
0.7878	0.8485	1211.40	8.031	5.75
1.0000	0.858	1228.00	7.729	5.64

Table 2. Density [d], ultrasonic velocity [U], isentropic compressibility [K_s], intermolecular free length [L_f], for acetone [1] – methanol [2] mixtures at 298.15, 303.15, 308.15 and 313.15 K.

X_1	d g cm ⁻³	U m sec ⁻¹	$K_s \times 10^{11}$ cm ² dyne ⁻¹	$L_f \times 10^9$ cm
T = 298.15 K				
0.0000	0.7864	1108.00	10.358	6.36
0.0602	0.7879	1114.40	10.220	6.32
0.1007	0.7900	1119.20	10.105	6.28
0.1913	0.7925	1124.00	9.988	6.25
0.2768	0.7949	1130.00	9.852	6.20
0.3551	0.7958	1136.00	9.737	6.17
0.4531	0.7954	1140.00	9.606	6.13
0.5594	0.7939	1153.00	9.465	6.08
0.6922	0.7915	1165.20	9.306	6.03
0.7889	0.7894	1173.60	9.197	5.99
0.8986	0.7869	1183.00	9.081	5.96
1.0000	0.7844	1192.00	8.972	5.92
T = 303.15 K				
0.0000	0.7698	1100.00	10.736	6.54
0.0602	0.7729	1103.50	10.625	6.50
0.1007	0.7760	1105.60	10.542	6.48
0.1913	0.7796	1107.80	10.452	6.45
0.2768	0.7830	1111.20	10.343	6.42
0.3551	0.7847	1115.20	10.247	6.39
0.4531	0.7853	1121.00	10.133	6.35
0.5594	0.7849	1128.20	10.010	6.31
0.6922	0.7837	1126.40	10.057	6.27
0.7889	0.7825	1144.20	9.761	6.23
0.8986	0.7808	1151.80	9.654	6.20
1.0000	0.7788	1166.00	9.444	6.16

X_1	d g cm^{-3}	U m sec^{-1}	$K_s \times 10^{11}$ $\text{cm}^2 \text{ dyne}^{-1}$	$L_f \times 10^9$ cm
T= 308.15 K				
0.0000	0.7652	1088.00	11.040	6.68
0.0602	0.7684	1091.40	10.926	6.65
0.1007	0.7715	1093.00	10.850	6.62
0.1913	0.7752	1094.40	10.770	6.60
0.2768	0.7782	1097.80	10.663	6.57
0.3551	0.7796	1101.80	10.566	6.54
0.4531	0.7801	1107.60	10.449	6.50
0.5594	0.7796	1114.80	10.321	6.46
0.6922	0.7784	1124.00	10.169	6.41
0.7889	0.7772	1131.00	10.059	6.38
0.8986	0.7753	1139.20	9.939	6.34
1.0000	0.7731	1148.00	9.815	6.30
T= 313.15 K				
0.0000	0.7607	1080.00	11.270	6.82
0.0602	0.7639	1079.80	11.227	6.80
0.1007	0.7669	1073.00	11.326	6.83
0.1913	0.7706	1067.80	11.381	6.85
0.2768	0.7734	1065.00	11.400	6.85
0.3551	0.7745	1064.80	11.388	6.85
0.4531	0.7750	1066.60	11.342	6.84
0.5594	0.7743	1071.20	11.255	6.81
0.6922	0.7731	1078.30	11.125	6.77
0.7889	0.7717	1084.40	11.020	6.74
0.8986	0.7698	1091.80	10.898	6.70
1.0000	0.7674	1100.00	10.769	6.66

Table 3. Deviation in isentropic compressibility [ΔK_s] and excess intermolecular free length [L_F^E] for benzene [1] –methanol [2] and acetone [1] – menthanol [2] mixtures at 298.15, 303.15, 308.15 and 313.15 K.

