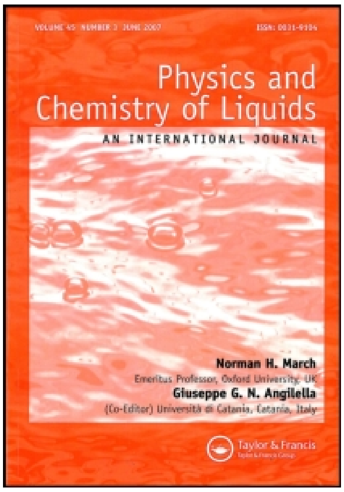

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Light Scattering from Binary Liquid Systems II. The Partial Pressure of Solutions

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LIGHT SCATTERING FROM BINARY LIQUID SYSTEMS

II. The Partial Pressure of Solutions

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The measured light scattering intensities of some binary liquid mixtures at 20°C using a He-Ne laser at $\lambda = 632.8$ nm and the calculated compositional fluctuation function, f, together with literature values of the vapour pressures for some of these liquids were utilized for evaluation of the partial pressures of the components of these mixtures as a function of mixture composition. The present work has confirmed that careful measurements of light scattering of binary mixtures can provide important thermodynamic data which are otherwise attainable only with some difficulty.

KEY WORDS: Binary mixtures, compositional fluctuations.

The thermodynamic function f which describes the compositional fluctuation level can be determined from the partial pressure of the vapour by analyzing the vapour's components. In such measurements it is very difficult to avoid, or even minimize, the large errors which add to the error in measuring the vapour pressures of solutions, so the thermodynamic f values are not obtainable with sufficient accuracy[1–3].

The advantage of the light scattering technique for calculating the partial pressure and other thermodynamic values is due to its facility for making measurements at high and low temperatures[4–5]. The method of vapour-liquid equilibria for determining the partial pressure encounters substantial difficulties when dealing with low temperatures. In the literature the bulk of thermodynamic data deals with high temperature. While a few experimental results can be found for the partial pressure of solutions at room temperature, for low temperatures such measurements are rare.

In this work, our previous results for light scattering from compositional fluctuations in binary liquid systems (part I of this series)[6] were used to evaluate the partial pressure for 14 binary mixtures of (CCl_4, benzene, toluene and chlorobenzene)-alcohol. The solutions of CCl_4-cyclohexane and benzene-cyclohexane were also tested.

The thermodynamic function of compositional fluctuations f can be expressed as,

$$1/f = (x_1 x_2/R_0 T)(\partial^2 G/\partial x^2)_{P,T} \qquad (1)$$

where x is the molar concentration of one of the components, whereas $x_1 + x_2 = 1$, R_0T has its usual meaning and G is the thermodynamic Gibbs potential. This expression is restricted in studying the dependence of the thermodynamical properties of solutions on the concentration. The molecular chemical potential in the liquid phase is similar to that in the vapour state. So, considering the vapour as an ideal gas we can write

$$\mu_1 = \mu_{10} + R_0T\ln P_1;$$

and

$$(\partial\mu_1/\partial x_1) = R_0T(\partial P_1/P_1\partial x_1)$$

where μ_1 and P_1 are the chemical potential and partial pressure of the first component of solution, respectively and μ_{10} is a constant. The thermodynamic function f becomes

$$1/f = (x_1\partial P_1/P_1\partial x_1) = (x_2\partial P_2/P_2\partial x_2) \tag{2}$$

We can see that f can be determined indirectly from the curves of the partial pressure—concentration dependence. For the ideal solution $P_1 = P_{10}x_1$ and $P_2 = P_{20}x_2$ where P_{10} and P_{20} are the vapour pressures of the pure components. Using the derivatives $(\partial P_1/\partial x_1) = P_1/x_1$ and substituting into expression (2) we have $f = 1$ so for ideal solution at all concentrations f is equal to one.

It is clear that we can solve the inverse problem by measuring the compositional scattering intensity in solutions at different concentrations from $x_2 = 0$ to $x_2 = 1$ and with the aid of the expression

$$R_C = (\pi^2/\lambda^4N_A)\{2n(\partial n/\partial x)\}^2\{9n^2/(2n^2 - 1)(n^2 + 2)\}^2x_1x_2V_{12}f, \tag{3}$$

we can determine the f values at all concentrations from which the partial pressure of the components can be calculated.

