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THERMODYNAMICS OF MOLECULAR INTERACTIONS IN MIXTURES OF 1,2-DIBROMOETHANE AND XYLENES AT 298.15 K

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ABSTRACT

The values of the excess molar Gibbs free energy of mixing for mixtures of 1,2-dibromoethane with *o*-, *m*- and *p*-xylene over the whole concentration range at 298.15 K have been obtained from vapour pressure data. The results have been analysed in terms of the Flory theory, the Sanchez and Lacombe theory and the ideal associated model approach. The ideal associated model, which assumes the presence of AB type molecular species, explains reasonably well the dependence of excess enthalpy of these systems on the mole fraction of the components. The equilibrium constant for the reaction $A + B \rightleftharpoons AB$ and the enthalpy of formation of AB molecular species have also been calculated.

INTRODUCTION

The study of excess molar volumes of mixing and excess molar enthalpies of mixing (H_m^E) of 1,2-dibromoethane (DBE) with aromatic hydrocarbons [1,2] has shown the interaction of two components as well as the disruption of the favourable order of the pure components. The excess permittivity and excess refractive index measurements [3] of these mixtures have also provided evidence for the existence of weak specific interactions of electron donor/acceptor type between DBE and aromatic hydrocarbons (aromatic hydrocarbons behave as electron donors). This has been supported further by NMR spectroscopic studies [3] of these mixtures.

In the present investigations, values of the excess molar Gibbs free energy of mixing, (G_m^E), for mixtures of DBE and xylenes over the whole concentration range at 298.15 K have been obtained. The data are critically examined in terms of the theories of Flory [4,5], Sanchez and Lacombe [6,7] and the ideal associated approach [8]. The G_m^E data have been coupled with our earlier reported H_m^E data [1] to obtain a better understanding of molecular interactions between the components of these mixtures.

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EXPERIMENTAL

1,2-Dibromoethane, *o*-xylene, *m*-xylene and *p*-xylene (BDH, A.R. grade) were purified by standard procedures [9]. The purity of the final samples was checked by density determinations at 298.15 ± 0.01 K (293.15 K in the case of *m*-xylene and 1,2-dibromoethane), which agreed to within $\pm 5 \times 10^{-5}$ g cm^{-3} with the corresponding literature values [10,11]. Total vapour pressures of these mixtures were measured as a function of the liquid phase mole fraction of DBE at 298.15 ± 0.01 K by a static method in the manner described by Nigam and Mahl [12]. The height of mercury in the manometer was read by a cathetometer to 0.001 cm and corrected to 273.15 K and standard gravity. The composition of the liquid phase was obtained by capacitance measurements (with a cell fitted in the vapour pressure still) using a dipole meter (type R1 09, S&I Instruments, India). The measured vapour pressures were reproducible within ± 0.02 Torr. The uncertainty in the liquid phase composition was ±0.01%. The agreement between experimentally observed and literature values [10,13] of vapour pressures was within ±0.3%.

RESULTS AND DISCUSSION

The G_m^E values for these mixtures were calculated by Barker's method [14] using vapour pressure for the respective mixtures. The form of function used for G_m^E, following Redlich and Kister [15], is

$$G_m^E = x_A x_B RT\left[G_0 + G_1(x_A - x_B) + G_2(x_A - x_B)^2\right] \tag{1}$$

where G_0, G_1 and G_2 are adjustable parameters. The values of these parameters, along with G_m^E values for DBE–xylene mixtures at 298.15 K, are given in Table 1. Virial coefficients needed in these calculations were obtained from Berthelot's equation [16] and the critical constants were taken from the literature [17]. We are not aware of any G_m^E data for mixtures of DBE with *o*-xylene, *m*-xylene or *p*-xylene at 298.15 K with which to compare our experimental results, as plotted in Fig. 1.