benzene [1] – methanol [2]			Acetone [1] – methanol [2]		
Φ_1	$\Delta K_s \times 10^{12}$ $\text{cm}^2 \text{ dyne}^{-1}$	$L_F^E \times 10^{10}$ cm	Φ_1	$\Delta K_s \times 10^{12}$ $\text{cm}^2 \text{ dyne}^{-1}$	$L_F^E \times 10^{10}$ cm
T = 298.15 K			T = 298.15 K		
0.0000	0.0000	0.0000	0.0000	0.000	0.000
0.0882	0.0619	0.1240	0.1043	0.055	0.031
0.1791	0.2254	0.5150	0.1997	0.234	0.097
0.2751	0.3542	0.8438	0.3006	0.458	0.176
0.3752	0.4189	1.1226	0.4102	0.617	0.233
0.4718	0.4788	1.2440	0.5001	0.723	0.269
0.5772	0.4752	1.3582	0.6009	0.805	0.296
0.6780	0.4237	1.2284	0.6976	0.733	0.270
0.7746	0.3243	0.9499	0.8034	0.605	0.222
0.8907	-0.1463	0.3335	0.8717	0.467	0.171
1.0000	0.0000	0.0000	0.9415	0.272	0.098
			1.0000	0.000	0.000
T = 303.15 K			T = 303.15 K		
0.0000	0.0000	0.0000	0.0000	0.000	0.000
0.0882	0.6200	0.0980	0.1030	0.126	0.049
0.1719	2.2600	0.5440	0.1975	0.429	0.149
0.2751	3.5460	0.9110	0.2976	0.717	0.245
0.3752	4.4250	1.3120	0.4068	0.929	0.315
0.4718	4.4788	1.1820	0.4966	1.040	0.352
0.5772	4.7470	1.3350	0.5975	1.103	0.373
0.6780	4.2330	1.2150	0.6946	1.022	0.347
0.7746	3.2460	0.9390	0.8012	0.830	0.282
0.8907	1.4630	0.4060	0.8701	0.631	0.215
1.0000	0.0000	0.0000	0.9405	0.409	0.138
			0.0000	0.000	0.000

Φ_1	$\Delta Ks \times 10^{12}$ $\text{cm}^2 \text{ dyne}^{-1}$	$L_F^E \times 10^{10}$ cm	Φ_1	$\Delta Ks \times 10^{12}$ $\text{cm}^2 \text{ dyne}^{-1}$	$L_F^E \times 10^{10}$ cm
T = 308.15 K			T = 308.15 K		
0.0000	0.0000	0.0000	0.0000	0.000	0.000
0.0870	0.4570	0.0480	0.1031	0.128	0.049
0.1769	1.9610	0.4450	0.1977	0.526	0.179
0.2721	3.1090	0.7610	0.2979	0.953	0.316
0.3717	3.9290	1.0040	0.4071	1.219	0.404
0.4681	4.3520	1.1480	0.4970	1.357	0.449
0.5736	4.4260	1.1710	0.5979	1.415	0.469
0.6747	3.8590	1.0650	0.6949	1.324	0.440
0.7720	2.9790	0.0829	0.8014	1.103	0.367
0.8892	1.3410	0.0354	0.8702	0.851	0.283
1.0000	0.0000	0.0000	0.9408	0.512	0.170
			1.0000	0.000	0.000
T = 313.15 K			T = 313.15		
0.0000	0.000	0.0000	1.0000	0.000	0.000
0.0870	0.152	0.0420	0.1032	0.092	0.030
0.1769	1.414	0.2770	0.1979	1.542	0.470
0.2721	2.491	0.5660	0.2982	2.608	0.793
0.3717	3.227	0.7760	0.4075	3.341	1.016
0.4681	3.612	0.9010	0.4973	3.672	1.118
0.5736	3.627	0.9320	0.5982	3.178	1.134
0.6747	3.254	0.8530	0.6952	3.327	1.018
0.7720	2.564	0.6810	0.8016	2.559	0.786
0.8892	1.555	0.2880	0.8704	1.849	0.570
1.0000	0.000	0.0000	0.9409	0.982	0.340
			0.0000	0.000	0.000

Table 4. Comparison of the calculated and experimental ultrasonic velocity values for binary mixtures at 298.15 K

