Dependence of the vapour pressure and activity coefficients on the composition of some two-component polar solvents

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In this paper the equilibrium $P-x$ data are presented for some binary solutions of polar solvents, *i.e.* dimethylformamide, dimethyl sulfoxide, ethylene glycol, amyl alcohol, and aniline at 100°C. The data have been measured by static method. From the $P-x$ data the coefficients of the relationship between the excess free enthalpy and composition have been calculated according to the Redlich—Kister and Renon NRTL equation. Half of the eight systems studied shows a positive and half a negative deviation from the properties of ideal solution, this deviation being small in the case of four pairs. In five cases of the reverse calculation of the vapour pressure of solution, the Redlich—Kister equation gives the results with equal average deviation as the NRTL equation; in two cases it is better to use the Redlich—Kister equation and in one case the Renon equation is more convenient.

The research of mixed solvents for the BTX aromates showed the need for determination of the dependence of the activity coefficients of components on the composition of some binary solutions of polar solvents at 100°C. This concerned the following pairs: dimethylformamide (DMFA)—dimethyl sulfoxide (DMSO); DMFA—ethylene glycol (EG); DMSO—EG; DMFA—aniline; amyl alcohol—aniline; amyl alcohol—DMFA; amyl alcohol—DMSO; amyl alcohol—EG.

The most reliable source for determining such relationships is based on the liquid——vapour equilibrium data. Since a direct determination of the composition of $l-g$ equilibrium phases is usually less accurate provided the components show a greater difference in boiling temperatures and the pressure of saturated vapour is relatively low, we have determined the dependence of saturated vapour pressure of solutions on the composition by static method. The data obtained have been processed numerically by the method described later in this paper using the Redlich—Kister (R—K) equation of fourth order and the so-called Renon NRTL equation.

Experimental technique

In principle, the device for measuring the isothermal $P-x$ data is based on the scheme for measuring the vapour pressure of pure substances described by *Waddington et al.* [2] and the apparatus for measuring the equilibrium liquid—vapour data by the static method according to *Renon et al.* [3]. In Fig. 1 the block diagram of the device used by us is presented and Fig. 2 shows a sketch of the equilibrium vessel. The measuring procedure was as follows.
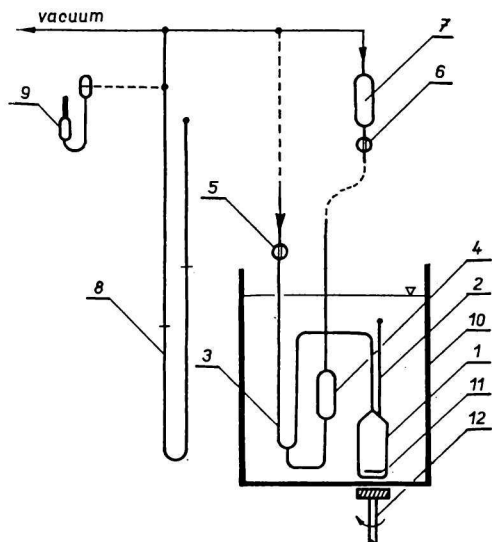
Fig. 1. Block diagram of the device for measuring vapour pressure.

1. flask with solution; 2. filling tube; 3. differential manometer; 4. reservoir of mercury, 5., 6. cocks; 7. vessel for filling manometer with mercury, 8. mercury manometer; 9. McLeod manometer; 10. glass thermostatting vessel; 11., 12. magnetic stirrer.
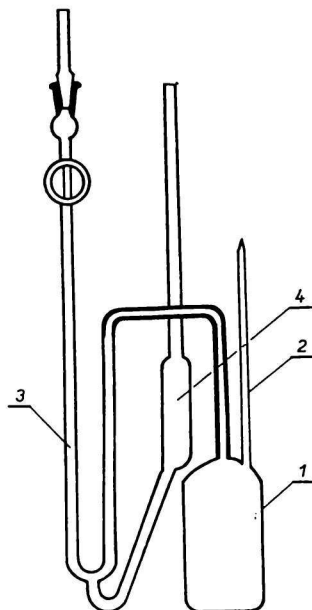
- - - elastic connection.

