

Measurements and Modeling of Excess Molar Enthalpy of Binary Mixtures of Oxygenate and Hydrocarbons

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The thermodynamic properties of the binary mixtures having potential oxygenates, biodiesel, aromatic and aliphatic compounds are of considerable importance to chemical engineers in formulation of motor fuel. In order to study the interactions of oxygenate with fuel components, excess molar enthalpy for 2-propanol (1) + aromatic hydrocarbon (2) mixtures were measured with flow microcalorimeter at 303.15 K. At equimole fraction, excess enthalpy values follow the order as: *n*-hexane > cyclohexane and 2-propanol > 1-propanol. The data have also been interpreted in terms of graph-theoretical approach and Prigogine-Flory-Patterson (PFP) theory and Flory-Treszczanowicz-Benson association (FTB) model. It has been observed that while Prigogine-Flory-Patterson theory fails to predict the excess enthalpy (H_m^E) values for these system in the composition range $x_1 > 0.05$, agreement with experimental values is reasonably good in propanol lean region. Flory-Treszczanowicz-Benson (FTB) association model and graphtheoretical approach predict the measured H_m^E quite well.

Keywords: Fuel oxygenate, 2-Propanol, Prigogine-Flory-Patterson theory, Flory-Treszczanowicz-Benson model.

INTRODUCTION

Due to price hikes, rapid depletion of fossil fuels and strict emission regulation, considerable concern has been raised over diesel-powered vehicles using alternative fuels. Bio-fuels for internal combustion engines as oxygenated compounds are also becoming important because of diminishing petroleum reserves and increasing air pollution [1-5]. The oxygenated compounds used worldwide as gasoline additives to reduce pollutants from vehicle exhaust gases [4]. Oxygenates are the compounds that contain oxygen such as alcohol, ethers, glycol ethers, methylal and carbonates or biomass products such as esters of vegetable oils [6]. Oxygenates have many advantages as they are octane enhancers, have significant anti-knock properties important for unleaded fuel, can be produced from renewable agricultural and raw materials instead of fossil sources and they reduce carbon monoxide pollution from vehicle exhaust [7-9].

Thus, the thermo-physical properties of oxygenate additive with aromatic hydrocarbons as well as with aliphatic hydrocarbon would be of great significance in process engineering design and in formulating motor gasoline and diesel [10]. As the excess properties are measure of departure from ideality, excess enthalpy of mixtures having oxygenate would also be of

great interest to chemists in getting information about the energetics of intermolecular interactions in these binary mixtures [11,12]. These considerations led us to carry out a systemic study of the thermodynamics of binary mixtures of alkanol with alkane or aromatic hydrocarbon. In continuation of earlier work, this paper reports the excess molar enthalpy (H_m^E) of 2-propanol + aromatic hydrocarbons mixtures at 303.15 K [13-15].

EXPERIMENTAL

Cyclohexane, *n*-hexane and isomer of propanol (Merck) were purified by the standard procedures [16,17]. The purities of purified sample were checked by measuring their densities and refractive indices using specially designed densimeter and Abbe refractometer (OSAW, India) in the manner described earlier [13-15]. The accuracy in the measurement of density and refractive indices were $\pm 0.05 \text{ kg m}^{-3}$ and ± 0.001 unit. Measured value of densities and refractive indices of the pure compounds agree well with their respective literature values and shown in earlier work [13-15]. The purified samples were also analyzed by gas chromatography for their purity and found to have better than 99.6 wt. %.

The excess molar enthalpy of mixing (H_m^E) values at 303.15 ± 0.01 K for the various (1+2) mixtures were measured using flow microcalorimeter (LKB-2107, Bromma, Sweden) in the

manner described by Monk *et al.* [18] and recorded in Table-1. Details and the operating procedure of the apparatus have been described elsewhere [19,20]. The accuracy of the measurement was checked by measuring the enthalpy of mixing for benzene + carbon tetrachloride mixtures at 298.15 K and these agreed with the literature values within $\pm 2 \text{ J mol}^{-1}$ [21].

