Binary Systems Containing Hydrocarbons

Note II. Miscibility Gaps in the Nitromethane + Alkanes Systems

MARIO ROLLA, PAOLO FRANZOSINI, RICCARDO RICCARDI, and LUIGI BOTTELLI

Institute of Physical Chemistry, University of Pavia, Italy

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The miscibility gaps (which can be represented through a unique generalized curve on the $T_d/T_{\max}$ vs. z plane) in the binary liquid systems of nitromethane with $13(C_5-C_9)$-alkanes have been measured. Moreover, it has been shown that for the title systems and for those of MeOAc or MeOH with alkanes the temperatures $T_{\max}$ obey a simple additive rule, at least as a first approximation.

Note I of this series[1] was dealing with miscibility gaps (MG's) in liquid binary mixtures of a number of alkanes with methylacetate (MeOAc): in the present paper the investigation has been extended to mixtures with nitromethane ($MeNO_2$).

All chemicals ($MeNO_2$ C. Erba RP and alkanes Fluka *puriss.*) have been dried by flowing their vapours through a tube filled with P_2O_5 [2]. The freezing point we obtained for $MeNO_2$ was -29.1_5 °C, in agreement with the value (-29.2) tabulated by UTERMARK et al.[3].

The visual method employed has been described elsewhere[2].

Results and Discussion

1. In Table 1 the compositions of the samples as N_{alkane}, together with the corresponding demixing temperatures t_d °C (taken by shaking and slowly cooling), are summarized. All the demixing curves look more or less asymmetric in the t_d vs. N_{alkane} plane.

In Table 2 the coordinates $(N_{\text{alkane}})_{\max}$ and $T_{\max}$ °K of the critical solution points (CSP's) are given: available data by previous authors are also reported for comparison.

As for n-alkanes, the temperatures $T_{\max}$ increase as the chain length increases, while at the same time the maxima of the demixing curves are displaced towards increasing $MeNO_2$ concentrations.

Alkanes, having the same number n_C of carbon atoms, show not far different $(N_{\text{alkane}})_{\max}$ values, which vary in a satisfactory agreement with the equation:

$$(N_{\text{alkane}})_{\max} = 0.929 - 0.119_5\, n_C + 0.005_5\, n_C^2 \quad (1)$$

valid for $5 \leqq n_C \leqq 9$.

According to MALESINSKA's procedure[6], the compositions of the mixtures have also been calculated as fractions z, by using the following asymmetry factors $q_2/q_1 \sim (N_{MeNO_2}/N_{\text{alkane}})_{\max}$: 1.2 for C_5-, 1.3_5 for C_6-, 1.8 for C_7-, 2.0_5 for C_8- and 2.3 for C_9-alkanes. By plotting the experimental data on the $(T_d/T_{\max}, z)$ plane, the MG's concerning the 13 investigated systems can be represented through a unique generalized demixing curve, symmetric with respect to $z = 0.5$ (see Fig. 1).

2. TATEVSKII et al.[8] have verified for a number of physico-chemical properties (P) of the alkanes the validity of the simple equation:

$$P = \sum_{i=0}^{3} n_i\, p_i + \sum_{i \le j = 1}^{4} n_{ij}\, p_{ij}\,, \quad (2)$$

where n_i and n_{ij} respectively are the number of the C−H bonds type C_i-H and the number of the C−C bonds type C_i-C_j in the molecule; p_i and p_{ij}

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[7] For the ($MeNO_2$ + 2,2,5-Trimethylhexane)-system we also measured the monotectic temperature (−29.5 °C).

[8] V. M. TATEVSKII, V. A. BENDERSKII, and S. S. YAROVOI, Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons, Pergamon Press, London 1961.

