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Solubility of anthracene in the seven-component liquid system 1-propanol+2-propanol+1-butanol+2-butanol+cyclohexane+heptane+2,2,4-trimethylpentane at 298.15 K

Michael Hoch*

Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

Abstract

The solubility of anthracene in the seven-component liquid system 1-propanol+2-propanol+1-butanol+2-butanol+cyclohexane+heptane+2,2,4-trimethylpentane at 298.15 K was calculated and compared to measured values. The agreement was excellent, better than 1% at all compositions studied. The eight component system requires seven binary interaction parameters anthracene+solvent, and 21 binary interaction parameters between the solvents. All the solvent+solvent interaction parameters are positive, thus increasing the solubility in the large system. The solubility is determined 80% by the seven anthracene+solvent interactions, and 20% by the 21 solvent+solvent interaction parameters. © 2001 Published by Elsevier Science B.V.

Keywords: Anthracene; Solubility; Interaction parameters

1. Introduction

We have measured and calculated from binary interaction parameters the enthalpy of mixing in the liquid Bi–Cd–Ga–In–Pb–Sn–Zn system [1–3] and the activity of Bi in the Bi–Cd–Pb–Sn–Zn system [4]. In ceramic systems we calculated the thermodynamic properties and phase diagrams in the quaternary systems SiO_2–CaO–MgO–Al_2O_3 [5] and B_2O_3–PbO–SiO_2–ZnO [6].

In organic systems we treated the liquid ethyl alcohol+*n*-hexane+benzene+methylcyclopentane [7] system. In all cases only binary and no ternary or higher order interaction parameters were needed, and we used the Hoch–Arpshofen solution model.

The solubility of anthracene in the seven-component liquid system at 298.15 K was measured by Acree [10].

2. The Hoch–Arpshofen model

In an earlier paper Hoch and Arpshofen [8] derived a model for binary solutions. In a subsequent paper Hoch [9] derived the model for ternary, quaternary, and higher order systems. The model is an extended regular solution model, taking into account that the maximum in the enthalpy, excess Gibbs energy and entropy of mixing is not always at $x=0.5$, and that in some cases at one end of the binary system the energy terms are positive, at the other negative.

In a multicomponent system with the components A, B, C, D, etc. and their mole-fractions x, y, z, u, etc. the effect of the mixing function F_m (H_m, enthalpy of mixing, G_m^{ex}, excess Gibbs energy of mixing, S_m^{ex}, excess entropy of mixing) of the binary system A–B (mole-fraction x and y) in the multicomponent system is

$$F_m = Wnx[1-(1-y)^{\{n-1\}}] \tag{1}$$

and the partial quantities are

$$F_x = Wn[1-(1-y)^{\{n-1\}} - xy(n-1)(1-y)^{\{n-2\}}] \tag{2}$$

$$F_y = Wnx(n-1)(1-y)^{\{n-1\}} \tag{3}$$

$$F_z = H_u = -Wnxy(n-1)(1-y)^{\{n-2\}} \tag{4}$$

W is the interaction parameter for the binary A–B and n, the size of the complex, is an integer (2, 3, 4, etc). The term x is the mole-fraction of the component so that in Eq. (1) F_m is maximum (positive or negative) at $x>0.5$.

In a binary system A–B, where x is the mole fraction of A and y is that of B

$$x+y=1. \tag{5}$$

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*E-mail address: michael.hoch@uc.edu (M. Hoch).

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The maximum effect of Eq. (1) will occur at the composition $A_{n-1}B$.

In the multicomponent system (A–B–C–D–etc.) the other binary systems (A–C, A–D, A–etc., B–C, B–D, B–etc., C–D, C–etc., and D–etc.) contribute similarly to the thermodynamic properties of the multicomponent system.

The partial quantities, Eqs. (2)–(4), do not change sign in a binary system when the composition changes from $x=0$ to $x=1$ or in a higher order system when x changes from $x=0$ to $x=1$ and y changes from $y=0$ to $y=1$.

