

Research Article

Estimation of the Critical Temperatures of Some More Deep Eutectic Solvents from Their Surface Tensions

Yizhak Marcus 

Institute of Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Correspondence should be addressed to Yizhak Marcus; ymarcus@vms.huji.ac.il

Received 22 January 2018; Accepted 11 April 2018; Published 2 May 2018

Academic Editor: Luca De Stefano

Copyright © 2018 Yizhak Marcus. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The critical temperatures of two dozen deep eutectic solvents, for only some of which these have been estimated previously, were estimated from the temperature dependences of their surface tensions and densities available in the literature according to the Eötvös and the Guggenheim expressions.

1. Introduction

Deep eutectic solvents are binary mixtures of a hydrogen bond accepting component (HBA), typically quaternary ammonium or phosphonium salt, and a hydrogen bond donating component (HBD), typically polyol, at a definite molar ratio. These mixtures are liquid at room temperature and freeze at a temperature considerably below the freezing points of the components, and hence, they are eutectics. Mirza et al. [1] reported a group additivity method for the estimation of the critical temperatures T_c (also the boiling points and densities) of deep eutectic solvents. An alternative path for the estimation of the critical temperatures is described here for deep eutectic solvents that for most of them no previous estimates were reported.

The surface tensions σ of liquids over a temperature range are related to their critical temperatures T_c according to either of two relationships. One relationship, according to Eötvös [2], is

$$\sigma V^{2/3} = A \left(1 - \frac{T}{T_c} \right), \quad (1)$$

where $V = M/\rho$ is the molar volume of the liquid, M is its molar mass, and ρ is its density. The other relationship, according to Guggenheim [3], is

$$\frac{\sigma}{\sigma_0} = \left(1 - \frac{T}{T_c} \right)^{11/9}. \quad (2)$$

These relationships may be inverted in order to deduce the critical temperatures from $\sigma(T)$ and $\rho(T)$ data that are available in the literature. In order to apply these expressions, it is necessary to determine the parameters A of (1) and σ_0 of (2). The experimental functions $\sigma(T)$ and $\rho(T)$ are linear over a wide temperature range:

$$\sigma(T) = \sigma(T = 298.15 \text{ K}) - \left(\frac{\partial \sigma}{\partial T} \right) \left(\frac{T}{K} - 298.15 \right), \quad (3)$$

$$\rho(T) = a - b \left(\frac{T}{K} - 273.15 \right). \quad (4)$$

The molar volume $V = M/\rho$ is therefore also linear with the temperature (because $b \ll a$). Therefore, extrapolation to the nominal temperature $T = 0$ yields according to (1) and (2), respectively, $A_0 = \sigma(0)V(0)^{2/3}$ and $\sigma_0 = \sigma(0)$.

Thus, the critical temperature T_c^E according to (1) is

$$T_c^E = \frac{T}{\left[1 - \sigma(T)V(T)^{2/3}/A_0 \right]}, \quad (5)$$

and T_c^G according to (2) is

$$T_c^G = \frac{T}{\left[1 - \sigma(T)/\sigma_0 \right]^{9/11}}. \quad (6)$$

TABLE 1: The surface tension σ at 298.15 K and its temperature coefficient $(\partial\sigma/\partial T)_p$; the molar masses M and the density coefficients of $\rho = a - b(t/^\circ\text{C})$ of deep eutectic solvents; and the derived critical temperatures: T_c^E according to (3), T_c^G according to (4), T_c^M from Mirza et al. [1], and T_c^H from Haghbakhsh et al. [17].

