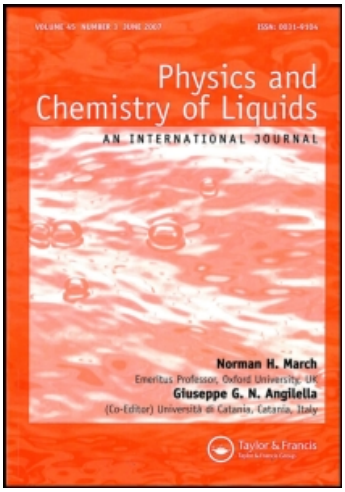

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Das, K. N. , Habibullah, M. , Ghosh, M. and AkberHossain, N. K. M.(2004) 'Regression alternative to the redlich-kister equation in the determination of the excess partial molar volumes of the constituents in a binary mixture', Physics and Chemistry of Liquids, 42: 1, 89 — 94
To link to this Article: DOI: 10.1080/00319100310001625035
URL: http://dx.doi.org/10.1080/00319100310001625035

Physics and Chemistry of Liquids
Vol. 42, No. 1, February 2004, pp. 89–94

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REGRESSION ALTERNATIVE TO THE REDLICH–KISTER EQUATION IN THE DETERMINATION OF THE EXCESS PARTIAL MOLAR VOLUMES OF THE CONSTITUENTS IN A BINARY MIXTURE

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(Received 17 October 2001)

A regression analysis of excess molar volume of tri-*n*-butyl amine (TBA) in binary mixtures of TBA + Toluene at 30°C has been performed using MS Excel 2000 and by Redlich–Kister equation in order to calculate the partial excess molar volume ($\bar{V}^E$). The data obtained by Redlich–Kister equation show less consistence than those given by MS Excel application software.

Keywords: Regression; Excess molar volume; Tri-*n*-butylamine; Toluene

1. INTRODUCTION

The excess partial molar volume of a constituent in a binary mixture is conventionally determined from a plot of excess molar volume (V^E) at constant temperature (T) and pressure (P) *vs* mole fraction (x) of one of the constituents (Fig. 1) [1] by the method of intercepts. Drawing the correct tangent at any point of a correctly drawn curve is a significant problem as in most scientific measurements. Hence, alternative numerical analytic methods are being proposed.

2. THEORY

Any dependent variable can be expressed as

$$y = f(x) = a + bx + cx^2 + dx^3 + \cdots \tag{1}$$

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ISSN 0031-9104 print: ISSN 1029-0451 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00319100310001625035

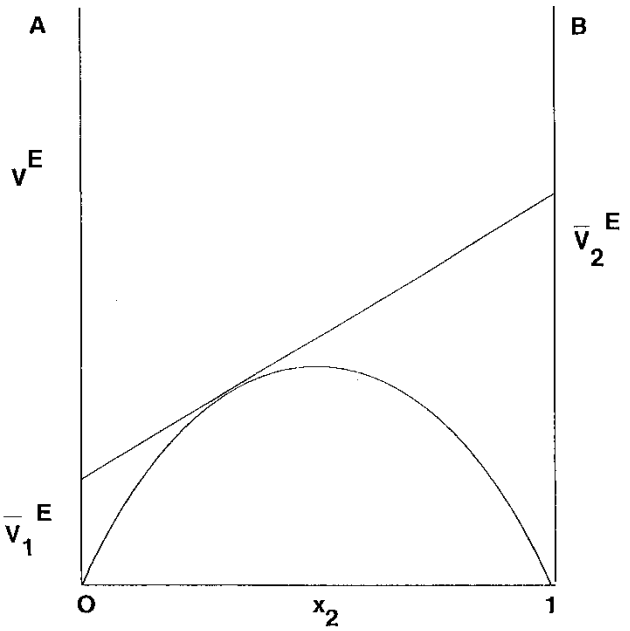

FIGURE 1 Determination of partial molar volume by the method of intercepts.

where x is the independent variable, and a, b, c, d etc. are the coefficients of polynomial expansion. Their numerical values are determined by the regression analysis [2] routinely performed by MS Excel, SSPS, Mathcad, or by any standard application software.

The excess molar volume of a binary mixture can be experimentally measured or derived by the equation:

$$V^E = x_1 M_1(\rho^{-1} - \rho_1^{-1}) + x_2 M_2(\rho^{-1} - \rho_2^{-1}) \tag{2}$$

where x, M and ρ are the mole fraction, molar mass, and density terms respectively, while 1 and 2 designate the constituents.