One major advantage of our method is that by using regression analysis, we can calculate the binary interactions from the large systems and can compare them with the values calculated from binary data.

It is possible, that in a binary system on one side attractive, on the other repulsive forces are present (Au–Si, $CaO–SiO_2$). In this case two terms of Eq. (1) are needed:

$$F_m = W_1 xn[1-(1-y)^{\{n-1\}}] + W_2 ym[1-(1-x)^{\{m-1\}}] \tag{1a}$$

or

$$F_m = W_1 xn[1-(1-y)^{\{n-1\}}] + W_2 xm[1-(1-y)^{\{m-1\}}] \tag{1b}$$

with $W_1 > 0$ and $W_2 < 0$ or vice versa.

In a binary system A–B, where x is the mole fraction of A and y is the mole fraction of B and which follows Eq. (1a), the maximum effects will occur at the compositions $A_{n-1}B$ and AB_{m-1}. These effects are also followed in a multicomponent system.

Though we talk about 'complexes', the ideal Gibbs energy of mixing is

$$G_m^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + \ldots) \tag{6}$$

We refer the reader to Refs. [1–9] for derivation of the model and the method of application. A great advantage of our model is that we have never needed ternary interaction parameters. More important, we can obtain the binary interaction parameters from ternary or quaternary data by regression analysis; the latter must agree with data obtained from binary data.

The interaction parameters are designated depending on what experimental data they were calculated from: W_h from H_m enthalpy of mixing, W_s from S_m^{ex}, excess entropy of mixing, and W_g from G_m^{ex}, excess Gibbs energy of mixing.

In all of our calculations the thermodynamic quantities are divided by R, the gas constant. Thus the enthalpy H/R and the Gibbs energy G/R are expressed in kK (kiloKelvin); the entropy S/R and the heat capacity C_p/R are dimensionless.

3. Results

To calculate the solubility we need interaction parameters between the eight components of the system, in total 28 binary interaction parameters. Acree et al. [11,12] measured at 298.15 K the solubility of anthracene in binary solution of the solvents. From these data we extracted the solubility of anthracene in each of the seven solvents. The solubility of anthracene in each solvent is small, thus in Eq. (1) we used $n=2$, x being anthracene. At the solubility limit the activity of solid anthracene in the liquid solvent is 1. The interaction parameters calculated are given in Table 1. The solvent + solvent interactions were calculated from binary data in the literature and are also shown in Table 1. The first two columns contain the components A and B, the third n and x, the fourth the anthracene + solvent interaction parameters, the fifth and sixth columns the solvent + solvent interaction parameters and the seventh the literature references. The literature data were taken from the Handbook of Heats of Mixing [13], International Data Series [14], Battler et al. [15], Singh et al. [16], Heintz et al. [17], Bender et al. [18]. Fig. 1 shows the enthalpy of mixing of binary alcohol + alcohol systems. Note that the ordinate scale is small, the largest absolute value is -0.015 kK. Fig. 2 shows the enthalpy of mixing of binary alkane + alkane systems. Again the ordinate scale is small, the maximum value is 0.03 kK. The data in these two figures contribute almost negligible amounts to the solubility of anthracene. Fig. 3 shows G_m^{ex}, the excess Gibbs energy of mixing in the systems 2-propanol + heptane, and 2-propanol + 2,2,4,-trimethylpentane and the enthalpy of mixing in the systems 2-propanol + heptane, 2-propanol + 2,2,4,-trimethylpentane and 2-propanol + cyclohexane. Here the ordinate scale is 0.15 kK, 10 times larger than the scale in Fig. 1 and five times larger than in Fig. 2. Thus the alcohol + alkane binaries contribute mainly to determining the solubility of anthracene. 2-Propanol is the most 'inorganic' alcohol among the ones used here: the –OH is on the center carbon atom, and only two $–CH_3$ are 'organic'. In Fig. 3 there is a very large difference between the G_m^{ex} and H_m values in the 2-propanol + heptane, and 2-propanol + 2,2,4,-trimethylpentane binary system. The maximum in the G_m^{ex} data is twice that in the H_m data. This however, will have a small effect on the solubility of anthracene.