HBA	HBD	σ (mN·m ⁻¹)	$(\partial\sigma/\partial T)_p$ (mN·m ⁻¹ ·K ⁻¹)	Reference	M (g·mol ⁻¹)	a (g·cm ⁻³)	10^3b (g·cm ⁻³ ·K ⁻¹)	Reference	T_c^E (K)	T_c^G (K)	T_c^M (K)	T_c^H (K)
ChCl	EG 1:2	48.91	-0.0932	[4]	263.8	1.1314	0.572	[10]	836	669	602,611	602
	Gly 1:2	58.05	-0.1353	[5]	323.8	1.2051	0.532	[7]	832	605	681,681	681
	Fru 2:1	74.0	-0.200	[6]	432.4	1.3081	1.179	[11]	869	564	757,903	
	Glu 2:1	71.71	-0.0516	[4]	432.4	1.267	1.000	[11]		1191	887,887	
	Mea 1:7	49.18	-0.0694	[13]	567.2	1.0843	0.73	[13]	1486	790		
DEANCl	EG 1:4	47.51	-0.0956	[4]	402.0	1.1149	0.618	[12]	982	651	612,667	
	Gly 1:2	54.54	-0.0888	[5]	337.9	1.1881	0.599	[12]	1158	728	641,696	704
Pr ₄ NBr	EG 1:4	47.05	-0.0877	[7]	514.5	1.1509	0.682	[7]	1068	677		642
	Gly 1:3	53.12	-0.0883	[7]	536.5	1.2214	0.664	[7]	1159	720		
	TEG 1:3	46.57	-0.0814	[7]	908.4	1.1681	0.700	[7]	1146	701		
Bu ₄ NCl	EG 1:3	40.49	-0.0817	[8]	464.1	1.0423	0.639	[8]	1002	650		
	Gly 1:5	47.35	-0.0700	[8]	738.4	1.1579	0.650	[8]	1312	769		
	TEG 3:1	40.22	-0.0849	[8]	920.0	1.0197	0.618	[8]	963	635		
Bu ₄ NBr	Gly 1:4	36.57	-0.1409	[5]	690.7	1.3537	0.6	[5]	609	558		
	Mea 1:4	35.83	-0.0392	[13]	566.7	1.0729	0.73	[13]	2072	919		
	Asa 1:9	38.5	-0.1150	[14]	1520.4	0.9795	0.584	[14]	720	563		
	Gla 1:10	37.6	-0.1375	[14]	1793.8	0.9791	0.601	[14]	633	518		
	Arg 1:6	40.4	-0.0750	[14]	1367.7	1.0223	0.603	[14]	1044	708		
MePh ₃ PBr	EG 1:4	51.29	-0.1056	[9]	605.5	1.2504	0.709	[12]	906	642	708,989	
	Gly 1:3	58.94	-0.1259	[9]	633.5	1.3132	0.651	[12]	914	631	832,996	802
	Mea 1:8	50.27	-0.0828	[13]	845.9	1.1209	0.81	[13]	1289	724		
BzPh ₃ PBr	Gly 1:16	53.24	-0.1205	[5]	1857.7	1.2512	0.7	[5]	894	613		741
AllPh ₃ PBr	Gly 1:14	41.57	-0.1409	[5]	1646.5	1.2805	0.7	[5]	671	512		739
	DEG 1:4	49.37	-0.0996	[15]	707.7	1.2160	0.74	[16]	980	748	898 ^a	
	TEG 1:4	48.25	-0.1326	[15]	883.9	1.2150	0.74	[16]	768	581	738 ^a	

^aReference [15].

2. The Data Employed and the Results

Table 1 presents the surface tension data $\sigma(T = 298.15 \text{ K})$ and their temperature coefficients $(\partial\sigma/\partial T)_p$ as well as the molar masses M and the density coefficients of (4), a and b , for obtaining the molar volumes. The derived critical temperature values T_c^E and T_c^G for those deep eutectic solvents are also included in Table 1, for which the required data have been reported. Table 1 also shows the values of T_c^M according to the group contribution estimates; the first entries are from Mirza et al. [1] and the second ones are from Mjalli et al. [4]. The following abbreviations are used for the HBA components of the solvents: ChCl = choline chloride; DEANCl = diethylethanolammonium chloride; Pr₄NBr = tetrapropylammonium bromide; Bu₄NCl = tetrabutylammonium chloride; MePh₃PBr = methyltriphenylphosphonium bromide; BzPh₃PBr = benzyltriphenylphosphonium bromide; and AllPh₃PBr = allyltriphenylphosphonium bromide. The HBD components are EG = 1,2-ethanediol, Gly = glycerol, Fru = fructose, Glu = glucose, TEG = triethylene glycol, Mea = monoethanolamine, Asa = aspartic acid, Gla = glutamic acid, and Arg = arginine, and the molar ratios for the eutectics are also shown.

The resulting T_c^E estimates of the critical temperatures according to the Eötvös relationship are on the average by 50% larger than the T_c^G estimates according to the

Guggenheim relationship. However, the T_c^G estimates are nearer the values of T_c^M from the group contributions according to Mirza et al. [1] than are the T_c^E ones. On the whole, the T_c^G values appear to be the more trustworthy.

3. Discussion

The normal boiling points T_b of deep eutectic solvents are generally not relevant for their applications but represent the upper limit of their usage, if they do not decompose below these T_b . Therefore, the critical temperatures T_c , which are on the average about $4/3(T_b/K)$ [1], are not the quantities that are relevant to their applications but have found use for the estimation of other properties that have not been measured as functions of the temperature [1, 4]. Still, the critical temperatures are physical properties that ought to be known; hence, the present estimates for two dozens of deep eutectic solvents of which only eight had their T_c estimated previously make sense. The values are based on the nominal extrapolation of the experimental surface tension data to $T = 0$ for the T_c^G estimates (to obtain σ_0) and of both these and the densities for the T_c^E estimates (to obtain A_0), but these parameters do not have any real significance.