We analysed our G_m^E data in terms of Flory theory [4,5], which takes into consideration the shape and size of the molecule, and according to this theory G_m^E is given by

$$G_m^E = 3T\left[(x_A P_A^* V_A^*/T_A^*)\ln(\tilde{V}_A^{1/3} - 1)/(\tilde{V}_{cal}^{1/3} - 1) + (1 - x_A)(P_B^* V_B^*/T_B^*)\ln(\tilde{V}_B^{1/3} - 1)/(\tilde{V}_{cal}^{1/3} - 1)\right] + H_m^E \quad \text{(Flory)} \tag{2}$$

where $\tilde{V}_{cal} = \tilde{V}_0 + \tilde{V}_{cal}^E$ and all parameters have the same significance as described by the authors in their original papers [4,5] and have been

TABLE 1

Measured total vapour pressure P, partial pressures P_A and P_B, activity coefficients γ_A and γ_B, residual vapour pressure. $R = P_{exp} - P_{cal}$, Gibbs free energy of mixing G_m^E, and the parameters of eqn. (1) for different mole fractions x_A of 1,2-dibromoethane (A) in mixtures with xylenes (B) at 298.15 K

x_A	P (Torr)	P_A (Torr)	P_B (Torr)	γ_A	γ_B	R (Torr)	G_m^E (J mol^{-1})
1,2-Dibromoethane–o-*xylene*							
0.0000	6.45	–	–	–	–	–	–
0.0931	6.70	1.13	5.85	0.7659	0.9913	−0.04	−81.18
0.2026	7.10	2.45	5.14	0.8526	0.9741	0.00	−131.85
0.2923	7.50	3.53	4.57	0.8765	0.9658	0.00	−156.59
0.3914	7.90	4.73	3.93	0.8775	0.9655	0.04	−179.70
0.4991	8.38	6.03	3.23	0.8732	0.9692	0.02	−206.57
0.5715	8.74	6.91	2.76	0.8762	0.9651	−0.02	−224.90
0.6356	9.09	7.68	2.35	0.8857	0.9491	−0.06	−238.39
0.7446	9.72	9.00	1.65	0.9175	0.8749	−0.02	−243.63
0.8409	10.45	10.17	1.03	0.9564	0.7430	0.04	−210.04
0.9361	11.33	11.32	0.41	0.9908	0.5554	0.11	−114.65
1.0000	12.09	–	–	–	–	–	–
$RTG_0 = -827.21$ J mol^{-1},			$RTG_1 = -517.50$ J mol^{-1},			$RTG_2 = -838.73$ J mol^{-1}	
1,2-Dibromoethane–m-*xylene*							
0.0000	7.95	–	–	–	–	–	–
0.0898	8.12	1.09	7.24	0.8360	0.9943	0.01	−31.32
0.1724	8.38	2.08	6.58	0.8966	0.9842	0.04	−55.51
0.2506	8.61	3.03	5.96	0.9286	0.9752	−0.02	−74.52
0.3479	8.95	4.21	5.18	0.9447	0.9683	−0.04	−92.90
0.4465	9.36	5.40	4.40	0.9475	0.9666	−0.01	−105.19
0.5631	9.82	6.81	3.47	0.9482	0.9657	0.01	−110.49
0.6856	10.38	8.29	2.50	0.9567	0.9505	0.07	−103.22
0.7889	10.78	9.54	1.68	0.9719	0.9080	−0.02	−84.60
0.9124	11.41	11.03	0.70	0.9929	0.7984	−0.10	−43.77
1.0000	12.09	–	–	–	–	–	–
$RTG_0 = -435.82$ J mol^{-1},			$RTG_1 = -99.81$ J mol^{-1},			$RTG_2 = -433.38$ J mol^{-1}	
1,2-Dibromoethane–p-*xylene*							
0.0000	8.46	–	–	–	–	–	–
0.0957	8.62	1.16	7.65	0.8664	0.9962	−0.01	−42.63
0.1965	8.88	2.38	6.80	0.9119	0.9877	−0.01	−69.49
0.2816	9.17	3.40	6.08	0.9345	0.9803	0.03	−82.72
0.3994	9.51	4.83	5.08	0.9510	0.9717	−0.02	−92.47
0.5011	9.85	6.06	4.22	0.9590	0.9651	−0.03	−95.94
0.5936	10.24	7.18	3.44	0.9654	0.9572	0.02	−95.78
0.6793	10.60	8.21	2.71	0.9727	0.9446	0.05	−91.93
0.7784	10.94	9.41	1.88	0.9828	0.9181	−0.03	−80.38
0.8711	11.38	10.53	1.09	0.9926	0.8755	−0.03	−58.60
0.9405	11.79	11.37	0.50	0.9981	0.8289	0.03	−32.06
1.0000	12.09	–	–	–	–	–	–
$RTG_0 = -383.69$ J mol^{-1},			$RTG_1 = -32.63$ J mol^{-1},			$RTG_2 = -206.85$ J mol^{-1}	

