

COMPARISON OF THE VOLUME AND SURFACE MODIFICATIONS OF THE REGULAR SOLUTION MODEL*

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Possibilities of the volume and surface modifications of the regular solution model were evaluated by comparing calculated and experimental values of the vapour phase composition in a set of 129 different binary systems and with all calculations being performed by using the properties of pure components only. This comparison showed that the region of practical applicability of the surface modification is larger than that of the volume modification, especially in the case of systems containing highly polar or chemically considerably different substances.

In relation to problems connected with the calculation of the vapour-liquid equilibrium from the properties of pure components, a necessity appeared of an objective comparison between the Hildebrand-Scatchard volume^{1,2} and Erdős surface³ modifications of the regular solution model. In view of the pressure independence of activity coefficients derived from the above mentioned modifications and after an evaluation of the amount and quality of equilibrium data in the regions of normal and elevated pressures, the comparative calculations were performed on a set of binary systems at normal pressures.

The dependence between the compositions of vapour and liquid phases in a binary system of non-electrolytes is given by the relations

$$y_1 = (a_{12}x_1/x_2)/(1 + a_{12}x_1/x_2) \quad (1)$$

$$y_2 = 1/(1 + a_{12}x_1/x_2), \quad (2)$$

where x_1 and x_2 (resp. y_1 and y_2) are mole fractions of components 1 and 2 in the liquid (resp. vapour) phase. The relative volatility, a_{12} , defined by

$$a_{12} = y_1x_2/(y_2x_1) \quad (3)$$

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can be, in the region of normal and low pressures, expressed by the equation

$$a_{12} = \gamma_1 P_1^0 / (\gamma_2 P_2^0) \quad (+_g), \quad (4)$$

where P_1^0 and P_2^0 are saturated vapour pressures of the pure components at a given temperature, γ_1 and γ_2 are activity coefficients of the components in the solution and the symbol $(+_g)$ denotes the ideal behaviour of the vapour phase. For an ideal solution, Eq. (4) passes to the form

$$a_{12} = P_1^0 / P_2^0, \quad (\text{id}), \quad (5)$$

where the symbol (id) denotes an ideal system.

To express the temperature dependence of the saturated vapour pressure of the pure component, we can employ the Antoine equation⁴

$$\log P_i^0 = A_i - B_i / (T + C_i - 273.15), \quad (6)$$

where T is absolute temperature and A_i, B_i, C_i are constants characteristic for the given component i and the temperature range.

It follows from the given relations that for a calculation of the vapour phase composition in a binary system we must know the liquid phase composition, temperature, constants in the Antoine equation and values of the activity coefficients. The first two quantities, x and T , are results of experiment, values of constants in the Antoine equation were taken from literature⁵. Values of the activity coefficients were derived from the volume and surface modifications of the regular solution model in a manner described below.

Hildebrand and Scatchard^{1,2} started from the assumption of the central character of intermolecular forces in a solution and derived the following relations for activity coefficients of components in a binary system

$$RT \ln \gamma_1 = V_1 \Phi_2^2 (\delta_1 - \delta_2)^2, \quad (7)$$

$$RT \ln \gamma_2 = V_2 \Phi_1^2 (\delta_1 - \delta_2)^2, \quad (8)$$

where V_1 and V_2 are molar volumes of pure liquid components, the solubility parameter, δ , is defined through the molar heat of vaporization, ΔH_v , as

$$\delta_i = [(\Delta H_{vi} - RT) / V_i]^{1/2} \quad i = 1, 2 \quad (9)$$

the volume fraction Φ_i is given by

$$\Phi_i = x_i V_i / (x_1 V_1 + x_2 V_2) \quad i = 1, 2 \quad (10)$$

and R is the gas constant. Values of volume V at temperature T were obtained from literature values⁶ of volume V_0 at temperature T_0 , which were re-calculated by the Watson relation⁷

$$V = V_0(1 + 0.4802T_0/T_c)/(1 + 0.4802T/T_c), \quad (11)$$

where T_c is critical temperature. The value of the molar heat of vaporization in relation (9) was determined from the differential form of the Clausius–Clapeyron equation

$$\Delta H_v = RT^2 \ln P/dT \quad (12)$$

and from the Antoine equation (6).