RESULTS AND DISCUSSION

The measured H_m^E data were fitted to the following Redlich and Kister equation [22]:

$$H_m^E (\text{J mol}^{-1}) = x_1(1-x_1) \left(\sum_{n=0}^3 H^{(n)}(1-2x_1)^n \right) \quad (1)$$

where $H^{(n)}$ are the adjustable parameters and x_1 is the mole fractions of isomer of propanol (1) in binary (1+2) mixture. These parameters were evaluated by fitting H_m^E data to eqn. 1 by least squares method and recorded in Table-2 along with the standard deviations of H_m^E , ($\sigma(H_m^E)$) [15]. The measured and smoothened values from eqn. 1 are shown in Fig. 1 as a function of mole fraction of isomer of propanol (1).

The H_m^E versus x_1 plots for isomer of propanol (1) + cyclohexane or *n*-hexane systems are skewed with positive H_m^E values over the whole composition range (Fig. 1).

At equimolar composition, excess enthalpy values for binary mixtures follow the order: *n*-hexane > cyclohexane and 2-propanol > 1-propanol. The positive contribution to H_m^E values arises from the breaking of self-associated isomer of propanol and dipole-dipole interactions between monomers and dimers of isomer of propanol and also from the disruption in favourable orientation order of hydrocarbons. Next we analyzed

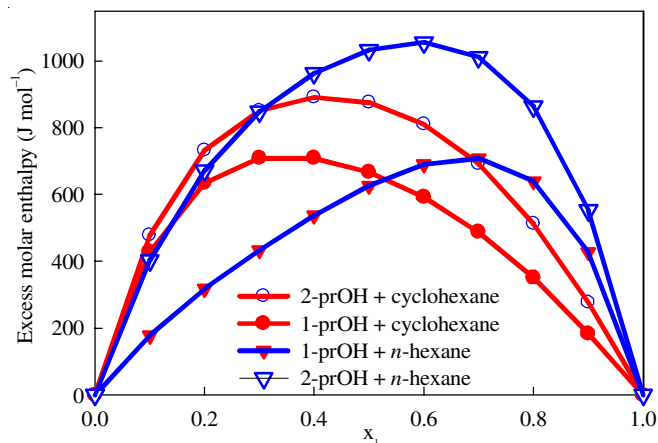


Fig. 1. Excess molar enthalpy (H_m^E) of isomer of propanol (1) + cyclohexane or *n*-hexane (2) mixture as a function of mole fraction of propanol (x_1) at 303.15 K; symbols represent experimental values and lines represent values calculated from eqn. 1

the present H_m^E values in terms of graph theoretical approach [23,24], Prigogine-Flory-Patterson theory [25-30] and Flory-Treszczanowicz-Benson association model [31].

Graph theoretical approach: In order to understand the energetics of the various interactions present in isomer of propanol (1) + cyclohexane or *n*-hexane mixtures, it is assumed that the process of mixtures formation requires:

- a mixing of (1_n) with (2) to establish (1_n)–(2) contacts,
- these (1_n)–(2) contacts would then cause rupture of intermolecular association in isomer of propanol to yield monomers and
- the monomers of 2-propanol then interact with aromatic hydrocarbon to give (1)–(2) molecular entity.

TABLE-1
MEASURED EXCESS MOLAR ENTHALPIES, H^E (J mol^{-1}) FOR BINARY MIXTURE OF ISOMER OF PROPANOL (1) + HYDROCARBONS (2) AS FUNCTIONS OF MOLE FRACTION OF PROPANOL AT 303.15 K

