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Note

Correlation of excess enthalpies of mixing in tributylphosphate-N-alkane system*

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We have reported recently[1] direct calorimetric data on the heat of mixing of tri-n-butylphosphate with n-hexane, n-dodecane and benzene at 303.15 K, and compared these new sets of excess enthalpies with those in the literature[2–4]. In continuation of the project, we now report a quantitative interpretation of our experimental data in terms of a simple statistical thermodynamic model previously used for alkylamine–hydrocarbon systems[5], which is based on a combination of the group interaction model and the zeroth approximation form of the lattice theory of mixtures for molecules of different sizes at a completely random arrangement.

The model[5] requires that each molecule, i, consists of m_i segments, each occupying one site on a lattice of coordination number z. The number of contact points for each type of molecule i is thus given by

$$s_i = m_i(z-2)+2 \tag{1}$$

Each segment on the surface of the molecule has a characteristic capability of interaction which is proportional to a group cross-section s^u and s^v of u and v type surfaces of molecule i. The combined molecular cross-sections are thus given as

$$s_i = \Sigma m_i^u s^u \tag{2}$$

representing the sum of the appropriate group cross-sections of the molecule. The corresponding molecular coverages are defined by the ratio

$$\alpha_{is} = m_i^u s^u / s_i \tag{3}$$

For the binary systems of tributylphosphate and the normal alkane diluents under consideration we have the simplest possible combination that the surface of the tributylphosphate molecule (component 1) is composed of aliphatic (CH_3 and CH_2) and phosphatic (PO_4) elements, and that of the normal aliphatic hydrocarbons (component 2), of aliphatic elements only. Thus, in terms of the theory, the two interacting surfaces are the aliphatic (u) and the phosphatic (v), assuming that the methyl and methylene surfaces are of the same kind.

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The experimentally determined excess enthalpy of mixing per mole of mixture is defined as:

$$H^E = s_1 s_2 \frac{x_1 x_2}{s_1 x_1 + s_2 x_2} A_{12} \tag{4}$$

where x is the mole fraction of components 1 and 2, s the corresponding molecular cross-section, and A_{12} the molecular interaction parameter defined as:

$$A_{12} = -k^{uv}(\alpha_1^u - \alpha_2^u)(\alpha_1^v - \alpha_2^v) \tag{5}$$

where k^{uv} is the molar interchange enthalpy per conventional unit area of the interacting aliphatic (u) and phosphatic (v) surfaces. Since the sum of all molecular coverages for any given molecule is equal to unity

$$\alpha_1^u + \alpha_1^v = \alpha_2^u + \alpha_2^v = 1 \tag{6}$$

and $\alpha_2^v = 0$, eqn (5) reduces to

$$A_{12} = k^{uv}(\alpha_1^v)^2 \tag{7}$$

The group and molecular cross-sections were calculated by adopting a lattice coordination number $z = 8$, thus an area of 0.125 for each bond. Accordingly, each methyl and methylene group constitutes one section which would have a value of unity in the isolated state, but have the values of $s^{CH_2} = 0.750$ and $s^{CH_3} = 0.875$ when chemically bond. In the tributylphosphate molecule, the phosphatic group has the value of $s^{PO_4} = 0.625$ (three bonds per group). From these values of group sections, the molecular cross-sections are calculated by a simple addition: that for tributylphosphate is $s_{TBP} = 10.00$, and the corresponding molecular coverage, $\alpha_1^v = s^{PO_4}/s_{TBP} = 0.0625$; that for n-hexane is $s_{C_6} = 4.75$ and for n-dodecane $s_{C_{12}} = 9.25$.

The molar interchange enthalpy, k^{uv}, as derived from the experimental data[1] for TBP-hexane and TBP-dodecane systems by eqns (4) and (7) has the value of $k^{uv} = 130{,}600 \pm 6400$ J mol^{-1}. The fit of the calculated H^E values is satisfactory in the TBP-hexane system, but the deviation from the experimental points at low TBP content in the TBP-dodecane system may be as high as 20%. A better agreement may be expected by employing a more sophisticated model which will take into account the cross-sections and interchange parameters of the etheric oxygen and the phosphoryl group in TBP separately, rather than the overall phosphatic group as in the present model. We are now engaged in generating additional heat of mixing data, which then will enable calculations based on the more elaborate model.

In the meantime, we have calculated the excess enthalpies of mixing of tributylphosphate with several n-alkanes at 303.15 K using the k^{uv} value derived here. The results, estimated to be reliable to $\pm 5\%$, are given in Table 1 at 0.1 mole fraction intervals.

TABLE 1

EXCESS ENTHALPIES OF MIXING OF TRIBUTYLPHOSPHATE WITH n-ALKANES CALCULATED USING EQNS (4) AND (7)

x_{TBP}	H^E ($J\ mol^{-1}$), 303.15 K			
	n-Pentane $s = 4.00$	*n-Heptane* $s = 5.50$	*n-Octane* $s = 6.25$	*n-Nonane* $s = 7.00$
0.1	399	424	433	440
0.2	628	701	729	751
0.3	739	860	908	949
0.4	765	874	987	1045
0.5	729	904	980	1050
0.6	644	821	900	974
0.7	522	681	754	824
0.8	371	493	551	607
0.9	195	264	310	331
	n-Decane $s = 7.75$	*n-Undecane* $s = 8.50$	*n-Tetradecane* $s = 10.75$	*n-Hexadecane* $s = 12.25$
0.1	446	449	462	468
0.2	771	788	828	847
0.3	985	1017	1094	1133
0.4	1097	1143	1259	1321
0.5	1113	1172	1321	1404
0.6	1042	1107	1277	1376
0.7	890	953	1126	1229
0.8	662	715	864	956
0.9	364	396	490	550

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