By plotting the curves $f = f(x_2)$ and dividing the x-axis into equal intervals $\Delta x_1 = \Delta x_2 = 0.1$. For the calculation we use the equality

$$(\Delta P_1/\Delta x_1)(x_1/P_1) = 1/f$$

For the first interval we can write

$$(\Delta P_{11}/\Delta x_{11})(x_{10}/P_{10}) = (\Delta P_{11}/0.1)(1/P_{10}) = 1/f_0 = 1$$

or

$$\Delta P_{11} = 0.1P_{10}$$

Table 1 The calculated values of the function, f and the partial pressure components P_1 and P_2 for the Mixture Systems Studied at 20°C.

x_2	f	$P_{1'}$ (Torrs)	$P_{2'}$ (Torrs)	x_2	f	$P_{1'}$ (Torrs)	$P_{2'}$ (Torrs)
CCL$_4$-Methanol				CCl$_4$-Ethanol			
0.00	1.00	79.41	00.00	0.00	1.00	79.41	00.00
0.10	4.85	77.59	48.24	0.10	4.06	77.23	19.00
0.20	6.74	76.15	60.77	0.20	5.21	75.37	25.22
0.30	10.02	75.06	65.64	0.30	6.43	73.69	27.90
0.40	11.61	73.98	67.90	0.40	6.38	71.76	29.43
0.50	9.30	72.39	69.40	0.50	4.46	68.54	30.63
0.60	7.86	70.08	70.93	0.60	3.42	63.53	32.07
0.70	2.68	61.36	72.47	0.70	3.01	56.49	33.72
0.80	1.90	45.21	76.55	0.80	1.86	41.30	35.40
0.90	1.48	14.66	81.95	0.90	1.34	10.48	37.95
1.00	1.00	00.00	88.60	1.00	1.00	00.00	41.39
CCl$_4$-Cyclohexane				Benzene-Methanol			
0.00	1.00	79.41	00.00	0.00	1.00	57.76	00.00
0.10	3.10	76.56	21.92	0.10	3.85	56.09	42.92
0.20	3.26	73.62	32.36	0.20	6.74	55.05	57.98
0.30	3.41	70.53	38.23	0.30	7.68	54.02	62.63
0.40	3.31	66.98	42.38	0.40	7.07	52.74	65.48
0.50	3.02	62.54	45.85	0.50	6.10	51.01	67.88
0.60	2.61	56.54	49.10	0.60	4.65	48.26	70.18
0.70	2.06	47.40	52.45	0.80	1.93	23.25	75.60
0.80	1.74	33.77	56.36	0.90	1.27	04.94	80.84
0.90	1.21	05.86	60.73	1.00	1.00	00.00	88.60
1.00	1.00	00.00	66.88				
Benzene-Ethanol				Benzene-Cyclohexane			
0.00	1.00	57.76	00.00	0.00	1.00	57.76	00.00
0.10	2.70	55.38	12.56	0.10	2.46	55.15	13.45
0.20	3.98	53.64	19.95	0.20	2.61	52.51	22.67
0.40	4.23	49.41	26.65	0.40	2.35	45.06	36.76
0.60	2.62	39.98	30.23	0.60	2.05	34.07	46.70
0.80	1.81	17.89	34.64	0.80	1.64	13.29	55.76
0.90	1.10	01.62	37.21	0.90	1.14	01.63	60.36
1.00	1.00	00.00	41.39	1.00	1.00	00.00	66.88
Toluene-Methanol				Toluene-Ethanol			
0.00	1.00	21.08	00.00	0.00	1.00	21.08	00.00
0.20	5.80	20.17	63.07	0.20	3.48	19.56	23.69
0.30	8.55	19.83	69.02	0.30	5.00	19.00	27.67
0.40	0.30	19.50	71.82	0.40	5.10	18.38	29.65
0.50	9.20	19.07	73.61	0.50	4.30	17.52	31.18
0.57	7.72	18.66	74.75	0.70	2.65	13.11	34.38
0.60	7.00	18.46	75.28	0.80	2.05	09.91	36.34
0.70	5.05	17.24	77.12	1.00	1.00	00.00	41.39
0.80	2.40	13.65	79.37				
1.00	1.00	00.00	88.60				

(*continued*)

Table 1 (*continued*)