Alkane	N_{alkane}	t_{d} °C
Isopentane	0.160	77.7
	0.173	80.9
	0.224	89.4
	0.235	90.8
	0.302	94.8
	0.322	95.2
	0.407	96.1
	0.442	96.2
	0.472	96.2
	0.511	96.1
	0.586	95.1
	0.628	94.4
	0.693	90.5
	0.798	81.3
n-Hexane	0.151	91.6
	0.180	95.0
	0.273	101.1
	0.303	101.7
	0.408	102.2
	0.429	102.2
	0.507	101.6
	0.510	101.6
	0.512	101.4
	0.621	98.6
	0.685	95.4
	0.789	84.5
2-Methylpentane	0.096	71.9
	0.154	88.0
	0.230	97.2
	0.255	97.9
	0.343	100.4
	0.408	100.4
	0.414	100.5
	0.425	100.3
	0.542	99.4
	0.583	98.4
	0.608	97.5
	0.608	97.2
	0.712	90.7
	0.797	82.9
3-Methylpentane	0.128	77.1
	0.198	91.9
	0.215	94.0
	0.255	96.5
	0.361	98.5
	0.459	98.5
	0.522	97.9
	0.652	93.7
	0.672	93.3
	0.680	92.2
	0.822	75.7
2,2-Dimethylbutane	0.085	59.5
	0.171	85.3
	0.267	94.7
	0.303	95.9
	0.381	96.6
	0.483	96.4
	0.508	96.5
	0.559	95.1
	0.617	93.5
	0.729	86.9
	0.812	77.7
2,3-Dimethylbutane	0.108	71.4
	0.137	78.7
	0.227	91.8
	0.241	93.2
	0.357	96.1
	0.477	96.1
	0.531	95.4
	0.539	95.5
	0.597	93.9
	0.655	91.3
	0.704	88.6
	0.718	87.5
	0.745	85.4
n-Heptane	0.140	99.5
	0.247	107.2
	0.315	107.8
	0.325	107.8
	0.443	107.4
	0.530	105.4
2,4-Dimethylpentane	0.102	85.7
	0.124	90.5
	0.161	97.3
	0.255	102.8
	0.314	103.3
	0.404	103.3
	0.467	102.8
	0.558	100.5
	0.642	96.5
	0.783	82.5
n-Octane	0.087	98.0
	0.093	100.1
	0.131	107.6
	0.178	111.9
	0.212	113.1
	0.264	113.9
	0.272	113.9
	0.375	113.8
	0.446	112.9
	0.544	110.0
	0.639	104.0
	0.756	92.2
2,2,4-Trimethylpentane	0.132	96.0
	0.231	103.6
	0.314	104.5
	0.398	104.3
	0.509	102.4
	0.531	101.7
	0.594	98.9
2,3,4-Trimethylpentane	0.103	89.4
	0.113	92.0
	0.155	98.8
	0.174	100.7
	0.256	103.9
	0.379	104.2
	0.468	103.3
	0.469	103.4
	0.603	98.9
	0.604	99.1
	0.683	93.5
	0.697	92.2

Table 1.

Alkane	N_{alkane}	t_d °C	Alkane	N_{alkane}	t_d °C
n-Nonane	0.054	94.8	2,2,5-Trimethylhexane	0.070	90.4
	0.073	103.2		0.138	106.2
	0.110	113.1		0.210	110.3
	0.151	117.5		0.305	110.8
	0.259	120.6		0.384	110.5
	0.296	120.6		0.424	109.9
	0.413	119.6		0.470	109.0
	0.455	118.7		0.546	105.9
	0.575	112.1		0.644	99.5
	0.704	101.0		0.722	91.6
	0.771	93.6			

Table 1. Systems of nitromethane with alkanes.

Alkane	This paper		Previous Authors		
	$(N_{\text{alkane}})_{\text{max}}$	T_{max} °K	$(N_{\text{alkane}})_{\text{max}}$	T_{max} °K	Ref.
Isopentane	0.46	369.4	—	305.5	4
n-Hexane	$0.41_5 \pm 0.01$	375.4	—	333.2 ?	5
			—	379.2	5
			0.3775	375.55	6
2-Methylpentane		373.6	—	—	—
3-Methylpentane		371.8	—	—	—
2,2-Dimethylbutane		369.9	—	—	—
2,3-Dimethylbutane		369.4	—	—	—
n-Heptane	0.36 ± 0.005	381.0	—	388.2	5
			0.350	381.45	6
2,4-Dimethylpentane		376.6	—	—	—
n-Octane	0.33 ± 0.01	387.2	—	>293	5
			0.315	387.65	6
2,2,4-Trimethylpentane		377.8	—	380.2	5
			0.335	378.20	6
2,3,4-Trimethylpentane		377.5	—	—	—
n-Nonane	$0.30_5 \pm 0.005$	393.8	—	>358	5
			0.280	393.45	6
2,2,5-Trimethylhexane		384.0	—	—	7

Table 2. CSP's in the systems of nitromethane with alkanes.

respectively the values of P corresponding to 6.023×10^{23} $C_i - H$ and $C_i - C_j$ bonds.

According to these authors, and by excluding the terms which concern methane and ethane, it can also be written:

$$P = n_{12} P_{12} + n_{13} P_{13} + n_{14} P_{14} + n_{22} P_{22} + n_{23} P_{23} + n_{24} P_{24} + n_{33} P_{33} + n_{34} P_{34} + n_{44} P_{44} \tag{3}$$

where $P_{ij} = p_{ij} + (4-i)\, p_i/i + (4-j)\, p_j/j$.

