LIQUID–VAPOUR EQUILIBRIUM. LIX.*

THE SYSTEMS DIISOPROPYL ETHER–ACRYLIC ACID, ISOPROPYL ACETATE–ACRYLIC ACID, ACRYLIC ACID–2-ETHYLHEXANOL AND METHYL ISOBUTYL KETONE–ACRYLIC ACID

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Isobaric vapour–liquid equilibrium has been measured in the systems diisopropyl ether–acrylic acid at 200 and 300 Torr, isopropyl acetate–acrylic acid at 200 Torr, acrylic acid–2-ethylhexanol at 100 Torr and methyl isobutyl ketone–acrylic acid at 200 Torr. The specially modified circulation still of the Gillespie type has been used for the measurements. The Margules third and fourth order equations have been used for the correlation of measured data.

As part of a systematic study of thermodynamic properties of binary mixtures whose components belong to various groups of Ewell's classification of liquids, isobaric vapour–liquid equilibria were measured for four acrylic acid–organic solvent systems.

EXPERIMENTAL

Preparation of pure substances. Diisopropyl ether (Shell product, Holand) was refluxed for ten hours with lithium aluminium hydride (about 5 g/l) and then rectified on an 80 cm long column packed with stainless steel helices[2]. To prevent the formation of peroxides, the product obtained was stabilized by hydroquinone (2 mg/l). Isopropyl acetate (99·2% technical reagent from Chemické závody, Záluží u Mostu) was rectified on a forty plate bubble-cup column. 2-Ethylhexanol (99·5% technical reagent from Chemické závody, Záluží u Mostu) was rectified on an 80 cm long column packed with stainless steel helices under reduced pressure (about 25 Torr). Methyl isobutyl ketone (technical reagent from Chema, Počernice) was shaken with alumina[2] and then rectified on an 80 cm long column packed with Raschig rings under reduced pressure (about 30 Torr). Acrylic acid (pure, product of BASF) was distilled on an 80 cm long column packed with copper helices under reduced pressure about 40 Torr. The collected main distillation fraction was stabilized by adding 500 p.p.m. of hydroquinone. The acid was prepared, as far as possible, immediately before the measurements because it polymerizes spontaneously very easily on longer storage[1]. Physical constants of the substances used are given in Table I.

Analytical method. The content of acrylic acid in the equilibrium vapour and liquid samples was determined by alkalimetric titration. The ethanolic 0·1M-NaOH solution prepared from distilled ethanol and metallic sodium and Thymol Blue indicator (yellow to blue transition) were used. The titrations were carried out in a nitrogen atmosphere. The accuracy of the acid determination was better than $\pm 0\cdot2$ per cent.

Apparatus and procedure. Owing to the easy polymerization of acrylic acid, a specially modified circulation still of the Gillespie type had to be used for the measurements. The apparatus was described in detail in another communication[9]. The description of the measuring procedure including the vacuum system can be found in the literature[10]. The pressure in the system was measured indirectly by measuring the boiling point of water in an ebulliometer connected parallel to the equilibrium still. Temperature was measured by mercury standards calibrated by means of a Mueller bridge with platinum resistance thermometer Leeds and Northrup. The accuracy

TABLE I

Physical Constants of Pure Substances

Compound	Constant	Measured	Published
Diisopropyl ether	d_4^{20}, g/cm^3	0·7257	0·7257[3]
			0·72565[4]
	n_D^{20}	1·3681	1·3682[3,4]
Isopropyl acetate	d_4^{20}, g/cm^3	0·8713	0·8718[5]
	n_D^{20}	1·3771	1·3773[5]
2-Ethylhexanol	d_4^{20}, g/cm^3	0·8328	0·8328[6]
	n_D^{20}	1·4311	1·4318[6]
Methyl isobutyl ketone	d_4^{20}, g/cm^3	0·8004	0·8006—0·8007[7]
	n_D^{20}	1·3959	1·3958[5]
Acrylic acid	d_4^{20}, g/cm^3	1·0490	1·0497[1]
	n_D^{20}	1·4204	1·4210[8]

TABLE II

Vapour Pressure of 2-Ethylhexanol

t, °C	101·0	109·1	112·3	116·2	120·3	124·9
P_{exp}^0, Torr	36·2	49·6	58·3	70·0	83·2	100·0
ΔP^0, Torr^a	−0·1	2·2	1·1	0·1	−0·2	−0·1

^{a} $\Delta P^0 = P_{calc} - P_{exp}$.

of the temperature measurements was $\pm 0.02°C$. The equilibrium samples were taken for analysis only if the boiling point in the still did not change for 20 minutes. The samples were taken by syringes, weighed, diluted with distilled ethanol into volumetric flasks, pipetted and analyzed in the above mentioned way.