x_2	f	$P_{1'}$ (*Torrs*)	$P_{2'}$ (*Torrs*)	x_2	f	$P_{1'}$ (*Torrs*)	$P_{2'}$ (*Torrs*)
Toluene-Propanol				Toluene-Butanol			
0.00	1.00	21.08	00.00	0.00	1.00	21.08	00.00
0.20	2.80	19.19	14.38	0.20	2.40	18.88	03.19
0.30	3.65	18.43	17.51	0.30	2.30	17.70	04.03
0.40	3.30	17.50	19.27	0.40	2.15	16.32	04.72
0.60	2.35	13.77	22.71	0.60	1.70	11.52	06.15
0.70	1.95	11.41	24.45	0.70	1.50	08.96	06.82
0.80	1.60	07.84	26.39	0.80	1.35	05.64	07.54
1.00	1.00	00.00	31.28	1.00	1.00	00.00	09.26
Toluene-Octane				Chlorobenzene-Methanol			
0.00	1.00	21.08	00.00	0.00	1.00	09.10	00.00
0.10	1.15	19.04	00.11	0.10	3.96	08.84	45.32
0.20	1.25	17.13	00.89	0.20	4.60	08.60	60.63
0.40	1.50	13.32	04.48	0.30	5.63	08.38	68.03
0.50	1.45	11.48	05.38	0.40	7.25	08.18	72.32
0.60	1.35	09.35	06.25	0.50	7.20	07.95	74.91
0.80	1.20	01.55	08.30	0.60	6.91	07.66	77.05
1.00	1.00	00.00	10.49	0.80	4.00	05.74	80.96
				0.90	1.96	02.81	83.57
				1.00	1.00	00.00	88.60
Chlorobenzene-Propanol				Chlorobenzene-Butanol			
0.00	1.00	09.10	00.00	0.00	1.00	09.10	00.00
0.10	2.40	08.68	08.71	0.10	1.48	08.41	00.92
0.20	2.82	08.29	14.94	0.20	2.39	07.97	02.85
0.30	3.61	07.96	18.16	0.30	2.28	07.47	03.61
0.40	3.54	07.58	20.01	0.40	1.96	06.83	04.23
0.50	3.36	07.12	21.54	0.60	1.48	04.52	05.68
0.60	3.00	06.52	22.91	0.80	1.20	00.75	07.33
0.70	2.11	05.49	24.26	1.00	1.00	00.00	09.26
0.80	1.50	03.66	26.03				
0.90	1.21	00.63	28.40				
1.00	1.00	00.00	31.28				

The partial pressure for $i + 1$ interval can be written as

$$P_{i+1} = P_i[1 - (0.1/x_i f_i)] \tag{4}$$

Table 1 and Figure 1–4 show the dependence of the partial pressure of 14 systems on the volume fraction of the second component x_2. At low concentrations all solutions become near to ideal because the partial pressure of the solute materials increases proportionally with the concentration x_2, whereas the partial pressure of the solvent falls proportionally with the decreasing of the concentration x_1. It is similar with that in the ideal solution. So, the function f always started out from the value $f = 1$ at $x_2 = 0$ and finished with $f = 1$ at $x_2 = 1$.

The light scattering method has a disadvantage when the components of the solution have equal, or nearly equal, refractive indices, in which case the method

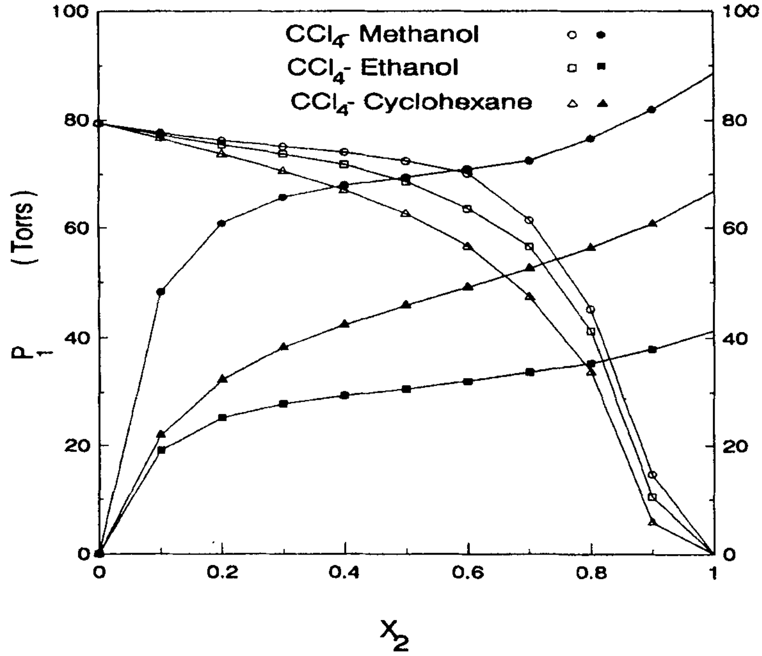

Figure 1 The partial pressures of CCl_4 solutions at 20°C, obtained from the experimental results of light scattering in solutions.