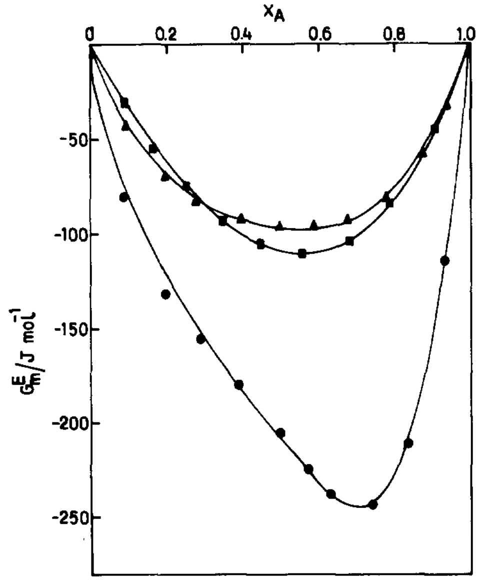

Fig. 1. Experimentally measured G_m^E values for DBE–*o*-xylene (●), DBE–*m*-xylene (■) and DBE–*p*-xylene (▲) mixtures as a function of mole fraction of DBE at 298.15 K.

calculated in our earlier work [1]. Using our earlier reported H_m^E, obtained by Flory theory [1], the values of G_m^E at 0.1, 0.3, 0.5, 0.7 and 0.9 mole fractions of DBE have been calculated, and are reported in Table 2, along with the corresponding experimental values; the agreement between these values appears to be good only in the case of DBE–*p*-xylene mixtures.

Next we examined our data using the Sanchez and Lacombe theory [6,7] which is also a lattice theory similar to that of Flory but incorporates Guggenheim's [18,19] idea of vacant sites/holes in the lattice fluids. According to this theory, G_m^E is given by

$$G_m^E = H_m^E(\text{Sanchez and Lacombe}) - RT\Big\{\Sigma x_A \ln \phi_A + r_{\text{mix}}\big(\tilde{V}_{\text{mix}} - 1\big) \times \ln\big(1 - \tilde{l}_{\text{mix}}\big) + \ln \tilde{l}_{\text{mix}} - \Sigma x_A\big[r_A^0\big(\tilde{V}_A - 1\big)\ln\big(1 - \tilde{l}_A\big) + \ln \tilde{l}_1\big]\Big\} \qquad (3)$$

where all the parameters have the same significance as that described by the authors in their original papers [6,7] and have been reported elsewhere [1]. The G_m^E values at 0.1, 0.3, 0.5, 0.7 and 0.9 mole fractions of DBE computed from this theory are given in Table 2, and these values are many times larger than the corresponding experimental values.

The H_m^E and activity coefficient data for these binary mixtures were then analysed in terms of the ideal associated model [8]. It is assumed that in these mixtures the equilibrium process occurs according to the reaction

$$A + B \rightleftharpoons AB \qquad (4)$$

TABLE 2

Comparison of experimentally measured G_m^E values at 298.15 K with the values calculated from Flory theory and Sanchez and Lacombe theory for various mixtures of 1,2-dibromoethane (A) and xylenes (B)

x_A	G_m^E (exp) (J mol^{-1})	G_m^E (Flory) (J mol^{-1})	G_m^E (Sanchez and Lacombe) (J mol^{-1})
1,2-Dibromoethane–o-*xylene*			
0.1	−85.50	14.65	5662.33
0.3	−158.43	23.79	5075.34
0.5	−206.80	27.44	4662.64
0.7	−245.37	25.15	4455.57
0.9	−160.02	15.98	4482.36
1,2-Dibromoethane–m-*xylene*			
0.1	−57.00	22.76	5564.32
0.3	−97.70	38.19	5005.41
0.5	−108.96	51.85	4633.66
0.7	−114.47	46.42	4463.70
0.9	−71.37	25.59	4532.76
1,2-Dibromoethane–p-*xylene*			
0.1	−44.10	−37.13	5259.46
0.3	−84.78	−101.79	4715.86
0.5	−95.92	−129.25	4357.68
0.7	−90.27	−110.76	4209.84
0.9	−48.80	−45.95	4302.20