The solubility measurements were carried out at eight compositions in the system: at the center, where the mole fraction of each component was $x=1/7=0.143$ and close to one solvent, halfway between center and pure component $x=(1+1/7)/2=0.572$, and the other six components $x=(1-0.571)/6=0.071$. From the interaction parameters, Eq. (4) determines the effect of the interaction parameters on the solubility of anthracene. Eq. (4) determines the contribution to the activity coefficient $T\ln(Y)$ of anthracene. If it is negative, the mole fraction $T\ln(x)$ of anthracene must be larger. In Table 2 and Fig. 4 we show

Table 1
Binary interaction parameters W in the eight component system anthracene + 1-propanol + 2-propanol + 1-butanol + 2-butanol + cyclohexane + heptane + 2,2,4-trimethylpentane

Compound		Interaction parameters			
A	B	n,(x)	W, kK	±	Ref.
Anthracene	1-Propanol	2,(A)	1.1069		[12]
Anthracene	2-Propanol	2,(A)	1.1577		[11]
Anthracene	1-Butanol	2,(A)	1.0639		[12]
Anthracene	2-Butanol	2,(A)	1.1115		[12]
Anthracene	Cyclohexane	2,(A)	0.9616		[11]
Anthracene	Heptane	2,(A)	0.9701		[11]
Anthracene	2,2,4-Trimethylpentane	2,(A)	1.0229		[11]
Average			1.0564		
1-Propanol	2-Propanol	2,(A)	−0.0117	0.0003	[13]
1-Propanol	1-Butanol	2,(A)	0.0013	0.0001	[14]
1-Propanol	2-Butanol	2,(A)	−0.0237	0.0010	[13]
1-Propanol	Cyclohexane	4,(B)	0.0422	0.0029	[16]
1-Propanol	Heptane	4,(B)	0.1030	0.0094	[18]
1-Propanol	2,2,4-Trimethylpentane	2,(A)	0.2658	0.0085	[13]
2-Propanol	1-Butanol	2,(A)	0.0001	0.0252	[13]
2-Propanol	2-Butanol	2,(A)	−0.0046	0.0155	[13]
2-Propanol	Cyclohexane	3,(B)	0.0915	0.0072	[15,16]
2-Propanol	Cyclohexane	2,(A)	0.3155	0.0177	[17]
2-Propanol	Heptane	2,(A)	0.3155	0.0177	[17]
2-Propanol	Heptane	3,(B)	0.1030	0.0094	[13]
2-Propanol	2,2,4-Trimethylpentane	2,(A)	0.3121	0.0114	[17]
2-Propanol	2,2,4-Trimethylpentane	4,(B)	0.0603	0.0094	[13]
1-Butanol	2-Butanol	2,(A)	−0.0237	0.0010	[13]
1-Butanol	Cyclohexane	4,(B)	0.0423	0.0028	[13,14]
1-Butanol	Heptane	4,(B)	0.0466	0.0028	[13]
1-Butanol	2,2,4-Trimethylpentane	5,(B)	0.0326	0.0023	[13,14]
2-Butanol	Cyclohexane	3,(B)	0.1032	0.0071	[14]
2-Butanol	Heptane	3,(B)	0.1032	0.0071	[13,14]
2-Butanol	2,2,4-Trimethylpentane	3,(B)	0.1032	0.0071	[13,14]
Cyclohexane	Heptane	3,(A)	0.0269	0.0016	[13,14]
Cyclohexane	2,2,4-Trimethylpentane	2,(A)	0.0435	0.0022	[13]
Heptane	2,2,4-Trimethylpentane	2,(A)	0.0435	0.0022	[14]