Fig. 2. Equilibrium measuring vessel of the device for determining vapour pressure.

1. flask with solution (volume *ca.* 30 cm³); 2. filling tube; 3. differential manometer (U tube); 4. reservoir of mercury for deaeration.

Vessel 7 was filled with a measured amount of mercury and cocks 5 and 6 were closed. Flask 1 was filled through a tube 2 with about 20 cm³ of solution. The individual components of solution were weighed as a weight difference by syringes. Tube 2 was sealed and the flask dipped into a cooling mixture (solid CO_2 + acetone), and the vacuum was connected. After reaching the required vacuum (max. pressure 0.1 torr) and cooling the solution in the flask, cock 5 was opened and the differential manometer was filled with mercury by opening cock 6. The content of flask was heated under constant stirring with a magnetic stirrer and the solution was deaerated. After a few minutes the content of the flask was cooled again (without stirring to prevent a reverse absorption of air) and by tilting, by approx. 45° for a few seconds the mercury from manometer was poured into flask 4 while the liberated air was sucked off. The flask was heated again and the deaeration was repeated until after cooling a constant difference of mercury levels in a U tube was achieved.

During measurements the equipment was connected to an evacuated reservoir and the whole measuring vessel was dipped into a thermostatting bath (see Fig. 1), the temperature of which was kept at 100°C accurate to ±0.05°C. In order to prevent the formation

of a concentration gradient, the solution was stirred. The pressure difference between the vapour space and reservoir of vacuum was equalized according to the difference of mercury levels in the U tube by letting the air into the reservoir. The saturated vapour pressure of solution was given as the sum of the pressure data of the U tube and manometer. The height of mercury level was measured with the accuracy ± 0.05 mm with a cathetometer.

Interpretation of the measured data

The pressure of the saturated vapour of solution was calculated from relationship

$$P = \frac{P_1^0 \, \gamma_1 \, x_1}{\Phi_1} + \frac{P_2^0 \, \gamma_2 \, x_2}{\Phi_2} \,. \tag{1}$$

Because of a low pressure in the system, the correction coefficients for a real behaviour of vapour phase Φ_1, Φ_2 were considered to be dependent only on the properties of pure components at a given pressure and temperature. The relationship put forward by *Scheibel* [4] and *Chidabaram* [5] was applied to the calculation of these coefficients.

The activity coefficients of components were evaluated by means of the excess free enthalpy from

a) the Redlich—Kister expansion of fourth order [9]

$$\frac{\Delta G^{\mathrm{E}}}{2.3 \, RT} = x_1 \, x_2 [b + c(x_1 - x_2) + d(x_1 - x_2)^2] \,, \tag{2}$$

b) the Renon NRTL equation [3, 6]

$$\frac{\Delta G^{\mathrm{E}}}{RT} = x_1 \, x_2 \left[\frac{\tau_{21} \, G_{21}}{x_1 + x_2 \, G_{21}} + \frac{\tau_{12} \, G_{12}}{x_2 + x_1 \, G_{12}} \right], \tag{3}$$

where

$$\tau_{12} = \frac{C_{12}}{RT}, \qquad \tau_{21} = \frac{C_{21}}{RT} \tag{4}$$

and

$$G_{12} = \exp(-\alpha_{12} \, \tau_{12}), \qquad G_{21} = \exp(-\alpha_{21} \, \tau_{21}). \tag{5}$$

The coefficients of eqns (2) and (3) which may be regarded in a not too wide pressure range only as a function of temperature were calculated as follows:

a) By the method proposed by *Tao* [7] the activity coefficients of components were calculated on the basis of the $P-x$ data. The activity coefficients thus calculated were used for the calculation of the coefficients in the Redlich—Kister equation by the method of least squares. Since the calculation according to Tao starts from a not very accurate graphically estimated value of the limiting activity coefficient of a more volatile component; the more precise value was obtained by using few iterations. The procedure is described in papers [1, 8].