The three species (A, B, AB) are assumed to mix ideally. If Z_A, Z_B and Z_{AB} are the equilibrium mole fractions of species A, B and AB respectively, then the equilibrium constant K for this process is given by

$$K = \frac{Z_{AB}}{Z_A Z_B} \text{ or } Z_{AB} = K Z_A Z_B \qquad (5)$$

Also at equilibrium

$$Z_A + Z_B + Z_{AB} = 1 \qquad (6)$$

and combining the eqns. (5) and (6) we get

$$\frac{1 - Z_A - Z_B}{Z_B} = K Z_A \qquad (7)$$

Since the three chemical species are assumed to form an ideal solution, each equilibrium mole fraction Z_i is equal to the corresponding activity a_i and hence eqn. (7) becomes

$$\frac{1 - a_A - a_B}{a_B} = K a_A \qquad (8)$$

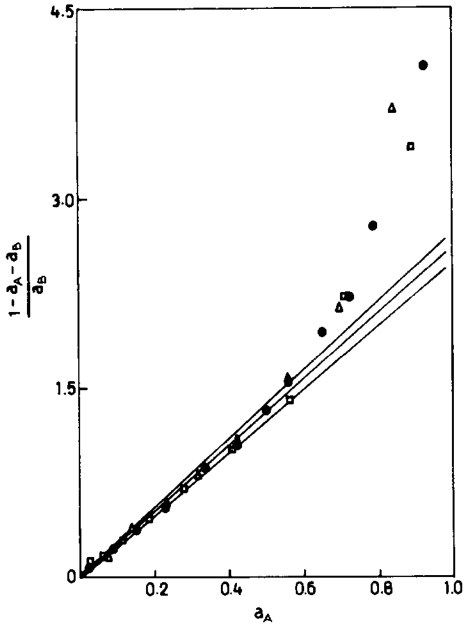

Fig. 2. Plot of $(1-a_A-a_B)/a_B$ vs. a_A for DBE–*o*-xylene (○), DBE–*m*-xylene (□) and DBE–*p*-xylene (△).

In order to evaluate K using eqn. (8), the observed activities of the components of these binary mixtures were corrected for their dispersion contribution using the expression

$$a_A = \frac{x_A \gamma_A}{\gamma_A^*} \text{ and } a_B = \frac{x_B \gamma_B}{\gamma_B^*} \tag{9}$$

where γ_A^* and γ_B^* are the activity coefficients of a reference mixture. A mixture of DBE (A) and cyclohexane (B) was chosen as the reference system, since cyclohexane is inert and has nearly the same molar volume as the xylenes. The values of $(1-a_A-a_B)/a_B$ for all these systems were computed and plotted against a_A, and the plots were found to be good straight lines (Fig. 2) passing through the origin. The values of the equilibrium constants K for these systems were evaluated from the slopes of the straight lines and are found to be 2.6774, 2.5350 and 2.8276 for *o*-xylene, *m*-xylene and *p*-xylene respectively. The molar excess enthalpy H_m^E for an equilibrium of the type A + B $\rightleftharpoons$ AB is given by

$$H_m^E = \frac{n_{AB}\Delta H}{N_A + N_B} \tag{10}$$

and the material balance equations are

$$N_A = n_A + n_{AB} \tag{11}$$

$$N_B = n_B + n_{AB} \tag{12}$$

In these equations n_A, n_B and n_{AB} represent the amounts of substance of species A, B and AB respectively, and N_A and N_B are the stoichiometric amounts of substance of A and B. Using eqns. (5), (6) and (10)–(12), we obtain

$$H_m^E \frac{(1+KZ_A)}{(1-x_A)} = K\Delta H Z_A \tag{13}$$

Further algebraic manipulation of eqns. (5), (6), (11) and (12) gives

$$x_A = \frac{(1+K)Z_A}{1+KZ_A(2-Z_A)} \tag{14}$$

The experimental values of H_m^E were also corrected for their dispersion contributions by subtracting earlier reported H_m^E values [20] for the DBE–cyclohexane system from the experimental values. Thus in eqn. (13)

$$H_m^E(\text{experimental corrected}) = H_m^E(\text{experimental}) - H_m^E(\text{DBE–cyclohexane}) \tag{15}$$

the values of x_A were calculated for various values of Z_A using the values of K as obtained from the plots of $(1-a_A-a_B)/a_B$ vs. a_A (Fig. 2). The values of x_A were used in eqn. (13) for plotting a graph of $H_m^E(1+KZ_A)/(1$