Obviously,

$$V^E = f'(x_1, x_2) = f(x) \tag{3}$$

$$\text{since} \quad x_1 + x_2 = 1 \tag{4}$$

and for the sake of convenience, we can use

$$x = x_1, \quad V^E = y, \quad \text{and} \quad \bar{V}^E = z \quad \text{etc.} \tag{5}$$

Since, $y = 0$ when $x = 0,1$; the boundary conditions of Eq. (3) is given by

$$\text{(i)} \quad a = 0 \quad \text{and} \quad \text{(ii)} \quad b + c + d = 0 \tag{6}$$

follows the same boundary conditions, e.g., when $i=3$, the above equation can be expanded in the form of Eq. (1) with $a=0$, $b=a_0-a_1+a_2-a_3$, $c=-(a_0-3a_1+5a_2-7a_3)$, $d=-2(a_1-4a_2+9a_3)$, $e=-4(a_2-5a_3)$, and $f=-8a_3$, and hence $b+c+d+e+f=0$

The Redlich–Kister equation [3] is difficult to expand, or derivatize, and is less convenient than Eq. (1) for any purpose. On derivation, Eq. (1) yields

$$y' = \frac{dy}{dx} = b + 2cx + 3dx^2 \tag{9}$$

The excess partial molar volume of the components in a binary mixture is given by the following equation [4]

$$z_1 = y + (1-x)y' \tag{10}$$

$$z_2 = y - xy' \tag{11}$$

3. EXPERIMENTAL

Ghosh [5] measured the excess molar volume of series of binary mixtures of tri-*n*-butylamine (TBA) and Toluene at 30°C and obtained the following results are shown in Table Ia.

The Redlich–Kister curve-fitting yields the following values (Table Ib) for the expansion coefficients.

TABLE Ia Excess molar volume *vs* mole fraction of TBA

Mole fraction of TBA (x)	*Excess molar volume* (cm^3/mole)
0.0000	0.0000
0.0978	0.0699
0.2033	0.1351
0.2991	0.1701
0.4018	0.2572
0.4978	0.2516
0.6027	0.2402
0.7025	0.2189
0.7947	0.1395
0.8935	0.0883
1.0000	0.0000

TABLE Ib The Redlich–Kister constants

$a_0 = 1.0199$
$a_1 = 0.1345$
$a_2 = -0.3925$
$a_3 = -0.1152$

4. RESULTS AND DISCUSSION

Regression analysis of the data was performed using MS Excel 2000 and the following polynomial was obtained:

$$y = 1.016x - 4.711x^2 + 21.612x^3 - 45.406x^4 + 40.813x^5 - 13.324x^6; \quad R^2 = 0.9875 \tag{12}$$

The consequent results are tabulated below (Table II).

Curve fitting by the Redlich–Kister equation yields the polynomial

$$y = 0.608x + 0.540x^2 - 1.366x^3 - 0.732x^4 + 0.920x^5 \tag{13}$$

The Eq. (13) is quite different from Eq. (12) with consequently different results; (Table III, Fig. 2).

TABLE II MS Excel results (based on 6th degree polynomial)

x	y	y'	z_1	z_2
0.00	0.000	1.016	1.016	0.000
0.10	0.072	0.560	0.576	0.016
0.20	0.127	0.573	0.586	0.013
0.30	0.186	0.580	0.592	0.012
0.40	0.237	0.402	0.478	0.076
0.50	0.261	0.067	0.294	0.228
0.60	0.249	−0.297	0.131	0.427
0.70	0.206	−0.547	0.041	0.589
0.80	0.146	−0.629	0.020	0.649
0.90	0.182	−0.670	0.015	0.685
1.00	0.000	−1.073	0.000	1.073

TABLE III Redlich–Kister results

x	y	y'	z_1	z_2
0.00	0.000	0.608	0.608	0.000
0.10	0.065	0.673	0.671	−0.002
0.20	0.132	0.645	0.650	0.005
0.30	0.191	0.530	0.562	0.032
0.40	0.235	0.329	0.433	0.104
0.50	0.255	0.068	0.289	0.221
0.60	0.247	−0.221	0.159	0.380
0.70	0.211	−0.497	0.062	0.559
0.80	0.150	−0.708	0.009	0.717
0.90	0.074	−0.783	−0.004	0.779
1.00	0.000	−0.647	0.000	0.647