1-Propanol (1) + hydrocarbon (2)				2-Propanol (1) + hydrocarbon (2)			
Cyclohexane		<i>n</i> -Hexane		Cyclohexane		<i>n</i> -Hexane	
x_1	H^E	x_1	H^E	x_1	H^E	x_1	H^E
0.0695	325	0.0331	620	0.0348	202	0.0288	134
0.1234	493	0.1021	181	0.0766	390	0.0696	294
0.1893	617	0.1752	282	0.1159	532	0.1159	452
0.2348	675	0.2338	362	0.1834	703	0.1734	611
0.2895	707	0.2971	433	0.2474	804	0.2374	748
0.3560	716	0.3569	494	0.3086	856	0.3186	873
0.4253	697	0.4342	565	0.3709	882	0.3809	943
0.4817	674	0.4944	618	0.4561	886	0.4361	993
0.5301	648	0.5651	673	0.5159	869	0.5059	1038
0.5880	604	0.6039	694	0.5834	822	0.5634	1052
0.6353	560	0.6670	710	0.6362	776	0.6162	1056
0.6901	497	0.7138	702	0.6904	703	0.6704	1031
0.7734	395	0.7704	676	0.7502	612	0.7202	994
0.8315	302	0.8531	551	0.8036	506	0.8036	856
0.8902	199	0.8898	457	0.8666	361	0.8466	744
0.9325	120	0.9509	239	0.9390	169	0.9490	316

TABLE-2
ADJUSTABLE PARAMETERS OF REDLICH KISTER EQUATION AND STANDARD DEVIATION (σ , J mol^{-1}) AT 303.15 K

System	$H^{(1)}$	$H^{(2)}$	$H^{(3)}$	$H^{(4)}$	σ
1-Propanol (1) + Cyclohexane (2)	2664	1174	1151	843	3
1-Propanol (1) + <i>n</i> -Hexane (2)	2503	1592	1349	222	3
2-Propanol (1) + Cyclohexane (2)	3501	802	1081	932	3
2-Propanol (1) + <i>n</i> -Hexane (2)	4133	-957	1837	-136	2

The total enthalpy change due to processes (a), (b) and (c) [13-15] is given as:

$$H_m^E = \left(\frac{x_1 x_2 (\xi_1^3 / \xi_2^3)}{x_1 + x_2 (\xi_1^3 / \xi_2^3)} \right) [(1 + x_2) \chi_{12}^* + x_1 \chi_{11}] \quad (2)$$

Calculation of H_m^E from eqn. 2 requires the knowledge of connectivity parameter of third degree of i th component (ξ_i) (Table-3), two unknown interaction parameters χ_{12}^* and χ_{11} . These parameters were calculated using H_m^E values at two compositions ($x_1 = 0.4$ and 0.5) for various binary mixtures and tabulated in Table-4. These parameters χ_{12}^* and χ_{11} were subsequently used to evaluate H_m^E at other mole fractions (Table-5). The calculated H_m^E values found to agree well with their corresponding experimental values (Fig. 2). This lends additional support to the assumptions made in the derivation of eqn. 2.

Prigogine-Flory-Patterson (PFP) theory: According to Prigogine-Flory-Patterson theory [28], excess molar enthalpy (H_m^E) is expressed as sum of two contributions (i) interactional contribution and (ii) free volume contribution. Thus, H_m^E be expressed as:

$$H_m^E = H_{\text{inter}}^E + H_{\text{free vol}}^E \quad (3)$$

$$H_m^E = (x_1 U_1^* + x_2 U_2^*) [-\tilde{U}(\tilde{T}) + \tilde{T} \tilde{C}_p(\tilde{T})] \chi_{12} \psi_1 \theta_2 / P_1^* + (x_1 U_1^* + x_2 U_2^*) \tilde{C}_p(\tilde{T}) (\psi_1 \tilde{T}_1 + \psi_2 \tilde{T}_2 - \tilde{T}) \quad (4)$$

where all the terms have usual meaning [25,26]. The Flory interaction parameters χ_{12} in eqn. 4 were calculated employing equimolar experimental H_m^E values, which were subsequently used to calculate H_m^E at other mole fraction (x_1) and compared with experimental values in Fig. 2 and Table-5. The calculated values of interactional contribution and free volume contribution