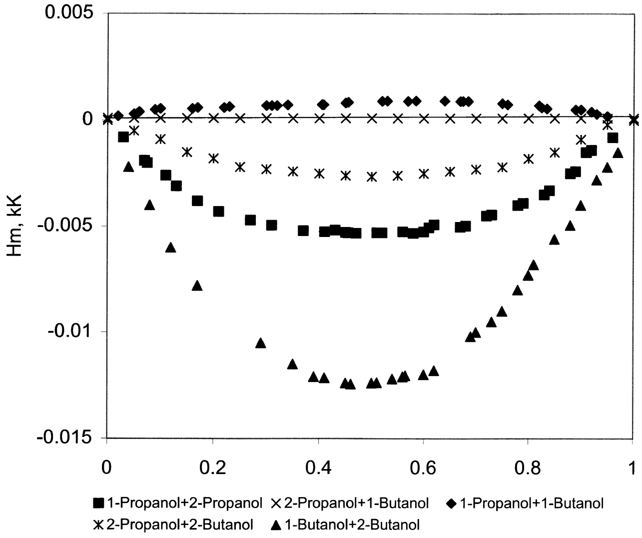


Fig. 1. Enthalpy of mixing at 298.15 in alcohol–alcohol binary systems. Data from Ref. [15].

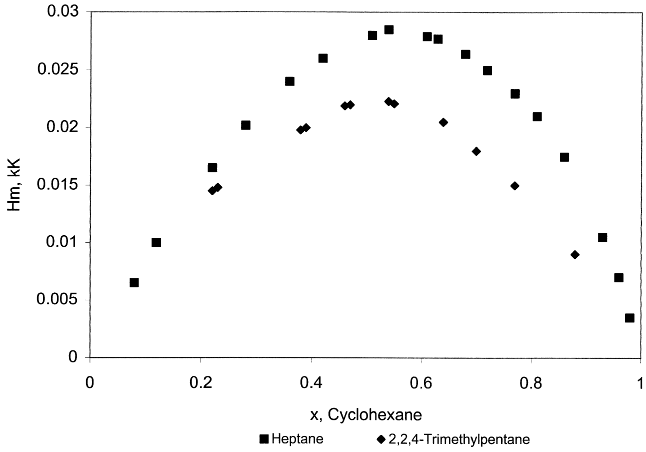
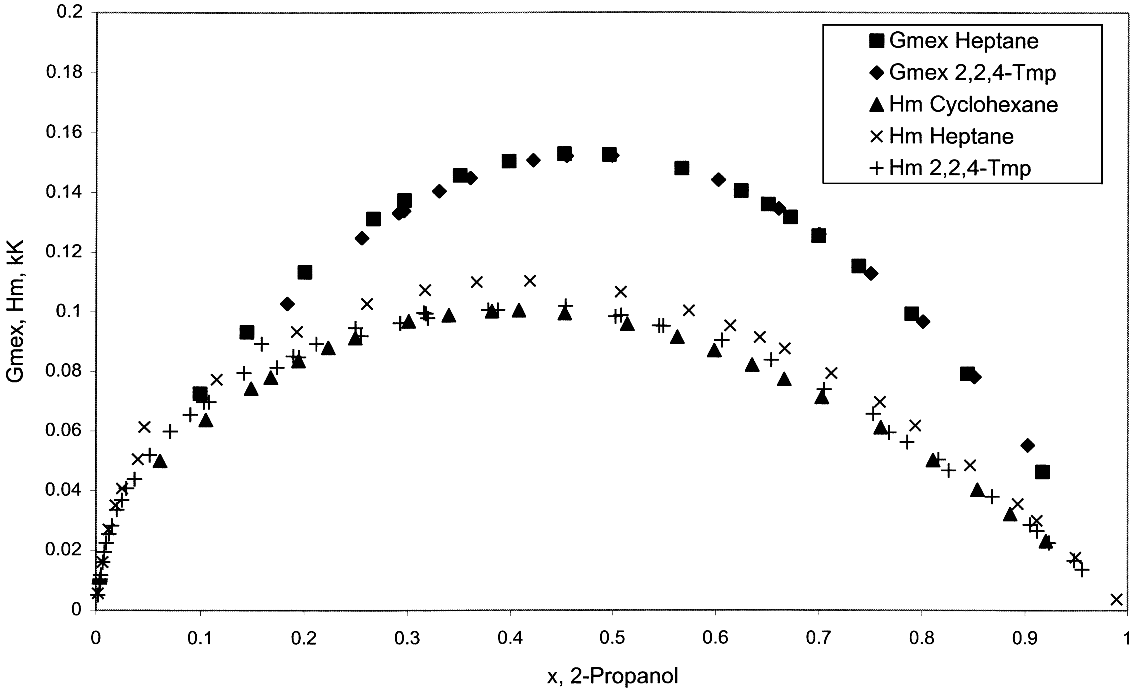


