

EVALUATION OF THE DEPENDENCE OF EXCESS VOLUME
OF THE BENZENE-CYCLOHEXANE MIXTURE ON COMPOSITION
AT 298.15 K FROM LITERATURE DATA

Ivan CIBULKA and Robert HOLUB

*Department of Physical Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

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The results of foregoing attempts in the literature to evaluate the mean dependence of excess volume of the benzene-cyclohexane mixture on composition at 298.15 K are summarized and a new equation for this dependence is presented. This equation is compared with the literature data.

The benzene-cyclohexane system was recommended by Powell and Swinton¹ as a test system for measuring excess volume of liquid mixtures. This recommendation has been widely accepted, and consequently, there exists a great number of data in the literature now with which (or with some of them) every new measurement is compared.

Majority of the literature data was measured at a temperature of 298.15 K. For this temperature, two works can be found in the literature whose authors have evaluated the literature data with the aim to obtain the concentration dependence with which the future measurements could be compared.

Tasič and coworkers² correlated 238 experimental points measured by the authors^{1,3-15} and reported the relation (x_1 denotes henceforth the benzene mole fraction, v^E the excess volume in $\text{cm}^3 \text{mol}^{-1}$)

$$v^E = x_1 x_2 [2.590 + 0.078(x_2 - x_1) + 0.067(x_2 - x_1)^2] \quad (1)$$

with a standard deviation $\sigma(v^E) = 0.0098 \text{ cm}^3 \text{mol}^{-1}$.

Handa and Benson¹⁶ selected three sets of data^{10,17,18} which are mutually in very good accordance and correlating altogether 164 experimental points, taking into account the standard deviations of single sets, too, they obtained the relation

$$v^E = x_1 x_2 [2.60725 + 0.09271(x_2 - x_1) + 0.04476(x_2 - x_1)^2] \quad (2)$$

with a standard deviation $\sigma(v^E) = 0.0016 \text{ cm}^3 \text{mol}^{-1}$.

TABLE I

Comparison of the literature data with the reference equation (3)

$D_1 \cdot 10^3$ ^a cm ³ mol ⁻¹	$D_2 \cdot 10^3$ ^b cm ³ mol ⁻¹	Max. dev. ^c ($v_{lit}^E - v_{ref}^E$) · 10 ³ cm ³ mol ⁻¹	Std. dev. $\sigma(v_{lit}^E) \cdot 10^3$ cm ³ mol ⁻¹	Number of exp. points	Author (ref.)
0.86	0.02	- 0.99 + 1.5	1.6	164	Handa(16), Eq. (2)
1.3	0.45	- 1.4 + 2.3	0.4	13	Goates(19)
1.6	- 1.2	- 3.0 + 0.09	0.7	42	Kumaran(17)
1.7	0.08	- 2.3 + 2.6	1.5	31	Weeks(13)
1.8	1.2	- 1.1 + 3.4	0.43	50	Tanaka(18)
1.9	- 1.7	- 2.7 -	0.8	72	Stokes(10)
1.9	- 0.7	- 3.6 + 2.1	4.8	9	Oba(20)
2.1	1.4	- 0.9 + 4.0	0.19	20	Takenaka(21)
2.1	- 1.7	- 4.0 + 0.1	1.7	30	Cibulka(22)
2.2	- 1.9	- 3.8 -	1.4	7	Stokes(10)
2.3	- 0.5	- 3.8 + 3.1	1.7	29	Kiyohara(7)
2.5	- 2.1	- 3.4 + 0.3	9.8	238	Tasič(2), Eq. (1)
2.6	- 0.6	- 4.1 + 3.3	2.0	17	Kimura(23)
2.7	- 0.2	- 3.9 + 4.8	4.0	10	Grolier(5)
3.0	- 2.6	- 5.1 -	2.9	10	Kowalski(24)
3.1	- 0.4	- 6.4 + 3.2	1.4	11	Meyer(25)
3.1	- 2.8	- 5.1 -	0.9	45	Cibulka(26)
3.3	2.0	- 1.5 + 5.8	1.3	10	Goates(27)
3.4	- 3.2	- 5.0 -	1.6	11	McLure(28)
3.6	- 2.2	- 7.1 + 1.3	4.0	13	Stookey(11)
3.9	- 0.2	- 6.2 + 5.0	6.0	9	Gracia(29)
4.0	- 1.9	- 6.2 + 3.6	0.5	7	Wood(14)
4.7	- 1.0	- 8.5 + 3.9	5.0	13	Letcher(30)
5.1	- 4.4	- 8.8 -	1.3	18	Palta(31)
5.4	- 4.7	- 8.1 -	1.6	15	Brennan(32)
5.9	- 5.1	- 8.1 -	3.0	12	Jain(33)
7.1	- 6.4	- 9.6 -	1.9	8	Radojkovič(9)
7.4	- 7.0	- 10.5 -	5.5	30	Beath(3)
7.5	- 6.8	- 10.5 -	1.3	14	Diaz Pena(34)
7.7	- 7.2	- 11.0 -	3.0	5	Dixon(35)
7.7	- 5.7	- 13.1 + 1.2	8.0	9	Woycicki(15)
9.8	- 9.1	- 13.0 -	0.5	6	Powell(1)
10.9	- 10.5	- 14.0 -	7.0	34	Watson(12)
11.9	- 8.9	- 19.7 + 1.3	14	9	Janssens(6)
14.6	- 1.9	- 23.5 + 16.8	33	16	Mathieson(8)
29.9	- 28.9	- 35.3 -	5.0	6	Ridgway(36)
50.2	- 34.2	- 99.7 + 10.4	28	7	Mato(37)

^a $D_1 = [\int_0^1 (v_{lit}^E - v_{ref}^E)^2 dx_1]^{1/2}$, ^b $D_2 = \int_0^1 (v_{lit}^E - v_{ref}^E) dx_1$, ^c where v_{lit}^E and v_{ref}^E are the values calculated from the respective correlation equation of literature data and from Eq. (3).

The concentration dependence of excess volume was obtained in this work by evaluating all the available literature data at a temperature of 298.15 K (Table I). It was required that the dependence should go through the places of the highest density of experimental points. Each data set has been represented in calculations in terms of an equation of the type (1), (2), by the standard deviation of excess volume and by the number of experimental points in set, assuming normal distribution of deviations of experimental points from the equation and a uniform distribution of points in the entire concentration range. With respect to a great number of sets and a relatively great number of points in majority of them, the above-mentioned assumptions are acceptable. In the way described, the equation

$$v_{ref}^E = x_1 x_2 [2.60357 + 0.07521(x_2 - x_1) + 0.06252(x_2 - x_1)^2 + 0.03249(x_2 - x_1)^3] \quad (3)$$

was obtained. The comparison of Eq. (3) with equations representing the single sets of the literature data is given in Table I. Discussion of the results extends beyond the framework of this work and will be published³⁸ along with a detailed survey of literature data (including data for further temperatures).

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