TABLE-3
CONNECTIVITY PARAMETERS OF THIRD ORDER ξ_i , MOLAR VOLUME (V), ISOBARIC EXPANSIVITY (α), ISOTHERMAL COMPRESSIBILITY (κ_T), CHARACTERISTIC PRESSURE (P^*), CHARACTERISTIC MOLAR VOLUME (V^*) AND CHARACTERISTIC TEMPERATURE (T^*) OBTAINED FROM FLORY THEORY FOR THE PURE LIQUIDS AT 303.15 K

Compound	ξ_i	V (cm ³ mol ⁻¹)	10 ³ α (K ⁻¹)	10 ⁶ κ_T (cm ³ J ⁻¹)	P* (J cm ⁻³)	V* (cm ³ mol ⁻¹)	T* (K)
1-Propanol	0.4082	75.503	1.0344	679.79	730.272	60.010	5175
2-Propanol	0.4710	77.359	1.1437	828.66	730.272	60.010	5175
Cyclohexane	1.5000	109.401	1.2320	1237.00	508.147	84.329	4732
n-Hexane	0.9500	131.610	1.4040	780.90	422.277	99.011	4452

TABLE-4
VALUES OF THE VARIOUS PFP CONTRIBUTIONS TO EXCESS ENTHALPY (J mol⁻¹), PFP INTERACTION PARAMETER (χ_{12}^*), FTB ASSOCIATION MODEL PARAMETERS K^0 AND χ_{12} AND GRAPH THEORY INTERACTION PARAMETER ξ_{12}^* OR χ_{11} AT 303.15 K

System	H_{inter}^E	$H_{\text{free vol}}^E$	χ_{12}^*	K^0	χ_{12}	ξ_{12}^*	χ_{11}
1-Propanol (1) + cyclohexane (2)	681	-15.05	38.80	234.4	11.34	5623	1205
1-Propanol (1) + n-hexane (2)	674	-47.91	36.38	234.4	-2.302	1312	1723
2-Propanol (1) + cyclohexane (2)	882	-2.76	49.83	232.9	28.68	5489	3657
2-Propanol (1) + n-hexane (2)	1055	-21.79	56.42	232.9	31.63	3625	-552

TABLE-5
COMPARISON OF EXCESS MOLAR ENTHALPY (H_m^E , J mol⁻¹) VALUES CALCULATED FROM GRAPH THEORY, PFP THEORY AND FTB MODEL WITH THEIR CORRESPONDING EXPERIMENTAL VALUES FOR THE VARIOUS BINARY MIXTURES AS FUNCTION OF MOLE FRACTION OF PROPANOL, x_1 , AT 303.15 K

x_1	Exptl.	FTB	PFP	Graph	Exptl.	FTB	PFP	Graph
1-Propanol (1) + cyclohexane (2)					2-Propanol (1) + cyclohexane (2)			
0.1	429	468	220	408	478	536	290	433
0.2	634	597	400	611	732	722	526	693
0.3	708	663	536	697	851	825	705	836
0.4	708	683	625	708	891	880	822	891
0.5	666	666	666	666	875	875	875	875
0.6	592	606	653	585	810	824	859	799
0.7	488	514	584	473	692	707	768	669
0.8	351	388	456	336	513	528	599	490
0.9	183	221	263	177	277	287	345	267
1-Propanol (1) + n-hexane (2)					2-Propanol (1) + n-hexane (2)			
0.1	178	485	199	137	403	612	330	334
0.2	318	602	364	280	671	843	604	608
0.3	434	647	493	417	848	970	816	820
0.4	537	648	581	537	963	1028	961	963
0.5	626	626	626	626	1033	1033	1033	1033
0.6	690	571	622	669	1056	980	1024	1023
0.7	708	475	564	649	1012	848	927	925
0.8	639	347	445	546	864	647	731	730
0.9	428	195	260	338	553	370	426	426