b) The coefficients C_{12}, C_{21}, and α_{12} of the NRTL equation were determined by the Newton iteration method using the minimizing function

$$Q = \sum_j \left(\frac{100}{P_{\exp}} \right)_j^2 (P_{\mathrm{calc}} - P_{\exp})_j^2 \,. \tag{6}$$

The numerical procedure and the corresponding block diagram are presented in the monograph by *Renon* [6].

Table 1a

Measured and calculated data on the saturated vapour pressure of some two-component
solvents with varying composition at 100°C

DMFA (1)−DMSO (2)

x_1	P_{exp} [torr]	R−K equation $b = 0.0593; c = 0.0060; d = 0.0235$		NRTL equation $C_{12} = -251.8; C_{21} = 413.8; \alpha_{12} = 0.3973$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\,P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\,P_{exp}}$
0.000	38.3				
0.102	50.7	50.5	+0.4	50.6	+0.2
0.197	60.9	60.9	±0	61.1	−0.4
0.307	72.4	72.5	−0.1	72.6	−0.3
0.406	83.4	82 7	+0.8	82.5	+1.1
0.502	92.4	92.6	−0.2	91.9	+0.5
0.614	104.1	103.8	+0.3	102.8	+1.3
0.705	111.9	112.7	−0.7	111.5	+0.3
0.799	123.8	121.6	+1.8	120.6	+2.6
0.903	130.5	131.2	−0.5	130.7	−0.2
1.000	140.2				
Average deviation [%]			±0.5		±0.8

Table 1b

DMFA (1)−EG (2)

x_1	P_{exp} [torr]	R−K equation $b = 0.0685; c = 0.0261; d = 0.0212$		NRTL equation $C_{12} = -384.6; C_{21} = 718.0; \alpha_{12} = 0.4651$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\,P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\,P_{exp}}$
0.000	15.8				
0.104	32.1	31.3	+2.6	31.8	+1.0
0.201	43.4	43.9	−1.1	44.4	−2.3
0.325	59.3	58.9	+0.7 ·	59.2	+0.1
0.412	68.2	69.3	−1.6	69.3	−1.6
0.481	79.4	77.6	+2.3	77.4	+2.5
0.593	91.7	91.1	+0.7	90.5	+1.3
0.789	104.0	105.0	−1.0	104.3	−0.3
0.799	114.9	115.9	−0.9	115.4	−0.4
0.898	127.8	127.8	±0	127.6	+0.2
1.000	140.2				
Average deviation [%]			±1.2		±1.1

Table 1c

DMSO (1)—EG (2)

x_1	P_{exp} [torr]	R−K equation $b = -0.4778; c = -0.1502;$ $d = 0.0368$		NRTL equation $C_{12} = -4175; C_{21} = 5417;$ $\alpha_{21} = 0.0689$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$
0.000	15.8				
0.149	16.3	16.3	± 0	15.7	$+3.8$
0.210	16.8	16.5	$+1.8$	15.8	$+5.9$
0.283	17.7	17.0	$+4.1$	16.2	$+8.4$
0.401	17.8	18.1	-1.7	17.7	$+0.7$
0.505	19.6	20.0	-2.0	20.0	-1.9
0.597	22.4	22.4	± 0	22.8	-1.6
0.706	27.1	26.2	$+3.4$	26.8	$+1.1$
0.791	29.8	29.7	$+0.3$	30.2	-1.5
0.899	34.4	34.4	± 0	34.6	-0.6
1.000	38.3				
Average deviation [%]			± 1.5		± 2.8