Starting from the assumption of a surface character of intermolecular forces, Erdős³ derived the relations for activity coefficients:

$$RT \ln \gamma_1 = S_1 \Theta_2^2 (q_1 - q_2)^2 \quad (13)$$

$$RT \ln \gamma_2 = S_2 \Theta_1^2 (q_1 - q_2)^2, \quad (14)$$

where S_1 and S_2 are molar surfaces of molecules of corresponding components, the surface solubility parameter, q , is given by the relation

$$q_i = [(\Delta H_{vi} - RT)/S_i]^{1/2} \quad i = 1, 2 \quad (15)$$

and the surface fraction, Θ_i , by

$$\Theta_i = x_i S_i / (x_1 S_1 + x_2 S_2) \quad i = 1, 2. \quad (16)$$

Two alternative procedures for determining the molar surface S_i were used in this work: a) the original Erdős correlation with parachor $[P]$

$$S_i = k_i [P_i]^{2/3} \quad (17)$$

with the proportionality constant k_i being for simplicity considered as characteristic for all of the substances employed, *i.e.*, the validity of the relation

$$k_1/k_2 = 1 \quad (18)$$

was assumed; b) a possibility was investigated of using the surface contributions from van der Waals molecular radii as proposed by Bondi⁸. The molecular surface

TABLE I
Physico-Chemical Properties of the Pure Substances

Substance	Class ⁹	T_c , K	T_{nbp} , K	Density at 20°C, g cm ⁻³	Parachor	Molar volume ³ 10 ⁹ cm ² mol ⁻¹
n-Heptane	5	469.65	309.22	0.62624	231.0	8.29
n-Hexane	5	507.37	341.89	0.65937	270.4	9.64
n-Heptane	5	540.2	371.57	0.68376	310.8	10.99
1-Octene	5	566.6	394.43	0.71492	335.2	11.81
n-Octane	5	568.8	398.82	0.7022	351.0	12.34
2-Methylheptane	5	595.6	390.80	0.69792	348.8	12.33
2,2,4-Trimethylpentane	5	543.89	372.39	0.69192	343.8	12.52
2,2,5-Trimethylhexane	5	568.0	393.23	0.70721	383.8	13.87
n-Decane	5	617.4	447.27	0.72245 ^a	431.1	15.04
Benzene	5	562.65	353.25	0.87901	206.1	6.00
Toluene	5	591.72	383.77	0.86694	245.7	7.45
Ethylbenzene	5	617.09	409.34	0.86702	284.3	8.80
<i>m</i> -Xylene	5	616.97	412.25	0.8641	284.2	9.57
<i>p</i> -Xylene	5	616.2	411.50	0.86105	284.5	9.57
Tetrachloromethane	5	556.30	349.86	1.5940	219.8	7.28
Ethyl bromide	5	503.8	311.54	1.45939	165.4	5.55
1,2-Dibromoethane	5	650.15	404.89	2.17920	213.0	6.86
1-Chlorobutane	5	542.15	351.73	0.88621	230.3	7.97
Chlorobenzene	5	632.4	404.87	1.10578	244.1	7.14
Bromobenzene	5	670.	429.24	1.4948	257.8	7.46
Dichloromethane	4	510.	313.34	1.32554	149.9	4.99
Trichloromethane	4	536.4	334.35	1.48316	183.4	6.03
1,1-Dichloroethane	4	523.	330.43	1.1757	188.5	6.33
1,2-Dichloroethane	4	561.	356.96	1.25309	186.4	6.30
Trichloroethylene	4	571.15	360.45	1.46422	209.10	7.15
Acetone	3	508.2	329.21	0.79082	161.5	5.84
Diethyl ether	3	466.70	307.75	0.7135	211.5	7.54
Methyl acetate	3	506.85	330.08	0.9336	176.7	6.44
Ethyl acetate	3	523.2	350.21	0.9004	216.2	7.79
1-Nitropropane	3	675.	404.52	0.99546 ^b	208.8	7.37
Nitrobenzene	3	755.95	483.80	1.2032	262.5	7.88
Triethylamine	3	535.	361.92	0.7280	296.5	10.64
Methyl alcohol	2	512.58	337.69	0.78655 ^b	88.2	3.58
Ethyl alcohol	2	516.2	351.45	0.78506 ^b	126.6	4.93
n-Propyl alcohol	2	536.71	370.30	0.8035	164.7	6.28
Isopropyl alcohol	2	508.31	355.39	0.78512	164.4	6.27
n-Butyl alcohol	2	562.93	390.88	0.80961	203.4	7.63
n-Pentyl alcohol	2	586.	411.15	0.80764 ^a	243.3	8.98
Phenol	2	694.2	454.90	1.0576 ^c	221.3	6.79