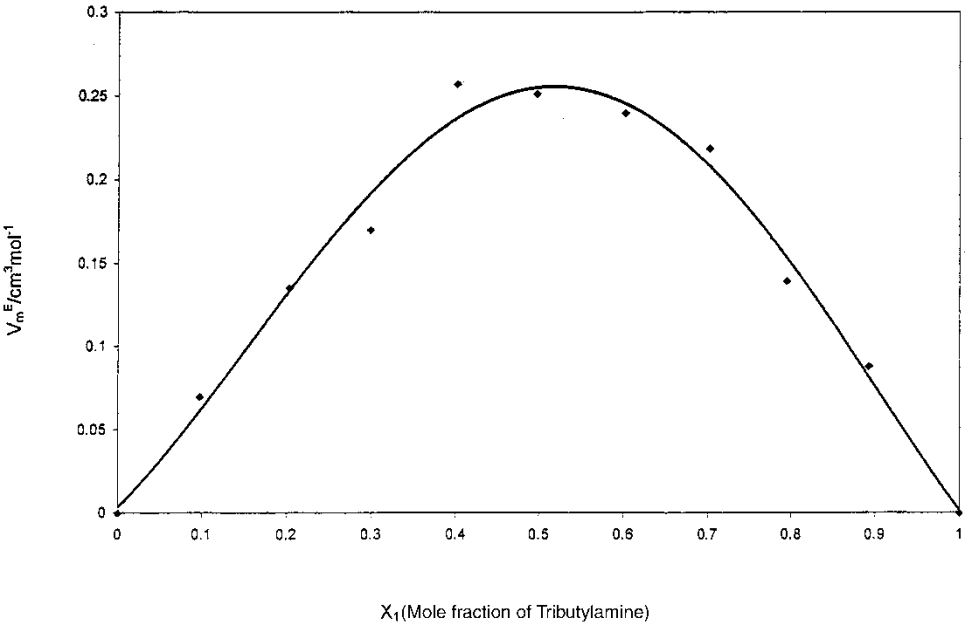

FIGURE 2 Excess molar volume of the mixture of tributylamine + toluene *vs* mole fraction of tributylamine (Redlich–Kister equation fitting).

The results are less consistent than those given by MS Excel program. Hence, in our opinion, numerical analysis by MS Excel is more acceptable than the conventional use of the Redlich–Kister equation.

The Table III results can be conveniently compared with the MS Excel results for a 5th degree polynomial as shown below:

$$y = 0.5781x + 0.6588x^2 - 1.5203x^3 - 0.6290x^4 + 0.9123x^5;$$
$$R^2 = 0.9849 \tag{14}$$

with consequent results tabulated below (Table IV, Fig. 3).

TABLE IV

x	y	y'	z_1	z_2
0.00	0.0000	0.5781	0.5781	0.0000
0.10	0.0628	0.6622	0.6588	−0.0034
0.20	0.1291	0.6464	0.6462	0.0002
0.30	0.1818	0.5319	0.5611	0.0292
0.40	0.2326	0.3331	0.4313	0.1001
0.50	0.2529	0.0673	0.2865	0.2193
0.60	0.2451	−0.2255	0.1548	0.3804
0.70	0.2083	−0.5022	0.0577	0.5599
0.80	0.1470	−0.7066	0.0057	0.7123
0.90	0.0716	−0.7718	−0.0055	0.7662
1.00	0.0000	−0.6197	0.0000	0.6197

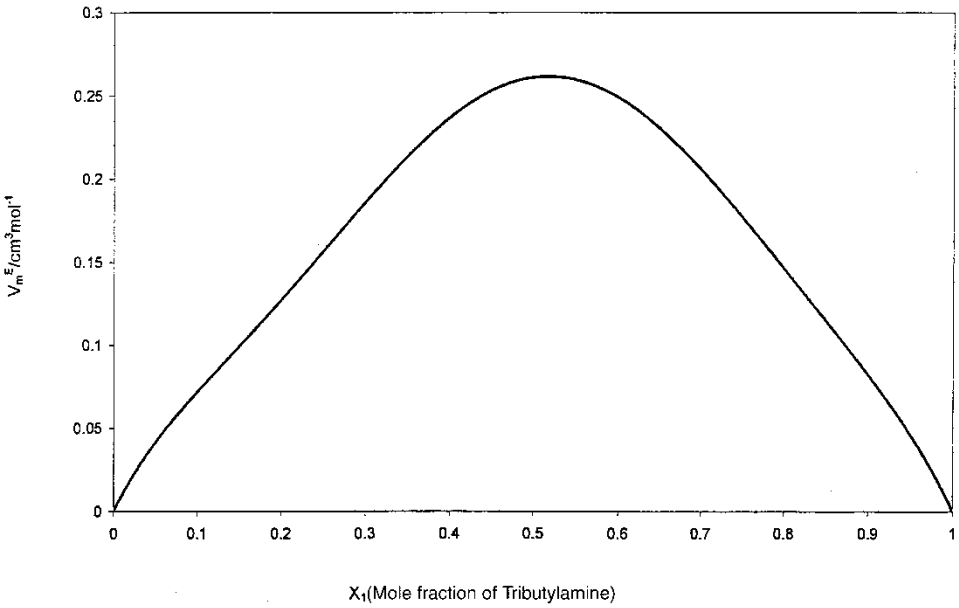

FIGURE 3 Excess molar volume of the mixture of tributylamine + toluene *vs* mole fraction of tributylamine (MS Excel fitting).

The results are comparable to the Table III within limits.

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