EXTENSION OF A LATTICE MODEL OF ELECTROLYTES TO A TERNARY SYSTEM OF A SALT AND TWO SOLVENTS. THE SYSTEM $CH_3OH-H_2O-LiCl$

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A lattice model proposed to describe the thermodynamic properties of binary electrolyte solutions over the whole concentration range has been extended to ternary systems involving two solvents. The relationships derived for the excess Gibbs energy and the activity coefficients of all the components have been tested with published experimental data on vapour pressures of methanol and water in the system $CH_3OH-H_2O-LiCl$ at 60°C. Examination of the ability of the model to predict the behaviour of the ternary system on the basis of binary data has shown that the expression for the excess Gibbs energy must be extended to include a ternary contribution

In a previous paper[1] a lattice model of electrolytes has been developed by analogy with the model of regular solutions, account being taken of the nature of the species present in the system. The aim was to propose a model which would represent the quantities of mixing over the whole concentration range, even at the price of a lower precision. The relationship for the excess Gibbs energy derived from this model turned out to provide a surprisingly good fit of experimental data for the vapour pressure and the decrease in the melting point of the solvent[2].

Because of the importance of multicomponent electrolyte systems with mixed solvents for the chemical engineering practice, an attempt has been made to extend the above model in that direction. For a start, attention was devoted to the ternary system of a simple electrolyte and two solvents.

THEORETICAL

Basic Assumptions of the Model

Let us consider a system with a completely dissociating electrolyte,

$$MA-R-S,$$

where R and S are polar solvents, and MA represents a salt dissociating into a cation

M^+ and an anion A^-. The composition of the system will be expressed in terms of the mole fractions x_1, x_2, and x_3, with x_1 and x_2 relating to the solvents R and S, respectively, and x_3 to the salt. It goes without saying that $x_1 + x_2 + x_3 = 1$.

As in the original model, we consider two sublattices, a cationic and an anionic one, and assume the solvent molecules to enter the sublattices in the ratio of the stoichiometric coefficients of the salt, in the present case in the ratio 1 : 1. In common with other lattice models, we now aditionally assumed that the molecules of the two solvents can occupy the nodes of the sublattices with equal probability, so that their relative amounts in each sublattice are given by the ratio of the mole fractions, $x_1 : x_2$.

The number of interactions to be considered in the present case is greater than that in the original model. As given by the combinatory analysis, they involve the following pairs: R–R, R–S, S–S, R–M, R–A, S–M, S–A, M–M, M–A, and A–A. If the number of lattice sites in both the cationic and anionic sublattices is $N_M + (N_R + N_S)/2$, then the possibilities of finding the species M, A, R, and S at the nodes of the individual sublattices are given by

$$p_M = p_A = 2x_3/(1 + x_3); \quad p_R = x_1/(1 + x_3); \quad p_S = x_2/(1 + x_3). \qquad (1)$$

These relationships were used to calculate the number of pairs of interacting species appearing in the equation for the total energy of the system which, in turn, entres into the expression for the partition function.

The Quantities of Mixing

The methods of statistical thermodynamics lead to the following expression for the excess Gibbs energy (for the meaning of the symbols the reader is referred to ref.[1])

$$\Delta G^E = (\varepsilon_{RM} + \varepsilon_{RA} - \varepsilon_{RR}) zNx_1x_3/(1 + x_3) + (\varepsilon_{SM} + \varepsilon_{SA} - \varepsilon_{SS}) zNx_2x_3/$$
$$/(1 + x_3) + (\varepsilon_{RS} - \varepsilon_{RR} - \varepsilon_{SS})(zN/2) x_1x_2/(1 + x_3) +$$
$$+ \varepsilon_{MA}N\{[2x_3/(1 + x_3)]^{1/3} - 1\}. \qquad (2)$$

By introducing four interaction parameters, Eq. (2) can be simplified to

$$\Delta G^E = L_{12}x_1x_2/(1 + x_3) + L_{13}x_1x_3/(1 + x_3) + L_{23}x_2x_3/(1 + x_3) +$$
$$+ L_3\{[2x_3/(1 + x_3)]^{1/3} - 1\}. \qquad (3)$$