Fig. 2. Enthaly of mixing in the binary systems. Cyclohexane + Heptane and Cyclohexane + 2,2,4-Trimethylpentane. Data from Ref. [15].



2,2,4-Tmp is 2,2,4-Trimethylpentane

Fig. 3. Excess Gibbs energy and enthalpy of mixing in the binary systems. 2-Propanol + Cyclohexane, 2-Propanol + Heptane, and 2-Propanol + 2,2,4-Trimethylpentane.

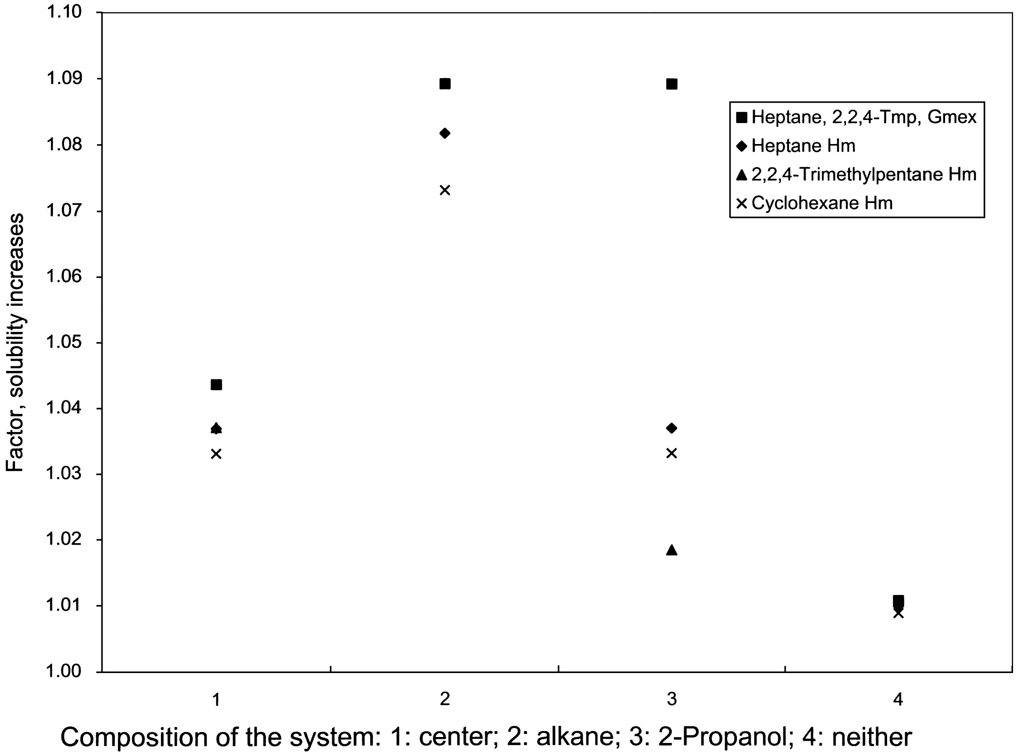


Fig. 4. Increase in solubility of Anthracene due to 2-Propanol-Alkane binary interactions.