Table 1d

DMFA (1)—aniline (2)

x_1	P_{exp} [torr]	R−K equation $b = -0.5485; c = 0.0293;$ $d = 0.0601$		NRTL equation $C_{12} = -2188; C_{21} = 3102;$ $\alpha_{12} = 0.2002$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$
0.000	48.4				
0.098	48.4	48.2	$+0.4$	48.2	$+0.4$
0.199	48.6	49.2	-1.2	49.1	-1.0
0.303	53.1	52.7	$+0.8$	52.6	$+0.9$
0.402	59.5	59.2	$+0.5$	59.3	$+0.3$
0.543	74.3	74.4	-0.1	74.5	-0.3
0.600	81.5	82.2	-0.9	82.2	-0.8
0.700	96.5	97.3	-0.8	96.8	-0.3
0.800	112.8	112.7	$+0.1$	112.0	$+0.7$
0.897	126.9	126.8	$+0.1$	126.3	$+0.4$
1.000	140.2				
Average deviation [%]			± 0.5		± 0.6

Table 1e

Amyl alcohol (1)—aniline (2)

x_1	P_{exp} [torr]	R—K equation $b = 0.3170; c = -0.0134;$ $d = -0.0009$		NRTL equation $C_{12} = 255.2; C_{21} = 333.9;$ $\alpha_{12} = 0.4223$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01 \, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01 \, P_{exp}}$
0.000	48.4				
0.100	76.4	76.4	±0	76.2	+0.3
0.202	96.4	97.2	−0.8	96.9	−0.6
0.302	112.6	112.7	−0.1	112.5	+0.1
0.407	126.4	125.6	+0.6	125.6	+0.6
0.487	133.7	133.9	−0.2	134.1	−0.3
0.602	145.5	144.7	+0.6	145.0	+0.4
0.683	151.5	151.7	−0.1	152.0	−0.4
0.792	160.8	160.9	−0.1	161.2	−0.2
0.897	169.6	169.6	±0	169.8	−0.1
1.000	178.0				
Average deviation [%]			±0.3		±0.3

Table 1f

Amyl alcohol (1)—DMFA (2)

x_1	P_{exp} [torr]	R—K equation $b = -0.0892; c = -0.0382;$ $d = -0.0048$		NRTL equation $C_{12} = -1163; C_{21} = 1660;$ $\alpha_{12} = 0.2405$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01 \, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01 \, P_{exp}}$
0.000	140.2				
0.105	142.4	141.9	+0.4	142.5	−0.1
0.203	143.6	143.6	±0	144.0	−0.3
0.296	146.0	145.4	+0.4	145.5	+0.3
0.398	147.6	147.8	−0.1	147.6	±0
0.495	150.1	150.5	−0.3	150.3	−0.1
0.616	155.2	154.9	+0.2	155.0	+0.1
0.704	159.2	159.0	+0.1	159.2	±0
0.799	164.6	164.2	+0.2	164.6	±0
0.902	170.8	170.9	−0.1	171.3	−0.3
1.000	178.0				
Average deviation [%]			±0.2		±0.1

Table 1g

Amyl alcohol (1) — EG (2)

| x_1	P_{exp} [torr]	R—K equation $b = 0.5765; c = -0.1286;$ $d = 0.1154$		NRTL equation $C_{12} = 478.0; C_{21} = 1115;$ $\alpha_{12} = 0.6550$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$
0.000	15.8				
0.034	48.0	47.0	+2.1	46.9	+2.2
0.101	77.5	79.1	−2.0	77.4	+0.1
0.208	97.7	99.3	−1.6	98.1	−0.5
0.313	110.6	109.6	+0.9	110.1	+0.5
0.400	118.8	117.3	+1.3	118.4	+0.4
0.503	127.8	127.0	+0.6	127.8	±0
0.599	135.9	136.6	−0.5	136.5	−0.4
0.681	143.7	144.8	−0.8	144.1	−0.2
0.796	154.6	156.3	−1.1	155.2	−0.4
0.902	168.8	167.0	+1.1	166.4	+1.4
1.000	178.0				
Average deviation [%]			±1.2		±0.6