For a binary system of two solvents $(x_3 = 0)$, we obtain

$$\Delta G^E_{12} = L_{12}x_1x_2. \qquad (4)$$

The expressions for a binary solvent-salt system $(x_2 = 0, x_1 = 0)$,

$$\Delta G_{13}^E = L_{13} x_1 x_3 / (1 + x_3) + L_3 \{[2x_3/(1 + x_3)]^{1/3} - 1\} \tag{5}$$

$$\Delta G_{23}^E = L_{23} x_2 x_3 / (1 + x_3) + L_3 \{[2x_3/(1 + x_3)]^{1/3} - 1\}, \tag{6}$$

are identical with the relationship derived on the basis of the original model. The relationships for the activity coefficients of the three components are obtained from Eq. (3) in the form

$$RT \ln \gamma_1 = L_{12} \frac{x_2(1 - x_1 + x_3)}{(1 + x_3)^2} + L_{13} \frac{x_3(1 - x_1 + x_3)}{(1 + x_3)^2} -$$
$$- L_{23} \frac{2x_2 x_3}{(1 + x_3)^2} - L_3/6 \left(\frac{2x_3}{1 + x_3}\right)^{4/3} \tag{7}$$

$$RT \ln \gamma_2 = L_{12} \frac{x_1(1 - x_2 + x_3)}{(1 + x_3)^2} - L_{13} \frac{2x_1 x_3}{(1 + x_3)^2} +$$
$$+ L_{23} \frac{x_3(1 - x_2 + x_3)}{(1 + x_3)^2} - L_3/6 \left(\frac{2x_3}{1 + x_3}\right)^{4/3} \tag{8}$$

$$RT \ln \gamma_3 = L_{12} \frac{-2x_1 x_2}{(1 + x_3)^2} + L_{13} \frac{x_1(1 - x_3)}{(1 + x_3)^2} +$$
$$+ L_{23} \frac{x_2(1 - x_3)}{(1 + x_3)^2} + L_3 \left\{\left(\frac{2x_3}{1 + x_3}\right)^{1/3} \frac{4 + 2x_3}{3 + 3x_3} - 1\right\}. \tag{9}$$

RESULTS

Application of the Model to Experimental Data

For the testing of the proposed extension of the model, we chose data obtained by Broul and co-workers[3] on vapour pressures of the solvents in the ternary system $CH_3OH-H_2O-LiCl$ and the corresponding binary systems at 60°C. Interpolation of temperature dependences of vapour pressure expressed by the Antoine equation provided the following values for the vapour pressure of the pure solvents:

$$P_1^0 = 633 \cdot 43 \text{ Torr} = 84 \cdot 451 \text{ kPa} (CH_3OH)$$

$$P_2^0 = 149 \cdot 42 \text{ Torr} = 19 \cdot 921 \text{ kPa} (H_2O)$$

The experimental data for vapour pressures, P, above solution and for mole fractions of methanol and water in the gas phase were used to calculate the partial pressures:

$P_1 = Py_1$ and $P_2 = Py_2$. These values were then used to obtain the activity coefficients from the relationships $\gamma_i = (P_i/P_i^0)/a_i^*$, where a_i^*, the activities of ideal mixtures[4], are given for the present system (1 : 1 salt) by the expression $a_i^* = x_i/(1 + x_3)$; $i = 1, 2$.

Evaluation of Data for the Binary System CH_3OH-H_2O

The application of the proposed simple model to a binary solvent system leads to a one-parameter equation, which cannot be adequate for experimental data so precise as those cited above. The use of the two-parameter Margules equation (the one used by Broul and co-workers) did not provide any marked improvement of the fit. Such an improvement was, however, achieved by application of a relationship for ΔG^E with the two concentrations raised each to an adjustable exponent,

$$\Delta G_{12}^E = L_{12} x_1^n x_2^m , \qquad (10)$$

which, de facto, is a three-parameter equation.