Previous estimates of the critical temperatures of deep eutectic solvents were conducted according to two paths. One was the use of the modified Lydersen–Joback–Reid

group contribution method to obtain first values of T_b and from them the values of T_c , which is applicable to organic liquids for which at least T_b is known and then extended [1, 4, 17] to the deep eutectic solvents. It was applied to twenty different deep eutectic solvents (shown as T_c^M [1, 4] and T_c^H [17] in Table 1 for those also studied here) as well as to noneutectic compositions of some of them. Some disagreements between the results of the application of this method are noted in Table 1. The other path was the application of the Eötvös [4, 15] and the Guggenheim [15] expressions, but in a different manner than done here. The former expression was recast in the linear form:

$$\sigma V^{2/3} = A' + BT. \quad (7)$$

and from the intercept and slope of its plots $T_c = -A'/B$ resulted [4]. The agreement with the values of T_c^M from the group contributions is poor. Better agreement was obtained in [15] between values derived from the Eötvös and Guggenheim expressions.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

References

- [1] N. R. Mirza, N. J. Nicholas, Y. Wu, S. Kentish, and G. W. Stevens, "Estimation of normal boiling temperatures, critical properties, and acentric factors of deep eutectic solvents," *Journal of Chemical and Engineering Data*, vol. 60, no. 6, pp. 1844–1854, 2015.
- [2] R. Eötvös, "Über den zusammenhang der oberflächenspannung der flüssigkeiten mit ihrem molecularvolumen," *Annalen der Physik und Chemie*, vol. 263, no. 3, pp. 448–459, 1886.
- [3] E. A. Guggenheim, "The principle of corresponding states," *Journal of Chemical Physics*, vol. 13, no. 7, pp. 253–261, 1945.
- [4] F. S. Mjalli, G. Vakili-Nezhaad, K. Shahbaz, and I. M. AlNashef, "Application of Eötvös and Guggenheim empirical rules for predicting the density and surface tension of ionic liquids analogues," *Thermochimica Acta*, vol. 575, pp. 40–44, 2014.
- [5] M. K. AlOmar, M. Hayyan, M. A. Alsaadi, S. Akib, A. Hayyan, and M. A. Hashim, "Glycerol-based deep eutectic solvents: physical properties," *Journal of Molecular Liquids*, vol. 215, pp. 98–105, 2016.
- [6] A. Hayyan, F. S. Mjalli, I. M. AlNashef, T. Al-Wahaibi, Y. M. Al-Wahaibi, and M. A. Hashim, "Fruit sugar-based deep eutectic solvents and their physical properties," *Thermochimica Acta*, vol. 541, pp. 70–75, 2012.
- [7] B. Jibril, F. S. Mjalli, J. Naser, and Z. Gano, "New tetrapropylammonium bromide-based deep eutectic solvents: synthesis and characterizations," *Journal of Molecular Liquids*, vol. 199, pp. 462–469, 2014.
- [8] F. S. Mjalli, J. Naser, B. Jibril, V. Alizadeh, and Z. Gano, "Tetrabutylammonium chloride based liquid analogues and their physical properties," *Journal of Chemical and Engineering Data*, vol. 59, no. 7, pp. 2242–2251, 2014.
- [9] K. Shahbaz, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Prediction of surface tension of deep eutectic solvents," *Fluid Phase Equilibria*, vol. 319, pp. 48–54, 2012.
- [10] T. B. Leron and M. H. Li, "Molar heat capacities of choline chloride-based deep eutectic solvents and their binary mixtures with water," *Thermochimica Acta*, vol. 530, pp. 52–57, 2012.
- [11] F. S. Mjalli, K. Shahbaz, and I. M. AlNashef, "Modified Rackett equation for modelling the molar volume of deep eutectic solvents," *Thermochimica Acta*, vol. 614, pp. 185–190, 2015.
- [12] K. Shahbaz, S. Baroutian, F. S. Mjalli, M. A. Hashim, and I. M. AlNashef, "Densities of ammonium and phosphonium based deep eutectic solvents: prediction using artificial intelligence and group contribution techniques," *Thermochimica Acta*, vol. 527, pp. 59–66, 2012.
- [13] F. S. Mjalli, G. Murshid, S. Al-Zakwami, and A. Hayyan, "Monoethanolamine-based deep eutectic solvents, their synthesis and characterization," *Fluid Phase Equilibria*, vol. 448, pp. 30–40, 2017.
- [14] F. S. Mjalli, "Novel amino acid based ionic liquids analogues: acidic and basic amino acids," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 61, pp. 64–74, 2016.
- [15] H. Ghaedi, M. Ayoub, S. Sufian, A. N. Shariff, and B. Lal, "The study on the temperature dependence of viscosity and surface tension of several phosphonium-based deep eutectic solvents," *Journal of Molecular Liquids*, vol. 241, pp. 500–510, 2017.
- [16] H. Ghaedi, M. Ayoub, D. Sufian, B. Lal, and A. N. Shariff, "Measurement and correlation of physicochemical properties of phosphonium-based deep eutectic solvents at several temperatures (293.15 K–343.15 K) for CO₂ capture," *Journal of Chemical Thermodynamics*, vol. 113, pp. 41–51, 2017.
- [17] R. Haghbakhsh, K. Parvaneh, S. Raeissi, and A. Shariati, "A general viscosity model for deep eutectic solvents: the free volume theory coupled with association equations of state," *Fluid Phase Equilibria*, 2017, In press.