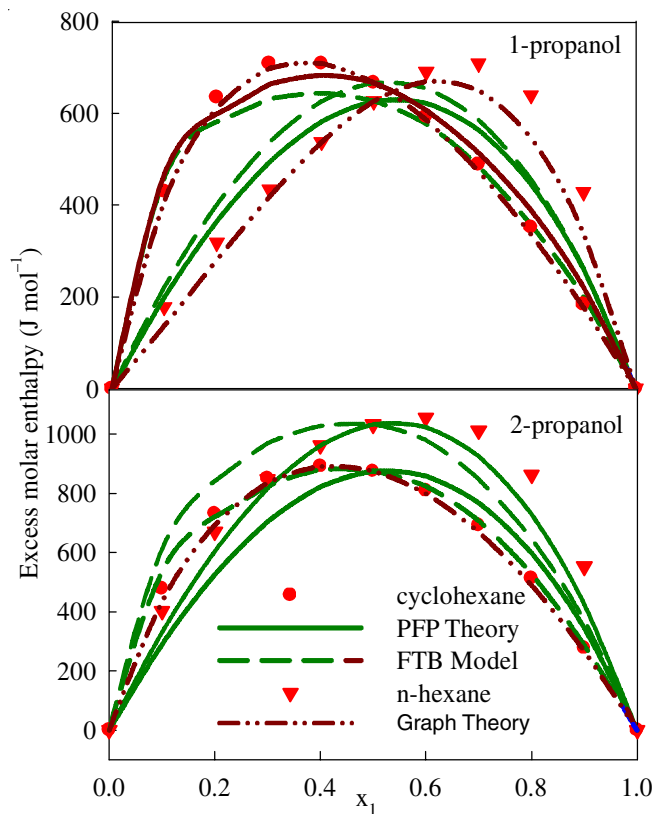


Fig. 2. Excess molar enthalpy (H_m^E) of isomer of propanol (1) + cyclohexane or n -hexane (2) as a function of mole fraction of propanol (x_1) at 303.15 K

to the value of H_m^E for equimolar composition and Flory interaction parameters are recorded in Table-3. It has been observed from Fig. 2 that PFP theory fails to predict H_m^E values for propanol (1) + n -hexane (2) systems in the composition range $x_1 > 0.5$, agreement with experimental values is reasonably good in propanol lean region.

Flory–Treszczanowicz–Benson (FTB) model [31]

This model expresses H_m^E as:

$$H_m^E = H_{\text{Chem}}^E + H_{\text{Phys}}^E \quad (5)$$

where

$$H_{\text{Chem}}^E = \Delta h_H^0 x_1 h(K^\phi, \phi_1) \quad (6)$$

In eqn. 6, K^ϕ is an association constant expressed in volume fraction and given as:

$$\ln K^\phi = 1 + \ln (K_H/r_1) \quad (7)$$

where $K_H = \exp\left(-\frac{(\Delta h_H^0 - T\Delta S_H^0)}{RT}\right)$ and $r_1 = (V_1^*/17.12 \text{ cm}^3 \text{ mol}^{-1})$.

The physical contribution H_{Phys}^E is given by Flory theory [25,26]:

$$H_{\text{Phys}}^E = H_F^E = x_1 \theta_2 \left(\frac{V_1^*}{\tilde{V}} \right) \chi_{12} + \sum_{i=1}^2 \left[x_i P_i^* V_i^* (\tilde{V}_i^{-1} - \tilde{V}^{-1}) \right] \quad (8)$$

In these equations all the terms have their usual meaning [25,26,31]. The values of association parameters Δh_H^0 , ΔS_H^0 and ΔS_H^0 used to calculate H_{Chem}^E from eqn. 6 are taken as -10 cm^3

mol^{-1} , $-24400 \text{ J mol}^{-1}$ and $-33 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively [31]. Method of calculation of χ_{12} using equimolar experimental excess enthalpy was reported earlier [32,33] and their values were calculated for the present systems using equimolar V_m^E data [14] and given in Table-4. The parameters required for the calculation of H_{Phys}^E from Flory theory were also given in Table-3. A good agreement of calculated and experimental H_m^E values was observed in Fig. 2 and Table-5.