In this case, the activity coefficients in the binary system are given by

$$RT \ln \gamma_1 = L_{12} x_1^n x_2^m (1 - m + n x_2/x_1) \qquad (11)$$

$$RT \ln \gamma_2 = L_{12} x_1^n x_2^m (1 - n + m x_1/x_2) . \qquad (12)$$

The best fit was obtained for the empirical values $n = 1$ and $m = 1.2$. The interaction parameter L_{12} was calculated by an optimization procedure as 0.698784. The corresponding vapour pressures and the values of the ratio $y = P_1/P$ are listed in Table I along with experimental results.

In Fig. 1 a plot of the partial vapour pressures of the two solvents and the total vapour pressures can be compared with curves calculated on the basis of the interaction parameter L_{12}.

Evaluation of Experimental Data for the Binary Systems
$CH_3OH-LiCl$ *and* $H_2O-LiCl$

Since the interaction parameter L_3 appears in both Eqs (5) and (6), both the systems must be evaluated simultaneously. Optimization yielded the following values of the interaction parameters L_{13}, L_{23}, and L_3:

$$L_{13} = -21.7273 ; \quad L_{23} = -24.46435 ; \quad L_3 = -12.4538 .$$

These values were used to calculate the vapour pressures of methanol and water. The results are listed in Tables II and III, along with the experimental values. Figure 2

TABLE I

Vapour–liquid equilibrium in the system methanol(1)–water(2) at 60°C. Values calculated from Eq. (4)

x_2	y_{exp}	P	y_{calc}	Δy	ΔP	$\Delta P, \%$
0·0343	0·2106	183·64	0·2224	−0·0118	−2·11	−1·13
0·0446	0·2699	196·92	0·2698	0·0001	1·09	0·56
0·0594	0·3312	211·65	0·3279	0·0033	1·93	0·92
0·0793	0·3920	228·70	0·3917	0·0003	1·36	0·60
0·1092	0·4714	254·74	0·4661	0·0053	2·98	1·19
0·1634	0·5698	291·74	0·5605	0·0093	1·11	0·38
0·1961	0·5989	309·50	0·6020	−0·0031	−1·78	−0·57
0·2705	0·6699	353·18	0·6722	−0·0023	0·99	0·28
0·3670	0·7462	395·79	0·7354	0·0108	−0·45	−0·11
0·4619	0·7889	431·10	0·7827	0·0062	−2·34	−0·54
0·5665	0·8223	466·95	0·8273	−0·0050	−3·91	−0·83
0·7582	0·9010	538·25	0·9034	−0·0024	0·51	0·09
			Average	0·0050		0·60

TABLE II

Vapour–liquid equilibrium in the system methanol(1)–lithium chloride(3) at 60°C. Values calculated from Eq. (5)

x_1	P_{exp}	P_{calc}	ΔP	$\Delta P, \%$
0·8084	224·48	220·27	4·21	1·91
0·8413	288·88	294·06	−5·18	−1·76
0·8638	346·43	351·03	−4·60	−1·31
0·8828	402·67	401·68	0·99	0·25
0·8961	439·90	437·55	2·35	0·54
0·9161	494·79	490·28	4·51	0·92
0·9242	512·13	510·64	1·49	0·29
0·9360	539·48	538·63	0·85	0·16
0·9505	568·48	569·41	−0·93	−0·16
0·9650	591·65	595·09	−3·44	−0·58
0·9783	610·49	613·38	−2·89	−0·47
0·9894	624·01	624·67	−0·66	−0·11
		Average	2·68	0·70

shows the dependences of the vapour pressure on the concentration for both systems, as well as the respective experimental points. The fit is generally better than that obtained by Broul and co-workers[3], who used a total of five parameters for each system.

Evaluation of the Ternary System

The experimental data for the vapour pressures in the system methanol–water–LiCl involve four data subsets, three for the binary systems and one for the ternary system. This offers several variants for their treatment (see Tables IV and V).