Table 1h

Amyl alcohol (1) — DMSO (2)

x_1	P_{exp} [torr]	R—K equation $b = -0.1706; c = -0.1064;$ $d = 0.0097$		NRTL equation $C_{12} = 567.4; C_{21} = -689.7;$ $\alpha_{12} = 0.4649$	
		P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$	P_{calc} [torr]	$\dfrac{P_{exp} - P_{calc}}{0.01\, P_{exp}}$
0.000	38.3				
0.102	49.5	49.4	+0.2	47.1	+4.9
0.200	59.6	59.2	+0.7	56.5	+5.2
0.303	70.2	70.0	+0.3	67.7	+3.5
0.399	80.5	80.9	−0.5	79.4	+1.3
0.499	93.4	93.9	−0.5	93.1	+0.3
0.593	107.0	107.7	−0.6	107.3	−0.3
0.693	126.3	124.1	+1.8	123.8	+1.9
0.791	140.9	141.4	−0.4	141.1	−0.2
0.895	160.7	160.1	+0.4	160.0	+0.5
1.000	178.0				
Average deviation [%]			±0.6		±2.0

Results

The preparation method of the solvents used, their purity as well as the critical parameters applied to the calculation of coefficients Φ_1 and Φ_2 are given in an original report[1].

Tables $1a-h$ contain the measured values of saturated vapour pressures of the respective binary solvents at 100°C for different mole fractions of the more volatile component. Moreover, the calculated coefficients of the Redlich—Kister equation of fourth order and the NRTL equation are also reported in these tables. Both the equations are compared
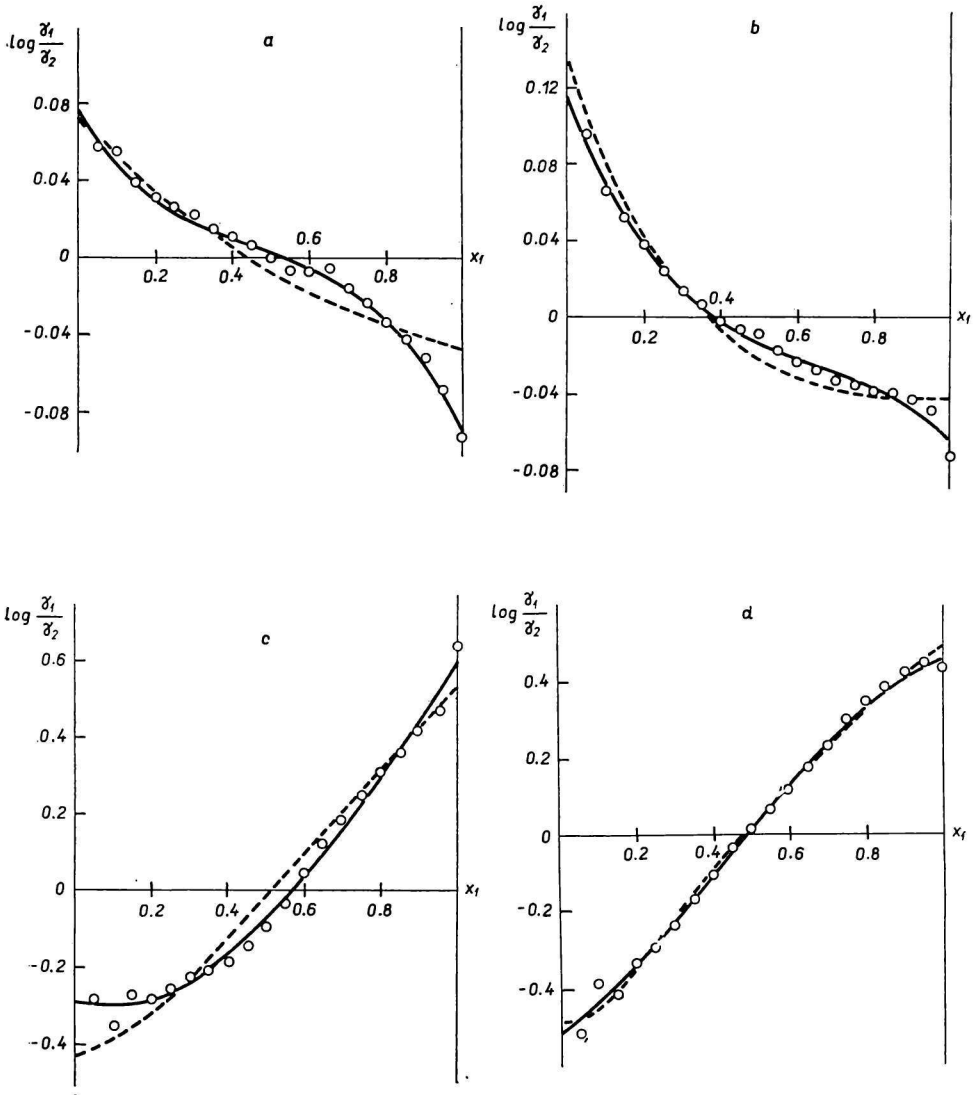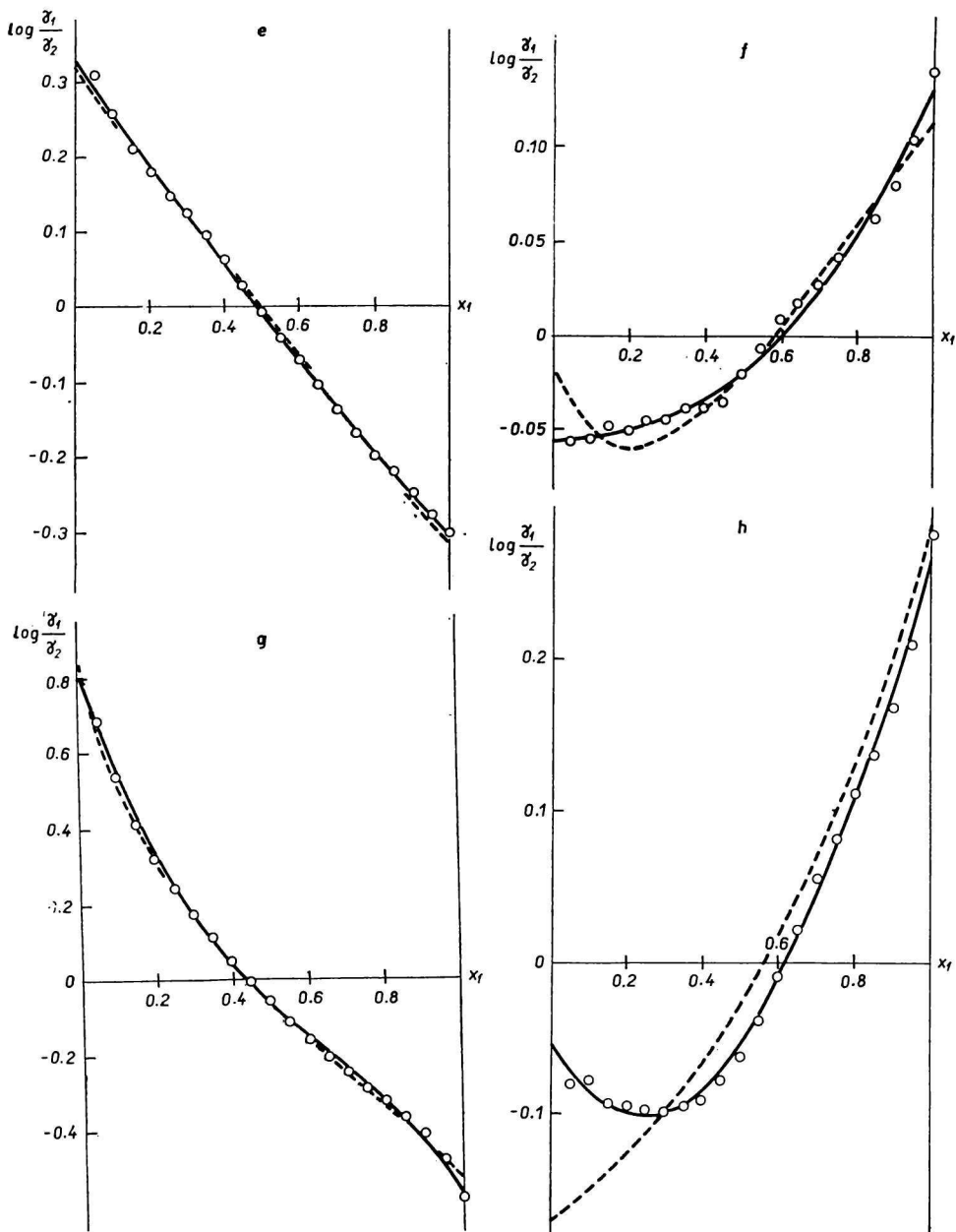
Fig. 3. Plots of the relationship log γ_1/γ_2 = f(x_1) for the solutions of solvents; $t = 100°C$. ○ calculated by the method of Tao; ———— calculated from the Redlich—Kister equation; - - - - calculated from the NRTL equation.