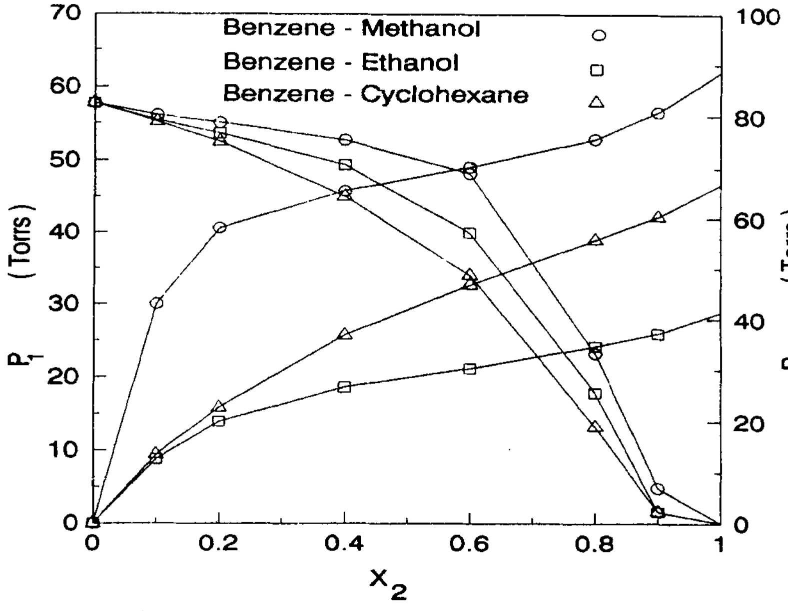

Figure 2 The partial pressures of benzene solutions at 20°C.

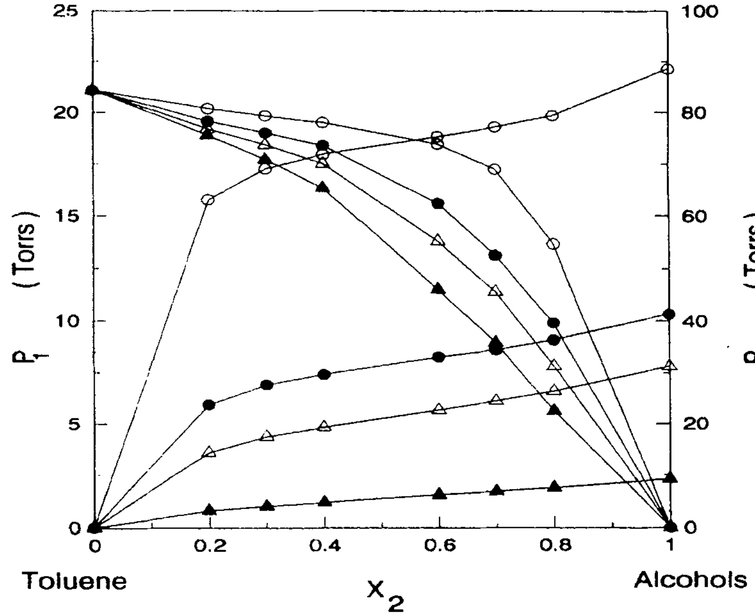

Figure 3 Dependence of the partial pressures on the volume fraction of component 2 for the binary systems: ○-toluene-methanol; ●-toluene-ethanol; △-toluene propanol; ▲-toluene-butanol.

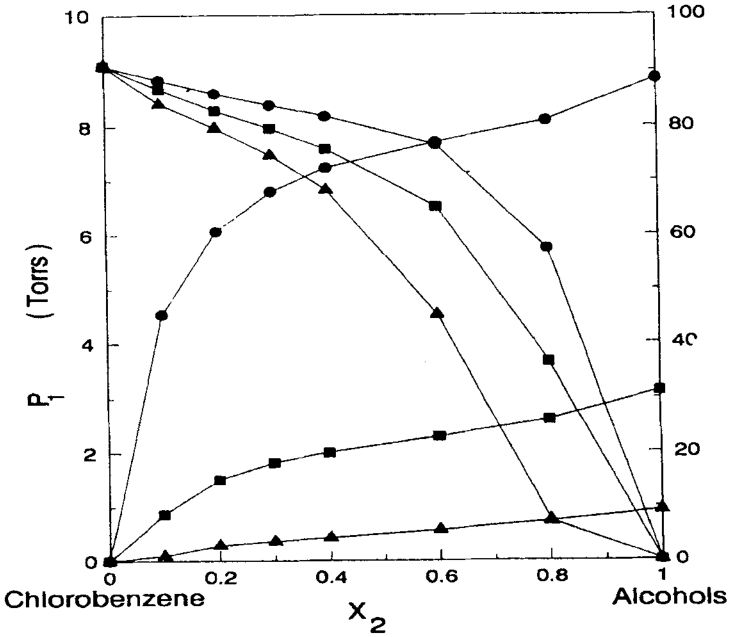

Figure 4 The partial pressure for the binary systems: ●-chlorobenzene-methanol; ■-chlorobenzene-propanol; ▲-chlorobenzene-butanol.

gives poor accuracy. It is clearly preferable to apply the light scattering method to these cases in which values of the refractive indices of pure components are different (when the derivative $\partial n/\partial x$ has a sufficiently large value). Such solutions give significant compositional scattered light even in these cases when few compositional fluctuations occurred and the function f is near to the unity.

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