The first variant is the conventional attempt to predict the behaviour of a ternary system from the knowledge of binary data. The results of this variant are listed in the first columns of Tables IV and V. The optimized quantity is the sum of standard deviations of the binary data (the optimized values for each variant are set in bold-face type). As seen, the statistical characteristics for this variant are not very satisfactory (such results usually serve as crude estimates). Thus it turns out that the approximation

$$\Delta G^E = \Delta G^E_{12} + \Delta G^E_{13} + \Delta G^E_{23}, \qquad (13)$$

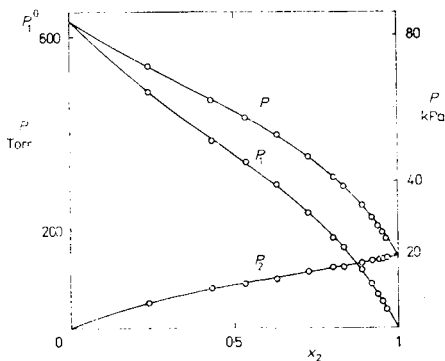which neglects the ternary contribution ΔG^E_{123}, is too rough.

FIG. 1

Dependences of the vapour pressure of methanol and water on the composition of the system methanol(1)–water(2)
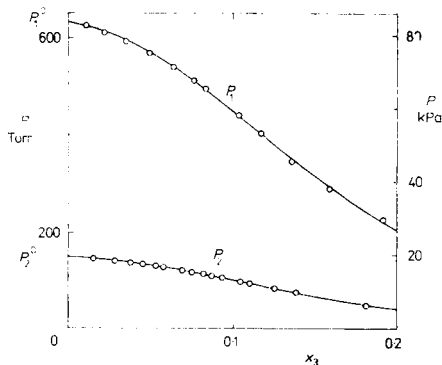

FIG. 2

Dependences of the vapour pressure of methanol and water on the composition of the systems methanol(1)–lithium chloride(3) and water(2)–lithium chloride(3)

TABLE III

Vapour–liquid equilibrium in the system water(2)–lithium chloride(3) at 60°C. Values calculated from Eq. (6)

x_2	P_{exp}	P_{calc}	ΔP	$\Delta P, \%$
0·8191	49·67	50·64	−0·97	−1·91
0·8618	75·55	75·49	0·06	0·08
0·8741	83·88	83·56	0·32	0·38
0·8744	84·01	83·76	0·25	0·30
0·8894	94·76	93·93	0·83	0·89
0·8955	98·72	98·11	0·61	0·62
0·9063	106·32	105·48	0·84	0·79
0·9126	110·16	109·74	0·42	0·39
0·9181	113·60	113·39	0·21	0·19
0·9249	117·80	117·80	−0·00	−0·00
0·9311	121·32	121·69	−0·37	−0·31
0·9420	127·23	128·15	−0·92	−0·72
0·9464	129·39	130·59	−1·20	−0·92
0·9548	133·36	134·92	−1·56	−1·16
0·9621	136·53	138·30	−1·77	−1·28
0·9719	140·42	142·21	−1·79	−1·26
0·9843	144·68	146·05	−1·37	−0·94
		Average	*0·79*	*0·71*

TABLE IV

Interaction parameters for different variants of handling the sets of experimental data

Parameter	Variant			
	1	2	3	4
L_{12}	0·69831	0·69831	0·66896	0·63245
std	*0·00781*	*0·00781*	*0·02021*	*0·03718*
L_{13}	−21·81373	−21·81373	−20·41863	−20·37257
std	*0·89173*	*0·89173*	*1·62315*	*2·57215*
L_{23}	−24·44176	−24·44176	−24·60993	−24·46347
std	*0·96349*	*0·96349*	*1·62455*	*2·57034*
L_3	−12·51783	−12·51783	−11·39105	−12·34585
std	*1.05854*	*1.05854*	*1·99823*	*3·29600*
L_{123}	—	4·92550	3·56180	3·53420
std	—	—	*0·42017*	*0·59861*

Extension of the expression for ΔG^{E} to include the ternary contribution, for example, in the form

$$\Delta G^{E}_{123} = L_{123}x_1x_2x_3 \qquad (14)$$

results in a much improved fit.