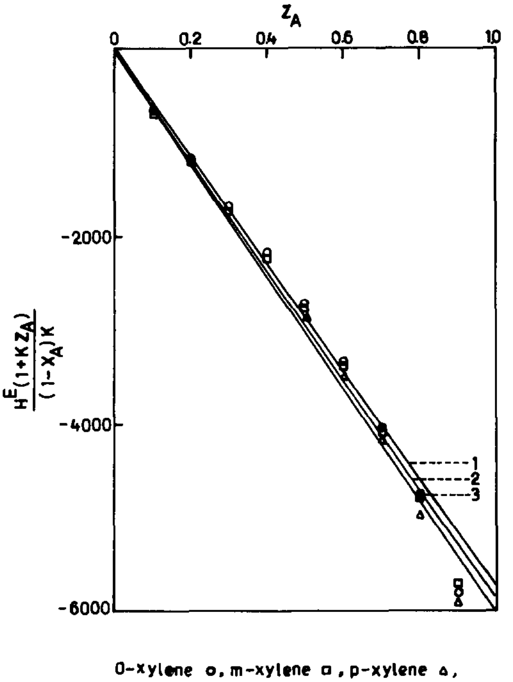

Fig. 3. Plot of $H^E(1+KZ_A)/(1-x_A)K$ vs. Z_A: curve 1, DBE–*o*-xylene (○); curve 2, DBE–*m*-xylene (□); curve 3, DBE–*p*-xylene (△).