TABLE III

Antoine Vapour Pressure Constants

Substance	A	B	C	Range of validity, °C	Ref.
Diisopropyl ether	6·84159	1 135·034	218·23	23— 68	4
Isopropyl acetate	7·33395	1 436·530	233·665	−38— 89	12
2-Ethylhexanol	8·12502	2 173·89	230	100—125	This work
Methyl isobutyl ketone	6·67278	1 168·443	191·948	21—115	11[a]
Acrylic acid	7·80806	1 827·90	230	65—140	9

[a] The constants calculated from direct vapour pressure data[11].

TABLE IV

Vapour–Liquid Equilibrium in the Diisopropyl Ether(1)–Acrylic Acid(2) System at 200 Torr

x_1	y_1	t	$y_{calc} - y_{exp}$	
			Marg. 3	Marg. 4
0·028	0·250	93·20	−0·011	0·017
0·048	0·384	88·50	−0·012	0·013
0·119	0·678	74·70	−0·013	−0·013
0·208	0·813	63·40	0·012	0·006
0·288	0·885	57·00	0·005	0·004
0·330	0·920	53·60	−0·007	−0·006
0·378	0·939	50·55	−0·008	−0·004
0·466	0·957	46·15	−0·003	0·003
0·656	0·984	39·55	−0·004	0·000
0·857	0·995	34·80	−0·002	−0·003
Mean			*0·008*	*0·007*

Constants of correlation equations: Marg. 3 $A_{12} = -0.0069$, $A_{21} = 0.0729$; Marg. 4 $A_{12} = 0.0912$, $A_{21} = 0.4831$, $D = 0.8578$.

TABLE V

Vapour–Liquid Equilibrium in the Isopropyl Acetate(1)–Acrylic Acid(2) System at 200 Torr

x_1	y_1	t	$y_{calc} - y_{exp}$	
			Marg. 3	Marg. 4
0·014	0·062	101·00	−0·006	0·002
0·034	0·159	98·65	−0·023	−0·011
0·052	0·234	97·00	−0·025	−0·013
0·084	0·339	93·80	−0·013	−0·005
0·116	0·418	91·05	0·015	0·017
0·195	0·624	83·65	0·010	0·004
0·245	0·725	80·25	−0·006	−0·010
0·468	0·902	67·05	−0·002	0·005
0·629	0·959	61·05	−0·015	−0·008
0·907	0·995	53·65	−0·011	−0·015
Mean			*0·012*	*0·009*

Constants of correlation equations: Marg. 3 $A_{12} = -0.1474$, $A_{21} = 0.2778$; Marg. 4 $A_{12} = -0.0791$, $A_{21} = 0.5184$, $D = 0.5217$.

TABLE VI

Vapour–Liquid Equilibrium in the Acrylic Acid(1)–2-Ethylhexanol(2) System at 100 Torr

x_1	y_1	t	$y_{calc} - y_{exp}$	
			Marg. 3	Marg. 4
0·138	0·352	121·90	−0·007	0·008
0·161	0·423	120·90	−0·015	−0·007
0·166	0·423	120·70	0·000	0·006
0·224	0·583	118·70	−0·020	−0·026
0·289	0·683	114·60	0·004	−0·003
0·306	0·707	115·10	0·002	−0·003
0·331	0·729	113·30	0·014	0·011
0·341	0·758	112·70	−0·002	−0·004
0·461	0·857	107·70	−0·005	0·006
0·637	0·941	98·45	−0·027	−0·014
0·757	0·969	93·85	−0·036	−0·032
0·855	0·986	90·05	−0·037	−0·047
Mean			*0·014*	*0·014*

Constants of correlation equations: Marg. 3 $A_{12} = -0.3349$, $A_{21} = 0.5178$; Marg. 4 $A_{12} = -0.1275$, $A_{21} = 0.9367$, $D = 0.9768$.