In the second variant, the binary parameters are determined as in the previous case, i.e., from the binary data, but the calculation involves the ternary parameter L_{123} obtained independently from the ternary data. This approach represents a sort of correction in predicting ternary data from the binary ones. The statistical characteristics listed in the second column of Table IV indicate a marked improvement of the fit compared to the first variant.

The third variant is an absolute treatment in which all the parameters are determined by processing all experimental data for the system. The optimized quantity is the sum of the squares of all deviations, and the statistical characteristics attest to the best fit of all the data.

TABLE V

Statistical characteristics for different variants of handling the sets of experimental data

Parameter	Variant				Ref.[3]
	1	2	3	4	
Standard deviations of calculated vapour pressures					
s_{12}	1·973	1·973	3·174	5·870	
s_{13}	3·122	3·122	4·430	9·622	
s_{23}	0·975	0·975	2·022	0·993	
$s_{12} + s_{13} + s_{23}$	2·094	2·094	3·223	6·131	
s_{123}	15·891	6·405	3·364	2·400	
$s_{12} + s_{13} + s_{23} + s_{123}$	11·266	4·742	3·294	4·677	
Mean relative deviations of vapour pressures: $\Delta p = 100(P_{\text{exp}} - P_{\text{cal}})/P_{\text{cal}}$					
ΔP_{12}	0·60	0·60	1·02	1·85	
ΔP_{13}	0·70	0·70	0·83	2·07	0·85
ΔP_{23}	0·71	0·71	1·89	0·81	0·47
ΔP_{123}	6·83	2·10	1·33	0·88	
Mean deviations of vapour pressure ratio: $\Delta y = y_{\text{exp}} - y_{\text{cal}}$					
Δy_{12}	0·0050	0·0050	0·0067	0·0099	0·0053
Δy_{123}	0·0307	0·0117	0·0090	0·0066	0·0191

TABLE VI

Vapour–liquid equilibrium in the system methanol(1)–water(2)–lithium chloride(3) at 60°C. Values calculated from Eqs (13) and (14). The quantities Δy_1, Δy_2, and ΔP represent the differences between experimental and calculated values.