Conclusion

Excess molar enthalpy (H_m^E) for isomer of propanol + cyclohexane or n -hexane mixtures were measured by flow microcalorimeter at 303.15 K. In order to study the interactions of oxygenate with fuel components, excess molar enthalpy for isomer of propanol (1) + cyclohexane or n -hexane (2) mixtures were measured with flow microcalorimeter at 303.15 K. At equimolar fraction, excess enthalpy values for binary mixtures follow the order: n -hexane > cyclohexane and 2-propanol > 1-propanol. The data have also been interpreted in terms of graph-theoretical approach, Prigogine-Flory-Patterson (PFP) theory and Flory-Treszczanowicz-Benson association (FTB) model. It has been observed that PFP theory fails to predict the H_m^E values for propanol (1) + n -hexane (2) systems in the composition range $x_1 > 0.5$, agreement with experimental values is reasonably good in propanol lean region. However, Flory-Treszczanowicz-Benson (FTB) association model and graph-theoretical approach predict the measured H_m^E values quite well.

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REFERENCES

1. F. Aguilar, F.E.M. Alaoui, J.J. Segovia, M.A. Villamañán and E.A. Montero, *Fluid Phase Equilib.*, **315**, 1 (2012); <https://doi.org/10.1016/j.fluid.2011.11.005>.
2. F.E.M. Alaoui, E.A. Montero, J.-P. Bazile, F. Aguilar and C. Boned, *J. Chem. Thermodyn.*, **43**, 1768 (2011); <https://doi.org/10.1016/j.jct.2011.06.006>.
3. F. Ancillotti and V. Fattore, *Fuel Process. Technol.*, **57**, 163 (1998); [https://doi.org/10.1016/S0378-3820\(98\)00081-2](https://doi.org/10.1016/S0378-3820(98)00081-2).
4. P. McKendry, *Bioresour. Technol.*, **83**, 37 (2002); [https://doi.org/10.1016/S0960-8524\(01\)00118-3](https://doi.org/10.1016/S0960-8524(01)00118-3).
5. S. Zhang, Y. Yan, T. Li and Z. Ren, *Bioresour. Technol.*, **96**, 545 (2005); <https://doi.org/10.1016/j.biortech.2004.06.015>.
6. A. Murcak, C. Hapimoglu, I. Çevik, M. Karabektas and G. Ergen, *Fuel*, **109**, 582 (2013); <https://doi.org/10.1016/j.fuel.2013.03.014>.
7. E.W. de Menezes, R. Cataluña, D. Samios and R. Silva, *Fuel*, **85**, 2567 (2006); <https://doi.org/10.1016/j.fuel.2006.04.014>.
8. I.-C. Hwang, S.-J. Park and S.-J. In, *J. Ind. Eng. Chem.*, **20**, 3292 (2014); <https://doi.org/10.1016/j.jiec.2013.12.010>.
9. M. Karabektas, G. Ergen and M. Hosoz, *Fuel*, **115**, 855 (2014); <https://doi.org/10.1016/j.fuel.2012.12.062>.
10. Q.N. Chan, Y. Bao and S. Kook, *Fuel*, **130**, 228 (2014); <https://doi.org/10.1016/j.fuel.2014.04.015>.
11. A. Mejía, H. Segura and M. Cartes, *Fuel*, **116**, 183 (2014); <https://doi.org/10.1016/j.fuel.2013.07.107>.
12. R. Sharma, R.C. Thakur and B. Saini, *Asian J. Chem.*, **28**, 2331 (2016); <https://doi.org/10.14233/ajchem.2016.20010>.