RESULTS AND DISCUSSION

The mutual dependence of equilibrium compositions of the liquid and vapour phases
in a binary system, for a low pressure region, is given by

$$\alpha_{12} = (y_1/y_2)/(x_1/x_2) = (\gamma_1/\gamma_2)(P_1^0/P_2^0), \qquad (1)$$

TABLE VII

Vapour–Liquid Equilibrium in the Methyl Isobutyl Ketone(1)–Acrylic Acid(2) System at 200 Torr

x_1	y_1	t	$y_{calc} - y_{exp}$	
			Marg. 3	Marg. 4
0·044	0·087	100·60	−0·029	0·002
0·121	0·220	98·55	−0·026	0·000
0·166	0·298	97·40	−0·013	−0·002
0·214	0·387	95·70	−0·005	−0·009
0·235	0·424	95·05	0·001	−0·009
0·322	0·555	92·40	0·024	0·010
0·379	0·660	90·70	0·001	−0·005
0·430	0·722	89·30	−0·002	0·001
0·491	0·793	87·35	−0·015	−0·002
0·621	0·874	84·05	−0·014	0·005
0·698	0·920	82·00	−0·026	−0·013
0·818	0·964	79·35	−0·028	−0·032
Mean			*0·015*	*0·008*

Constants of correlation equations: Marg. 3 $A_{12} = -0·3418$, $A_{21} = 0·1319$; Marg. 4 $A_{12} = -0·0403$, $A_{21} = 0·5809$, $D = 1·1655$.

TABLE VIII

Comparison of Measured and Calculated Vapour–Liquid Equilibrium Data in the Diisopropyl
Ether(1)–Acrylic Acid(2) System at 300 Torr

The superscript exp denotes the direct measured data and calc the values calculated by means
of the method[13] on the basis of the data at 200 Torr.

x_1^{exp}	y_1^{exp}	y_1^{calc}	Δy_1	t^{exp}	t^{calc}	Δt
0·212	0·819	0·810	−0·009	74·8	75·0	−0·2
0·256	0·864	0·852	−0·012	70·4	70·8	0·4
0·317	0·904	0·896	−0·008	65·6	65·7	0·1

where α_{12} is relative volatility, x_1, x_2 are mole fractions of the components 1, 2 in the liquid phase and y_1, y_2 mole fractions in the vapour phase, resp., P_1^0, P_2^0 denote the vapour pressures of pure components 1, 2 at a given temperature and γ_1, γ_2 activity coefficients of both components. The concentration dependence of the activity coefficients was expressed by the third order and the fourth order Margules equations:

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 (A_{12} - A_{21}), \tag{2}$$

$$\log(\gamma_1/\gamma_2) = x_2^2 A_{12} - x_1^2 A_{21} - 2x_1 x_2 [A_{12} - A_{21} + (x_2 - x_1) D], \tag{3}$$

where A_{12}, A_{21}, D are constants characteristic for the given equation and binary mixture. The constants were evaluated by means of the least squares method using the statistical weights.

The temperature dependence of the vapour pressures of pure substances, which is necessary for the computations, was expressed by means of the Antoine equation

$$\log P^0 = A - B/(t + C), \tag{4}$$

where P^0 is vapour pressure (Torr), t temperature (°C) and A, B, C are constants. For most compounds, the constants were taken over from the literature. However, no vapour pressure data were found for 2-ethylhexanol and therefore they were measured and correlated in the way described in another paper[9] (Table II). The published vapour pressure data for methyl isobutyl ketone[11] were correlated by Eq. (4), too, using the least squares method (with statistical weights). The survey of the Antoine vapour pressure constants used is given in Table III.

The measured data on the vapour–liquid equilibrium in four systems said and their comparison with calculated ones according to Eqs (2) and (3) are given in Tables IV–VII. To establish the dependence of equilibrium behaviour on pressure in the diisopropyl ether–acrylic acid system, three equilibrium points at 300 Torr were measured in addition to the measurements at the basic pressure 200 Torr. It was found that this dependence was not very marked and accordingly the vapour–liquid equilibrium data can be converted to a different pressure using the simple Ho and Lu method[13]. In Table VIII, the comparison is given of the measured and by means of this method calculated data for the pressure 300 Torr.

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