a) DMFA (1)—DMSO (2); b) DMFA (1)—EG (2); c) DMSO (1)—EG (2); d) DMFA (1)—aniline (2); e) amyl alcohol (1)—aniline (2); f) amyl alcohol (1)—DMFA (2); g) amyl alcohol (1)—DMSO (2); h) amyl alcohol (1)—EG (2).

on the basis of the value of the vapour pressure of solution calculated by means of eqn *(1)*, its percentage deviation from the measured value, and average percentage deviation.

The results of measurements of saturated vapour pressure show that the deviations from the Raoult law are positive for four systems and negative for the other four systems investigated. In one system the $P-x$ curve exhibits poorly pronounced minimum (DMFA— —aniline). Figs. *3a—h* represent the calculated relationship $\log \gamma_1/\gamma_2 = f(x_1)$ for both equations used while the coordinates of the points marked in the plots have been calculated by the method of Tao and thus are substituted for experimental points. From the plots it is obvious that four of the investigated systems closely resemble ideal solution. The variety in the properties of individual solutions is caused by the fact that the dissociation as well as the solvation of components may take place during the formation of solution from the solvents used.

In five cases both the NRTL equation and the Redlich—Kister equation of fourth order are equally convenient for expressing the character of solution. For one system (amyl alcohol—EG) the NRTL equation gives better results while for the systems amyl alcohol—DMSO and DMSO—EG the average deviation of the calculated vapour pressure from the experimental value is smaller when Redlich—Kister equation has been applied. It is also to be pointed out that the latter two solutions exhibit a negative deviation from the Raoult law with a minimum on the curve $\log \gamma_1/\gamma_2 = f(x_1)$.

Symbols

P saturated vapour pressure of solution
P_1^0, P_2^0 saturated vapour pressure of pure component
P_{exp} measured pressure of the saturated vapour of solution
P_{calc} calculated pressure of the saturated vapour of solution
C_{12}, C_{21} coefficients of the NRTL equation
$\varDelta G^E$ molar excess free enthalpy of solution
Q minimizing function
R gas constant
T absolute temperature
b, c, d coefficients of the Redlich—Kister equation of fourth order
x_1, x_2 mole fractions of components
α_{12}, α_{21} the third coefficients of the NRTL equation ($\alpha_{12} = \alpha_{21}$)
γ_1, γ_2 activity coefficients of the components in solution (standard state corresponds to a pure component at the pressure and temperature of system)
Φ_1, Φ_2 correction for the real behaviour of a component in vapour phase
Subscripts 1 and 2 denote respectively more volatile and less volatile components.

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