X ₁	U _{exp.} m sec ⁻¹	U _{cal.} in m sec ⁻¹			
		C F T	Nomoto	Van Dael	F L T
System Benzene + Methanol					
0.0000	1108.00	1108.00	1108.00	1108.00	1527.52
0.0422	1121.40	1134.15	1124.12	1092.13	1527.66
0.0904	1142.80	1159.58	1140.89	1077.06	1522.38
0.1474	1165.40	1184.51	1158.78	1062.96	1509.80
0.2149	1168.40	1208.96	1177.66	1050.96	1493.03
0.2893	1209.40	1230.74	1196.05	1043.06	1473.01
0.3836	1231.40	1252.00	1216.33	1040.60	1445.99
0.4897	1250.80	1259.31	1235.94	1047.77	1414.55
0.6103	1267.00	1282.48	1254.93	1069.59	1378.77
0.7878	1282.80	1293.50	1278.01	1134.85	1331.75
1.0000	1300.00	1300.00	1300.00	1300.00	1294.04
System Acetone + Methanol					
0.0000	1108.00	1108.00	1108.00	1108.00	1772.42
0.0602	1114.40	1126.57	1116.57	1099.31	1726.02
0.1007	1119.20	1143.69	1124.45	1092.41	1690.01
0.1913	1124.00	1161.15	1132.82	1086.60	1654.40
0.2768	1130.00	1178.37	1141.96	1082.58	1613.16
0.3551	1136.00	1189.48	1149.50	1081.75	1569.42
0.4531	1144.00	1198.29	1157.99	1084.51	1510.68
0.5594	1153.60	1202.93	1166.17	1092.39	1447.05
0.6922	1165.20	1204.08	1175.16	1109.94	1375.11
0.7889	1173.60	1202.15	1180.99	1128.75	1327.01
0.8986	1183.00	1197.79	1186.98	1157.33	1277.08
1.0000	1192.00	1192.00	1192.00	1192.00	1234.71

On the basis of the model for sound propagation proposed by Eyring and Kincaid¹¹, intermolecular free length decreases and consequently ultrasonic velocity increases in benzene – methanol and acetone – methanol mixtures. This implies that Eyring and Kincaid model

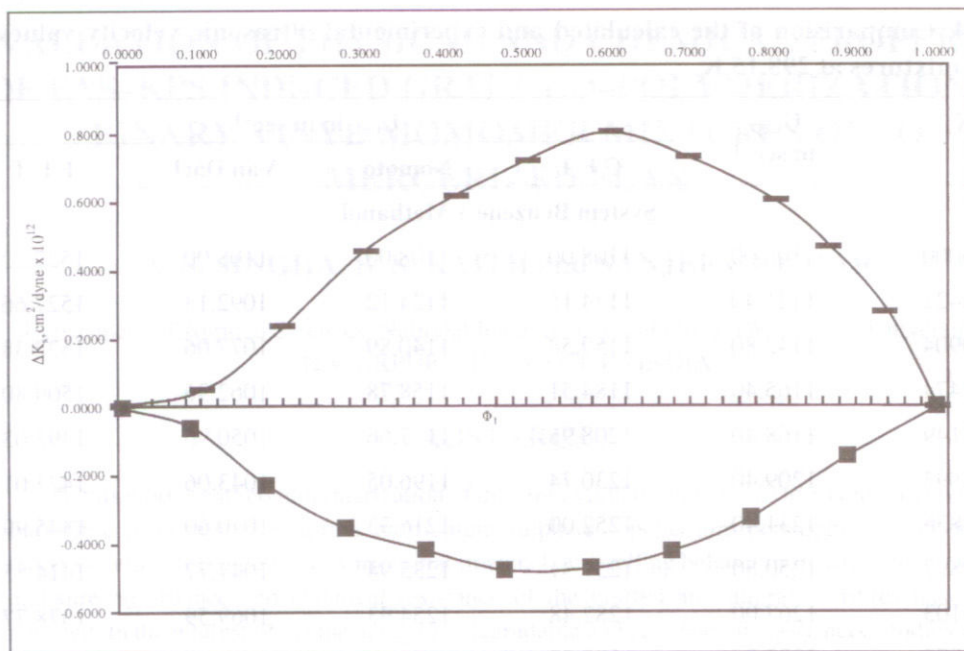


Fig.1. ΔK_s at 298.15 K for $[\Phi_1]$ [benzene] $[1-\Phi_1]$ methanol [■], $[\Phi_1]$ [acetone] $[1-\Phi_1]$ [methanol] [●] mixture