x_1	x_2	x_3	y_1	y_2	P	Δy_1	Δy_2	ΔP	$\Delta P, \%$	N
0·0048	0·8384	0·1568	0·0926	0·9074	69·87	−0·0054	0·0054	2·28	3·38	1
0·0061	0·8457	0·1476	0·1144	0·8856	77·86	−0·0111	0·0111	2·10	2·78	2
0·0074	0·9630	0·0296	0·0418	0i9582	144·70	−0·0281	0·0281	−5·59	−3·72	3
0·0119	0·9550	0·0331	0·1026	0·8974	151·08	−0·0073	0·0073	−3·48	−2·25	4
0·0125	0·8644	0·1231	0·1664	0·8336	101·38	−0·0209	0·0209	1·42	1·42	5
0·0189	0·9463	0·0348	0·1555	0·8445	159·75	−0·0094	0·0094	−2·68	−1·65	6
0·0202	0·8669	0·1129	0·2450	0·7550	119·65	−0·0129	0·0129	2·40	2·05	7
0·0236	0·9728	0·0036	0·1565	0·8435	171·76	−0·0085	0·0085	−2·03	−1·17	8
0·0299	0·9324	0·0377	0·2430	0·7570	174·11	0·0029	−0·0029	−0·27	−0·16	9
0·0362	0·8619	0·1019	0·3352	0·6648	143·72	−0·0293	0·0293	−1·25	−0·86	10
0·0516	0·8535	0·0949	0·4139	0·5861	167·06	−0·0218	0·0218	−0·58	−0·35	11
0·0555	0·9085	0·0360	0·3405	0·6595	195·64	−0·0224	0·0224	−7·21	−3·55	12
0·0637	0·9305	0·0058	0·3396	0·6604	211·19	−0·0067	0·0067	−1·21	−0·57	13
0·0757	0·8371	0·0872	0·4990	0·5010	198·33	−0·0152	0·0152	0·23	0·11	14
0·0815	0·8843	0·0342	0·4317	0·5683	222·11	−0·0167	0·0167	−6·54	−2·86	15
0·0896	0·6930	0·2174	0·7249	0·2751	100·98	0·0112	−0·0112	6·71	7·12	16
0·1077	0·8597	0·0326	0·4989	0·5011	245·10	−0·0126	0·0126	−6·79	−2·70	17
0·1137	0·8036	0·0827	0·5880	0·4120	235·88	−0·0123	0·0123	0·87	0·37	18
0·1178	0·8760	0·0062	0·4896	0·5104	258·82	0·0005	−0·0005	1·58	0·61	19
0·1428	0·8240	0·0332	0·5712	0·4288	275·43	−0·0065	0·0065	−3·85	−1·38	20
0·1666	0·6308	0·2026	0·8011	0·1989	140·64	0·0033	−0·0033	2·90	2·10	21
0·1712	0·7474	0·0814	0·6726	0·3274	277·41	−0·0108	0·0108	0·96	0·35	22
0·1720	0·7941	0·0339	0·6162	0·3838	297·82	−0·0040	0·0040	−1·70	−0·57	23
0·1984	0·7679	0·0337	0·6457	0·3543	313·95	−0·0048	0·0048	−2·22	−0·70	24
0·2420	0·6833	0·0747	0·7295	0·2705	319·84	−0·0097	0·0097	0·18	0·06	25
0·2501	0·7089	0·0410	0·7088	0·2912	340·35	0·0020	−0·0020	−3·03	−0·88	26
0·2765	0·5409	0·1826	0·8488	0·1512	189·30	0·0036	−0·0036	1·68	0·90	27
0·3316	0·5988	0·0696	0·7761	0·2239	359·64	−0·0107	0·0107	−0·18	−0·05	28
0·3423	0·6138	0·0439	0·7607	0·2393	378·71	−0·0073	0·0073	−3·92	−1·02	29
0·3822	0·6045	0·0133	0·7522	0·2478	401·47	−0·0052	0·0052	−1·35	−0·33	30
0·4094	0·4349	0·1557	0·8786	0·1232	249·89	0·0030	−0·0030	1·79	0·72	31
0·4210	0·5291	0·0571	0·8078	0·1922	399·48	−0·0076	0·0076	−0·61	−0·15	32
0·4428	0·5078	0·0494	0·8105	0·1895	410·72	−0·0075	0·0075	−2·52	−0·61	33
0·4816	0·4710	0·0474	0·8267	0·1733	425·26	−0·0047	0·0047	−1·15	−0·27	34
0·5297	0·4177	0·0526	0·8503	0·1497	434·90	−0·0022	0·0022	−0·27	−0·06	35
0·5298	0·3385	0·1317	0·8996	0·1004	311·38	0·0040	−0·0040	4·56	1·48	36
0·5661	0·3606	0·0733	0·8759	0·1241	422·48	−0·0013	0·0013	4·63	1·11	37
0·5951	0·3901	0·0148	0·8465	0·1535	476·88	−0·0042	0·0042	−1·22	−0·26	38
0·6400	0·2966	0·0634	0·8953	0·1047	454·68	−0·0007	0·0007	4·35	0·97	39
0·7619	0·1636	0·0745	0·9421	0·0579	470·53	0·0000	−0·0000	7·27	1·57	40
					Average	*0·0090*	*0·0090*	*2·64*	*1·33*	

The fourth variant is mentioned here just for completeness. It is, in fact, the inverse of the first variant, because it handles the ternary data only (the optimized quantity is s_{123}), and the statistical characteristics of the binary data are obtained by extrapolation from the ternary data.