It seemed interesting to us to check the applicability of Eq. (3) to the temperatures T_{max} of the MG's in liquid binary mixtures formed with a fixed component and a series of alkanes: in fact a favourable result would mean an improvement towards predicting the position of the MG's in systems not yet investigated.

It is obvious that, in order to evaluate all the nine P_{ij} parameters in Eq. (3), it would be necessary to know the T_{max} values corresponding to at least nine different hydrocarbons having suitable structures, while in the alkanes we used, some kinds of bonds were missing. However, assuming the T_{max} in the mixtures of $MeNO_2$ with n-Hexane, n-Octane, 2-Methylpentane, 3-Methylpentane, 2,2-Dimethylbutane and 2,3,4-Trimethylpentane to be exact, and, as a first approximation, the dependence of T_{max} from n_C to be linear in the mixtures of $MeNO_2$ with n-alkanes, numerical values could be obtained for the fol-

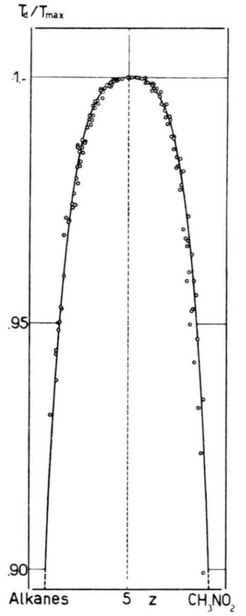

Fig. 1. Plot of reduced temperatures T_d/T_{max} vs. fraction *z* for 13 systems formed by **$MeNO_2$ with** C_5-C_9 alkanes.

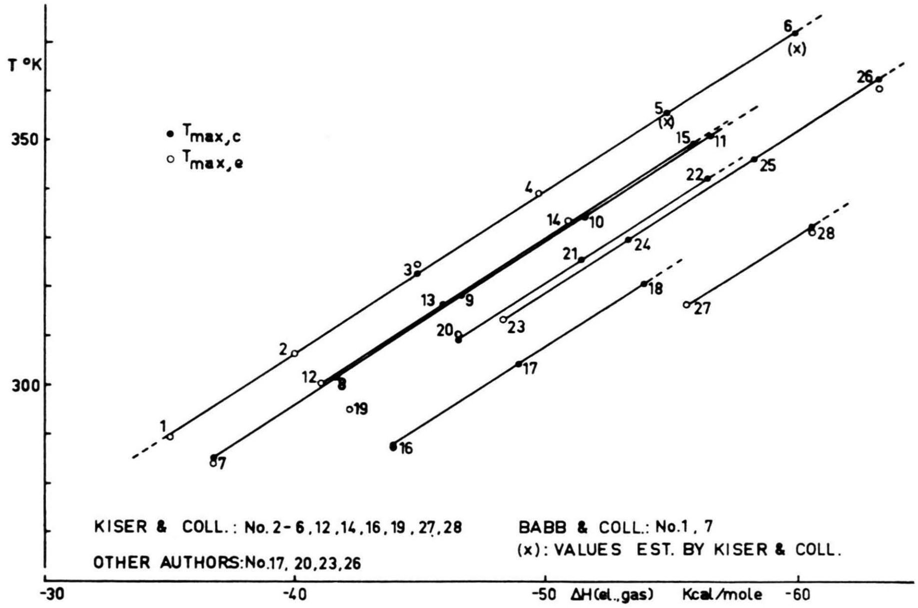

Fig. 2. Plot of calculated and experimental T_{max} values vs. ΔH_{298} (el., gas) for systems formed by MeOH with C_5-C_{10} alkanes (as for the serial numbers, see Table 3).

lowing parameters: P_{12} (+178.9), P_{13} (+121.2), P_{22} (+5.9), P_{23} (−53.6), P_{33} (−114.3), $3\,P_{14}+P_{24}$ (+191.1).