Table 2
Factor by which solubility of Anthracene is increased due to 2-Propanol + Alkane binary interactions (Tmp, trimethylpentane)

	G_m^{ex} Heptane 2,2,4-T	H_m Heptane	H_m 2,2,4-Tmp	H_m Cyclohexane
Center	1.0436	1.0369	1.0371	1.0331
Alkane	1.0892	1.0817	1.0892	1.0731
2-Propanol	1.0892	1.0369	1.0184	1.0331
Neither	1.0107	1.0099	1.0107	1.0089

the factor by which the solubility of anthracene is increased due to the various binary systems 2-propanol + alkane, at the center of the system, at the points close to the alkanes, close to 2-propanol, and neither, when the mole fraction of each component in question is $x = 0.071$. Only at the point close to 2-propanol is there a significant difference.

Table 3 shows the measured and calculated solubility of anthracene in the seven-component liquid. The eight compositions are given above. The first column indicates

Table 3
Solubility of anthracene in solutions of 1-propanol + 2-propanol + 1-butanol + 2-butanol + cyclohexane + heptane + 2,2,4,-trimethylpentane (Tmp, trimethylpentane)

Sample close to	x 1-Propanol	x 2-Propanol	x 1-Butanol	x 2-Butanol	x Cyclohexane	x Heptane	x 2,2,4-Tmp	x Anthracene measured	x Anthracene calculated, G_m^{ex}	Ratio calc. G_m^{ex}/ measured	x Anthracene calc., H_m	Ratio calc. H_m/ measured	Calc. H_m/ calc. G_m^{ex}	x Anthracene calc., no solvent–solvent interaction	Calc. (no solve.)/ measured
Center	0.1474	0.1419	0.1452	0.1400	0.1421	0.1429	0.1405	0.001116	0.001181	1.0578	0.001152	1.0323	0.9759	0.0008835	0.7917
2,2,4-Tmp	0.0794	0.0719	0.0729	0.0728	0.0747	0.0855	0.5428	0.001164	0.001214	1.0427	0.001210	1.0395	0.9970	0.0009660	0.8299
1-Propanol	0.5344	0.0727	0.0985	0.0742	0.0731	0.0736	0.0735	0.000875	0.000799	0.9130	0.000796	0.9097	0.9964	0.0007783	0.8895
2-Propanol	0.0745	0.5387	0.0733	0.0944	0.0743	0.0730	0.0718	0.000784	0.000830	1.0589	0.000709	0.9043	0.8540	0.0006150	0.7844
2-Butanol	0.0753	0.0765	0.0752	0.5466	0.0751	0.0762	0.0751	0.000888	0.000846	0.9532	0.000843	0.9493	0.9960	0.0007144	0.8045
1-Butanol	0.0722	0.0724	0.5364	0.0742	0.0985	0.0744	0.0719	0.000996	0.000949	0.9533	0.000946	0.9498	0.9964	0.0008490	0.8524
Cyclohexane	0.0731	0.0689	0.0760	0.0795	0.5513	0.0765	0.0747	0.001467	0.001589	1.0832	0.001563	1.0654	0.9836	0.0012545	0.8551
Heptane	0.0884	0.0681	0.0741	0.0752	0.0777	0.5432	0.0733	0.001412	0.001465	1.0374	0.001452	1.0283	0.9913	0.0011330	0.8024
Average										1.0124		0.9808	0.9738		0.8262
Maximum										1.0832		1.0654	0.9970		0.8895
Minimum										0.9130		0.9043	0.8540		0.7844