In order to provide comparison with the results of Broul and co-workers[3], Table V includes other statistical characteristics, namely the mean relative deviation in the vapour pressure and the relative mean deviation Δy. If we adopt as the criterion for assessing the adequacy of the treatment the same quantity as used by the above authors, i.e. Δy_{123}, we arrive at the following conclusion: while the seven-parameter treatment used by Broul and co-workers[3] gives better results than the four-parameter
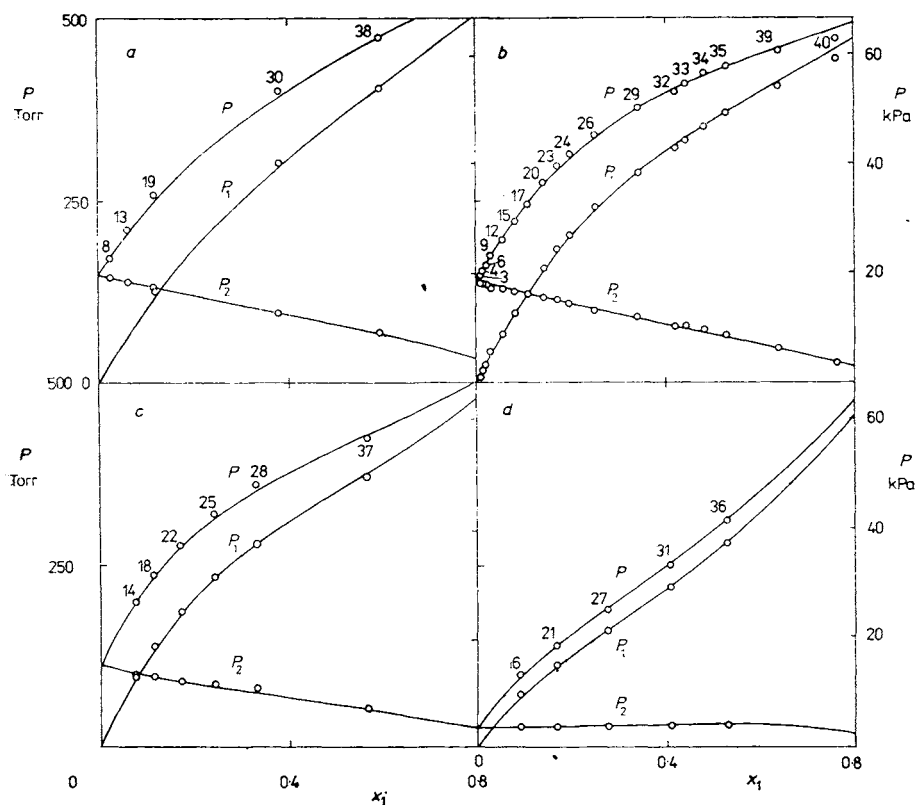

Fig. 3

Dependences of the vapour pressure of methanol and water on the composition of the system methanol(1)–water(2)–lithium chloride(3) in cuts for a $x_2 = 0.9959 - 1.0198 x_1$, b $x_2 = 0.97028 - 1.0494 x_1$, c $x_2 = 0.91465 - 0.9712 x_1$, and d $x_2 = 0.76472 - 0.8054 x_1$. The numbers on the points correspond with the serial numbers in Table V

variant 1, all the five-parameter variants (2 to 4) are superior to the seven-para meter treatment.

In searching for correlation between the vapour pressures for the ternary system, it was found that most of the 40 ternary data might be divided into four groups in which the concentrations x_1 and x_2 were interdependent and could be represented by a simple linear relationship. This permitted the experimental data to be graphically represented in comparison with curves obtained by the corresponding cuts of the ternary diagram. Figures 3a to 3d show plots of the parameter values from the fourth column of Table IV, each point being labelled by a serial number from Table VI.

Even though this work has not confirmed the feasibility of describing vapour pressures of a ternary system on the basis of the binary data alone and, owing to the precision of the experimental data used, has pointed to the necessity of introducing a ternary contribution to the excess Gibbs energy, it nevertheless has demonstrated that a relatively simple lattice model is able to describe data of importance in chemical engineering practice.

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Translated by M. Škubalová.