Availing ourselves of the above values, we obtained the following results for the remaining systems (c = calculated, e = experimental):

$MeNO_2$ + Isopentane[9]	$T_{max,\,c}$ = 367.7 °K	$T_{max,\,e}$ = 369.4 °K
2,3-Dimethylbutane	370.5	369.4
n-Heptane	381.4	381.0
2,4-Dimethylpentane	377.6	376.6
2,2,4-Trimethylpentane	379.9	377.8
n-Nonane	393.2	393.8
2,2,5-Trimethylhexane	385.8	384.0

A similar calculation has been carried out also for the systems of MeOAc with alkanes, investigated in Note I[1]. By using the T_{max} values concerning the mixtures of MeOAc with thet same six hydrocarbons already considered in the case of $MeNO_2$, it has been found: $P_{12} = +103.6$; $P_{13} = +70.8$; $P_{22} = +6.9_5$; $P_{23} = -27.5$; $P_{33} = -62.6$; $3\,P_{14} + P_{24} = 113.5$. For the remaining systems it has been calculated:

MeOAc + n-Pentane	$T_{max,\,c}$ = 221.1 °K	$T_{max,\,e}$ = 220.6 °K
Isopentane	217.7	217.2
2,3-Dimethylbutane	220.6	218.9
n-Heptane	235.0	235.1
2,4-Dimethylpentane	228.2	227.6
2,2,4-Trimethylpentane	227.6	227.3
n-Nonane	248.9	248.2
2,2,5-Trimethylhexane	234.6	235.5

[9] As for the ($MeNO_2$+Isopentane)-system, $T_{max,\,c}$ is 367.7, in satisfactory agreement with our experimental result (369.4), while A. W. Francis [4] tabulates 305.5 °K.

[10] A. L. Babb and H. G. Drickamer, J. Chem. Phys. **20,** 290 [1952] (data at 7 atm.).

[11] R. W. Kiser, G. D. Johnson, and M. D. Shetlar, J. Chem. Eng. Data **6,** 338 [1961].

No	Alkanes	ΔH_{298} (el., gas)[13] Kcal/mole	$T_{\max, c}$ °K	$T_{\max, e}$ °K	Ref. for $T_{\max, e}$
1	n-Pentane	−35.00	290.0	289.3 287.5	10 11,14
2	n-Hexane	−39.96	306.3	312.1 306.4	10,14 11
3	n-Heptane	−44.92	322.6	324.4	11
4	n-Octane	−49.88	338.9	338.9	11
5	n-Nonane	−54.84	355.2	353.2	11,15
6	n-Decane	−59.80	371.5	368.2	11,15
7	2-Methylbutane	−36.70	285.3	283.9	10
8	2-Methylpentane	−41.66	301.6	—	
9	2-Methylhexane	−46.62	317.9	—	
10	2-Methylheptane	−51.58	334.2	—	
11	2-Methyloctane	−56.54	350.5	—	
12	3-Methylpentane	−41.03	300.0	300.4	11
13	3-Methylhexane	−45.99	316.3	—	
14	3-Methylheptane (or 4-Methylheptane)	−50.95	332.6	333.4	11,16
15	3-Methyloctane (or 4-)	−55.91	348.9	—	
16	2,2-Dimethylbutane	−43.98	287.9	287.4	11
17	2,2-Dimethylpentane	−48.94	304.2	313.2	5,14
18	2,2-Dimethylhexane	−53.90	320.5	—	
19	2,3-Dimethylbutane	−42.18	294.4	293.6	11
20	2,3-Dimethylpentane	−46.51	309.1	310.2	5
21	2,3-Dimethylhexane	−51.47	325.4	—	
22	2,3-Dimethylheptane	−56.43	341.7	—	
23	2,4-Dimethylpentane	−48.32	313.2	313.2	5
24	2,5-Dimethylhexane	−53.28	329.5	—	
25	2,6-Dimethylheptane	−58.24	345.8	—	
26	2,7-Dimethyloctane	−63.20	362.1	360.0	5
27	2,2,4-Trimethylpentane	−55.60	315.8	316.2	11
28	2,2,5-Trimethylhexane	−60.56	332.1	330.7	11

Table 3. $T_{\max}$ values in systems of MeOH with alkanes [12].

For both families of systems the agreement between calculated and experimental $T_{\max}$ is satisfactory.

3. Finally, in order to confirm a wider validity of Eq. (3), the mixtures of methanol (MeOH) with alkanes (for which, among other data, two reliable series of measurements by Babb et al.[10] and by Kiser et al.[11] are available from literature) have been considered.

Availing ourselves of the following empirical parameter values: $P_{12} = +128.7$; $P_{13} = +90.2$; $P_{22} = +16.3$; $P_{23} = -23.8$; $P_{33} = -66.4$; $3P_{14} + P_{24} = +159.2$ the $T_{\max}$'s for the mixtures of MeOH with the initial terms of the families constituted by the n-alkanes, 2-methylalkanes, 3- or 4-methylalkanes, 2,2- and 2,3-dimethylalkanes, and also by 2,4-Dimethylpentane, 2,5-Dimethylhexane, etc., and by 2,2,4-Trimethylpentane, 2,2,5-Trimethylhexane, etc., have been calculated. The results are summarized in Table 3, while in Fig. 2 calculated and experimental $T_{\max}$'s (once more in a rather satisfactory agreement) are plotted vs. a "structural" property of the alkanes, i. e. ΔH_{298} (el., gas) [8].