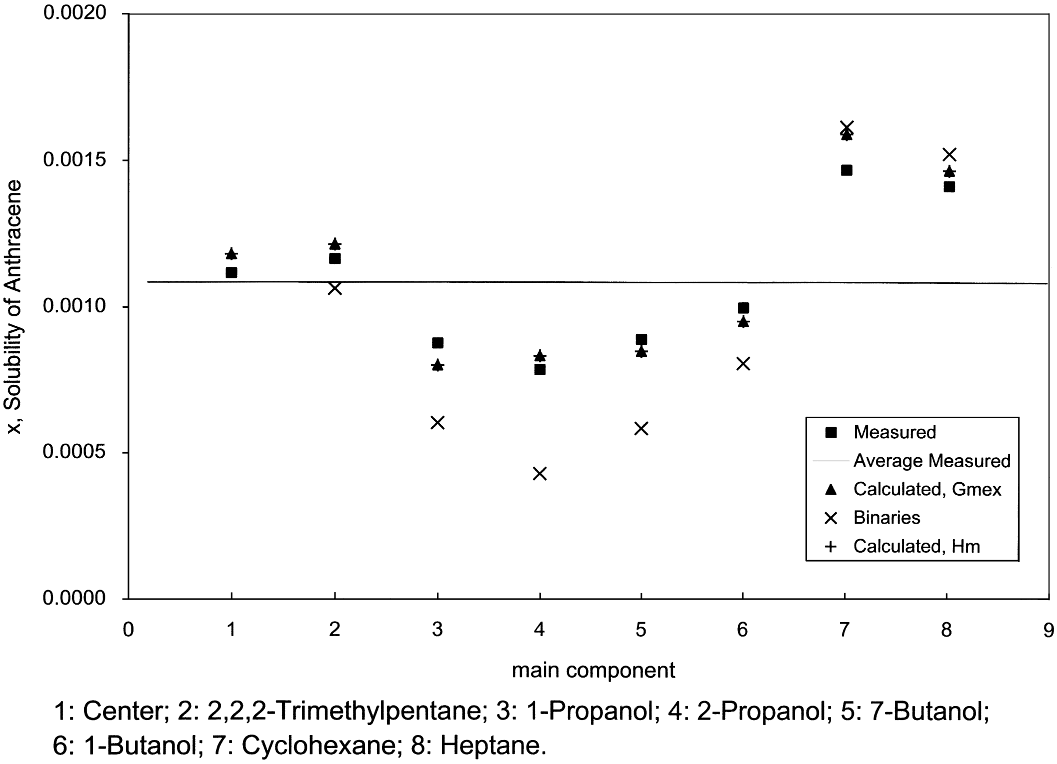


Fig. 5. Solubility of Anthracene in a seven component solvent system. At 1: $x = 1/7 = 0.143$; at others: $x = (1 + 0.143)/2 \sim = 0.572$.

which solvent with $x=0.571$ controls the system, the second to eighth the mole fraction of the components, the ninth the measured solubility of anthracene. The 10th column gives the calculated (with G_m^{ex}) solubility of anthracene. The 11th gives the ratio calculated/measured. At the bottom of this column we show the average, maximum and minimum values of the ratio. The average value is extremely close to one, and the spread is small. The 12th and 13th give the calculated value (with H_m) and the ratio calculated/measured. There is no significant difference between the two calculations. In the G_m^{ex} calculation we also assumed that the 2-propanol + cyclohexane data are the same as the 2-propanol + heptane data. To see the importance of the solvent + solvent interaction, we calculated the solubility of anthracene using only the anthracene + solvent interactions. The data are shown in columns 15 and 16. The calculated/measured ratio is 20% lower than when the solvent + solvent interactions were also used, in spite of the fact that we have seven anthracene + solvent interactions, and 21 solvent + solvent interactions. This is due mainly to the low solubility of anthracene in each solvent. Finally Fig. 5 shows the solubility of anthracene in the seven-component solutions: the measured values, the average of the measured values, the calculated values (both with G_m^{ex} and H_m) and the values using only the 'direct interactions'.

4. Conclusions

We have calculated the solubility of anthracene in the seven-component liquid system 1-propanol + 2-propanol + 1-butanol + 2-butanol + cyclohexane + heptane + 2,2,4-trimethylpentane at 298.15 K. There are 21 binary solvent + solvent interaction parameters not involving anthracene, thus each plays a small role in the calculations. The seven anthracene + solvent 'direct' interactions play a much larger role than the 'indirect' solvent + solvent interactions.

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