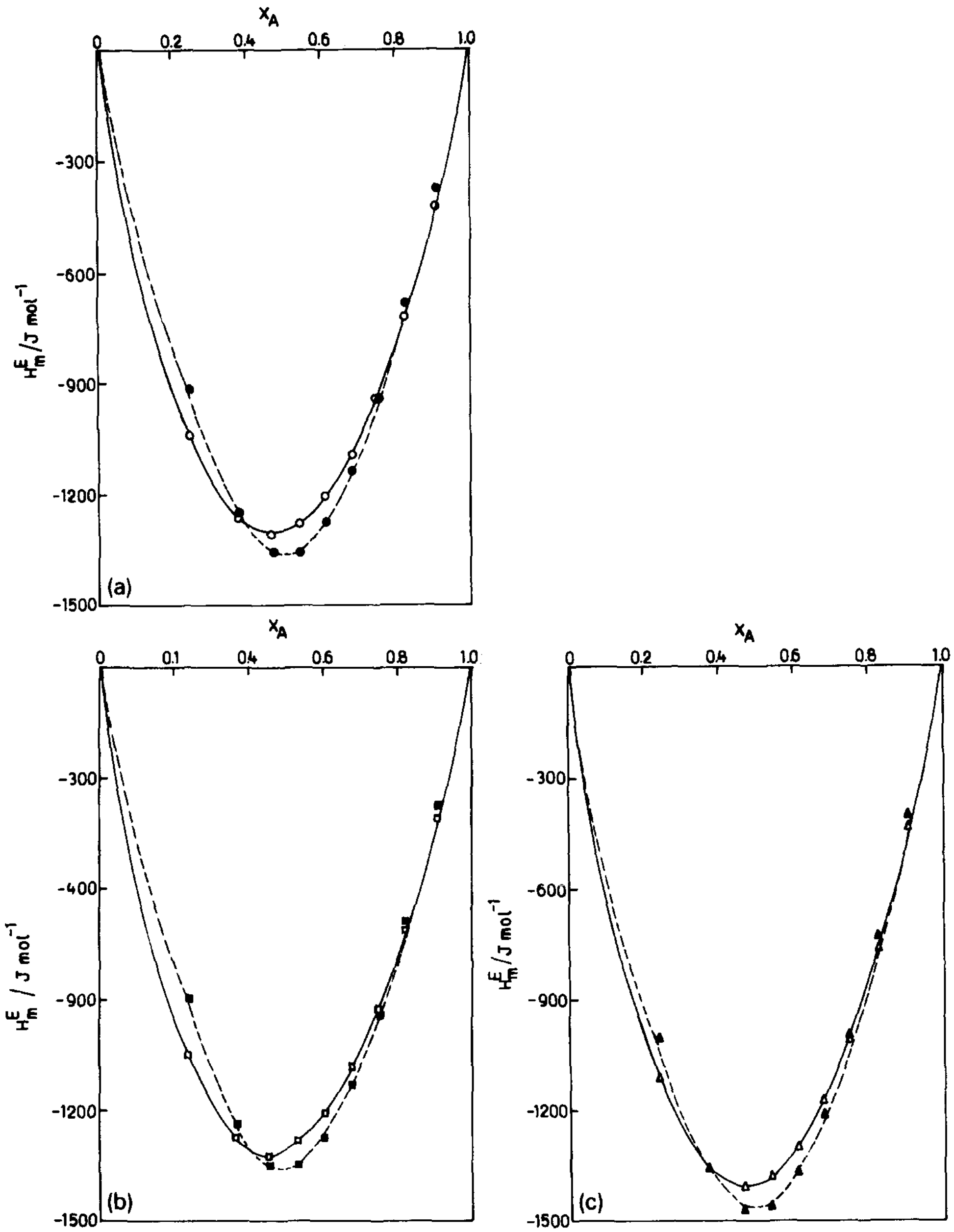

Fig. 4. (a) Comparison of H^{E}_{exp}(corrected) (○) with H^{E}_{cal} (●) at 298.15 K for DBE–*o*-xylene. (b) Comparison of H^{E}_{exp}(corrected) (□) with H^{E}_{cal} (■) at 298.15 K for DBE–*m*-xylene. (c) Comparison of H^{E}_{exp}(corrected) (△) with H^{E}_{cal} (▲) at 298.15 K for DBE–*p*-xylene.

$- x_A)K$ against Z_A (Fig. 3) and were found to give good straight lines over the entire range of composition. From the slopes of these graphs, the values of ΔH for DBE–*o*-xylene, DBE–*m*-xylene and DBE–*p*-xylene systems were observed to be -5.733 kJ mol^{-1}, -5.818 kJ mol^{-1} and -5.995 kJ mol^{-1} respectively. Using K and ΔH in eqn. (13), H_m^E values were calculated and compared with the corresponding H_m^E (experimental corrected) values in Figs. 4(a)–4(c). The agreement between the calculated H_m^E and experimental corrected H_m^E values is reasonably good, suggesting that DBE–*o*-xylene, DBE–*m*-xylene and DBE–*p*-xylene mixtures are characterised by the presence of A, B and AB molecular species in their solutions.

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REFERENCES

1 D.C. Spah, P.K. Verma, K.C. Singh and K.C. Kalra, Thermochim. Acta, 146 (1989) 187.
2 D.C. Spah, K.C. Singh and K.C. Kalra, Indian J. Chem., Sect. A, 29A (1990) 546.
3 K.C. Kalra, K.C. Singh and D.C. Spah, J. Solution Chem., in press.
4 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
5 A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
6 I.C. Sanchez and R.H. Lacombe, J. Phys. Chem., 80 (1976) 2352.
7 I.C. Sanchez and R.H. Lacombe, J. Phys. Chem., 80 (1976) 2568.
8 D.V. Fenby and L.G. Hepler, J. Chem. Thermodyn., 6 (1974) 185.
9 A.I. Vogel, A Text-Book of Practical Organic Chemistry, Longmans, London, 3rd edn., 1978.
10 J. Timmermans, Physicochemical Constants of Pure Organic Compounds, Elsevier, Amsterdam, 1950.
11 A.H. Buep and M. Baron, J. Phys. Chem., 92 (1988) 840.
12 R.K. Nigam and B.S. Mahl, J. Phys. Chem., 9 (1971) 1250.
13 D.E. Gray (Ed.), American Institute of Physics Handbook, McGraw-Hill, 3rd edn., 1972, Section 4, p. 270.
14 J.A. Barker, Aust. J. Chem., 6 (1953) 207.
15 O. Redlich and A.T. Kister, Ind. Eng. Chem., 40 (1948) 345.
16 D.C. Berthelot, R. Acad. Sci., 126 (1898) 1703.
17 R.C. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 67th edn., 1986–87.
18 E.A. Guggenheim, Mixtures, Oxford University Press, London, 1952, Chapters 10 and 11.
19 E.A. Guggenheim, Application of Statistical Mechanics, Oxford University Press, London, 1966, Chapters 4 and 7.
20 K.C. Kalra, K.C. Singh and D.C. Spah, J. Chem. Thermodyn., 22 (1990) 321.