TABLE I
(Continued)

Substance	Class ⁹	T_c , K	T_{nbp} , K	Density at 20°C g cm ⁻³	Parachor	Molar volume ³ 10 ⁹ cm ³ mol ⁻¹
<i>m</i> -Cresol	2	699.15	475.35	0.986	261.1	8.91
Aniline	2	699.	457.14	1.02173	230.2	7.07
Dimethylformamide	2	641.85	422.71	0.94873	170.7	6.84
Nitromethane	2	588.	374.34	1.12453 ^a	132.1	4.67
Acetonitrile	2	548.	354.75	0.7857	121.9	4.31
Water	1	647.15	373.14	0.99897	52.71	2.80

^a Value at 30°C, ^b value at 25°C, ^c value at 41°C.

is given by the sum of surface increments, A_w , over individual functional groups:

$$S_i = \sum_k A_{wk} \quad (19)$$

Values of parachor were taken from literature⁶, the molar heat of vaporization was determined from relations (6) and (12). The temperature, T , was determined in the case of isobaric equilibrium data (only systems at the normal pressure of 101.3 kPa were considered) from the relation

$$T = \left(\sum_{i=1}^N T_i + T_{nbp1} + T_{nbp2} \right) / (N + 2), \quad (20)$$

where T_{nbp1} and T_{nbp2} are normal boiling point temperatures of the components, T_i are experimental temperatures and N is the number of experimental points.

RESULTS

The outlined modifications of the regular solution model were, together with the ideal solution model (relation (5)), tested by comparing calculated and experimental values of the vapour phase composition for a set of 129 different binary systems, which on the whole represented 181 isothermal and isobaric systems with 2478 experimental points. The physico-chemical properties necessary for the calculations are, for 45 pure substances which constitute the set of tested systems, given in Table I. The substances were divided into 5 classes in accordance with the classification proposed by Ewell, Harrison and Berg⁹. A combination of these 5 classes gave, in the

case of our set, 12 types of binary systems, results of calculations of which are evaluated in Table II. The overall results of the comparison are also reported in Table II.

The results of our calculations can be summarized as follows: all of the relations employed yield good results for systems whose components belong to the same Ewell's class. In view of the fact that values of activity coefficients calculated from the corresponding relations are always higher than unity, no satisfactory results can be expected for systems exhibiting negative deviations from Raoult's law, *i.e.*, for the type 4-3. Relatively poor agreement was observed for systems of the type 4-2 (all of the systems tested form an azeotropic mixture) and for the type 3-1 (acetone-water and triethylamine-water systems). The volume modification fails completely in the case of highly polar systems of the type 2-1.

It follows from the overall comparison that the surface modification of the regular solution model is more suitable for practical applications than the volume modification and that the original Erdős variant with parachor yields better results than the direct evaluation of the molecular surface through Bondi's structural contributions.

TABLE II

Mean Absolute Percent Deviation^a in the Calculated Vapour Phase Composition for Different Modifications of the Regular Solution Model

System ⁹	Number			Ideal solution	Regular solution		
	systems	isotherms and isobars	exptl. points		H-S ^b	Erdős	Bondi
5-5	20	25	341	4.5	3.5	3.3	5.6
5-4	9	12	190	3.4	3.2	3.2	3.2
5-3	12	15	188	10.1	6.7	8.3	8.1
5-2	38	54	716	27.5	19.9	13.0	18.7
4-4	4	4	57	6.5	6.2	6.2	6.3
4-3	5	5	79	20.4	16.3	18.9	17.5
4-2	6	11	171	25.0	21.8	16.1	15.8
3-3	2	2	24	9.4	11.4	9.6	9.8
3-2	11	23	327	13.2	16.0	5.2	10.6
3-1	2	4	44	25.9	66.6	38.6	43.6
2-2	11	12	126	6.4	8.7	6.6	8.2
2-1	9	14	215	24.2	183.4	6.2	8.1
Total	129	181	2 478	16.8	27.5	9.4	12.4

^a Mean deviation = $\sum 100|(y_{1,\text{calc}} - y_{1,\text{exp}})|/N_{\text{exp}}y_{1,\text{exp}}$ ^b Hildebrandt-Scatchard.

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