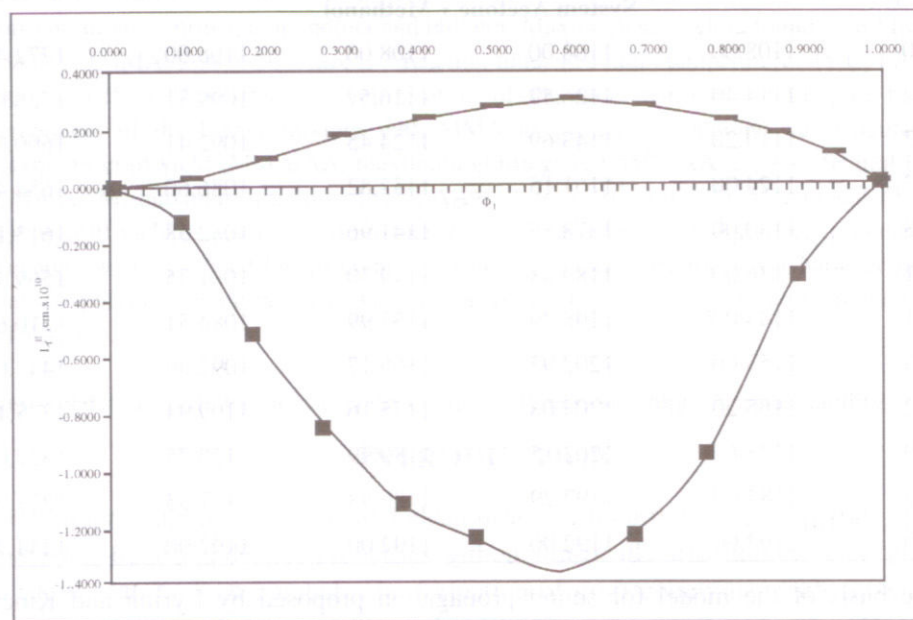


Fig.2. L_F^E at 298.15 K for $[\Phi_1]$ [benzene] $[1-\Phi_1]$ methanol [■], $[\Phi_1]$ [acetone] $[1-\Phi_1]$ [methanol] [●] mixture

explains well the variation of U with composition of binary mixtures. Negative values of ΔK_s and L_F^E in benzene – methanol mixture indicate donor – acceptor type of interactions resulting in H – II bonding. Positive values of ΔK_s and L_F^E in the mixtures of acetone – methanol suggest interstitial accommodation of acetone molecules into clusters of methanol.

Table 4 includes a comparison between experimental ultrasonic velocity values with those calculated using collision factor theory [CFT]¹², free length theory [FLT]¹³, Nomoto¹⁴ and van Dael¹⁵ equations at 298.15 K. Similar observations are made at other temperatures. In both binary mixtures, ultrasonic velocity calculated from Nomoto and CFT are close to the experimentally observed values. Nomoto equation is based on the assumption of the linearity of the molecular sound velocity versus mole fraction and additivity of molar volumes in liquid mixture¹⁴, a behaviour which has been observed in the present system. The FLT is not strictly applicable to system, where the components are self associated as in the present study.

REFERENCES

1. P. S. Nikam, Smt. Neena Nikam, Mehdi Hasan and B. S. Suryawanshi. *Asian J. Chem.*, **6**, 237 (1994).
2. P. S. Nikam, Smt. Neena Nikam, Mehdi Hasan and A. R. Hirey. *Asian J. Chem.*, **7**, 500 (1995).
3. P. S. Nikam, Smt. M. C. Jadhav and Mehdi Hasan, *Acustica. acta acustica*, **83**, 86 (1997).
4. P. S. Nikam, T. R. Mahale and Mehdi Hasan, *Acustica acta acustica*, **84**, 579 (1998).
5. P. S. Nikam, B. S. Jagadale, A. B. Sawant and Mehdi Hasan, *Acoustics Letters*, **22**, 1999 (1999).
6. P. S. Nikam, Mehdi Hasan and Smt. V. U. Patil, *Indian J. Pure Appl. Phys.* **38**, 693 (2000).
7. P. S. Nikam, Mehdi Hasan and V. M. Kapade, *J. Pure. Appl Ultrason.*, **22**, 16 (2000).
8. P. S. Nikam, H. R. Ansari and Mehdi Hasan, *J. Mol. Liq.*, **8**, 169 (2000).
9. P. S. Nikam and R. B. Pathak, *J. Pure Appl. Ultrason*, **18**, 19 (1996).
10. P. S. Nikam and R. B. Pathak, *J. Pure Appl. Ultrason*, **18**, 19 (1996).
11. H. Eyring and J. F. Kincaid, *J. Chem. Phys.*, **6**, 620 (1938).
12. W. Schaff, *Molecular Akustics* (1963).
13. B. Jacobson, *Acta. Chem. Sca*, **6**, 1485 (1952).
14. O. J. Nomoto, *Phy. Soc. Japan*, **13**, 1528 (1958).
15. W. Van Dael and E. Vangeel, *Proceedings of the First International Conference on Calorimetry, Thermodynamics, Warsa*, 535 (1969).