4. As a conclusion, it seems that a reasonable validity is to be attributed to the hypothesis that the $T_{\max}$ values in the three above considered families of systems obey an additive rule (at least as a first approximation, and when $5 \leqq n_C \leqq 9$ or 10).

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[12] When data by Babb et al. and/or by Kiser et al. are available, the data by previous authors have been neglected.

[13] Heat of formation at 25 °C calculated by Tatevskii et al. (loc. cit.).

[14] Value not drawn in Fig. 2.

[15] Estimated value (by Kiser et al.).

[16] $T_{\max, e}$ refers to 3-Methylheptane.

The investigation of more families of systems containing hydrocarbons is in progress.

Acknowledgments

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Miscibility Gaps in Fused Salts

Note III. Systems of Mercury Halides with Alkali Nitrates *

Cesare Sinistri, Giorgio Flor, Paolo Franzosini, and Mario Rolla

Institute of Physical Chemistry, University of Pavia, Italy

(Z. Naturforschg. **22 a**, 53—58 [1967]; received 1 October 1966)

Molten mixtures of $HgCl_2$, $HgBr_2$ and HgJ_2 with alkali nitrates have been investigated. Two liquids regions occur in the following systems: $HgCl_2 +$ (Li, Na) NO_3, $HgBr_2 +$ (Li, Na, K, Rb) NO_3 and $HgJ_2 +$ (Li, Na, K, Rb, Cs) NO_3. The ability of demixing progressively increases in the sense Cs → Li and Cl → J. Moreover the composition squares of the systems Na, Hg/NO_3, Cl and (Na, K, Rb), Hg/NO_3, Br have been partially drawn.

Following our previous work on liquid-liquid (LL) equilibria in molten salt mixtures, in the present paper we have investigated the occurrence of demixing in type Me, Hg/NO_3, X systems, where Me = Li, Na, K, Rb, Cs and X = Cl, Br, J.

Little is known in literature about such systems, which are formed by salts predominantly covalent mixed with salts predominantly ionic. Bergman[1] has studied the behaviour of some mixtures of HgJ_2 with (Li, Na, K) NO_3. He found that the solubility of the first salt is particularly low in molten lithium nitrate. More recently Guenther[2] has performed distribution experiments between the two immiscible salt phases in the system $HgBr_2 + LiNO_3$ at 254 °C.

Apparatus and Materials

The apparatus used is the same already described in Note I[3]: however it has been found expedient to keep the Pyrex test-vessels immersed in a fused salt bath, rather than in an air bath.

All chemicals used (C. Erba, Merck or Light) were of reagent grade purity and were carefully dried before use.

Results and Discussion

a) $MeNO_3 + HgX_2$ *mixtures.* In Fig. 1 the LL and SL (solid-liquid) curves of 15 mixtures $MeNO_3 + HgX_2$ are shown. They are principal diagonal sections in the composition squares of the corresponding Me, Hg/NO_3, X systems. In Fig. 1 the empty circles represent experimental data, the filled ones extrapolated data (in the way specified later on). The areas in which LL equilibria occur are dashed.

As regards mercury chloride, demixing occurs in the mixtures with lithium and sodium nitrate, the extent of the miscibility gap (MG) being larger in the first case. In the mixtures with potassium, rubidium, and caesium nitrates a eutectic and, respectively, the congruent compounds $(RbNO_3)_2 \cdot HgCl_2$ and $CsNO_3 \cdot HgCl_2$ are formed.

As regards mercury bromide, demixing occurs with lithium, sodium, potassium, and rubidium nitrates, the MG being the largest in the case of $LiNO_3$. In the $CsNO_3 + HgBr_2$ system the formation of a eutectic occurs.

Finally, as regards mercury iodide demixing occurs with all the five alkali nitrates.

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[1] A. G. Bergman, Z. Anorg. Chem. **157**, 83 [1926].

[2] K. F. Guenther, J. Inorg. Nucl. Chem. **27**, 1427 [1965].

[3] C. Sinistri, P. Franzosini, A. Timidei, and M. Rolla, Z. Naturforschg. **20 a**, 561 [1965].