13. S. Gahlyan, M. Rani, S. Maken, H. Kwon, K. Tak and I. Moon, *J. Ind. Eng. Chem.*, **23**, 299 (2015);
<https://doi.org/10.1016/j.jiec.2014.08.032>.
14. S. Gahlyan, M. Rani and S. Maken, *J. Mol. Liq.*, **199**, 42 (2014);
<https://doi.org/10.1016/j.molliq.2014.08.011>.
15. S. Gahlyan, M. Rani, I. Lee, I. Moon and S. Maken, *Korean J. Chem. Eng.*, **32**, 168 (2015);
<https://doi.org/10.1007/s11814-014-0200-6>.
16. J.A. Riddick, W.B. Bunger and T.K. Sakano, *Organic Solvents. Physical Properties and Methods of Purification*, Wiley, New York, edn 4 (1986).
17. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, ELBS Longman, London, edn 4 (1978).
18. P. Monk, I. Wadsö, P. Karvonen, A.I. Virtanen and J. Paasivirta, *Acta Chem. Scand.*, **22**, 1842 (1968);
<https://doi.org/10.3891/acta.chem.scand.22-1842>.
19. D.S. Adcock and M.L. McGlashan, *Proc. R. Soc. Lond. A Math. Phys. Sci.*, **226**, 266 (1954);
<https://doi.org/10.1098/rspa.1954.0253>.
20. A. Maken and S. Maken, *J. Ind. Eng. Chem.*, **18**, 1013 (2012);
<https://doi.org/10.1016/j.jiec.2011.11.139>.
21. R.H. Stokes, K.N. Marsh and R.P. Tomlins, *J. Chem. Thermodyn.*, **1**, 211 (1969);
[https://doi.org/10.1016/0021-9614\(69\)90059-7](https://doi.org/10.1016/0021-9614(69)90059-7).
22. O. Redlich and A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948);
<https://doi.org/10.1021/ie50458a036>.
23. S. Kumar, A. Maken, S. Agarwal and S. Maken, *J. Mol. Liq.*, **155**, 115 (2010);
<https://doi.org/10.1016/j.molliq.2010.05.023>.
24. A. Maken and S. Maken, *J. Ind. Eng. Chem.*, **18**, 1013 (2012);
<https://doi.org/10.1016/j.jiec.2011.11.139>.
25. P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965);
<https://doi.org/10.1021/ja01087a002>.
26. A. Abe and P.J. Flory, *J. Am. Chem. Soc.*, **87**, 1838 (1965);
<https://doi.org/10.1021/ja01087a003>.
27. I. Prigogine, N. Trappeniers and V. Mathot, *Discuss. Faraday Soc.*, **15**, 93 (1953);
<https://doi.org/10.1039/df9531500093>.
28. D. Patterson and G. Delmas, *Discuss. Faraday Soc.*, **49**, 98 (1970);
<https://doi.org/10.1039/df9704900098>.
29. I. Prigogine, N. Trappeniers and V. Mathot, *J. Chem. Phys.*, **21**, 559 (1953);
<https://doi.org/10.1063/1.1698950>.
30. I. Prigogine, A. Bellemans and V. Mathot, *The Molecular Theory of Solutions*, North-Holland Publishing Company, Amsterdam, edn. 1 (1957).
31. A.J. Treszczanowicz and G.C. Benson, *Fluid Phase Equilib.*, **23**, 117 (1985);
[https://doi.org/10.1016/0378-3812\(85\)90001-9](https://doi.org/10.1016/0378-3812(85)90001-9).
32. M. Rani, S. Agarwal, P. Lahot and S. Maken, *J. Ind. Eng. Chem.*, **19**, 1715 (2013);
<https://doi.org/10.1016/j.jiec.2013.02.011>.
33. S. Gahlyan, S. Verma, M. Rani, S. Maken, *J. Mol. Liq.*, **244**, 233 (2017);
<https://doi.org/10.1016/j.molliq.2017.09.015>.